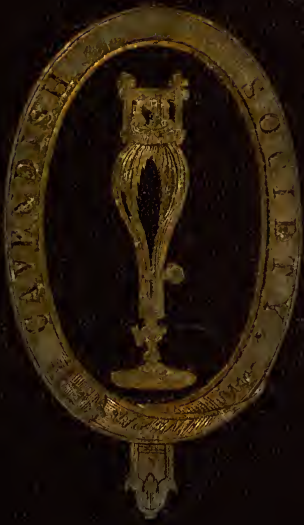
CAVENDISH SOCIETY

HAND-BOOK

OF

CHEMISTRY.

BY

LEOPOLD GMELIN.

ORGANIC CHEMISTRY,

VOL. VIII.

ORGANIC COMPOUNDS CONTAINING TWENTY AND TWENTY-TWO ATOMS OF CARBON.

TRANSLATED BY

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COMPOUNDS CONTAINING 20 AT. CARBON.

Naphthalin Series.

Naphthalin. $C^{20}H^{8}$.

Garden. (1820.) *Thoms. Ann.* 15, 74; *J. Phys.* 90, 238; *Pogg.* 7, 104.
Kidd. *Phil. Trans.* 1821; *Schw.* 34, 426; *Pogg.* 7, 104.
Ure. *Phil. Trans.* 1822, 473.
Chamberlain. *Phil. Ann.* 6, 135; *Pogg.* 7, 106.
Faraday. *Phil. Trans.* 1826, 140; *Schw.* 47, 335 and 459; abstr. *Pogg.* 7, 104.
Reichenbach. *Schw.* 61, 175; *Schw.* 68, 233; *Pogg.* 28, 484.
Saussure. *N. Gehl.* 4, 69.
Fremy. *Ann. Chim. Phys.* 59, 18.
A. Connel. *N. Edinb. Phil. J.* 1832, No. 26, 231; *Schw.* 61, 104.
Brooke. *Repert.* 38 265.
Mansfield. *Chem. Soc. Qu. J.* 1, 248.
Pelletier & Walter. *Ann. Chim. Phys.* 67, 274.
Liebig & Wöhler. *Pogg.* 24, 169; *Berzel. Jahresber*, 13, 358.
Laurent. *Ann. Chim. Phys.* 49, 214; *Pogg.* 25, 376; abstr. *Schw.* 65, 86; *Ann. Pharm.* 3, 9; *Ann. Chim. Phys.* 52, 275; abstr. *Ann. Pharm.* 8, 8; *Pogg.* 29, 77; *Schw.* 68, 316; *Ann. Chim. Phys.* 61, 113; abstr. *Ann. Pharm.* 19, 38; *J. pr. Chem.* 8, 13; *Ann. Chim. Phys.* 61, 125; abstr. *J. pr. Chem.* 8, 201; *Ann. Chim. Phys.* 66, 124; *Ann. Chim. Phys.* 74, 26; abstr. *Ann. Pharm.* 35, 292; *Rev. sc.* 6, 76; abstr. *Ann. Pharm.* 41, 114; *Rev. sc.* 11, 361; *ibid.* 12, 193; *ibid.* 13, 66 and 579; *ibid.* 14, 313; *Compt. rend.* 14, 318; *Rev. sc.* 14, 818; abstr. *J. pr. Chem.* 27, 29; *Compt. rend.* 29, 363; *Rev. sc.* 15, 739; *ibid.* 21, 36; *Compt. chim.* 1850, 1; abstr. *Pharm. Centr.* 1850, 310; *Ann. Pharm.* 76, 298; *Liebig & Kopp's Jahresb.* 1850, 497.
Dumas. *Ann. Chim. Phys.* 50, 182; *Ann. Pharm.* 5, 6; *Pogg.* 26, 517; *Schw.* 66, 89.
Dumas & Stass. *Ann. Chim. Phys.* 76, 40; *N. Ann. Chim. Phys.* 1, 42.
Liebig. *Ann. Pharm.* 25, 19.
Woskressensky. *Ann. Pharm.* 26, 66.
Mitscherlich. *Pogg.* 31, 631.
Erdmann & Marchand. *J. pr. Chem.* 23, 177.
Berzelius. *Pogg.* 44, 377; *Ann. Pharm.* 28, 9.
Marignac. *Ann. Pharm.* 38, 18.

MAGNUS. *Pogg.* 90, 1; *Phil. Mag. J* 6, 420; abstr. *Berl. Acad. Ber.* 1853, 446; *Ann. Pharm.* 88, 349; *J. pr. Chem.* 60, 86; *Pharm. Centr*, 1853, 597; *Instit.* 1853, 416; *Liebig & Kopp's Jahresb.* 1853, 525.

BERTHELOT. *N. Ann. Chim.* 33, 295; abstr. *Ann. Pharm.* 81, 108; *J. pr. Chem.* 55, 76; *Pharm. Centr.* 1851, 861; *Liebig & Kopp's Jahresb.* 1851, 437, 504; *Compt. rend.* 33, 210; *N. Ann. Chim. Phys.* 53, 69; abstr. *Compt. rend.* 43, 236; *Ann. Pharm.* 108, 188; *J. pr. Chem.* 70, 253; *Chem. Centr.* 1858, 535.

H. KOPP. *Ann. Pharm.* 95, 329; abstr. *Pharm. Centr.* 1855, 771; *Liebig & Kopp's Jahresb.* 1855, 37.

SCHWARZ. *Dingler. pol. J.* 147, 229; abstr. *Chem. Centr.* 1858, 558.

Coal-tar camphor; Naphtum or *Naphtalène.* (Laurent.) *Two-fifths hydrocarbon, Decaoctyl.* (Berzelius.) *Normal-Naphten.* (Gerhardt.) *Hydride of Naphtyl.* (Kolbe.)

Discovered in coal-tar oil, by Garden (1820); recognised by Reichenbach as one of the products of decomposition by heat, of the distillate from coal. Faraday determined the composition of naphthalin, and, as well as Berzelius and Laurent, investigated its derivation.

Formation. A. Very frequently produced in the dry distillation of organic bodies, especially when decomposition takes place at a very high temperature.

1. From *Ethylene.* At a red heat, olefiant gas splits up into marsh-gas, and tar of various degrees of volatility, but containing on the average 93·3 p. c. C and 6·5 p. c. H, (and accordingly having nearly the composition of naphthalin). — This tar sometimes deposits crystals of naphthalin, especially when the more volatile part is evaporated off:

$$8\,C^4H^4 = C^{20}H^8 + 6\,C^2H^4.$$

The marsh-gas is mixed with undecomposed olefiant gas and hydrogen, the latter having been formed by the decomposition of the tar into hydrogen and carbon; at a white heat, olefiant gas yields only these two products, but no tar. (Magnus.)

2. By passing the vapour of *alcohol, ether, rock-oil,* or of *essential oils* through a red-hot porcelain tube. (Saussure, Berthelot.) Charcoal and empyreumatic oil are likewise produced in this operation. (Reichenbach.) Benzene, phenylic alcohol, and other products are likewise formed, and, as well as the naphthalin, are in part simply condensed and partly collected in nitric acid, and obtained as nitrobenzene, nitro-naphthalin, &c. (Berthelot.)

3. From *Acetic Acid.* If vapour of acetic acid be passed through a red-hot porcelain tube filled with fragments of pumice, naphthalin and a large quantity of undecomposed acetic acid condense in the receiver, together with a brown oil which forms picric acid with nitric acid. (Berthelot.)

4. Naphthalin is found amongst the decomposition-products of camphor, the vapour of which has been passed over strongly ignited lime, and condenses in the receiver in fine, perfectly pure crystals. (Fremy.)

5. Naphthalin is found, in quantity varying according to the circumstances under which the decomposition takes place, amongst the products of the dry distillation of *coal,* (compare ix. 135.) (Garden, Laurent); of *fat oils* when illuminating gas is prepared from them (A. Connel); of *resins,* when fused and dropped into red-hot cylinders (Pelletier & Walter). Naphthalin is produced, not by the carbonization of coal, but by the decomposition of the first formed distillation-products,

when these products in the state of liquid or vapour come in contact with the red-hot sides of the retorts (vapour-carbonization). It is for this reason that no naphthalin is obtained on distilling coal in iron retorts, of which only the bottom is heated, while the sides are protected from the heat; or when the products of distillation are repeatedly rectified, or cooled to —20°; or acted upon by chlorine (as Dumas affirms) (Reichenbach). Neither is naphthalin produced by distilling tarry residues or wood (Reichenbach), or lignite (Schwarz), if a very strong heat be avoided. — Naphthalin exists ready formed in commercial coal-tar (Garden, &c.); but not invariably (Laurent), (which is owing, not, as Laurent supposed, to varying age, but to the different modes of preparation) (Reichenbach). Coal-tar sometimes contains $\frac{1}{4}$ of its weight of naphthalin, and sometimes only traces (London tar contains large quantities) (Mansfield, *Chem. Soc. Qu. J.* 1,248). Tar prepared by distilling coal in iron retorts (in the manner formerly adopted for the preparation of gas), contains but little naphthalin. If retorts of Charmotte clay are employed instead of iron, the tar contains considerable quantities of naphthalin, and a little volatile oil, formed either by the decomposition of the naphthalin, or of the gas itself. (Schwarz.) — Kidd obtained naphthalin by dropping coal-tar upon red-hot iron cylinders. — Naphthalin is found in lamp black, to which it imparts its peculiar odour, and may be separated by simple distillation, or by distillation with water. It is also found in the soot obtained by the burning of wood-tar (Reichenbach); likewise in the vapour which penetrates into rooms from leaky stove-flues (Berzelius), since a deposit of soot is produced by the red hot flue. (Reichenbach.) — Dumas believed that naphthalin exists ready-formed in coal, but Reichenbach showed that this is not the case.

B. By *synthesis*, from inorganic substances. Since olefiant gas may be formed from inorganic materials,—and from olefiant gas, alcohol and then acetic acid may be produced, the modes of formation of naphthalin A, 1, 2, and 3 may be regarded as syntheses of this description.

1. If a perfectly pure and dry mixture of bisulphide of carbon vapour and sulphuretted hydrogen, or a mixture of these two gases and carbonic oxide, be passed over porous copper or iron at a dull red heat, the products obtained are: a little naphthalin and empyreumatic oil, much hydrogen, marsh-gas, and olefiant gas, and a residue of sulphide of copper mixed with charcoal. (Berthelot.) Perhaps this mode of formation is identical with that from olefiant gas (A, 1), olefiant gas being probably produced, in the first instance and yielding naphthalin (Carius), by its decomposition.

2. When vapour of dichloride of carbon (viii, 160) mixed with hydrogen, is passed through a glass tube filled with fragments of pumice, at a bright red-heat, it yields large quantities of naphthalin. (Berthelot.)

Preparation. Naphthalin is obtained in large, but varying quantities as an almost useless by-product in the distillation of tar on the large scale, especially of that from coal; but it is also a product of the distillation of wood, lignite, and animal offal. (Comp. *Benzene*, xi, 135.)

1. Tar (whether produced from wood, coal, or animal refuse) is first distilled with steam, as long as naphtha (*light naphtha*), of sp. gr. 0·91 at the utmost, is obtained, and afterwards with the aid of heat, whereupon water and oil of naphthalin (*dead oil, heavy naphtha*) pass over, until this latter attains a sp. gr. of 0·99. Every 100 gallons of the distillate

last obtained are now intimately stirred up with 15 gallons of oil of vitriol (sp. gr. 1·83) and allowed to settle, after which the clear upper liquid is decanted. This is stirred up with one-tenth of its volume of caustic alkali-solution of sp. gr. 1·35, and after it has been completely neutralized, the whole is allowed to settle. The upper layer is then poured off and distilled alone, until the distillate attains a sp. gr. of 0·94. If this first distillate be now mixed in a still with quick lime (1 pound of lime to every gallon of oil), and distilled at a gentle heat, it yields, first a light oil till the sp. gr. reaches 0·91; and if the receiver be then changed and the remainder collected by itself, and cooled to — 4° C, it deposits naphthalin, which may be purified by filtration and pressure. If the distillation of the crude oil of naphthalin be continued in another still, as long as anything passes over, the purified heavy oil of naphthalin is obtained, which, if treated in a similar manner with lime, yields an additional quantity of naphthalin. (G. Shand & A. Maclean, *Chem. Gaz.* 1854, No. 270; *Dingler pol. J.* 133, 309.)

The black flaky masses which are deposited on the ground in places where coal-tar is heated in open pans in order to free it from water, consist, according to Schwarz, of almost pure naphthalin. Coal-tar which has been subjected to heat in the above-mentioned process, yields by distillation two oils, one of which distils at 160° C and contains 0·46 p. c. naphthalin, while the second passes over between 160° and 220° C. and contains 0·65 p. c. naphthalin. Crude tar, which has not been previously heated, yields by distillation, first a light oil together with strongly ammoniacal water; then between 210° and 230° C., after the water has been driven off, so large a quantity of naphthalin, that the distillate, if collected in a separate receiver, assumes at ordinary temperatures the consistence of butter. (Schwarz.) — Garden obtained naphthalin by distilling coal-tar, the naphthalin passing over with the empyreumatic oil, from which it was afterwards deposited. — When coal-tar is distilled, but little naphthalin passes over at first, the quantity gradually increasing till the operation is half over, and then again becoming less; the greatest amount passes over with the last portions of the distillate, insomuch that these become completely solid in the receiver (the final products contain sulphur); 100 gallons yielded 5 lbs. naphthalin. If the distillation be hastened a larger quantity is obtained; but if oil of vitriol be added to the tar, little or no naphthalin is produced. (Chamberlain).

2. Coal-tar is boiled in a copper kettle till all the water is driven off (which would otherwise cause the retort to crack), and then distilled in a glass retort to half its bulk. The naphthalin is separated from the distillate: *a* by cooling to —10° C, whereupon large quantities of naphthalin, mixed with a small quantity of a yellow unctuous substance, are deposited. The product is collected on fine linen and pressed. — *b*. The following is a better method: the distillate is placed in a tubulated retort through which chlorine gas is passed for four days, whereupon it becomes hot, evolves hydrochloric acid gas and vapours having an offensive odour (if the condenser be cooled to 0° C. these vapours condense to a wine-red liquid), and finally assumes the dark colour of tar. The product is washed with water, which removes hydrochloric acid and bad smelling bodies, and distilled alone, the distillate being collected in two portions. Both of these, when cooled to — 10° C. deposit large quantities of naphthalin. (Laurent, *Ann. Chim. Phys.* 49, 214.)

3. When commercial coal-tar oil is submitted to fractional distillation, the portion passing over between 170° and 190° C. deposits a very large

amount of naphthalin (20 ℔s. of oil yields 5 ℔s.) which may be collected on a filter, drained, and distilled. (Laurent, *N. Ann. Chim. Phys.* 3, 296.)

4. Coal-tar is passed through red-hot iron tubes, and the thin tar, obtained by the condensation of the vapours, is distilled, whereupon first water and oil, then naphthalin pass over. (Kidd.) — 5. Coal-tar (especially such as has been long exposed to the air) is heated with chloride of lime, water, and oil of vitriol. Much naphthalin is evolved with the steam. (Brook.)

Purification. Commercial naphthalin, or naphthalin prepared by any of the above described methods, is generally contaminated with varying proportions of an empyreumatic oil which turns brown on exposure to the air (as well as by a yellow unctuous substance, Laurent). To free naphthalin from these impurities, the following processes may be employed :—

a. Sublimation. 1. The naphthalin is gently heated in retorts or other suitable vessels, and the vapours are collected in wooden chambers, wherein they condense in white flakes. (G. Shand & A. Maclean.) — 2. About half a pound of crude naphthalin is gently heated for several hours on the sand-bath in a large porcelain dish, over which a sheet of filter-paper has been pasted ; after the whole has cooled, the dish is found to be full of dazzling white crystals of naphthalin. These are removed and the remaining cake of naphthalin pressed with blotting paper (in order to soak up the oil), and again heated, the operation being repeated as long as any sublimate is obtained. The last portion is yellow. This is the only method of obtaining pure, colourless naphthalin. (Otto, *Ann. Pharm.* 93, 383.)

b. Washing with cold alcohol and recrystallizing from hot alcohol. (Garden, Laurent.) The most convenient method is to put the powdered naphthalin upon 4 or 5 funnels (without paper) placed one above the other, and to pour the alcohol upon the uppermost ; by this means 1¼ lb. alcohol are sufficient for 5 lbs. naphthalin. (Laurent.)

Properties. Brilliant white scales, soft to the touch. Crystallizes in six-sided tables. (Kidd, Chamberlain.) — More frequently in rhombic tables of 100° — 105° (Kidd). Regular crystals may be obtained but only with great difficulty, by sublimation or from alcohol ; they are rhombic tables of about 122° and 78°, the acute angles being generally truncated, so that the crystals appear hexagonal. By very slow spontaneous evaporation from ether, it may be obtained in crystals which are often of considerable size and completely developed ; they are prisms belonging to the oblique prismatic system, generally like Fig. 106, but reduced to the tabular form by the predominance of the *i*-faces. $u' : u' = 82°$: $u' : i = 111°$; $u' : t = 125°$; $i : t = 94° \ 30'$. (Laurent.) — Crystallizes from oil of turpentine in prisms terminated by pyramids. (Chamberlain.) Naphthalin when slowly sublimed, forms such an extremely light bulky mass, that sometimes ¼ gramme will fill a litre-flask. (Handwörterb, 5, 432.) — Heavier than water (Kidd). Sp. gr. 1·048 (Ure); 1·153 at 18° (the naphthalin had been fused, but was still somewhat porous: — Reichenbach) Melts at 84° 5′ (Garden), between 77° and 82° (Kidd), at 75·5° (Ure), forming an oil which on cooling solidifies in a mass consisting of flexible interlaced laminæ ; melts at 79° (Dumas), at 79·2° (H. Kopp). — (The naphthalin used by Kopp for his determination was absolutely pure; when it was melted and allowed to solidify slowly, the thermometer remained constant at 79·2°.)

Sp. gr. of liquid naphthalin at its melting-point (water at 0° C. being taken as unity) = 0·9778 (average). The true volume at 8° above the melting point is given by the formula:

$$V = 1 + 0{\cdot}000747 \times 8 + 0{\cdot}0000018095 \times 8^2$$

Spec. vol. = 149·2 at the boiling point (calculated, according to Kopp = 154) (H. Kopp). Boils at 210° (Kidd), at 212° (Dumas), at 220° (Gerhardt); boils constantly between 216·4° and 216·8° (barometer at $0^{\cdot m}$ 7476), or at 218·0° (barometer at 760^{mm}) (H. Kopp). (Determined by Kopp's method, and rectified according to the corrections proposed by him.) Sublimes even at a low temperature (Garden), but more slowly than common camphor; heated alone, it sublimes in brilliant flakes (Ure), without previous fusion. (Laurent.) Thrown into a red-hot crucible, it volatilises undecomposed, and condenses in the air in snowy spangles. (Laurent.) May be distilled with water (Ure, Chamberlain); when heated with water, it rises to the surface in oily drops, and then evaporates with a motion similar to that exhibited by common camphor. (Ure.)

Smells aromatic, like the narcissus, (Garden and others.) Tastes aromatic and pungent. (Garden.) Neutral to vegetable colours. (Kidd.) Vapour-density = 4·528 (Dumas), 4·621 (average, Woskressensky, *Ann. Pharm.* 26, 66), 4·46 (Natanson, *Ann. Pharm.* 93, 801). Consequently, 1 litre of vapour weighs 5·882 grammes (Dumas), 5·939 grammes (Woskressensky).

			Faraday.		Oppermann.	Laurent.
			a.	*b.*		*mean.*
20 C	120	93·75	93·75	93·484	94·39	94·00
8 H	8	6·25	6·25	6·516	5·61	6·10
$C^{20}H^{8}$	128	100·00	100·00	100·000	100·00	100·10

	Dumas.	Mitscherlich.	Woskressensky. *mean.*	Marchand.	Erdmann & Marchand.	Dumas & Stass. *average.*
20 C	94·2	94·39	94·41	93·65	93·58	93·83
8 H	6·5	6·21	6·07	6·35	6·27	6·30
$C^{20}H^{8}$	100·7	100·60	100·48	100·00	99·85	100·13

	Vol.	Density.
C-vapour	20	8·3200
H-gas	8	0·5544
Naphthalin-vapour	2	8·8744
	1	4·4372

The composition as stated by Faraday has been proved to be correct. Thomson regarded $C^{3}H^{2}$, Ure $C^{2}H$ as more probable. According to Woskressensky's analysis, the formula is $C^{3}H$ (with which, however, his determination of the vapour-density does not agree: Gm.), in which case, naphthalin would be isomeric or polymeric with idrialin, and probably also with paranaphthalin, scheererite, and pyrene. The analyses made in Liebig's laboratory, gave as the average, 94·4 p. c. C, and 6·15 p. c. H, from which we get $C^{8}H^{3}$, after making the correction for hydrogen. (Liebig, 1838; *Ann. Pharm.* 25, 19.) — Faraday supposed the atomic weight of naphthalin to be $C^{20}H^{8}$, (which has since been found to be the only admissible formula); Berzelius supposed it to be $C^{10}H^{4}$; the last supposition was *once* made by Laurent (*Ann. Chim. Phys.* 61, 124). — According to Marignac, naphthalin may be regarded as a compound of two hydrocarbons:

$$C^{20}H^{8} = C^{16}H^{4} + C^{4}H^{4},$$

for the following reasons: *a.* The formation of chlorine-compounds which are very analogous to those formed from olefiant gas (the chlorine removing only half the hydrogen from the naphthalin ?); *b*. The resolution of naphthalin into compounds of the two hydrocarbons in the formation of nitrophthalic acid, $C^{16}XH^5O^8$ and of phthalic acid, together with the compound $C^2X^2Cl^2$ (ii, 360). According to Kolbe, it is hydride of naphthyl = $C^{20}H^7,H$ (comp. *Ann. Pharm.* 76, 39.)

Decompositions. Naphthalin yields by sublimation a liquid which at first tastes sweet and aromatic, afterwards pungent, and from which a considerable quantity of prussic acid may be obtained; *Chamberlain.*) 1. When naphthalin is heated in the air, the vapour is difficult to set on fire; when once ignited, it *burns* very rapidly with a thick smoke. (Kidd.) — 2. Naphthalin vapour, passed over red-hot *hydrate of baryta,* yields carbonate of baryta and hydrogen. —(Pelouze and Millon, *Ann. Pharm.* 33, 182.) — 3. *Chlorine* forms new compounds with naphthalin, heat being evolved and hydrochloric acid gas produced. (Laurent, *Ann. Chim. Phys.* 49, 214.) The naphthalin melts, but solidifies again if the action of chlorine be continued; the solid mass contained 44·69 p. c. C, 3·12 p. c. H, and 52·19 p. c. Cl, corresponding to the formula $C^{10}Cl^4H^4$ (Dumas). Dry chlorine acts immediately and with great violence at ordinary temperatures. The naphthalin melts, and if the stream of chlorine be rapid, sublimes in part as bihydrochlorate of bichloro-naphthalin, while hydrochloric acid is evolved. The mass gradually thickens, and becomes like solidified olive oil. The products formed in this reaction are hydrochlorate of chloronaphthalin, $C^{20}ClH^7,HCl$, and bihydrochlorate of bichloronaphthalin, $C^{20}Cl^2H^6,2HCl$ (modification α and β); by the further action of chlorine and heat, new chlorides are formed from the first, with fresh evolution of hydrochloric acid gas, especially bihydrochlorate of trichloronaphthalin, $C^{20}Cl^3H^5,2HCl$. (Laurent.) Chlorine replaces the hydrogen of naphthalin, atom for atom, but the resulting hydrochloric acid remains in combination with the new radical (comp. also vii. 21). The chlorine which these compounds contain, outside the radical, may be removed in the form of hydrochloric acid, either by distillation or by treatment with potash, while the chlorinated radicals thus set free cannot be further decomposed by distillation or by treatment with potash. (Laurent.) If these radicals are again treated with chlorine, the hydrochlorates of new radicals, richer in chlorine are formed, which, in their turn, may be set free by distillation or treatment with potash, and are finally converted by chlorine into perchloronaphthalin. (Laurent.) The number of the chlorine-compounds obtained by Laurent is very much increased by the fact that almost all of them vary in physical properties when prepared in different ways. (This seems to be frequently caused by impurities.) (Carius.) Besides such radicals and their hydrochlorates as only contain whole atoms of Cl and H to 20 At. C, others are described by Laurent, containing a fractional number of Cl and H atoms, as well as Br and H, or ClBr and H together; the whole of these are probably mixtures of two or more compounds. (Carius.) Several of these radicals, and likewise their hydrochlorates, bear a great resemblance to one another; thus bihydrochlorate of bichloronaphthalin and bihydrochlorate of trichloronaphthalin (the latter recrystallised from alcohol) are isomorphous. (Laurent.) Laurent distinguishes the isomeric compounds of like composition by the letters A, B, &c., and even compounds of different composition, when agreeing in certain properties, *e. g.*, crystalline form, are denoted by the same letters. Thus all radicals marked A are soft, like wax, and crystallise in regular six-sided prisms of 120°. (Laurent, *Rev. Scient.* 14, 74.)

4. *Bromine* acts violently upon naphthalin, with rise of temperature and evolution of hydrobromic acid, leaving oily bromo-

naphthalin. From this it appears that the bromine replaces the hydrogen, while the free radical is formed with evolution of hydrobromic acid. (Laurent.) By the further action of bromine upon bromonaphthalin, hydrobromic acid and bi- or tri-bromonaphthalin are formed, and from the latter, the hydrobromates $C^{20}Br^4H^4,2HBr$, and $C^{20}Br^4H^4,HBr$ (from which the radical $C^{20}Br^4H^4$ may be separated by distillation or by potash), and as the final product of the action of bromine, bihydrobromate of pentabromonaphthalin is formed — $C^{20}Br^5H^3,2HBr$. (Laurent.) The bromine-compounds generally bear a great resemblance to one another and to the chlorine-compounds, *e. g.*, isomorphism, and like these last, occur in different isomeric modifications (Laurent.) The chlorine-compounds which still contain hydrogen, are converted by bromine into radicals containing both bromine and chlorine, or into their hydrochlorates and hydrobromates. On the other hand, by the action of chlorine on the bromine compounds, the hydrochlorates of radicals containing bromine (or bromine and chlorine) are obtained; but the latter, as well as the radicals which may be separated from them, are not identical with those obtained by the action of bromine on the chlorine-compounds, but isomeric, and generally isomorphous with them at the same time. (Laurent.) — 5. Naphthalin melts with *iodine* at a gentle heat to a brown liquid, which solidifies to a graphitoïdal mass on cooling, dissolves readily in alcohol, and is precipitated therefrom by water. (Ure.) *Iodine* is without action upon naphthalin; on warming them together, they melt, but separate on cooling. (Laurent.) Phosphorus, sulphur, and chloride of carbon are equally inert with naphthalin. (Laurent.) 6. *Hydrochloric acid* does not act on naphthalin (Reichenbach); it dissolves naphthalin, and assumes a dark colour. (Löwig. *Chemie der. org. Verb.* 2nd. pt. 2, 865.) — 7. *Chloride of Sulphur* (which?) heated with naphthalin, produces bichloronaphthalin, with separation of plastic sulphur and evolution of hydrochloric acid gas. (Laurent.) — 8. *Cyanogen* does not act upon naphthalin. If chlorine gas be passed over a powdered mixture of naphthalin and cyanide of mercury made into a paste with weak alcohol, an odour of chloride of cyanogen is evolved, mercurous chloride is formed, and the naphthalin is replaced by a yellow oil which is partly dissolved and may be precipitated by water. (Laurent.) — 9. A mixture of *bichromate of potash and sulphuric* (or *hydrochloric*) *acid*, acts but slightly on naphthalin, if much water is present; but if the quantity of water be small, a violent action takes place, and the naphthalin is partly converted into naphthesic acid ($C^{20}H^6O^8$). (Laurent, *Rev. scient.* 14, 560). — According to another statement of Laurent (*Comp. rend.* 21, 36), a beautiful rose-coloured substance is formed in the above manner, viz., Carminaphthone; $C^{18}H^4O^8$, soluble in alkalis and reprecipitated by acids.

10. Strong *nitric acid* does not act upon naphthalin in the cold (Laurent); it forms nitronaphthalin, in the course of 5 or 6 days, without evolution of red vapours. (Piria, *N. Ann. Chim. Phys.* 31, 217). On gently warming the liquid, a brown oil is formed, which afterwards dissolves; the liquid on cooling deposits yellow crystals (Garden), readily decomposible and inflammable. (Kidd.) Naphthalin evolves red vapours on boiling with nitric acid, and forms a mixture of nitronaphthalin and an oil, which floats on the liquid in the fluid form; hence 1 At. H in the naphthalin is replaced by 1 At. O, with formation of water, and the resulting compound then combines with the residue of the nitric acid:

$$C^{20}H^8 + NO^5 = (C^{20}H^7O + NO^3) + HO \text{ (Laurent).}$$

On continuing the boiling with nitric acid, binitronaphthalin, $C^{20}X^2H^6$

(and nitronaphthaleise $C^{20}X^{2\cdot5}H^{5\cdot5}$) is produced. (Laurent.) By boiling with nitric acid for several days, ternitronaphthalin, $C^{20}X^3H^5$, nitronaphthale, phthalic and oxalic acids (Laurent), and nitrophthalic acid (Marignac, Laurent) are formed.

11. *Nitrous acid* acts violently in the cold and forms nitronaphthalin and an oil. — 12. *Aqua regia* acts slowly in the cold; in this reaction, an oil is formed, which by distillation leaves a residue of carbon, and yields a distillate of nitronaphthalin and an oil.

13. *Oil of vitriol* dissolves naphthalin very slowly in the cold, forming a brown liquid (Reichenbach); at a moderate heat, sulphonaphthalic acid is formed, and another acid, which is distinguished from the first by the fact that its salts do not burn with flame. (Faraday.) Oil of vitriol, when gently warmed, dissolves naphthalin without evolution of sulphurous acid, and forms a brownish red liquid, which, after complete saturation with naphthalin, is clear and viscid when cold. Water precipitates from the solution unaltered naphthalin, together with sulphonaphthalin and a little sulphonaphthalide, while the solution contains sulphonaphthalic acid, $C^{20}H^8,2SO^3$, and bisulphonaphthalic acid, $C^{20}H^8,4SO^3$, and acquires a red colour. (Berzelius.)

With *sulphuric anhydride,* naphthalin melts to a dark red mass, which turns blackish-green, and contains principally sulphonaphthalic acid (Liebig and Wöhler); in this reaction, sulphurous acid is always evolved, even when naphthalin is placed with sulphuric anhydride under a bell-jar; the products are the same as those obtained by the action of sulphuric acid; only the colouring matter, bisulphonaphthalic acid, and sulphonaphthalide are formed in larger quantity, and hyposulphoglutic acid is likewise obtained. (Berzelius.)

Warmed with *phosphoric anhydride,* naphthalin volatilizes unchanged (Laurent); it is not attacked by concentrated *acetic* or *oxalic* acid; or by *caustic potash-solution* even on boiling (Reichenbach); or by fused *potassium* (Laurent).

14. When equal parts of naphthalin and fat are exposed to the air for a week, the mixture absorbs oxygen, which, together with part of the oxygen of the fat, is taken up by the naphthalin, giving rise to naphtholeic acid and a hydrocarbon; at the same time, a little carbonic acid is evolved and the mixture turns black. Naphtholeic acid, extracted from the mixture by ether, is a semi-fluid body becoming fluid at 20° C., yellowish, and transparent, and smells like crude naphthalin; it contains 65·65 p. c. C, 14·22 H, and 20·13 O, and forms soaps with the alkalis, uncrystallisable salts with baryta, strontia, lime, lead, copper, and silver; and decomposes partly at 75^c, evolving strong suffocating vapours. (Rossignon.) It is rancid fat. (Gm.) — The hydrocarbon remains in the residue when the mixture is extracted with ether, and is purified by washing with ether, pressing between blotting paper, and crystallising from boiling alcohol. Forms thick silky flakes, soft to the touch, softening between the fingers, its consistence varying according to the nature of the fat; contains C and H in the proportion of 2:2·5 (has not been analysed!) (Rossignon, *Compt. rend.* 14, 61.) — It is impure naphthalin. (Gmelin.)

Combinations. 1. Naphthalin does not dissolve in cold *water*, or in aqueous alcohol. (Garden.) It dissolves slightly in boiling water; the solution deposits most of the naphthalin on cooling, but remains turbid, and in that state passes through the filter. (Kidd.) — 2. Dissolves very rapidly in *bisulphide of carbon.* (Reichenbach.) — 3. Dissolves in *alcohol,* especially in hot alcohol, and is precipitated from the solution by water (Garden, Reichenbach); the solution in 4 pts. hot alcohol yields on cooling a solid crystalline mass, the solution in 11 pts. yields fine crystals. (Kidd.) — 4. In *ether* it dissolves more readily (Kidd, Ure), and very rapidly. (Reichenbach.) — 5. Dissolves in aqueous *oxalic* and *acetic acids* with bright red colour, the warm-saturated solution solidifying in a crystalline mass on cooling. (Garden, Kidd.) 6. Dissolves in *oils both fat and volatile* (Garden); in *oil of turpentine,* the temperature falling 4·2°, and the hot solution on cooling yields fine crystals. (Chamberlain.) Dissolves slowly in *eupione,* gradually in *creosote,* slowly in *picamar* and in *cold olive-oil.* (Reichenbach.)

Insoluble in aqueous *alkalis.* (Garden.) Does not absorb *ammonia-gas.* (Kidd.)

7. With *Picric acid.* — 1. A mixture of naphthalin and picric acid is dissolved in warm alcohol (or in benzene); and the golden yellow needles which separate on cooling are washed with a little alcohol, gently pressed between blotting paper, and dried by exposure to the air. — 2. This compound is precipitated in much smaller crystals than those obtained according to 1, when the cold-saturated solutions of naphthalin and picric acid in alcohol are mixed. — Golden-yellow crystals, melting at 149° to a clear orange-yellow liquid and at the same time evolving a little naphthalin. It is superficially decomposed by cold water, which removes picric acid, and more freely by boiling water, part of the naphthalin passing off in vapour; nevertheless microscopic needles of the compound are obtained from the filtered solution. It yields all its picric acid to warm dilute aqueous ammonia. Dissolves in alcohol, ether, and benzene, separating out undecomposed on evaporation. (Fritzsche, *Petersb. Acad. Bull.* 16, 120; *J. pr. Chem.* 72, 282.)

			Fritzsche.
1 At. naphthalin $C^{20}H^8$	128	35·84	
1 At picric acid $C^{12}X^3H^3O^2$	229	64·16	64·40
$C^{20}H^8 + C^{12}X^3H^3O^2$	357	100·00	

Appendix to Naphthalin.

A. Metanaphthalin. $C^{20}H^8$.

Pelletier & Walter. (1837.) *Ann. Chim. Phys.* 67, 269; *Pogg.* 44, 81.

Dumas. *Compt. rend.* 6, 460; *Pogg.* 44, 110; *J. pr. Chem.* 14, 214.

Retiserin. (Pelletier and Walter.)

Formation. Found accompanying naphthalin in the tar formed when illuminating gas is prepared by dropping melted pine-resin into red-hot iron cylinders; it probably exists also in many other empyreumatic products. (Pelletier & Walter.)

Preparation. Resin is submitted to distillation; the buttery mass passing over towards the end is collected apart; all adhering liquid is removed as completely as possible by pressure between blotting paper;

and the residue is dissolved in absolute alcohol. The solution, treated with animal charcoal at a temperature a little above 40° C., then filtered and allowed to cool, yields crystals of metanaphthalin, which may be purified by repeated recrystallisation. (Pelletier & Walter.)

Properties. White nacreous crystalline flakes, unctuous to the touch, having a feeble odour of wax but no taste. Melts at 67° C.; distils over at 325° as an oil, which solidifies in a crystalline mass on cooling. Unaffected by light and air. (Pelletier & Walter.)

			Pelletier & Walter *mean.*	Dumas. *mean.*
20 C	120	93·75	93·72	93·4
8 H	8	6·25	6·72	7·0
$C^{20}H^8$	128	100·00	100·44	100·4

According to Dumas, the formula is perhaps $C^{32}H^{14}$, which requires 93·2 p. c. C and 6·8 p. c. H.

Decompositions. 1. Metanaphthalin is not acted upon by aqueous *chlorine*, but if chlorine gas be passed into the melted substance, it is converted, with evolution of hydrochloric acid gas, into a green resin, which is not crystallisable, and is still less soluble in absolute alcohol than metanaphthalin. (Pelletier & Walter.) — 2. Cold *nitric* acid acts but slightly upon metanaphthalin; heated acid converts it into an ochre-yellow resin which decomposes by heat, without volatilising. (This distinguishes it from naphthalin.) (Pelletier and Walter.) 3. *Oil of vitriol* does not act in the cold or on gently warming; but if metanaphthalin be boiled with a large excess of oil of vitriol, it becomes carbonized. No sulphometanaphthalic acid appears to be formed in this reaction. (Pelletier & Walter.)

Combinations. Insoluble in *water.* — Dissolves *sulphur* by heat. (Pelletier & Walter.) — Metanaphthalin is not attacked by *potassium* or by other metals; neither does it combine with the *alkalis.* — Dissolves slightly in cold, and very abundantly in hot *alcohol,* crystallising therefrom on cooling; it is still more soluble in *ether* (paranaphthalin is insoluble in ether), and most soluble in *rock-oil, oil of turpentine,* and other *hydrocarbons.* (Pelletier & Walter.)

B. Bodies isomeric with Naphthalin, and obtained by the dry distillation of the Benzoates.

LAURENT & CHANCEL. *Compt. chim.* 1849, 117; *J. pr. Chem.* 46, 510; *Liebig & Kopp's Jahresb.* 1849, 326.

CHANCEL. *Compt. chim.* 1849, 87; *Compt. rend.* 28, 83; *Instit.* 1849, 19; *Ann. Pharm.* 72, 279; *Pharm. Centr.* 1849, 216; *Liebig & Kopp's Jahresb.* 1849, 326; Further, *Compt. chim.* 1851, 85; *Ann. Pharm.* 80, 285; *J. pr. Chem.* 53, 252; *Liebig & Kopp's Jahresb.* 1851, 432.

LIST & LIMPRICHT. *Ann. Pharm.* 90, 209.

a. Hydrocarbon $C^{20}H^8$, *melting at* 92°.

Formation. Formed together with *b.* in the preparation of benzone (xii, 40), by the dry distillation of benzoate of lime; on rectifying the crude liquid, *a* and *b* are obtained in the portion which passes over up to 315° C, before the benzone. — *a.* and *b.* are doubtless secondary products formed by the decomposition of benzone (Chancel.)

$$2\,C^{26}H^{10}O^2 = C^2O^4 + C^{20}H^8 + C^{30}H^{12}.$$

Preparation. The various products from the dry distillation of benzoate of lime are dissolved in oil of vitriol, whereupon the hydrocarbon *a* rises almost instantly to the surface of the liquid. This substance is removed, washed with water, repeatedly pressed between blotting paper, and recrystallised once or twice from boiling alcohol. (Chancel.)

Properties. Crystallises readily in fine needles, melts at 92°, and volatilizes at a high temperature only (Chancel).

		[illegible]	Chancel. *average.*
20 C	120	93·75	93·46
8 H	8	6·25	6·49
$C^{20}H^8$	128	100·00	99·95

From the high boiling point of *a* (and *b*), Chancel concludes that the atomic weight of *a* (and of *b* as well) must be very high; perhaps $C^{20}H^8$ or $C^{30}H^{12}$.

Dissolves more readily in *alcohol* and in *ether*, than *b*. (Chancel.)

b. Hydrocarbon $C^{20}H^8$, *melting at* 65°.

Formation. (Comp. p. 11.) 2. By passing the vapour of benzoate of ammonia over red-hot baryta, much benzonitrile, $C^{14}NH^5$ (xii, 161) being at the same time produced. (Laurent & Chancel.) — 3. By the dry distillation of benzoate of potash. (Chancel). — 4. When benzoate of copper is submitted to dry distillation (see xii, 43), the products there mentioned are obtained, together with an oil boiling at 260° which, by heating with oil of vitriol, is resolved into sulpho-carbolic acid and crystals, the latter separating out as the sulphuric acid solution cools, and more completely by the addition of water. These crystals appear to be identical with Chancel's hydrocarbon *b.* (List & Limpricht.)

Preparation. 1. The following is the best method. When benzoate of lime is mixed with potash-lime, and submitted to dry distillation, a solution of *b* in benzene is obtained. The solvent is removed by distillation in a water bath, and the residue is purified by crystallisation from alcohol (Chancel). — The vapour of benzoate of ammonia is passed through a tube containing red-hot baryta, and the small quantity of crystals obtained together with benzonitrile, is purified by sublimation and crystallisation from alcohol. (Laurent & Chancel.)

Properties. Colourless (nacreous, iridescent (List & Limpricht) laminæ, crystallising with difficulty, and melting at 65° (69° according to List & Limpricht). Volatilises without decomposition at a very high temperature. (Laurent & Chancel). Has a faint agreeable smell of roses.

			Chancel. *average.*	Laurent & Chancel.	List & Limpricht.
20 C	120	93·75	93·54	93·9	93·41
8 H	8	6·25	6·47	6·4	6·66
$C^{20}H^8$	128	100·00	100·01	100·3	100·07

According to Gerhardt (*Traité* 3, 984) the body is perhaps $C^{24}H^{10}$ phenyl (by calculation, 93·5 p. c. C, 6·5 p. c. H).

Forms a crystallisable substance with *bromine* (this distinguishes it from naphthalin). (Chancel.)

It is far less soluble in *alcohol* and in *ether* than *a*. (Chancel.)

Conjugated compounds of the nucleus $C^{20}H^8$.

Sulphonaphthalic Acid.

$C^{20}H^8S^2O^6 = C^{20}H^8,2SO^3$.

Faraday. *Phil. Trans.* 1826, 140; *Schw.* 47, 355 and 459; Extr. *Pogg.* 7, 104.
Berzelius. *Pogg.* 44, 377; *Ann. Pharm.* 28, 9; abstr. *Berz. Jahresb.* 18, 468.
Regnault. *Ann. Chim. Phys.* 65, 87; *J. pr. Chem.* 12, 99.
Liebig & Wöhler. *Pogg.* 24, 169.
Gregory. *Ann. Pharm.* 22, 272.
Wöhler. *Ann. Pharm.* 37, 197.
Laurent. *Compt. rend.* 21, 33; *Compt. chim.* 1849, 390; Extr. *Ann. Pharm.* 72, 297.

Sulphonaphthalic acid (Faraday); *Hyposulphonaphthalic acid* (Berzelius); *Sulphonaphthanic acid* (Laurent); *Dithiononaphthylic acid* (Kolbe). — First prepared and investigated by Faraday.

Formation. Produced by melting naphthalin with oil of vitriol (Faraday), or with sulphuric anhydride (Liebig & Wöhler), or with Nordhausen sulphuric acid, — bisulphonaphthalic acid, sulphonaphthalin, sulphonaphthalides, and a red colouring matter, being in all cases simultaneously formed. (Berzelius.) — The last four products are obtained in larger quantity, when Nordhausen sulphuric acid or sulphuric anhydride is employed (in which case hyposulphoglutic acid is formed, and sulphurous acid is always evolved), the proportion increasing with the violence of the reaction. (Berzelius). — When oil of vitriol is employed, a particular acid is likewise formed, yielding with baryta, Faraday's *smouldering baryta-salt.* (Faraday.) Regnault did not obtain this salt, but Berzelius produced it in small quantity. — If an excess of sulphuric anhydride is employed, no undecomposed naphthalin is left. (Liebig & Wöhler.) If oil of vitriol is used, the whole of the sulphuric acid does not pass into combination, even when the naphthalin is in excess and the mixture is warmed for several hours (Faraday); on the contrary, when 14 atoms of boiled oil of vitriol are digested at 100° C, for 12 hours, with an excess of naphthalin, 5 At. of sulphonaphthalic acid at the most are formed, and there remain 4 At. of 3½-hydrated sulphuric acid, which is no longer capable of forming sulphonaphthalic acid. Bi- and even terhydrated sulphuric acid still form a certain quantity of sulphonaphthalic acid. (Regnault.)

Preparation. A. *Free acid.* 1. The thick liquid which is obtained by saturating the most highly concentrated oil of vitriol at 90° with naphthalin, and does not solidify when kept from the air, is allowed to absorb moisture from the air, whereby it is converted after a few days into a dirty violet mass. The same reaction is produced, by directly mixing the thick liquid with a little water. When the solidified mass has been as far as possible freed from adhering sulphuric acid by spreading it upon a porous tile, and then by pressure between two other tiles, it yields almost white talc-like scales, which are a mixture of sulphonaphthalic acid, bisulphonaphthalic acid, and a little free sulphuric acid. (Wöhler.) — 2. May be obtained pure, when prepared as above from the baryta or lead-salt, either by decomposing the lead-salt with sulphuretted hydrogen (Regnault), or by decomposing the baryta-salt with sulphuric acid (Faraday), removing the excess of sulphuric acid by carbonate of lead, and precipitating the lead from the solution by sulphuretted hydrogen; the filtered solution, evaporated in vacuo over sulphuric acid, yields a syrupy liquid, which after several days solidifies in a crystalline mass. (Berzelius.)

B. *Baryta-salt. a. With Oil of Vitriol.* 1. Seven hundred pts. of naphthalin are melted with 520 pts. oil of vitriol, and the whole shaken together. After the mass has become solid, the cake of crystals is removed from the liquid beneath it, and melted with 300 pts. more of naphthalin. On cooling, an opaque liquid is obtained, which separates into two strata. The lower stratum is warmed and shaken with $\frac{1}{5}$ of its bulk of water, whereby most of the excess of naphthalin (and the rest on further dilution) is precipitated, after which the liquid is diluted with more water and neutralized with carbonate of baryta, whereupon the slight coloration of the liquid completely disappears. The whole is then filtered and the precipitate slightly washed. The precipitate contains, besides carbonate and sulphate of baryta, Faraday's smouldering baryta salt, which may be extracted by boiling water. The filtered solution yields on evaporation sulphonaphthalate of baryta. (Faraday.)

2. Naphthalin is digested with 2 pts. oil of vitriol between 70° and 80° for several hours, and the resulting dark-red solution is diluted with water, neutralized with carbonate of baryta, filtered hot, and crystallised by cooling. The mother-liquor yields more crystals on evaporation, and the residues on the filter when boiled with water, likewise yield a little more of the same salt. The baryta-salt is purified by recrystallisation. (Regnault.)

3. *The best method.* Naphthalin, freed from water by melting at 100°, is added in small portions to oil of vitriol which has been distilled and perfectly dried by prolonged heating, and the whole heated in a water bath to 100° C. (90° Wöhler), whereupon the naphthalin melts, and dissolves, without evolution of gas, forming a yellowish red solution Naphthalin is continually added till the liquid, after being warmed for half-an-hour, deposits undecomposed naphthalin when diluted with water; further addition is superfluous. The liquid, which when cool is homogeneous, red and viscid, is diluted, and the naphthalin, part of which is deposited immediately and the rest in the form of scales on cooling, is separated by filtration. The residue on the filter partly dissolves in the wash-water (the soluble portion appears to consist of naphthalin together with sulphonaphthalic acid.) The bright brown-yellow filtrate contains sulphonaphthalic acid, bisulphonaphthalic acid, free sulphuric acid and a red colouring matter. To purify the first two and to separate them from one another, either of the following methods may be adopted. (*a.*) The impure acids are

saturated with carbonate of baryta; the baryta is precipitated from the filtrate by sulphuric acid, whereupon the red colouring matter is likewise precipitated; and the now colourless filtrate is again saturated with carbonate of baryta, filtered, concentrated by evaporation, and mixed with twice its volume of alcohol, whereupon the mixture becomes turbid, and deposits for several hours a pulverulent precipitate of bisulphonaphthalic acid. The greatest part of the alcohol is then distilled off from the residual solution, which on cooling deposits part of the suplhonaphthalate in brilliant scales. On evaporating down the mother-liquor and adding alcohol, a fresh portion of the nearly insoluble bisulphonaphthalin is deposited; and the filtrate, which when treated with acetate of lead gives only a slight precipitate after long standing, deposits sulphonaphthalate of baryta in scales. — (*b.*) The impure acids are completely freed from sulphuric acid by carbonate of baryta, and the solution only half neutralized with carbonate of baryta, whereupon the liquid solidifies in a thick mass of small scaly crystals. In this manner, only the stronger sulphonaphthalic acid is neutralized of which the baryta-salt being, almost insoluble in the cold acid liquid, is separated; but if the whole were completely neutralized or merely warmed, the precipitate would redissolve. The salt is collected on a filter, washed with cold water, and dissolved to saturation in boiling water, from which it crystallises in scales on cooling. In this way, pure sulphonaphthalate of baryta is obtained (the concentrated solution of which is not precipitated by alcohol, and only after several days by acetate of lead), bisulphonaphthalic acid remaining in solution. (Berzelius.)

b. With Sulphuric Anhydride. The vapour of sulphuric anhydride is passed into a receiver, wherein naphthalin is kept in fusion. The mass, which at first turns red, and afterwards dark brown, is dissolved in boiling water, and the naphthalin, which partly solidifies on the surface, and partly crystallises out on cooling, is separated by filtration. The sulphonaphthalic and bisulphonaphthalic acids thus obtained, are purified and separated by methods *a* or *b*.

Properties. Known only as a bihydrated acid. — White, solid mass, hard and brittle when completely dry. (Faraday.) Solidifies in an irregular crystalline mass when the aqueous or alcoholic solution is evaporated (Regnault). Melts below 100° without decomposition and solidifies in a crystalline mass on cooling (Faraday). Melts between 85° and 90° (Regnault). Tastes bitter, acid, and somewhat metallic, like copper salts.

			Regnault. *in vacuo.*
20 C	120	53·08	53·71
10 H	10	4·43	4·69
8 O	64	28·32	
2 S	32	14·17	
$C^{20}H^8,2SO^3+2Aq$	226	100·00	

Sulphonaphthalic acid is a compound of unaltered naphthalin with sulphuric acid $= C^{20}H^8 + 2SO^3$. (Faraday, Laurent.) Contains hyposulphuric acid, and is formed by the simple combination of naphthalin with sulphuric acid:

$$C^{20}H^8 + 2SO^3 = C^{20}H^7S^2O^5,HO,$$

the 1 At. of water being replaceable by bases. (Regnault.) Contains hyposulphuric acid, as is rendered probable by the behaviour of the potash-salt when boiled with potash, and of the mixture when evaporated to dryness and strongly heated. If the acid (according to Regnault) = $C^{20}H^7S^2O^5,HO$, the baryta salt should give on analysis 22·61 p. c. water; Regnault obtained 23·73, Berzelius 24·65 p. c. (average) of water; hence the formula of the acid = $C^{20}H^8S^2O^5,HO$. The formation of sulphonaphthalic acid by the action of sulphuric acid upon naphthalin, is not so simple as Regnault supposes, since other products are always formed as well as this acid. — The acid may also be viewed as a compound of 1 At. sulphonaphthalin with 1 At. sulphuric acid. (Berzelius.)

Decompositions. Melts between 85° and 90°, evolving part of its water of crystallisation, but decomposes before all the water has been driven off; at about 120° C, it begins to smell of naphthalin; at a higher temperature, it swells up and leaves a very brittle shining residue of carbon (Regnault). At a gentle heat, sulphonaphthalic acid turns red, without evolution of sulphurous acid, gives off a little water, and then contains free sulphuric acid; if a stronger heat be applied, it evolves a little naphthalin, and assumes a dark brown colour, carbonization then suddenly setting in from the bottom of the vessel, and spreading rapidly through the entire mass; at a still greater heat, naphthalin, sulphurous acid, and charcoal are obtained; but even after ignition, the residue still contains a little sulphonaphthalic acid. (Faraday.)

If the concentrated aqueous solution be warmed, it first turns yellow, then brown, and is found to contain a yellow colouring matter, which also passes into most of the salts; it can only be separated from the baryta-salt, by adding a few drops of sulphuric acid, and afterwards treating the solution with a little oxide of lead. (Berzelius.)

2. The aqueous acid placed in the circuit of the *voltaic battery*, gives off hydrogen at the negative pole, and oxygen and sulphuric at the positive pole; the sulphuric acid acting upon the naphthalin, produces a dark yellow colour. (Faraday.)

3. *Nitric Acid* converts it, first into nitro-sulphonaphthalic acid, and afterwards, by prolonged action, into binitrosulphonaphthalic acid. (Laurent.)

4. The potash-salt, boiled for a long time with an excess of *potash*, yields neither naphthalin nor sulphuric acid, but crystallises out unchanged on cooling. If the mixed solution be evaporated to dryness and the residue of potash-salt and potash be heated till naphthalin begins to sublime, and the mass turns dark, its solution in water smells of creosote, a blackish brown residue remains undissolved, and the dark yellow solution gives with hydrochloric acid, a whitish precipitate of fine, slowly subsiding crystalline scales. More of this substance is extracted by alcohol from the residue; the solution acidified with hydrochloric acid, smells of sulphurous acid, and evolves that gas on boiling. (Berzelius.)

5. The potash-salt, heated with *sulphide of hydrogen and potassium*, yields a very foul-smelling liquid which is soluble in water and does not precipitate lead-salts (naphthalin-mercaptan) (Gregory).

Combinations.. The acid deliquesces in the air, and is very soluble in *water*. (Faraday.)

Sulphonaphthalates. The acid neutralises alkalis. The concentrated solution precipitates chloride of barium, but the precipitate dissolves on addition of water. The formula of the salts is $C^{20}H^7MS^2O^6$. Submitted to dry distillation, they yield first water and a little naphthalin, then sulphurous and carbonic acids, and leave a residue of sulphate, sulphide, and charcoal. Heated in the air, they burn with flame, and leave a residue of sulphate mixed with charcoal. (Faraday.) They deflagrate violently with nitre; do not give off naphthalin when boiled with potash; decompose slowly when the dried residue is strongly heated, (Regnault.) They are all soluble in water, and mostly soluble in alcohol. (Faraday.)

Sulphonaphthalate of Ammonia. Ill-defined crystals having a cooling saline taste. Melts and blackens by heat, burns with flame, and leaves a residue of acid sulphate of ammonia mixed with charcoal. If the aqueous solution be evaporated at ordinary temperatures, even when containing an excess of ammonia, it acquires the property of reddening litmus. Readily soluble in water, but not deliquescent. (Faraday.)

Sulphonaphthalate of Potash. Obtained by decomposing the baryta salt with sulphate of potash. (Regnault.) Colourless, soft crystals, unctuous to the touch, sometimes transparent, sometimes opaque, occasionally forming efflorescences composed of small needles. (Faraday.) Small, white, very brilliant flakes, giving off in vacuo 3·78 p. c. aq. (1 At.=3·53 p. c.) (Regnault.) Permanent in the air; taste bitter and saline. (Faraday.)

	In vacuo.		Regnault.
20 C	120·0	48·73	48·98
7 H	7·0	2·84	3·04
KO	47·2	19·16	19·09
2 S	32·0	12·99	13·24
5 O	40·0	16·28	15·65
$C^{20}H^7K,2SO^3$	246·2	100·00	100·00

The salt burns with flame in the air, and leaves a residue of sulphate of potash having a very feeble alkaline reaction. (Faraday.) Dissolves readily in water; the colourless solution is not decomposed by repeated evaporation and crystallisation. Dissolves in alcohol, forming a colourless liquid. (Faraday.)

Soda-salt. — White nacreous crystals permanent in the air and having a peculiar and decided metallic taste. (Faraday.)

Sulphonaphthalate of Baryta. (*Burning with flame,* Faraday.) *Preparation* (comp. p. 14.) Crystallises in tufts when the aqueous solution is slowly evaporated (Faraday), in cruciform laminæ resembling prehnite (Regnault). Deposited in grains on cooling the hot aqueous solution (Faraday). Crystallises in foliated masses from the hot solution (Regnault). Crystallises from boiling alcohol in large transparent scales, which, on drying, cohere in a mass having a silvery lustre. (Berzelius.) After drying it appears white and tender, soft to the touch. Tastes bitter. Permanent in the air. The salt dried in vacuo, as well as that dried in the air, still contains 1 at. water, and gives off at 100°, 3·485 p. c. water =1 at. (Regnault.) Contains 1 at. of water of crystallisation, which is completely expelled at 50°. (Berzelius.)

			Regnault.	Liebig & Wöhler.	Faraday.
			at 160°.	*at* 100°.	
20 C	120	43·55	43·80	43·40	41·90
7 H	7	2·54	2·66	2·86	2·86
BaO	76·5	27·76	27·59	26·58	27·57
2 S	32	11·61	11·76		
5 O	40	14·54	14·19		
$C^{20}H^7Ba,2SO^3$	275·5	100·00	100·00		

Berzelius obtained on the average 41·83 p. c. sulphate of baryta from the salt dried at 100°.

Sulphonaphthalate of baryta, heated in a tube, evolves naphthalin, but not till the temperature exceeds 260° (a non-inflammable gas is evolved according to Regnault), then sulphurous acid and a little tarry matter, and at a very high temperature, leaves a blackish mixture of charcoal, sulphate of baryta, and sulphide of barium. (Faraday and Regnault.) — Heated on platinum foil, it burns with a brilliant, very smoky flame, and leaves the same blackish residue. — Not decomposed by boiling with moderately strong nitric or nitro-hydrochloric acid, so that no sulphate of baryta is precipitated from the solution; if, however, the acids are very concentrated, sulphuric acid is then liberated and other special decomposition-products are formed. (Faraday.) — Chlorine does not decompose the dry salt, unless heat is applied, whereupon the chlorine acts upon the naphthalin as it is liberated. — Soluble in alcohol, insoluble in ether.

Sulphonaphthalate of Strontia. — White, imperfectly crystalline substance, resembling the baryta-salt; it is permanent in the air. Burns with a brilliant, but not red flame, leaving a residue similar to that of the baryta-salt. Soluble in water and in alcohol. (Faraday.)

Suphonaphthalate of Lime crystallises imperfectly and has a bitter taste. Heated in a tube, it yields the same products as the baryta-salt. Burns with flame. Dissolves slightly in water; soluble in alcohol. (Faraday.)

Sulphonaphthalate of Magnesia. — White, crystallisable salt, of moderately bitter taste. Behaves like the baryta-salt when heated in a tube; burns with flame. (Faraday.)

Sulphonaphthalate of Manganese is neutral, has an astringent taste, and gives the same results on heating as the baryta-salt. Dissolves in water and in alcohol. (Faraday.)

Sulphonaphthalate of Zinc. — Obtained by dissolving the metal (in which case hydrogen is evolved), or the hydrated oxide, in sulphonaphthalic acid. White, bitter needles, permanent in the air, and burning with flame. Soluble in hot water. (Faraday.)

Sulphonaphthalate of Lead is prepared by dissolving oxide of lead in the free acid. (Regnault.)

a. Neutral. White salt, permanent in the air (Faraday); crystallises still more irregularly than the baryta-salt. (Regnault.) Exactly like the baryta-salt, but more soluble; crystallises by spontaneous evaporation in crystals which may be split into plates like mica. (Berzelius.) Tastes bitter, metallic, and slightly sweet.

			Regnault. *at* 180°.
20 C	120	38·63	38·50
7 H	7	2·26	2·40
PbO	111·7	35·93	35·75
2 S	32	10·29	10·21
5 O	40	12·89	13·14
$C^{20}H^7Pb,2SO^3$	310·7	100·00	100·00

Behaves like the other salts when heated. (Faraday.) Decomposes by heat with increase of volume, and forms ramifications in all directions. (Regnault.)

Dissolves in water and in alcohol. (Faraday.) It is less soluble in water containing free acid, than in pure water; the warm-saturated solution solidifies on cooling in an interwoven mass of scales. (Berzelius.)

b. Basic. The neutral salt *a* is dissolved in water, and the solution boiled for some time with oxide of lead. The diluted solution on cooling deposits the new salt in crystalline flakes. Contains 53·81 p. c. oxide of of lead, which is expressed by the formula: $C^{20}H^7Pb,2SO^3 + PbO$. (Regnault).

c. When the solution of *b* is boiled for a considerable time longer with massicot, the decanted liquid deposits an abundant white powder, and scarcely anything remains in solution. (Regnault, Berzelius.) Regnault found 70·36 p. c. oxide of lead, corresponding to the formula, $C^{20}H^7Pb, 2SO^3 + 3PbO$.

Berzelius obtained a fourth basic salt of lead by prolonged boiling of the neutral salt with oxide of lead. A mass was deposited insoluble in water, soft and viscid when warmed, but becoming hard on cooling.

Ferrous Sulphonaphthalate is obtained by dissolving the metal (hydrogen being evolved), or the hydrated ferrous oxide in the acid. Crystallisable. The aqueous solution absorbs oxygen from the air. (Faraday.)

Sulphonaphthalate of Nickel. — *a. Neutral.* Formed by dissolving the carbonate of the base in the acid. Green crystals decomposible in the ordinary way by heat; soluble in water. (Faraday.)

b. Basic. Insoluble in water.

Sulphonaphthalate of Copper is prepared by dissolving hydrated oxide of copper in the acid. Laminæ united so as to present a radiated appearance; very pale green. Contains water of crystallisation, which it partly loses in dry air. Melts by heat, and burns with flame attended with the usual phenomena. (Faraday.)

Mercurous Sulphonaphthalate.—Formed by dissolving the freshly precipitated carbonate in the acid. White, slightly crystalline salt, having a metallic taste and feebly acid reaction. Destroyed by heat. When dissolved in water or alcohol, it leaves a yellow basic salt. (Faraday.)

Mercuric Sulphonaphthalate. — The solution of the recently precipitated oxide leaves on evaporation a yellow deliquescent residue. May be set on fire in the air. (Faraday.)

Sulphonaphthalate of Silver. — When the freshly precipitated hydrated oxide is dissolved in the acid, the almost neutral, brown solution, leaves on evaporation a brilliant, white, crystalline salt, permanent in the air, and having an intensely metallic taste. (Faraday.) Micaceous laminæ soluble in 9·7 pts. water at 20° C. (Regnault.) Regnault found 36·03 p. c. AgO (calculation, $C^{20}H^7Ag,2SO^3 = 36{\cdot}84$ p. c. AgO). The aqueous solution deposits by prolonged boiling a black insoluble mass and then yields by evaporation abundant yellow crystals. (Faraday.) Does *not* decompose, even after several hours' boiling. (Regnault.) Burns with flame, leaving as final residue pure metallic silver.

Sulphonaphthalic acid dissolves in *alcohol*, slightly in *ether*. Dissolves in *oil of turpentine*, *olive-oil*, and melted *naphthalin*, and in greater proportion the more anhydrous it is. The solution in naphthalin forms on cooling two strata, the upper of which is a solution of the anhydrous acid, the lower a solution of the hydrated acid in naphthalin. (Faraday.)

Acid of Faraday's Smouldering Baryta-salt.

$C^{20}H^8,2SO^3$?

Faraday. *Phil. Trans.* 1826, 140; *Schw.* 47, 355 and 459; abstr. *Pogg.* 7, 104.
Berzelius. *Pogg.* 44, 377; *Ann. Pharm.* 28, 9.

Formation and Preparation. By acting on naphthalin with sulphuric acid, Faraday obtained, besides sulphonaphthalic acid, a second acid, which, he says, is formed in proportionally smaller quantity, as the oil of vitriol is allowed to act upon the naphthalin at a lower temperature and in smaller quantity. The baryta-salt remains upon the filter, after the saturation of the impure sulphonaphthalic acid, together with the sulphate of baryta and a little sulphonaphthalate of baryta. The matter is extracted with boiling water, and the two baryta-salts are separated by crystallisation. (Faraday.) To obtain the acid, the lead-salt is decomposed with sulphuretted hydrogen, and the filtrate evaporated in vacuo over sulphuric acid. (Berzelius.)

Mass crystallising in scales, soft to the touch, tasting acid and bitter like sulphonaphthalic acid.

Does not absorb moisture from the air, but gradually turns yellowish-brown by the action of sunlight.

The *potash-salt* crystallises in scales, readily soluble in alcohol. It is not decomposed by boiling with concentrated potash-solution, but crystallises out unchanged on cooling.

Baryta-salt.—Small, translucent prisms, grouped in tufts, perfectly neutral, and almost tasteless.

			Faraday. *at* 100°.
20 C	120	43·55	42·40
7 H	7	2·54	2·66
BaO	76·5	27·76	28·03
2 S	32	11·61	
5 O	40	14·54	
$C^{20}H^7Ba,2SO^3$	275·5	100·00	

Since this salt is just as neutral as that of sulphonaphthalic acid, it appears to differ from the latter only by a slightly lower percentage of naphthalin. (Faraday.) The baryta-salt contains exactly as much baryta as the common sulphonaphthalate; hence it is probable that the acid contains hyposulphuric acid in combination with an isomeric modification of naphthalin. (Berzelius.)

The baryta-salt, heated in a tube, evolves only a little naphthalin together with a vapour having an empyreumatic odour, and a little sulphurous acid, and leaves the same residue as sulphonaphthalate of baryta. Heated on platinum foil, it gives only a slight flame, but rather smoulders away like tinder. The salt, heated for three hours to 227°, increases by only 0·8 per cent. of its weight in the air. Soluble in water, but much less than the sulphonaphthalate of baryta. (Faraday.)

Lead-salt. — Exactly like the baryta-salt. (Berzelius.)

Bisulphonaphthalic Acid.

$C^{20}H^8S^4O^{12} = C^{20}H^8,4SO^3$.

BERZELIUS. *Pogg.* 44, 393; *Ann. Pharm.* 28, 9; abstr. *Berz. Jahresb.* 18, 468.

LAURENT. *Compt. chim.* 1845, 177; *Compt. rend.* 21, 33; *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 297; *Liebig & Kopp's Jahresb.* 1849, 440.

Hyposulphonaphthalic acid. (Berzelius.) *Sulphonaphthalic acid, Thionaphthalic acid, Thionaphthyl-Dithionschwefelsäure.* (Kolbe.) *Disulfonaphtalinsäure.*

Formation. Comp. p. 14. (*Sulphonaphthalic acid.*)

Preparation. The bisulphonaphthalate of baryta precipitated by alcohol in the preparation of sulphonaphthalate of baryta (p. 14, 3, *a*), is washed with alcohol, dried, and dissolved in boiling water, whereby a yellow solution is generally formed. In order to get rid of the colour, part of the baryta is precipitated with sulphuric acid; the acid solution is saturated with carbonate of lead and filtered; the oxide of lead reprecipitated by baryta, and filtered; and the liquid free from oxide of lead, is slightly acidified with dilute sulphuric acid, then filtered, and evaporated down, whereupon the baryta-salt crystallises. The crystals are washed with alcohol till the liquid ceases to redden litmus. The acid mother-liquor, evaporated almost to dryness, mixed with the wash-alcohol, and then washed with fresh alcohol, yields a fresh portion of the salt. The baryta-salt is dissolved in water, and precipitated by sulphuric acid; the excess of sulphuric acid is removed by carbonate of lead, and the lead in solution is precipitated by sulphuretted hydrogen. The filtrate is first evaporated on a water-bath, till the sulphuretted hydrogen is driven off, and then in vacuo over sulphuric acid. The solution acquires the consistence of syrup, and then dries up to a lamino-crystalline, slightly yellow mass. (Berzelius.)

In the solid form, bisulphonaphthalic acid feels soft like powdered talc, and tastes acid and bitter, like suphonaphthalic acid. It becomes coloured by exposure to the air, especially if repeatedly allowed to absorb moisture and afterwards dried in the sun.

Bisulphonaphthalates. Bisulphonaphthalic acid is *bibasic.* Its salts $= C^{20}H^6M^2,4SO^3$; according to Berzelius, they are $C^{11}H^{4\cdot5}O,MO,S^2O^5$. They resemble the sulphonaphthalates and have the same bitter taste. They require a very high temperature to decompose them, and then yield naphthalin and sulphurous acid. They are not changed by boiling with concentrated potash, but if the mixture is evaporated down till the residue chars, the solution therefrom treated with sulphuric acid, evolves sulphurous acid. The salts are readily soluble in water. To ascertain whether a small quantity of one of these salts is mixed with a sulphonaphthalate, the substance is dissolved in alcohol of sp. gr. 0·84 and a few drops of acetate of lead are added to the solution, whereupon a precipitate is formed, bisulphonaphthalate of lead being almost insoluble in alcohol. (Berzelius.)

Bisulphonaphthalate of Ammonia exactly resembles the potash-salt; evaporated at a gentle heat, it becomes coloured, and the residue contains free acid.

Bisulphonaphthalate of Potash is obtained by spontaneous evaporation, as a white granular mass; crystallises from a warm solution of aqueous potash, in scales united in arborescent groups. Readily soluble in water, slightly soluble in alcohol.

Bisulphonaphthalate of Soda does not afford good crystals by spontaneous evaporation; it is more soluble in alcohol than the potash-salt.

Bisulphonaphthalate of Baryta is deposited, by evaporation of the solution on a water-bath, in crystalline crusts on the bottom of the vessel and on the surface of the liquid. If the hot solution be allowed to cool slowly, the liquid becomes filled with a non-crystalline woolly vegetation of the salt. — Snow-white substance, resembling chalk.

The anhydrous salt, exposed to heat, yields a sublimate of naphthalin, but not till charring has commenced, and gives acid vapours which however do not smell of sulphurous acid. Dissolves very slowly in water, even at the boiling heat. The solution may be evaporated down to a considerable extent before yielding any deposit; it generally turns yellow on evaporation, but, when containing free acid, deposits a white salt; if however, it is neutral, it deposits a coloured salt, which leaves a small brown residue when dissolved in water.

Very slightly soluble in alcohol, and precipitated from the aqueous solution by alcohol.

			Berzelius. *at* 100°.
20 C	120	28·37	29·24
6 H	6	1·42	1·78
2 BaO,SO^3	233	55·08	50·93
2 SO^2	64	15·13	
$C^{20}H^6Ba^2,4SO^3$	423	100·00	

According to Berzelius, the formula is $C^{11}H^{4·5}O,BaO,S^2O^5$ (calculation requires 51·13 p. c. BaO,SO^3), comp. p. 22. The discrepancy between his analysis and the formula assigned, cannot easily be accounted for.

Bisulphonaphthalate of Lead is exactly like the baryta-salt. It dissolves in water, but is so little soluble in alcohol, that it is almost completely precipitated thereby from its aqueous solution. (Berzelius.)

Parts with 7 p. c. water at 220° C. (4 At. = 6·82 p. c.), and then contains 60·6 p. c. PbO,SO^3 (calculated, 61·5 p. c.). (Laurent.)

			Laurent. *at* 100°.
20 C	120	22·65	23·00
10 H	10	1·89	1·67
2 PbO,SO^3	303·6	57·33	
2 S	32	6·04	
8 O	64	12·09	
$C^{20}H^{10}Pb^2,4SO^3, + 4Aq.$	529·6	100·00	

Hyposulphoglutic Acid.

Berzelius. *Pogg.* 44, 377; *Ann. Pharm.* 28, 9.

Preparation. 1. When the red sulphate of baryta, obtained in the preparation of sulphonaphthalic acid (p. 14), is boiled for a long time with an excess of carbonate of soda, hyposulphoglutic acid, is extracted together with a red colouring matter and a resin. The liquid, at a certain degree of concentration, deposits impure hyposulphoglutate of soda, in brown, viscid, glutinous masses, which however redissolve on dilution. The liquid filtered from baryta is concentrated and separated from the glutinous deposit, a small quantity of which still remains dissolved; the mother-liquor is mixed with a large quantity of sulphuric acid, whereby the hyposulphoglutic acid still in solution is precipitated, and the precipitate is washed with hydrochloric acid, in which it is insoluble. The viscid resinous soda-salt is dissolved in as little water as possible and treated in the same way as the mother-liquor, and the precipitated acid is dried. To purify the product, it is dissolved in ammonia; the excess of ammonia is expelled by evaporation; and the solution is filtered and precipitated with acetate of lead, whereupon a brownish-yellow precipitate is formed, while the pure lead-salt remains in solution. The filtered solution is heated till the precipitated lead-salt redissolves, then concentrated, and precipitated with basic acetate of lead, and the precipitate is washed and decomposed by sulphuretted hydrogen. The precipitated acid is coloured brown by sulphide of lead; the liquid is therefore digested for 24 to 48 hours between 60° and 80° in a well corked flask, and then filtered. (The brown undissolved lead-salt, treated in a similar manner, yields a clear yellow liquid, containing the same acid, but contaminated with a resin and a colouring matter.) It is best to evaporate the acid thus freed from lead, in vacuo over sulphuric acid, since it becomes coloured in the air. — 2. The acid may be obtained from the mother-liquor of sulphonaphthalate of baryta (p. 14, 3, *a*), which dries up to a gummy mass. This gummy mass is dissolved in water, and precipitated to a certain extent with subacetate of lead; the precipitate is decomposed by sulphuretted hydrogen, and the filtrate concentrated and mixed with fuming hydrochloric acid, whereby the acid is precipitated almost colourless, while sulphonaphthalic acid remains in solution. (This process yields but little acid, since most of the acid is contained as baryta-salt in the sulphate of baryta employed in the first method of preparation.)

Properties. Transparent, uncrystallisable, slightly yellow mass, fissured like glass (when spontaneously evaporated in the air, it forms a yellow mass without cracks). Dissolves after the glass has been completely dried. Inodorous, and bitter, like sulphonaphthalic acid, but has a slightly acid taste. Reddens litmus.

Dissolved by *nitric acid,* and decomposed on boiling; water precipitates from the solution a pale yellow substance, insoluble in water; the filtrate is colourless, and gives sulphate of baryta with chloride of barium. If the potash-salt be fused with excess of potash until charring begins, and the mass be then treated with dilute sulphuric acid, it evolves sulphurous acid; hence it contains hyposulphuric acid.

With a small quantity of water, it forms a viscid glutinous substance. Dissolves readily in water, and is precipitated from the solution by sulphuric or hydrochloric acid (but not by nitric acid) as a viscid, glutinous mass.

The Hyposulphoglutates are destroyed by ignition, with formation of sulphates; they are slightly soluble in cold water, more abundantly in warm water; the portion which remains undissolved melts by heat and becomes opaque.

The *potash, soda,* and *ammonia-salts,* resemble in appearance the free acid. If caustic alkali or carbonate (carbonate of ammonia in the case of the ammonia-salt) be added to their solution, the greater part of the dissolved salt is precipitated in white scales, which gradually unite into a glutinous mass. The solution of the ammonia-salt yields by evaporation a residue which reddens litmus, still contains ammonia, and exactly resembles the free acid.

Hyposulphoglutate of Baryta. — Melts below 100°. Dissolves in warm water, and is precipitated on cooling; dissolves in warm alcohol. Leaves when ignited 37·3 p. c. BaO,SO^3.

Hyposulphoglutate of Lead. Melts below 100°. Dissolves in warm water, and is precipitated on cooling. Dissolves in warm alcohol.

Hyposulphoglutic acid is soluble in *alcohol,* less soluble in *ether.*

Oxygen-nucleus $C^{20}H^7O$?

Naphthalase. $C^{20}H^7O$?

LAURENT. *Ann. Chim. Phys.* 59, 326; *Rev. scient.* 13, 68.

Naphthase.

Formation. By heating nitronaphthalin with hydrate of lime or hydrate of baryta.

Preparation. 1. Nitronaphthalin is heated (as slowly as possible, lest it should take fire, and but little product be obtained), with from 8 to 10 pts. of hydrate of lime in a retort filled up to the neck, whereupon ammonia is evolved and a brown oil (containing much naphthalin) and undecomposed nitronaphthalin pass over, while a thick oil condenses in the neck of the retort, and solidifies on cooling. The lime is blackened from separation of carbon. The neck of the retort is cut off near the bulb and washed, as well as the condenser, with ether, which leaves naphthalase undissolved. — 2. A mixture of 1 pt. nitronaphthalin and 8 to 10 pts. hydrate of lime or baryta, is distilled by small portions; the naphthalase condensing in the neck of the retort is collected, washed with ether, and distilled; and the solidified distillate is again washed with ether.

Properties. Yellow substance, which begins to sublime at 250°, but does not melt till a stronger heat is applied, when it begins to boil. The vapour is yellow and condenses in small spangles, which are deposited on the neck of the retort in long, yellow needles. When melted, it solidifies in a fibrous mass on cooling.

			Laurent.
20 C	120	88·8	85·9
7 H	7	5·1	4·8
O	8	6·1	9·3
$C^{20}H^7O$	135	100·0	100·0

The analysis should be repeated. Perhaps 1 At. nitronaphthalin forms with 1 At. water of the hydrate of lime, 1 At. naphthalin, while another portion is converted into naphthalic and nitric acid, the latter being immediately decomposed by the excess of lime.

Combinations. Naphthalase dissolves in *water.* — It dissolves in cold *oil of vitriol,* even in the smallest quantity, with a very intense and beautiful bluish violet colour. The solution in hermetically sealed tubes does not change colour even after two years. On the addition of a little water, the colour turns reddish-violet, and on the addition of more water, pure naphthalase is precipitated, which may again be turned blue by oil of vitriol. The solution in oil of vitriol may be evaporated down for a few moments without losing its colour; but it gradually turns red, and then brown. Even if the naphthalase be first heated with nitric acid or treated with chlorine, the blue colour is still produced on dissolving it in oil of vitriol.

Insoluble in *alcohol,* scarcely soluble in *ether.*

Oxygen-nucleus $C^{20}H^6O^2$.

Naphthulmin.

$$C^{20}H^6O^4 = C^{20}H^6O^2,O^2 ?$$

SCHÜTZENBERGER & WILLM. *Compt. rend.* 46, 894 ; *J. pr. Chem.* 74, 75.

Formation and Preparation. When hydrochlorate of naphthalidine is treated with aqueous nitrite of potash, a large quantity of nitrogen is evolved, and a light brown substance insoluble in water is formed, which, when treated with alcohol or with ether, yields a red substance, nitrosonaphthylin, turning blue with acids. There remains a tolerably bulky, ulmin-black, non-azotised residue, which is naphthulmin, and may be purified by solution in oil of vitriol and precipitation with water.

			Schützenberger & Willm.
20 C	120	75·95	76·18
6 H	6	3·79	3·79
4 O	32	20·26	20·03
$C^{20}H^6O^4$	158	100·00	100·00

It is therefore the hydride of oxynaphthyl, or at least isomeric (?) with that substance. (Schützenberger & Willm.)

Insoluble in almost all solvents, especially in *acids* and *alkalis*. Dissolves in *oil of vitriol* with indigo-blue colour, and is precipitated therefrom in its original state by water.

Vanillin.

$$C^{20}H^6O^4 = C^{20}H^6O^2,O^2 ?$$

GOBLEY. (1858.) *N. J. Pharm.* 34, 401.
AM. VÉE. *N. J. Pharm.* 34, 412.

Givre de vanille. Mistaken by Buchholz (*Repert.* 2, 253) and by Vogel for benzoïc acid, previously by Gobley for coumarin, and by others for cinnamic acid ; first recognized as a distinct body by F. L. Bley (*Br. Arch.* 28, 132).

Source. In vanille, the fruit of *Vanilla aromatica.* — It constitutes the crystals which effloresce from the pods (Gobley, Vée) ; and is deposited from tincture of vanille which has been kept for a long time. (Gobley.)

Preparation. The tincture of vanille, prepared with alcohol of 85 p. c., is evaporated to the consistence of extract, diluted to a syrup with water and shaken up with ether, as long as that liquid takes up colouring matter. The ethereal extracts leave on evaporation a brown, strongly smelling residue, from which boiling water extracts the vanillin, to be purified by animal charcoal and recrystallisation.

Properties. Colourless, long, four-sided, acicular prisms. Has a strong aromatic odour of vanille, and a hot pungent taste. It is hard and cracks between the teeth. Melts at 76° and volatilizes almost completely at 150° in small, brilliant, white crystals. Neutral. (Gobley.) The vanillin effloresced on vanilla-pods melts between 77 and 78°., and reddens litmus (Vée), very slightly (Gobley).

			Gobley.
20 C	120	75·95	75·22
6 H	6	3·79	3·98
4 O	32	20·26	20·80
$C^{20}H^6O^4$	158	100·00	100·00

Almost insoluble in cold, readily soluble in boiling *water*. (Gobley, Vée.)

Dissolves without decomposition, in dilute *acids*, with yellow colour in *oil of vitriol*. (Gobley.) Dissolves easily in *caustic potash*, from which it is precipitated unchanged by acids. It does not expel carbonic acid from *alkaline carbonates*, even on boiling; neither does it combine with bases. (Gobley.)

Dissolves readily in *alcohol*, *ether*, and in *oils* both *fat* and *volatile*. (Gobley.)

Naphthesic Acid.

$C^{20}H^6O^8 = C^{20}H^6O^2,O^6$?

LAURENT. *Rev. scient.* 14, 560.

Naphtessäure.

Formation and Preparation. (See page 8.) Naphthalin placed in contact with bichromate of potash, water, and sulphuric acid, is violently attacked if little water is present, slightly if much water be present. If, after the reaction is over, the mass be treated with water, and the solution filtered from undecomposed naphthalin, and left to itself for one or two months, crystals of chrome-alum are deposited, at first pure, but afterwards covered with white granules of the size of a pin's head. When these granules are dissolved in alcohol, they remain, on evaporating the filtered solution, as a crystalline mass, which may be purified by sublimation.

Properties. Crystallises in rhombic needles of 58° and 122°; melts below 100°.

			Laurent.
20 C	120	63·14	62·94
6 H	6	3·16	2·93
8 O	64	33·70	34·13
$C^{20}H^6O^2,O^6$	190	100·00	100·00

According to a preliminary experiment, the atomic weight is much less than is expressed by this formula. (Laurent.)

Very slightly soluble in *water*.

Sulphi-nucleus, $C^{20}H^7(SO^2)$.

Sulphonaphthalin. $C^{20}H^7(SO^2)$.

BERZELIUS. *Pogg.* 44, 404; *Ann. Pharm.* 28, 9.
REGNAULT. *Ann. Chim. Phys.* 65, 87; *J. pr. Chem.* 12, 99.
LAURENT. *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 297.
GERIKE. *Ann. Pharm.* 100, 216; *Liebig & Kopp's Jahresbericht*, 1856, 613 (note).

Oxide of Thiononaphthyl. (Kolbe.)

Formation. (p. 8.) 1. Produced, together with sulphonaphthalide, by the action of fuming sulphuric acid or sulphuric anhydride on naphthalin. (Berzelius.) 2. By dissolving naphthalin in warm sulphuric acid, whereby only a small quantity of sulphonaphthalide is formed. (Berzelius.)

Preparation. Naphthalin is treated with sulphuric anhydride, as in the preparation of sulphonaphthalic acid (p. 15), and by the addition of water to the red product, a mixture of sulphonaphthalin, sulphonaphthalide, and undecomposed naphthalin is precipitated. The last is volatilised by prolonged boiling of the mixture with water. The residue is fatty, sticks to the glass vessel and dissolves very slightly in boiling water, which then becomes opaline on cooling. The residue is treated with cold alcohol, which dissolves scarcely anything but sulphonaphthalin, and the solution is crystallised by spontaneous evaporation. If the solution be evaporated by heat, it becomes turbid on cooling, and deposits a pulverulent mixture of both products, whilst the liquid contains merely traces of sulphonaphthalide. (Berzelius.)

Properties. Soft, laminated nodules (Berzelius); crystalline (Gerike). Melts far below 100° (Berzelius); at 70° (v. Fehling, *Handwörterb.* v. 439); between 90° and 95° (Gerike), to a yellowish liquid, solidifying in a transparent (gummy, Gerike), highly electric mass. (Berzelius.)

			Berzelius.
20 C	120	75·47	74·974
7 H	7	4·40	4·879
S	16	10·06	10·000
2 O	16	10·07	10·147
$C^{20}H^7(SO^2)$	159	100·00	100·000

According to Berzelius, sulphonaphthalin consists of $C^{20}H^8$ combined with 1 At. SO^2; it is not probable however, that naphthalin exists as such in the compound; neither can it be determined whether sulphonaphthalin is $C^{20}H^8O^2 + S$, or $C^{20}H^8O,SO$, or $C^{20}H^8,SO^2$. (Berzelius.) It appears to be analogous to sulphobenzide, and therefore its formula is probably $2(C^{20}H^7SO^2)$. — (Gericke.)

Decompositions. Heated above its melting point, it gives off fumes, and sublimes as a mealy substance, portions of which are crystalline; the product is partly decomposed sulphonaphthalin. Heated in small tubes, it distils partly in drops, and then evolves sulphurous acid and turns yellow, brown, and finally black. (Berzelius.) Sublimes partly undecomposed. (Gerike.)

2. Decomposes with *fuming nitric acid;* water precipitates white flakes from the solution. (Gerike.)

3. *Aqua regia* does not form sulphuric acid, even after prolonged boiling; but dissolves the substance after 24 hours' boiling; water precipitates from the solution a substance which exactly resembles sulphonaphthalide, and partly dissolves in ammonia with dark yellow colour. (Berzelius.) 4. *Alcoholic potash* does not decompose it at a high temperature. (Gericke.)

Combinations. 1. Does not dissolve in *water* (Gericke), boiling *water* dissolves only a trace of it, and becomes opaline on cooling (Berzelius). — 2. Dissolves in cold *alcohol*, especially in anhydrous alcohol (Berzelius); scarcely in cold, and somewhat more in hot alcohol. (Gericke.) It is precipitated on cooling from the boiling saturated solution in the form of powder; but if separated before the liquid has cooled down below the melting point of sulphonaphthalin, it is deposited in drops, just as when the solution is evaporated by heat. (Berzelius.)

Appendix to Sulphonaphthalin.

Sulphonaphthalide. $C^{24}H^{10}SO^2$?

Berzelius. *Pogg.* 44, 404; *Ann. Pharm.* 28, 9; *J. pr. Chem.* 12, 99.

Formation and Preparation. Formed, according to Berzelius, together with sulphonaphthalin, when naphthalin is treated with sulphuric acid, and in still greater quantity, when sulphuric anhydride is employed. The residue left on treating sulphonaphthalin and sulphonaphthalide with cold alcohol (p. 28), is dissolved in boiling alcohol, whereupon the sulphonaphthalide separates on cooling out as a snow-white powder.

Properties. Colourless; becomes strongly electric when rubbed or stroked with the back of a knife. Melts at a temperature much above 100° C. to a colourless liquid. Does not lose weight at 100°.

			Berzelius.
24 C	144	77·72	77·146
10 H	10	5·29	5·131
S	16	8·50	
2 O	16	8·49	
$C^{24}H^{10}SO^2$	186	100·00	

According to v. Fehling (Handwörterb, v. 439) it is a mixture of a little naphthalin with sulphonaphthalin. Gerhardt was of the same opinion (*Tr.* 3, 460). This is rendered very improbable by the much higher melting point of sulphonaphthalide. (Carius.)

Decompositions. 1. *Heated* above its melting point, it fumes and sublimes with decomposition as a partly crystalline powder. This sublimate melts and solidifies in a crystalline mass on cooling; if the sublimate be dissolved in alcohol, it crystallises out by spontaneous evaporation in small, short, needles acuminated at both ends, and appearing like elongated octahedrons; they have a slight yellow tinge, and are insoluble both in dilute acids and in caustic alkalis. Heated in a glass tube, sulphonaphthalide behaves like sulphonaphthalin.

2. Sulphonaphthalide is but slowly attacked by *aqua regia;* it coheres, then melts on the surface, and slowly evolves nitric oxide. After prolonged boiling, it dissolves completely, if enough nitric acid is present; and the solution gives with water a white precipitate which assumes a lemon colour on the filter. The filtered liquid does not contain a trace of sulphuric acid, even when heat has been applied for several days; hence the sulphonaphthalide must be converted into another sulphurized body.

3. Heated with *nitrate of baryta,* it volatilises without oxidation of the sulphur. — 4. On heating it with *chlorate of potash* and *carbonate of soda,* a partial decomposition is effected, and the solution of the residue contains sulphuric acid.

Combinations. Insoluble in *water,* concentrated *nitric acid,* and *caustic potash.*

Dissolves very slightly, if at all, in cold, and slightly in boiling *absolute alcohol,* separating out for the most part, on cooling. Very slightly soluble in *ether.*

Bromine-nucleus $C^{20}BrH^7$.

Bromonaphthalin. $C^{20}BrH^7$.

LAURENT. *Ann. Chim. Phys.* 59, 216; *Ann. Pharm.* 12, 187; *Pogg.* 31, 320; Further, *Rev. scient.* 12, 195.

Bromonaphtalase, Bronaphtase. (Laurent.) *Bromide of naphthyl.* (Kolbe.) *Brominated naphthalin.* (Gerhardt.)

Formation and Preparation. Formed when bromine is brought in contact with excess of naphthalin, a violent action taking place, heat being developed, and hydrobromic acid evolved. With excess of bromine, bibromonaphthalin is likewise formed, and is very difficult to separate from bromonaphthalin, since both are equally soluble in alcohol and ether. They may be incompletely separated by distilling the crude oily mixture, bibromonaphthalin passing over towards the last.

Properties. Colourless oil, volatile without decomposition. The crude oil, not previously purified, gave on analysis 50·90 p.c. C. and 2·95 p.c. H, (Laurent.) In accordance with this analysis, Laurent considers the crude oil to be a mixture of 1 At. bromonaphthalin, $C^{20}BrH^7$, and 1 At. bibromonaphthalin, $C^{20}Br^2H^6$.

Decompositions. 1. Bromonaphthalin is not attacked by *alcoholic potash.* — 2. *Bromine* converts it into bibromonaphthalin and other brominated products, hydrobromic acid being evolved. — 3. *Chlorine* forms hydrochlorate of bromochloronaphthalin and an oily compound containing bromine and chlorine. — 4. *Sulphuric acid* converts it into bromosulphonaphthalic acid.

Conjugated compound of the Bromine-nucleus, $C^{20}BrH^7$.

Bromosulphonaphthalic Acid.

$$C^{20}BrH^7S^2O^6 = C^{20}BrH^7, 2SO^3.$$

LAURENT. *Compt. rend.* 21, 33; *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 297; *Liebig & Kopp's Jahresb.* 1849, 441.

Brominaphtilinschwefelsäure; Bromonaphthylodithionic acid; Brominated Sulphonaphthalic acid.

Known only in combination with bases.

Formation and Preparation of the Potash-salt. Bromonaphthalin is heated with fuming sulphuric acid till complete solution takes place, after which the liquid is diluted with water and neutralised with potash. The whole is then heated to boiling, filtered from a little free bromonaphthalin, and allowed to cool. The crystalline mass which now separates out is washed on a filter and dissolved in boiling alcohol. On cooling, the potash-salt is deposited in crystals.

Decomposition. By boiling *nitric acid.* If the solution of the potash-salt be evaporated to dryness with nitric acid, and the residue taken up with water and neutralised with potash, a yellow powder, almost insoluble in water, separates out, which deflagrates when heated in sealed vessels, and is therefore probably a nitro-compound.

Bromosulphonaphthalate of Potash. — Colourless, crystallises in nodules.

			Laurent. *mean.*
$C^{20}BrH^6SO^2$	238·0	73·3	
KO,SO^3	87·2	26·7	25·95
$C^{20}BrKH^6,2SO^3$	325·2	100·0	

Bromosulphonaphthalate of potash produces in a moderately dilute solution of *chloride of calcium*, a white precipitate; also in *acetate of lead*. It does not precipitate salts of *magnesium, manganese, cobalt, nickel, zinc,* or *silver*.

Bromosulphonaphthalate of Baryta obtained by double decomposition, separates out from its warm and slightly dilute solution as a crystalline precipitate.

			Laurent.
$C^{20}BrH^6SO^2$	238·0	67·3	
BaO,SO^3	116·5	32·7	32·4
$C^{20}BrBaH^6,2SO^3$	354·5	100·0	

Bromine-nucleus $C^{20}Br^2H^6$.

Bibromonaphthalin. $C^{20}Br^2H^6$.

LAURENT. *Ann. Chim. Phys.* 59, 216; *Ann. Pharm.* 12, 187; *Pogg.* 31, 320; Further, *Rev. scient.* 12, 204.

Bromnaphtalese, Bronaphtese. (Laurent.) *Dekahexylbromür.* (Berzelius.) *Bromide of bromonaphthyl* (Kolbe).

Formation and Preparation. Bromine is added to naphthalin or to bromonaphthalin till no more hydrobromic acid is evolved; and the mass, which solidifies when the reaction is completed, is dissolved in alcohol and left to crystallise. Also formed when Laurent's first *bromure de bronaphtine* is heated, together with free bromine and terbromonaphthalin. (Comp. p. 34.)

Properties. Long, white, inodorous needles, whose section forms a hexagon with two very acute angles. Melts when heated and solidifies in a fibrous mass when cooled to 59°. Volatile without decomposition.

			Laurent.
20 C	120	41·95	42·17
6 H	6	2·12	2·25
2 Br	160	55·93	
$C^{20}Br^2H^6$	286	100·00	

Decompositions. Heated on platinum-foil in the flame of a lamp, it *burns* with a smoky flame, which goes out as soon as the lamp is taken away. — 2. *Chlorine* does not act upon it in the cold; but on heating, quadrichloronaphthalin is formed. 3. Cold *nitric acid* does not attack it; the boiling acid decomposes it. — 4. *Sulphur* dissolves in bibromonaphthalin when heated; on cooling, both bodies separate in crystals. If heat be applied till the mixture of the two bodies assumes the colour of bromine, it remains fluid for a long time after cooling to 10°. If the mixture be ultimately heated to boiling, it evolves hydrobromic and hydrosulphuric acids, and deposits charcoal. — 5. *Sulphuric acid* appears to be without action on bibromonaphthalin, even when warmed, but chars it slightly. *Fuming sulphuric acid* forms bibromosulphonaphthalic acid. — 6. *Potassium* decomposes it slightly at a gentle heat, and becomes covered with bromide of potassium; at a strong heat, decomposition suddenly takes place, with evolution of light, and charcoal is deposited. — 7. It is not attacked by *hydrate of potash.*

Combinations. Insoluble in *water;* very soluble in *alcohol* and in *ether.*

Conjugated compounds of the Bromine-nucleus $C^{20}Br^2H^6$.

Bibromosulphonaphthalic Acid.

$C^{20}Br^2H^6S^2O^6 = C^{20}Br^2H^6,2SO^3$.

Laurent. *Compt. rend.* 21, 33; *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 297; *Liebig & Kopp's Jahresb.* 1849, 441.

Bibromonaphthylodithionic acid; Bibrominated sulphonaphthalic acid.

Known only in combination with bases.

Formation and Preparation. Prepared from bibromonaphthalin with fuming sulphuric acid, in the same way as bromosulphonaphthalic acid from bromonaphthalin. The solution is diluted with water, neutralised with potash, and heated to boiling; and the liquid is filtered from the free bibromonaphthalin, and allowed to crystallise by cooling. The bibromosulphonaphthalate of potash thus obtained is purified by recrystallisation.

Potash-salt.			Laurent.
$C^{20}Br^2H^5SO^2$	317	78·4	
KO,SO^3	87·2	21·6	21·5
$C^{20}Br^2KH^5,2SO^3$	404·2	100.0	

Bibromosulphonaphthalate of Baryta is obtained by mixing the solution of the potash-salt with a very dilute, boiling solution of chloride of barium. Deposited on cooling as a flocculent precipitate, consisting of microscopic crystals.

			Laurent.
$C^{20}Br^2H^5SO^2$	317	73·2	
BaO,SO^3	116·5	26·8	26·6
$C^{20}Br^2BaH^5,2SO^3$	433·5	100·0	

Bromine-nucleus $C^{20}Br^3H^5$.

Terbromonaphthalin.

$C^{20}Br^3H^5$.

Laurent. *Rev. scient.* 12, 213; 13, 95.

Bromnaphtalise, Bronaphtise. (Laurent.) *Bromide of bibromonaphthyl.*

Formation and Preparation. 1. Bibromonaphthalin is heated with excess of bromine. — 2. Laurent's first *bromure de bronaphtine* is heated in a retort, whereupon bromine is evolved and a crystalline mixture passes over, consisting of bi- and ter-bromonaphthalin, which are separated by ether. By spontaneous evaporation, the terbromonaphthalin crystallises first, mixed however with bibromonaphthalin.

Properties. Fine yellow needles; melts at about 60°, and then does not sometimes solidify till it has cooled down to the common temperature.

			Laurent.
20 C	120	32·87	34·30
5 H	5	1·37	1·46
3 Br	240	65·76	
$C^{20}Br^{3}H^{5}$	365	100·00	

It still contained a little bibromonaphthalin.

Very slightly soluble in *alcohol,* moderately soluble in *ether.*

Appendix to Terbromonaphthalin.

Bronaphthin. $C^{20}H^{5.5}Br^{2.5}$?

Laurent. *Rev. scient.* 12, 204.

Formation and Preparation. Formed, together with several other products, by pouring bromine over bibromonaphthalin. The mixture is extracted with ether and the compound is obtained in crystals by spontaneous evaporation.

Properties. Opaque, white, microscopic needles, united in slightly radiated scales. Melts at 48°, and volatilises undecomposed.

			Laurent.
20 C	120	37·40	38·17
5·5 H	5·5	1·75	1·82
2·5 Br	200	60·85	
$C^{20}Br^{2.5}H^{5.5}$	325·5	100·00	

It is perhaps = $C^{20}Br^{2}H^{6}$ + $C^{20}Br^{3}H^{5}$.

Laurent's First Bromide of Bronaphthin.

$C^{20}H^{5.5}Br^{2.5}, Br^{4}$.

Laurent. *Rev. scient.* 13, 95.

Formation and Preparation. When bibromonaphthalin is exposed to sunshine, with an excess of bromine, hydrobromic acid is evolved, and after one or two days, a crystalline mass is deposited, which either consists wholly of the bromide, or contains the compound $C^{20}Br^{5}H^{3},2HBr$ as well. If enough bromine has been used, the bromide crystallises in prisms which may be picked out with a pair of forceps. Should the compound

$C^{20}Br^{5}H^{3},2HBr$ have been likewise formed, the mixture, after repeated washing, must be triturated with ether and dissolved therein, the solution allowed to evaporate slowly, and the crystals picked out.

Properties. Right rhombic prisms, (*Fig.* 65); $i : t = 115° 30'$; $u' : t = 109°$; $u' : u = 142°$.

			Laurent.
20 C	120	18·59	19·40
5·5 H	5·5	0·85	0·88
6.5 Br	520	80·56	
$C^{20}H^{5\cdot5}Br^{6\cdot5}$	645·5	100·00	

According to v. Fehling (*Handwörterb*, 5, 456), it is a mixture of $C^{20}Br^{4}H^{4},2HBr$ and $C^{20}Br^{5}H^{3},2HBr$. It is decomposed by distillation, bromine being evolved and a mixture of bi- and terbromonaphthalin passing over. (Laurent.)

Laurent's Second Bromide of Bronaphthin.

$C^{20}H^{5\cdot5}Br^{2\cdot5}, Br^{4}$.

LAURENT. *Rev. scient.* 13, 97.

Formation and Preparation. Bibromonaphthalin is heated with excess of bromine, and allowed to stand for two days, the whole being repeatedly heated. A body very slightly soluble in ether is formed, apparently of the same formula as the first bromide of bronaphthin, but crystallising in a different form.

Oblique rectangular prisms $m : t = 90°$; $y : t = 90°$; $y : m = 127°$. Sometimes the angles y, m, t are truncated by the faces a, which obliterate all the others. $a : m = 130°$; $a : t = 120°$.

Laurent's analysis gave 18·94 p. c. C and 0·86 p. c. H.

Evolves bromine and a little hydrobromic acid when heated, and leaves an oil which solidifies in needles on cooling.

Bromine-nucleus $C^{20}Br^{4}H^{4}$.

Quadribromonaphthalin.

$C^{20}Br^{4}H^{4}$.

LAURENT. *Rev. scient.* 12, 221.

Bronaphtose. (Laurent.) *Bromide of tribromonaphthyl.*

Formation and Preparation. When the bromide $C^{20}Br^{4}H^{4},2HBr$ is distilled, hydrobromic acid and a little bromine are evolved, and a white substance distils over, which is a mixture of quadribromonaphthalin with another body. In order to effect their separation, they are washed with ether, then warmed with ether in a strong sealed tube placed in a water bath at 100°, and after the whole has cooled, the short brilliant prisms of quadribromonaphthalin are picked out from the other substance, which crystallises in very fine needles.

Properties. Oblique prisms with oblique base, exactly resembling quadrichloronaphthalin *b.* Inclination of the lateral edges = 101° 30′. Inclination of the base to either side = between 101° 30′ and 102°. Volatile without decomposition.

	Prisms.		Laurent. *mean.*
20 C	120	27·45	27·17
4 H	4	0·91	0·93
4 Br	320	71·64	
$C^{20}Br^{4}H^{4}$	444	100·00	

Hydrate of potash has not the slightest action on this compound. It is slightly soluble in *alcohol* and in *ether.*

The substance crystallising in fine needles which accompanies quadribromonaphthalin, is probably isomeric with that compound. The angles of the needles are of 120°; the crystals are very elastic, brittle, and very slightly soluble in ether. (Laurent.)

Hydrobromate of Quadribromonaphthalin.

$C^{20}Br^{5}H^{5} = C^{20}Br^{4}H^{4},HBr.$

LAURENT. *Rev. scient.* 13, 94.

Sousbromure de bronaphtise. (Laurent.) *Bromure de naphtaline tribromée.* (Gerhardt.)

Formation. Sometimes formed, together with the compound $C^{20}Br^{4}H^{4},2HBr$, when bibromonaphthalin is treated with bromine. To separate the mixture, it is boiled with ether, in which the bromide $C^{20}Br^{4}H^{4},HBr$ chiefly dissolves, and is deposited in microscopic needles by the spontaneous evaporation of this solution.

	Needles.		Laurent.
20 C	120	22·85	23·61
5 H	5	0·95	1·00
5 Br	400	76·20	
$C^{20}Br^{4}H^{4},HBr$	525	100·00	

Decomposed by *distillation,* evolving bromine with a little hydrobromic acid, and yielding a crystalline sublimate very slightly soluble in ether (quadribromonaphthalin ?)

Bihydrobromate of Quadribromonaphthalin.

$C^{20}Br^{6}H^{6} = C^{20}Br^{4}H^{4}, 2HBr.$

Laurent. *Rev. scient.* 13, 94.

Bronaphtesbromür, Decahexylsuperbromid.

Formation and Preparation. By pouring bromine over naphthalin or bibromonaphthalin. Sometimes after a few hours a white powder is deposited, which is washed with ether.

Properties. Crystallises by spontaneous evaporation from its boiling ethereal solution, in microscopic rhombic tables.

	Tables.		Laurent.
20 C	120	19·80	20·49
6 H	6	0·99	1·01
6 Br	480	79·21	
$C^{20}Br^{4}H^{4},2HBr$	606	100·00	

Decompositions. 1. Decomposes by distillation into hydrobromic acid, a little bromine, and quadribromonaphthalin, which condenses in the neck of the retort. — 2. Decomposed with great difficulty by *alcoholic potash,* with formation of bromide of potassium.

Very slightly soluble in boiling *ether.*

Bromine-nucleus $C^{20}Br^{5}H^{3}$.

Bihydrobromate of Pentabromonaphthalin.

$C^{20}Br^{7}H^{5} = C^{20}Br^{5}H^{3}, 2HBr.$

Laurent. *Rev. scient.* 13, 579.

Bromure de bronaphtise. (Laurent.) *Quadribromnaphtylbromür-bibromwasserstoff.* (Kolbe.)

Formation and Preparation. By the prolonged action of bromine on bibromonaphthalin or on naphthalin, at a gentle heat, and finally in sunshine. The substance is recrystallised from ether, and the crystals picked out with forceps.

Properties. Crystallises in prisms belonging to the doubly oblique prismatic system, very closely resembling prisms of the oblique prismatic system; like Fig. 112, together with the sides *a*; $u : u = 110°$; $i : h$ right $= 132°$, left $= 130° 30'$; $i : a$ left $= 120°$; $i : u = 105°$.

	Prisms.		Laurent.
20 C	120	17·52	18·01
5 H	5	0·73	0·75
7 Br	560	81·75	
$C^{20}Br^{5}H^{3},2HBr$	685	100·00	

Decomposed by *distillation*, bromine being evolved and another product formed which has not yet been investigated.

Very slightly soluble in *ether*.

Chlorine-nucleus $C^{20}ClH^{7}$.

Chloronaphthalin. $C^{20}ClH^{7}$.

Laurent. *Ann. Chim. Phys.* 59, 196; abstr. *Ann. Pharm.* 8, 8; *Berz. Jahresb.* 16, 350. — *Rev. scient.* 13, 78, & 92. — Zinin. *J. pr. Chem.* 33, 36.

Chlornaphtalas, Chlornaphtas. (Laurent.) *Ikodekatesserylchlorür.* (Berzelius.) *Naphtaline chlorée.* (Gerhardt.) *Chloronaphthalid.* (Mitscherlich.) *a- Chloronaphthalid.* (Löwig.)

Formation and Preparation. 1. Hydrochlorate of chloronaphthalin is repeatedly distilled over hydrate of lime. — 2. Hydrochlorate of chloronaphthalin is boiled with alcoholic potash, and the oily compound thus liberated is precipitated by adding water, and purified by distillation. (Laurent.)

Properties. Colourless, transparent oil; combustible; distils without decomposition.

	Oil.		Laurent. *mean.*
20 C	120	73·84	72·75
7 H	7	4·31	4·00
Cl	35·5	21·85	
$C^{20}ClH^{7}$	162·5	100·00	

Decompositions. 1. Heated with *oil of vitriol*, it is converted into chlorosulphonaphthalic acid (Zinin); it is not attacked by sulphuric acid (Laurent). 2. Decomposed by *bromine* with violent effervescence; hydrobromic acid being evolved, and bihydrobromate of terbromochloronaphthalin ($C^{20}Br^{3}ClH^{4},2HBr$), being formed. — 3. *Chlorine* converts it into a peculiar oil which is changed into *α*-terchloronaphthalin by hydrate of potash. If the action of the chlorine is aided by a gentle heat, ter- or quadrichloronaphthalin is directly formed. — 4. Not attacked by *hydrate of potash.* (Laurent.)

Conjugated compounds of the Chlorine-nucleus $C^{20}ClH^{7}$.

Chlorosulphonaphthalic Acid.

$C^{20}ClH^{7}, 2SO^{3}$.

Zinin. *J. pr. Chem.* 33, 36.

Chlorsulfonaphtalinsäure, Chlorohyposulphonaphthalasic acid. (Laurent.) *Acide sulfonaphtalique chloré.* (Gerhardt.)

Formation and Preparation. 1 vol. of purified chloronaphthalin is mixed with 2 vols. of sulphuric acid, and the mixture heated for a quarter of an hour in an oil-bath to 140°. A transparent, brownish liquid is thereby obtained, which is not changed by cooling, but on the addition of a few drops of water, solidifies in a white, buttery, crystalline mass, which must be placed upon a porous tile to absorb the excess of sulphuric acid. (Zinin.) The same acid is also probably obtained by treating hydrochlorate of chloronaphthalin with fuming sulphuric acid, hydrochloric acid gas being evolved. (Laurent.)

Properties. Melts by heat to a brownish liquid, and then decomposes, diffusing an odour of naphthalin.

Combinations. Readily soluble in *water*.

Forms with bases chiefly soluble *salts;* with ammonia, a white, easily soluble, non-crystalline mass; with potash, a dull, white powder, but slightly soluble in water and in alcohol; this gave according to Zinin's analysis, 16·71 p. c. KO, (the formula $C^{20}ClH^6K,2SO^3$ requires 16·8 p. c. KO).

Chlorosulphonaphthalate of Baryta. Dull white, microscopic needles, difficultly soluble.

			Zinin. *at.* 150°.
20 C	120	38·69	38·77
6 H	6	1·94	2·13
Cl	35·5	11·46	11·18
BaO	76·6	24·69	25·65
5 O	40	12·90	11·96
2 S	32	10·32	10·31
$C^{20}ClH^6Ba,2SO^3$	310·1	100·00	100·00

Cuprous chlorosulphonaphthalate is a white flocculent precipitate; the *cupric salt* is bluish and readily soluble; the *lead-salt* a white, almost insoluble body; the *silver-salt* a white, curdy, precipitate, slightly soluble in water, and decomposing at 100° C.

Chlorosulphonaphthalic acid dissolves easily in *alcohol.*

Hydrochlorate of Chloronaphthalin.

$C^{20}Cl^2H^8 = C^{20}ClH^7, HCl.$

LAURENT. *Ann. Chim. Phys.* 52, 275; *Ann. Chim. Phys.* 59, 196; *Ann. Pharm.* 8, 8; *Pogg.* 29, 77; abstr. *Berz. Jahresb.* 16, 350; *Rev. scient.* 13, 76.

Hydrochlorate of Chlornaphthalase, or *Chlonaphthase.* (Laurent.) *Bichloride of naphthalin.* (Berzelius.) *Naphtalidchlorür.* (Mitscherlich.) *Naphtylchlorür-chlorwasserstoff.* (Kolbe.) *Chlorure de naphtaline.* (Gerhardt.)

Formation. Hydrochlorate of chloronaphthalin is the first product of the action of chlorine upon naphthalin.

Preparation. 1. When dry chlorine gas is passed at the common temperature over naphthalin, a violent action immediately sets in; the naphthalin melts, and when the stream of chlorine is rapid, partly sublimes as solid $C^{20}Cl^2H^6,2HCl$, hydrochloric acid being liberated at the same time. The mass gradually thickens, owing to the formation of a granular substance, and after a while assumes the consistence of solidified olive oil. The same product is formed, when, in preparing naphthalin according to the method given at p. 4, chlorine is passed too long into the tar. If all the naphthalin has not been attacked, the mass must be gently warmed till it melts, and again treated with chlorine. After the reaction is terminated, the mass consists of solid and liquid hydrochlorate of chloronaphthalin; it is shaken up with ether in a glass tube, the liquid decanted, and the mass treated in the same way three or four times, and then filtered. The whole of the ethereal solutions are distilled till the greater part of the ether is volatilised, and the residue, which still contains ether, is maintained at a temperature of — 10°, as long as it continues to deposit solid chloride. The oily chloride is now removed with a pipette from the crystals, and the ether is evaporated by a gentle heat. The fluid chloride thus obtained, invariably contains a small quantity of the solid chloride. (Laurent, *Ann. Chim. Phys.* 52, 275.)

2. The following is a better method. Chlorine is passed over naphthalin, till the resulting oily compound, which had become heated during the reaction, begins to deposit a white granular mass. The oily liquid thus formed is a mixture of naphthalin, the oil $C^{20}ClH^7,HCl$, and the crystalline body $C^{20}Cl^2H^6,2HCl$. (If an attempt were made to convert all the naphthalin, there would be a risk of transforming the two chlorine-compounds into other compounds closely resembling them.) In order to partially remove the naphthalin, the mixture is heated in a dish for a long time between 50° and 60°; the residue is afterwards dissolved in ether, and the solution is kept for some time at —10°. The residual ethereal solution is mixed with alcohol and exposed to the air in an open beaker, until $\frac{2}{5}$ of the oil have been deposited; this portion contains the oily chloride. The third-fifth is collected apart; it is the solid chloride in a state of perfect purity; while the $\frac{2}{5}$ still in solution contain naphthalin. (Laurent, *Ann. Chim. Phys.* 59, 196.)

Properties. Pale yellow oil, heavier than water, and smelling like the solid bihydrochlorate of bichloronaphthalin ($C^{20}Cl^2H^6,2HCl$).

			Laurent.	
	Oil.		*1st analysis.*	*2nd analysis.*
20 C	120	60·30	61·435	60·60
8 H	8	4·02	3·525	3·60
2 Cl	71	35·68		
$C^{20}ClH^7,HCl$	199	100·00		

Decompositions. 1. Hydrochlorate of chloronaphthalin cannot be made to *burn* of itself, but must first be mixed with some combustible body, such as paper or wood, when it burns with a green-edged smoky flame. — 2. Decomposes partly by *distillation*, hydrochloric acid gas being evolved and chloronaphthalin ($C^{20}ClH^7$) being formed. When redistilled six times, whereupon a little hydrochloric acid is each time evolved, it is converted into a colourless oil, which has the composition of a sub-hydrochlorate, since it contains 67·81 p. c. C and 3·86 p. c. H, and probably corresponds to the formula $2(C^{20}ClH^7),HCl$; it may however not be a pure product, since it loses by repeated distillation as much hydrochloric acid as it had already parted with. (Laurent.) — 3. Hydrochlorate of chloronaphthalin is decomposed very slowly by *potassium*, even at the boiling heat, into chloride of potassium and an oil; it was for this reason that Laurent (*Ann. Chim. Phys.* 52, 275) formerly supposed that it was not decomposed by potassium, but that the formation of chloride of potassium was owing to decomposition of solid chloride contained in the liquid. (Laurent.) 4. Distilled over fragments of *potash*, it parts with hydrochloric acid; the decomposition is more complete than by distillation *per se*, chloride of potassium being formed and chloronaphthalin obtained as distillate; but to decompose the oil effectually, it is necessary to repeat the operation three or four times. (Laurent, *Ann. Chim. Phys.* 59, 196.) Alcoholic potash decomposes it readily and completely into chloride of potassium and chloronaphthalin. (Laurent, *Rev. Scient.* 13, 76.) — 5. By *bromine* it is converted into chlorenbronaphtone B (?). — 6. *Chlorine* converts it slowly into solid $C^{20}Cl^2H^6,2HCl$; but when heat is applied, bihydrochlorate of terchloronaphthalin is formed. This last body is produced in this reaction in two modifications:

$$C^{20}ClH^7,HCl + Cl^4 = HCl + C^{20}Cl^3H^5,2HCl.$$

If too great a heat be applied during the action of the chlorine, terchloronaphthalin A is also formed, or the products of its decomposition by the action of chlorine. (Laurent.)

7. *Nitric acid* slowly converts it into a yellow, glutinous, and viscid mass. — 8. Dissolves in hot *fuming sulphuric acid*, with evolution of hydrochloric acid gas; the resulting liquid diluted with water and saturated with carbonate of baryta, yields an almost insoluble salt. (Laurent.)

Combinations. Insoluble in *water*. Dissolves readily in *alcohol*, still more and in every proportion in *ether*.

Chlorine-nucleus $C^{20}Cl^2H^6$.

Bichloronaphthalin. $C^{20}Cl^2H^6$.

LAURENT. *Ann. Chim. Phys.* 59, 196; abstr. *Ann. Pharm.* 8, 8; *Berz. Jahres.* 16, 350; Further, *Compt. rend.* 21, 35; *Rev. scient.* 12, 196; *Compt. chim.* 1850, 1 & 7; abstr. *Ann. Pharm.* 76, 399.

Chlornaphtalese, Chlornaphtese. (Laurent.) *Dekahexylchlorür.* (Berzelius.) *Naphtalidchlorid.* (Mitscherlich.) *Napthaline bichlorée.* (Gerhardt.) *Chloride of chloronaphthyl.* (Kolbe)

Formation. According to Laurent, bichloronaphthalin *exists in seven different modifications.* It is formed: 1. from *a*-hydrochlorate of bichloronaphthalin; *a.* by *distillation*, in the modifications A, C, F, and X; — *b.* by decomposition with *potash*, in modifications E, and AD — *c.* by *alcoholic ammonia*, in the modification C. — It is formed: 2. from β-bihydrochlorate of bichloronaphthalin; *a.* by *distillation*, in the modification C.; — *b.* by decomposition with *potash*, in the modification F, together with an oil. — Formed: 3. in the modification G, by treating binitronaphthalin with chlorine.

Chief characteristics of the Bichloronaphthalins. (Laurent. *Rev. scient.* 12, 203.)

	A.	C.	AD.	E.	F.	X.	Y.
Form	Fluid	Needles of 112° 30′	Needles of 122°	Needles of 94°	Tables 103°	Fluid	Sublimed laminæ
Melting point	....	50°	28 –30°	31°	101°		
Forms with chlorine	Oily A-bihydrochlorate of quadrichloronaphthalin, which is converted by potash into A-quadrichloronaphthalin	Bihydrochlorate of quadrichloronaphthalin C	Trichloronaphthalin AC	....	Laminæ of chlonaphtone	Oily X-bihydrochlorate of quadrichloronaphthalin, which is converted by potash into E quadrichloronaphthalin	
Forms with bromine	....	Bihydrobromate of bibromobichloronaphthalin	Bromobichloronaphthalin A	....	Bibromobichloronaphthalin B	An oil	

a. Isomeric bichloronaphthalins formed by the distillation of a - $C^{20}Cl^{2}H^{6}$, 2HCl.

1. *Modification* C. Obtained by the distillation of *a* - $C^{20}Cl^{2}H^{6}$,2HCl, hydrochloric acid gas being evolved. It is obtained mixed with a peculiar oil (the quantity of which increases with the rapidity of the distillation), and with undecomposed chloride; for this reason, the distillation must be repeated in order to decompose the latter. The product is pressed between blotting paper, dissolved in alcohol at the common temperature, and crystallised by cooling the solution to — 5° or — 10° C. (Laurent, *Ann. Chim. Phys.* 59, 196.) — 2. The oily distillate of *a* - $C^{20}Cl^{2}H^{6}$,2HCl deposits, after varying intervals of time, at first chiefly rhombic tablets of bichloronaphthalin F, from which the oil is decanted, and then needles of C. — Bichloronaphthalin X, which is likewise present, but in very varying proportions, is removed with a pipette when the quantity is considerable; the crystals are further pressed between blotting paper, dissolved in ether-alcohol (more advantageously in ether, if the substance still contains rhombic tablets); and the liquid is allowed to evaporate spontaneously in a flat-bottomed flask. As soon as all the ether is evaporated, but not the small quantity of alcohol, the crystals are thrown upon paper, and if any rhombic tablets are mixed with them, they are picked out with forceps. (Laurent.)

3. Chloride of sulphur (which ?) is heated in a flask, and naphthalin gradually added, whereupon hydrochloric acid is evolved. After the action has ceased, water and ammonia are added, whereupon a soft,

brown mixture of sulphur and a crystallisable substance is produced, from which bichloronaphthalin C is extracted by boiling alcohol and crystallises out on cooling. (Laurent.)

Properties. Crystallises from alcohol in long transparent needles having a rhombic section (of 111° or 112°) and terminated by very acute pyramids. Generally two such prisms are joined together lengthways, so that hemitrophy results, just as in the case of sphene. The crystals obtained from ether, though tolerably large, are nevertheless extremely irregular. Melts about 50° to a colourless oil, solidifying at 44° in a fibrous mass. Distils without decomposition. Inodorous and tasteless.

	Needles.		Laurent. *average.* *a.*	*b.*
20 C	120	60·87	61·62	60·73
6 H	6	3·04	2·90	2·96
2 Cl	71	36·09		
$C^{20}Cl^2H^6$	197	100·00		

b was prepared by the third method.

Decompositions. 1. Forms with *chlorine* at ordinary temperatures, bihydrochlorate of quadrichloronaphthalin; by heat, chiefly the modifications *b* and *c* of quadrichloronaphthalin. — 2 With *bromine* at ordinary temperatures it forms bihydrobromate of bibromobichloronaphthalin. — 3. *Nitric, hydrochloric* and *sulphuric acids* are without action upon it. — (Laurent.) Fuming sulphuric acid dissolves it when heated, with formation of bichlorosulphonaphthalic acid (Zinin, *J. pr. Chem.* 33, 37.) — 4. It is not attacked by *potassium* in the cold, but between 30° and 40° it is decomposed, with evolution of light and deposition of carbon. — 5. Very concentrated *solution of potash* does not attack it, even on boiling.

Insoluble in *water;* very soluble in *alcohol* and in *ether.*

2. *Modification* F, is contained, according to Laurent, in the oily distillate from the chloride *a* - $C^{20}Cl^2H^6$,2HCl (see modification C; preparation 2, p. 40). The oil above the rhombic tablets is decanted; the crystals are dissolved in ether; and the solution is placed in a flat-bottomed flask, and allowed to evaporate very slowly. After two or three days beautiful rhombic tablets are formed, mixed with a few acicular groups of C; these latter are first picked out as completely as possible, and the crystals are then washed with ether, which dissolves the tablets less rapidly than the needles. The tablets are finally recrystallised once or twice from ether. (Laurent.)

Properties. Colourless, inodorous, rhombic tablets, with angles of 77° and 103°. Melts at 101°, and on cooling solidifies in a scaly mass. Distils without decomposition.

			Laurent.
20 C	120	60·85	60·45
6 H	6	3·05	3·08
2 Cl	71	36·10	
$C^{20}Cl^2H^6$	197	100·00	

Decompositions. 1. Not attacked by *alcoholic potash.* — 2. Converted by *bromine* into bibromo-bichloronaphthalin *b.* — 3. Forms a substitution-product with *chlorine.* — 4. Dissolved by warm *fuming sulphuric acid;* the solution is not precipitated by water.

Dissolves readily in *alcohol* and in *ether.*

3. *Modification* X is produced, together with the two previous modifications C and F, by distilling *a*- $C^{20}Cl^2H^6,2HCl$ and forms the oil decanted from these two. According to Laurent, the more rapid the distillation, the more abundantly is the oil formed; but he does not mention how this liquid modification X, is to be separated from the oily modification A (4), which is also produced in the distillation. (Carius.) Sometimes the distillate does not solidify on cooling, or only becomes partially solid. In order to purify the decanted oil, it is dissolved in alcohol; the solution is cooled to — 8° or — 10°, and decanted from the crystals hereby deposited; and the oil is precipitated by the addition of water. (Laurent.)

Properties. Distils without decomposition. Contains 60·5 p. c. C and 3·0 p. c. H. (Laurent.)

Converted by *chlorine* into oily bihydrochlorate of quadrichloronaphthalin X. — It is not decomposed by *alcoholic potash.*

4. *Modification* A is obtained by redistilling the chloride *a* $C^{20}Cl^2H^6$,-2HCl four or five times, whereby the modification C is completely decomposed.

Properties. Oil, not decomposed by distillation, and containing 60·5 p. c. C. and 3·2 p. c. H. (Laurent.)

Converted by *chlorine* into oily hydrochlorate of quadrichloronaphthalin A. — Not attacked by *hydrate of potash.*

b. Isomeric bichloronaphthalins obtained by decomposing *a*-bihydrochlorate of bichloronaphthalin with alcoholic potash.

5. *Modification* AD. *Parachloronaphthalose* (Laurent). *a*-bihydrochlorate of bichloronaphthalin is distilled upwards for an hour in a long-necked flask with concentrated alcoholic potash; the liquid is precipitated with water; and the precipitated oil is redistilled with alcoholic potash in the same way, then reprecipitated by water, freed from adhering potash, chloride of potassium and alcohol by washing with water, and finally dried. The colourless or faintly yellowish oil thus obtained, gradually solidifies in a white nacreous mass, which is purified from adhering oil by pressing between blotting paper, and then dissolved in ether-alcohol. By cooling the solution to — 5 or — 10°, crystals are obtained, which are separated from the mother-liquor and dried. The crystals may sometimes contain a little bihydrochlorate of bichloronaphthalin; in this case, the ethereal solution, by slow evaporation, first deposits this substance in rhombic laminæ which are less readily fusible and less soluble in ether than AD. (Laurent.)

Properties. Colourless, acute laminæ, or rather long rhombic needles of 122° (Laurent, *Rev. scient.* 13, 72). Melts between 28 and 30°; but does not solidify till cooled to 18° or 20°, and then forms a nacreous, but not fibrous mass. Volatile without decomposition. Inodorous.

Needles or laminæ.			Laurent.
20 C	120	60·87	61·35
6 H	6	3·04	2·90
2 Cl	71	36·09	
$C^{20}Cl^2H^6$	197	100·00	

Decompositions. 1. Unattacked by *acids.* — 2. Fuming *sulphuric acid* behaves with this compound as with the isomeric compound C-bichloronaphthalin. — 3. With *chlorine* it forms, when warmed, terchloronaphthalin AC. — 4. With *bromine,* hydrobromate of bromobichloronaphthalin A, with evolution of hydrobromic acid. — 5. Decomposed by *potassium* between 40° and 50°, with evolution of light and separation of carbon. — 6. Not attacked by *hydrate of potash.*

Insoluble in *water;* very soluble in *alcohol* and in *ether.*

6. *Modification* E is found in the alcoholic mother liquor from which AD has crystallised by refrigeration (comp. p. 44), and is obtained by spontaneous evaporation.

Properties. Very well defined, brilliant six-sided prisms of 94°, larger than the crystals of AD. Melts at 31°, and distils unchanged. Laurent found 60·76 p. c. C. and 3·06 p. c. H.

Decompositions. 1. Treated with *bromine,* it evolves hydrobromic acid. — 2. Behaves with *sulphuric acid* like the other modifications of bichloronaphthalin. — 3. It is not acted upon by *hydrate of potash.*

c. *Bichloronaphthalin* formed by treating *binitronaphthalin* with chlorine gas.

7. *Modification* Y. Chlorine is passed through fused binitronaphthalin. If the heat does not exceed the melting point of binitronaphthalin, and the decomposition is not thoroughly effected, a mixture of undecomposed binitronaphthalin, oily hydrochlorate of terchloronaphthalin, and bichloronaphthalin Y is obtained, nitrous fumes being evolved. If more chlorine is used and the temperature raised higher, terchloronaphthalin A is formed. First the oily chloride is removed with a little ether, and then the bichloronaphthalin is extracted from the residue by more ether, (the binitronaphthalin remains undissolved), and it is purified by recrystallising once or twice, and finally sublimed or distilled. (Laurent, *Rev. scient.* 12, 202.)

Properties. Forms by sublimation, white needles, the exact form of which cannot be determined. In order to obtain fine sublimed scales, the substance is put on a small dish and placed on a sand-bath heated to 100°, the whole being covered with a low bell-jar. It melts at 35°, and crystallises in needles on cooling. Laurent found 60·45 p. c. C. and 3·03 p. c. H.

Of all the modifications of bichloronaphthalin, this is the least soluble in *alcohol* and in *ether.*

Conjugated Compounds of the Chlorine-nucleus $C^{20}Cl^2H^6$.

Bichlorosulphonaphthalic Acid.

$C^{20}Cl^2H^6S^2O^6 = C^{20}Cl^2H^6,2SO^3$.

Zinin. *J. pr. Chem.* 33, 37.

Chlorohyposulphonaphthalesic acid. (Laurent.) *Bichloronaphthylodithionic acid.* (Kolbe.) *Acide sulfonaphtalique bichloré.* (Gerhardt.) *Bichlornaphtalinschwefelsäure.*

Sulphuric acid acts upon bichloronaphthalin as upon chloronaphthalin, and forms a white buttery acid, somewhat more consistent than chlorosulphonaphthalic acid. (Zinin.)

The *ammonia-salt* is exceedingly soluble.

The *potash-salt* forms small needles having a fatty lustre, sparingly soluble. Contains 14·74 p. c. KO.

Baryta-salt. Small, white needles having a fatty lustre; sparingly soluble.

			Zinin. *at* 150°.
20 C	120	34·82	34·85
5 H	5	1·46	1·50
2 Cl	71	20·60	20·57
BaO	76·6	22·20	22·07
5 O	40	11·63	11·42
2 S	32	9·29	9·59
$C^{20}Cl^2H^5Ba,2SO^3$	344·6	100·00	100·00

Silver-salt. White, brilliant laminæ sparingly soluble. Zinin found 29·89 p. c. AgO; the calculation requires 30·23 p. c.

Bihydrochlorate of Bichloronaphthalin.

$$C^{20}H^8Cl^4 = C^{20}Cl^2H^6, 2HCl.$$

DUMAS. *Ann. Chim. Phys.* 50, 182.

LAURENT. *Ann. Chim. Phys.* 52, 275; 59, 196; Further, *Rev. scient.* 6, 29; 13, 72; Further, *Ann. Chim. Phys.* 74, 26; Further, *Compt. rend.* 21, 35; *Compt. chim.* 1850, 1; abstr. *Ann. Pharm.* 76, 298; *Liebig & Kopp's Jahresb.* 1850, 497.

DE MARIGNAC. *Ann. Pharm.* 38, 40.

Hydrochlorate de chloronaphtalese. (Laurent.) *Bichlorure de naphtaline.* (Gerhardt.) *Chlornaphtylchlorür-bichlorwasserstoff.* (Kolbe.)

Formation. By the action of chlorine upon naphthalin. If the stream of chlorine-gas be not too long continued, hydrochloric acid gas is evolved and a buttery mass resembling frozen olive-oil is obtained, which, together with undecomposed naphthalin, contains hydrochlorate of chloronaphthalin, and the *modifications* a and β of *bihydrochlorate* of *bichloronaphthalin.* (Laurent.)

1. *Modification a.*

Preparation. The buttery mixture of the chloride (see formation) is washed four or five times by decantation with ether, collected on a filter, pressed between blotting paper, dried and fused. (Laurent, *Ann. Chim. Phys.* 52, 275; De Marignac.) Since the chloride may be converted by excess of chlorine into new compounds closely resembling it, the stream of chlorine must be interrupted before all the naphthalin is decomposed; and in order to partly remove the latter, the product is warmed for a long time in a dish, between 50° and 60° C, then dissolved in ether, and the solution maintained for some time at a temperature of —10°C, whereupon the greater part of the solid chloride separates out; or the product is mixed with a little ether, in order to make it more liquid; the oil is decanted after 24 hours; and the residue is repeatedly washed on a filter with ether. (Laurent.)

To *purify* the product, it is either (*a.*) dissolved in boiling ether, the substance yielding on cooling, very white, more or less crystalline chloride.

Or, (*b.* a cheaper method, since less ether is required for solution) the mass, after being washed with ether, is dissolved in rock-oil, which dissolves the chloride very abundantly, and on cooling rapidly deposits it at even a few degrees below the boiling point, and when quite cold retains only traces in solution. The crystals are collected on a funnel and washed with a little ether. (Laurent, *Rev. scient.* 13, 72.)

Properties. Obtained either as a white, shining powder, or, when crystallised from ether, in transparent, vitreous, rhombic laminæ. As however only a small quantity of the chloride is dissolved by ether, it is better to heat it with 30 or 40 times its bulk of ether, in a sealed flask to a few degrees above the boiling point of ether, and then to cool the solution slowly. (Laurent.) Crystallises from rock-oil in crystals resembling rhombohedrons, with the cracked laminated appearance of calc-spar. Crystallised from ether, it forms oblique rhomboidal tablets; — Lateral angles = 109°, inclination of bases to side = 108° 30′ (Laurent, *Compt. rend.* 20, 363); or in oblique rhombic prisms; — Angles of the rhombic base = about 75° and 105°, the obtuse angles being truncated. (Laurent, *Ann. Chim. Phys.* 52, 275.) Heated with ether to 100° in a sealed glass tube, it crystallises on cooling in the form of fig. 113; a and a much more upright, the faces k being wanting; faces i, u, u' predominating; h- faces are always present; on the other hand, faces a, m, and a, (which are wanting in Fig. 113) seldom occur, $u : u = 109°$ (hence they more resemble fig. 86: Gm.), $i : u = 108° 30'$; $i : f$ (behind) 121° 40′; $h : h$ (below) = 118°; $u : h = 129° 50'$; $i : t$ $(y : m) = 113°$; $t : f = 147°$; $i : a = 144°$ (about); m (Fig. 115) : a = 139° 30′ or, on the other side, 137° 30′; $i : m$ left = 92° and right = 88°. (Laurent, *Rev. scient.* 13, 72.) Melts at 160°, and solidifies in a crystalline mass on cooling. (Laurent.) If a crystal thereof be thrown into the partly fused chloride, the whole mass solidifies at about 150° in perfectly well defined rhombic tablets. If, however, the substance has been completely fused, and is then allowed to cool without adding a crystal, the mass solidifies sometimes at 150° in rhombic crystals, sometimes between 110° and 100° in radiated needles. Very brittle, pulverisable, inodorous, and permanent in the air. May be volatilised undecomposed in a glass tube through which a stream of gas is passing. (Laurent.)

			Laurent. *mean.*	Dumas.	Marignac.
20 C	120	44·43	45·13	44·69	44·72
8 H	8	2·96	2·49	3·12	3·04
4 Cl	142	52·61			52·20
$C^{20}Cl^2H^6,2HCl$	273	100·00			99·96

Laurent formerly considered the chloride to be bihydrochlorate of bichloronaphthalin; afterwards $C^{20}H^8Cl^4$.

Decompositions. 1. Strongly *heated* in a retort, it begins to boil, evolves hydrochloric acid, and yields an oily distillate, which soon solidifies in crystals, and is a mixture of the four bichloronaphthalins C, F, H, and A (occurring in different proportions according to the temperature at which the distillation takes place), and a little undecomposed chloride. There remains in the retort a small quantity of porous charcoal, amounting, after washing with alcohol, to 1 or 2 p. c. of the chloride employed. (Laurent.) 2. It is not combustible of itself, even in the gaseous state; melted on paper, and lighted, it *burns* with a fuliginous, deeply green-edged flame. (Laurent.) — 3. *Bromine* converts it in sunshine into bibromo-terchloronaphthalin and other compounds. (Laurent.) 4. It is converted by *chlorine*, at a gentle heat, into bihydrochlorate of chloronaphthalin, taking up 2 At. chlorine, and parting with 1 At. HCl; at a higher temperature, other products are likewise formed. — 5. The chloride is attacked only by boiling *nitric acid*, and yields (even when a portion still remains undecomposed) phthalic and oxalic acids, a thick oil being at the same time obtained, from which ether precipitates oxychloronaphtalose, $C^{20}H^4Cl^2O^4$ (Laurent). During the reaction abundant nitrous fumes are evolved, and a little chloride of binitromethylene (C^2X^2,Cl^2) passes over with the nitric acid (vii, 360); the acid in the residue appears to differ from Laurent's phthalic acid (Marignac). — 6. *Hydrochloric acid* is without action on this compound. — 7. *Sulphuric acid* is also inert in the cold; but on prolonged boiling, decomposition takes place, with evolution of hydrochloric acid, and formation of:—1, a substance which is insoluble in water, soluble in ether, leaves a transparent varnish on the evaporation of the ethereal solution, and is decomposed by heat, yielding an oil which on cooling solidifies in a transparent fissured mass; 2, a substance which remains dissolved in the sulphuric acid — the solution saturated with baryta yielding a salt resembling sulphonaphthalate of baryta. (Laurent, *Ann. Chim. Phys.* 59, 196.) — 8. Heated with *fuming sulphuric acid*, it evolves hydrochloric acid; — the liquid, diluted with water, saturated with baryta, filtered and evaporated down, yields a very soluble baryta-salt, which crystallises with difficulty, and contains both chlorine and sulphur. (Laurent, *Rev. scient.* 13, 72.) — 9. Decomposed by *potassium* at, or a little above, the common temperature, with slight explosion and evolution of light, chloride of potassium being formed and much carbon separated; Laurent, by performing the experiment in a glass tube, obtained a small quantity of a gas which burned with a green flame. — 10. It is not attacked by *potash* in the cold; on boiling, chloride of potassium and a new crystallisable substance are formed. (Laurent.) It is decomposed by boiling *alcoholic potash* into chloride of potassium and the two modifications E and AD of bichloronaphthalin. (Laurent, *Rev. scient.* 13, 72.) — 11. Decomposed by *alcoholic ammonia*, but slowly, bichloronaphthalin C being apparently formed. (Laurent.) — 12. Boiled with *alcoholic sulphide of ammonium*, it forms a new compound, soluble in alcohol and in ether, and containing sulphur, chlorine, and oxygen. (Laurent.)

Combinations. Insoluble in *water*. Scarcely soluble in cold, and very slightly soluble in boiling *alcohol*, from which, on cooling, it is almost completely deposited in small scales. It dissolves somewhat more freely in *ether*, especially at 100° (in a sealed tube). Dissolves very sparingly in cold, and abundantly in boiling *rock-oil*. (Laurent.)

2. *Modification β.*

Formation (p. 46).

Preparation. That portion of the buttery mixture, obtained by the action of chlorine upon naphthalin, which remains liquid after cooling, is dissolved in a little ether, and maintained at 0° for 48 hours, whereupon the mixture solidifies like frozen olive-oil. The deposit is collected at 0° on a piece of fine linen, and the mother-liquor again cooled, whereby more of the solid product is obtained. Both portions are pressed and dissolved in a little ether containing $\frac{1}{8}$ or $\frac{1}{10}$ of alcohol. The solution, allowed to stand in an imperfectly closed vessel, deposits in the course of a few days a crystalline mass, which is filtered off and pressed. This is a mixture of the modification *a*, which is slightly soluble in ether, and scarcely soluble in alcohol, and of the modification *β*, which dissolves readily in alcohol, and still more in ether. The whole is dissolved in boiling alcohol, and very slowly cooled, and the modification *a*, which crystallises first, is separated by decanting the liquid; this liquid, by spontaneous evaporation, yields first the modification *a*, and then mixtures of the two modifications, which are treated separately with a little ether, whereby the modification *β* is dissolved immediately, and the modification *a* more slowly in proportion as the crystals are larger. The product is now repeatedly recrystallised, till the crystalline mass is dissolved by ether immediately and without residue. (Laurent, *Compt. Chim.* 1850, 1.)

Properties. Colourless, inodorous; crystallises in small flakes, often united in large balls. When fused and cooled to 10° C., it does not solidify immediately, but gradually, in radiated spheres often more than an inch in diameter.

			Laurent.
20 C	120	44·51	44·11
8 H	8	2·95	2·83
4 Cl	142	52·54	
$C^{20}Cl^2H^6,2HCl$	270	100·00	

Decompositions. 1. Resolved by *distillation* into hydrochloric acid and oil, and bichloronaphthalin C. (needles of 112°). — 2. *Bromine* converts it into bihydrochlorate of bromochloronaphthalin, $C^{20}ClBrH^6,2HCl$. — 3. Decomposed by boiling *alcoholic potash* into chloride of potassium, an oil, and bichloronaphthalin F. — 4. If *alcoholic sulphide of ammonium* be poured into a boiling alcoholic solution of the chloride, the liquid turns brown, becomes turbid in a few seconds, and deposits an abundant precipitate resembling flowers of sulphur, and containing chlorine, sulphur, and oxygen.

Chlorine-nucleus $C^{20}Cl^3H^5$.

Terchloronaphthalin. $C^{20}Cl^3H^5$.

LAURENT. *Ann. Chim. Phys.* 66, 152, and 199; Further, *Rev. scient.* 12, 206; Further, *Compt. rend.* 15, 739; Further, *Compt. rend.* 21, 35; *Compt. chim.* 1850, 1; abstr. *Ann. Pharm.* 76, 300; *Liebig & Kopp's Jahresb.* 1850, 498.
ZININ. *J. pr. Chem.* 27, 152.

Chlornaphtalis, Chlornaphtis. (Laurent.) *Dekapentylchlorid.* (Berzelius.) *Naphtaline trichlorée.* (Gerhardt.)

Obtained by Laurent *in seven different modifications, formed under different circumstances.* — Laurent (*Ann. Chim. Phys.* 66, 152) states his belief that he had often previously obtained terchloronaphthalin; but as the crystals were soft like wax, he mistook them for a mixture of quadrichloronaphthalin with an oil, and indeed he was ultimately of opinion that, in every case in which he formerly supposed that he had obtained quadrichloronaphthalin by the action of chlorine on various compounds, the compound, described as such, was really terchloronaphthalin, with the exception of that obtained by the decomposition of bihydrochlorate of quadrichloronaphthalin.

Formation. 1. *Modification* A. 1. Obtained by treating hydrochlorate of chloronaphthalin with chlorine, and boiling the oily product with potash. (Laurent.) 2. By treating nitro- or binitro-naphthalin with chlorine. (Laurent.)

2. *Modification* AC. By treating fused bichloronaphthalin with chlorine, hydrochloric acid being evolved. (Laurent.)

3. *Modification* D, is formed together with A, when bihydrochlorate of terchloronaphthalin is distilled.

4. *Modifications* C and (5) G are formed simultaneously, together with A, when bihydrochlorate of terchloronaphthalin is boiled with potash.

6. *Modification* AD. Obtained by Laurent by decomposing the bihydrochlorates of bi- and terchloronaphthalin with potash.

7. *Modification* AE is formed, together with A and an oil, with evolution of hydrochloric acid, when bihydrochlorate of bichloronaphthalin is warmed with fuming oil of vitriol.

Chief characteristics of the Terchloronaphthalins. (Laurent, *Rev. scient.* 12, 213.)

	A.	AC.	C.	G.	D.	AD.
Form	6-sided prisms of 120°	6-sided prisms, rhombus of 113°	Long needles, rhombus of 113°	Prisms terminated by needles, rhombus of 130°	Like G, rhombus of 124°	Needles of silky lustre, rhombus of 122°
Hardness, &c.	Soft	Soft	Elastic, brittle	Unelastic, brittle	Like G	
Melting-point	75°	66°	Between 78° & 80°	Between 69° & 70°	Between 88° & 90°	160°
State after fusion	Soft rectangular parallelograms.	Like A	Transparent rosettes, becoming slowly opaque when left to themselves.	Transparent rosettes, becoming suddenly opaque by friction with foreign bodies	Needles, with moirated surface transparent, becoming opaque on standing.	Transparent rosettes, becoming opaque on standing
In ether	Exceedingly soluble.	Very soluble	Soluble	Soluble	Soluble	Slightly soluble
In alcohol	Very slightly soluble.	Soluble	Soluble	Soluble	Soluble	Slightly soluble

1. *Modification* A. 1. Chlorine gas is passed over naphthalin; and the oily hydrochlorate of chloronaphthalin (p. 39) is separated from the solid chlorides by means of ether, and again treated with chlorine, either with the aid of heat, or in the sun. A thick mixture of oily hydrochlorate of terchloronaphthalin, solid bihydrochlorate of terchloronaphthalin, and other solid chlorides is obtained. — In order to separate the products, they are mixed with ether, and the whole is maintained for several hours at 0°, whereupon the solid chlorides separate out.—(Amongst these, Laurent discovered a new chloride crystallising in right prisms with rectangular base; this form does not in any other instance occur in the series of chlorides of naphthalin, and could be isolated only by picking out the crystals with the aid of a magnifying-glass.) The oil is decanted and boiled with alcoholic potash, which is renewed two or three times. Above $\frac{7}{8}$-ths of the oil employed are obtained. (Laurent.) — 2. The oily hydrochlorate of terchloronaphthalin may also be subjected to distillation, whereby hydrochloric acid gas is evolved. The chloride thus prepared is, however, not pure, but must be separated from a little oil by dissolving in 3 or 4 pts. ether and 1 pt. alcohol, with the aid of heat. Crystals are obtained by the cooling of the solution, and still more by spontaneous evaporation in an open vessel. The crystals must be recrystallised once or twice from ether-alcohol, and can be obtained colourless only by recrystallisation from equal pts. of ether and alcohol, or rather more alcohol. (Laurent, *Ann. Chim. Phys.* 66, 197.) — 3. By treating nitro- or binitronaphthalin with chlorine, with the aid of heat. (Laurent, *Ann. Chim Phys.* 66, 152.) — 4. Zinin obtained terchloronaphthalin by treating chloronaphthalin (he afterwards thought that it contained the terchloronaphthalin ready formed) with oil of vitriol at 140° C., as a clear oil, which on cooling became solid like wax and floated on the brown liquid containing chlorosulphonaphthalic acid. (This part of Zinin's research has not since been noticed; it seems to show that Zinin's compound is identical with Laurent's terchloronaphthalin A; its formation in Zinin's experiment may be explained by supposing that chloronaphthalin is converted by chlorine into compounds of the nucleus $C^{20}Cl^3H^5$. (Carius.)

Properties. Inodorous, tastelelss. Crystallises from boiling alcohol in crystals grouped like the feather of a quill (Laurent); in long, flexible crystals of silky lustre (Zinin). It may be obtained by very slow evaporation of the ethereal solution in long, striated, irregular, six-sided prisms of 120°. — Soft like wax; the crystals soften by being pressed together, and yield a transparent mass. (Laurent, Zinin.) Melts at 75° (Laurent); at 74° (Zinin), and solidifies in crystals on cooling. Begins to boil at 200° (Zinin), and distils without decomposition. (Zinin, Laurent.)

	Crystals.		Zinin. *average.*	Laurent.
20 C	120	51·90	52·61	52·32
5 H	5	2·16	2·36	2·25
3 Cl	106·5	45·94	44·12	
$C^{20}H^5Cl^3$	231·5	100·00	99·09	

Since terchloronaphthalin is formed by treating the oily chloride with hydrate of potash, the latter oil must have the composition $C^{20}Cl^3H^5 + HCl$, or $+ 2HCl$ (Laurent).

Decompositions. 1. The compound is dissolved by warm *fuming sulphuric acid;* water does not produce a precipitate with the solution as long as it is warm, but on cooling it assumes a gelatinous appearance, and a crystalline body is obtained (Laurent). 2. With *chlorine,* aided by heat, it forms a new compound, probably $C^{20}Cl^{4}H^{4},HCl$. (Laurent.) 3. *Nitric acid* is without action. (Laurent.) 4. *Potassium* decomposes it with evolution of light. 5. It is not attacked by *aqueous potash;* by *alcoholic potash* it is dissolved, and deposited unchanged. (Zinin.)

Terchloronaphthalin A is insoluble in *water.*

Ether dissolves more than its own weight of it; in *alcohol,* on the contrary, it dissolves but sparingly, even on boiling, and is therefore precipitated by alcohol from its ethereal solution. (Laurent.)

2. *Modification* AC is obtained by passing chlorine through fused bichloronaphthalin AD, whereby hydrochloric acid is evolved; it is purified by one or two recrystallisations from ether.

Properties. Fine 6-sided needles (inclination of the faces = 113°); it is soft like wax, and the crystals may be bent in all directions. (Laurent, *Rev. scient.* 14, 74.) Melts at 66°, and on cooling crystallises like A. Distils without decomposition.

Laurent found 51·6-8 p. c. C and 2·16 p. c. H.

Unacted upon by *hydrate of potash.* — *Fuming sulphuric acid* behaves with this modification as with A.

Dissolves more readily in *alcohol* than A; very soluble in *ether.*

3. *Modification* D. When bihydrochlorate of terchloronaphthalin A is distilled, it is completely decomposed; hydrochloric acid is evolved and modifications A and D of terchloronaphthalin are obtained, a small residue of carbon being left. A is first extracted from the mixture by ether; the residue is dissolved in ether with a little alcohol; and the solution allowed to evaporate spontaneously, whereupon D crystallises out. (Laurent, *Rev. scient.* 12, 211.)

Properties. Beautiful brilliant needles, the section of which forms a rhomb of 124°; it resembles terchloronaphthalin G. Melts between 88° and 90°, and on cooling solidifies in a transparent mass of long needles; in this state it is soft like wax, but gradually becomes hard and opaque. Distils without decomposition.

Laurent found 51·5 p. c. C and 2·2 p. c. H.

Behaves with *sulphuric acid* like the other terchloronaphthalins; and is not acted upon by *hydrate of potash.*

Dissolves very readily in *ether,* much less in *alcohol.*

4. *Modification* G. If powdered crystallised bihydrochlorate of terchloronaphthalin be boiled with alcoholic potash, it is decomposed, with formation of chloride of potassium; and on adding water to the solution, a precipitate of the three modifications A, C, and G of terchloronaphthalin is produced. In order to effect their separation, the modification A is first removed with a little ether (or alcohol might first be used, which dissolves C and G more readily than A), and the residue dissolved in ether with a little alcohol. The solution is placed in a loosely covered vessel, and allowed to evaporate spontaneously. G, which is present in greater quantity than C, first crystallises; the solution is poured off from the crystals and again left to evaporate spontaneously, and this treatment is continued as long as homogeneous crystals are obtained.

Finally G and C crystallise together; G in groups of very brilliant crystals, C in fine regular needles, which traverse the liquid in every direction. The crystals are picked out and recrystallized. (Laurent, *Rev. scient.* 12, 209.)

Properties. Brilliant, colourless, transparent prisms, the section of which is a rhomb of 50 and 130°. The crystals are brittle, unelastic, and may be readily pulverised. Melts between 69° and 70° C. If one gramme of the substance be melted on a glass plate, it solidifies on cooling in a slightly transparent mass, which, by examination with the microscope, is found to consist of small striated rosettes; after a minute or so, the mass becomes perfectly opaque. If touched with a hard body immediately after solidification, it will be found to be soft, like the modification A; but as soon as it has become opaque, it is found to be brittle and easily pulverisable. If the transparent mass be touched with a feather, it suddenly becomes opaque (Laurent).

Laurent found 51·60 p. c. C, and 2·14 p. c. H.

It is not decomposed either by *distillation*, or by *potash*.

Dissolves in warm *fuming sulphuric acid;* and on addition of water, a precipitate is formed which redissolves in warm water.

Dissolves readily in *ether*, less readily in *alcohol.*

5. *Modification* C is obtained mixed with G (p. 52), by boiling solid bihydrochlorate of terchloronaphthalin with alcoholic potash. It is separated from G by picking out the crystals, and purified by one or two recrystallisations from ether-alcohol.

Properties. Long, brittle, elastic needles, the section of which forms a rhomb of 113°. Melts between 78° and 80° and exhibits on cooling the same phenomena as G.

Laurent found 51·45 p. c. C and 2·22 p. c. H.

6. *Modification* AD is obtained by boiling bihydrochlorate of bi- and terchloronaphthalin with alcoholic potash. The solution is precipitated by water and the precipitate treated with a little ether, whereupon the modification AD alone remains in the residue. (Laurent, *Rev. scient.* 12, 212.)

Properties. Crystallises from ether in needles of silky lustre. Does not melt till about 160° C, and solidifies on cooling in microscopic, slightly transparent rosettes; it is then soft like wax, but gradually hardens and becomes opaque.

It has not been analysed.

Readily soluble in *alcohol,* moderately in *ether.*

7. *Modification* AE. The crude oil, obtained in the preparation o bihydrochlorate of terchloronaphthalin (p. 55) is treated with gently warmed fuming sulphuric acid (whereupon hydrochloric acid gas is evolved), and the brown solution is precipitated with water and left to cool. After a few hours, a brown semi-plastic mass is deposited, which is first washed with water, then with a little alcohol, and afterwards dissolved in ether. On evaporation, a deposit is formed which is a mixture of the terchloronaphthalins A, AE, and of a small quantity of an oil. Since A, as well as the oil, is more soluble in ether than AE, the product is crystallised a second time from ether, and afterwards twice recrystallised from ether-alcohol.

Properties. Fine, colourless needles, the section of which is a hexagon, derived from a rhomb of 122°. Melts at 93°, and on cooling crystallises like A in rectangular parallelograms, crossed by two diagonals. After cooling, it remains soft like A, but becomes hard and brittle after a time. Distils undecomposed.

			Laurent.
20 C	120	51·90	51·50
5 H	5	2·16	2·10
3 Cl	106·5	45·94	
$C^{20}Cl^{3}H^{5}$	231·5	100·00	

Decompositions. 1. In contact with *bromine,* it evolves hydrobromic acid, and gives rise to a crystalline and almost insoluble substance. — 2. With *fuming sulphuric acid* it forms terchlorosulphonaphthalic acid.

It is less soluble in *ether,* but more soluble in *alcohol* than the modification A. (Laurent, *Compt. rend.* 21, 35; further *Compt. chim.* 1850, 1; extr. *Ann. Pharm.* 76, 300; *Liebig & Kopp's Jahresb.* 1850, 499.)

Conjugated compounds of the Chlorine-nucleus, $C^{20}Cl^{3}H^{5}$.

Terchlorosulphonaphthalic Acid.

$$C^{20}Cl^{3}H^{5}S^{2}O^{6} = C^{20}Cl^{3}H^{5},2SO^{3}.$$

LAURENT. *Compt. rend.* 21, 33; Further, *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 298; *Liebig & Kopp's Jahresb.* 1849, 441.

Chlorohyposulphonaphthalic acid. (Laurent.) *Trichloronaphthylodithionic acid.* (Kolbe.) *Acide sulfonaphtalique trichloré.* (Gerhardt.) *Trichlornaphtalinschwefelsäure.*

Formation. Obtained by treating terchloronaphthalin with fuming sulphuric acid. In preparing terchloronaphthalin AE by means of fuming sulphuric acid (p. 53) part of the terchloronaphthalin is directly converted into this acid.

Preparation. Terchloronaphthalin is dissolved in warm fuming sulphuric acid, and the solution is diluted with water and neutralised with potash, whereby an abundant gelatinous precipitate is immediately produced; the whole is then heated to boiling and filtered. On cooling, the liquid, even when very dilute, solidifies as a transparent jelly, appearing under the microscope to consist of long and exceedingly fine needles, which being interwoven give to the salt its gelatinous appearance. The salt is thrown on a filter, washed with cold water, then dissolved in boiling water and poured into a solution of acetate of lead, whereupon a white, gelatinous precipitate, consisting of microscopic needles, is formed. If this be decomposed under water by dilute sulphuric acid, the solution filtered from sulphate of lead solidifies on cooling as a transparent jelly of terchlorosulphonaphthalic acid, consisting of microscopic needles, which, when dried and dissolved in boiling alcohol, is deposited on cooling, as a crystalline magma.

It displaces the strongest acids from their compounds, and precipitates the dilute solutions of sulphate and nitrate of potash, soda, magnesia, or oxide of nickel, as well as chloride of barium or calcium.

Ammonia-salt. Readily soluble in water and in aqueous ammonia.

Potash-salt. Opaque, microscopic laminæ; readily soluble in boiling, and almost insoluble in cold water. It is but slightly dissolved by boiling alcohol.

Baryta-salt. When a dilute, boiling solution of chloride of barium is decomposed by terchlorosulphonaphthalate of ammonia; a gelatinous precipitate, consisting of microscopic needles, is deposited from the solution on cooling. Contains 31·5 p. c. BaO,SO^3 ($C^{20}Cl^3BaH^4,2SO^3$ = 30·6 p. c.) Dissolves in from 300 to 400 pts. of boiling water.

Lime-salt. The ammonia salt added to a warm dilute solution of chloride of calcium, throws down a transparent starch-like jelly.

Cuprammonium-salt. Prepared by pouring the ammonia-salt into acetate of copper, adding ammonia, and heating. On cooling, the solution solidifies in a thready jelly. The washed salt is lilac-blue, and becomes blue on drying. Its water cannot be estimated, as it parts with ammonia on drying.

Laurent found 6·3 p. c. N and 9·1 p. c. CuO; the formula $C^{20}Cl^3CuH^4,2SO^3 + 2NH^3 + 4HO$ requires 6·7 p. c. N and 9·5 p. c. CuO.

Hydrochlorate of Terchloronaphthalin.

$C^{20}Cl^3H^5,HCl$.

LAURENT. *Ann. Chim. Phys.* 66, 199.

If chlorine-gas be passed through crude oily hydrochlorate of chloronaphthalin (p. 39), and its action promoted by warming or by sun-light, a thick oil is obtained, from which a mixture of solid chlorides is precipitated by a small quantity of ether at 0°. The decanted ethereal solution contains an oil, which Laurent supposed to be hydrochlorate of terchloronaphthalin, since it is resolved by boiling with potash or by distillation, into hydrochloric acid and terchloronaphthalin A (see also *Preparation* 1, p. 51).

Bihydrochlorate of Terchloronaphthalin.

$C^{20}Cl^3H^5,2HCl$.

LAURENT, *Rev. scient.* 13, 78.

Chloride of Chloronaphthase. (Laurent.) *Bichlorure de naphtaline chlorée.* (Gerhardt.) *Bichlornaphtylchlorür-Bichlorwasserstoff.* (Kolbe.) *Zweifach-Hydrochlor-Trichlornaphtalin.*

Formation. Exists in two different modifications, which are simultaneously formed when bihydrochlorate of bichloronaphthalin is treated with chlorine-gas.

A. *Solid modification.* 1. Fused bihydrochlorate of bichloronaphthalin is treated with chlorine-gas. It is difficult to conduct the operation successfully, since if the temperature be too low no reaction takes place; and if too strong a heat is applied, the chloride formed is further decomposed. — 2. Crude hydrochlorate of chloronaphthalin is treated with chlorine-gas. After the solid bihydrochlorate of bichloronaphthalin has been separated by ether from the buttery product of the action of chlorine on naphthalin (p. 46; *preparation*) and the ether expelled by heat from the oily chloride, chlorine is passed through the oil for two or three days; if the liquid thereby becomes too thick, it is gently warmed. A few drops of ether are now added, to render the mass more fluid, and it is allowed to stand in a cool place, whereupon a crystalline precipitate, exactly like $C^{20}Cl^2H^6,2HCl$ *a*, is formed. The supernatant oil is decanted, and the deposit thrown on a filter, washed with a little ether, and finally dissolved in boiling ether. The solution is allowed to stand for several days in a wide-mouthed vessel covered with paper. The crystals which are then deposited on the bottom of the vessel, are sometimes a mixture of $C^{20}Cl^2H^6,2HCl$ and $C^{20}Cl^3H^5,2HCl$. The crystals of the last compound being much larger than those of the first and easy to distinguish, may be readily picked out. The selected crystals are dissolved in the mother-liquor by a gentle heat, then recrystallised, again picked out, and finally recrystallised once or twice from ether.

Properties. Crystallises from ether in rhombic prisms (Fig. 68), the obtuse lateral edges being truncated; $u' : u = 70° \, 15'$; $u' : u$ over $t = 109° \, 45'$; $t : i = 115° \, 55'$; $i : u = 111° \, 25'$. Sometimes several other bevelling faces occur, belonging to different acute and obtuse horizontal prisms, as well as the octahedral faces *a*. The crystals are transparent and colourless. Crystallised from alcohol it presents an entirely dissimilar form, viz., an oblique rhombic prism (Fig. 91); $a : a = 110°$ (about); $i : u$ between 118° and 119; $a : u =$ between 127° and 128°.

Melts at 105°, and when completely fused may be cooled down to 84° without becoming solid; it then crystallises slowly in nodules formed of concentric rings; the last portions remain fluid, or rather viscid, until they reach the common temperature. If the substance has been melted at 105° or 110°, and a crystal is then thrown into the liquid, it rapidly solidifies at 105° in beautiful oblique rhombic tablets. If the liquid becomes solid between 105° and 54°, a mixture of both forms is obtained, *i.e.*, nodules and tablets, but the latter much more acute than those previously obtained. (Laurent.)

			Laurent. mean.
20 C	120	39·41	39·43
7 H	7	2·30	2·31
5 Cl	177·5	58·29	
$C^{20}Cl^3H^5,2HCl$	304·5	100·00	

Decompositions. 1. Completely decomposed by *distillation*, evolving hydrochloric acid, yielding the terchloronaphthalins A and D, and leaving no residue. — 2. Converted by boiling *nitric acid* into chloroxynaphthalic phthalic, and oxalic acids, together with crystalline oxychloronaphthalose. — Converted by boiling *alcoholic potash* into chloride of potassium and the terchloronaphthalins A, C, and G.

Insoluble in *water*; slightly soluble in *alcohol*, rather soluble in *ether* (more readily than the chloride $C^{20}Cl^2H^6,2HCl$).

B. *Liquid modification.* — This is the oil obtained in the preparation of the solid modification (p. 54, 2).

			Laurent.
20 C	120	39·41	38·30
7 H	7	2·30	2·30
5 Cl	177·5	58·29	
$C^{20}Cl^3H^5,2HCl$	304·5	100·00	

It is completely converted by *distillation* into hydrochloric acid and terchloronaphthalin A, mixed with a little oil. With boiling *alcoholic potash*, it yields the same products as the solid modification A.

Appendix to the Chlorine-nucleus, $C^{20}Cl^3H^5$.

Laurent's Chlorure de Chlonaphtane.

$C^{20}Cl^{0\cdot5}H^{7\cdot5},Cl^4$.

LAURENT. *Rev. scient.* 13, 77.

Found 1: — in crude hydrochlorate of chloronaphthalin prepared by the method described at page 39; secondly, in the ethereal mother-liquor, from which bihydrochlorate of terchloronaphthalin has been crystallised. (Comp. p. 56.)

Preparation. Crude hydrochlorate of chloronaphthalin (p. 39) left for several weeks in a cool place, deposits a white granular mixture of the chloride $C^{20}Cl^2H^6,2HCl$ and of chlorure de chlonaphtane. The oil is decanted; the crystals are laid upon paper, until the paper no longer shows grease spots; and the product is treated with a little ether, which dissolves the last traces of oil together with all the chlorure de chlonaphtane and a small quantity of bihydrochlorate of bichloronaphthalin. Chlorure de chlonaphtane then crystallises from the solution, the oil remaining dissolved. The crystals are treated with alcohol, which does not dissolve the bihydrochlorate of chloronaphthalin, and the crystals obtained by evaporating the alcoholic solution are purified by recrystallisation.

Properties. Crystallises in needles. Melts at 57° C, and does not solidify on cooling, but if a crystal of the chloride be added to the liquid it is immediately converted into a transparent mass of crystals.

	Needles.		Laurent.
20 C	120	41·77	42·20
7·5 H	7·5	2·61	2·75
4·5 Cl	160	55·62	
$C^{20}H^{7.5}Cl^{4.5}$	287·5	100·00	

Decompositions. 1. Decomposed by repeated *distillation* into hydrochloric acid and three substances, the first of which crystallises out after the distillate has stood for a long time, and appears to be the wax-like terchloronaphthalin A. The second crystallises from alcohol in needles; the third is oily; both appear to be modifications of bichloronaphthalin and to have been formed as represented by the equation:

$$2\,C^{20}H^{7.5}Cl^{4.5} = 4\,HCl + C^{20}H^{5}Cl^{3} + C^{20}H^{6}Cl^{2}.$$

2. Decomposed by *alcoholic potash* into chloride of potassium and a substance which is perhaps $C^{20}Cl^{2.5}H^{5.5}$.

Chlorure de chlonaphtane cannot be a mixture of the chlorides $C^{20}Cl^{2}H^{6},2HCl$ and $C^{20}Cl^{3}H^{5},2HCl$, since both are much less fusible and less soluble in ether and in alcohol. (Laurent.)

Laurent's Chloride of Naphthalin and Chlonapthtise.

$C^{80}H^{29}Cl^{19}$.

LAURENT. *Rev. scient.* 13, 83.

Preparation. Difficult to prepare. Chlorine is passed through fused bihydrochlorate of bichloronaphthalin. If insufficient heat be applied, the substance is not attacked, and too great a heat decomposes it. If the action of the chlorine be too long continued, bihydrochlorate of quadrichloronaphthalin is formed. If the operation has been conducted successfully, the double chloride is obtained, mixed with bihydrochlorate of quadrichloronaphthalin and some other crystallisable and oily substances. These last are extracted by cold ether, and the residue, consisting of the two first substances, is dissolved in boiling ether, and the solution allowed to evaporate spontaneously in an imperfectly closed vessel. In a few days, rhombic tablets of the double chloride and right rhombic prisms of bihydrochlorate of quadrichloronaphthalin are obtained. The first is picked out with a forceps, redissolved in ether, allowed to crystallise, and the rhombic tablets are again picked out. These are finally dissolved in boiling alcohol and crystallised by cooling the solution.

Crystals: fig. 86 without the faces *m* and *f*; $i : h$ behind = 120° (about); $u : h$ below = 130° (about); $i : u$ = about 110°; and accordingly it has the same form as bihydrochlorate of bichloronaphthalin *a*. Melts at 160°. (Laurent.)

	Tablets.		Laurent. *mean.*
80 C	480	40·55	40·52
29 H	29	2·46	2·50
19 Cl	674·5	56·99	
$C^{80}H^{29}Cl^{19}$	1183·5	100·00	

Hence it has the composition of a compound of 3 At. bihydrochlorate of terchloronaphthalin $= C^{60}H^{21}Cl^{15}$, and 1 At. bihydrochlorate of bichloronaphthalin $= C^{20}H^{8}Cl^{4}$. — It is not a mixture, since on *distillation*, it yields terchloronaphthalin A, and an oil, together with hydrochloric acid gas. Boiled with *alcoholic potash*, it parts with 2 At. hydrochloric acid, and yields microscopic needles, which are not obtained from a mixture of the two chlorides. Its melting point is also higher than that of either chloride. (Laurent.)

Chlorine-nucleus $C^{20}Cl^{4}H^{4}$.

Quadrichloronaphthalin. $C^{20}Cl^{4}H^{4}$.

LAURENT. *Ann. Chim. Phys.* 59, 196; Further, *Ann. Chim. Phys.* 66, 203; Further, *Rev. scient.* 12, 218.

Tetrachloronaphtaline, Chloronaphtalose, Chlonaphtose. (Laurent.) *Dekatetrylchlorid.* (Berzelius.) *Chloride of terchloronaphthyl.* (Kolbe.) *Naphtaline quadrichlorée.* (Gerhardt.)

Formation. Exists, according to Laurent, *in four different modifications.* A, B, E, and K, *which are formed in different ways.*

Chief characteristics of the Quadrichloronaphthalins. (Laurent, *Rev. scient.* 12, 221.)

	A.	B.	E.	K.
Elasticity	Soft	Brittle	Flexible	Flexible
Form	6-sided prisms of 120°	Oblique prisms with oblique base of 100°, 101°, 103°	Long needles, rhombus of 94°	Short needles, rhombus of 100°
Melting-point	106°	124°	170°	125°
Crystalline form after fusion	Microscopic rosettes	Needles	Needles	Rosettes
In ether	Very soluble	Very slightly soluble	Very slightly soluble	Very slightly soluble

1. Modification A. Formed when naphthalin, or one of the first products thereof by the action of chlorine, is heated to boiling and treated with chlorine-gas.

Preparation. Chlorine is passed through fused terchloronaphthalin A. — 2. (Very advantageous.) Chlorine is passed through impure hydrochlorate of chloronaphthalin, until the mass, which has been kept fused, solidifies when slightly cooled, and the white crystalline product, which generally contains an admixture of oil, is recrystallised two or three times from boiling alcohol. Thus prepared it sometimes still contains perchloronaphthalese, which may be easily recognised by its crystalline form. — 3. On distilling bihydrochlorate of quadrichloronaphthalin, hydrochloric acid is evolved and a mixture of quadrichloronaphthalin A and B passes over, from which A is extracted by ether.

Properties. Long, white or yellowish needles. Crystallises in 6-sided prisms of 120°; the crystals are very like those of terchloronaphthalin A, but are more brilliant, and are not terminated by needles, but generally rounded at the angles; almost all the crystals have an opening parallel to the axis. Melts at 106°, and on cooling solidifies in microscopic rosettes. Soft like wax and plastic. It sublimes at higher temperature unchanged in small needles.

			Laurent.
20 C	120	45·12	44·5
4 H	4	1·51	1·5
4 Cl	142	53·37	
$C^{20}Cl^4H^4$	266	100·00	

Decompositions. 1. Heated on a combustible body, it *burns* with a green-edged, smoky flame. — 2. With *chlorine* at a gentle heat it forms hexachloronaphthalin. 3. It is not attacked by boiling *acids.* 4. Converted by *fuming sulphuric acid* into quadrichlorosulphonaphthalic acid. — 5. When it is heated with *potassium,* light is evolved and carbon deposited. — 6. Not decomposed by boiling *alcoholic potash.* It may be melted and volatilised on fragments of potash, without undergoing decomposition. If its vapour be passed over lime heated nearly to redness, carbon is deposited and chloride of calcium formed.

Combinations. Very slightly soluble in boiling *alcohol.* It requires four or five times as much *ether* for its solution as terchloronaphthalin.

2. *Modification* B. (Preparation, *vid. sup.*)

Properties. Highly lustrous prisms of the doubly oblique prismatic system. Fig. 124, without z-faces; $y : u = 100°$; $y : v = 101° 30'$; $v : u = 103°$. Melts about 125°, and solidifies in beautiful needles on cooling. Distils without decomposition.

Laurent found 45·00 p. c. C and 1·50 p. c. H.

It is not attacked by *potash.* Dissolves very slightly in *ether,* less than A.

3. *Modification* E. (*Parachloronaphtalose.* Laurent.)

Formation. By distilling bihydrochlorate of quadrichloronaphthalin X, hydrochloric acid being evolved; or by boiling the same substance with alcoholic potash.

Preparation. Oily bichloronaphthalin A (p. 41) is cooled in order to free it from the accompanying solid modifications, and chlorine is passed through it in the cold for a long time (whereupon it acquires the consistence of honey); it is then warmed and treated with more chlorine. The product, after standing for 4 days, does not yield a deposit, but when shaken with half of its volume of ether, it gives a white pulverulent precipitate. It is the crystallised modification of $C^{20}Cl^4H^4,2HCl$, since the oil contained a little bichloronaphthalin C. When the ethereal liquid is evaporated, and the residual X-$C^{20}Cl^4H^4,2HCl$, boiled with alcoholic potash, which is renewed four or five times, it yields a crystalline substance, contaminated with a brown oil. The same product is likewise formed when the chloride is distilled. To separate the crystals from the oil, they are pressed between blotting paper and boiled with ether-alcohol. The product is finally distilled.

Properties. Crystallises from ether or rock-oil in microscopic silky needles. Melts at 170°, and solidifies in a radiated mass. Distils without decomposition. Inodorous.

	Needles.		Laurent.
20 C	120	45·12	45·79
4 H	4	1·51	1·65
4 Cl	142	53·37	
$C^{20}Cl^4H^4$	266	100·00	

It is not attacked by *potash.*

It is but very slightly soluble in boiling *alcohol*, and not much more in warm *ether;* the accompanying brown oil considerably increases its solubility.

At the ordinary temperatures, it is almost insoluble in rock-oil, but readily soluble at the boiling point; on cooling, the solution becomes completely filled with long needles.

4. *Modification* K. Crystallised bihydrochlorate of quadrichloronaphthalin C is boiled with alcoholic potash as long as chloride of potassium is formed; the whole is then diluted with water, the residue washed with alcohol or with ether, and dissolved in boiling ether or rock-oil. The solution deposits crystals on cooling.

Properties. Very fine and short needles, forming nodular groups; their section is a rhombus of 100° + 80°. Melts at 125°, and on cooling solidifies in an opaque mass. Distils without decomposition.

Laurent found 44·90 p. c. C and 1·50 p. c. H.

It is not attacked by *potash.* Dissolves very sparingly in *alcohol* and in boiling *ether,* likewise in cold *rock-oil,* but to a greater amount in boiling rock-oil. The solution in rock-oil deposits on cooling nodular grouped needles, which occupy but a very small portion of the liquid.

Appendix to Quadrichloronaphthalin.

Chloronaphtone F. $C^{20}H^{4.5}Cl^{3.5}$.

LAURENT. *Rev. scient.* 12, 215.

Formation & Preparation. By passing chlorine through fused bichloronaphthalin F, hydrochloric acid being evolved; purified by recrystallization from *boiling* alcohol.

Colourless laminæ. It is the only radical without definite form. After fusion, it solidifies in a scaly mass. Distils without decomposition.

Laurent found 48·0 p. c. C, and 2·0 p. c. H; by calculation, 48·3 p. c. C, and 1·8 p. c. H.

It is possibly an isomorphous mixture of the unknown modifications F, of bi- and terchloronaphthalin. (Laurent.) Somewhat readily soluble in *alcohol,* very soluble in *ether.*

Conjugated compound of the Chlorine-nucleus, $C^{20}Cl^4H^4$.

Quadrichlorosulphonaphthalic Acid.

$C^{20}H^4Cl^4S^2O^6 = C^{20}Cl^4H^4,2SO^3$.

Laurent. *Compt. rend.* 21, 33; further, *Compt. chim.* 1849, 397; abstr. *Ann, Pharm.* 72, 300; *Liebig & Kopp's Jahresb.* 1849, 442.

Quadrichloronaphthylodithionic acid. Acide sulfonaphtalique quadrichloré. (Gerhardt.) *Quadrichlornaphtalinschwefelsäure.*

Known only in combination with potash.

Formation and Preparation. Produced by heating quadrichloronaphthalin with fuming sulphuric acid. When the whole is completely dissolved, the liquid is diluted with water, neutralised with potash, heated to boiling, and rapidly filtered. On cooling, the potash-salt is deposited in crystalline flakes, which are washed on a filter and dried. These contain 22·0 p. c. KO, SO^3, corresponding to the formula $C^{20}Cl^4KH^3,2SO^3$ which requires 22·6 p. c. KO,SO^3. Almost insoluble in cold and only slightly soluble in hot *water;* readily soluble in boiling *alcohol.*

The alcoholic solution of the potash-salt does not precipitate *acetate of baryta;* but the liquid is rendered gelatinous by the addition of water.

Bihydrochlorate of Quadrichloronaphthalin.

$C^{20}H^6Cl^6 = C^{20}H^4Cl^4,2HCl$.

Laurent. *N. Ann. Chim. Phys.* 59, 196; 66, 196 and 203; further (complete description of the three modifications), *Rev. scient.* 13, 85.

Perchloronaphtalèse, Chlorure de chlonaphtèse. (Laurent.) *Dekahexylsuperchlorid.* (Berzelius.) *Trichlornaphtylchlorür-Bichlorwasserstoff.* (Kolbe.) *Bichlorure de naphtaline bichlorée.* (Gerhardt.) *Zweifach-Hydrochlor-Quadrichlornaphtalin.*

Formation. Produced by treating bichloronaphthalin with chlorine, and in three different modifications, according as the modifications C, A, or X *are employed.*

1. *Modification* C. 1. Bichloronaphthalin C is kept in fusion and treated with chlorine; no hydrochloric acid is evolved. The product is purified by washing with a little ether, dissolving in boiling ether, and crystallising. — 2. Chlorine is passed through the crude mixture of bichloronaphthalin obtained by distilling $C^{20}Cl^2H^6,2HCl$ (p. 42); the thick transparent product is diluted with a little ether; and the white

crystalline powder, which is deposited after a few minutes, is recrystallized from boiling alcohol.

Properties. Crystallises from ether on cooling, or better by slow evaporation, in small, brilliant, oblique, rhombic prisms: fig. 99, with faces m and without i; $u' : u$ = between 90° and 91°; $x : x$ = between 122° and 123°; $x : u$ = between 128° and 129°. Colourless, inodorous. Melts at 141°; and after complete fusion, solidifies in needles; when only partly melted, it crystallises in prisms, and apparently at a higher temperature.

	Prisms.		Laurent.
20 C	120	35·40	35·33
6 H	6	1·77	1·89
6 Cl	213	62·83	
$C^{20}Cl^4H^4,2HCl$	339	100·00	

Decompositions. 1. By *distillation*, it evolves hydrochloric acid and yields a small quantity of quadrichloronaphthalin A, and much B. — 2. With boiling *alcoholic potash* it forms chloride of potassium and quadrichloronaphthalin K. — 3. *Potassium* decomposes it at a gentle heat, with evolution of light and deposition of carbon.

Slightly soluble in *ether*, still less in *alcohol*.

2. *Modification* A. Bichloronaphthalin A is treated with chlorine, whereupon only a very small quantity of hydrochloric acid is evolved.

Properties. Oily liquid.

On *distillation* it evolves hydrochloric acid and yields quadrichloronaphthalin A, together with traces of an oil. Boiled with *alcoholic potash*, it is resolved into chloride of potassium and quadrichloronaphthalin A.

3. *Modification* X. Bichloronaphthalin X is treated with chlorine, whereupon no appreciable quantity of hydrochloric acid is evolved. The oil becomes very viscid, owing to the formation of small quantities of modification C, which are separated by shaking up the liquid with a small quantity of ether. The ethereal solution is evaporated.

Properties. Oily liquid.

On *distillation*, it evolves hydrochloric acid and yields quadrichloronaphthalin E: the same products are obtained with *alcoholic potash*.

Chlorine-nucleus $C^{20}Cl^6H^2$.

Sexchloronaphthalin. $C^{20}Cl^6H^2$.

LAURENT. *Rev. scient.* 12, 233; further, *Compt. rend.* 16, 861.

Chlonaphtalase A. (Laurent.) *Chloride of quintichloronaphthyl.* (Kolbe.) *Sechsfach-Chlornaphtalin.*

Formation and Preparation. Terchloronaphthalin A is treated with chlorine for a long time at an elevated temperature. If the product contains perchloronaphthalin, it is extracted with ether, wherein the last substance is but sparingly soluble.

Properties. Six-sided prisms with angles of 120°. Soft like wax and may be bent in every direction. Melts and solidifies at 143°. Distils without decomposition.

		Prisms.	Laurent.
20 C	120	35·88	36·00
2 H	2	0·60	0·66
6 Cl	213	63·52	
$C^{20}Cl^6H^2$	335	100·00	

Decompositions. It is not attacked by *potash,* or by dilute *sulphuric* or *hydrochloric acid.* It is dissolved sparingly by warm *oil of vitriol.* — Boiling *nitric acid* converts it slowly into oxide of chloroxynaphthalise, $C^{20}Cl^6O^2,O^2$. (Laurent.)

Soluble in about 20 pts. *ether;* dissolves more abundantly in *rock-oil,* scarcely at all in *alcohol.*

Appendix to Sexchloronaphthalin.

Chlonaphthalane A. $C^{20}Cl^{5.5}H^{2.5}$.

LAURENT. *Rev. scient.* 12, 232.

Formation and Preparation. On treating bichloronaphthalin C with chlorine, aided by a gentle heat, a mixture of sexchloronaphthalin A and of chlonaphthalane A is obtained, which is separated by crystallisation from its solution in ether mixed with a little alcohol. By spontaneous evaporation, fine needles of sexchloronaphthalin crystallise out, then fine as well as thicker needles. The liquid is then decanted, and chloronaphthalane is obtained on further evaporation.

Properties. Six-sided prisms of 120°, pierced parallel to the axis. Slightly yellow, and soft like wax. After melting, it crystallises at 131° C in microscopic rosettes. Volatile without decomposition; not decomposed by hydrate of potash.

Laurent found 37·53 p. c. C, and 0·83 p. c. H; calculation, 37·7 p. c. C and 0·8 p. c. H.

Dissolves in *ether,* but less freely than quadrichloronaphthalin A; scarcely soluble in *alcohol.*

Chlorine-nucleus $C^{20}Cl^8$.

Perchloronaphthalin. $C^{20}Cl^8$.

LAURENT. *Rev. scient.* 12, 234.

Chloronaphtalis A. (Laurent.) *Chloride of perchloronaphthyl.* (Kolbe.) *Naphtaline perchlorée.* (Gerhardt.)

Formation and Preparation. Chlorine is allowed to act for a long time upon terchloronaphthalin A kept in fusion. The sexchloronaphthalin is removed from the product by means of ether, and the residue is treated with boiling rock-oil.

Properties. Light yellow, easily friable, acicular prisms with angles of 112° 30′ and 67° 30′. Melts at 172°; volatile without decomposition.

	Prisms.		Laurent.
20 C	120	29·75	29·88
8 Cl	284	70·25	
$C^{20}Cl^{8}$	404	100·00	

Laurent obtained in his analysis 0·06 p. c. H, in addition.

The compound is not attacked by *potash*.
Very slightly soluble in boiling *alcohol* and *ether*.

Oxychlorine-nucleus $C^{20}ClH^{5}O^{2}$.

Chloronaphthalic Acid.

$C^{20}ClH^{5}O^{6} = C^{20}ClH^{5}O^{2},O^{4}$.

LAURENT. *Compt. rend.* 16, 861; *Ann. Chim. Phys.* 74, 26; *Rev. scient.* 13, 592; abstr. *Ann. Pharm.* 35, 292.
WOLFF & STRECKER. *Ann. Pharm.* 75, 14.

Acide chloronaphtisique. (Laurent.) *Acide chloroxynaphtalique.* (Gerhardt.)

Formation. By boiling hydrochlorate of terchloronaphthalin with nitric acid; Laurent afterwards obtained only chloride of chloroxynaphthalin, and therefore thought it probable that the acid was formed from this substance when the two bodies were separated by very dilute alcoholic potash.

2. By boiling chloroxynaphthalin with concentrated alcoholic potash:

$$C^{20}Cl^{2}H^{4}O^{4} + KO,HO = C^{20}ClH^{5}O^{6} + KCl.$$

Preparation. Bihydrochlorate of terchloronaphthalin (Laurent) is boiled with nitric acid, till a yellow oil, which becomes very thick on cooling, is formed. This is mixed with ether, whereupon a yellow substance (chloride of chloroxynaphthalin with or without chloronaphthalic acid) is precipitated; on boiling the latter with alcoholic potash, it dissolves completely. The liquid is diluted with a small quantity of water and neutralised with an acid, whereupon chloronaphthalic acid gradually crystallises out on cooling. (Laurent.) — Wolff & Strecker once obtained by this method an acid, which did not yield the common golden-yellow baryta-salt, but a purple-red salt, perhaps bi- or terchloronaphthalic acid. (Wolff & Strecker.)

Properties. Long, yellow, transparent, inodorous, very delicate needles, permanent in the air; their ends show under the microscope re-entering angles, because they consist of two twin crystals. Sometimes short irregular crystals are met with, which, however, also show the re-entering angle. Melts about 200° C., and on cooling crystallises in laminæ, which, being composed of rectangular prisms, likewise exhibit a re-entering angle at their ends. Distils without decomposition. (Laurent.)

			Laurent. *at* 100° *in vacuo.* *mean.*
20 C	120	57·6	57·00
5 H	5	2·4	2·45
Cl	35·5	16·8	16·68
6 O	48	23·2	23·87
$C^{20}ClH^5O^6$	208·5	100·0	100·00

This compound is alizarin, in which 1 At. H is replaced by 1 At. Cl, as is evident from the analogy between the two substances, in composition, properties and decomposition-products, especially with nitric acid. (Wolff & Strecker.)

Decompositions. Resolved by boiling *nitric acid* into phthalic, oxalic, and hydrochloric acids (unless perhaps a chlorophthalic acid, $C^{16}ClH^5O^6$, is formed: Wolff & Strecker):

$$C^{20}ClH^5O^6 + 4\,HO + 6\,O = C^{16}H^6O^8 + C^4H^2O^8 + HCl. \quad \text{(Laurent.)}$$

2. Chloronaphthalic acid cannot be reduced to alizaric acid either by Melsens' method (reduction by *potassium-amalgam*, ix, 211), or by that of Kolbe (reduction in the *voltaic circuit*, vii, 295). The aqueous acid produces with potassium-amalgam the dark red solution of the potash-salt, which does not appear blue by reflected light; only a small quantity of the acid is decomposed in this reaction. The potash solution of the acid becomes light in the electric current. (Wolff & Strecker.)

Combinations. It does not dissolve appreciably in *water*.

Dissolves in strong *sulphuric acid*, and is precipitated therefrom by water.

With Bases. — *Chloronaphthalates.* The acid forms very beautiful salts, varying between yellow, orange, and carmine-red. A piece of paper saturated with the aqueous solution of the acid, is immediately turned red by ammonia-vapour. The salts yield by distillation a new crystalline substance, and leave a residue of metallic chloride and charcoal. — Hydrochloric acid precipitates the acid from them. — They are almost insoluble in water, and are, with the exception of the potash-salt, obtained by double decomposition from the solution of the ammonia-salt in 30 pts. water.

Chloronaphthalate of Ammonia. The acid is added to a hot dilute solution of ammonia in alcohol or water, whereupon the salt crystallises on cooling in radiated crimson needles. By distillation it yields much carbon and a white sublimate. (Laurent.)

Chloronaphthalate of Potash. Hydrate of potash is heated to boiling with 10 or 15 pts. water or alcohol, and the acid is added till the alkali is saturated. Crystallises on cooling in striated carmine-coloured needles, which must be washed with a little alcohol. Dried at 100° in vacuo, it contains 18·07 p. c. KO, corresponding to the formula $C^{20}ClKH^4O^6 + Aq$. Calculation = 18·46 p. c. KO. (Laurent.)

Chloronaphthalate of Baryta. Chloride of barium precipitates from the ammonia-salt (when dilute, after a short time) very friable silky needles, which are orange-coloured when dry, and become red under the burnisher. Dried in vacuo at 100°, it contains 27·27 p. c. BaO, corresponding to $C^{20}ClBaH^4O^6$. (Laurent.) (By calculation = 27·7 p. c. BaO.)

Chloride of Strontium precipitates orange-yellow needles.

Chloronaphthalate of Lime. When chloride of calcium is added to a solution of the ammonia-salt, the liquid after a few minutes becomes filled with long orange-yellow needles.

The ammonia-salt immediately yields with *potash-alum* an orange-yellow precipitate; with *sulphate of cadmium*, an instantaneous brilliant vermilion-red precipitate, which under the microscope is seen to consist of yellow cruciform crystals.

With *acetate of lead*, it forms an orange-yellow precipitate. The solution of the acid in boiling alcohol, forms with alcoholic acetate of lead, beautiful, silky, orange-coloured, four-sided needles. It precipitates *subacetate of lead*, orange-red; *ferrous and ferric sulphates*, brown; with *chloride of cobalt* it produces an instantaneous crimson-red precipitate, which is blood-red after drying, and then becomes vermilion-red under the burnisher. It yields a crystalline carmine-coloured precipitate with *cupric acetate*; with *mercuric chloride* a reddish-brown; and with *nitrate of silver* a blood-red precipitate, which is dense when precipitated from hot solutions, and, when examined with the microscope, is found to consist of carmine-red needles.

Chloronaphthalic dissolved with difficulty in boiling *alcohol* and in *ether*. It does not dye fabrics either mordanted with alumina or oiled and mordanted for Turkish-red. (Wolff & Strecker.)

Appendix to Chloronaphthalic Acid.

1. Peculiar acid obtained from Bihydrochlorate of Terchloronaphthalin by the action of Nitric Acid.

LAURENT. *Ann. Chim. Phys.* 74, 26.

Formation and Preparation. Formed by boiling the oily modification of bihydrochlorate of terchloronaphthalin for two or three days with 6 pts. concentrated nitric acid. The acid liquid is separated from the oil, then evaporated, and the phthalic acid, which now crystallises out, is separated from the solution, which is further evaporated till the residue solidifies in a crystalline mass. This neutralised with aqueous ammonia, evaporated to dryness, taken up with boiling water, filtered from a brown, viscid substance, and again evaporated, leaves a residue, which, being dissolved in boiling alcohol, deposits after 24 hours a very small quantity of a sparingly soluble, scarcely crystalline salt, which has not been further investigated. The remaining solution is precipitated by chloride of calcium, the precipitate after standing 24 hours, thrown on a filter, washed with a little cold water, then heated to boiling with 20 pts. water, whereby only a part is dissolved, and oxalic acid is gradually added till the salt is almost completely decomposed. The liquid is then filtered and evaporated, whereupon it separates into an aqueous and an oily stratum; the latter, on being dissolved in ether, filtered from a slight residue, and evaporated, yields a peculiar oily acid.

Yields by distillation a substance which crystallises on cooling, is insoluble in water, but soluble in ammonia.

The acid dissolves in *water*, and separates by evaporation as an oily stratum.

Forms crystallisable salts with *ammonia*, *potash*, and *lime*.

2. Oxychloronaphthalenose. $C^{18}H^8Cl^6O^2$?

LAURENT. *Ann. Chim. Phys.* 74, 26.

Formation and Preparation. In the preparation of chloride of chloroxynaphthalin with nitric acid from *oily* bihydrochlorate of terchloronaphthalin. The ethereal solution, filtered from the chloride of chloroxynaphthalin (*q. v.*), deposits by spontaneous evaporation, small colourless prisms and a yellowish substance. The oil is decanted (it is almost completely converted by distillation into terchloronaphthalin), and the crystals are washed with a little ether, then with alcoholic potash, and dissolved in boiling alcohol. On cooling, oxychloronaphthalenose crystallises from the solution.

Properties. Oblique rhombic prisms or needles, colourless, and very brilliant. Melts about 160°, and distils at a higher temperature apparently without decomposition.

			Laurent.
18 C	108	31·30	31·00
8 H	8	2·32	2·22
6 Cl	213	61·73	61·07
2 O	16	4·65	5·71
$C^{18}H^8Cl^6O^2$	345	100·00	100·00

Insoluble in *water*. — Dissolves in strong *sulphuric acid* without coloration, slightly in *alcohol* and in *ether*.

Oxychlorine-nucleus $C^{20}Cl^2H^4O^2$.

Chloride of Chloroxynaphthalin.

$$C^{20}Cl^2H^4O^4 = C^{20}Cl^2H^4O^2,O^2.$$

LAURENT. *Compt. rend.* 16, 861; *Ann. Chim. Phys.* 74, 26; *Rev. scient.* 13, 592; abstr. *Ann. Pharm.* 35, 299.

Oxychloronaphtalose, Oxide of Chloroxenaphtose. (Laurent.) *Chlorure de chloroxynaphtyle.* (Gerhardt.)

Formation. By boiling bihydrochlorate of terchloronaphthalin with nitric acid. (Laurent.)

Preparation. Crystalline bihydrochlorate of terchloronaphthalin is boiled with nitric acid, till a yellow oil, becoming very viscid on cooling, has been formed. (Phthalic acid crystallises from the acid solution on evaporation.) The oil mixed with a small quantity of ether, yields a pulverulent deposit, which, after standing for one or two days, is purified by decantation and washing with ether on a filter, and then dissolved in a large quantity of boiling alcohol. On cooling, needles of chloride of chloroxynaphthalin are deposited from the solution:

$$C^{20}Cl^3H^5,2HCl + 4O = C^{20}Cl^2H^4O^4 + 3HCl. \quad \text{(Laurent.)}$$

In the first preparation, Laurent obtained the chloride of chloroxynaphthalin mixed with chloronaphthalic acid, bihydrochlorate of quadrichloronaphthalin and another crystalline substance; afterwards (*Rev. scient.* 13, 592) he obtained only the above-mentioned oil, which contains only chloride of chloroxynaphthalin, but in a very small quantity.

Properties. Brilliant, yellow needles, bent like the knee. Melts at 98°; and sublimes at a higher temperature, without decomposition, in rhombic tablets.

			Laurent.
20 C	120	52·87	53·3
4 H	4	1·76	1·8
2 Cl	71	31·27	30·7
4 O	32	14·10	14·2
$C^{20}Cl^2H^4O^4$	227	100·00	100·0

Laurent found previously 56·04 p. c. C, and 2·54 p. c. H.

Decompositions. Blackens on exposure to *light.* — 2. Converted by boiling *nitric acid* into phthalic acid. — 3. It is instantaneously turned carmine-red by *alcoholic potash;* the whole then dissolves in water as chloride of potassium and chloronaphthalate of potash.

Combinations. Insoluble in *water.* Dissolves in *oil of vitriol* with mahogany colour, and is precipitated therefrom by water in its original state.

Dissolves very slightly in *alcohol* or in *ether.*

Oxychlorine-nucleus $C^{20}Cl^5HO^2$.

Perchloronaphthalic Acid.

$C^{20}Cl^5HO^6 = C^{20}Cl^5HO^2,O^4$.

LAURENT. *Compt. rend.* 16, 861; *Rev. scient.* 13, 596.

Chloroxenaphthalesic acid. (Laurent.) *Acide perchloroxynaphtalique.* (Gerhardt.)

Formation and Preparation. When chloride of perchloroxynaphthalin is treated with potash, a very beautiful carmine-red substance is instantaneously formed, from which perchloronaphthalic acid separates on the addition of an acid:

$$C^{20}Cl^{6}O^{4} + KO,HO = C^{20}Cl^{5}HO^{6} + KCl.$$

The product is purified by dissolving it in ether, evaporating the solution, dissolving the crystalline deposit in alcohol, and adding potash, whereby a precipitate of carmine-red needles is immediately formed. These being collected on a filter, washed and decomposed by an acid, yield perchloronaphthalic acid, which may be finally recrystallised from alcohol or from ether.

Properties. Yellow, crystalline.

			Laurent.
20 C	120	34·6	35·0
H	1	0·3	0·5
5 Cl	177·5	51·2	50·5
6 O	48	13·9	
$C^{20}Cl^{5}HO^{6}$	346·5	100·0	

Hence it is formed from chloride of perchloroxynaphthalin, in the same manner as chloronaphthalic acid from chloride of chloroxynaphthalin. (Laurent.)

Combinations. When added to boiling alcoholic solution of potash or ammonia, it forms red or carmine crystalline salts, which appear to dissolve to a slight extent only in boiling water.

Oxychlorine-nucleus $C^{20}Cl^{6}O^{2}$.

Chloride of Perchloroxynaphthalin.

$$C^{20}Cl^{6}O^{4} = C^{20}Cl^{6}O^{2},O^{2}.$$

LAURENT. *Compt. rend.* 16, 861; *Ann. Chim. Phys.* 74, 26; *Rev. scient.* 13, 595; abstr. *Ann. Pharm.* 35, 292.

Chloroxenaphtalisoxyd (Laurent); *Chlorure de Perchloroxynaphtyle* (Gerhardt).

Formation. Formed by boiling sexchloronaphthalin with nitric acid, (together with chloropthalic acid, which remains in the acid solution, also an oil, and a crystalline substance, neither of which have been further investigated):

$$C^{20}Cl^{6}H^{2} + 6\,O = C^{20}Cl^{6}O^{4} + 2\,HO. \quad \text{(Laurent.)}$$

Preparation. Sexchloronaphthalin is but feebly attacked by nitric acid, 10 grammes thereof require boiling for 3 or 4 days, whereby a yellow resin, melting in the boiling nitric acid, is formed. The whole is diluted with a little water, boiled, and decanted. The resin is pulverised, and after the oil has been extracted by digestion with ether, the residue is dissolved in boiling rock-oil, from which the chloride of perchloronaphthalin is deposited a few degrees below the boiling point, and again recrystallised from rock-oil.

The rock-oil solution, when perfectly cool, deposits a second substance, which appears under the microscope to consist of orange-coloured granules, and, according to Laurent, is gradually decomposed by boiling rock-oil, which thereby acquires a brown colour.

Properties. Crystallises from boiling ether or from rock-oil in light, yellow, highly brilliant laminæ. It melts at a rather elevated temperature, and then volatilises, for the most part undecomposed.

			Laurent.
20 C	120	33·0	33·3
6 Cl	213	58·2	56·7
4 O	32	8·8	10·0
$C^{20}Cl^6O^4$	365	100·0	100·0

Decompositions. 1. Converted by boiling *nitric acid,* probably into chlorophthalic acid. 2. With *potash* or *ammonia* it forms a chloride of the metal and perchloronaphthalic acid.

Insoluble in *water* and in *alcohol;* very slightly soluble in boiling *ether,* sparingly in boiling *rock-oil.*

Bromochlorine-nucleus $C^{20}BrClH^6$.

Hydrochlorate of Chlorobromonaphthalin.

$$C^{20}H^7BrCl^2 = C^{20}BrClH^6,HCl.$$

Laurent. *Rev. scient.* 13, 580.

Subchloride of Bronaphthase. (Laurent.) *Chlorure de naphtaline bromée.* (Gerhardt.) *Hydrochlor-Chlorbromnaphtalin.*

Formation and Preparation. When chlorine is passed into crude bromonaphthalin, the liquid gradually thickens, and deposits a crystalline substance. The product is diluted with a small quantity of ether, and allowed to stand for 24 hours; the oil is then decanted, and the crystalline powder is washed with ether and dissolved in a large quantity of boiling ether, whereupon it crystallises by spontaneous evaporation.

Properties. Rhombic tables, derived from an oblique rhombic prism, resembling bihydrochlorate of bichloronaphthalin. (*Fig.* 81.) Tabular, owing to the predominance of the *i*-face; $u' : i =$ between 121° and 122°. Melts at 165°, and on cooling crystallises in well-defined rhombic tables.

	Tables.		Laurent.
20 C	120	43·2	43·0
7 H	7	2·5	2·6
Br	80	28·8	
2 Cl	71	25·5	
$C^{20}BrClH^6,HCl$	278	100·0	

By *distillation* it evolves bromine and a hydracid.

Bihydrochlorate of Bromochloronaphthalin.

$C^{20}H^8BrCl^3 = C^{20}BrClH^6,2HCl$.

LAURENT. *Compt. rend.* 21, 25; *Compt. chim.* 1850, 1; abstr. *Ann. Pharm.* 76, 399; *Liebig & Kopp's Jahresb.* 1850, 498.

Bichlorobromure de naphtaline (Gerhardt).

Formation and Preparation. Bromine is poured over bihydrochlorate of bichloronaphthalin β, and the liquid is left to stand in a closed flask for 48 hours; the excess of bromine and the undecomposed chloride are then removed by lukewarm alcohol, and the residue is dissolved in boiling ether, from which the new product crystallises on cooling.

Properties. Colourless four or eight-sided rhombic prisms, the acute lateral edges of which are generally truncated by irregular faces (*Fig.* 81), $i : u = 103° 30'$; $u' : u' =$ about 103°; hence it is isomorphous with bihydrochlorate of bichloronaphthalin β. (Laurent.)

	Prisms.		Laurent.
20 C	120	38·20	38·06
8 H	8	2·55	2·56
Br	80	25·47	
3 Cl	106·5	33·78	
$C^{20}BrClH^6,2HCl$	314·5	100·00	

It is decomposed by *alcoholic potash*, as well as by *distillation*.

Dissolves more readily in *ether* than common bihydrochlorate of bichloronaphthalin α, and less readily than the modification β of the same chloride.

Bromochlorine-nucleus $C^{20}BrCl^2H^5$.

Bromobichloronaphthalin. $C^{20}BrCl^2H^5$.

LAURENT. *Rev. scient.* 12, 214.

Chlorbronaphtise A (Laurent). *Naphtaline bromobichlorée* (Gerhardt). *Chloride of chlorobromonaphthyl* (Kolbe).

Formation and Preparation. A slight excess of bromine is poured over bichloronaphthalin AD, and the whole is allowed to stand for one or two days in an imperfectly closed vessel, whereupon hydrobromic acid is evolved. The excess of bromine is first removed by washing the product with a small quantity of alcohol and a little ammonia, and the residue is then dissolved in boiling alcohol. The compound crystallises on cooling, while any bichloronaphthalin that may be present remains in the alcoholic mother-liquor.

Properties. Colourless; of the consistence of wax. Crystallises from alcohol in fine needles, and by spontaneous evaporation of its ethereal solution, in six-sided needles, with angles between 120° and 121°. Melts at about 80°, and on cooling solidifies in rectangular parallelograms, crossed by diagonals. When it is perfectly cold, the surface of the mass has a moiréd appearance. It distils without decomposition.

			Laurent.
20 C	120	43·5	44·5
5 H	5	1·8	1·9
Br	80	29·0	
2 Cl	71	25·7	
$C^{20}BrCl^{2}H^{5}$	276	100·0	

Unattacked by *potash*.
Sparingly soluble in *alcohol;* readily in *ether.*

Appendix to the Bromochlorine-nucleus $C^{20}BrCl^{2}H^{5}$.

Laurent's Chlorébronaphtine.

$C^{20}H^{5.5}Br^{0.5}Cl^{2}$.

LAURENT. *Rev. scient.* 12, 205.

Formation and Preparation. Bichloronaphthalin X is treated with bromine, and the resulting *oily bromide* is boiled with alcoholic potash (whereby bromide of potassium is formed), and the oily product, which speedily solidifies, is precipitated by water. The mass still contains an oil, from which it may be freed by pressing between paper and repeated recrystallisation from ether-alcohol.

Properties. Colourless needles. Melts at 47°, and solidifies in rectangular parallelograms crossed by two diagonals bristling with needles. Volatile without decomposition. It is not attacked by *potash.*

Laurent found 51·1 p. c. C. and 2·3 p. c. H.; by calculation, 51·0 p. c. C. and 2·3 p. c. H.

It is not a mixture of the radicals $C^{20}Cl^{2}H^{6}$ and $C^{20}BrCl^{2}H^{5}$, first, because the bichloronaphthalin could only be the modification X, which is liquid; secondly, because other compounds corresponding to this chloride exist, which are not mixtures. (Laurent.)

Bromochlorine-nucleus $C^{20}Br^{3}ClH^{4}$.

Bihydrobromate of Terbromochloronaphthalin.

$C^{20}Br^{5}ClH^{6} = C^{20}Br^{3}ClH^{4},2HBr$.

LAURENT. *Rev. scient.* 13, 92; further, *Compt. chim.* 1850, 8.

Bromure de chlorobronaphtèse (Laurent). *Bibromure de naphtaline bromo-chlorée* (Gerhardt).

Formation and Preparation. The first distillate of chloronaphthalin is treated with bromine. A lively effervescence then ensues, owing to evolution of hydrobromic acid, and with excess of bromine, crystals are formed on standing. These are dissolved in a very large quantity of boiling ether, which on cooling deposits very small, highly brilliant prisms of the compound.

Properties. Prisms belonging to the doubly oblique prismatic system. *Fig.* 132, without u- and x-faces; with q-faces; $w : v = 96^\circ$; $y : w = 85^\circ$; $y : v = 102^\circ\,30'$; $v : e = 125^\circ$; $y : e = 135^\circ$; $w : e = 124^\circ$; $e : q = 114^\circ$; $v' : q = 121^\circ$; $w : q = 120^\circ$; $v : q = 136^\circ$. (Laurent, *Compt. chim.* 1850, 8; corrected description.)

	Prisms.		Laurent. mean.
20 C	120	21·38	21·87
6 H	6	1·07	1·17
Cl	35·5	6·33	
5 Br	400·0	71·22	
$C^{20}Br^3ClH^4,2HBr$	561·5	100·00	

It turns red before melting; evolves bromine vapour at 100°; melts about 110°, and then evolves a large quantity of bromine and hydrobromic acid, leaving an oil which on cooling crystallises in quadrilateral figures, crossed by two diagonals bristling with needles (as is the case with terchloronaphthalin).

Bromochlorine-nucleus $C^{20}Br^2Cl^2H^4$.

Bibromobichloronaphthalin.

$C^{20}Br^2Cl^2H^4$.

LAURENT. *Rev. scient.* 12, 222; further, *Compt. rend.* 14, 380.

Formation. It exists, according to Laurent, *in two isomeric modifications; modification* a (*chlorebronaphtose b,* Laurent) *obtained by the action of bromine upon bichloronaphthalin, and modification* β (*bromechlonaphtose b,* Laurent), *by the action of chlorine on bibromonaphthalin.*

1. *Modification a.* Bromine is poured over bichloronaphthalin F, whereupon hydrobromic acid is evolved, and after a few minutes the liquid solidifies in needles. These are washed with ether, and dissolved in a small quantity of warm ether.

Properties. Small, brilliant, doubly oblique prisms. Facial angles = 101° 30′ to 102° 50′ and 101° 15′. Melts at about 170°. Crystallises in needles on cooling, and exhibits dimorphism, like the terchloronaphthalins; for, if a portion be again melted, part of the fused mass crystallises again in needles; but at the same time, a second crystallisation may be observed, of opaque four-sided bodies, which cover the needles. If the whole be melted, no more needles are obtained.

			Laurent.
20 C	120	34·25	34·43
4 H	4	1·14	1·26
2 Br,2Cl	231	64·61	
$C^{20}Br^2Cl^2H^4$	355	100·00	

It is not decomposed by *distillation*, or by *potash*.
Scarcely soluble in *ether* and in *alcohol*, even on boiling.

2. *Modification β*. Obtained by heating bibromonaphthalin with chlorine.

Properties. It is deposited by the spontaneous evaporation of its ethereal solution, in small doubly-oblique prisms, which are much longer than they are broad. Inclination of the faces = 102° 10′ – 103° – 101° 20′. Melts at 160°, and distils unchanged; solidifies on cooling in a fibrous mass.

Laurent found 33·90 p. c. C. and 1·11 p. c. H.

It is not attacked by *potash*.
Scarcely soluble in *ether* and in boiling *alcohol*.

Bihydrobromate of Bibromobichloronaphthalin.

$C^{20}H^6Br^4Cl^2 = C^{20}Br^2Cl^2H^4,2\,HBr.$

LAURENT. *Ann. Chim. Phys.* 59, 196; further, *Rev. scient.* 6, 79; 13, 87.

Bromure de chlonaphtèse (Laurent). *Dekahexylsuperbromid* (Berzelius). *Chlordibromnaphtylbromür-Bibromwasserstoff* (Kolbe). *Bibromure de naphtaline bichlorée* (Gerhardt).

Formation and Preparation. Bromine is poured upon bichloronaphthalin in a stoppered bottle, and the stopper is firmly tied down. The bichloronaphthalin first dissolves in the bromine, and then the whole gradually becomes one solid crystalline mass. On opening the bottle, no hydrobromic acid is evolved. The excess of bromine and any unattacked bichloronaphthalin that may be present are removed by washing the product with ether; the residue is dissolved in alcohol or in boiling ether, or heated in a *sealed* glass tube with ether to 100° (but not higher), and crystallised by cooling the solution.

Properties. Small, brilliant crystals, very like bihydrochlorate of bichloronaphthalin; *Fig.* 83; $u' : u = 101° 30'$; $i : u = 94° 30'$; sometimes the a-faces are completely removed by the enlargement of the faces i; $a : u = 133°$; $a : i =$ between 121° and 122°. It is colourless.

			Laurent.
20 C	120	23·99	23·50
6 H	6	1·05	1·05
2 Cl	71	13·83	
4 Br	320	61·13	
$C^{20}Cl^2Br^2H^4,2HBr$	517	100·00	

Decompositions. 1. Melts a little above 100°, immediately turning red and evolving bromine-vapour. If heat be applied as long as bromine continues to be evolved, bichloronaphthalin C remains in the residue, which may be reconverted into the bromide by means of bromine.— 2. It is decomposed with difficulty by boiling *alcoholic potash*; a substance is then precipitated by water from the solution, which, when crystallised from ether-alcohol, yields needles, while an oil remains in solution. The needles melt at 55°, volatilise without decomposition, are very readily soluble in alcohol and in ether, and contain 41·8 p. c. C. and 1·7 H.; hence Laurent considers them as $C^{20}H^{4\frac{5}{6}}Br1\frac{1}{6}Cl^2$, or as a mixture of 5 At. $C^{20}BrCl^2H^5$ and 1 At. $C^{20}Br^2Cl^2H^4$. Hence potash acts in the same way as heat, *i. e.*, it removes the bromine as such, and not as hydrobromic acid, and forms a radical or a mixture of two radicals, which cannot be decomposed by distillation. — 3. If the bromide be heated with *ether* in a sealed glass tube between 120° and 130°, it loses the property of crystallising on cooling, and on evaporation needles are obtained, which appear to be bichloronaphthalin C.

Sparingly soluble in cold *alcohol*, and in cold *ether*.

Bihydrochlorate of Bibromobichloronaphthalin.

$C^{20}H^6Br^2Cl^4 = C^{20}Br^2Cl^2H^4,2HCl.$

LAURENT. *Rev. scient.* 13, 582.

Chlorure de bronaphtèse. (Laurent.) *Bichlorobromnaphtyl-Bichlorwasserstoff.* (Kolbe.) *Bichlorure de naphtaline bibromée.* (Gerhardt.)

Preparation. By passing chlorine over fused bibromonaphthalin a very thick oil is hereby formed, which when diluted with a small quantity of ether, deposits the chloride as a crystalline powder. In this reaction, another oil is formed which, when treated with excess of chlorine, yields the chloride, together with bihydrochlorate of bibromoterchloronaphthalin and a new oil.

Properties. Long, colourless, oblique prisms; *Fig.* 79, without the *i*-faces; $u : u =$ between 90° and 91°; $x : x =$ between 122° and 123°; $u : x = 129°$. Melts about 155°, and solidifies in prisms on cooling.

			Laurent.
20 C	120	28·03	28·14
6 H	6	1·40	1·51
2 Br,4Cl	302	70·57	
$C^{20}Br^2Cl^2H^4,2HCl$	428	100·00	

It is decomposed by *distillation*, yielding bromine, a hydracid, bromoterchloronaphthalin β, and quadrichloronaphthalin A. — *Alcoholic potash* converts it into a product crystallising in needles, and rather soluble in ether.

Very slightly soluble in *alcohol* and in *ether*.

Appendix to the Bromochlorine-nucleus $C^{20}Br^2Cl^2H^4$.

1. Laurent's Bromure de Chlorébronaphtine.

$C^{20}H^{5.5}Br^{4.5}Cl^2$?

LAURENT. *Rev. scient.* 13, 89.

Formation and Preparation. Bichloronaphthalin C is treated with excess of bromine, and exposed for several days to the sun, whereupon crystals are deposited, which are washed with ether, then dissolved in ether in a sealed tube at 100°, and allowed to cool. Those crystals are selected which have the following shape: *Fig.* 65; $i : i = 108°$; $i : u$ behind $t = 102°$; $i : u' = 120°$; $u : u = 102° \, 30'$; i right : $u = 125°$. Hence they do not belong to the right prismatic system, but to the oblique or doubly oblique prismatic system.

			Laurent.
20 C	120	21·56	22·09
5·5 H	5·5	1·00	1·11
4·5 Br,2Cl	431	77·44	
$C^{20}H^{5 \cdot 5}Br^{4 \cdot 5}Cl^{2}$	556·5	100·00	

The analysis should be repeated, since the experimental composition, as well as the properties of the body, resemble those of bihydrobromate of bibromobichloronaphthalin.

It evolves bromine by *heat*, together with a small quantity of white vapour, and leaves an easily fusible substance.

It is scarcely soluble in *ether*.

2. Laurent's *Bromide a*. This compound crystallises from the ethereal solution together with the above-mentioned substance. Right rhombic prisms; *Fig.* 63; $u' : u = 106° \, 30'$; $p : y = 135°$. Evolves bromine on application of heat, and leaves an oily residue which solidifies very slowly.

It is almost insoluble in boiling *ether*.

3. Laurent's *Bromide β* is found mixed with the crystals of the bromide *a*. *Fig.* 75; without faces *m*. Right rhombic prisms: $u' : u = 100°$; $y : y = 126°$; $u' : u = 61°$.

Evolves bromine and white vapours when *heated*. Insoluble in *ether*.

4. Laurent's *radical δ* is likewise mixed with the preceding. Oblique, rhombic prisms. *Fig.* 121; $y : u = 109°$; $y : v = 107° \, 30'$; $u : v = 108°$. Volatilizes without decomposition, and must therefore be a radical; perhaps $C^{20}H^{5}BrCl^{2}$ or $C^{20}H^{4}Br^{2}Cl^{2}$; probably the ether had taken up bromine at 100°.

Almost insoluble in *ether*.

5. Laurent's Chlorenbronaphtone B.

$C^{20}H^{4 \cdot 5}Br^{2}Cl^{1 \cdot 5}$.

LAURENT. *Rev. scient.* 12, 215.

Formation and Preparation. When bromine is mixed with crude hydrochlorate of chloronaphthalin, a hydracid is evolved, and after 24 hours, the bottom of the vessel is found covered with small crystals, which may be easily purified by washing with ether after the oil has been poured off.

Properties. Brilliant, colourless, transparent and very small oblique prisms, with oblique base. Angles of faces = between 100° and 103°, inclination of base to one of the sides = about 100°. Volatilises without decomposition.

Laurent found 36·00 p. c. C. and 1·36 H.; by calculation, 35·9 p. c. C and 1·3 H.

According to Laurent, this compound may have been formed from hydrochlorate of chloronaphthalin; but since it is produced only in very small quantity, he considers it probable that the chloride may have contained a small quantity of chlonaphthene, $C^{20}Cl^{1.5}H^{6.5}$, and that it may have been derived from this body.

Almost insoluble in *alcohol* and in *ether*.

6. Bromenchlonaphtose A. (Laurent.)

$C^{20}H^4Br^{1.5}Cl^{2.5}$.

LAURENT. *Rev. scient.* 12, 228.

Formation and Preparation. Fused bibromonaphthalin treated with chlorine, yields amongst other substances, an oily product. If this be separated from the solid product by standing under a small quantity of ether for several days and the ether then driven off; the oil again treated with chlorine with the aid of heat; the liquid portion separated from the solid by ether; and after the ether has been driven off, treated with chlorine in sunshine: a very thick oil is obtained (probably $C^{20}Br^{1.5}Cl^{2.5}H^4,HCl$ or $C^{20}Br^{1.5}Cl^{2.5}H^4,2HCl$). If this be now separated from the solid products by ether, and boiled with alcoholic potash, it deposits a mixture of bromenchlonaphthose A (very soluble in ether), and of bromenchlonaphthose B (almost insoluble in ether), which is separated by means of ether, and purified by recrystallisation from ether.

Properties. It bears a close resemblance to terchloronaphthalin A; crystallises in six-sided prisms or in needles of 120°, the apices of which are rounded off. Soft like wax, and melts when pressed together. Melts at 115° C., and on cooling crystallises in microscopic rosettes. Volatile without decomposition. It is not decomposed by hydrate of potash.

			Laurent. *mean.*
20 C	120	36·4	36·17
4 H	4	1·2	1·65
1·5 Br	120	35·6	33·55
2·5 Cl	88·75	26·8	27·99
$C^{20}Br^{1.5}Cl^{2.5}H^4$	332·75	100·0	99·36

Very soluble in *ether*, slightly soluble in *alcohol*.

Bromochlorine-nucleus $C^{20}BrCl^3H^4$.

Bromoterchloronaphthalin. $C^{20}BrCl^3H^4$.

LAURENT. *Compt. rend.* 14, 380; further, *Rev. scient.* 12, 225.

Formation. Exists according to Laurent *in three different modifications, formed under different circumstances.*

1. *Modification a.* (Chloribronaphtose *a*, Laurent.) Bromine is poured over terchloronaphthalin *a*, whereupon this compound dissolves without

decomposing. When the solution is exposed to the sun for several days, it evolves hydrobromic acid, and yields bromoterchloronaphthalin, which is purified by repeated recrystallisation from ether-alcohol.

Properties. Colourless, six-sided prisms, with angles = 117° 30′ and two = 125°. It is soft, like wax, and may be bent in every direction without breaking. After it has been melted, it crystallises between 105° and 106° in microscopic rosettes. Volatile without decomposition.

			Laurent.
20 C	120	38·99	38·91
4 H	4	1·29	1·29
Br,3Cl	186·5	59·72	
$C^{20}BrCl^{3}H^{4}$	310·5	100·00	

2. *Modification β.* (Bromachlonaphtose *a*, Laurent.) A stream of bromine is passed over bichloronaphthalin, which at first is heated till it melts. A thick oily mixture of bihydrochlorate of bibromobichloronaphthalin and an oil is obtained. If this be mixed with ether and allowed to stand, it yields crystals of the solid chloride, while the oil remains in solution. On boiling the crystals with alcoholic potash, bromoterchloronaphthalin is formed, and may be purified by repeated crystallisation from ether-alcohol.

Properties. It exactly resembles quadrichloronaphthalin A, except that the crystals are far more beautiful and well-defined. Six-sided prisms, whereof four angles = 120° 30′, and two angles = 119°. Soft, like wax; after fusion, it solidifies at about 110° in microscopic rosettes. Volatile without decomposition. It is not attacked by *potash.*

Laurent found 38·91 p. c. C. and 1·30 p. c. H.

It is rather soluble in *ether,* but less than the modification *a*; scarcely soluble in *alcohol.*

3. *Modification γ.* (Bromachlonaphtose *b*, Laurent.) When bihydrobromate of bibromobichloronaphthalin is distilled, bromine and acid vapours are evolved, and a mixture of terchloronaphthalin A and bromoterchloronaphthalin γ condenses in the receiver. Ether extracts terchloronaphthalin from the mixture, and leaves a white powder which is boiled with more ether. This solution, when left to evaporate, deposits small, brilliant, perfectly defined prisms.

Properties. Oblique prisms, with oblique base. Inclination of the sides = 102° 30′; inclination of the faces to the base = 101° and 103°. Volatile without decomposition.

Laurent found 39·04 p. c. C. and 1·48 p. c. H.

Dissolves very slightly in *alcohol* and in boiling *ether.*

Bromanchlonaphtone A. (Laurent.)

$C^{20}H^{4.5}Br^{0.5}Cl^{3}$?

LAURENT. *Rev. scient.* 12, 216.

Formation and Preparation. Chlorine is passed into bromonaphthalin, and after a short time the oil thus obtained is freed from solid matter by mixing with a little ether, and after the ether has been driven off, the oil is gently warmed and again treated with chlorine till it deposits crystalline matter afresh. This is removed by ether, and the oil is boiled with alcoholic potash. (The oil is probably $C^{20}Br^{0\cdot5}Cl^{3}H^{4\cdot5}$ + HCl or + 2HCl). The product is purified by crystallisation from boiling ether containing a little alcohol, and by spontaneous evaporation.

Properties. It bears a close resemblance to terchloronaphthalin A, but forms much finer crystals: they are six-sided prisms of 120°, the cleavage being parallel to the axis. Soft, like wax, and may be bent in every direction. Melts at 106°, and solidifies in microscopic rosettes. Distils without decomposition.

			Laurent.
20 C	120	44·45	44·03
4·5 H	4·5	1·66	1·62
0·5 Br,3Cl	146·5	53·89	
$C^{20}Br^{0\cdot5}Cl^{3}H^{4\cdot5}$	271·0	100·00	

(0·500 bromanchlonaphtone being decomposed by lime, required 0·710 silver for the precipitation; by calculation 0·700 silver. The precipitate treated with chlorine evolved bromine.)

Dissolves somewhat readily in *ether*, and very slightly in *alcohol.*

Bromochlorine-nucleus $C^{20}Br^{2}Cl^{3}H^{3}$.

Bibromoterchloronaphthalin.

$C^{20}Br^{2}Cl^{3}H^{3}$.

LAURENT. *Rev. scient.* 12, 231.

Bromide of terchlorobromonaphthyl. (Kolbe.)

Exists, according to Laurent, *in two isomeric modifications.*

1. *Modification a.* (Bromèchlonaphtuse *b*; Laurent.) When bihydrochlorate of bibromoterchloronaphthalin is boiled with alcoholic potash, a white powder is formed, which is dissolved in a large quantity of boiling ether, or better still in boiling rock-oil, and allowed to crystallise. The ethereal mother-liquor contains in solution a small quantity of a substance crystallising in needles.

Properties. Crystallises from ether by spontaneous evaporation in small and very brilliant prisms of the doubly oblique prismatic system. *Fig.* 124, without *z*-faces, with *e*-faces; $v : u = 101° 30'$; $y : w = 101° 30'$; $y : v = 101°$; $e : u = 132°$; $e : y = 115°$; $e : v = 115° 30'$. After it has been melted, it crystallises at 165° in long prisms. Volatilises without decomposition.

It is not attacked by *potash.*

			Laurent.
20 C	120	31·13	31·27
3 H	3	0·80	0·90
2 Br,3Cl	266·5	68·07	
$C^{20}Br^{2}Cl^{3}H^{3}$	389·5	100·00	

2. *Modification β.* (Chloribronaphtuse.) Bromine is poured over bihydrochlorate of bichloronaphthalin, and the mixture is exposed for four weeks to the sun. On treating the mass with ether, an oil and a crystallisable substance are dissolved out, and a residue of bibromoterchloronaphthalin, which is almost insoluble in ether, remains :

$$C^{20}H^{8}Cl^{4} + 6\,Br = C^{20}Br^{2}Cl^{3}H^{3} + 4\,HBr + HCl.$$

White powder, which crystallises from fusion in rectangular parallelograms, crossed by two diagonals.

			Laurent.
20 C	120	30·80	30·90
3 H	3	0·78	1·10
3 Cl	106·5	27·35	
2 Br	160·0	41·07	
$C^{20}Br^{2}Cl^{3}H^{3}$	389·5	100·00	

Bihydrochlorate of Bibromoterchloronaphthalin.

$$C^{20}H^{5}Br^{2}Cl^{5} = C^{20}Br^{2}Cl^{3}H^{3},2HCl.$$

LAURENT. *Rev. scient.* 13, 583 ; further, *Compt. chim.* 1850, 1 ; abstr. *Ann. Pharm.* 76, 301.

Perchlorure de bronaphtèse (the compound was first described by Laurent under this name, and the formula written $C^{20}H^{6}Br^{2}Cl^{5}$). *Chlorure de bromichlonaphtèse* (Laurent). *Terchlorobromnaphthylchlorür Bichlorwassertoff* (Kolbe.)

Formation and Preparation. By the action of chlorine on bihydrochlorate of bibromobichloronaphthalin.

Properties. Prisms of the doubly oblique prismatic system, very similar to those of the oblique prismatic system. *Fig.* 124 without faces, *z*, with faces *q*, *b*, *k*, *d*; $u : v = 110°$; $y : k = 119°$; $w : y = 101°$; $k : l$ = about 77° ; $q : d = 93°$; $d : t = 106°$. It has also been obtained in rhombic prisms by Laurent. Melts at about 150°, and crystallises in rhombic tablets on cooling. If it be heated a little above its melting point, it remains soft and transparent on cooling, and solidifies but partially, in a non-crystalline mass, which, if gently heated, crystallises in rhombic tablets.

Decompositions. On *distillation* it evolves bromine and a hydracid, and yields three other substances. (Comp. *Bromachlonaphtune* B, p. 78.) — It is converted by boiling *alcoholic potash* into bibromoterchloronaphthalin *a*. (Laurent previously obtained in this reaction another radical, *chlorénbronaphtune* $C^{20}Br^{1\cdot5}Cl^{3}H^{3\cdot5}$; see *Rev. scient.* 12, 229.)

Dissolves very sparingly in *ether*.

Appendix to the Bromochlorine-nucleus, $C^{20}Br^2Cl^3H^3$.

Laurent's Bromochlonaphtune B.

$C^{20}BrCl^{3.5}H^{3.5}$.

LAURENT. *Rev. scient.* 12, 230.

Formation and Preparation. When bihydrochlorate of bibromoterchloronaphthalin is distilled, bromine and a hydracid are evolved, and the following products are obtained: 1. Bromachlonaphtune B; 2. A chloride or a chloro-bromide of the series A, crystallising in six-sided prisms of 120°, and melting in boiling water; 3. A very small quantity of a substance crystallising from ether in small opaque nodules; less soluble in ether than 2, but more soluble than 1. — 2 and 3 are extracted from the mixture by ether; the bromachlonaphtune is dissolved in a very large quantity of boiling ether, and crystallised by spontaneous evaporation of the solution.

Very minute oblique prisms, with oblique base; *Fig.* 81, $u : u' = 101°$; $i : m =$ between 100° and 103°; $i : u =$ between 100° and 103°. When fused, it sometimes solidifies suddenly in an opaque mass, sometimes in fine needles.

Laurent found 36·33 p. c. C. and 1·11 p. c. H.; by calculation, 36·83 p. c. C. and 1·07 p. c. H.

Nitro-nucleus $C^{20}XH^7$.

Nitronaphthalin.

$C^{20}NH^7O^4 = C^{20}XH^7$.

LAURENT. (1835.) *Ann. Chim. Phys.* 59, 376; *Ann. Pharm.* 19, 38; *J. pr. Chem.* 8, 13; *Ann. Chim. Phys.* 66, 152; *Rev. scient.* 6, 88; further, 13, 68.
MARIGNAC. *Ann. Pharm.* 38, 1.
ZININ. *J. pr. Chem.* 27, 140; *Ann. Pharm.* 44, 283.
PIRIA. *Compt. rend.* 31, 488; *N. Ann. Chim. Phys.* 31, 217; *Ann. Pharm.* 78, 32; *J. pr. Chem.* 52, 56; *Pharm. Centr.* 1850, 780; *Liebig & Kopp's Jahresber.* 1850, 500.
BECHAMP. *N. Ann. Chim. Phys.* 42, 186; *Ann. Pharm.* 92, 401.

Nitronaphtalase, Ninaphtase, $C^{20}XH^7$ (Laurent); *Nitrite de naphtalase*, $C^{20}H^7O,NO^3$ (Laurent, *Ann. Chim. Phys.* 66, 152), *Nitrite of Icodecatesseryl*, $C^{20}H^7O,NO^3$ (Berzelius); *Naphthylnitrür* (Kolbe).

Formation. 1. Nitronaphthalin was first prepared by Laurent by boiling naphthalin with nitric acid, whereby red vapours are evolved and nitronaphthalin and an oil are formed:

$$C^{20}H^8 + NO^5,HO = C^{20}XH^7 + 2HO.$$

2. From naphthalin and nitric acid in the cold, without formation of red vapours and an oil (Piria). — 3. By the action of hyponitric acid on naphthalin in the cold, whereby a peculiar oil is simultaneously formed; this oil, after being exposed for some time to the air, aquires the smell of bitter almonds. (Laurent.) According to Laurent, an oil is produced

by the action of aqua regia on naphthalin in the cold, which on distillation yields carbon and another oil from which a little nitronaphthalin is deposited on cooling.

Preparation. From 5 to 6 pts. nitric acid of sp. gr. 1·33 are added to 1 pt. of naphthalin, and the whole is allowed to digest for 5 or 6 days. The matter easily cakes and must therefore at first be frequently stirred. Lemon-yellow nitronaphthalin, without any by-products, is obtained, and is washed on a filter with water. (Piria.) — 2. Naphthalin is boiled with nitric acid, whereupon red vapours are evolved, till, after 15 or 20 minutes, a yellow oil has been formed, which on cooling solidifies very slowly in a crystalline mass, consisting of nitronaphthalin and a reddish-yellow oil. This is submitted to strong pressure between blotting paper and dissolved in hot alcohol. On cooling, the liquid first deposits an oil which must be removed with a pipette; afterwards nitronaphthalin crystallises out, and is collected after 12 hours and recrystallised once or twice. The oil which has been removed with the pipette, yields a fresh crop of crystals when redissolved in the alcoholic mother-liquid. (Laurent.)

Properties. Brittle, sulphur-yellow, six-sided rhombic prisms, derived from prisms with angles of 100° and 80°, the acute angles being truncated. Melts at 43°, the thermometer rising to 54° at the moment of solidification. A few crystals melted on a glass plate, form oily drops which remain fluid for some time at ordinary temperatures, but on slight agitation, instantly solidify in needles. Volatilises without decomposition and sublimes in small needles; when rapidly heated, a considerable quantity decomposes with emission of reddish light, and forms a large deposit of carbon. (Laurent.)

			Laurent. *mean.* earlier.	 later.
20 C	120	69·35	69·86	68·70
7 H	7	4·06	4·07	4·07
N	14	8·10	8·53	8·30
4 O	32	18·49	17·54	18·93
$C^{20}XH^7$	173	100·00	100·00	100·00

Decompositions. 1. *Chlorine* at a gentle heat converts it into an oil ($C^{20}Cl^3H^5,HCl$?), which yields with potash terchloronaphthalin A. If the nitronaphthalin be too strongly heated, terchloronaphthalin A or quadrichloronaphthalin A may be directly formed. (Laurent.) — 2. With *bromine*, aided by a gentle heat, it forms hydrobromic acid and bibromonaphthalin; the experiment should be repeated. (Laurent.) — 3. It is not attacked by *iodine*. — 4. It dissolves unchanged in fused *sulphur*; if a stronger heat be applied, the mass begins to boil, evolves sulphurous acid, and the heterogeneous green mass thus formed dissolves partially in ether with green colour; the portion insoluble in ether swells up by heat and leaves a very bulky residue of charcoal. (Laurent.) — 6. Nitronaphthalin boiled with *permanganate of potash*, yields nitrate and phthalate of potash. (Cloez and Guignet, *Compt. rend.* 47, 712; *J. pr. Chem.* 76, 500.) — 7. *Hydrochloric acid* is without action upon it. — 8. *Oil of vitriol* dissolves nitronaphthalin, and water reprecipitates it unchanged; on boiling, the solution becomes brown and is no longer precipitated by water; on neutralising the liquid with lime, filtering and evaporating, a saline mass, soluble in alcohol, is obtained. (Laurent.) — 9. It is converted by *fuming sulphuric acid* into nitrosulphonaphthalic acid, $C^{20}XH^7,2SO^3$. (Laurent, *Rev. scient.* 13, 590.) — 10. *Potassium* decomposes it suddenly at 43°, with evolution of light and deposition of carbon. (Laurent.) — 11. It is but slightly attacked by boiling *aqueous potash;* the liquid becomes brown, and on the addition of an acid deposits a few brown flakes. With *alcoholic potash* it forms a red liquid; on testing it from time to time with oil of vitriol, a dark green, blueish or violet-blue coloration is obtained; on continued boiling, the mass swells up, decomposes, and leaves a very bulky residue of charcoal. (Laurent.) — If nitronaphthalin be heated in a water-bath for 6 hours with a paste of 2 pts. hydrate of potash in as little water as possible, and 1 pt. fresh hydrate of lime, the water being replaced as it evaporates, it is completely decomposed, and yields the potash-salt of nitrophthalic acid, $C^{32}H^{14}N^2O^{10}$, which dissolves in water with dark yellow colour, and nitrophthalin, $C^{10}H^7NO^4$, to which a brown substance obstinately adheres. (Dusart, *N. Ann. Chim. Phys.* 45, 332.) — 12. Heated with an excess of *hydrate of baryta* or *lime,* it evolves ammonia, naphthalin, an oil, and naphtalase, $C^{20}H^7O$ (p. 25). (Laurent.)

13. When nitronaphthalin is dissolved in alcohol and the warm solution is treated with *sulphuretted hydrogen,* naphthylamine, $C^{20}NH^9$, is formed, and the liquid turns greenish-yellow and deposits sulphur. This decomposition is more rapidly effected by sulphide of ammonium. (Zinin.) — 14. When 1 pt. of nitronaphthalin is heated to 100° with a moderately concentrated solution of *ferrous acetate* (2 pts. iron) for a quarter of an hour, it yields naphthylamine and ferric oxide; the same reaction takes place with lively effervescence, when 1 pt. nitronaphthalin is heated with 1½ pts. iron filings and sufficient acetic acid to cover the mixture (Béchamp); at the same time another base, phthalamine ($C^{16}H^9NO^4$) is formed. (Schützenberger & Willm., *Compt. rend.* 47, 82; *J. pr. Chem.* 75, 117.) — 15. When nitronaphthalin in alcoholic solution is boiled for 8 hours with aqueous *sulphite of ammonia,* it is converted into the two isomeric compounds thionaphthamic acid and naphthionic acid, $C^{20}H^9NS^2O^6$. (Piria.) — 16. An alcoholic solution of nitronaphthalin, heated with *bisulphide of carbon* in a sealed tube to 160°, yields naphthylamine and sulphur. (Schlagdenhaufen, *N. J. Pharm.* 34, 175.)

Combinations. Insoluble in *water;* very soluble in *alcohol, ether,* and in *chloride of sulphur.* (Laurent.)

Conjugated Compounds of the Nitro-nucleus $C^{20}XH^7$.

Nitrosulphonaphthalic Acid.

$$C^{20}H^7NS^2O^{10} = C^{20}XH^7,2SO^3.$$

LAURENT. *Rev. scient.* 13, 68, 587 and 588; *Compt. rend.* 21, 33; *Compt. chim.* 1849, 390; abstr. *Ann. Pharm.* 72, 297; *Liebig & Kopp's Jahresber.* 1849, 440; *Compt. rend.* 31, 537; *J. pr. Chem.* 52, 58; *Pharm. Centr.* 1851, 157; *Liebig & Kopp's Jahresb.* 1850, 508.

Acide sulfaninaphtèsique and nitrasulnaphtèsique; Acide sulfonaphtalique nitré (Laurent); *Nitronaphthylodithionic acid* (Kolbe). *Nitronaphtalinschwefelsäure.*

Formation. 1. By boiling sulphonaphthalic acid with nitric acid (acide sulfaninaphtésique) ; or 2. By dissolving nitronaphthalin in fuming sulphuric acid (acide nitrasulnaphtésique). (Laurent.)

Preparation. Nitronaphthalin is heated with fuming sulphuric acid, wherein it dissolves with a red colour, gradually turning to brown ; the solution is then mixed with water, filtered from undecomposed nitronaphthalin, neutralised with chalk, filtered, and evaporated ; whereupon the lime-salt crystallises out and is purified by dissolving in alcohol, filtering, and evaporating the solution. — 2. Sulphonaphthalate of lime is boiled with nitric acid ; the acid solution is evaporated to dryness ; the residue washed with a little alcohol, then dissolved in weak alcohol, and the solution is decomposed by sulphuric acid ; the filtered solution is saturated with baryta, and the excess of baryta precipitated by carbonic acid, and the liquid is filtered and evaporated ; it then deposits crusts of the baryta-salt. — The free acid is separated from the baryta-salt by means of sulphuric acid, care being taken to avoid an excess of acid, or from the lead-salt by sulphuretted hydrogen, and the filtrate is finally evaporated in vacuo.

Properties. Microscopic, rhombic laminæ.

With sulphide of ammonium it yields *acide sulfonaphtalidamique* (naphthionic acid ?).

Very soluble in *water.*

The *nitrosulphonaphthalates* take fire when heated in closed vessels.

Ammonia-salt. The solution left to evaporate sometimes yields rhombic laminæ, sometimes long needles.

Potash-salt. May be obtained in irregular crystals by the spontaneous evaporation of its solution ; slightly soluble in alcohol.

Nitrosulphonaphthalate of Baryta. Crusts.

			Laurent. *dried in vacuo.*
20 C	120	37·5	36·43
6 H	6	1·8	1·75
N	14	4·4	
SO^2	32	10·0	9·60
BaO,SO^3	116·5	36·3	36·36
4 O	32	10·0	
$C^{20}XBaH^6,2SO^3$	320·5	100·0	

Nitrosulphonaphthalate of Lime. The salt dried in vacuo, loses at 140° 3·00 p. c. water; 1 At. = 3·20 p. c.

			Laurent. *in vacuo (mean).*
20 C	120	42·60	42·00
7 H	7	2·48	2·50
NO^4	46	16·35	
2 SO^3	80	28·46	28·75
CaO	28	10·11	10·22
$C^{20}XCaH^6,2SO^3 + Aq$	281	100·00	

Nitrosulphonaphthalic acid is very soluble in *alcohol* and in *ether.*

Nitro-nucleus $C^{20}X^2H^6$.

Binitronaphthalin.

$C^{20}H^6N^2O^8 = C^{20}X^2H^6$.

Laurent. *Ann. Chim. Phys.* 59, 376; *Ann. Pharm.* 19, 38; *J. pr. Chem.* 8, 13; *Rev. scient.* 6, 88; 13, 68.
Marignac. *Ann. Pharm.* 38, 1.

Binitrite de naphtalèse, $C^{20}H^6O^2,2NO^3$; *Nitronaphthalèse*, *Ninaphtèse* C (Laurent). *Nitronaphtylnitrür.* (Kolbe.)

Formation. Naphthalin or nitronaphthalin is boiled for a long time with nitric acid. (Laurent, Marignac.)

Preparation. Nitric acid is boiled in a large bolt-head and naphthalin gradually added as long as it continues to dissolve; on cooling, the liquid deposits pale yellow needles, which are washed, first with nitric acid, then with water, and finally with alcohol. (Laurent.) — 2. If nitronaphthalin be rapidly boiled down with nitric acid in a glass bolt-head, the oily stratum at first formed dissolves in the nitric acid, as soon as both occupy about equal volumes. The bolt-head is now taken off the fire, and on cooling, the whole solidifies in a mass which is first washed with hot water, then with hot alcohol. (Laurent.) — 3. Naphthalin is boiled with nitric acid for several days in a retort, the acid distillate being poured back in small portions by means of a funnel drawn out to a fine point. After each addition of acid, it is necessary to wait till no more red vapours are evolved, and the mass in the retort must be washed out every evening. In this manner, the following products are obtained: 1. An aqueous solution of nitronaphthalic acid; 2. An insoluble residue, principally of ternitronaphthalin (p. 88), and a small quantity of a yellowish, viscid resin, insoluble in water; 3. Binitronaphthalin, partly sublimed in the neck of the retort, and partly dissolved in nitric acid in the distillate. The greater part of the nitric acid is evaporated off at a gentle heat, and water is then added to the residue, whereby the binitronaphthalin is completely precipitated. (Marignac.)

Properties. Light powder consisting of microscopic needles; crystallises from its nitric acid solution in rhombic prisms of 67° and 113°, (Laurent); and from its solution in a very large quantity of boiling alcohol, in fine, flexible, slightly yellow needles, (Marignac). Melts at 185°, and when heated strongly in small quantities, sublimes without decomposition, in small needles. When large quantities are rapidly heated, or when it is heated in close vessels, it suddenly decomposes, evolves gas with violence, and yields much carbon with emission of red light. (Laurent.) Neutral to test-papers.

			Laurent. *mean.*	Marignac.
20 C	120	55·05	54·83	54·92
6 H	6	2·75	2·90	2·83
2 N	28	12·84	12·70	12·46
8 O	64	29·36	29·57	29·79
$C^{20}X^2H^6$	218	100·00	100·00	100·00

Decompositions. 1. Treated with *chlorine* aided by a gentle heat, it evolves nitrous fumes; and if the action of the chlorine is discontinued at the proper time, bichloronaphthalin Y is obtained together with an oil, which by distillation or treatment with hydrate of potash, yields hydrochloric acid and terchloronaphthalin A, and hence must be a souschlorure de chlonaphtèse, (Laurent.) — 2. By prolonged boiling with *nitric acid* it is converted into ternitronaphthalin, (Laurent, *Rev. scient.* 13, 70.) — 3. Fused with *sulphur*, it evolves sulphurous acid and sulphuretted hydrogen, leaving a residue of very porous charcoal. (Laurent.) — 4. Binitronaphthalin is but slightly attacked by concentrated *aqueous potash;* with *alcoholic potash*, it forms a red liquid in the cold, and on boiling, rapidly turns brown and evolves ammonia, the reaction being completed in a quarter of an hour. A body resembling ulmic acid, viz., *nitronaphtalesic acid*, is precipitated from the solution by nitric acid. (Laurent.) In order to purify this body, it is washed on a filter with boiling water, dried, and treated with ether, which extracts a small quantity of a brown substance. — The acid is brownish black, and tasteless. Laurent found in it 62·2 p. c. C, 2·3 p. c. H. and 13·1 p. c. N. Heated on platinum-foil, it decomposes without melting, and leaves a bulky residue of carbon. It is rather easily attacked by boiling nitric acid, being converted into a light brown substance, completely soluble in a large quantity of nitric acid. Water precipitates from the solution yellow flakes, which deflagrate by heat, and form salts with ammonia and potash, which decompose with deflagration when heated in closed vessels. The nitric acid mother-liquid from the flakes, yields another *crystalline* acid by evaporation. *Nitronaphthalesic acid* is insoluble in water, in alcohol and in ether, and forms salts which glow when heated in close vessels. Its alkaline salts are brown, crystallisable, and soluble. (Laurent.)

5. Binitronaphthalin, heated with *hydrate of lime*, evolves naphthalin, ammonia, and a brown oil. (Laurent.)

6. With *sulphuretted hydrogen* it forms a carmine-coloured base, which melts on warming, and, deflagrates when heated in close vessels; probably nitronaphthylamine (?). (Laurent, *Compt. rend.* 31, 537; *J. pr. Chem.* 52, 58.) — 7. Treated with *sulphide of ammonium*, like nitronaphthalin for the preparation of naphthylamine, it yields fine red needles of seminaphthylamine, $C^{20}N^2H^{10}$. (Zinin, *J. pr. Chem.* 27, 152, and 33, 29.) — Its feebly ammoniacal, boiling solution is reduced by sulphuretted hydrogen in about three hours to ninaphthylamine, $C^{20}H^8N^2O^2$ (isomeric with nitrosonaphthylin), (Ch. S. Wood, *Chem. Gaz.* 1859, 218; *Chem. Centr.* 1859, 1836.)

$$C^{20}X^2H^6 + 8\,HS = 6\,HO + 8\,S + C^{20}H^8N^2O^2.$$

8. Its alcoholic solution is converted by *zinc* and *hydrochloric acid* into nitrosonaphthylin, $C^{20}H^8N^2O^2$. (Church & Perkin, *Chem. Soc. Qu. J.* 9, 1; *J. pr. Chem.* 68, 248.)

Conjugated compounds of the Nitro-nucleus $C^{20}X^2H^6$.

Binitrosulphonaphthalic Acid.

$$C^{20}H^6N^2S^2O^{14} = C^{20}X^2H^6,2SO^3.$$

LAURENT. *Compt. rend.* 31, 537; *J. pr. Chem.* 52, 58; *Pharm. Centr.* 1851, 157; *Liebig & Kopp's Jahresb.* 1850, 508.

Binitronaphtalinschwefelsäure.
Known only in combination with *ammonia*.

Formation and Preparation. By long continued treatment of sulphonaphthalic acid with nitric acid.

Binitrosulphonaphthalate of ammonia. Crystallises in beautiful yellow needles, and treated with sulphuretted hydrogen, it deposits sulphur, and yields a new nitro-acid, apparently *acide sulfonaphtalidamique nitré,* (nitronaphthionic acid ?).

Nitro-nucleus $C^{20}X^3H^5$.

Ternitronaphthalin.

$$C^{20}H^5N^3O^{12} = C^{20}X^3H^5.$$

LAURENT. *Rev. scient.* 6, 84 and 86 ; 13, 71.
MARIGNAC. *Ann. Pharm.* 38, 1.

Nitronaphtalise, Ninaphtise. (Laurent.)

Formation. By prolonged boiling of naphthalin with nitric acid, in three isomeric modifications, α, β, and γ, which differ only in crystalline form, melting-point, and solubility.

Modification α. (*Ninaphtise* G Laurent.) When naphthalin is boiled for a day or two with nitric acid, almost colourless crystals are obtained, which are a mixture of binitronaphthalin, naphthaleïse and ternitronaphthalin α and β, the last being formed in the largest quantity. Binitronaphthalin and naphthaleïse are extracted by ether, and the residue is heated with such a quantity of alcohol, that on cooling about half remains dissolved. This solution yields by spontaneous evaporation, long rhombic laminæ of ternitronaphthalin α, mixed with needles, which are separated by shaking up the whole and pouring off the suspended crystals. By repeatedly recrystallising the laminæ from boiling alcohol and picking out the needles, ternitronaphthalin α is obtained in a state of purity. (Laurent.)

Properties. Pale yellow, inodorous. Crystallises from boiling alcohol on cooling in long rhombic tablets, which are generally very irregular and indented like a saw. If it be heated to 100° with ether in a sealed tube, six-sided prisms are obtained, derived from a rhombus of 50° and 130°. Melts at 210°, and solidifies in a fibrous mass on cooling. Heated on a glass plate in the air, it volatilises undecomposed; but if it be heated in a tube, it takes fire, gives off a brown smoke, and leaves a residue of charcoal.

			Laurent. *mean.*
20 C	120	45·6	45·5
5 H	5	1·9	2·0
3 N	42	16·0	16·3
12 O	96	36·5	36·2
$C^{20}X^3H^5$	263	100·0	100·0

Decompositions. 1. By *chlorine* it is first turned red, and then completely decomposed. (Laurent.) — 2. Heated with *lime,* it undergoes combustion. (Laurent.) — 3. It dissolves in *alcoholic potash* and forms a red solution, which turns brown on boiling and evolves ammonia. On neutralising the solution with an acid, a voluminous brown precipitate of nitronaphthalesic acid is obtained. This acid resembles nitronaphthalesic (p. 87) and nitronaphthaleïsic acids, and decomposes with deflagration on heating in a close vessel. Its compounds with the alkalis are brown, uncrystallisable. Nitronaphthalesic acid contains more carbon than ternitronaphthalin (?), (Laurent). — 4. It dissolves slowly and with difficulty in a saturated alcoholic solution of *ammonia,* forming a rose-coloured liquid, which, if saturated with *sulphuretted hydrogen,* turns yellowish and reddish brown, and then dissolves a considerable quantity more of the excess of ternitronaphthalin. The solution turns green when heated but does not deposit sulphur. If the liquid be distilled almost to dryness, and the residue treated with boiling water, it yields a carmine-red solution, which on cooling deposits a reddish-brown powder, not possessing basic properties. (Zinin, *J. pr. Chem.* 33, 34.)

Combinations. 1. Dissolves very sparingly in boiling *alcohol.* — 2. It dissolves in *nitric acid,* and *oil of vitriol* without decomposition, if they be not too strongly heated. (Laurent.)

Modification β. (*Ninaphtise* GL, *Nitronaphtale,* Laurent). All the residues from the previously described modification are mixed together and boiled with nitric acid for five or six days. On cooling, beautiful needles are obtained, which are washed on a funnel (without paper) first with nitric acid, and then with water and with alcohol. If the crystals be immediately washed with water, a resin is precipitated, which mixes with the ternitronaphthalin. The crystals when dry must be washed with ether, to remove traces of this resin. (Laurent.)

Properties. Colourless when freshly crystallised, becomes slightly yellow and dull after washing with water and drying. It closely resembles terchloronaphthalin *a,* but has a different crystalline form. Heated in a sealed tube to 100° with ether, it crystallises on cooling in brilliant, yellow, exceedingly small, oblique rhombic prisms: Fig. 93, with faces $t.\,u : u = 50°$; $i : t$ behind $= 126$; $t : u = 124$; $i : t = 110°$; $i : u = 98° 15'$; $f : u = 104° 30'$. Although the crystals of *a* and *β* have one angle in common, yet they cannot be confounded with one another. (Laurent.) Melts at 215°; 0·1 gramme melted on a glass plate, remains transparent on solidifying, and then crystallises suddenly when it is again heated below its melting point, or when gently stirred with a pointed instrument. Heated on platinum-foil, it appears to volatilise undecomposed; but when heated in closed vessels, it suddenly decomposes with emission of light.

			Laurent.	
			first analysis.	*later.*
20 C	120	45·6	45·45	45·6
5 H	5	1·9	1·92	2·0
3 N	42	16·0	17·25	16·8
12 O	96	36·5	55·38	35·6
$C^{20}X^3H^5$	263	100·0	100·00	100·0

Laurent previously considered the compound to be $C^{19}H^5N^3O^{11}$; Berzelius (*Jahresbericht,* 23, 534) considered it to be isomeric with ternitronaphthalin *a,* which Laurent afterwards found to be the fact.

Decompositions. 1. Dissolves readily in hot *oil of vitriol* without decomposition; but if the solution be too strongly heated, it turns brown and evolves sulphurous acid. — 2. It takes fire when heated with *hydrate of baryta* in a closed vessel. — 3. Boiling *alcoholic potash* first turns it orange-red, then brown, and decomposes it; the brown solution gives with acids a brown precipitate resembling nitronaphthalisic acid. (Laurent.) — 4. Boiling *nitric acid* decomposes it in a similar manner. (Laurent.)

Of all the nitro-compounds of naphthalin, it is the most insoluble in *alcohol* and in *ether*.

Modification γ. Marignac's *ternitronaphthalin.* The insoluble residue which remains when binitronaphthalin is prepared by boiling naphthalin for a long time with nitric acid (p. 87, 3), is impure ternitronaphthalin γ. To purify it, it is again washed with water, finely pulverised, and treated with cold ether; which thereby acquires a yellow colour and yields a viscid resin on evaporation. (Marignac.)

Properties. Slightly yellow; it is deposited from boiling alcohol as a crystalline powder. Melts a little above 100°. When carefully heated it volatilises without residue, but often decomposes very rapidly, with slight explosion and reddish flame, leaving a large residue of carbon.

			Marignac. *mean.*
20 C	120	45·6	46·12
5 H	5	1·9	1·96
3 N	42	16·0	16·59
12 O	96	36·5	35·33
$C^{20}X^3H^5$	263	100·0	100·00

Hence it is $C^{20}H^5O^3,3NO^3$ or $C^{20}H^5,3NO^4$ (Marignac).

Decomposition. Dissolves with beautiful red colour in *caustic alkalis* and their *carbonates,* slowly in *aqueous* and rapidly in *alcoholic potash.* The red alcoholic potash-solution becomes dark or blackish-brown, slowly in the cold, but almost instantly when heated, evolving a large quantity of ammonia; the liquid having absorbed carbonic acid, effervesces when it is saturated with an acid, and yields a flocculent, bulky, brownish-black precipitate = $C^{12}H^3NO^5$. The brown body dries up to a hard, black, shining mass, resembling anthracite.

			Marignac. *mean.*
12 C	72	56·21	56·22
3 H	3	2·30	2·69
N	14	10·85	10·79
5 O	40	30·64	30·30
$C^{12}H^3NO^5$	129	100·00	100·00

When the liquid separated from the brown body is distilled, it yields formic acid and exhales a feeble odour of prussic acid, which however cannot be detected in the solution. Since prussic acid is decomposed by potash into formic acid and ammonia, the decomposition is perhaps as follows:

$$2\,C^{20}X^3H^5 + HO = 2\,C^{12}H^3NO^5 + 4\,C^2NH + C^2HO^3 + 6\,CO^2. \text{ (Marignac.)}$$

The brown body *heated* in a tube, evolves water and empyreumatic vapours and leaves a large amount of carbon; it decomposes when rapidly heated on platinum-foil, emitting red sparks. It is not acted upon by concentrated *hydrochloric acid*, or by diluted *nitric* and *sulphuric acids*, but is decomposed by *oil of vitriol* with evolution of sulphurous acid. It dissolves in concentrated *nitric acid*, nitrous acid being set free; the yellow solution gives with water a pulverulent precipitate insoluble in water, soluble in ether.

Almost insoluble in *water* and in *alcohol*, to which it nevertheless imparts a yellow colour. Quite insoluble in *ether*.

The dry brown substance also dissolves readily in *caustic alkalis* and their *carbonates*, forming brown solutions, without expelling carbonic acid from the carbonates. The solutions yield viscid masses by slow evaporation. When the ammoniacal solution is boiled, it gradually parts with its ammonia and deposits the brown substance. *Salts of silver, lead, baryta*, and *lime* precipitate the brown substance from its solutions in combination with small quantities of the salt employed, or of the corresponding metallic oxide; the precipitates have, however, no definite composition, and appear to decompose by prolonged washing. The brown body is precipitated by *acids* from its solution in alkalis. (Marignac.)

Combinations. 1. Ternitronaphthalin γ is insoluble in cold water, and only so far soluble in boiling water, that the liquid becomes turbid on cooling.

2. Dissolves slightly in *nitric acid*, and is precipitated therefrom by water.

3. Dissolves sparingly in boiling *alcohol*. — 4. It is almost insoluble in *ether;* even in boiling ether.

Appendix to Ternitronaphthalin.

Nitronaphthaleïse (Laurent).

$$C^{20}H^{5.5}N^{2.5}O^{10} = C^{20}X^{2.5}H^{5.5}.$$

LAURENT. *Rev. scient.* 6, 88; 13, 70.

Ninaphtine. (Laurent.)

Formation and Preparation. The nitric acid mother-liquid which remains in the preparation of binitronaphthalin (p. 86, 2) still contains a large quantity of that substance in solution; this solution is boiled for several hours in a retort, whereupon, while the whole is still warm, an oily mixture of binitro- and ternitro-naphthalin (both of which are scarcely soluble in ether), and nitronaphthaléise (rather soluble in ether) is deposited at the bottom of the vessel. The oil solidifies in a yellow waxy mass; which is washed with alcohol and boiled with ether; whereupon the solution by spontaneous evaporation yields crystals of nitronaphthaleïse mixed with a little binitronaphthalin. The mother-liquid still contains some nitronaphthaleïse and an oil. The crystals are treated with warm but not boiling ether, the solution is evaporated, and the residue completely purified by repeated recrystallisation from alcohol.

Properties. Pale yellow. Crystallises from alcohol or from ether in small feathery needles. Melts in boiling alcohol (hence it cannot be a mixture of bi- and ter- nitronaphthalin, both of which melt near 200°), and on cooling solidifies in an opaque radiated mass. — Distils partly undecomposed, but decomposes suddenly after a few moments with evolution of light.

			Laurent. *mean.*
20 C	120	49·90	49·3
5·5 H	5·5	2·27	2·3
2·5 N	35	14·55	14·8
10 O	80	33·28	33·6
$C^{20}X^{2\cdot5}H^{5\cdot5}$	240·5	100·00	100·0

It imparts a red colour to *alcoholic potash* and then decomposes by boiling, evolving ammonia; the brown liquid gives with acids a brown precipitate of nitronaphthaleïsic acid. This compound resembles naphthaleïsic acid, and forms with alkalis brown uncrystallisable salts which decompose with deflagration when heated in closed vessels. Laurent found in the analysis of nitronaphthaleïsic acid, 51·8 p. c. C. 2·6 p.c. H., and 31·8 p. c. N.

Nitronaphthaleïse is insoluble in *water*. It dissolves unchanged in *nitric acid;* sparing in hot *oil of vitriol,* and is precipitated therefrom by water.

Slightly soluble in *alcohol,* rather soluble in *ether.*

Bromonitro-nucleus $C^{20}BrX^2H^5$.

Bromobinitronaphthalin.

$C^{20}H^5BrN^2O^8 = C^{20}BrX^2H^5$.

Laurent. *Compt. rend.* 21, 35; *Compt. chim.* 1850, 1; abstr. *Ann. Pharm.* 76, 298; *Pharm. Centr.* 1850, 310; *Liebig & Kopp's Jahresb.* 1850, 497.

Nitrobronaphtise. (Laurent.)

Formation and Preparation. When bibromonaphthalin is boiled with nitric acid, a solution is obtained from which water precipitates an oil solidifying in the cold. The product is purified by repeated crystallisation from ether. (The acid liquid, from which the bromobinitronaphthalin has crystallised, yields by evaporation a mixture of oxalic and bromophthalic acids.)

Properties. Yellow substance.

			Laurent.
20 C	120	40·50	40·35
5 H	5	1·67	1·55
Br	80	26·90	26·40
2 N	28	9·50	10·25
8 O	64	21·43	21·45
$C^{20}BrX^2H^5$	297	100·00	100·00

Thus 1 At. Br and 1 At. H of bibromonaphthalin are replaced by 2 At. X.

When rapidly *heated* in a glass tube, it explodes.

Insoluble in *water;* readily soluble in *ether,* less soluble in *alcohol.*

Azo-nucleus $C^{20}NH^{7}$.

Naphthylamine.

$$C^{20}NH^{9} = C^{20}NH^{7},H^{2}.$$

ZININ. (1842.) *J. pr. Chem.* 27, 140; *Ann. Pharm.* 44, 283; *Berz. Jahresb.* 23, 545. — *Petersb. Acad. Bull.* 10, 346; abstr. *Ann. Pharm.* 84, 346; *Chem. Gaz.* 1852, 441; *J. pr. Chem.* 57, 173; *Pharm. Centr.* 1852, 689; *Liebig & Kopp's Jahresb.* 1852, 627.

PIRIA. *Sull'azione del solfito d'ammoniaca sulla nitronaftalina*, Pisa, 1850; *Ann. Pharm.* 78, 31; *N. Ann. Chim. Phys.* 31, 217; abstr. *Pharm. Centr.* 1851, 380; *Compt. rend.* 31, 488; *J. pr. Chem.* 52, 56; *Liebig & Kopp's Jahresb.* 1850, 500.

BECHAMP. *N. Ann. Chim. Phys.* 42, 186; abstr. *Ann. Pharm.* 92, 401; *Compt. rend.* 39, 26; *J. pr. Chem.* 62, 469.

DELBOS. *N. Ann. Chim. Phys.* 21, 68; *Compt. rend*, 24, 1091; *N. J. Pharm.* 12, 237; *Ann. Pharm.* 64, 370; *J. pr. Chem.* 42, 244; *Pharm. Centr.* 1847, 637; *Liebig & Kopp's Jahresb.* 1847-8, 610.

W. H. PERKIN. *Chem. Soc. Qu. J.* 9, 8; *Chem. Gaz.* 1856, 119; *N. Phil. Mag. J.* 12, 226; *Instit.* 1856, 300 and 406; *J. pr. Chem.* 68, 152 and 441; *Chem. Centr.* 1856, 394; *Liebig & Kopp's Jahresb.* 1856, 538.

H. SCHIFF. Prelim. notice: *Ann. Pharm.* 101, 90; *J. pr. Chem.* 71, 108; more detailed: *Inaugural dissertation*, Göttingen, 1857; abstr. *Ann. Pharm.* 101, 299; *J. pr. Chem.* 70, 264; *N. Ann. Chim. Phys.* 52, 112; *Chem. Gaz.* 1857, 211; *Chem. Centr.* 1857, 166 and 362; *Liebig & Kopp's Jahresb*, 1857, 389.

A. W. HOFMANN. *Compt. rend.* 47, 425; *N. Ann. Chim. Phys.* 54, 204.

SCHÜTZENBERGER & WILLM. *Compt. rend.* 47, 82; *J. pr. Chem.* 75, 117; *Chem. Centr.* 1858, 654; *Chim. p.* 1, 38.

Naphthalidam (Zinin); *Naphthalidine* (Piria).

Formation. First prepared by Zinin in 1842, by treating nitronaphthalin with sulphuretted hydrogen, or with sulphuretted hydrogen and ammonia aided by a gentle heat:

$$C^{20}XH^{7} + 6\,HS = C^{20}NH^{7},H^{2} + 4\,HO + 6\,S.$$

2. A thionaphthamate is decomposed by an acid, and the thionaphthamic acid thereby liberated is resolved by water into sulphuric acid and naphthylamine:

$$C^{20}NH^{9},2SO^{3} + HO = C^{20}NH^{9},HO,SO^{3} + HO,SO^{3};$$

the same reaction is produced when a thionaphthamate is distilled with excess of hydrate of lime. (Piria.) — 3. Nitronaphthalin is warmed with excess of ferrous acetate:

$$C^{20}XH^{7} + 12\,FeO + 2\,HO = 6\,Fe^{2}O^{3} + C^{20}NH^{7},H^{2};$$

or with iron filings and acetic acid (Béchamp); in the last case, phthalamine, $C^{16}H^{4}NO^{4}$, is simultaneously formed, (Schützenberger & Willm). — 4. Nitronaphthalin is heated with bisulphide of carbon in a sealed tube to 160°, whereby sulphur is separated. (Schlagdenhauffen, *N. J. Pharm.* 34, 175.)

Preparation 1. One pt. of nitronaphthalin is dissolved in 10 pts. strong alcohol, the solution saturated with ammonia, whereupon a little nitronaphthalin may remain undissolved, and then saturated with sulphuretted hydrogen, till the whole is dissolved and the solution acquires a dirty dark-green colour. The liquid is then allowed to stand for a day, whereupon sulphur crystallises out, the odour of sulphuretted hydrogen ceases, an odour of ammonia becomes perceptible, and the solution now contains hydrosulphate of naphthylamine which decomposes on distillation. A portion of the alcohol is distilled off, whereupon a large quantity of sulphur is deposited, which causes violent bumping, so that the distillation cannot be continued unless the liquid be decanted from the sulphur; the distillation is now continued till bumping again occurs; and the liquid is again decanted and distilled till the portion remaining in the retort separates into two strata, the lower of which is impure naphthylamine, the upper a solution of naphthylamine in weak alcohol. Or sulphuretted hydrogen alone is passed into the warm alcoholic solution of nitronaphthalin; and after a time, the pale yellow solution is poured off from the precipitate which has been formed, and submitted to distillation, whereupon a thick dirty green oil is deposited (solidifying in crystals on cooling), and the liquid on standing deposits fine needles of naphthylamine.

To purify the product, either of the following methods may be adopted: *a.* the impure base is distilled, the fluid yellowish distillate then solidifying in a white crystalline mass. Or, *b.* sulphuric acid is added to the alcoholic liquid, whereby sulphuretted hydrogen is evolved and sulphur and sulphate of ammonia are precipitated, and on the addition of more sulphuric acid, the whole mass solidifies in a paste of sulphate of naphthylamine. This is purified by one or two recrystallisations from alcohol, dissolved in water and supersaturated with ammonia, whereupon the liquid becomes transiently turbid, and after a few minutes is completely filled with crystals of naphthylamine. (Zinin.)

2. A thionaphthamate, or better still, hydrochlorate of naphthylamine prepared therefrom (p. 99), is distilled with excess of slaked lime. (Piria.)

3. 20 grammes of nitronaphthalin are warmed for ¼ hour on a water-bath with tolerably concentrated ferrous acetate containing 40 grammes of iron, in a flask provided with a drawn out tube. The flask is then filled with boiling water, and after the liquid has become clear, it is decanted; if it deposits needles, these are collected, and only the liquid is poured away. After the residue has been several times treated with boiling water, it is collected on a filter and exhausted with alcohol of 86°; the alcoholic solution is distilled as rapidly as possible; and the residue is treated with sulphuric acid, whereupon, if the liquid be sufficiently concentrated, the whole solidifies in a crystalline mass of sulphate of naphthylamine. This is purified by recrystallisation from boiling alcohol or better, from boiling water, (since in contact with alcohol the red mass is formed with peculiar facility,) and its hot aqueous solution is decomposed by ammonia (Béchamp). — 4. A mixture of 1 pt. nitronaphthalin (which for this purpose need not be recrystallised from alcohol, but only freed from nitric acid by washing with water: *Schiff*) with 1½ pt. iron filings in sufficient common acetic acid to cover the whole, is gently warmed in a retort capable of containing ten times as much substance, till the nitronaphthalin is melted. It is then taken off the fire, lest the mass should go over. When the violence of the reaction has abated, it is distilled on a sand-bath, the retort being surrounded with sand up to the neck,

whereupon first the acetic acid, and afterwards at about 300°, the naphthylamine passes over and collects under the acetic acid as a yellow liquid, which is purified either by fractional distillation, or as described in method 3. (Béchamp.) Considerable quantities of naphthylamine are thus obtained, but impure; it is therefore dissolved in hydrochloric acid, and the filtrate is evaporated to dryness and distilled with hydrate of lime, whereupon the base passes over perfectly colourless and almost pure. (Perkin.) 5. The operation is conducted as in 4, and after the reaction is terminated, the excess of acetic acid (which always contains a little naphthylamine in solution) is distilled off; the residue when cooled is mixed with rather concentrated potash-solution, and allowed to stand for an hour, in order that the mass may become thoroughly saturated with potash; and the bulb, of the retort is then completely surrounded with ignited charcoal, whereupon the naphthylamine begins to pass over at 300°. It is advantageous to place some acetic acid in the receiver, in order that the vapours may be immediately absorbed. As soon as the distillation is over, the contents of the receiver, which always contains a small quantity of undecomposed nitronaphthalin, are repeatedly boiled with dilute acetic acid, and the naphthylamine is precipitated from the filtrate by potash. White flakes are obtained which impart a turbid, milky appearance to the liquid, and after standing for several hours unite in long needles. (Schiff.)

Purification. Naphthylamine obtained by method 4, (as well as that obtained by method 5, according to Carius), contains an admixture of phthalamine. To purify it, the crude product obtained in the first distillation is treated with sulphuric acid, and the more insoluble sulphate of naphthylamine is separated from the more soluble sulphate of phthalamine by crystallisation from water. (Schützenberger & Willm.)

Properties. Precipitated from the sulphate by ammonia, it forms fine, white, silky needles, pressed flat together; or when precipitated from the acetate by potash, white flakes, uniting in long needles after they have stood for several hours in the liquid. (Schiff.) Melts at 50°, and boils at about 300°, distilling without decomposition, as a pale-yellow, clear liquid, a single drop of which often remains fluid for some time on a watch-glass, but solidifies suddenly when touched. When the liquid is cooled to 0°, it solidifies in a yellowish white crystalline mass. (Zinin.) Carefully and gradually heated, it sublimes in long silky needles (Schiff), and when kept long in a closed vessel between 20° and 30°, in long, narrow, very thin, flexible and transparent laminæ. (Zinin.) It has a peculiar, strong, disagreeable odour, and a strong, pungent, bitter taste; it has not an alkaline reaction. (Zinin.)

			Zinin. *mean.*
20 C	120	83·91	83·91
9 H	9	6·30	6·51
N	14	9·79	9·21
$C^{20}NH^{9}$	143	100·00	99·63

Decompositions. 1. Heated on platinum-foil, it burns with a very smoky, yellow flame, and leaves a large residue of charcoal (Zinin). — 2. Turns violet in the *air* (Zinin); exposed to air and *light*, it turns yellow, and afterwards brown (Schiff); probably *absorbing oxygen* at the same time (Zinin). It becomes more rapidly coloured in the liquid form, and hence more especially after distillation, if it be not cooled to 0° and preserved in hermetically sealed vessels. (Zinin.) Sublimed naphthylamine becomes coloured only by prolonged exposure to the air and sun, and if protected from both, may be preserved unchanged for years. (Schiff.) — 3. It is not attacked by *chlorine* in the cold, but in the melted state it is violently attacked, being thereby converted into a resinous substance, while another portion forms hydrochlorate of naphthylamine with the hydrochloric acid produced, and sublimes in the upper part of the vessel. When the aqueous solution of hydrochlorate of naphthylamine is submitted to the action of chlorine, it assumes a violet colour and deposits a brown resin. No chloride of ammonium is formed in this reaction; but from the solution, which has become strongly acid, a new substance crystallises by spontaneous evaporation in long, transparent, golden-yellow needles. (Zinin.)

4. Naphthylamine, or one of its salts, gives with aqueous *ferric chloride, nitrate of silver, chloride of gold,* and in general with all oxidising agents, a beautiful, azure-blue precipitate of naphthameïne, which rapidly turns purple (Piria); the same reaction is produced by *nitrous acid* (Ganahl), as well as by, *platinic chloride, mercuric chloride, chloride of zinc, bichloride of tin,* and by *chromic acid.* (Schiff.) The blue precipitate is not formed, as Piria concluded, from naphthylamine by loss of hydrogen and the elements of ammonia, but consists of oxynaphthylamine, $C^{20}H^9NO^2$ (Schiff). The colour acquired by naphthylamine and its salts by exposure to the air is probably due to the formation of the same substance. (Piria, Schiff.) — 5. Naphthylamine, as well as its salts, is converted by *nitric acid,* especially if it contain *nitrous acid,* into a brown powder, which is almost insoluble in water, but readily soluble in alcohol, forming a red or violet liquid. It is deposited on evaporation unchanged, and sometimes together with crystals resembling murexid. (Zinin.) (Hence it is probably nitrosonaphthylin; Carius.) — 6. Naphthylamine or one of its salts is converted by *nitrous acid* or by *nitrite of potash,* into nitrosonaphthylin, $C^{20}H^8N^2O^2$ (Church & Perkin), with evolution of nitrogen gas (Schützenberger & Willm); according to Schützenberger & Willm (*Compt. rend.* 46, 894; *J. pr. Chem.* 74, 75), it is converted into a brown porous mass which is resolved by alcohol or ether, into nitrosonaphthylin, which dissolves, and an insoluble non-azotised substance, naphthulmin, $C^{20}H^6O^4$ (Comp. p. 26.) Naphthylamine suspended in water and treated with *nitrous acid,* yields at first naphthameïne, with evolution of gas, and if the action be prolonged, a resin and an acid which dissolves in alcohol with lemon-yellow colour, $C^{18}H^6N^2O^8$ (xiii, 352) — (Ganahl & Chiozza, *Ann. Pharm.* 99, 240; *J. pr. Chem.* 70, 125).

7. When naphthylamine is added by small portions to a mixture of *nitric* and *sulphuric acids,* a violent reaction sets in and the whole acquires a dark green colour. Water precipitates from the solution yellowish-red flakes, insoluble in water and hydrochloric acid, soluble with red colour in alcohol, sulphuric acid, nitric acid, and potash, and precipitated from the potash solution by neutralisation and from the other solutions by water; they are probably nitronaphthylamine, $C^{20}NXH^6,H^2$. From this solution iron and acetic acid precipitate brown flakes of a base resembling in reactions and insolubility Zinin's seminaphthylamine $C^{20}N^2H^{10}$. (Schiff.)

8. Naphthylamine heated on a water-bath with *oxychloride of phos-*

phorus, yields ternaphthylphosphamide and hydrochlorate of naphthylamine.

$$PO^2Cl^3 + 6\,C^{20}NH^9 = N^3(PO^2)(C^{20}H^7)^3H^3 + 3\,C^{20}NH^9,HCl. \quad \text{(Schiff.)}$$

9. When a solution of naphthylamine is anhydrous ether is saturated with *gaseous cyanic acid*, and allowed to evaporate spontaneously, it yields brilliant yellow laminæ of naphthyl-urea, $C^{22}H^{10}N^2O^2$. This urea is not formed from sulphate of naphthylamine and *cyanate of potash*, but these substances decompose by prolonged digestion of the concentrated solutions and evaporation in the water-bath, giving rise to naphthylamine, sulphate of potash, and common urea:

$$S^2(C^{20}NH^{10})HO^8 + KO,CyO + 2\,HO = C^2H^4N^2O^2 + C^{20}NH^9 + 2\,KO,SO^3 + 2\,CO^2. \quad \text{(Schiff.)}$$

this should perhaps be:

$$S^2(C^{20}NH^{10})^2O^8 + 2\,KO,CyO + 2\,HO = C^2H^4N^2O^2 + 2\,C^{20}NH^9 + 2\,KO,SO^3 + 2\,CO^2. \quad \text{(Carius.)}$$

When an ethereal solution of naphthylamine is saturated with *gaseous cyanic acid*, no naphthyl-urea is formed under certain circumstances, (probably when ether containing water is employed), but a red solution, yielding on evaporation a purple syrupy mass, which is turned violet by acids, and red again by alkalis. Paper saturated with the alcoholic solution gives the opposite reactions to litmus paper; like that formerly prepared by Sacc with tincture of madder. These colour-reactions are perhaps connected with the relation of the naphthalin-compounds to the colouring matters of madder. (Schiff.)

10. Alcoholic solution of naphthylamine combines with *oil of mustard*, forming allyl-naphthyl-sulphocarbamide, $C^{28}H^{14}N^2S^2$. (Zinin.) — 11. A mixture of naphthylamine and *sulphocyanide of phenyl* becomes almost immediately solid, phenyl-naphthyl-sulphocarbamide being formed. (A. W. Hofmann.) — 12. An alcoholic solution of naphthylamine yields with *bisulphide of carbon*, sulphocarbonaphthalide and sulphuretted hydrogen, (Laurent, *N. Ann. Chim. Phys.* 22, 104; Delbos); and the same reaction ensues when naphthylamine is heated for several hours with bisulphide of carbon in a sealed tube. (Schiff.)

$$2\,C^{20}NH^9 + 2\,CS^2 = C^{42}N^2H^{16}S^2 + 2\,HS.$$

When the vapours of naphthylamine and *bisulphide of carbon* are passed through a red-hot porcelain tube, much shining charcoal is deposited; and hydrosulphocyanic and hydrosulphuric acids are formed; probably naphtho-sulphocyanic acid, $C^{20}CyH^7,S^2$, together with sulphuretted hydrogen, is first formed, and is then resolved in carbon and hydrosulphocyanic acid. (Schlagdenhaufen, *N. J. Pharm.* 34, 175.)

13. Naphthylamine behaves with *chloride of cyanogen* like aniline, (Cahours & Cloez, *Compt. rend.* 38, 354; *Ann. Pharm.* 90, 91.) If chloride of cyanogen be passed through naphthylamine in the fused state, as in the preparation of melaniline by A. W. Hofmann's method, (xi, 351) heat is developed and a substance is produced which on cooling becomes a black resinous mass, and consists chiefly of hydrochlorate of menaphthylamine. (W. H. Perkin.)

$$2\,C^{20}H^9N + C^2NCl = C^{42}NH^{17},HCl.$$

14. When naphthylamine is heated with *bromide of ethyl* for several hours at a temperature between 40° and 50°, so that the vapour formed

condenses and flows back into the flask, a reddish-brown mass is produced, containing hydrobromate of ethyl-naphthylamine together with excess of bromide of ethyl; the same reaction takes place at the common temperature in about 14 days:

$$C^{20}NH^9 + C^4H^5Br = C^{24}H^{13}N,HBr. \quad \text{(Schiff.)}$$

15. *Naphthylamine* and *iodide of ethyl* form hydriodate of ethyl-naphthylamine. 16. With *iodide of methyl*, a sticky mass is formed, which cannot be crystallised from either alcohol, water, or ether. (Schiff.) — 17. Naphthylamine and *aniline* do not react upon one another either by distillation or by heating the mixture in a sealed tube in an oil-bath. (Schiff.)

Combinations. 1. Almost insoluble in *water*. (Zinin.) 2. Appears to combine with *iodine*. (Zinin.)

Naphthylamine is a strong base, and combines with all *oxyacids* and *hydracids*, forming salts, from all of which it is separated by *ammonia*. The salts of the hydracids are anhydrous, those of the oxyacids contain 1 At. water, which cannot be expelled without destroying the salt. (Zinin.) The salts of naphthylamine are white, and for the most part crystalline. (Zinin.) They turn violet on exposure to air and light (Zinin); they turn yellow, afterwards red, and then brown, (Schiff) — probably absorbing oxygen (Zinin), and in consequence of the formation of oxynaphthylamine. (Piria, Schiff.) Their solutions give with ferric chloride, nitrate of silver, chloride of gold, and generally with all oxidising agents, a beautiful azure-blue precipitate, rapidly acquiring a purple colour (comp. p. 96): naphthameïn, according to Piria; oxynaphthylamine, $C^{20}H^9NO^2$, according to Schiff; and with chromic acid, a green, blue, or black coloration, according to the concentration of the liquid. (A. W. Hofmann.) They impart a yellow colour to pine-wood, like aniline, only the colour is more intense. (A. W. Hofmann.)

Phosphate of Naphthylamine. a. Ordinary. Even weak solutions of naphthylamine solidify in a mass of acicular crystals with an aqueous solution of unignited phosphoric acid. These crystals are readily soluble in boiling alcohol and in water; the salt crystallises unchanged from the alcoholic solution, but is deposited from the aqueous solution as a mass of white, silvery scales. It turns red in the air more rapidly than the sulphate. (Zinin.)

b. Metaphosphate. An alcoholic solution of naphthylamine gives with alcoholic metaphosphoric acid, a white pulverulent precipitate, which is but very slightly soluble in water and in alcohol. (Zinin.)

Sulphate of Naphthylamine. Naphthylamine dissolves in gently heated oil of vitriol, forming a clear liquid, which yields no crystals even at 0°, but when diluted with water, deposits a large quantity of scaly crystals, so that the liquid becomes solid. The same crystals are obtained by cooling a solution of naphthylamine in dilute sulphuric acid. (Zinin.) If sulphuric acid be added to a solution of thionaphthamate of potash, soda, or ammonia, and the liquid warmed, a crystalline pulp is formed before the liquid begins to boil, provided it is sufficiently concentrated; on continuing the application of heat, the crystals dissolve, and on cooling, silvery laminæ are deposited, which may be purified by repeated recrystallisation from water or from alcohol (comp. p. 93.)

(Piria). White, silvery laminæ, possessing in a great degree the odour and taste of the free base. Reddens litmus. When dry, it does not suffer any change in the air; when moist, or in solution, it turns red like the base. The solution stains the skin first red and then dark brown. (Zinin.) At the temperature of boiling water, it effloresces to a light, mealy, dull powder. Heated in a retort, it melts, decomposes with evolution of sulphurous acid, and leaves a porous, shining charcoal, while part of the base distils over with the water. (Zinin.) It is difficultly soluble in cold water and alcohol; slowly, but rather abundantly soluble in boiling alcohol, so that the saturated boiling solution solidifies completely on cooling. (Zinin.) It is less soluble in water than *sulphate of phthalamine*, and can therefore be separated from this substance by crystallisation. (Schützenberger & Willm.)

			Zinin. *at* 100° (*mean*).
20 C	120	62·49	62·00
10 H	10	5·21	5·88
N	14	7·29	6·50
S	16	8·34	8·39
4 O	32	16·67	17·23
$C^{20}NH^9,HO,SO^3$	192	100·00	100·00

Bechamp found in the salts prepared by method 3 (p. 94), 22·812 p. c. SO^3; Schützenberger and Willm, in those obtained by method 4, and separated by crystallisation from sulphate of phthalamine, 62·3 p. c. C, 5·3 p. c. H, 20·8 p. c. SO^3, and 8·65 p. c. water of crystallisation.

Alcoholic solution of sulphate of naphthylamine yields with *iodide of potassium*, a precipitate of sulphate of potash; the solution deposits on evaporation a resinous mass containing iodine, burning without residue, and decomposing with hot water. (Schiff.)

Hydrobromate of Naphthylamine. A concentrated alcoholic solution of sulphate of naphthylamine mixed with an equivalent quantity of concentrated solution of bromide of potassium or of barium, yields in the first instance slowly, in the second immediately, a precipitate of sulphate. The coloured filtrate slowly evaporated, leaves a crystalline residue of hydrobromate of naphthylamine, readily soluble in alcohol, but less soluble in cold water. Schiff found in the salt 35·53 p. c. Br; the formula $C^{20}NH^9,HBr$ requires 35·72 p. c. Br. (Schiff.) Schiff explains the formation of this salt by the equation:

$$S^2(C^{20}NH^{10})HO^8 + KBr = C^{20}NH^9,HBr + S^2KHO^8.$$

Hydrochlorate of Naphthylamine. When concentrated alcoholic solution of naphthylamine is mixed with excess of hydrochloric acid, a white, solid mass is produced, which must be carefully freed from moisture by pressure between blotting paper and drying in vacuo over oil of vitriol and lime, and afterwards sublimed in a common beaker-glass placed in an oil-bath. (Zinin.)—A tolerably concentrated solution of thionaphthamate of potash, soda, or ammonia, is heated till it nearly boils, *pure* hydrochloric acid is then added, and the whole is boiled for a few moments. If the solution is very concentrated, a crystalline precipitate of sulphate and hydrochlorate of naphthylamine is formed, even while the liquid is still warm; in this case, a little water must be added and the whole warmed, till the precipitate redissolves. The sulphuric acid is now precipitated by excess of chloride of barium and the liquid filtered hot; on cooling, hydrochlorate of naphthylamine crystallises out. The mother-liquid yields, on addition of hydrochloric acid, more of the salt, which becomes less soluble therein the more hydrochloric acid is added. (Piria.) Crystallises from alcohol in brilliant scales resembling the sulphate; from water in asbestos-like needles. (Zinin.) Sublimes almost without decomposition (Zinin, Piria); at 200°, in a light, woolly mass, consisting of fine needles (Zinin); in snowy crystalline flakes (Piria). The sublimed salt is permanent in the air; if moist or in solution, it is rapidly decomposed in the air (Zinin, Piria); it then becomes red more quickly than the sulphate (Zinin), and can no longer be purified by crystallisation from alcohol or from water. (Piria.) Rather soluble in water, more soluble in alcohol and in ether. (Zinin.)

			Zinin. *sublimed (mean).*
20 C	120	66·85	66·36
10 H	10	5·58	5·74
N	14	7·80	
Cl	35·5	19·77	19·03
$C^{20}NH^9,HCl$	179·5	100·00	

Nitrate of Naphthylamine. Naphthylamine dissolves in boiling dilute nitric acid free from nitrous acid, forming a colourless or slightly red liquid, from which the salt crystallises on cooling in small, brilliant scales. (Zinin.)

Chloromercurate of Naphthylamine. Mercuric chloride produces with alcoholic solution of naphthylamine or of its salts, a yellow curdy precipitate, difficultly soluble in cold alcohol, but completely in boiling alcohol, from which it is deposited in crystals on cooling. (Zinin).

Chloroplatinate of Naphthylamine. When an alcoholic solution of hydrochlorate of naphthylamine is poured into a solution of platinic chloride, the liquid turns green and deposits the salt as a brownish green-yellow powder. Crystallises from the hot solution on cooling; difficultly soluble in water, and still less soluble in alcohol or in ether. (Zinin.)

Dried at 100°, it contains 28·21 p. c. platinum. (Zinin.)

Oxalate of Naphthylamine. *a. Neutral.* Crystallises in small, thin, silvery laminæ, grouped in stars. (Zinin.) Heated in a retort, it first melts, losing water of crystallisation; shortly afterwards, water and equal volumes of carbonic oxide and carbonic acid are evolved with effervescence, naphthylamine and carbonaphthalide, $C^{42}N^2H^{16}O^2$, distilling over at the same time:

$$C^{44}H^{20}N^2O^8 = C^{42}N^2H^{16}O^2 + 4\,HO + 2\,CO;$$

or better;

$$2\,C^{44}H^{20}N^2O^8 = C^{42}N^2H^{16}O^2 + 2\,C^{20}NH^9 + 6\,HO + 4\,CO + 2\,CO^2. \quad \text{(Delbos).}$$

The last named compound is a secondary decomposition-product from oxanaphthalide $C^{44}N^2N^{16}O^4$. The neutral salt behaves when heated like the acid salt, only that it yields more free naphthylamine and more oxanaphthalide (Zinin.)

			Zinin. *dried in vacuo over sulph. acid.*
44 C	264	70·20	66·13
20 H	20	5·32	5·33
2 N	28	7·45	
8 O	64	17·03	
$2(C^{20}NH^9),C^4H^2O^8$	376	100·00	

b. Acid. Crystallises in clumps of dull, white nodules, soluble in alcohol and in water. (Zinin.) Decomposed by dry distillation, yielding a brownish yellow powder, which is insoluble in water, and is deposited from its alcoholic solution unchanged. (Zinin.) Heated to complete fusion, it yields carbonaphthalide:

$$2\,C^{24}H^{11}NO^8 = C^{42}N^2H^{16}O^2 + 6\,HO + 4\,CO + 2\,CO^2. \quad \text{(Delbos.)}$$

The well dried substance begins to melt at 200°, then swells up, evolving water and a mixture of 2 vols. carbonic acid and 1 vol. carbonic oxide; after the whole has been completely melted, the liquid residue, which on cooling solidifies in a radiated crystalline mass, consists of oxanaphthalide and formonaphthalide $C^{22}H^9NO^2$. (Zinin, *Petersb. Acad. Bull.* 16,242; *Ann. Pharm.* 108,228; *J. pr. Chem.* 74,379.)

			Zinin.
24 C	144	61·79	62·18
11 H	11	4·73	4·88
N	14	6·01	
8 O	64	27·47	
$C^{20}NH^9,C^4H^2O^8$	233	100·00	

Appendix to Naphthylamine.

Oxynaphthylamine.

$$C^{20}NH^9O^2 = C^{20}NH^7,2\,HO\ ?$$

PIRIA. *Compt. rend.* 31, 488; *Ann. Pharm.* 78, 31; *N. Ann. Chim. Phys.* 31, 217; *J. pr. Chem.* 52, 56; *Pharm. Centr.* 1851, 380; *Liebig & Kopp's Jahresb.* 1850, 500.

H. SCHIFF. *Ann. Pharm.* 101, 90; *J. pr. Chem.* 71, 108; *Chem. Centr.* 1857, 166; *Chem. Gaz.* 1857, 211; *Liebig & Kopp's Jahresb.* 1857, 389.

Naphthameïne. (Piria.) *Oxynaphthalidine.*

Formation. 1. A solution of naphthylamine or of one of its salts is treated with an oxidising agent, such as ferric chloride, nitrate of silver, chloride of gold (Piria), or chromic acid, mercuric or stannic chloride, or chloride of zinc; in which reaction neither metal nor chlorine enters into the new compound. (Schiff.) — 2. By the first action of nitrous acid upon naphthylamine suspended in water, nitrogen gas being evolved. (Ganahl, *Ann. Pharm.* 99,240.) — The violet colour acquired by naphthylamine and its salts, as well as by the thionaphthamates, on exposure to the air, is probably owing to the formation of oxynaphthylamine. (Piria, Schiff.)

Preparation. Hydrochlorate of naphthylamine is dissolved in alcohol, the solution diluted with water, but not sufficiently to cause turbidity, and while the whole is continuously stirred, aqueous ferric chloride is added, drop by drop, until a slight excess is present. The whole is allowed to stand for an hour with repeated stirring, and the precipitate is then collected, and first washed with water, till the wash-waters cease to become turbid with nitrate of silver, afterwards with alcohol, and then dried in vacuo. (Piria.) — Schiff adopts the same method, or he precipitates sulphate or acetate of naphthylamine with aqueous chromic acid.

Properties. Light, amorphous, dark purple powder (closely resembling Robiquet's orceïn, xii, 358.) (Piria.) When moist, it has a peculiar odour, resembling that of iodine, especially if heated. It cannot be crystallised. (Schiff.)

			Schiff.		
			a.	*b.*	*c.*
20 C	120	75·47	75·41	74·09	75·34
9 H	9	5·66	5·71	5·70	5·39
N	14	8·80	8·84		
2 O	66	10·07	10·04		
$C^{20}NH^{9}O^{2}$	159	100·00	100·00		

a was obtained with chromic acid, *b* with ferric chloride; *c* was precipitated by water from the sulphuric acid solution. Hence it is a simple product of the oxidation of naphthylamine, and not, as Piria thinks, oxidised naphthylamine minus ammonia.

Decompositions. It melts when heated, and immediately decomposes, evolving an aromatic vapour smelling of naphthylamine; and finally leaves a residue of difficultly combustible charcoal, which, however may be completely burned. (Piria.) — Burns when heated in the air, and leaves a difficultly combustible charcoal. (Schiff.) When moist, or if placed under water, it rapidly becomes violet; hence it is difficult to obtain the dry product of a pure blue colour. (Schiff.)

Combinations. 1. It is insoluble in *water.* — 2. Dissolves in cold *sulphuric acid,* forming a blue liquid of the colour of indigo-solution, and is precipitated unchanged by water. — 3. Insoluble in *ammonia* and *caustic potash.* (Piria.) — 4. Dissolves sparingly in *alcohol,* imparting its colour to the liquid. (Piria.) — 5. Dissolves abundantly, with purple colour, in ether, and is precipitated from the solution by spontaneous evaporation as an amorphous powder. (Piria.) — 6. Dissolves in concentrated *acetic acid* with violet colour; the solution is not precipitated by water or by tartaric acid, but oxynaphthylamine is precipitated therefrom by most acids, alkalis, and metallic chlorides. (Piria.)

It does not combine with acids or with bases. (Schiff.)

Lepidine.

$C^{20}NH^9 = C^{20}NH^7,H^2$.

Gr. Williams. *Edinb. Roy. Soc. Trans.* 21, 2nd pt.; *Chem. Gaz.* 1855, 301 and 325; *J. pr. Chem.* 66, 334; abstr. *N. Ann. Chim. Phys.* 44, 491. Further, *Edinb. Roy. Soc. Trans.* 21, 377; *Chem. Gaz.* 3rd pt., 1856, 261 and 283; abstr. *J. pr. Chem.* 69, 355; *Chem. Centr.* 1856, 817; *Liebig & Kopp's Jahresb.* 1856, 532.

Isolated by Williams, after Gerhardt had already conjectured its presence in chinoline. (Comp. xiii, 243.)

Formation. 1. By submitting cinchonine to dry distillation. — 2. In the dry distillation of coal, passing over in the coal-tar oil. In either case accompanied by many other bases.

Preparation. 1. *From cinchonine.* The operation is conducted as described, xiii, 244, and the portion passing over above 270° (between 266° and 271° *J. pr. Chem.* 69, 363) is purified by repeated rectification. — 2. From coal-tar oil. The portions passing over between 250° and 267° C. in the fractional distillation of the bases as described (xiii, 244), are collected apart. The portions which pass over afterwards, *i.e.* at 274°, contain cryptidine, $C^{22}NH^{11}$.

Properties. Oil resembling chinoline. That obtained from cinchonine boils between 266° and 271°, that from coal-tar oil between 252° and 257°, and has a sp. gr. of 1·072 at 15°. Both products have the same odour. The vapour density of the first = 5·14, of the second = 5·15, at 15° above the boiling point, but the last was slightly decomposed.

	from Cinchonine.		Gr. Williams.
20 C	120	83·91	83·29
N	14	9·80	10·15
9 H	9	6·29	6·57
$C^{20}NH^9$	143	100·00	100·01

	Vols.	Vapour density.
C-vapour	20	8·3200
N-gas	1	0·9706
H-gas	9	0·6237
Lepidine vapour	2	9·9143
	1	4·9571

According to Williams, lepidine obtained by method 1 is probably only isomeric, and not identical with that obtained by method 2, which is rendered probable by the difference in boiling point (and the different behaviours of their salts).

Isomeric with methyl-chinoline (xiii, 252), and with naphthylamine.

Decompositions. 1. Lepidine 1 is slightly decomposed by boiling, yielding traces of pyrrhol and carbonate of ammonia. — 3. The iodides of methyl, ethyl, and amyl, convert it into methyl-, ethyl-, and amyl-lepidine.

Combinations. Lepidine 1 forms salts, which are crystallisable, but crystallise with difficulty. When bases of lower boiling point are *present,* the same holds good with lepidine. 2. The salts obtained from the latter smell of naphthalin.

Hydrochlorate of Lepidine. $C^{20}NH^{9},HCl$. — Small colourless needles, which do not melt at 100°.

Nitrate of Lepidine. When lepidine which has passed over between 260° and 266° is dissolved in moderately dilute nitric acid, it forms a pale red solution, yielding on evaporation a brownish red deliquescent mass. When this has been purified by repeated pressure and crystallisation from alcohol, it forms hard prisms (yellow, if impure) which are permanent in the air, and do not melt at 100° — Lepidine obtained from cinchonine, and that from coal-tar oil, behave in the same way with hydrochloric acid.

	Prisms.		G. Williams.
20 C	120	58·25	57·69 to 58·40
10 H	10	4·86	4·93 ,, 4·90
2 N	28	13·59	
6 O	48	23·30	
$C^{20}NH^{9},NO^{5}HO$	206	100·00	

Bichromate of Lepidine is obtained by mixing aqueous chromic acid with lepidine, and recrystallising from water the crystalline powder thus formed. Beautiful, long, golden-yellow needles, which decompose at 100°, when moist but not when dry, and leave chromic oxide on ignition. Lepidine, prepared from coal-tar oil, does not form crystals with chromic acid, but only oily compounds.

	Needles.		Gr. Williams.
20 C	120	47·36	47·05
N	14	5·52	
10 H	10	3·95	3·89
2 Cr	53·4	21·07	21·27
7 O	56	22·10	
$C^{20}NH^{9},HO,2CrO^{3}$	253·4	100·00	

Concentrated solutions of hydrochlorate of lepidine and chloride of *cadmium* yield a crystalline compound, corresponding to that formed by hydrochlorate of chinoline (xiii, 215). (*Chem. Gaz.* 1855, 450; *Liebig & Kopp's Jahresb.* 1855, 551.)

Chloroplatinate of Lepidine. — Obtained from lepidine passing over between 265° and 271°. If prepared from coal-tar oil, it remains soft for a short time after it has been precipitated, and afterwards becomes crystalline.

			Gr. Williams. *mean.*
20 C	120	34·36	34·04
N	14	4·01	
10 H	10	2·86	2·95
Br	98·7	28·27	28·13
3 Cl	106·5	30·50	
$C^{29}NH^{9},HCl,PtCl^{2}$	349·2	100·00	

Azo-nitroso-nucleus $C^{20}N(NO^2)H^6$?

Nitrosonaphthylin.

$$C^{20}H^8N^2O^2 = C^{20}N(NO^2)H^6,H^2.$$

A. H. Church & W. H. Perkin. *Chem. Soc. Qu. J.* 9, 1 ; *J. pr. Chem.* 68, 248 ; *Chem. Gaz.* 1856, 139 ; *Instit.* 1856, 299 ; *Liebig & Kopp's Jahresb.* 1856, 607.

Formation. 1. Formed by reducing binitronaphthalin with nascent hydrogen :

$$C^{20}H^6N^2O^8 + 8\,H = C^{20}H^8N^2O^2 + 6\,HO.$$

2. By the action of nitrous acid in naphthylamine :

$$C^{20}NH^9 + NO^3 = C^{20}H^8N^2O^2 + HO;$$

or of nitrite of potash on hydrochlorate of naphthylamine :

$$C^{20}NH^9,HCl + KO,NO^3 = C^{20}H^8N^2O^2 + 2\,HO + KCl. \quad \text{(Church \& Perkin.)}$$

In this reaction a large quantity of nitrogen is evolved, and a brown porous mass is formed, which is a mixture of nitrosonaphthylin and naphthulmin (p. 26). (Schätzenberger & Willm, *Compt. rend.* 46,894, *J. pr. Chem.* 74,75.) It is also probably formed by the action of nascent hydrogen on nitronaphthylamine. (Church & Perkin.)

Preparation. Nitrite of potash added to hydrochlorate of naphthylamine, yields a precipitate of almost pure nitrosonaphthylin. If the precipitate be washed with water, dried, and extracted with alcohol, and the solution slowly evaporated, the nitrosonaphthylin gradually crystallises out in small needles.

Properties. Small, very dark crystals having a green metallic lustre, like murexid ; when precipitated from its alcoholic solution by water, it is scarlet. Melts and sublimes partly, without decomposition. It imparts to alcohol an intense red colour, which is changed to a magnificent violet by acids : alkalis restore the original colour. Cotton wool, linen, paper, &c., may be dyed permanently orange by being dipped into the alcoholic solution of nitrosonaphthylin. When fabrics thus dyed are dipped in acids, they acquire an intense purple-blue colour, rapidly changing to orange in a stream of water.

			Church & Perkin.
20 C	120	69·77	69·76
2 N	28	16·28	16·39
8 H	8	4·65	4·80
2 O	16	9·30	9·05
$C^{20}H^8N^2O^2$	172	100·00	100·00

Assuming Laurent's theory of "substitutions nitrosées," nitrosonaphthalin is $C^{20}H^6(NO^2)N,H^2$ = naphthylamine, wherein 1 At. H is replaced by 1 At. NO^2. The discovery of nitrosonaphthylin and of the analogous nitrosophenylin point to the existence of an entirely new type of substitution-compounds. (Church & Perkin.)

Decompositions. 1. When nitrosonaphthylin is strongly heated, part of it sublimes undecomposed; afterwards white vapours are evolved, and charcoal is left behind. — 2. The *alcoholic* solution appears to decompose gradually; the amount of carbon in the substance thus altered is raised to 75 p. c. — 3. Nitrosonaphthylin is destroyed by strong *nitric acid.* — 4. Its colour is not affected by *alkalis,* but is destroyed by the prolonged action of *nascent hydrogen.*

Combinations. Insoluble in *water* and in *dilute acids.* Dissolves in *fuming sulphuric acid* with purple-blue colour. Dissolves in *alcohol* with intense red colour, and is precipitated from the solution by water. Soluble in *ether.*

Ninaphthylamine.

$$C^{20}H^{8}N^{2}O^{2} = C^{20}N(NO^{2})H^{6},H^{2}\ ?$$

CH. S. WOOD. *Chem. Gaz.* 1859, 218; abstr. *Chem. Centr.* 1859, 836.

Ninaphthalidin.

Formation. By reducing a weak ammoniacal solution of binitronaphthalin with sulphuretted hydrogen:

$$C^{20}X^{2}H^{6} + 8\,HS = C^{20}H^{8}N^{2}O^{2} + 6\,HO + 8\,S.$$

Preparation. Sulphuretted hydrogen is passed through an alcoholic and feebly ammoniacal, boiling solution of binitronaphthalin for about three hours, whereupon the greater part of the alcohol distils off; the residue is then supersaturated with dilute sulphuric acid, heated to boiling, and filtered. — On cooling, yellowish brown sulphate of ninaphthylamine crystallises out, from the solution of which the base is precipitated by ammonia.

Properties. Beautiful carmine-red needles. It is slightly decompose at 100°. It is a base, and differs totally in properties from the isomeric compound nitrosonaphthylin (p. 105).

Sulphate of Ninaphthylamine. $C^{20}H^{8}N^{2}O^{2},SO^{3},HO$. — White scales; decomposed by recrystallisation from its aqueous solution.

Hydrochlorate of Ninaphthylamine. $C^{20}H^{8}N^{2}O^{2},HCl$. — Acicular crystals.

Chloroplatinate of Ninaphthylamine. $C^{20}H^{8}N^{2}O^{2},HCl+PtCl^{2}$ is precipitated in yellowish-brown, rather soluble crystals when platinic chloride is added to a solution of the base in ether--alcohol.

Amidazo-nucleus $C^{20}NAdH^{6}$.

Seminaphthylamine.

$C^{20}N^{2}H^{10} = C^{20}NAdH^{6},H^{2}$.

ZININ. (1844.) *J. pr. Chem.* 33, 29; *Ann. Pharm.* 52, 362; *J. pr. Chem.* 57, 177; *Ann. Pharm.* 85, 329.

Azonaphthylamine, Seminaphthalidine.

Formation. By treating binitronaphthalin with sulphuretted hydrogen and ammonia. (Zinin.)

Preparation. Binitronaphthalin is dissolved in a saturated alcoholic solution of ammonia, and sulphuretted hydrogen is passed through the dark carmine-red solution, till, on complete saturation, it has become greenish-brownish yellow. The liquid is then boiled in a retort, whereupon a large quantity of pulverulent sulphur is deposited; hence in the distillation proper precautions must be taken, as in the case of naphthylamine (p. 94, 1.). When no more sulphur is deposited from the residue in the retort, water is added; and the whole is boiled, filtered boiling, and left to cool, whereupon a quantity of copper-red needles crystallise out. A dark brown, resinous mass, becoming viscid by heat, then remains in the retort, which is several times boiled out with water, as long as the solution continues to deposit crystals on cooling. The crystals are dissolved in hot water, and the filtered solution is left to cool in a well corked flask, whereupon crystals are obtained having an almost metallic lustre, and yellow colour, with copper-red iridescence; by repeated crystallisation from alcohol and water alternately, they may be obtained colourless. The red coloration is due to a resin which is more soluble in alcohol than the base, crystallises from water in fine, dull needles, melts to a red liquid when heated, and distils with partial decomposition, without explosion. (Zinin.)

Properties. Crystallises from alcohol in long and very brilliant needles. It is not affected by a temperature of 100°, melts at 160° to a yellowish-brown liquid, and sublimes in small quantity. Boils above 200°, partly subliming in the neck of the retort, and distilling partly undecomposed, while another part undergoes decomposition, leaves a large residue of carbon, and yields decomposition-products, which impart a brown colour to the sublimate and distillate, and render them impure. Permanent in the air.

			Zinin. *Average at* 100° *in dry air.*
20 C	120	75·79	75·60
10 H	10	6·31	6·31
2 N	28	17·90	18·00
$C^{20}NAdH^{8}$	158	100·00	99·91

The formula is $C^{10}H^{5}N$, and from its formation, the atomic weight of binitronaphthalin must be halved. (Zinin.) From binitronaphthalin $C^{20}X^{2}H^{6}$, a compound containing 10 C could not be formed; hence the formula must be $C^{20}H^{10}N$. (Laurent, *Compt. Chim.* 1849, 165.)

Decompositions. 1. The solutions of seminaphthylamine in water, ether, or in alcohol, especially the last, decompose rapidly in the *air*, becoming turbid and brown, and depositing a brown powder; they then yield only a small quantity of dark brown crystals on evaporation. 2. *Heated* on platinum foil, it burns with a yellow and very smoky flame, diffusing a not unpleasant odour of naphthalin. — 3. By strong *nitric acid* it is converted into a violet-brown powder, probably the same substance that is deposited from the solution on exposure to the air. — 4. When *chlorine gas* is passed through aqueous hydrochlorate of seminaphthylamine, the base is converted into a reddish brown powder, which is almost insoluble in water, but dissolves in hot alcohol with dark carmine colour, and is precipitated unchanged on cooling. — 5. By *chlorate of potash* (and hydrochloric acid?) it is converted into a similar, but somewhat lighter coloured powder.

Combinations. Dissolves with difficulty in *water*, forming a pale brownish red solution.

It combines with acids and forms salts; those with oxy-acids contain 2 At. water. Dry seminaphthylamine dissolves in oil of vitriol, forming a dark violet liquid, which remains unchanged for months, but on addition of water instantly solidifies to a reddish white crystalline mass. The alcoholic solution of seminaphthylamine is decolorised by all aqueous acids; the concentrated solution solidifies with sulphuric, phosphoric, or hydrochloric acid in a soft crystalline mass consisting of microscopic white needles or laminæ; ammonia precipitates from the aqueous solution of these crystals, unchanged seminaphthylamine in reddish needles.

Phosphate of Seminaphthylamine. Obtained by mixing the alcoholic solution of the base with aqueous phosphoric acid. It forms brilliant white crystalline scales, more stable than the sulphate. Difficultly soluble in water and in alcohol, crystallising therefrom almost unaltered.

Sulphate of Seminaphthylamine. Moderately dilute sulphuric acid is added to concentrated alcoholic seminaphthylamine, but in such quantity that the free base, which may be recognised by the colour of the liquid, is still present. The white precipitate is washed on a filter with alcohol till the washings are almost colourless, then pressed between blotting paper, dried in vacuo over sulphuric acid, and afterwards in a stream of dry air at 100°. Small, white, scaly crystals; or, when dried, a white, dull powder, permanent in the air. Above 100° it turns red and decomposes. Dissolves with difficulty and with partial decomposition, in water or alcohol; the boiling solution deposits brownish laminæ on cooling.

			Zinin. *at* 100°.
20 C	120	46·87	47·09
12 H	12	4·69	4·80
2 N	28	10·93	
2 O	16	6·25	
2 SO^3	80	31·26	31·00
$C^{20}NAdH^8,2HO,2SO^3$	256	100·00	

Hydrochlorate of Seminaphthylamine. To a cold alcoholic solution o seminaphthylamine, moderately strong hydrochloric acid is added drop by drop, and the mixture is cooled, lest it should become heated. The liquid solidifies to a thick white paste of silvery laminæ. These are washed on a filter with a small quantity of alcohol, pressed between blotting paper, and dried, first in vacuo over sulphuric acid and caustic lime, and then at 100° in a current of dry air. — White crystalline powder which may be preserved unaltered when dry, but decomposes readily in the moist state. It is decomposed by heat, and cannot be sublimed. Sparingly soluble in water and in alcohol ; the solutions turn brown in the air.

			Zinin. *at* 100°, *mean.*
20 C	120	51·91	51·81
12 H	12	5·19	5·21
2 N	28	12·27	
2 Cl	71	30·63	30·51
$C^{20}NAdH^{8},2HCl$	231	100·00	

Hydrochlorate of seminaphthylamine forms with *mercuric chloride* an easily soluble compound, crystallising in rather large, white, silvery laminæ.

Chloroplatinate of Seminaphthylamine. Yellowish brown, difficultly soluble powder. The well dried substance leaves on ignition 34·56 p. c. Pt.; $C^{20}N^{2}H^{10},2HCl + 2PtCl^{2} = 34{\cdot}63$ p. c. Pt.

Seminaphthylamine does not appear to combine with *hydrocyanic acid ;* it does not dissolve more abundantly in the aqueous acid than in water, and crystallises unchanged from its alcoholic solution which has been mixed with concentrated prussic acid.

Aqueous *hydrosulphocyanic acid* dissolves seminaphthylamine, readily and abundantly, especially when heated ; on cooling the solution, brilliant white laminæ of the sulphocyanide are deposited.

Oxalate of Seminaphthylamine. White crystalline powder, sparingly soluble in water, and still less in alcohol and ether. The hot solution deposits on cooling brilliant white laminæ.

Tartrate of Seminaphthylamine is prepared like the phosphate. Crystallises in fine, white needles, grouped in the form of stars. Rather soluble in water and in alcohol, sparingly soluble in ether ; its solution decomposes ; the dry salt is more stable.

Seminaphthylamine dissolves in *alcohol* and *ether* with much darker colour than in water. (These statements of Zinin's refer to coloured seminaphthylamine. *Carius.*)

Conjugated compounds of $C^{20}NH^{7}$, *or of similar nuclei.*

Sulphonaphthylamic Acid.

$$C^{20}NH^{9}S^{2}O^{6} = C^{20}NH^{9},2SO^{3}.$$

LAURENT. *Compt. rend.* 31, 537 ; *J. pr. Chem.* 52, 58 ; *Pharm. Centr.* 1851, 157 ; *Liebig & Kopp's Jahresb.* 1850, 508.

Acide sulfonaphtalidamique. (Laurent.) *Naphtalidinschwefelsäure.*

Formation. 1. By treating nitrosulphonaphthalic acid, $C^{20}XH^{2},2SO^{3}$, with sulphide of ammonium. — 2. By gently heating carbonaphthalide,

$C^{42}N^2H^{16}O^2$, with oil of vitrol, carbonic acid being evolved: the acid is precipitated on diluting the liquid with water.

$$C^{42}N^2H^{16}O^2 + 4(HO,SO^3) = 2(C^{20}NH^9,2SO^3) + 2CO^2 + 2HO.$$

It is uncertain whether this acid is merely isomeric with naphthamic and with naphthionic acid, $C^{20}NH^9S^2O^6$, or whether it is identical with naphthionic acid. (Carius.)

Naphthionic Acid.

$C^{20}NH^9S^2O^6 = C^{20}NH^9,2SO^3$.

PIRIA. *Sull'azione del solfito d'ammoniaca sulla nitronaftalina*, Pisa, 1850; *Ann. Pharm.* 78, 31; *N. Ann. Chim. Phys.* 31, 217; abstr. *Compt. rend.* 31, 488; *J. pr. Chem.* 52, 56; *Pharm. Centr.* 1851, 380; *Liebig & Kopp's Jahresb.* 1850, 500.

Formation. Produced, together with the isomeric body thionaphthamic acid, when nitronaphthalin is boiled with sulphite of ammonia. In this reaction the sulphite of ammonia converts the nitronaphthalin (like ammonia and sulphuretted hydrogen), into naphthylamine, which then combines with 2 At. SO^3, forming about equal proportions of the two isomeric acids. These acids cannot, however, be converted one into the other. (Piria.)

Preparation. 1 pt. nitronaphthalin (prepared by Piria's method, p. 1), and washed with water till the acid reaction ceases, is warmed with 5 pts. alcohol till completely dissolved, and mixed, while the liquid is kept warm, with 5 pts. aqueous sulphite of ammonia of sp. gr. 1·24. The mixture turns reddish, and then yellow; and, when kept simmering, deposits crusts of acid sulphite of ammonia on the sides of the flask, and becomes acid, whereby the thionapthamic acid is decomposed, and a large quantity of resin is formed, which greatly hinders the formation and purification of the acids. Hence it is necessary, as often as the liquid becomes acid, to add powdered carbonate of ammonia till the crusts redissolve completely, and the solution becomes alkaline. After boiling for eight hours, the decomposition is complete. This may be ascertained by adding a drop of the liquid to water, with which it should produce no turbidity. The liquid forms two strata, whereof the upper and more considerable stratum contains the decomposition-products of nitronaphthalin dissolved in ammonia—the lower stratum, aqueous sulphate and excess of sulphite of ammonia. The upper stratum is decanted, evaporated over a naked flame to an oily consistence, and allowed to stand in a cool place for 24 hours, whereupon it solidifies in a mass of orange-yellow laminæ of thionaphthamate of ammonia. The mother-liquid contains uncrystallisable naphthionate of ammonia; it is heated to 100°, and mixed with excess of hydrochloric acid, whereby naphthionic acid is precipitated as a reddish white powder, and sulphurous acid is evolved from the sulphite of ammonia contained in the liquid. The acid is first washed with water, and then with alcohol, till both flow off colourless; and by purifying it completely, it is converted into the lime- or soda-salt. The salt is obtained white by recrystallisation, decomposed with excess of hydrochloric acid, and the naphthionic acid washed as much as possible out of contact with the air, first with water freed from air by boiling, and then with alcohol. In this way, 200 grammes of nitronaphthalin yield 62·5 grammes of almost pure naphthionate of soda.

Properties. Precipitated from the cold solution of the lime- or soda-salt, it forms a bulky white powder; precipitated from the hot solution, small, light, silky crystals. It is tasteless and inodorous, and has an acid reaction. The crystals part with 1 At. water at 100°, but may be heated to 150° without losing more.

	Crystallised.		Piria.
20 C	120	51·72	51·54
10 H	10	4·31	4·48
N	14	6·03	6·14
2 S	32	13·80	14·14
7 O	56	24·14	23·70
$C^{20}NH^9,2SO^3 + Aq.$	232	100·00	100·00

Decompositions. Naphthionic acid, especially when moist, is readily decomposed by the *air*, and by *oxidising agents;* but presents great stability with most other chemical reagents. — 2. *Heated* on platinum foil, it burns, evolving sulphurous acid and a combustible aromatic vapour, smelling of oil of bitter almonds, and leaving a difficultly combustible charcoal which preserves the form of the substance. — 3. It is not affected by *dilute nitric acid,* but by *concentrated* nitric acid, especially if containing *nitrous acid,* or if *hot,* it is converted into a brown resin resembling that produced by other oxidising agents. — 4. *Chlorine* passed into an aqueous solution of a naphthionate, turns it brown, and finally precipitates a brown resin. *Chromate of potash* acts in a similar manner, especially if it be mixed with *sulphuric acid.* — 5. Naphthionic acid is neither dissolved nor decomposed by concentrated *hydrochloric acid;* neither is it attacked by concentrated *soda-ley.*

Combinations. — 1. Dissolves in 2,000 pts. cold *water;* readily in boiling water, from which it separates in crystals on cooling. — 2. Dissolves in *sulphuric acid,* especially with the aid of heat, and is precipitated therefrom by water unchanged; the solution does not blacken till 220°, at which temperature it evolves sulphurous acid.

Naphthionic acid is a strong acid; it expels acetic acid from its salts, and readily dissolves in a solution of acetate of potash. The salts of the alkalis are neutral, those of the heavy metallic oxides, acid. Mineral acids precipitate naphthionic acid as a white crystalline powder; acetic acid does not precipitate the aqueous solution, and only partially precipitates the alcoholic solution. It is difficult to obtain the naphthionates free from a red colouring matter; the best way is to recrystallise them from alcohol in the dark. Their solutions exhibit fluorescence like that of quinine, with red, blue, and violet colour; 1 pt. of naphthionate of soda in 200,000 pts. water still exhibits this property. In the solid state, the salts are permanent in the air; the solutions turn red on exposure to air and light, but not in the dark. — *Ferric chloride* produces with a solution of a naphthionate, a vermilion-red precipitate turning brown by heat; nitrate of silver a white, crystalline precipitate; *mercuric chloride,* a white precipitate, dissolving by heat, and reappearing as the liquid cools; *platinic chloride* gives a bright yellow precipitate; *chloride of gold* immediately turns the solution purple-red, and reduced gold is then precipitated; no reaction is produced by acetate of lead, chloride of barium, ferrocyanide of potassium, sulphate of zinc, or tartar-emetic.

Naphthionate of Potash. The brown solution of crude naphthionic acid in boiling concentrated potash, deposits, on cooling, crystals which must be recrystallised twice or thrice from the smallest possible quantity of alcohol. — Small, micaceous, slightly coloured laminæ, very soluble in water or in alcohol, sparingly soluble in aqueous or alcoholic potash. Contains 14·84 p. c. K. and 11·87 p. c. S, corresponding to the formula $C^{20}NH^9S^2O^6,KO$; by calculation 14·98 p. c. K. and 12·25 p. c. S.

Naphthionate of ammonia is exceedingly soluble in water and in alcohol, and crystallises with difficulty.

Naphthionate of Soda. The crude acid is heated with powdered carbonate of soda and a little alcohol of 60 p. c., the solution filtered boiling, and allowed to stand for 10 or 12 hours, whereupon it deposits naphthionate of soda in beautiful, large, transparent, and but slightly coloured prisms. The mother-liquid yields on evaporation more of the salt, but coloured. The crude salt is powdered, washed in a funnel with concentrated alcoholic soda (which dissolves the resinous matter very effectually, but not the salt), and the residue is repeatedly recrystallised with animal charcoal from a small quantity of weak boiling alcohol, till colourless crystals are obtained.—Large, well defined prisms of the oblique-prismatic system, or, when crystallised from water, ill-defined, indeterminable forms, containing apparently more water of crystallisation. When completely freed from water of crystallisation by heat, it reabsorbs it in moist air, and appears unchanged when dissolved in water, but does not dissolve in alcohol till it has been boiled for a long time, and this solution deposits on cooling a mass of small, ill-defined, cauliflower-like crystals, which are presently converted into thick prisms of the original form: *Fig.* 81 with *h*-faces; $i : u = 118° 56'$; $i : h = 96° 34'$; $u : u = 111° 55'$. Ratio of the axes, $a : b : c = 1 : 0·760 : 0·914$. — Viewed in masses, it is always slightly yellow. In dry air it does not undergo any change, or lose any water of crystallisation. The solution turns reddish brown in the air, especially in sunshine. Dissolves readily in water and in alcohol, but not in ether, and but slightly in alkaline water or alcohol; hence its saturated solution is completely precipitated by solutions of the fixed alkalis. Its taste is at first scarcely perceptible, but after a time it is sweet and persistent.

	Crystallised.		Piria. *mean.*
20 C	120	37·85	37·56
16 H	16	5·05	5·23
Na	23	7·26	7·15
N	14	4·42	4·50
2 S	32	10·09	9·76
14 O	112	35·33	35·80
$C^{20}NNaH^8S^2O^6 + 8Aq.$	317	100·00	100·00

Contains 8 Ats. water of crystallisation, whereof 7 At. 20·00 p. c. (average), by calculation 19·87 p. c. are expelled at about 80°, and the eighth atom, 2·67 p. c. at about 130°. (Piria.)

Naphthionate of Baryta is prepared: 1. By dissolving the acid in baryta-water and removing the excess of baryta by carbonic acid; it is then generally coloured deep red by a resinous substance, and must be purified by washing with cold alcohol, dissolving in boiling water, treating with animal charcoal and crystallising. — 2. (better than 1). 2 pts. crystallised naphthionate of soda and 1 pt. chloride of barium are dissolved in 10 pts. boiling water. As the solution cools, the salt immediately crystallises in a tolerable state of purity, and may be freed from every trace of chloride of barium by two recrystallisations from a small quantity of boiling water. — Crystallises in two different forms, depending on the temperature, and probably with different amounts of water of crystallisation. From rather concentrated solutions, micaceous, white, slightly amethystine laminæ are deposited while the liquid is still warm. The dilute solution does not crystallise till it is quite cold, and then deposits large, transparent, rhombic laminæ, resembling the lime-salt with which they are probably isomorphous. The last-named crystals effloresce very rapidly, become opaque before they are dry, and even when they are placed in alcohol or in water heated above 30°. It is rather soluble in water.

Naphthionate of Lime. Crude naphthionic acid is heated to boiling with milk of lime, and the filtered solution is evaporated on a water bath and allowed to stand from 12 to 24 hours, whereupon large, reddish crystals are deposited. The mother-liquid when evaporated yields more crystals, but more highly coloured. Of all the naphthionates this is the most easy to purify, viz. by washing the powdered salt on a funnel with cold alcohol, and then recrystallising it from boiling alcohol after previous treatment with animal charcoal.

White tablets having a fatty lustre, imperfectly transparent, appearing colourless singly, but rose-coloured when viewed in masses. When dry it is unaffected by the air, but its aqueous solution becomes coloured. Readily soluble in water, almost insoluble in alcohol. Neutral to test papers. *Fig.* 86 with a- and f-faces, without m. $i : u$ & $u' = 124° 19'$; $i : f = 115° 41'$; $i : a = 116° 30'$; $i : h = 59° 30'$; $u : u' = 117° 4'$. Ratio of the axes, $a : b : c = 1 : 1{\cdot}355 : 1{\cdot}662$. The crystals are mostly reversed twin-crystals with curved faces, in which the inclination of the two i-faces is about 172° 44′.

	Crystallised.		Piria. *mean.*
20 C	120	38·22	38·13
16 H	16	5·10	5·14
Ca	20	6·37	6·33
N	14	4·46	4·58
2 S	32	10·19	
14 O	112	35·66	
$C^{20}NCaH^8S^2O^6 + 8Aq$	314	100·00	

Gives off 7 At. (calculation = 20·05 p. c.) water of crystallisation at 100°, and the 8 At. between 100° and 160° (calculation = 2·86 p. c.); Piria found an average of 20·00 p. c. and 2·78 p. c. water.

Naphthionate of Magnesia is obtained by boiling 1 pt. of carbonate of magnesia with 2 pts. crude naphthionic acid for two hours. As the filtered solution cools, it deposits deep red needles, which may be freed from the greater part of the colouring matter by repeated recrystallisation from boiling weak alcohol. Crystallises in two different forms, containing different quantities of water of crystallisation, depending on the temperature. *a.* From concentrated solutions it crystallises on cooling in long prisms probably belonging to the square prismatic system, and having their extremities bevelled with two faces. They contain 3·92 p. c. Mg, and give off 23·15 p. c. water at 150°; hence they are probably $C^{20}NMgH^8S^2O^6 + 8$ Aq. (calculation = 3·92 Mg. and 23·52 p. c. Aq.). The crystals rapidly become opaque in the air, from absorption of water. — *b.* The mother-liquid from *a*, evaporated spontaneously or in vacuo, yields beautiful, large, red, oblique prismatic crystals; *Fig.* 91 with *f*- & *t*-faces . $u : u' = 76° 22'$; $i : t = 132° 51'$; $i : u$ and $u' = 114° 57'$; $i : f = 77° 43'$; Permanent in the air; becomes opaque in hot water, loses only part of its water of crystallisation at 100°, but the whole at 150° in all 27·56 p. c.; hence its formula is $C^{20}NMgH^8S^2O^6 + 10$ Aq. (By calculation 27·78 p. c. water.)

Naphthionate of Zinc. 2 pts. naphthionate of soda are dissolved with 1 pt. sulphate of zinc in a small quantity of boiling water. On cooling (sometimes the cold liquid requires stirring), large nacreous laminæ crystallise out, resembling naphthalin, and are purified by first crystallising from alcohol and then from water. — Rather long, transparent, red, rhombic laminæ; or when crystallised by cooling the hot alcoholic solution, short, four-sided prisms. Becomes opaque at 90°, but not anhydrous till it has been long heated in a stream of air between 150° and 160°. At a higher temperature, it is decomposed, yielding an aromatic vapour and afterwards sulphurous acid. Dissolves readily in water, and in absolute alcohol, especially when heated.

Naphthionate of Lead. Acetate of lead and naphthionate of soda do not react upon one another. — A solution of nitrate of lead in hot, concentrated, aqueous naphthionate of soda, deposits on cooling short, red needles grouped about a common centre, or small granules. Its aqueous solution turns red when boiled, and cannot afterwards be made to crystallise. Reddens litmus. Dissolves slightly in water, but not in alcohol. In dry air at 150° it parts with 5·15 p. c. water of crystallisation; 2 At. = 5·24 p. c. water.

Cuprous Naphthionate? A solution of naphthionate of soda turns red on addition of sulphate of copper. If the excess of sulphate of copper be precipitated by alcohol, and the liquid evaporated in vacuo, an uncrystalline, reddish-brown residue is left, the aqueous solution of which gives with potash a precipitate of hydrated cuprous oxide.

Naphthionate of Silver. Solution of naphthionate of soda produces with perfectly neutral nitrate of silver, a white precipitate, which at first redissolves but afterwards becomes permanent, being converted into a light, white, curdy powder. The salt sometimes remains in this state, and sometimes is rapidly converted into small, heavy, granular crystals of adamantine lustre. It is slightly soluble in water, especially in hot water, from which it crystallises on cooling. It turns grey on exposure to light, without suffering further change. It yields by heat the same volatile products as the other naphthionates, and leaves metallic silver mixed with exceedingly incombustible charcoal.

	Crystallised or amorphous.		Piria. *mean.*
20 C	120	34·48	34·35
10 H	10	2·88	3·04
Ag	108	31·03	31·38
N	14	4·02	4·16
2 S	32	9·20	9·22
8 O	64	18·39	17·85
$C^{20}NAgH^8S^2O^6 + 2Aq$	348	100·00	100·00

It parts with 5·23 p. c. water of crystallisation at 120°; 2 At. = 5·17 p. c.

Naphthionate of Silver with Ammonia. Naphthionate of silver gives with hot aqueous ammonia, a clear solution, which, on cooling, deposits whitish grey granular crystals. Resembles the silver-salt, and is very little affected by light. Decomposes by heat, with evolution of ammonia.

			Piria.
20 C	120	31·41	31·70
16 H	16	4·19	4·33
Ag	108	28·27	28·85
3 N	42	10·99	10·76
2 S	32	8·38	
8 O	64	16·76	
$2NH^3,C^{20}NAgH^8S^2O^6 + 2Aq$	382	100·00	

Naphthionic acid is barely soluble in alcohol.

Thionaphthamic Acid.

$$C^{20}NH^9S^2O^6 = C^{20}NH^9,2SO^3\,(?).$$

Piria. (1850.) *Sull'azione del solfito d'ammoniaca sulla nitronaftalina*, Pisa, 1850; *Ann. Pharm.* 78, 31; *N. Ann. Chim. Phys.* 31, 217; abstr. *Compt. rend.* 31, 488; *J. pr. Chem.* 52, 56; *Pharm. Centr.* 1851, 380; *Liebig* & *Kopp's Jahresb.* 1850, 500.

Formation. Obtained as impure thionaphthamate of ammonia, in orange-yellow laminæ, together with the isomeric compound, naphthionic acid (p. 110), and in about equal quantity, by boiling nitronaphthalin with sulphite of ammonia. The mother-liquid contains the naphthionate of ammonia.

Thionaphthamic acid cannot be separated from the ammonia-salt without undergoing decomposition, being converted on the addition of acids, even of cold acetic acid, into sulphate of naphthylamine, which crystallises out.

The *thionaphthamates* crystallise in large, reddish or amethyst-red, nacreous laminæ. Their solution rapidly turns brownish red in the air, owing doubtless to formation of oxynaphthylamine (p. 101), by the oxidising agency of the air upon the naphthylamine. (Piria.) This decomposition is especially promoted by the action of heat and light;

alkalis retard it; hence the salts are obtained with less colour when they are crystallised from solutions containing a slight excess of alkali. In a state of perfect purity, the salts are probably colourless. (Piria.) From 1 At. salt, 2 At. sulphuric acid are thus liberated, of which only 1 At. is neutralised by the naphthylamine; hence free sulphuric acid is formed, which hastens the decomposition. If the solution of the perfectly neutral ammonia-salt be heated to between 80° and 90°, and the evaporated water replaced, it becomes coloured, deposits a melted brown resin, turns very acid, and then contains sulphate of naphthylamine. The potash-salt to which a little caustic potash has been added, it is not decomposed by similar treatment. The salts, distilled with excess of hydrate of lime, yield oily naphthylamine which afterwards crystallises.

Thionaphthamate of Ammonia. Obtained in crystals by dissolving the crude salt in 2 pts. boiling water containing a few drops of ammonia (p. 110) and cooling the solution. — Small, reddish, micaceous laminæ, the solution of which becomes more rapidly coloured than that of the other salts. Dissolves very readily in water and in alcohol.

Thionaphthamate of Potash. The aqueous ammonia-salt is boiled with a slight excess of carbonate of potash, till ammonia ceases to be evolved; on cooling, broad, nacreous laminæ, resembling boracic acid, crystallise out. These crystals cannot be obtained perfectly colourless, even by recrystallisation with animal charcoal. — It does not lose weight in a stream of air at 150°. Dissolves very readily in pure water, and but very slightly in water containing potash or carbonate of potash; it scarcely dissolves in alcohol, and very slightly in dilute alcohol.

	Crystallised.		Piria. *mean.*
20 C	120	45·97	45·84
8 H	8	3·06	3·22
K	39·2	14·98	14·83
N	14	5·36	5·53
2 S	32	12·26	12·24
6 O	48	18·37	18·34
$C^{20}NKH^8S^2O^6$	261·2	100·00	100·00

Thionaphthamate of Soda is prepared in exactly the same manner as the potash-salt. Crystallises in reddish micaceous laminæ. Dissolves slightly in cold and readily in hot water, and very slightly in water containing carbonate of soda.

Thionaphthamate of Baryta. Reddish micaceous laminæ, which crystallise out on mixing boiling concentrated solutions of thionaphthamate of potash and chloride of barium.

	Crystals.		Piria.
20 C	120	37·75	37·32
11 H	11	3·46	3·78
Ba	68·5	21·59	21·45
N	14	4·41	
2 S	32	10·07	10·04
9 O	72	22·72	
$C^{20}NBaH^8S^2O^6 + 3Aq$	317·5	100·00	

Loses at 120°, 8·53 p. c. water of crystallisation (3 At. = 8·5 p. c.). (Piria.)

The *lime-* and *magnesia-salts* resemble the other salts, and are very soluble.

Thionaphthamate of Lead. Nitrate of lead is added to *excess* of the boiling concentrated solution of the potash-salt (if an excess of nitrate of lead be added, a double-salt is formed, containing apparently equal number of atoms of thionaphthamate and nitrate of lead). The salt which is deposited on cooling is purified by recrystallisation. — Light, reddish, crystalline powder, dissolving very slightly in water, and scarcely at all in alcohol.

Thionaphthamate and Acetate of Lead. When almost boiling concentrated solutions of thionaphthamate of potash and acetate of lead acidulated with acetic acid, are mixed together, this double-salt crystallises out on cooling, in reddish, nacreous laminæ grouped about a common centre. Gives with sulphuric acid, acetic acid and the ordinary decomposition-products of thionaphthamic acid. Heated in dry air, it does not part with any water. Slightly soluble in cold, more soluble in hot water.

	Crystallised.		Piria.
24 C	144	29·51	
11 H	11	2·25	
2 Pb	207·4	42·42	42·07
N	14	2·87	2·99
2 S	32	6·56	6·53
10 O	80	16·39	
$C^{20}NPbH^8S^2O^6 + C^4H^3PbO^4$	488·4	100·00	

Formylnaphthalide.

$$C^{22}H^9NO^2 = C^{20}(C^2H)AdH^6,O^2 ?$$

ZININ. *Petersb. Acad. Bull.* 16, 282 ; *Ann. Pharm.* 108, 228 ; *J. pr. Chem.* 74, 379 ; *Rep. Chim. pure* 1, 148.

Formation. Compare oxalate of naphthylamine *a* and *b* (p. 100.)

Preparation. Well dried acid oxalate of naphthylamine, $C^{20}NH^9, C^4H^2O^8$, is heated in a retort carefully and gradually to about 200° ; whereupon it melts and evolves with effervescence, water and a mixture of 1 vol. carbonic oxide with 2 vols. carbonic acid. After the whole has been completely melted, it is left to cool, whereupon the liquid product solidifies in a radiated crystalline mass, generally amounting to two-thirds of the salt employed. This is treated with alcohol, which dissolves formylnaphthalide and leaves insoluble oxynaphthalide, $C^{44}H^{16}N^2O^4$

Properties. Crystallises on cooling from boiling water in long silky needles. Melts at 102°, and distils almost entirely without decomposition. It acquires a slight rose tint in the air, especially when moist.

			Zinin.
22 C	132	77·19	77·14
9 H	9	5·26	5·34
N	14	17·55	
2 O	16		
$C^{20}(C^2H)AdH^6,O^2$	171	100·00	

Decompositions. 1. Aqueous and even dilute boiling *potash* readily decomposes it into naphthylamine and formic acid. 2. It is easily decomposed by *strong acids* with aid of heat.

Dissolves somewhat readily in boiling *water*, and very readily in *alcohol*.

Methyl-lepidine.

$C^{22}NH^{11} = C^{20}(C^2H^3)NH^6,H^2$.

GR. WILLIAMS. *J. pr. Chem.* 66, 340.

Formelepidin.

Obtained in crystals in combination with hydriodic acid, like hydriodate of methyl-chinoline (p. xiii, 252).

Isomeric with ethyl-chinoline and cryptidine.

Naphthalocyanic Acid.

$C^{22}NH^7O^2 = C^{20}CyH^7,O^2$.

V. HALL. *N. Phil. Mag. J.* 17, 304 ; *Chem. Gaz.* 1858, 477 ; *Liebig & Kopp's Jahresb.* 1858, 350.

A. W. HOFMANN. *Compt. rend.* 47, 425; *N. Ann. Chim. Phys.* 54, 204.

Cyanate of naphthyl.

Formation and Preparation. When carbonaphthalide (p. 125) is heated with phosphoric anhydride, a small quantity of cyanate of naphthyl passes over, while the greater part of the compound is charred. (Hall.) — 2. Menaphthoximide (p. 128) heated to 260° decomposes, puffing out white vapours, which have a very strong peculiar odour, and probably contain naphthalocyanic acid corresponding to anilocyanic acid. (Perkin, *Chem. Soc. Qu. J.* 9, 8.)

Properties. Magnificent and very fusible crystals. With chemical reagents, it gives reactions precisely analogous to those of anilocyanic acid. (Hofmann.)

Insoluble in *water*, very soluble in *alcohol* and in *ether*.

Naphthalosulphocyanic Acid.

$C^{22}H^7NS^2 = C^{20}CyH^7,S^2.$

V. HALL. *N. Phil. Mag. J.* 17, 304; *Chem. Gaz.* 1858, 477; *Liebig & Kopp's Jahresb.* 1858, 350.
A. W. HOFMANN. *Compt. rend.* 47, 425; *N. Ann. Chim. Phys.* 54, 204.

Sulphocyanide of naphthyl.

Formation and Preparation. By distilling sulphocarbonaphthalide, $C^{40}CyNH^{14},H^2S^2$. with phosphoric anhydride:

$$C^{42}N^2H^{16}S^2 = C^{20}NH^9 + C^{20}CyH^7,S^2.$$

Sulphocarbonaphthalide, obtained by digesting crude naphthylamine with bisulphide of carbon, is pure enough for the purpose. (Hall.)

Properties. Splendid, readily fusible crystals, having a peculiar odour. (Hall.)

Decompositions. 1. Boiled in alcoholic solution with *naphthylamine*, it again forms sulphocarbonaphthalide, which, from its insolubility in alcohol, may be easily separated from the naphthalosulphocyanic acid. — 2. With *aniline* it forms sulphocyanide of phenyl-naphthylamine, $C^{20}(C^{12}H^5)CyAdH^5,H^2S^2$. (Hall, Hofmann.)

Insoluble in *water*, readily soluble in *alcohol* and in *ether*.

Naphthyl-urea.

$C^{22}N^2H^{10}O^2 = C^{20}CyAdH^6,H^2O^2.$

H. SCHIFF. *Dissertation*, Göttingen 1857; *J. pr. Chem.* 70, 264; *Ann. Pharm.* 101, 299; *N. Ann. Chim. Phys.* 52, 112; *Chem. Gaz.* 1857, 211; *Chem. Centr.* 1857, 166 and 362; *Liebig & Kopp's Jahresb* 1857, 389.

Naphthalidinharnstoff; Naphthylharnstoff; Naphthylcarbamid. (Schiff.)

Formation. From naphthylamine and cyanic acid (p. 97, 9), but not from sulphate of naphthylamine and cyanate of potash.

Preparation. Solution of naphthylamine in anhydrous ether is saturated with gaseous cyanic acid (prepared by heating cyanuric acid), and left to evaporate spontaneously, whereby brilliant laminæ of the compound are obtained. In making this experiment, decomposition once took place, giving rise to a purple-red substance; probably owing to the presence of water in the ether (comp. p. 97, 9).

Properties. Brilliant laminæ; or when obtained by evaporating the alcoholic solution by heat, flat, brilliant, flexible needles. It retains a yellowish tint even after several recrystallisations.

			Schiff.
22 C	132	70·96	70·75
10 H	10	5·38	5·45
2 N	28	15·05	14·35
2 O	16	8·61	9·45
$C^{20}CyAdH^6,H^2O^2$	186	100·00	100·00

Decompositions. 1. Decomposed by *acids.* — 2. With *nitric acid* the solution evolves gas, and forms a blood-red liquid.

Combinations. It is scarcely soluble in *water*, and insoluble in *alkalis.* — 2. Dissolves sparingly in *ether*, but readily in *alcohol.* — 3. Its concentrated alcoholic solution mixed with *oxalic acid*, yields a crystalline compound.

Ethyl-naphthylamine.

$C^{24}NH^{13} = C^{20}(C^4H^5)NH^6,H^2.$

SCHIFF. Notice by Limpricht: *Ann. Pharm.* 99, 117. — *J. pr. Chem.* 70, 264; *Ann. Pharm.* 101, 299; *N. Ann. Chim. Phys.* 52, 112; *Chem. Gaz.* 1857, 211; *Chem. Centr.* 1857, 166 and 362; *Liebig* & *Kopp's Jahresb.* 1857, 389.

Vinenaphthalidin. (Gm.)

Known only in combination with hydrobromic and hydriodic acids.

Formation. When naphthylamine is treated for a long time with excess of bromide of ethyl between 40° and 50°, hydrobromate of ethyl-naphthylamine is formed, from which potash liberates the ethyl-naphthylamine, which at the same time decomposes.

Hydrobromate of Ethyl-naphthylamine. Purified naphthylamine mixed with excess of bromide of ethyl in a small flask (provided with an upright tube so as to condense the vapours and allow them to flow back) is heated for several hours to the boiling point of bromide of ethyl; the excess of bromide is then distilled off from the resulting reddish brown mass, and the residue is extracted with boiling water. The compound crystallizes from the cooling extracts, and is purified by recrystallisation:

$$C^{20}NH^9 + C^4H^5Br = C^{20}(C^4H^5)NH^8,HBr.$$

2. Naphthylamine sealed up in a glass tube with bromide of ethyl, yields in a few days, at ordinary temperatures, a small quantity of crystals, and after 14 days, the tube is almost completely filled with them. Pale, rose-coloured, small needles, grouped about a common

centre; they become less readily coloured in the air than naphthylamine. With potash, it forms a white curdy precipitate of naphthylamine, which after a time is converted into needles; at the same time alcohol is formed:

$$C^{20}(C^4H^5)NH^8,HBr + KO,HO = C^{20}NH^9 + C^4H^6O^2 + KBr.$$

Very slightly soluble in cold *water*, rather soluble in hot water, *alcohol*, and *ether*.

			Schiff.
24 C	144	57·14	
14 H	14	5·56	
N	14	5·56	
Br	80	31·74	31·55
$C^{20}(C^4H^5)NH^8,HBr$	252	100·00	

Hydriodate of Ethyl-naphthylamine is obtained from naphthylamine and iodide of ethyl, and crystallises in brilliant four-sided prisms. It is much more easily decomposed than hydrobromate of ethyl-naphthylamine; and has about the same solubility as the latter.

Ethyl-lepidine.

$$C^{24}NH^{13} = C^{20}(C^4H^5)NH^6,H^2.$$

GR. WILLIAMS. *Edinb. Roy. Soc. Trans.* 21, 3rd pt., 377; *Chem. Gaz.* 1856, 261 and 283; *J. pr. Chem.* 69, 355.

Vinelepidin. (Gm.)

If 1 At. more hydrogen be supposed to be added to this compound, it becomes ethyl-lepidine-ammonium. Known only in combination with acids.

Obtained as *hydriodate of ethyl-lepidine* in the same manner as the hydriodate of methyl- or ethyl-chinoline (xiii, 252, 254) in brown needles, which after recrystallisation exhibit a beautiful canary-yellow colour, become transiently blood-red at 100°, and have the formula $C^{24}H^{13}N,HI$.

Chloroplatinate of Ethyl-lepidine. Obtained in the same manner as the chloroplatinate of methyl-chinoline (xiii, 252). It is soft at first, but soon becomes crystalline. It must be washed with ether-alcohol.

			Gr. Williams.
24 C	144	38·14	38·00
N	14	3·71	
14 H	14	3·71	3·82
Pt	99	26·23	26·53
3 Cl	106·5	28·21	
$C^{24}NH^{13},HCl,PtCl^2$	377·5	100·00	

Allyl-naphthyl-sulphocarbamide.

$C^{28}H^{14}N^2S^2 = C^{20}(C^6H^5)CyAdH^5,H^2S^2$.

ZININ. *Petersb. Acad. Bull.* 10, 346; abstr. *Ann. Pharm.* 84, 346; *J. pr. Chem.* 57, 173; *Chem. Gaz.* 1852, 441; *Pharm. Centr.* 1852, 689; *Liebig & Kopp's Jahresb.* 1852, 627.

Senföl-Naphtalidin.

Formation. Naphthylamine combines with oil of mustard, like ammonia.

Preparation. If 30 pts. oil of mustard be added to 43 pts. naphthylamine, dissolved in 344 pts. alcohol of 90 p. c., the greater part of the compound (51 pts.) is gradually deposited in radiated, hemispherically grouped crystals, which soon form a crust; the mother-liquid evaporated to half its bulk yields 18 pts. more product.

Properties. Melts at 130° to a clear, colourless liquid, which on cooling solidifies in a granular crystalline mass. Carefully heated, it distils for the most part undecomposed, as an oily, colourless or slightly yellow liquid, which when cool does not crystallise in granules till it has stood for some time. Neutral.

			Zinin. *mean.*
28 C	168	69·42	69·66
14 H	14	5·79	5·95
2 N	28	11·57	
2 S	32	13·22	13·00
$C^{20}(C^6H^5)CyAdH^5,H^2S^2$	242	100·00	

Decompositions. Dissolves in *nitric acid* of sp. gr. 1·36, without coloration, if carefully heated, but is soon decomposed, with violent evolution of red vapours, the liquid turning yellow; water then precipitates a yellow resin. If the solution be still boiled till no more red vapours are evolved, water precipitates from the liquid an orange-yellow powder, dissolving readily in alcohol and in nitric acid, but sparingly in boiling water; heated on platinum foil, it melts to a brownish red liquid, and then burns with deflagration, leaving a large residue of carbon.— 2. Treated with *hydrated oxide of lead*, it parts with its sulphur, and forms a new substance crystallising from hot alcohol in white silky granules. More of these granules are precipitated from the mother-liquid by water, as well as an unctuous substance much more soluble in alcohol than the body granules.

Amyl-lepidine.

$C^{30}NH^{19} = C^{20}(C^{10}H^{11})NH^6,H^2$.

GR. WILLIAMS. *J. pr. Chem.* 66, 340.

When lepidine is heated with iodide of amyl for several hours in a sealed tube at 100°, *hydriodate of amyl-lepidine* is obtained in small crystals containing 37·49 p. c. iodine, and but slightly soluble in water. (By calculation 37·24 p. c. iodine.)

Sulphocyanide of Phenyl-naphthylamine.

$C^{34}H^{14}N^2S^2 = C^{20}(C^{12}H^5)CyAdH^5,H^2S^2$.

A. W. HOFMANN. *Compt. rend.* 47, 425; *N. Ann. Chim. Phys.* 54, 205.

Phenyl-naphthyl-Sulphocarbamide. (Hofmann.) *Sulfocyanphenyl-naphtalidin.*

Formation and Preparation. 1. When naphthylamine is mixed with sulphocyanide of phenyl, the two bodies unite almost immediately to a solid compound (Hofmann):

$$C^{12}CyH^5S^2 + C^{20}NH^9 = C^{20}(C^{12}H^5)CyAdH^5,H^2S^2.$$

2. Naphthalosulphocyanic acid forms the same compound with aniline. (Hall, *N. Phil. Mag. J.* 17, 304.)

Properties. Crystallises from its boiling solution in spangles; very like sulphocarbanilide, $C^{24}CyNH^{10},H^2S^2$.

Very sparingly soluble in *alcohol* and in *ether*.

Conjugated compounds containing 2 *At.* $C^{20}NH$.

Carbonaphthalide.

$C^{42}H^{16}N^2O^2 = C^{40}CyNH^{14},H^2O^2$.

DELBOS. *N. Ann. Chim. Phys.* 21, 68; *Compt. rend.* 24, 1091; *N. J. Pharm.* 12, 237; *Ann. Pharm.* 64, 370; *J. pr. Chem.* 42, 244; *Pharm. Centr.* 1847, 637; *Liebig & Kopp's Jahresb.* 1847-8, 610.
ZININ. *Petersb. Acad. Bull.* 16, 282; *Ann. Pharm.* 108, 228; *J. pr. Chem.* 74, 279; *Rep. Chim. pure.* 1, 148.

Naphthalidam-Carbamid. (Delbos.)

Formation. (Comp. p. 100; oxalate of naphthylamine *a* and *b*.) — 2. By boiling sulphocarbonaphthalide with alcoholic potash (Delbos):

$$C^{42}H^{16}N^2S^2 + 2HO = C^{42}H^{16}N^2O^2 + 2HS.$$

3. Oxanaphthalide is heated for a long time above its melting point or submitted to dry distillation, whereupon almost pure carbonic oxide is evolved. (Zinin.)

Preparation. 1. When neutral oxalate of naphthylamine is fused in a retort, it evolves water of crystallisation, and almost immediately decomposes, whereupon water, carbonic acid, and carbonic oxide are evolved with effervescence, and at a higher temperature naphthylamine and carbonaphthalide distil over, the latter condensing for the most part in the neck of the retort. The distilled yellowish mass is freed from naphthylamine by repeated boiling with alcohol, which leaves a residue of pure carbonaphthalide. It would be more advantageous to interrupt the distillation immediately after the evolution of carbonic oxide and carbonic acid, since a large quantity of carbonaphthalide is decomposed by distillation; but then a product would be obtained contaminated with undecomposed oxalate of naphthylamine. (Delbos.) — 2. *Best method:* Acid oxalate of naphthylamine is heated till it melts completely, and is purified as in method 1 (also from simultaneously formed naphthalide and undecomposed oxanaphthalide). (Delbos, Zinin.)

Properties. Pure white, light, and slightly silky mass. Distils above 300, undergoing partial carbonisation. Turns rapidly red in the air. (Delbos.)

			Delbos. *dried at* 100°.
42 C	252	80·76	80·17
16 H	16	5·13	4·98
2 N	28	8·98	
2 O	16	5·13	
$C^{40}CyNH^{14},H^2O^2$	312	100·00	

Decompositions. 1. Distilled with *phosphoric anhydride*, it yields amongst other products, a small quantity of naphthalocyanic acid (p. 118.) (Hall, *N. Phil. Mag. J.* 17, 304.) 2. It is not affected by dilute *acids.* (Delbos.) — 3. Dissolves without decomposition in *alcoholic potash,* and is precipitated therefrom by water. (Delbos.)

Insoluble in *water.* Dissolves very sparingly in boiling *alcohol* (less than oxanaphthalide, Zinin), from which it is deposited on cooling as a white powder consisting of microscopic needles.

Sulphocarbonapthalide.

$C^{42}H^{15}N^2S^2 = C^{40}CyNH^{14},H^2S^2$.

Delbos. *N. Ann. Chim. Phys.* 21, 68; *Compt. rend.* 24, 1091; *N. J. Pharm.* 12, 237; *Ann. Pharm.* 64, 370; *J. pr. Chem.* 42, 244; *Pharm. Centr.* 1847, 637; *Liebig & Kopp's Jahresb.* 1847-8, 610.

Naphthalidam-sulphocarbamid. (Delbos.)

Formation. From naphthylamine and bisulphide of carbon (comp. p. 97, 12.) — 2. From naphthalin and naphthalosulphocyanic acid, (comp. p. 119, 1).

Preparation. Bisulphide of carbon is mixed with a solution of naphthylamine in absolute alcohol. After one or two days, the liquid deposits sulphocarbonaphthalide, on the sides of the vessel, as a white crystalline vegetation. The mixture blackens if allowed to stand for three or four days, owing to the formation of sulphide of naphthalidam. By using a very dilute solution of naphthylamine in absolute alcohol, sulphocarbonaphthalide is obtained in brilliant, colourless needles. (Delbos.

Properties. Snow-white crystalline mass, or small and very brillian prisms.

			Delbos.
42 C	252	76·83	78·86
16 H	16	4·87	4·59
2 N	28	8·54	
2 S	32	9·76	9·69
$C^{40}CyNH^{14},H^2S^2$	328	100·00	

Decompositions. 1. By boiling with *alcoholic potash*, it is converted into carbonaphthalide (comp. p. 123. Delbos). 2. By *dry distillation* it is decomposed, naphthylamine being liberated and the substance at the same time becoming charred. (Delbos.) Distilled with *phosphoric anhydride* it yields naphthalosulphocyanic acid, (p. 119. Hall.) — 4. It is not affected by dilute *acids*. (Delbos.)

Insoluble in *water*, *alcohol*, and *bisulphide of carbon*. (Delbos.)

Menaphthylamine.

$C^{42}H^{17}N^3 = C^{40}CyNAdH^{13},H^2$.

W. H. Perkin. *Chem. Soc. Qu. J.* 9, 8; *Chem. Gaz.* 1856, 519; *N. Phil. Mag. J.* 12, 226; *Instit.* 1856, 300 and 406; *Ann. Pharm.* 98, 236; *J. pr. Chem.* 68, 152 and 441; *Chem. Centr.* 1856, 394; *Liebig & Kopp's Jahresb.* 1856, 538.

Menaphtalidin.

Formation. From naphthylamine and chloride of cyanogen (comp. p. 97). (Perkin.)

Preparation. By A. W. Hofmann's process for preparing melaniline, (xi, 351). A number of glass tubes are partly filled with naphthylamine maintained in fusion by a gentle heat, and gaseous chloride of cyanogen is drawn through them by means of an aspirator. As soon as the reaction commences, heat is developed; the liquid thickens, so that the passage of the gas is impeded; and at the end of the operation, the mass must be carefully warmed to keep it sufficiently fluid. The mass, which after cooling is black and resinous, and consists principally of hydrochlorate of menaphthylamine, is boiled with a large quantity of water, and the menaphthylamine is precipitated by ammonia or potash from the filtered solution, as a white precipitate, which is washed with water in order to free it from chloride of potassium or chloride of ammonium, and purified by one or two recrystallisations from alcohol.

Properties. Small, white needles, inodorous and having a bitter taste. It becomes coloured in the air; and restores the colour to reddened litmus.

			Perkin. *mean.*
42 C	252	81·0	80·89
17 H	17	5·4	5·54
3 N	42	13·6	
$C^{40}CyNAdH^{13},H^2$	311	100·0	

Decompositions. 1. Melts at about 200° to a transparent pale yellow oil, and decomposes at 260°, whereupon pure naphthylamine distils over, and a brown mass remains in the retort. This brown residue has probably a composition analogous to that of the substance formed under similar circumstances from melaniline. (Perkin.) — 2. It appears to form neutral compounds with *chlorine, bromine,* and *iodine.* 3. Menaphthylamine treated with *fuming sulphuric acid* becomes pasty, from formation of sulphate; the mixture becomes liquid again when heated; and if it then be diluted with water and treated with carbonate of lead, the soluble lead-salt of a new acid is obtained, which, however, decomposes partially every time its solution is evaporated. Sulphuretted hydrogen precipitates sulphide of lead from the solution of the lead-salt, and leaves a colourless solution, which on evaporation, yields a soluble alkaline and an insoluble neutral body as decomposition-products of the acid. — 4. *Fuming nitric acid* reacts very violently on menaphthylamine, giving rise to a series of substitution-products. — 5. *Chromic acid* acts but slowly. — 6. *Cyanogen gas,* passed into an alcoholic or ethereal solution of menaphthylamine, turns it first yellow, and then red, but gives no precipitate even after standing for a long time. Menaphthylamine suspended in ether and treated with gaseous cyanogen, dissolves completely, and the solution after a time deposits dark-yellow, crystalline bicyano-menaphthylamine. (Perkin.)

$$C^{42}H^{17}N^3 + 2\,C^2N = C^{40}Cy^3Ad^2H^{11},H^2.$$

Combinations. It is almost insoluble in *water.* It unites with *acids,* forming salts of menaphthylamine, many of which are amorphous or but very slightly crystalline; all of them are but sparingly soluble in water and neutral to litmus paper. The salts are precipitated from their solutions by acids and by saline solutions; potash and ammonia precipitate the base as a pure white powder.

Phosphate of Menaphthylamine. White, crystalline; very soluble in alcohol and in ether.

Sulphate of Menaphthylamine. Best obtained by neutralising the base with sulphuric acid. — White, perfectly amorphous substance, only moderately soluble in alcohol and in ether; on evaporating the solution it is reprecipitated as a white powder.

Hydriodate and *Hydrobromate of Menaphthylamine* are crystalline and very soluble in alcohol and in ether.

Hydrochlorate of Menaphthylamine. White, amorphous compound turning slightly red in the air. Rather soluble in water, very soluble in alcohol and in ether. Decomposed by heat, hydrochlorate of naphthylamine subliming, and a black residue remaining in the retort.

			Perkin.
$C^{42}H^{17}N^3$	311·0	89·6	
HCl	36·5	10·4	10·44
$C^{42}H^{17}N^3,HCl$	347·5	100·0	

Nitrate of Menaphthylamine is the most beautiful of all the salts of menaphthylamine. It is prepared by dissolving the pure base in dilute boiling nitric acid. It is deposited from this solution in small white prisms. Almost insoluble in cold water; dissolves abundantly in alcohol and in ether.

Chloroplatinate of Menaphthylamine is best obtained by mixing an alcoholic solution of platinic chloride with warm alcoholic solution of hydrochlorate of menaphthylamine; small, yellow, brilliant scales are then deposited. If aqueous solutions are employed, the compound is immediately precipitated as an amorphous powder, which is almost white but soon assumes a green colour. Perkin found 19·07 p. c. Pt.; the formula $C^{42}H^{17}N^{3},HCl + PtCl^{2}$ requires 19·08 p. c.

Terchloride of Gold gives a blue precipitate with solution of menaphthylamine.

Menaphthylamine dissolves in *alcohol* and in *ether*.

Bicyanomenaphthylamine.

$C^{46}H^{17}N^{5} = C^{40}Cy^{3}Ad^{2}H^{11},H^{2}$.

W. H. Perkin. *Chem. Soc. Qu. J.* 9, 8; *Ann. Pharm.* 98, 236; *J. pr. Chem.* 68, 152 and 441; *Liebig & Kopp's Jahresb.* 1856, 538.

Dicymenaphthylamine. (Perkin.) *Bicyanmenaphtalidin.*

Formation. Produced from menaphthylamine and gaseous cyanogen (comp. 126, 2).

Preparation. Gaseous cyanogen is passed through ether containing menaphthylamine in suspension. The whole is dissolved, and after a time, bicyanomenaphthylamine is deposited as a crystalline, dark-yellow substance, and is purified by washing with ether.

Properties. Pale yellow; crystallises with difficulty.

			Perkin. *at* 100°.
46 C	276	76·00	76·00
17 H	17	4·69	4·71
5 N	70	19·31	
$C^{40}Cy^{3}Ad^{2}H^{11},H^{2}$	363	100·00	

Insoluble in *water*.

Bicyanomenaphthylamine is a base, although a very unstable one; it dissolves with ease in dilute acids and may be reprecipitated by ammonia, if added immediately after dissolving the base; but, like cyananiline and bicyanomelaniline, it cannot remain longer in acid solution, without undergoing complete decomposition. If the solution of bicyanomenaphthylamine in acids be left to itself only a few seconds, it becomes turbid and deposits yellow menaphthoximide. (Perkin.)

$$C^{46}H^{17}N^{5} + 4\,HO + 2\,HCl = C^{40}(C^{4}HO^{2})CyNAdH^{12},O^{2} + 2\,NH^{4}Cl.$$

Bicyanomenaphthylamine is moderately soluble in *alcohol* and in *ether*.

Oxanaphthalide.

$C^{44}H^{16}N^2O^4 = C^{40}(C^4HO^2)NAdH^{13},O^2$.

ZININ. *Petersb. Acad. Bull.* 16, 282; *Ann. Pharm.* 108, 228; *J. pr. Chem.* 74, 379; *Rep. Chim. pure.* 1, 148.

Formation. By the action of heat on oxalate of naphthylamine (comp. 100, *a* and *b*).

Preparation. The residue which remains after fusing acid oxalate of naphthylamine, is treated with alcohol, whereby the formylnaphthalide (p. 117) is dissolved out, leaving insoluble oxanaphthalide.

Properties. Small scales. Melts at about 200°. Zinin found 77·78 p. c. C and 4·87 p. c. H; by calculation, 77·64 p. c. C and 4·70 p. c. H.

Decompositions. *Heated* for a long time above its melting-point, or submitted to *dry distillation*, it decomposes for the most part, yielding almost pure carbonic oxide, and forming carbonaphthalide $C^{40}CyNH^{12}, H^2O^2$. — 2. It is but very slightly affected by dilute aqueous *potash* or even by rather concentrated *acids* (nitric acid excepted); but if it be boiled with alcoholic potash or heated with concentrated aqueous potash (1 pt. potash to 3 or 4 pts. water), it is resolved into naphthylamine and oxalic acid.

Insoluble in water, sparingly soluble in boiling *alcohol*.

Menaphthoximide.

$C^{46}H^{15}N^3O^4 = C^{40}(C^4HO^2)CyNAdH^{12},O^2$(?).

W. H. PERKIN. *Chem. Soc. Qu. J.* 9, 8; *Ann. Pharm.* 98, 236; *J. pr. Chem.* 68, 152 and 441; *Liebig & Kopp's Jahresb.* 1856, 538.

Formation. (Comp. p. 127.)

Preparation. Warm, alcoholic solution of bicyanomenaphthylamine is mixed with hydrochloric acid and allowed to stand, whereupon menaphthoximide is deposited in small yellow spangles.

Properties. Small, yellow spangles.

			Perkin. *dried at* 100°.
46 C	276	75·66	75·6
15 H	15	4·10	4·2
3 N	42	11·50	
4 O	32	8·74	
$C^{46}H^{15}N^3O^4$	365	100·00	

Decompositions. 1. When *heated*, it melts at 245° and is decomposed at 260°, puffing out white vapours having a strong and most peculiar odour; the substance hereby formed is probably naphthalocyanic acid (p. 118.), analogous to anilocyanic acid. — 2. With aqueous *potash* it forms menaphthylamine and oxalic acid; and hence may be regarded as acid oxalate of menaphthylamine *minus* 4 At. water. (Perkin.) — 3. It is converted by *acids*, in a similar manner to melanoximide, into oxalic acid and menaphthylamine; a white neutral body being simultaneously formed.

Insoluble in *water;* very sparingly soluble in *alcohol* and in *ether* (it may be obtained crystallised from the latter, though with difficulty).

Ternaphthylphosphamide,

$C^{60}N^{24}N^{3}PO^{2} = C^{60}N^{3}(PO^{2})H^{18},H^{6}$ (?).

H. Schiff. *Ann. Pharm.* 101, 299; *J. pr. Chem.* 70, 264; *Chem. Gaz.* 1857, 211; *Chem. Centr.* 1857, 166; *Liebig & Kopp's Jahresb.* 1857, 389.

Formation and Preparation. Naphthylamine heated with oxychloride of phosphorus on a water-bath, yields a reddish uncrystalline product, while the excess of liquid contains hydrochlorate of naphthylamine.

This, as Schiff proved, is ternaphthylphosphamide, since from oxychloride of phosphorus and ammonia or aniline, terphosphamide, $N^{3}PO^{2}H^{6}$, or terphenylphosphamide, $C^{36}H^{18}N^{3}PO^{2}$, is produced. (Schiff.)

The dried substance is readily decomposed by hot *water*, or by boiling *alkalis* or *acids;* melted with *potash*, it evolves naphthylamine, and yields phosphate of potash.

Primary nucleus, $C^{20}H^{10}$; *Oxygen-nucleus*, $C^{20}H^{6}O^{4}$.

Alizarin.

$C^{20}H^{6}O^{6} = C^{20}H^{6}O^{4},O^{2}$.

Colin & Robiquet. *Ann. Chim. Phys.* 34, 225; *J. Pharm.* 12, 407; *Berz. Jahresb.* 7, 265; *N. Tr.* 14, 1, 174.

Kuhlmann. *J. Pharm.* 14, 354; *Berz. Jahresb.* 8, 275.

Zenneck. *Pogg.* 13, 261.

Gaultier de Claubry & Persoz. *Ann. Chim. Phys.* 48, 69; *N. Tr.* 25, 2, 186.

F. F. Runge. *Verhandl. des Vereins zur Beförderung des Gewerbfleisses in Preussen*, 1835, Heft 2; *J. pr. Chem.* 5, 374; abstr. *Ann. Chim. Phys.* 63, 282.

Robiquet. *J. Pharm.* 21, 387; *J. pr. Chem.* 6, 130;—against Runge: *Ann. Chim. Phys.* 63, 297;—against Decaisne: *Ann. Chim. Phys.* 73, 274.

Decaisne. *J. Pharm.* 24, 424; *J. pr. Chem.* 15, 393.

J. Schiel. *Ann. Pharm.* 60, 79.

J. Higgin. *Phil. Mag. J.* 33, 282; *J. pr. Chem.* 46, 1.
Schunck. References given under Rubian.
Debus. *Ann. Pharm.* 66, 351; *N. Ann. Chim. Phys.* 38, 498.
J. Wolff & Strecker. *Ann. Pharm.* 75, 20; *Pharm. Centr.* 1850, 593; *Chem. Soc. Qu. J.* 3, 243.
Rochleder. *Wien. Akad. Ber.* 6, 433; *J. pr. Chem.* 55, 388; *Ann. Pharm.* 80, 321; *Wien. Akad. Ber.* 7, 804; *Ann. Pharm.* 82, 205; *J. pr. Chem.* 66, 85.

Extractive or resinous Madder-red, Erythrodanum, Alizarine (Colin & Robiquet); *Matière colorante rouge* (Gaultier & Persoz); *Krapp-roth* (Runge, Schiel); *Lizaric acid* (Debus). Constitutes, together with purpurin (xiii, 325), the red colouring matter of the roots of *Rubia tinctorum* and *R. peregrina.* Discovered in 1826 by Colin & Robiquet, after Buchholz (*Taschenb.* 1811, 60) and Kuhlmann (*Ann. Chim. Phys.* 24, 225; *N. Tr.* 8, 2, 111) had in vain sought to isolate the red colouring matter of madder.

Source. In madder root. According to Colin and Robiquet and others, it exists ready formed, but according to Decaisne's microscopic researches, it is derived from a yellow substance disseminated unequally through the entire root. According to Schunck, the substance from which alizarin is derived is rubian; according to Higgin, it is xanthin; and according to Rochleder, ruberythric acid; the two last-named bodies are regarded by Schunck as mixtures or decomposition-products of rubian. (See Rubian.) Part of the alizarin yielded by madder is found ready formed in the dried root, and may be extracted therefrom by alcohol.

Formation. 1. Schunck's rubian yields when heated a sublimate of alizarin; by boiling acids or alkalis, or by contact with erythrozym, it is resolved into alizarin and other products (see *Rubian*). — 2. Schunck's rubianic acid is decomposed under the same circumstances as rubian, yielding alizarin and sugar (comp. Rubianic Acid). — 3. Rochleder's ruberythric acid, boiled with acids or alkalis, yields the same decomposition-products (see *Ruberythric Acid*).

4. *In madder. Phenomena accompanying the formation of alizarin in madder.* Extract of madder, prepared with cold or luke-warm water, becomes after a time thick and gelatinous, and loses its bitter taste and yellow colour. (Higgin, Schunck.) — In this reaction, the erythrozym (see below) decomposes the rubian in the extract of madder in the same manner as pure rubian is decomposed (see *Rubian*). (Schunck.) — The xanthin and the greater part of the rubiacin disappear, giving rise to alizarin. (Higgin.) — Fresh cold-prepared extract of madder is reddish brown, has at first a sweet, then an unpleasantly bitter taste, and dyes cotton fabrics a pure yellow, like xanthin. After an hour or two, it becomes gelatinous, and, if sufficiently concentrated, deposits orange flakes of alizarin and rubiacin, more of which are precipitated by sulphuric acid; and after filtration, a perfectly sweet and no longer bitter liquid remains, which dyes calico pale red, and (tested by the method given under xanthin) contains no more xanthin. (Higgin.)

If the alizarin is precipitated from fresh extract of madder by acetate of lime, and the filtrate divided into three parts, whereof *a* is immediately examined, *b* diluted with water and allowed to stand for four hours, and *c* allowed to stand for three hours; hydrochloric acid precipitates from *a*, pure rubiacin, while xanthin remains in the filtrate; *b* on the contrary is no longer bitter, yields with hydrochloric acid a precipitate of rubiacin, but contains no xanthin; *c* has become lighter, has deposited flakes of alizarin, and contains rubiacin in solution. — Hence xanthin is converted into rubiacin and this into alizarin. This change also takes place in vacuo, and accordingly without the influence of oxygen (as Decaisne supposed), being in fact due to a nitrogenised constituent of madder (see *Erythrozym*) of which good madder contains sufficient to decompose an addition of 20 p. c. of its weight of xanthin. The decomposition takes place most rapidly between 50° and 55°, at which temperature all the xanthin in madder over which water has been poured, is converted in half an hour into rubiacin, and in 4½ hours almost all the rubiacin is converted into alizarin. By prolonged standing, the alizarin becomes fixed on the madder-fibres, and cannot then be extracted by water till the whole has been treated with acid. — This change is retarded by boiling the madder. Decoction of madder retains its bitter taste and deep yellow colour after long standing. A cold-prepared infusion deposits on boiling, flakes of a nitrogenised substance, and the filtrate then undergoes no further change. Acids precipitate from the cold infusion the same substance, together with rubiacin, alizarin, and pectin, leaving a filtrate which contains xanthin, and does not decompose. The nitrogenised substance, together with pectin, is precipitated as a jelly from the cold infusion by alcohol, and the filtrate undergoes no further change; but if the liquid be heated with the precipitate till all the alcohol is driven off, it redissolves, and the clear solution suffers the usual decomposition. (Higgin.)

Preparation. A. *From madder.* 1. The operation is conducted as described at page 326, vol. xiii, and the alizarite of alumina thus obtained is decomposed by boiling dilute hydrochloric acid. The precipitated alizarin is dissolved in boiling alcohol, crystallised by slowly evaporating the solution, and purified by recrystallisation. (Debus.) — In the same way Schunck decomposes the alizarite of alumina obtained in the first method of preparing rubian (see below); whereupon, however, on cooling the alcoholic solution of alizarin and allowing it to stand, a brown pulverulent resin is generally deposited between the crystals, and must be removed by levigating with alcohol. — Wolff & Strecker boil the alizarite of alumina obtained by method 1 (xiii. 326,) repeatedly with concentrated aqueous carbonate of soda, as long as the liquid acquires a deep colour, whereby purpurin is extracted; an admixture of resin is then removed by repeated washing with warm ether, and the residue is decomposed as above.

2. Madder washed as described (xiii, 326, 3), is boiled with solution of alum for four days; whereupon the brownish red precipitate containing the alizarin which is deposited from the extracts, is repeatedly boiled with dilute hydrochloric acid, the residue washed and dissolved in alcohol. On evaporating down the alcoholic solution and allowing it to cool, it deposits crystals of alizarin, which is freed from the purpurin contained in it by dissolving in a small quantity of alcohol and repeatedly boiling with solution of alum, as long as the liquid becomes coloured; whereupon the alizarin is precipitated and the purpurin passes into solution. The alizarin is obtained in crystals by washing the product, dissolving the ether, and abandoning the solution to spontaneous evaporation. (Runge.) Schiel adopts a similar method, boiling with alcoholic solution of alum,

the precipitate, which is deposited on cooling from the madder-extract prepared with alum, whereupon the colouring matters form two strata on cooling. He removes the upper light red flocculent stratum; again treats the lower dark-brown stratum with alcoholic alum; boils; and thus continues the operation, till the upper flakes give a pure violet solution with potash, whereupon he separates the alizarin from the undissolved portion by boiling with hydrochloric acid, recrystallising from alcohol, and finally from ether.

3. Rochleder proceeds as described (xiii, 327), or precipitates the alizarin and purpurin from the aqueous decoction of madder by baryta-water, filters off the violet precipitate, and decomposes it with moderately strong hydrochloric acid, whereby chloride of barium is dissolved out, leaving a residue of alizarin containing a little purpurin, which may be separated by recrystallisation.

4. Commercial garancin is warmed two or three times with $\frac{1}{2}$ pt. ammonia-alum dissolved in water; the liquid evaporated with constant stirring; the residue dried, pulverised, treated with boiling bisulphide of carbon (or with absolute alcohol), and filtered from undissolved alum; and the brilliant golden-yellow solution is allowed to cool; whereupon alizarin crystallises out in silky needles. (L. Vilmorin, *J. Chim. Méd.* 1859, 255; *Dingl. pol. Journ.* 152, 159; *Chem. Centr.* 1859, 380.)

5. When the extract prepared from madder with wood-spirit is triturated with 10 pts. water, and heated in closed vessels for 15 minutes at 250°, the water after cooling is found full of crystals of alizarin, which may readily be separated from the fused extract at the bottom of the vessel; and by repeating the operation three times, the whole of the alizarin may be extracted. (Plessy & Schützenberger, *Compt. rend.* 43, 167; *J. Pr. Chem.* 70, 314.)

Older methods. Alsatian madder is softened with 3 or 4 pts. of cold water for 10 minutes, and the mass is pressed between linen. The brownish red liquid coagulates in a trembling jelly, which is gradually pressed through several folds of thick linen, then moistened with water and again pressed out. The residue may be sublimed; or else it may be exhausted with alcohol; the tincture reduced to $\frac{1}{5}$th of its volume; the residue mixed with a little sulphuric acid and a large quantity of water; and the resulting bulky, brownish yellow precipitate washed by decantation with a large quantity of water, as long as the wash-water exhibits an acid reaction. It is then dried, and the alizarin is either separated by sublimation or extracted with ether. (Colin & Robiquet.) — Kuhlmann recommended to extract with boiling alcohol either the crude madder, or madder previously washed with cold water, then to evaporate the tincture, and when the residue has become almost thick, but still contains alcohol, to precipitate it with sulphuric acid and water, and either to sublime the precipitate or extract it with ether. (*J. Pharm.* 14, 363.) — Zenneck washes madder with cold water, then with dilute sulphuric acid; exhausts the dried residue with ether; and sublimes the residue left by evaporating the ether. An oil obstinately adheres to sublimed alizarin, and may be removed by rincing the crystals with ether and pressing them hard between blotting paper. (Robiquet.)

Gaultier and Persoz prepared their *matière colorante rouge*, which appears to be impure alizarin, by precipitating the alkaline decoction of madder obtained as described (xiii, 326, 2) with an acid, washing the precipitate, dissolving it in alcohol, and evaporating.

Useful for comparing different kinds of Madder. 10 kilogr. madder are boiled for 30 minutes with 2 kilogr. alum and 20 kilogr. water, then poured upon linen, and the residue is pressed and treated three times in the same manner. The united extracts are allowed to stand for a certain time, and after they are quite cold, decanted, and mixed, during constant stirring, with 625 grammes of sulphuric acid (previously diluted with twice its weight of water), whereupon thick reddish flakes are precipitated, which, after having been thoroughly washed, are dried in the air. Alizarin thus obtained still contains lime, xanthin, and purpurin. To remove these substances, it is dissolved in aqueous carbonate of potash and the filtrate is precipitated by sulphuric acid. Avignon-madder yields from 2 to 3 p. c. alizarin. (Meillet, *Rev. scient.* 1, 213.)

B. *From Rubian.* 1. *By boiling with acids.* Aqueous rubian (or extract of madder prepared with boiling water) is boiled with a large quantity of dilute sulphuric acid as long as orange-coloured flakes continue to deposit; it is then allowed to cool, and the flakes are collected and washed (the filtrate from them sometimes yields an additional quantity when again boiled with fresh acid). They contain alizarin, rubiretin, verantin, and rubianin, and are submitted to the following treatment:

a. In case only Alizarin is required. The substance is dissolved in alcohol, precipated with hydrate of alumina, and filtered; the precipitate is treated with aqueous carbonate of potash or soda, as long as anything is dissolved; the residue is collected and decomposed by an acid; and the precipated alizarin is crystallised from alcohol. (Schunck.)

In case Rubiretin, Verantin, and Rubianin are also required. — The substance is dissolved in boiling alcohol; the reddish yellow solution filtered boiling; and the residue boiled with fresh alcohol as long as the latter acquires a dark yellow colour. The yellow or brownish yellow crystalline mass left in the residue is chiefly rubianin, which, however, may also be dissolved by frequent treatment with boiling alcohol, whence it crystallises on cooling, as well as from the first extracts. The solutions are left to cool, and the crystals of rubianin containing verantin (see further treatment of this below) are separated from the mother-liquid (which, however, still contains a little rubianin). Acetate of alumina is now added to the liquid, whereby all the alizarin together with a small quantity of verantin is precipitated as a dark red powder, which is collected and washed with alcohol till the washings are colourless. The mother-liquid serves for the preparation of rubiretin, rubianin, and verantin. The precipitate is decomposed with hydrochloric acid; the flakes of alizarin and verantin thus separated are washed with water and dissolved in alcohol; and all the verantin is precipitated from the solution as a reddish brown copper-compound by acetate of copper, while the alizarite of copper remains dissolved in the dark purple filtrate, from which alizarin is prepared by precipitating with hydrochloric acid, thoroughly washing the precipitate, dissolving in alcohol, and recrystallising. (Schunck.)

The following method is adopted to purify the rubianin, rubiretin, and verantin, likewise obtained—

a. Rubianin. When an aqueous decoction of madder is employed instead of rubian, rubiacin is obtained in place of rubianin. — *a.* The crystals of rubianin containing verantin obtained as above are dissolved in boiling alcohol; the verantin is precipitated by acetate of lead as verantite of lead; and the liquid is filtered and left to cool, whereupon large lemon-yellow needles of rubianin are deposited. — β. The mother-liquid remaining after the precipitation of the alizarite of alumina, and still containing rubiretin, rubianin, and verantin, is evaporated to dryness, and the residue is mixed with hydrochloric acid and washed with water till all traces of acid and alumina have been removed. The residue is boiled with water, whereupon brown drops of resin are precipitated, and brownish yellow flakes float on the water. These are poured off with the liquid from the resinous drops (rubiretin and verantin), and this treatment is repeated as long as flakes are obtained. The flakes consist of rubianin and verantin, the first of which dissolves by repeated decoction with water, and is deposited in orange-coloured flakes on cooling. These are dissolved in boiling alcohol, and as the liquid cools, crystals of rubianin are obtained, while a small quantity of alizarin and rubiretin remains in the mother-liquid. (Schunck.)

b. Rubiretin. When the resinous drops obtained above are treated with cold alcohol, they yield rubiretin, verantin remaining undissolved. (Schunck.)

c. Verantin. Obtained in the preceding processes partly as verantite of lead, partly as verantite of copper, and partly as insoluble residue (*a* and *b*). The first two are decomposed with dilute sulphuric acid, and the verantin is extracted with boiling alcohol, then dissolved in a small quantity of boiling alcohol, and the dark reddish or yellowish brown powder deposited on cooling is purified by redissolving in alcohol. (Schunck.)

The madder-root exhausted with boiling water for the preparation of rubian, still contains alizarin, rubiacin, and verantin. It is boiled with hydrochloric acid, washed with water, and boiled with potash, whereby a dark red solution is formed, which being filtered and supersaturated with an acid, yields a dark, brownish red precipitate. This being boiled with water, yields alizarin and pectic acid, and leaves a residue of rubian and verantin. The alizarin is separated from the pectic acid by recrystallisation. The mixture of rubiacin and verantin boiled with ferric nitrate, yields a solution of rubiacic acid, which may be precipitated by hydrochloric acid, while verantin remains undissolved. (Schunck.) See below, rubiacinic acid.

2. *By boiling with alkalis.* Rubian is boiled with an excess of caustic soda, till the colour of the liquid, which was at first blood-red, has turned purple-red, and the liquid having become more concentrated, deposits dark purple-red alizarite of soda. The solution is now decomposed with excess of dilute sulphuric acid, whereupon it becomes colourless, depositing orange-coloured flakes, which, having been thoroughly washed with water, form a mixture of alizarin, verantin, rubiretin, and rubiadin. The flakes are treated with boiling alcohol, which dissolves them leaving a dark-brown substance (formed from sugar); the liquid is filtered, and the filtrate is precipitated with acetate of alumina, whereby alizarite of alumina, together with a small quantity of verantin, is precipitated, and is further treated as above described. (Schunck.) — For the further treatment of the mother-liquid containing rubiadin, rubiretin, and verantin, see *Rubiadin.*

3. *By fermentation — Action of Erythrozym on Rubian — or by Fermentation of Madder.* By this method alizarin, rubiretin, and verantin are obtained in smaller quantity than by methods 1 and 2, and are more difficult to purify. Erythrozym is added to aqueous rubian, and the liquid is allowed to stand in a moderately warm place until it has become tasteless and colourless, owing to the deposition of a brown jelly. If this deposit should not take place in 24 hours, more erythroxym must be added. Or madder is stirred up with cold or warm water, and left in a warm place till a jelly is formed. In both cases, the mass is mixed with a little water, and the jelly is collected on a filter and washed with a small quantity of water. It contains alizarin, rubiretin, verantin, rubiafin, rubiagin, and rubiadipin, which are separated as follows:—

The mass is well boiled with alcohol as long as the liquid acquires a yellow colour, and acetate of alumina is added to the filtrate, whereby alizarin, verantin, and rubiafin are precipitated in combination with alumina, but only partially. The whole is then filtered (for the further treatment of the precipitate, see below), and sulphuric acid and a large quantity of water are added to the dark brownish-red filtrate, whereby the whole of the dissolved substances are precipitated as a yellow powder, which, having been thoroughly washed with water, is redissolved in boiling alcohol and mixed with excess of acetate of lead. The dark purple-red lead-precipitate, which is filtered boiling, contains alizarin, rubiretin, verantin, and rubiafin; the dark yellow filtrate rubiagin and rubiadipin. The lead-precipitate is decomposed with boiling hydrochloric acid, and the precipitated yellow flakes are washed and covered with cold alcohol, which extracts *rubiretin*, leaving alizarin, rubiafin, and verantin. On the other hand, the above-mentioned precipitate produced by acetate of alumina is decomposed with boiling hydrochloric acid; the orange flakes thereby separated are added to the residue of alizarin, rubiafin, and verantin, which was left undissolved by cold alcohol; and the whole is dissolved in boiling alcohol and mixed with acetate of copper, which forms a purple precipitate (rubiafite, verantite with a small quantity of alizarite of copper). After filtering off the precipitate, alizarin alone remains in solution and is precipitated by hydrochloric acid and water, and purified by crystallisation. (Schunck.)

Treatment of the Verantite and Rubiafite of copper. The purple copper precipitate, decomposed by hydrochloric acid, deposits insoluble red flakes, which, after washing, are dissolved in boiling alcohol, and treated with hydrated stannous oxide, whereupon only *rubiafin* remains dissolved, and crystallises from the filtrate in brilliant needles and laminæ, while verantin, together with a small quantity of alizarin, is precipitated as a stannous oxide-lac. (Schunck.) See *Verantin.*

Higgin obtains his alizarin (rubiacin and xanthin), the first of which is probably a mixture of alizarin and purpurin (see Wolff & Strecker, *Ann. Pharm.* 75, 3), in the following manner: — Madder is exhausted in a digesting funnel with hot water, till the washings run off almost colourless; the cold extract is precipitated with dilute sulphuric acid; the precipitated flakes, containing alizarin, rubiacin, and a small quantity of pectin, are collected; and the filtrate, containing xanthin, traces of alizarin, and a small quantity of sugar, is kept for the preparation of xanthin. The flakes are first washed with water acidulated with sulphuric acid, then with pure water, afterwards mixed with an equal bulk of powdered chalk, and boiled with water, till the washings assume a bright red colour. This aqueous solution contains *rubiacin,* which is separated by acidulating the filtrate with sulphuric acid, collecting and washing the greenish yellow precipitate, and recrystallising from alcohol. The residual chalk contains Higgin's *alizarin,* which is extracted by digesting with dilute hydrochloric acid, filtering, washing the residue, and recrystallising from alcohol.

Preparation of Higgin's Xanthin. The filtrate obtained as above is neutralised with carbonate of soda; the rubiacin and alizarin still in solution are precipitated by digesting the liquid for half an hour at 55° with a small quantity of hydrate of alumina; the phosphoric and sulphuric acids are separated from the filtrate by means of baryta-water; and the xanthin is precipitated from the filtrate as a red lac by subacetate of lead. This being washed with water, suspended in water, and decomposed by sulphuretted hydrogen, deposits xanthin together with sulphide of lead. The mixture is then washed with cold water and the xanthin extracted by boiling water; the solutions are evaporated to a syrup (neutralised with baryta, if necessary), and then, to complete dryness; the residue is extracted with absolute alcohol; and the alcoholic solution is evaporated. (Higgin.)

The madder, after thorough washing with hot water, still contains the greater part of the alizarin (p. 135) together with only a small quantity of rubiacin. To separate the alizarin, the madder residue is boiled three or four times with a weak solution of alum, whereby the rubiacin is removed, and the residue is then boiled for a quarter of an hour with a saturated solution of alum and filtered, this treatment being repeated till the madder is exhausted and has become ash-grey. The united decoctions are cooled to 32° and strongly acidified with dilute sulphuric acid, whereupon the alizarin is precipitated, the precipitation being promoted by rapidly stirring the liquid. The product is collected and purified as above. Higgin's alizarin differs from that prepared by other chemists, by its property of dissolving with purple-red colour in boiling aqueous alum. Since this solution does not yield much deposit on cooling, it perhaps consists of purpurin (p. xiii, 325), or according to Schunck, of alizarin containing verantin (see below, *Verantin*). When boiled with aqueous sulphate of ammonia (or sulphate of potash) it is converted into a purple-red powder, without dissolving (the behaviour of pure alizarin is not known), and may thus be separated from Higgin's rubiacin.

Properties. Hydrated alizarin (p. 138) parts with its water between 100° and 120°, becomes opaque, assumes a darker red colour, like native chromate of lead, and is converted into anhydrous alizarin (Schunck), which melts at a higher temperature, solidifies in a reddish brown crystalline mass on cooling, and sublimes, according to Schunck, at 215°, according to Schiel, at 225°, in long, brilliant, golden yellow needles, reflecting light with red colour. (Colin & Robiquet.) Sublimed alizarin forms four-sided, flexible (Zenneck), brilliant, orange-coloured (Runge, Schiel), reddish yellow (Debus), red, transparent needles. (Robiquet.) It is brighter in colour than before sublimation, bright orange, transparent, and very brilliant. (Schunck.) In the first sublimation there always remains a residue of carbon, according to Colin & Robiquet, Runge & Shunck, Wolff & Strecker, but not on resublimation, according to Colin & Robiquet & Runge. Neutral (Colin & Robiquet). Reddens litmus. (Zenneck.) Heavier than water. Tastes bitter and acid. (Zenneck.)

Wolff & Strecker's calculation.			Schunck's calculation.			Robiquet.	Schist. *mean.*
20 C	120	68·96	14 C	84	69·42	70·09	67·46
6 H	6	3·45	5 H	5	4·13	3·73	4·22
6 O	48	27·59	4 O	32	26·45	26·18	28·32
$C^{20}H^{6}O^{6}$	174	100·00	$C^{14}H^{5}O^{4}$	121	100·00	100·00	100·00

	Debus. *mean.*	Wolff & Strecker.	Schunck. *earlier.* *dried.*	*mean.* *sublimed.*
C	68·97	68·4	69·13	69·61
H	3·79		4·01	3·73
O	27·24		26·86	26·66
	100·00		100·00	100·00

	Schunck. *later.* *a.*	*b.*	*c.* *mean.*	*d.* *mean.*	Rochleder. *at* 100°.
C	69·37	69·07	69·59	69·38	67·93
H	4·07	4·70	4·15	4·16	3·77
O	26·56	26·23	26·26	26·46	28·30
	100·00	100·00	100·00	100·00	100·00

a was obtained from rubian by sulphuric acid; *b* by soda; *c* by erythrozym; *d* from rubianic acid by sulphuric acid and soda. (Schunck.)

Earlier formulæ of alizarin: $C^{37}H^{24}O^{10}$ (Robiquet); $C^{28}H^{9}O^{9}$ (Schiel); $C^{30}H^{10}O^{9}$ (Debus); $C^{60}H^{19}O^{19} = 3C^{20}H^{6}O^{6} + Aq$ for the alizarin which Rochleder investigated. (Rochleder.) The formula $C^{20}H^{6}O^{6}$ given by Wolff & Strecker is most generally adopted; this does not exactly correspond with Schunck's analyses, and according to him does not explain the connection of alizarin with rubian and rubianic acid, and especially of the formation of alizarin observed by Schunck in decomposing rubianic acid (see *Rubianic Acid*); Schunck's formulæ are therefore likewise given in the following pages.

Decompositions. 1. Alizarin heated on platinum-foil, melts and burns with flame. (Schunck.) When Schiel filled a glass bulb with alizarin, and passed a current of oxygen into it, an explosion took place as the substance was fused, and shattered the apparatus. 2. It is converted by boiling dilute *nitric acid* into oxalic acid and a peculiar acid (Schunck), into phthalic acid. (xiii, 10.) (Laurent & Gerhardt.)

$$C^{20}H^{6}O^{6} + 2\,HO + 8\,O = C^{16}H^{6}O^{8} + C^{4}H^{2}O^{8}.$$

3. When alizarin is suspended in water and *chlorine* gas passed through the liquid, it turns yellow, gives by heat a colourless sublimate, and dissolves in alkalis without much colour. (Schunck.) — It remains apparently unchanged by the action of chlorine, but if mixed with potash after the excess of chlorine has been removed, it gives a deep red solution like purpurin and a purple-red precipitate with baryta; hence it has probably been converted into purpurin:

$$C^{20}H^{6}O^{6} + 4\,O = C^{18}H^{6}O^{6} + 2\,CO^{2}. \quad \text{(Wolff \& Strecker.)}$$

Aqueous alizarin is rapidly turned pale brown by chlorine. (Zenneck.) 4. It is converted into phthalic acid by *ferric nitrate* or *chloride at the boiling heat.* (Schunck.) (For the behaviour of the alkaline solution with ferrous sulphate, see xiii, 329.) 6. It is decomposed by boiling with *chromate of potash and sulphuric acid.* (Debus, Schunck.) — 6. It reduces *terchloride of gold* on addition of caustic potash. (Schunck.) — 7. According to Wolff & Strecker, alizarin is converted into purpurin by the fermentation of madder, inasmuch as these chemists were able to obtain only purpurin, but no alizarin, from fermented madder. This is denied by Schunck.

Combinations. With water. — a. Hydrated Alizarin. Crystallised from alcohol: long, transparent, dark-yellow prisms of high lustre, resembling isatin, without any shade of brownish yellow or red, which they have only when contaminated with verantin. (Wolff & Strecker.) Large, rose-coloured needles. (Debus.) Brownish yellow, crystalline powder (Runge); brownish red mass, having a brilliant fracture. (Gaultier & Persoz.) It parts with 18·12 p. c. water at 100°, ($C^{20}H^6O^6 + 4Aq = 17{\cdot}14$; $C^{14}H^5O^4 + 3Aq = 18{\cdot}24$ p. c.), without changing its form, and is converted into anhydrous alizarin. (Schunk.)

Wolff & Strecker's calculation.			Schunck's calculation.			Schunck. *mean.*
20 C	120	57·14	14 C	84	56·75	56·98
10 H	10	4·76	8 H	8	5·40	5·06
10 O	80	38·10	7 O	56	37·85	37·96
$C^{20}H^6O^6$,4Aq	210	100·00	$C^{14}H^5O^4$,3Aq	148	100·00	100·00

b. Aqueous Alizarin. Alizarin is with difficulty moistened by cold *water* (Wolff & Strecker), and dissolves in it very slightly, but more readily in boiling water. (Colin & Robiquet.) It dissolves sparingly with yellow colour in boiling water, and is deposited in flakes on cooling. (Schunck.) The solution is rose-coloured (Colin & Robiquet), only when the water contains alkali. (Schunck, Wolff & Strecker.) The solution prepared with boiling water does not yield any deposit on cooling (Gaultier & Persoz); it is precipitated by acids. (Kuhlmann.) The solubility of alizarin in water rapidly increases when the mixture is heated in a sealed tube above 200°. 100 pts. water dissolve at 200°, 0·82, at 225°, 1·70 and at 250°, 3·16 parts. (Plessy & Schützenberger. *Compt. rend.* 43, 167; *J. pr. chem.* 60, 314.)

It is not affected by weak *acids* (Gaultier & Persoz), by *hydrochloric acid.* (Schunck.) Boiled with dilute acids, it dissolves with yellow colour, and is deposited in orange-yellow flakes on cooling. (Runge.)

Dissolves in *sulphuric acid* without evolution of sulphurous acid, forming a blood-red solution from which it is precipitated by water unchanged. (Colin & Robiquet and others.) The colour of the solution in sulphuric acid is dark yellowish brown, and is not changed by heat. (Schunck.)

Dissolves in *bisulphide of carbon*, with reddish yellow colour. (Zenneck.) Alizarin combines with *salifiable bases.* These compounds, which are regarded by Debus as salts, *lizarates*, are red, violet (or blue), and are insoluble in water and in alcohol with the exception of the ammonia, soda, and potash-salts. They seldom, if ever, contain 1 At. metallic oxide to 1 At. alizarin.

When dry *gaseous ammonia* is passed over alizarin, the mass becomes warm and turns violet, but parts by heat with all the ammonia it has taken up and reassumes its yellow colour. Heated in a stream of ammonia, alizarin sublimes unchanged, but acquires a violet colour. (Rochleder.)

Dissolves in aqueous *ammonia* with orseille-colour, without any blue lustre on the surface. (Wolff & Strecker.) The ammonia-solution is purple-red (Runge), violet-red (Colin & Robiquet), red (Schiel); it becomes turbid as the ammonia evaporates (Gaultier & Persoz); leaves a violet-brown film. (Schunck.) Dissolves in *sulphide of ammonium* with beautiful reddish brown colour. (Gaultier & Persoz.)

Dissolves readily in aqueous *caustic alkalis;* at a certain concentration, the solution appears of a deep purple colour by transmitted light, and pure blue by reflected light; when more diluted, it appears uniformly violet. (Wolff & Strecker.) The solution is pure blue (Colin & Robiquet); of a beautiful red, permanent in the air (Gaultier & Persoz); of a magnificent violet-blue, and, when saturated, purple (Runge); violet (Schiel); purple, and leaves on evaporation a purple uncrystalline mass. (Schunck.)

Dissolves in aqueous *alkaline carbonates* as in ammonia (Wolff & Strecker), with magnificent purple colour. (Schunck.) The solution is orange-red (Gaultier & Persoz); red. (Schiel.) Dissolves in *arsenite, arseniate,* and *silicate of potash.* (Gaultier & Persoz.) — It does not dissolve in cold *bicarbonate of soda,* till the solution is warmed, whereupon carbonic acid is evolved. (Zenneck.)

Alizarin is precipitated by acids from its alkaline solutions in deep orange-coloured flakes. (Schunck.)

Alizarite of Soda. Alizarin is dissolved by heat in a cold-saturated solution of carbonate of soda, and the compound which is deposited on cooling is dried, then dissolved in absolute alcohol and precipitated by ether. Purple flakes, insoluble in concentrated solution of carbonate of soda and in cold concentrated saline solutions, but soluble in water and in alcohol with orseille colour, which is turned blue by caustic soda. (Wolff & Strecker.)

Alizarite of Baryta. Baryta produces a beautiful blue precipitate in the solution of alizarin in ammonia (Robiquet & Colin); it precipitates and decolorises the potash solution. (Schunck.) Alcoholic alizarin boiled with baryta, turns lilac, and deposits a lilac precipitate. (Zenneck.)

a. Bibasic. Alcoholic alizarin is precipitated with excess of baryta-water; the precipitate is washed out of contact of air with water and warm alcohol, till the washings are no longer coloured by addition of potash; and the residue is dried at 100°. (Wolff & Strecker.)

			Wolff & Strecker.
$C^{20}H^6O^6$	174	50·43	
2 BaO	153	44·35	44·0
2 HO	18	5·22	
$C^{20}H^6O^6 + 2BaO,HO$	345	100·00	

b. Sesquibasic. 1. Ammoniacal solution of alizarin yields with chloride of barium a magnificent purple (Schunck), almost pure blue precipitate, above which a colourless liquid remains. (Wolff & Strecker.) When dry, it forms a dark-brown, almost black mass, which acquires a yellow metallic lustre by trituration in an agate mortar. (Schunck.) 2. It was once obtained by precipitating alcoholic alizarin with baryta-water as in the preparation of the bibasic salt, and contained, at 100°, 38·3, and at 120°, 39·8 p. c. baryta. (Wolff & Strecker.)

	at 100°.		Schunck.	Wolff & Strecker.
2 $C^{20}H^{6}O^{6},3HO$	375	62·04		
3 BaO	229·5	37·96	38·03	38·3
$2C^{20}H^{6}O^{6}, + 3BaO,HO$	604·5	100·00		

At 120° = $2C^{20}H^{6}O^{6},3BaO$ (by calculation, 39·7 p. c. BaO). (Wolf & Strecker.) According to Schunck, the formula is $C^{14}H^{5}O^{4},BaO$ or $C^{14}H^{4}BaO^{4},HO$, which requires 38·78 p. c. BaO.

c. Sesqui-acid. Alizarin is dissolved in aqueous ammonia, and after the excess of ammonia has been evaporated off, the solution is precipitated with chloride of barium. After drying at 100°, the salt still loses weight at 120°. (Wolff & Strecker.)

	at 120°.		Wolff & Strecker. *mean.*
60 C	360	53·3	53·35
18 H	18	2·7	2·85
18 O	144	21·3	20·90
2 BaO	153	22·7	22·90
$3C^{20}H^{6}O^{6},2BaO$	675	100·0	100·00

Strontia-water produces a beautiful blue precipitate with ammoniacal alizarin. (Colin & Robiquet.)

Alizarite of Lime. Lime-water decolorizes alizarite of potash and precipitates alizarite of lime (Schunck); it behaves with ammoniacal alizarin like baryta-water. (Colin & Robiquet.) Alcoholic alizarin boiled with *hydrate of lime* acquires a lilac colour and deposits a lilac precipitate. (Zenneck.) *Carbonate* (and *phosphate*) *of lime* take up the colouring matter from aqueous (but not from alcoholic) alizarin; it is to this affinity between alizarin and phosphate of lime that the red colour of the bones of animals feeding on madder is owing. (Berzelius, *A. Gehlen,* 4, 124.) Alizarin dissolves in *calcareous* waters and forms a blue lac. (Runge.)

To prepare alizarite of lime an ammoniacal solution of alizarin is precipitated with chloride of calcium. Magnificent purple precipitate, like the baryta compound. (Schunck.)

	at 100°.		Schunck. *mean.*
2 $C^{20}H^{6}O^{6},3HO$	375	81·7	
3 CaO	84	18·3	18·44
$2C^{20}H^{6}O^{6} + 3CaO,HO$	459	100·0	

The formula is thus given by Wolff & Strecker; Schunck writes it $C^{14}CaH^{4},O^{4},HO$, which requires 10·03 p. c. CaO.

Ammoniacal alizarin produces a violet precipitate with *chloride of magnesium* (Zenneck), a purple precipitate. (Schunck.) Alcoholic alizarin boiled with *magnesia,* behaves as with lime or baryta. (Zenneck.)

Alizarite of Alumina. Alizarin is scarcely soluble in alum-solution (Colin & Robiquet), insoluble. (Gaultier & Persoz and others.) When concentrated solution of alum is boiled with alizarin, it turns yellow, and on cooling becomes almost colourless, depositing what it had dissolved (Wolff & Strecker); it acquires a red iridescence, and on cooling deposits small crystals of alizarin, none of which remains in solution. (Schunck.) The solutions of alizarin in alcohol and in potash are decolorised by hydrate of alumina, while the whole of the alizarin is precipitated, imparting a red or reddish purple colour to the alumina. (Schunck.) Alizarin dissolves in aluminate of potash. (Gaultier & Persoz.) It forms the base of madder-lake.

Alcoholic or ethereal solution of alizarin is precipitated by *oxide of zinc.* (Debus.) Alizarin dissolves readily in *stannous chloride,* and in large quantity in *stannous oxide* mixed with potash (Gaultier & Persoz); it is thereby reduced. (Schunck.) Ammoniacal alizarin forms a brown precipitate with tin-salts. (Zenneck.)

Alizarite of Lead. Ammoniacal alizarin produces a purple-red precipitate with acetate of lead. — *a. Two-thirds?* Alcoholic alizarin is precipitated with alcoholic acetate of lead. Purple precipitate, becoming deep red on standing. (Schunck.) *b. Three-fourths?* Alcoholic alizarin feebly acidulated with acetic acid is precipitated with alcoholic acetate of lead, so that the first remains in excess; whereupon a violet precipitate is formed, stable at 160°, insoluble in water, soluble in acetic acid and in potash. (Debus.)

a.

According to Wolff & Strecker.			According to Schunck.			Schunck. *mean.*
40 C	240	36·1	14 C	84	37·57	37·23
10 H	10	1·5	4 H	4	1·78	1·64
10 O	80	12·1	3 O	24	10·75	11·67
3 PbO	336	50·3	PbO	112	49·90	49·46
$2C^{20}H^5O^5$,3PbO	666	100·0	$C^{14}H^4O^3$,PbO	224	100·00	100·00

Prepared with alizarin obtained by decomposing rubian, it gave 50·44 p. c. PbO. (Schunk.)

b.

According to Wolff & Strecker.			Debus. *at* 120° (*mean*).
60 C	360	38·2	38·35
15 H	15	1·6	1·97
15 O	120	12·8	12·06
4 PbO	448	47·4	47·62
$3C^{20}H^5O^5$,4PbO	943	100·0	100·00

According to Debus, it is $C^{30}H^8O^7$,2PbO.

Ammoniacal alizarin produces purple precipitates with *ferrous* and *ferric-salts* (Schunck); brown precipitates. (Zenneck.) Alcoholic and potash solutions of alizarin are precipitated dark purple by *ferric oxide.* (Schunck.) Ammoniacal alizarin produces a purple precipitate with salts of *copper* (Schunck), a brown precipitate (Zenneck); and likewise with salts of *mercury* and *gold.* *Silver-salts* are precipitated bright violet (Zenneck), purple, and then reduced. (Schunck.)

Alizarin dissolves in cold and more abundantly in boiling *alcohol,* with yellow colour. (Schunck, Wolff, & Strecker.) The solution turns red on the addition of a small quantity of ammonia. (Wolff & Strecker.) It dissolves in alcohol in almost every proportion (Colin & Robiquet), at 12° in 210 pts. of alcohol of sp. gr. 0·84. (Zenneck.) The hot-prepared solution does not deposit crystals on cooling, but on dilution. (Schunck.) It is precipitated by water and by acids. (Kuhlmann, Schunck.)

Alizarin dissolves more readily in *ether* than in alcohol, with golden yellow colour (Colin & Robiquet, and others); at 12°, in 160 pts. ether of sp. gr. 0·73. (Zenneck.) The solution is not reddened by small quantities of alkalis, since the compound of alizarin with the alkali is precipitated. (Wolff & Strecker.)

Alizarin dissolves sparingly in boiling *acetic acid*, and imparts to it a yellow colour. (Schunck.) Dissolves slowly in cold, rapidly and more abundantly in hot *glycerin*, forming an intensely scarlet liquid, which deposits red flakes when mixed with water. (Arnodon, *Dingl. pol. Journ.* 147, 465.)

Alizarin dissolves in *rock-oil, oil of turpentine*, and in *fatty oils.* (Zenneck.) It produces on *mordanted fabrics* all the colours which can be produced by madder. (Colin, Robiquet, and others.)

Primary nucleus $C^{20}H^{12}$.

Paranicene. $C^{20}H^{12}$.

St. Evre. *N. Ann. Chim. Phys.* 25, 503; *J. pr. Chem.* 46, 465.

Formation. (xi, 176.)

According to Gerhardt (*N. Ann. Chim. Phys.* 45, 101), Pisani & E. Kopp (*Compt. Chim.* 1847, 198) obtained only chlorobenzoïc acid by the action of chlorine upon benzoic acid dissolved in potash, and not St. Evre's chloroniceic acid. If this opinion be correct, and St. Evre had described as chloroniceic acid a mixture of benzoic and chlorobenzoic acids, chloronicene may be identical with chlorobenzene or chloride of phenyl (xi, 173), and chloronicene with chloraniline. Nitrochloronicene would be the unknown nitrochlorobenzene. It remains therefore to shew whether the formulæ of paranicene, nitroparanicene, and paracinin are to be changed in a corresponding manner, and to indicate the origin of these bodies. (Kr.)

Passes over when chloroniceate of baryta or a mixture of chloroniceic acid with excess of baryta or lime, is submitted to dry distillation, after the chloronicene ($C^{20}Cl^2H^{10}$), and contaminated thereby, as a white sublimate, which must be pressed between paper, carefully washed with cold ether, and passed in the state of vapour through a tube containing lime heated to redness.

Lemon-yellow, broad laminæ, of sp. gr. 1·24, and boiling at 365°. It has a penetrating taste and smell. Vapour-density = 4·79.

			St. Evre. *mean.*
20 C	120	90·90	90·77
12 H	12	9·10	9·04
$C^{20}H^{12}$	132	100·00	99·81

	Vols.	Vapour-density.
C-vapour	20	8·3200
H-gas	12	0·8316
Paranicene-vapour	2	9·1516
	1	4·5758

It is violently attacked by *fuming nitric acid* and finally dissolves, depositing needles of paranicene on cooling. A small quantity of resin is formed at the same time.

Dissolves in *alcohol* and in *ether*.

Cuminic Alcohol.

$$C^{20}H^{14}O^{2} = C^{20}H^{12},H^{2}O^{2}.$$

KRAUT. *Dissertation über Derivate des Cuminols und Cymens*, Gött. 1854; abstr. *Ann. Pharm.* 92, 66; *J. pr. Chem.* 64, 159; *Pharm. Centr.* 1855, 107; *N. Ann. Chim. Phys.* 43, 347.

Cymylic alcohol.

Formation. Produced by the action of alcoholic potash on cuminol at mean temperature, or more rapidly at the boiling heat.

Preparation. 1 vol. of cuminol is distilled upwards with 2 vols. of alcoholic potash for an hour; a large quantity of water is then added, and the whole is distilled, as long as oil-drops float on the distillate. A mixture of cuminic alcohol and cymene then passes over together with alcohol and water. This is collected, shaken up with very dilute solution of alkaline bisulphite in order to remove any undecomposed cuminol that may be present, then washed with water, dried over chloride of calcium, and distilled alone. The cymene which first passes over is collected apart, and thus separated from the cuminic alcohol which distils between 240° and 250°. The product is purified by several fractional distillations, the first portion of the distillate being rejected.

Properties. Colourless oil, having a feeble and pleasant aromatic odour and a burning taste. Boils at 243°. Taking into account the correction necessary for the temperature of the column of mercury, it must boil at a higher temperature, probably at 270°. (H. Kopp. *Ann. Pharm.* 96, 23.)
Permanent in the air. Neutral.

			Kraut. *mean.*
20 C	120	80·00	79·58
14 H	14	9·33	9·36
2 O	16	10·67	11·06
$C^{20}H^{14}O^{2}$	150	100·00	100·00

Decompositions. 1. Cuminic alcohol is converted by *nitric acid* into cuminic acid. — 2. When cuminic alcohol is mixed with strong *sulphuric acid*, heat is developed and a brown resin is formed, which is brittle at ordinary temperatures but becomes semi-fluid in boiling water; no conjugated sulphuric acid is produced. — 3. It dissolves *potassium* with evolution of hydrogen, and on the application of heat is converted into a yellow granular mass, which is decomposed by water into hydrate of potash and cuminic alcohol. — 4. Boiled continuously for 10 or 12 hours with 5 or 6 vols. of *alcoholic potash*, it is almost completely converted into cymene and cuminate of potash:

$$3\,(C^{20}H^{14}O^{2}) + KO,HO = C^{20}H^{11}KO^{4} + 2\,C^{20}H^{14} + 4\,HO.$$

5. Heated with *chloride of benzoyl* to 80°, it evolves a large quantity

of hydrochloric acid, and leaves a brown residue becoming buttery on cooling, probably benzoate of cumyl.

Combinations. Cuminic alcohol is insoluble in *water.* It does not unite with the alkaline bisulphites. It mixes with *alcohol* and *ether* in all proportions.

Cuminol.

$C^{20}H^{12}O^2 = C^{20}H^{12},O^2$.

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 63; *J. pr. Chem.* 23, 321; *Ann. Pharm.* 38, 67; *N. Br. Arch.* 27, 155.
CAHOURS. *N. Ann. Chim. Phys.* 23, 345; *J. pr. Chem.* 45, 143; abstr. *Ann. Pharm.* 70, 44.
BERTAGNINI. *Ann. Pharm.* 85, 275.
CHIOZZA. *N. Ann. Chim. Phys.* 39, 216.
KRAUT. *Dissert. über Cuminol und Cymen,* Gött. 1854; abstr. *Ann. Pharm.* 92, 66; *J. pr. Chem.* 64, 159; *N. Ann. Chim. Phys.* 43, 347.
SIEVEKING. *Dissert. über Cuminol und Cymen,* Gött. 1857; abstr. *Ann. Pharm.* 106, 257; *J. pr. Chem.* 74, 505.
J. TRAPP. *Petersb. Acad. Bull.* 16, 298; *J. pr. Chem.* 74, 428; *Ann. Pharm.* 108, 386.

Cuminic aldehyde, Hydride of cumyl.

Sources. Occurs together with cymene in Roman oil of cumin, the volatile oil of *Cuminum cyminum.* (Gerhardt & Cahours.) It exists ready formed in the seeds, and may be extracted by absolute alcohol, and, precipitated with water, after evaporation. (Gerhardt & Cahours.) Roman cumin seeds, distilled four times with water, yield 3·27 p. c. oil. (Noad, *Ann. Pharm.* 63, 286), 2·8 p. c. (Zeller, *N. Jahrb. Pharm.* 1854, 1, 225.) The oil is bright golden-yellow, of sp. gr. 0·975, very mobile, and has a sharp, aromatic, and slightly bitter taste. (Bley, *N. Tr.* 19, 1, 3.) Roman cumin oil is coloured pale yellow by a small quantity of resin, formed by the action of the air on cuminol; hence its colour gradually deepens. It becomes acid on exposure to the air. It begins to boil at 170°, and the portion passing over at 175° contains 88·27 p. c. C, 10·83 p. c. H, and 0·88 p. c. O; the portions which come over afterwards up to 230°, are progressively richer in oxygen, till at 255° an oil passes over containing 85·88 p. c. C, 10·46 p. c. H, and 3·66 p. c. O. (Gerhardt & Cahours.) Roman cumin oil is resinised by fuming nitric acid, and when treated with sulphuric acid, becomes viscid dark brownish red, and then milky on addition of water, owing to the deposition of resin. It turns greenish yellow with bromine, without undergoing further change, and dissolves iodine with brownish red colour, without evolving heat or detonating. It forms a liniment with caustic potash, also with ammonia. It dissolves abundantly (?) in water, and readily in alcohol and in ether. (Bley.)

Cuminol occurs also in the volatile oil of the seeds of the water-hemlock (*Cicuta virosa.*) (J. Trapp.) Ten pounds of the seeds of this plant gave by distillation with water 2 oz. of a colourless, limpid oil, lighter than water, and possessing the odour and taste of Roman cumin seeds. When this oil is shaken with concentrated aqueous bisulphite of soda, it becomes milky and solidifies in 12 hours in a white crystalline mass of bisulphite of soda and cuminol to which cymene still adheres. The cymene is removed by pressing the product between blotting paper (whereby the oil is absorbed, and may be afterwards separated by distillation), and the mass is completely purified by recrystallisation from weak alcohol. (T. Trapp.)

Preparation. From *Roman Cumin oil.* 1. The oil is distilled in an oil-bath till the temperature has reached 200°, when all the cymene passes over together with a large quantity of cuminol; after prolonged heating, the residue consists of pure cuminol. This is distilled in a stream of carbonic acid, and preserved out of contact with the air. (Gerhardt & Cahours.) — 2. By submitting Roman cumin oil to repeated fractional distillation, it is divided into two parts, one boiling below 190° and containing almost all the cymene; the other boiling above 190°, and containing cuminol together with small quantities of cymene and cuminic acid. When 1 vol. of the latter is shaken up with 2 or 3 vols. concentrated aqueous bisulphite of soda, it forms a granular crystalline mass, which, after standing for 24 hours, during which time it becomes quite hard, is collected and pressed between blotting paper frequently renewed, and distilled with water and an alkaline carbonate or caustic alkali; pure cuminol then passes over with the vapour of water.

The cymene which has passed over below 190° contains a little more cuminol, which may be separated by shaking the liquid with dilute bisulphite of soda, removing the precipitate, and distilling the solution with aqueous carbonate of potash. (Bertagnini, Kraut.) — If the compound of cuminol with bisulphite of soda be decomposed with dilute sulphuric acid and submitted to distillation, an oil no longer capable of combining with bisulphite of soda, remains in the residue; it is therefore better to rectify alone the cuminol separated by sulphuric acid from the compound with bisulphite of soda. (Sieveking.)

Properties. Colourless or yellowish oil. Boils at 220°, without decomposition, if air be excluded (Gerhardt & Cahours); from platinum, at 229·4°, or, taking into account the correction necessary for the mercury column of the thermometer, at 236·6°, under 748 mm. pressure. Sp. gr. = 0·9727, at 13·4°, = 0·9832 at 0°. (H. Kopp, *Ann. Pharm.* 94, 317.) Vapour-density = 5·24, but at the high temperature required for the determination the cuminol decomposes slightly. (Gerhardt & Cahours.) It has a strong smell of cumin, and a sharp, burning taste. (Gerhardt & Cahours.)

Dried over chloride of calcium.			Gerhardt & Cahours. *mean.*
20 C	120	81·08	80·89
12 H	12	8·11	8·45
2 O	16	10·81	10·66
$C^{20}H^{12}O^{2}$	148	100·00	100·00

	Vols.	Vapour-density.
C-vapour	20	8·3200
H-gas	12	0·8316
O-gas	1	1·1093
Cuminol-vapour	2	10·2609
	1	5·13045

Decompositions. 1. Oxidises at mean temperature in the *air*, especially in moist air. It becomes resinised and acid by distillation in vessels containing air. (Gerhardt & Cahours.) — 2. It is very slowly decomposed by *water* at mean temperature, without evolution of hydrogen, into cuminic acid and an oil richer in hydrogen (probably cuminic alcohol, Kr.). (Gerhardt & Cahours.) — 3. If *fuming nitric acid* be gradually dropped upon cuminol, avoiding all elevation of temperature, till the brown colour of the mixture just disappears, the liquid on standing deposits white crystals of cuminic acid. If heat be applied, a large quantity of resin and nitrocuminic acid are obtained, even if dilute nitric acid be employed. (Gerhardt & Cahours.) — 4. *Sulphuric acid* dissolves cuminol, if the liquid be kept cool, with dark red colour; on adding water, a brown tar is precipitated. (Gerhardt & Cahours.) — 5. It is converted by *moist bromine* or *chlorine*, in diffuse daylight, into bromo- or chloro-cuminol. In the sun, chlorine is taken up more freely, probably because several atoms of hydrogen are replaced by chlorine. (Gerhardt & Cahours.) — 6. Cuminol, evaporated with *hydrochloric acid*, leaves a mixture of resin and cuminic acid. (Gerhardt & Cahours.) — 7. By *pentachloride of phosphorus* it is converted into chlorocuminol. (Cahours.) — 8. Dry *gaseous ammonia* converts it, after a while, into a product analogous to hydrobenzamide. (Gerhardt & Cahours.) Sieveking was unable to obtain this product. Even on prolonged contact with *aqueous ammonia*, it does not form crystals, but only a yellow mass, which cannot be obtained in crystals, even after solution in ether and evaporation. (Sieveking.) Sieveking once obtained crystals by passing ammonia into alcoholic cuminol, but the quantity was too small for analysis. — 9. Its alcoholic solution is converted by *sulphide of ammonium* into thiocumol, $C^{20}H^{12}S^2$. (Cahours, *Compt. rend.* 25, 459.) — 10. *Potassium* acts but slightly in the cold on cuminol, becoming dull but not evolving any gas-bubbles. On gently warming the tube, a violent action ensues, hydrogen is evolved in large quantity, and cuminol-potassium formed. (Gerhardt & Cahours.) — 11. When cuminol is dropped on fused *hydrate of potash*, each drop as it comes in contact with the potash, turns first red, then white, and solidifies, forming cuminate of potash. (Gerhardt & Cahours.)

$$C^{20}H^{12}O^2 + KO,HO = C^{20}H^{11}KO^4 + 2H.$$

When a piece of hydrate of potash is covered with cuminol and a gentle heat applied, it becomes covered with a gelatinous cauliflower-like mass (without evolution of hydrogen), which, on being separated from the potassium and pressed between paper, deposits, in contact with water, cuminol (cuminic alcohol, according to Kraut), while cuminate of potash remains in solution. (Gerhardt & Cahours.) It is decomposed by *aqueous potash* (Gerhardt & Cahours), and more rapidly by *alcoholic potash* (Kraut), without evolution of hydrogen, into cuminate of potash and an oil (Gerhardt & Cahours); into cuminic alcohol. (Kraut.)

$$2C^{20}H^{12}O^2 + KO,HO = C^{20}H^{14}O^2 + C^{20}H^{11}KO^4.$$

Decomposition with evolution of hydrogen also takes place when cuminol is acted upon by fused potash not too strongly heated. (Gerhardt & Cahours.) — In this reaction, cymene is liberated, the cuminol being first decomposed into cuminate of potash and cuminic alcohol, and the latter further decomposed into cuminate of potash and cymene. (Kraut.) — 12. By a mixture of *bichromate of potash* and sulphuric acid, it is converted into cuminic acid (Gerhardt & Cahours); if the action be prolonged, insolinic acid is formed (xiii, 318). (Hofmann, *Ann. Pharm.* 97, 207.) By heating Roman cumin oil with chromate of potash and sulphuric acid, Persoz obtained cyminic and cumino-cyminic acids, the first being identical with cuminic acid, the second with insolinic acid. (*Compt. rend.* 13, 431.) — 13. By the action of *cyanide of potassium* on cuminol, Gerhardt & Cahours once obtained a product analogous to benzoin, which, however they were unable to produce again. — 14. Heated with *chloride of cumyl*, it forms cumyl. (Chiozza.)

Combinations. With Potassium. Cuminol-potassium. When cuminol is carefully heated with a slight excess of potassium, a violent reaction, accompanied by abundant evolution of hydrogen, takes place, and the whole of the cuminol is converted into gelatinous cuminol-potassium. (Gerhardt & Cahours.) Chiozza heats cuminol with potassium in a covered platinum crucible, presses the product between blotting paper, and places it in vacuo over sulphuric acid, which absorbs with avidity the adhering cuminol. — According to Gerhardt & Cahours, it is also produced by the action of fragments of caustic potash on cuminol at ordinary temperatures (p. 146).

It is decomposed by water into cuminol and hydrate of potash, and rapidly converted by moist air into cuminate of potash. (Gerhardt & Cahours.) With chloride of cumyl, it forms chloride of potassium and cumyl; with chloride of benzoyl a similar product, which is rapidly converted by aqueous potash into cumyl. (Chiozza.)

With Bisulphite of Ammonia. When Roman cumin oil (mixture of cymene and cuminol) is mixed and shaken up with aqueous bisulphite of ammonia of 29° B., it forms almost immediately a crystalline mass, which, when separated from the mother-liquid and dissolved in boiling alcohol, deposits after a time beautiful groups of needles. (Bertagnini.) If the compound is kept in a sealed glass tube in the dark, it remains unchanged for several months, and then turns yellowish, probably from spontaneous decomposition. (Bertagnini.)

With Bisulphite of Potash. When Roman cumin oil is gently warme with aqueous bisulphite of potash of between 28° and 30° B., a large part of it dissolves, and is deposited on cooling in brilliant laminæ of the compound of bisulphite of potash and cuminol. The undissolved portion yields all its cuminol when shaken up with fresh quantities of bisulphite of potash, so that only cymene remains. (Bertagnini.)

The compound is decomposed by water. Heated in a test tube, it evolves sulphurous acid and cuminol. It dissolves in water containing a small quantity of a bisulphite, without decomposition, even when heat is applied. It is insoluble in concentrated solutions of the alkaline bisulphites. (Bertagnini.)

With Bisulphite of Soda. Roman cumin oil, shaken up with aqueous bisulphite of soda of 27° B., forms a buttery mass, becoming hard in the course of a few hours. This is separated from the mother-liquid, and dissolved in very dilute boiling alcohol; whereupon it crystallises from the solution on cooling, in needles which may be purified by recrystallisation from dilute alcohol. (Bertagnini.)

Brilliant, white, inodorous needles (bulky, nacreous scales: Trapp), which turn yellow on prolonged exposure to the air (Bertagnini); they effloresce in the air. (Trapp.) When heated, it evolves sulphurous acid and cuminol, and leaves sulphite of soda and charcoal (Bertagnini.) It is decomposed by boiling water, depositing a white powder, and forming a turbid milky liquid. (Trapp.)

It is decomposed by (aqueous ?) ammonia; after prolonged contact, a thick oil is precipitated, probably resembling the oil produced from cuminol by ammonia. (Sieveking.) Insoluble in cold water. (Trapp.) Dissolves in water containing a small quantity of a sulphite, especially with the aid of heat. The solution is decomposed by heating with bases or acids. It is decomposed by iodine or bromine, with formation of sulphuric acid and separation of cuminol; an excess of bromine forms a crystalline, easily fusible substance, which combines with bisulphites and is probably bromide of cumyl (bromocuminol ?). (Bertagnini.)

It does not dissolve in concentrated solutions of the sulphites, or (slightly, Trapp) in cold alcohol or in ether. (Bertagnini.)

			Bertagnini. *mean.*
NaO	31	11·48	11·84
20 C	120	44·44	44·71
15 H	15	5·55	5·33
2 S	32	11·85	
10 O	80	26·68	
$C^{20}H^{12}O^2,NaO,2SO^2+3Aq$	278	100·00	

Cuminol prepared from the seeds of the water-hemlock contains 8·67 p. c. Na (calculation = 8·52 p. c.). (Trapp.)

Cuminic Acid.

$$C^{20}H^{12}O^4 = C^{20}H^{12},O^4$$

GERHARDT & CAHOURS (1841). *N. Ann. Chim. Phys.* 1, 70; *J. pr. Chem.* 23, 329; *Ann. Pharm.* 38, 76.

PERSOZ. *Compt. rend.* 13, 431; *J. pr. Chem.* 25, 55; *Ann. Pharm.* 44, 311.

GERHARDT. *Compt. chim.* 1, 75; *N. Ann. Chim. Phys.* 37, 404; *Ann. Pharm.* 87, 77.

CAHOURS. *Compt. rend*, 24, 554; *N. Ann. Chim. Phys.* 25, 36; *Ann. Pharm.* 69, 243; *N. Ann. Chim. Phys.* 23, 347; *J. pr. Chem.* 45, 144; abstr. *Ann. Pharm.* 70, 45; *N. Ann. Chim. Phys.* 52, 201.

FR. FIELD. *Ann. Pharm.* 65, 51; *Mem. Chem. Soc.* 3, 408; *J. pr. Chem.* 44, 136.

A. W. HOFMANN. *Ann. Pharm.* 74, 344; further, 97, 197.

CHIOZZA. *N. Ann. Chim. Phys.* 39, 219.

KRAUT. *Dissert. über Cuminol und Cymen*, Gött. 1854; *Ann. Pharm.* 98, 366; *N. Br. Arch.* 96, 274.

Acide cuminique.—*Acide cyminique* (Persoz), *Cuminsäure.* Discovered by Gerhardt & Cahours. The acid observed by Chevalier (x, 109) in Roman cumin oil which had become acid by exposure to the air was, doubtless, cuminic and not succinic acid. (Kr.)

Formation. Produced by the oxidation of cuminol by air, moist bromine or chlorine, nitric acid or chromic acid; with evolution of hydrogen, when cuminol is fused with hydrate of potash. (Gerhardt & Cahours.) With simultaneous formation of cuminic alcohol (Kraut): by the action of water, or of aqueous (Gerhardt & Cahours), or alcoholic potash on cuminol. — From cuminic alcohol, by oxidation with nitric acid; by fusing it with hydrate of potash, hydrogen being evolved; by boiling it with alcoholic potash, cymene being simultaneously produced. (Kraut.)

Preparation. Hydrate of potash is fused in a retort, into the tubulus of which a funnel-tube, drawn out to a fine point, has been fitted, and cuminol or Roman cumin oil is gradually dropped into the retort, each drop becoming solid and white as it comes in contact with the hydrate of potash, while (if Roman cumin oil be used) cymene distils over. When all the cumin oil is decomposed, the residue is dissolved in water, and any unvolatilised cymene that may be present is removed with a pipette. Nitric acid in slight excess is then added, whereby cuminic acid is precipitated in white or yellowish flakes; these are collected on a filter, washed and fused in a dish; the fused mass, which solidifies on cooling, is separated from adhering water and distilled *per se*; and the distillate is crystallised from alcohol. — If it is not required to collect the cymene, the Roman cumin oil may be dropped on potash fused in a dish, whereby the operation may be more rapidly conducted. (Gerhardt & Cahours.)

When the hydrate of potash is fused in glass retorts, the vessels are rapidly corroded; and the use of an open dish occasions much loss from the volatilisation of cuminol; it is therefore preferable to decompose Roman cumin oil with alcoholic potash, so that the cuminic alcohol at first formed may be completely decomposed into cuminic acid and cymene (Kr.) — Persoz heats Roman cumin oil with a mixture of 5 pts. bichromate of potash, 11 pts. oil of vitriol, and 40 pts. water, whereby a distillate containing acetic acid and a mixture of cuminic and insolinic acids is obtained (xiii, 319), and is separated by alcohol, in which insolinic acid is insoluble.

Properties. Beautiful, white, tabular prisms. (Gerhardt & Cahours.) (Rhombic, according to Persoz.) Melts at 115°. (Persoz, Gerhardt.) In the earlier investigations of Gerhardt and Cahours, its melting point was found to be 92°; but this acid contained cymene. (Gerhardt, *Compt. rend.* 20, 1443.) — It floats on boiling water as a colourless oil, which solidifies on cooling. Boils above 250°, but volatilises with the vapour of water. Sublimes readily without decomposition in beautiful long needles. The vapour has an acid suffocating smell. Tastes strongly acid (it is tasteless, Persoz), and has a faint odour of bugs. (Gerhardt & Cahours.)

			Gerhardt & Cahours.	Hofmann.	Gerhardt.
	Crystals.		mean.		
20 C	120	73·17	73·12	72·66	72·91
12 H	12	7·32	7·53	7·37	7·38
4 O	32	19·51	19·35	19·97	19·71
$C^{20}H^{12}O^4$	164	100·00	100·00	100·00	100·00

Hofmann analysed cuminic acid which had passed unchanged through the system into the urine; Gerhardt the acid obtained from aceto-cuminic anhydride. It is isomeric with eugenic acid.

Decompositions. 1. Cuminic acid is converted by boiling fuming *nitric acid* (and by cold nitrosulphuric acid: Kraut) into nitrocuminic acid; by heated *nitrosulphuric acid,* into binitrocuminic acid. (Cahours.) — 2. By *pentachloride of phosphorus,* into chloride of cumyl. (Cahours.) Its soda-salt mixed with terchloride of phosphorus forms chloride of cumyl and phosphite of soda. (Gerhardt.) *Chlorophosphoric acid* converts cuminate of soda into cuminic anhydride. (Gerhardt.) — 4. By boiling with *bichromate of potash* and *sulphuric acid,* it is converted into insolinic acid. (Hofmann.) — 5. By dry distillation with excess of *caustic baryta,* it is decomposed into carbonate of baryta and cymene. (Gerhardt & Cahours.) — 6. It passes through the system unchanged into the urine. (Hofmann.) — 7. The potash-salt heated with *bromide of cyanogen* yields cumonitrile and bromide of potassium. (Cahours.) — 8. The soda-salt heated with *chloride of acetyl, benzoyl,* or *cumyl,* forms the corresponding conjugated anhydride. (Gerhardt.)

Combinations. The acid is scarcely soluble in cold *water,* slightly in boiling water, from which it is deposited on cooling. (Gerhardt & Cahours; Persoz.) — It is more soluble in acidulated water, hence it must not be precipitated with too much nitric acid. (Gerhardt and Cahours.)

Dissolves in strong *sulphuric acid* without coloration. If the acid has not been purified by sublimation and then by crystallisation from alcohol, it still contains an oil, and turns red with sulphuric acid. (Gerhardt & Cahours.)

Cuminic acid forms salts with bases: *Cuminates.* They resemble the benzoates. (Persoz.) — It decomposes the alkaline carbonates. (Gerhardt & Cahours.)

Cuminate of Ammonia. Friable tufts, becoming dull in the air, probably from loss of ammonia. (Gerhardt & Cahours.) It is decomposed by heat, partly into cuminic acid and ammonia, partly into cuminamide and cumonitrile. Heated in a sealed tube, or heated almost to fusion for a long time in a retort, it is for the most part principally converted into cuminamide, and when rapidly distilled, into cumonitrile. (Field.)

Cuminate of Potash. Ill-defined, deliquescent crystals. (Gerhardt & Cahours.)

Cuminate of Baryta. Carbonate of baryta is decomposed by cuminic acid. The concentrated solution, filtered hot, deposits immediately on cooling, nacreous scales, each of which at the moment of its formation exhibits the prismatic colours. Tastes very bitter; dissolves readily in alcohol and in ether. (Gerhardt & Cahours.)

	Dried at 100°.		Gerhardt & Cahours.
Ba	68·6	29·61	29·88
20 C	120	51·82	51·41
11 H	11	4·75	4·81
4 O	32	13·82	13·90
$C^{20}H^{11}BaO^{4}$	231·6	100·00	100·00

Cuminate of Copper. Greenish powder, becoming stongly electric by pressure. Remains unchanged at 250°. Melts at 260°, and swells up slightly, without volatilising. The residue contains a small quantity of metallic copper, cuminic acid, cuprous cuminate, and a copper-salt, which, when decomposed by acids, deposits a semi-fluid oil. (Chiozza.) By dry distillation, it yields cuminic acid and cymene. (Kraut.)

Cuminate of Silver. Nitrate of silver gives with cuminate of ammonia a white curdy precipitate which rapidly blackens in the light. Subjected to dry distillation, it yields carbonic acid and cuminic acid (part of which is decomposed into carbonic acid and cymene), and leaves a residue of charcoal and carbide of silver, the latter remaining unchanged even when the salt is ignited in the air.

	Dried at 100°.		Gerhardt & Cahours. *mean.*
Ag	108·1	39·87	40·06
20 C	120·0	44·22	44·19
11 H	11·0	4·05	4·11
4 O	32·0	11·86	11·64
$C^{20}H^{11}AgO^4$	271·0	100·00	100·00

When prepared with cuminic acid obtained by acting on cuminic alcohol with nitric acid, it contains 39·69 p. c. Ag. (Kraut.)

Cuminic acid is readily soluble in *alcohol* and *ether*, and crystallises from the solutions by evaporation. (Gerhardt & Cahours, Persoz.) It dissolves in warm *glacial acetic acid* in all proportions, and crystallises therefrom on cooling. (Persoz.)

Oxycuminic Acid.

$C^{20}H^{12}O^6 = C^{20}H^{12},O^6$?

Cahours. *N. Ann. Chim. Phys.* 53, 338; *Ann. Pharm.* 109, 20.

Acide oxycuminique.

Formation and Preparation. Amidocuminic acid is dissolved in excess of moderately concentrated nitric acid, and nitric oxide is passed through the solution; whereupon nitrogen gas is evolved, and, after prolonged action, oxycuminic acid is obtained.

Properties. Small, yellowish brown prisms.

			Cahours.
20 C	120	66·66	66·18
12 H	12	6·66	6·81
6 O	48	26·68	27·01
$C^{20}H^{12}O^6$	180	100·00	100·00

It bears the same relation to cuminic acid as glycolic (xii, 508) to acetic acid.

Dissolves sparingly in cold, readily in boiling *water*.

Combines with *salifiable bases,* forming compounds some of whic crystallise well.

Oxycuminate of Silver. Yields on ignition 37·41 p. c. Ag, corresponding to the formula $C^{20}AgH^{11}O^6$, which requires 37·63 p. c. Ag.

Oxycuminic acid is more readily soluble in *alcohol* than in water.

Chlorocumol.

$$C^{20}H^{12}Cl^2 = C^{20}H^{12},Cl^2.$$

CAHOURS. (1848.) *N. Ann. Chim. Phys.* 23, 345; *J. pr. Chem.* 45, 143; abstr. *Ann. Pharm.* 70, 44.

J. P. SIEVEKING. *Dissert. über Cuminol und Cymen,* Gött. 1857; abstr. *Ann. Pharm.* 106, 258; *J. pr. Chem.* 74, 505.

J. TÜTTSCHEFF. *Petersb. Acad. Bull. No.* 392; *J. pr. Chem.* 75, 370; abstr. *Rep. Chim. pure.* 1, 268.

Chlorocuminol.

Formation and Preparation. Pentachloride of phosphorus reacts violently and rapidly on cuminol; the mixture becomes hot, and yields by distillation oxychloride of phosphorus boiling at 111°, and chlorocumol, leaving but a small residue. The portion distilling between 250° and 265° is collected apart, washed with water and dilute potash till all traces of oxychloride of phosphorus have been destroyed; then again with water; afterwards dried over chloride of calcium and rectified. (Cahours.) In the action of pentachloride of phosphorus on cuminol, charcoal is deposited. (Tüttscheff.) If the product obtained from equal numbers of atoms of pentachloride of phosphorus and cuminol be heated to 150°, after the oxychloride of phosphorus has distilled over, it blackens, evolves large quantities of hydrochloric acid, and on being further heated to 250° or 260°, yields scarcely any chlorocumol. It is therefore preferable to place 5 pts. pentachloride of phosphorus in a tubulated retort, into the tubulus of which a glass tube is fitted by means of a perforated cork, and to connect with this a dropping burette, by which 2 pts. cuminol may be introduced by small portions. After the action has ceased, the whole is heated to 150°, or till almost all the oxychloride of phosphorus has passed over, and the residue is mixed with water; whereupon the chlorocumol is deposited at the bottom of the vessel. This is collected, carefully separated from adhering water, and distilled by itself. The portion distilling between 250° and 260°, amounting to $\frac{4}{5}$ths of the cuminol employed, is collected apart. (Sieveking.)

Properties. Limpid liquid, heavier than water. (Cahours.) Boils between 255° and 260° (Cahours) at 255°, with slight decomposition, evolving hydrochloric acid and depositing charcoal. (Tüttscheff.) It smells like chloride of benzoyl (Cahours); penetrating, and not disagreeable. (Sieveking.)

			Cahours. *mean.*
20 C	120	59·11	60·01
12 H	12	5·91	6·11
2 Cl	71	34·98	34·18
$C^{20}H^{12}Cl^2$	203	100·00	100·30

Decompositions. 1. Heated with alcoholic *ammonia* in a sealed tube, it forms chloride of ammonium and a thick yellow oil. (Sieveking.) — 2. It does not appear to be decomposed by aqueous *potash.* (Cahours.) — 3. With *hydrosulphate of potassium,* it yields chloride of potassium, and a viscid product of repulsive odour. (Cahours.) — The alcoholic solution, treated for some time with *sulphide of ammonium,* yields a dark red resin soluble in ether. (Sieveking.) — 4. By freshly precipitated *oxide of silver* it is converted into cuminol. (Tüttscheff.) — 5. When 2 At. *ethylate of soda* are heated with 1 At. chlorocumol, chloride of sodium and a red liquid are obtained. When this product is distilled, first alcohol, and then, between 170° and 238°, an oil passes over, which behaves with alkaline bisulphites like cuminol. (Sieveking.) — 6. With *acetate of silver,* it forms acetate of cumo-glycol (Sieveking); with *benzoate of silver,* benzoate of cumoglycol. (Tüttscheff.)

Insoluble in *water.* (Cahours.) Readily soluble in *alcohol* and in *ether.* (Cahours.)

Conjugated compounds of the Primary Nucleus, $C^{20}H^{12}$.

Acetate of Cumoglycol.

$$C^{28}H^{18}O^{8} = 2C^{4}H^{3}O^{3},C^{20}H^{12}O^{2}.$$

J. P. Sieveking. (1857.) *Dissert. über Cuminol und Cymen,* Gött, 1857; *Ann. Pharm.* 106, 258; *J. pr. Chem.* 74, 505.

Acetate of Cumylene. Essigsäure Cumol-äther.

Preparation. Chlorocumol is mixed with excess of acetate of silver, and the reaction, which immediately ensues, is finally aided by a gentle heat. The product is treated with ether; the solution evaporated; and the residue washed with aqueous carbonate of soda, and crystallised from ether, whereby yellowish crystals, contaminated with an oil, are obtained.

Properties. Colourless crystals, resembling the swallow-tail crystals of gypsum. Melts at a moderate heat, and diffuses a powerful odour of acetic acid and cuminol.

			Sieveking. *mean.*
28 C	168	67·2	70·7
18 H	18	7·2	7·5
8 O	64	25·6	21·8
$2C^{4}H^{3}O^{3},C^{20}H^{12}O^{2}$	250	100·0	100·0

It gave too much carbon in the analysis, owing to the presence of an oil.

Benzoate of Cumoglycol.

$$C^{48}H^{22}O^{8} = 2C^{14}H^{5}O^{3},C^{20}H^{12}O^{2}.$$

J. Tüttscheff. *Petersb. Acad. Bull.* No. 392; *J. pr. Chem.* 75, 370.

Bibenzoate of Cumol; Benzoate of Cumylene.

Formation and Preparation. Seven pts. chlorocumol are mixed in a porcelain dish with 16 pts. benzoate of silver; the mass thereby formed is treated with ether, which leaves the chloride of silver undissolved; and the resulting solution of benzoate of cumoglycol is left to evaporate spontaneously, whereupon a brownish yellow oil, solidifying in crystals in a few days, is deposited. This is pressed between paper, washed with aqueous ammonia, and recrystallised alternately from ether-alcohol and absolute alcohol.

Properties. Brilliant, colourless needles, melting at 88°, and solidifying in crystals on cooling.

	Needles.		Tüttscheff. *mean.*
48 C	288	77·01	76·94
22 H	22	5·88	5·93
8 O	64	17·11	17·13
$2C^{14}H^{5}O^{3},C^{20}H^{12}O^{2}$	374	100·00	100·00

Decompositions. It cannot be volatilised without decomposition. — 2. It is dissolved by cold *sulphuric acid* with dark redcolour; the solution blackens by boiling. — 3. It is not attacked by boiling *nitric acid.* — 4. It is not affected by *ammonia* or by concentrated *baryta-water.* — 5. Distilled with *caustic potash,* it yields benzoate of potash and cuminol.

Dissolves in *alcohol,* especially in warm strong alcohol, and is precipitated by water. Dissolves readily in *ether, acetone,* and *chloroform.*

Cumyl.

$$C^{40}H^{22}O^{4} = C^{20}H^{11}(C^{20}H^{11}O^{2})O^{2}.$$

Chiozza. (1852.) *Compt. rend.* 35, 225; *Ann. Pharm.* 84, 102; *J. pr. Chem.* 57, 178; in detail, *N. Ann. Chim. Phys.* 39, 216.

Cumyle.

Formation. 1. By heating cuminol with chloride of cumyl. The reaction takes place only at a high temperature, at which the hydrochloric acid evolved further decomposes the cumyl and turns it brown. — 2. Cuminol-potassium is heated with chloride of cumyl. — 3. Cuminol-potassium is acted upon by chloride of benzoyl, whereby an uncrystallisable oil is formed, which, when heated with aqueous potash, yields cumyl together with other products.

Preparation. To freshly prepared cuminol-potassium (p. 147), an equivalent quantity of chloride of cumyl is added; whereupon the mixture liquifies, and when gently heated, becomes pasty, and deposits chloride of potassium. The excess of chloride of cumyl and any cuminic anhydride that may have been formed are removed by washing the product with weak potash; the mixture is shaken with ether, which takes up the cumyl; the ethereal stratum is decanted, and dried over chloride of calcium; and the ether is evaporated over the water-bath.

Properties. Viscid oil. Cooled to −18° in a freezing-mixture, it solidifies in a clear, uncrystalline mass. Heavier than water. It has a faint odour at ordinary temperatures, and an agreeable odour of geraniums when heated.

			Chiozza.	
			a. *mean.*	*b.*
40 C	240	81·6	80·55	81·5
22 H	22	7·5	7·97	7·8
4 O	32	10·9	11·48	10·7
$C^{40}H^{22}O^4$	294	100·0	100·00	100·0

a was obtained by method 2, *b* by method 3.

Decompositions. 1. Cumyl *takes fire* with difficulty and burns with a smoky flame. — 2. *Heated* above 300°, it decomposes with ebullition, into cuminic acid and other products poorer in oxygen, leaving a residue of charcoal. — 3. It is attacked by cold strong *sulphuric acid*, and on heating the mixture, it blackens and gives off sulphurous acid. — 4. Dissolves in fuming *nitric acid* without evolving red vapours, and on addition of water, a yellow, neutral, soft resin is deposited, with which flakes of cuminic acid mix as the liquid cools. — 5. Gently warmed with fragments of *caustic potash*, it is decomposed into cuminol and cuminate of potash. Alcoholic potash exercises the same action. It is likewise attacked by aqueous potash, but more slowly, and when boiled with it, is converted into an oil containing 81·6 p. c. C & 8·6 p. c. H.

It is scarcely soluble in cold, readily in boiling *alcohol*.

Cuminate of Ethyl.

$$C^{24}H^{16}O^4 = C^4H^5O,C^{20}H^{11}O^3.$$

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 77.
CAHOURS. *N. Ann. Chim. Phys.* 23, 348.

Cuminic ether, Ether cuminique, Cuminvinester.

Formation and Preparation. 1. A solution of cuminic acid in absolute alcohol is saturated with gaseous hydrochloric acid; the chloride of ethyl and excess of alcohol are expelled by heating the liquid on a water bath; the ether is distilled off; and the distillate is washed with carbonate of soda and rectified over oxide of lead. (Gerhardt & Cahours.) —

2. When chloride of cumyl is added to strong alcohol, the mixture becomes hot, and on addition of water, deposits cuminate of ethyl. (Cahours.)

Properties. Colourless liquid. Lighter than water. Boils at 240°. Vapour density = 6·65. It has a very agreeable odour of pippins.

			Gerhardt & Cahours. *mean.*
24 C	144	75·00	74·45
16 H	16	8·33	8·65
4 O	32	16·67	16·90
$C^4H^5O,C^{20}H^{11}O^3$	192	100·00	100·00

	Vols.	Density.
C-vapour	24	9·9840
H-gas	16	1·1088
O-gas	2	2·2186
Ether-vapour	2	13·3114
	1	6·6557

Decompositions. The vapour is readily inflammable, and burns with a blueish flame. — Heated with *potash,* it yields alcohol and cuminate of potash. (Gerhardt & Cahours.)

Insoluble in *water.* Dissolves in every proportion in *alcohol* and in *ether.* (Gerhardt & Cahours.)

Acetocuminic Anhydride.

$C^{24}H^{14}O^6 = C^4H^3O^3,C^{20}H^{11}O^3$.

GERHARDT. (1852.) *Compt. rend.* 34, 904; *Ann. Pharm.* 83, 114; in detail, *N. Ann. Chim. Phys.* 37, 304; *Ann. Pharm.* 87, 82.

Cuminate acétique, Acétate cuminique, Anhydrous Cuminacetic Acid.

Obtained in the same way as acetobenzoïc anhydride (xii, 95), from cuminate of soda and chloride of acetyl.

Properties. Neutral oil having an agreeable odour of Spanish wine. Heavier than water.

			Cahours.
24 C	144	69·90	70·14
14 H	14	6·80	6·93
6 O	48	23·30	22·93
$C^4H^3O^3,C^{20}H^{11}O^3$	206	100·00	100·00

Decompositions. 1. When *moist,* it rapidly becomes acid, depositing laminæ of cuminic acid, and diffusing an odour of acetic acid. — 2. It is decomposed by *distillation* into acetic anhydride and cuminic anhydride. — 3. By alkalis it is converted into a mixture of cuminate and acetate.

Cuminate of Phenyl,

$C^{32}H^{16}O^{4} = C^{12}H^{5}O,C^{20}H^{11}O^{3}$.

WILLIAMSON & SCRUGHAM. *Phil. Mag.* 7, 370; *Chem. Gaz.* 1854, 193; *Ann. Pharm.* 92, 316; *J. pr. Chem.* 62, 365; *Pharm. Centr.* 1854, 506; *N. Ann. Chim. Phys.* 41, 491.
KRAUT. *Dissertation,* Gött. 1854; *N. Br. Arch.* 96, 272.

Cuminsaure-Carbolsäure, Cumyl-phenyl.

Formation. By the action of chloride of cumyl on phenylate of potash. (Williamson & Scrugham.) — By the dry distillation of cumosalicylic acid, or of a mixture of chloride of cumyl and salicylate of soda in equal numbers of atoms. (Kraut.)

Preparation. 16 pts. salicylate of soda are heated with 18¼ pts. chloride of cumyl in a retort, at first gently, till the mixture has become pasty and the odour of chloride of cumyl has disappeared, then more strongly, as long as oil continues to pass over. The distillate is heated to boiling with dilute aqueous potash, whereupon cuminic and carbolic acids dissolve in the potash, and cuminate of phenyl is deposited on cooling as a crystalline mass which is purified by washing, freezing, and repeated recrystallisation from alcohol. (Kraut.)

Properties. Long, white needles, melting between 57° and 58°. Distils without decomposition. It has an agreeable odour, resembling that of benzoate of phenyl, especially when heated.

			Kraut. *mean.*
32 C	192	80·00	80·58
16 H	16	6·60	6·87
4 O	32	13·40	12·55
$C^{12}H^{5}O,C^{20}H^{11}O^{3}$	240	100·00	100·00

Decompositions. 1. When a mixture of cuminate of phenyl and *nitrate of soda* is heated with strong *sulphuric acid,* binitrocuminic acid (and probably nitrocuminic acid) is formed. (Kraut.) — 2. It is resolved by strong *sulphuric acid* into cuminic acid and sulpho-carbonic acid. (Kraut.) — 3. It is not decomposed by aqueous potash, but *alcoholic potash* decomposes it, yielding cuminate and phenylate of potash. (Kraut.)

It is insoluble in *water.* Dissolves readily in hot *alcohol* and in *ether.*

Benzo-cuminic Anhydride.

$C^{34}H^{16}O^{6} = C^{14}H^{5}O^{3},C^{20}H^{11}O^{3}$.

GERHARDT. (1852.) *Ann. Pharm.* 82, 114; *N. Ann. Chim. Phys.* 37, 285; *Ann. Pharm.* 87, 79.

Anhydrous Benzocuminic acid, Cuminate of benzoyl, Benzoate of cumyl, Wasserfreie Benzoesäure-Cuminsäure.

Preparation. 20 pts. dried cuminate of soda are heated in a retort with 15 pts. chloride of benzoyl, till the odour has disappeared; after which the whole is allowed to cool. A thick, almost colourless syrup is thus obtained, which is warmed with water to dissolve out the chloride of sodium; whereupon the benzo-cuminic anhydride collects at the bottom of the vessel as an oil. This is washed first with aqueous carbonate of soda, then with water, and after pouring off the water, dissolved in ether and gently warmed till the ether and adhering water have evaporated.

Properties. Thick, almost colourless, and inodorous oil. Sp. gr. = 1·115 at 23°. Heated in open vessels, it appears to volatilise without decomposition, and yields very pungent vapours.

			Gerhardt.
34 C	204	76·12	75·89
16 H	16	5·97	6·18
6 O	48	17·91	17·93
$C^{14}H^5O^3,C^{20}H^{11}O^3$	268	100·00	100·00

Decompositions. 1. When kept *moist,* it turns acid. 2. It cannot be distilled without decomposition, but yields an acid, buttery distillate solidifying in the neck of the retort. 3. *Ammonia* converts it into benzamide, or benzoate of ammonia, and cuminamide. 4. By *alkalis* it is converted into a mixture of benzoate and cuminate.

Cumosalicyl.

$$C^{34}H^{16}O^6 = C^{16}H^5O^3,C^{20}H^{11}O^3.$$

CAHOURS. *Compt. rend.* 44, 1252; *Ann. Pharm.* 104, 109; in detail, *N. Ann. Chim. Phys.* 52, 197; *Ann. Pharm.* 108, 317.

Cumosalicyle.

Formation and Preparation. Chloride of cumyl does not act in the cold on salicylous acid; but on applying heat, abundance of hydrochloric acid is evolved, and solid cumosalicyl is formed, which is purified by pressing between blotting paper, washing with warm aqueous potash and boiling water, and repeated recrystallisation from strong alcohol.

Properties. Brilliant, colourless, friable prisms, melting at a gentle heat to a clear oil, and solidifying on cooling.

			Cahours.
34 C	204	76·1	75·79
16 H	16	5·9	5·97
6 O	48	18·0	18·24
$C^{14}H^5O^3,C^{20}H^{11}O^3$	268	100·0	100·00

It is attacked by *chlorine, bromine,* and *fuming nitric acid,* giving rise to crystallisable products. It is not attacked by solid *caustic potash* or by aqueous potash, either in the cold or when heated.

Insoluble in cold, slightly soluble in boiling *water.*

Dissolves in *alcohol,* especially in warm alcohol. Dissolves readily in *ether.*

Cuminate of Methyl-salicyl.

$C^{36}H^{18}O^{8} = C^{2}H^{3}O,C^{20}H^{11}O^{3},C^{14}H^{4}O^{4}$.

GERHARDT. (1854.) *Compt. rend.* 38, 32; *Ann. Pharm.* 89, 362; *Chem. Centr.* 1854, 131; *Traité*, 3, 327.

Cuminsaure Methylsalicylsäure.

When chloride of cumyl is heated with salicylate of methyl, a viscid oil is obtained, which crystallises when mixed with ether, and evaporated.

Properties. Crystallises from alcohol in very brilliant laminæ, and from ether, by spontaneous evaporation, in thick, oblique prisms. It is deposited from its hot saturated alcoholic solution as an oil which remains fluid for a long time.

Insoluble in *water*, slightly soluble in cold *alcohol*. Very soluble in *ether*.

Oenantho-cuminic Anhydride.

$C^{34}H^{24}O^{6} = C^{14}H^{13}O^{3},C^{20}H^{11}O^{3}$.

CHIOZZA & MALERBA. *Ann. Pharm.* 91, 102; *Chem. Centr.* 1854, 793; *J. pr. Chem.* 64, 32.

Cumyl-oenanthylal, Anhydrous Oenantho-cuminic acid, Oenanthylate of Cumyl.

Obtained by the action of chloride of cumyl on oenanthylate of potash.

Colourless oil, smelling feebly of apples and slightly aromatic in the cold. Lighter than water. Heavier than water (Chiozza & Malerba). (Gerhardt, *Traité*, 3, 601.) When heated, it yields vapours which attack the organs of respiration.

			Chiozza & Malerba.
34 C	204	73·91	74·0
24 H	24	8·69	8·2
6 O	48	17·40	17·8
$C^{14}H^{13}O^{3},C^{20}H^{11}O^{3}$	276	100·00	100·0

Cuminic Anhydride.

$C^{40}H^{22}O^{6} = C^{20}H^{11}O^{3},C^{20}H^{11}O^{3}$.

GERHARDT. (1852.) *Compt. rend.* 34, 904; *Ann. Pharm.* 83, 114; more detailed, *N. Ann. Chim. Phys.* 37, 304; *Ann. Pharm.* 87, 77.

Anhydrous cuminic acid, Cuminate cuminique.

Formation. 1. By the action of chloride of cumyl on cuminate of soda. — 2. By the action of oxychloride of phosphorus on cuminate of soda. — 3. Aceto-cuminic anhydride is resolved by distillation into acetic anhydride and cuminic anhydride.

Preparation. Similar to that of benzo-cuminic anhydride (p. 157). The ethereal solution is generally rendered milky by chloride of sodium ; This is removed by evaporating the solution and again treating the residue with ether.

Properties. Viscid, almost colourless oil, solidifying in crystals after a time. Tasteless. It has a faint odour like the ethers of the fatty acids. Neutral.

			Gerhardt.	
			oil.	*solidified mass.*
40 C	240	77·42	77·43	77·35
22 H	22	7·10	7·15	7·17
6 O	48	15·48	5·42	15·48
$C^{20}H^{11}O^3,C^{20}H^{11}O^3$	310	100·00	100·00	100·00

Decompositions. Exposed to *moist air*, it gradually becomes filled with brilliant laminæ of cuminic acid, into which it is at last completely converted. — By *aqueous ammonia* it is gradually converted into solid cuminamide.

Cuminuric Acid.

$C^{24}NH^{15}O^6 = C^{24}AdH^{13}O^2,O^4$.

CAHOURS. *N. Ann. Chim. Phys.* 53, 356 ; *Ann. Pharm.* 109, 31.

Formation and Preparation. When the compound of glycocol and oxide of silver is acted upon by chloride of cumyl, chloride of silver is formed, together with cuminuric acid, which is soluble in warm alcohol and crystallises on cooling or by slow evaporation, in yellowish brown prisms. The product is purified by pressure between blotting paper and recrystallisation.

			Cahours.
24 C	144	65·15	64·91
N	14	6·33	
15 H	15	6·78	6·65
6 O	48	21·74	
$C^{24}NH^{15}O^6$	221	100·00	

It bears the same relation to cuminic acid, as hippuric to benzoïc acid.

Boiled with *hydrochloric acid*, it takes up water and is converted into cuminic acid and hydrochlorate of glycocol.

Cuminurate of silver contains 32·61 p. c. Ag ($C^{24}AgNH^{14}O^6$ = 32·92 p. c.).

Cuminuric acid dissolves in *alcohol*, especially when warm.

Oxygen-nucleus $C^{20}H^{10}O^2$.

Sassafras-Camphor.

$$C^{20}H^{10}O^4 = C^{20}H^{10}O^2,O^2.$$

Binder. (1821.) *Repert.* 11, 346.
Saint-Evre. *N. Ann. Chim. Phys.* 12, 107; *J. pr. Chem.* 34, 372; abstr. *Compt. rend.* 18, 735; *N. J. Pharm.* 10, 314.

In oil of Sassafras. Rectified oil of sassafras is cooled by an artificial freezing mixture, and the crystals, which are deposited after a few hours from the turbid liquid, are collected, pressed between paper, melted, and recrystallised by means of a freezing mixture. (St. Evre.)

Hard, white, oblique four-sided or irregular six-sided prisms, bevelled with two faces, and somewhat truncated on the bevelling edge.

It crackles when pressed together. Sp. gr. = 1·245 at 6°; 1·11 in the liquid state at 12° 5′. It remains liquid at 5°, but solidifies below 17°; solidifies at 7·5°. (Binder.) — Vapour-density = 5·85. (St. Evre.)

It has an odour of sassafras, and tastes at first sweetish and warm, afterwards burning. (Binder.)

			St. Evre.		
20 C	120	74·07	73·86	73·34	73·83
10 H	10	6·17	6·61	6·24	6·29
4 O	32	19·76	19·53	19·82	19·83
$C^{20}H^{10}O^4$	162	100·00	100·00	100·00	100·00

It becomes rapidly altered in the *air.* (St. Evre.) — When set on fire, it burns with a very smoky flame. — Mixed with *nitric acid,* it turns yellow, dissolves with reddish brown colour, and is partly converted into a brown viscid resin. — With fuming *sulphuric acid* it effervesces, evolving sulphurous acid and depositing spongy charcoal. (Binder.)

Appendix to Sassafras-camphor.

Oil of Sassafras.

Binder. (1821.) *Repert.* 11, 346.
Bonastre. *J. Pharm.* 14, 645; abstr. *J. Chim. méd.* 4, 484; *N. Tr.* 19, 1, 210.
Saint-Evre. *N. Ann. Chim. Phys.* 12, 107; *J. pr. Chem.* 34, 372; abstr. *Compt. rend.* 18, 735; *N. J. Pharm.* 10, 314.
Zeller. *Stud. über aether. Oele.*, 1850.

Essence of sassafras.

Source and Preparation. Occurs in the wood and bark of the roots of *Laurus sassafras* L. — The wood is rasped and distilled with water, and the oil which sinks to the bottom of the aqueous distillate is collected. Commercial oil of sassafras is generally adulterated (*a*) with *oil of* *lavender;* it is then specifically lighter than the pure oil; (*b.*) with *oil of turpentine,* which, when the oil is submitted to distillation, passes over and floats on the distillate; *c* with *oil of cloves,* the impurity remaining in the residue, when the oil is distilled with potash.

Properties. Yellow (St. Evre); varies between pale-brown and reddish yellow. (Zeller.) — Sp. gr. = 1·09 at 10° (St. Evre), between 1·07 and 1·09. (Zeller.) — Begins to boil at 115°, the boiling point rising to 228°, when it remains nearly constant. (St. Evre.) — It has an odour of fennel and a sharp (St. Evre), fiery taste. (Bonastre.) — It is neutral. (Zeller.)

	St. Evre.
C	72·19
H	6·40
O	21·41
	100·00

The analysis corresponds to the formula $C^{18}H^{10}O^2$,* but oil of sassafras is a mixture (St. Evre) of two oils, one heavier, the other lighter than water. (Bonastre.)

Decompositions. 1. When kept for some time or *cooled,* it deposits crystalline sassafras-camphor. (Binder, St. Evre.) 2. On *distillation,* it leaves a brownish yellow residue. (St. Evre.) — 3. Distilled through a *tube heated to redness* or over *heated soda-lime,* it yields naphthalin and phenylic alcohol. (St. Evre.) — 4. Saturated with *chlorine,* it becomes opaque, milky, and viscid. (Bonastre.); evolves hydrochloric acid and is converted into a viscid mass containing common camphor. (Faltin, *Ann. Pharm.* 87, 376.) — 5. It is violently attacked by *bromine,* being converted into bromide of oil of sassafras and evolving hydrobromic acid. (St. Evre.) — 6. With *iodine,* it turns yellowish brown without becoming viscid. — 7. Mixed with cold *nitric acid,* it gradually becomes flesh-coloured (Bonastre), reddish brown with slight elevation of temperature. (Zeller.) With hot nitric acid it turns red (Daryk); warmed with weak nitric acid, it yields oxalic acid (Daryk, St. Evre); with moderately concentrated acid, a brittle resin. (Zeller.) It readily takes fire with *fuming nitric acid* (St. Evre), leaving a brown resin. (Hasse, *Crell. Ann.* 1785, 1,422.) — 8. Treated with strong *sulphuric acid,* it frequently takes fire, and is converted into a red, acid resin, mixed with charcoal. (St. Evre.) Mixed with ½ pt. strong sulphuric acid, it turns greenish, yellowish-brown. (Zeller.) — 9. Saturated with *sulphurous acid,* it turns green, and afterwards orange-coloured, deposits sulphur, becomes hot, and yields a mixture which on standing separates into two strata, the upper, consisting of undecomposed oil, the lower of an oil boiling at 235°, and represented by the formula $C^{10}H^{10}O^3$. If the action of sulphurous acid be continued for a longer period, an oil containing sulphur is formed, corresponding in composition to the formula $C^{20}H^{20}O^2S$. — 10. It is not altered by *phosphoric anhydride.* — 11. Distilled with *pentachloride of phosphorus,* it is converted into chloride of oil of sassafras, with violent evolution of hydrochloric acid. — 12. It is not attacked by *potassium.* — 13. Saturated with *ammonia* it yields bulky prisms containing 73·17 p. c. C, 6·18 p. c. H, and 20·65 O. (St. Evre.) Cooled oil of sassafras is rendered turbid by

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* This is wrong, $C^{18}H^{10}O^2$ = 80·60 C, 7·46 H, 11·94; perhaps it is $C^{18}H^{10}O^4$ = 72·00 C; 6·66 H; and 21·340.

ammonia, and becomes viscid, but not crystalline. (Bonastre.) — 14. It is not altered by *bichromate of potash* and *sulphuric acid* (St. Evre); deposits yellowish-brown, resinous flakes. (Zeller.) — 15. It is not affected by *chloride of zinc*. (St. Evre.)

Combinations. Dissolves in 4 or 5 pts. *alcohol* of sp. gr. 0·85, and sparingly in aqueous *alkalis*. (Zeller, Bonastre.)

Oxygen-nucleus $C^{20}H^8O^4$.

Pyroxanthin.

$C^{20}H^8O^4$?

SCANLAN. (1855.) *Phil. Mag. J.*, [3], 41, 395; also *J. pr. Chem.* 7, 94.
APJOHN & GREGORY. *Proc. of the Roy. Irish Acad.* 1836, 33; *J. pr. Chem.* 13, 70.
SCHWEIZER. *J. pr. Chem.* 44, 129.

Eblanin. Discovered simultaneously by Pasch & Scanlan (1835), and named after the place of residence of the latter. (Dublin, *lat.* Eblana.)

Formation. 1. By heating the precipitate formed by lime in crude wood-spirit. — 2. By saturating the most volatile portion of crude wood spirit with *lime*, and heating. — 3. By the action of potash on the pyroxanthogen contained in crude pyroligneous acid. (Schweizer.)

Preparation. 1. Crude wood spirit is distilled till 15 p. c. has passed over; the distillate containing acetic acid is saturated with lime and redistilled; and from the dry, dark-coloured residue, consisting of acetate of lime, lime, brown resin, and pyroxanthin, the first two substances are extracted with hydrochloric acid, after which it is repeatedly boiled with alcohol. The first extracts contain almost exclusively a brown resin, smelling like pitch; the last contain principally pyroxanthin; these are evaporated, and the crystals thereby deposited are recrystallised from alcohol. (Apjohn & Gregory.) — 2. The most volatile part of crude pyroligneous acid (from ash-wood) is distilled in a water-bath, till the distillate will scarcely take fire, and the residue is distilled alone over a naked flame, till nothing but water containing acetic acid passes over. This second distillate is supersaturated with potash, and the orange-yellow flakes thereupon deposited are washed on a filter, first with water, and then repeatedly with a small quantity of hot alcohol, to remove the resin, which is especially deposited when the liquid has been nearly saturated. It is then dissolved in boiling alcohol, and the crystals deposited on cooling are recrystallised from alcohol. If the flocculent precipitate produced by potash is immediately crystallised from alcohol instead of being first washed with a small quantity of warm alcohol, in order to remove the greater part of the adhering resin, the crystals obtained are difficult to purify. (Schweizer.)

Properties. Long, yellow needles which begin to sublime in a current of air at 134°, melt at 144°, solidify in crystals on cooling. (Apjohn & Gregory.)

			Apjohn.	Gregory.
20 C	120	75·00	74·1	74·3
8 H	8	5·00	6·1	5·5
4 O	32	20·00	19·8	20·2
$C^{20}H^8O^4$	160	100·00	100·0	100·0

$C^{21}H^9O^4$, according to Gregory, $C^{24}H^{10}O^4$, according to Gmelin.

Decompositions. 1. It is decomposed by heat in closed vessels. 2. It is partly decomposed by dry *gaseous chlorine* between 80° and 100° into a blackish brown resin, with evolution of hydrochloric acid. — 3. It is violently attacked by *fuming nitric acid*, being converted into oxalic acid and a substance which explodes by heat. Dissolves in concentrated nitric acid without evolution of gas; the solution mixed with water deposits a brownish yellow substance, which explodes by heat when dried, dissolves in potash, and is not reprecipitated from this solution by acetic acid. — 4. With cold strong *sulphuric acid*, it turns reddish brown, afterwards blackish brown, and finally deposits blackish brown flakes. Strong sulphuric acid, diluted with an equal bulk of water, dissolves pyroxanthin, even at a gentle heat, with fine purple-red colour; the solution, after a few days, deposits blackish brown flakes, but as long as it remains purple red, it deposits unchanged pyroxanthin on addition of water. — 5. Dissolves in *concentrated hydrochloric acid*, forming a magnificent purple red solution. The freshly prepared solution deposits unchanged pyroxanthin on addition of water, but after a time loses its colour, especially in the air, and deposits blackish brown flakes. (Apjohn & Gregory.)

Combinations. Pyroxanthin is insoluble in *water*, slightly soluble in *aqueous potash* and in *ammonia*.

Dissolves in *glacial acetic acid*, and is precipitated therefrom by water.

Dissolves in *alcohol* and in *ether*; crystallises from the hot concentrated solution on cooling, and is precipitated therefrom by water. (Apjohn & Gregory.)

Appendix to Pyroxanthin.

Pyroxanthogen.

SCHWEIZER. (1848.) *J. pr. Chem.* 44, 129.

Source and Preparation. Occurs in crude pyroligneous acid. The wood-spirit is first distilled from this liquid, and the residue is then distilled alone, as long as water containing acetic acid passes over. This second distillate is then mixed with ether and allowed to stand for 24 hours with frequent shaking; the stratum of ether swimming on the surface of the liquid is poured off and distilled; the residue is mixed with water; and the heavy brownish oil thereby precipitated is repeatedly washed with water and distilled several times with water.

Properties. Transparent, colourless, or yellowish oil, heavier than water. Solidifies at —28° in a white, fatty mass. It has a disagreeable odour of smoked fish, and a strong pungent taste.

It is probably a mixture. (Schweizer.)

Decompositions. 1. It acquires a darker colour on exposure to *air* and *light.* — 2. Yields a dark distillate by heat, and leaves a dark yellow and, finally, black resinous residue. — 3. Its aqueous or alcoholic solution is decomposed by *potash, lime*, or *baryta* (also by *carbonate of potash* and by *ammonia* with the aid of heat); yielding (1) a precipitate of pyroxanthin; (2) a reddish-brown, easily fusible resin, insoluble in water, sparingly soluble in aqueous potash, and readily soluble in alcohol and in ether; (3) a soft resin smelling of creosote, precipitated from the solution by sulphuric acid; (4) a yellowish oil, which may be extracted from the solution by ether, resembles pyroxanthogen, but no longer yields pyroxanthin with potash; and (5) a peculiar acid.—4. It reduces mercury from mercurous salts. — 5. Its alcoholic solution precipitates *acetate of lead* on addition of ammonia, in thick white flakes.

Combinations. Dissolves very sparingly in cold *water*, more readily in hot water; readily in *wood-spirit, alcohol*, and *ether*. (Schweizer.)

Bromine-nucleus $C^{20}BrH^{11}$.

Bromocuminol.

$C^{20}BrH^{11}O^2 = C^{20}BrH^{11},O^2$.

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 86.

Hydrure de bromocumyle.

Dry bromine reacts on cuminol in the same manner as chlorine, and forms bromocuminol as a heavy oil, which is readily resolved by water into cuminic acid and hydrobromic acid. The aqueous solution of bisulphite of soda and cuminol is decomposed by bromine, with formation of sulphuric acid and separation of cuminol, which is converted by excess of bromine into a crystalline, readily fusible substance, which combines with the bisulphites and is probably bromide of cumyl (bromocuminol ?). (Bertagnini, *Ann. Pharm.* 87, 277.)

Chlorine-nucleus $C^{20}ClH^{11}$.

Chloride of Cumyl.

$C^{20}H^{11}ClO^2 = C^{20}ClH^{11},O^2$.

CAHOURS. (1841.) *Compt. rend.* 22, 846; *Ann. Pharm.* 60, 254; *Compt. rend.* 25, 724.—*N. Ann. Chim. Phys.* 23, 347; *J. pr. Chem.* 45, 144; extr. *Ann. Pharm.* 70, 45.

Chlorcumyl, Cumylchlorür.

Formation and Preparation. Pentachloride of phosphorus reacts on cuminic acid below 60°, evolving large quantities of hydrochloric acid, and yields a mixture of oxychloride of phosphorus and chloride of cumyl. The product is rectified, and the portion distilling between 250° and 260° is collected apart, washed with cold water, dried over chloride of calcium and rectified. (Cahours.)—Oxychloride of phosphorus with 3 at. cuminate of soda yields chloride of cumyl. — Terchloride of phosphorus reacts at common temperatures on the alkaline cuminates, forming chloride of cumyl and an alkaline phosphite, which readily attacks the chloride of cumyl, so that the distillate is rendered impure by substances containing phosphorus. (Gerhardt, *Ann. Pharm.* 87, 64.)

Properties. Colourless, very mobile liquid of sp. gr. 1·07 at 15°. Boils between 256° and 258°.

			Cahours.
20 C	120	65·79	65·75
11 H	11	6·03	6·17
Cl	35·5	19·41	19·71
2 O	16	8·77	8·37
$C^{20}ClH^{11}O^2$	182·5	100·00	100·00

Isomeric with chlorocuminol.

Decompositions. 1. It is decomposed by moist *air* into hydrochloric and cuminic acids. — 2. Boiled with *aqueous potash*, it quickly yields the same products. — 3. By dry *gaseous ammonia* (Cahours) and by *carbonate of ammonia* (Gerhardt and Chiozza, p. 167), it is converted into cumamide. — 4. It becomes strongly heated with *alcohol*, and, on adding water to the liquid, cuminate of ethyl is separated as a light oil. With the *silver-compound of glycocol*, it forms cuminuric acid (Cahours, p. 160); with *phenylate of potash*, cuminate of phenyl (Williamson & Scrugham, p. 157); with *aniline*, cumanilide (Cahours, p. 177); with *sulphophenylamide*, cumylosulphophenylamide (p. 177), and at a higher temperature, cumonitrile and sulphophenylic acid; with *benzoylsulphophenylargentamide*, cumylbenzoylsulphophenylamide (p. 179) (Gerhardt & Chiozza); with *salicylous acid*, cumosalicyl (Cahours, p. 158); with *salicylate of soda*, cumosalicylic anhydride, and on distillation, cuminate of phenyl (Kraut, p. 157); with *salicylamide*, cumosalicylamide (Gerhardt & Chiozza, p. 179); with *oenanthylate of potash*, oenanthocuminic anhydride (Chiozza & Malerba, p. 159); with *nitranisidine*, the compound corresponding to benzonitranisidide (xii, 269); with *nitrocumidine*, a crystallisable product (Cahours, p. 352); with *cuminol-potassium*, cumyl (Chiozza, p. 154); with *cuminate of potash*, cuminic anhydride (Gerhardt, p. 159); with *eugenic acid*, cumeneugenyl (Cahours); with *piperidine*, cumylopiperide. (Cahours.)

Chlorocuminol.

$C^{20}ClH^{11}O^2 = C^{20}ClH^{11},O^2$.

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 82.

Hydrure de chlorocumyle.

Preparation. Dry chlorine gas passed in daylight through cuminol previously dried over chloride of calcium, is absorbed with evolution of hydrochloric acid. The liquid becomes heated, turns red, and is then gradually decolorised, and after a few hours becomes saturated with chlorine, whereupon the excess of chlorine and the hydrochloric acid are expelled by a stream of carbonic acid, and the product is kept so as to preserve it from air and moisture.

Properties. Yellowish liquid, heavier than water. It has a very powerful odour, differing from that of cuminol.

			Gerhardt & Cahours. *average.*
20 C	120	65·79	64·64
11 H	11	6·03	6·54
Cl	35·5	19·41	22·18
2 O	16	8·77	6·64
$C^{20}H^{11}ClO^2$	182·5	100·00	100·00

Isomeric with chloride of cumyl.

According to Gerhardt & Cahours, it had absorbed hydrochloric acid, and consequently gave too little C, and too much H and Cl.

Decompositions. 1. Decomposed by moist air into hydrochloric and cuminic acids. It does not keep well, even in stoppered bottles, but turns red, becomes turbid, and evolves fumes of hydrochloric acid; perhaps a spontaneous decomposition takes place without the intervention of moist air. — 2. It is decomposed by *distillation* into hydrochloric acid, carbon, and a peculiar volatile oil. — 3. It dissolves completely in a few moments in boiling *aqueous potash*, as chloride of potassium and cuminate of potash. — 4. Strong *sulphuric acid* dissolves chlorocuminol with evolution of hydrochloric acid, forming a crimson solution which in contact with moist air soon deposits crystals of cuminic acid. — 5. When dry *gaseous ammonia* is passed through chlorocuminol, it becomes thick and stops up the tube; if the chlorocuminol is dissolved in absolute alcohol, a large quantity of chloride of ammonium is immediately deposited, and on adding water to the decanted liquid, a chlorinated oil is precipitated, which with potash yields cuminic acid, and when heated by itself, hydrochloric acid, charcoal, and a peculiar *volatile oil.* Hence ammonia appears merely to combine with the hydrochloric acid formed by the slow decomposition of the chlorocuminol, and not to act on the compound itself. — 6. It does not yield cuminate of ethyl with *absolute alcohol.*

Chlorine-nucleus $C^{20}Cl^2H^{10}$.

Chloronicene.

$C^{20}Cl^2H^{10}$.

St. Evre. (1849.) *N. Ann. Chim. Phys.* 25, 495; also *Ann. Pharm.* 70, 263; also *J. pr. Chem.* 46, 458.

Nicène monochloré.

Formation and Preparation. By distilling chloroniceic acid ($C^{12}ClH^5O^4$, xi, 176) with excess of lime or baryta:

$$2C^{12}ClH^5O^4 = C^{20}Cl^2H^{10} + 4CO^2.$$

Chloronicene then passes over first, as a brown-yellow liquid, then paranicene, $C^{10}H^{6}$ or $C^{20}H^{12}$, in yellow crystals.

Impure chloronicëic acid may be used for the preparation, in which case the distillate will contain benzene, $C^{12}H^{6}$. This may be distilled off at 90° in a stream of carbonic acid or hydrogen (air would decompose it); and if the receiver be then changed, chloronicene may be collected between 290° and 295°, and there remains a liquid mixture of chloronicene and a solid hydrocarbon which solidifies on cooling.

Properties. Pale yellow oil, of sp. gr. 1·141 at 10°, boiling between 292° and 294°, and having a vapour-density of 7·52. In vessels containing air, it turns brown after some weeks.

			St. Evre. *mean.*
20 C	120·0	59·76	60·71
2 Cl	70·8	35·26	34·69
10 H	10·0	4·98	5·52
$C^{20}Cl^{2}H^{10}$	200·8	100·00	100·92

	Vol.	Density.
C-vapour	20	8·3200
Cl-gas	2	4·9086
H-gas	10	0·6930
Vapour	2	13·9216
	1	6·9608

Thus according to Laurent & Gerhardt. (*Compt. chim.* 1849, 163). According to St. Evre, the atomic weight is only half as great. Gerhardt afterwards regarded it as identical with chloride of phenyl, $C^{12}H^{5}Cl$ (see page 142).

Fuming nitric acid attacks the compound with violence, converting it into nitrochloronicene and a resin.

Oxybromine-nucleus $C^{20}Br^{8}H^{2}O^{2}$.

Brom-sassafras Oil.

$$C^{20}H^{2}Br^{8}O^{4} = C^{20}H^{2}Br^{8}O^{2},O^{2}.$$

ST. EVRE. (1846.) *N. Ann. Chim. Phys.* 12, 107; also *J. pr. Chem.* 34, 372; abstr. *Compt. rend.* 18, 735; *N. J. Pharm.* 10, 314.

Formation and Preparation. When bromine is slowly dropped into sassafras oil, a large quantity of hydrobromic acid is evolved, and the oil becomes crystalline. The crystalline mass is pressed between paper, washed with the smallest possible quantity of ether, which separates free bromine and a fibrous substance resembling solid chloride of carbon, and dried in vacuo at 130°.

Properties. White needles united in tufts.

			St. Evre.
20 C	120	15·12	14·64
2 H	2	0·25	0·25
8 Br	640	80·60	79·84
4 O	32	4·03	5·27
$C^{20}H^{3}Br^{8}O^{4}$	794	100·00	100·00

Decompositions. 1. By *chlorine* in sunshine, it is converted into a tough mass, free from hydrogen and resembling sesquichloride of carbon — 2. Heated with *aqueous potash,* it yields a brittle translucent resin still containing bromine.

It dissolves in boiling *ether.*

Oxychlorine-nucleus $C^{20}Cl^9HO^2$.

Chlor-sassafras Oil.

$C^{20}HCl^9O^4 = C^{20}Cl^9HO^2,O^2$.

St. Evre. (1846.) *N. Ann. Chim. Phys.* 12, 107; also *J. pr. Chem.* 34, 372; abstr. *Compt. rend.* 18, 735; *N. J. Pharm.* 10, 314.

Formation and Preparation. By distilling in the oil-bath a mixture of sassafras oil and pentachloride of phosphorus, washing the oily distillate with water to remove oxychloride of phosphorus and hydrochloric acid, and rectifying it over oxide of lead in a stream of carbonic acid.

Properties. Boils at 238°.

Nitro-nucleus $C^{20}XH^{11}$.

Nitroparanicene.

$C^{20}NH^{11}O^4 = C^{20}XH^{11}$.

Paranicène nitrogéne. (Compare page 142.)

Formation and Preparation (p. 142.) Paranicene is dissolved in fuming nitric acid, and the needles which separate on cooling are freed from resin by recrystallisation from alcohol and ether.

			St. Evre. *mean.*
20 C	120	67·79	67·63
N	14	7·91	8·12
11 H	11	6·21	5·87
4 O	32	18·09	18·38
$C^{20}XH^{11}$	177	100·00	100·00

Hydrosulphate of Ammonia converts it into paranicene (St. Evre, *N. Ann. Chim. Phys.* 25, 506.)

Nitrocuminic Acid.

$C^{20}NH^{11}O^{8}=C^{20}XH^{11},O^{4}$.

CAHOURS. (1848.) *Compt. rend.* 24, 554; *N. Ann. Chim. Phys.* 25, 36; *J. pr. Chem.* 46, 346; *Ann. Pharm.* 69, 243.—*N. Ann. Chim. Phys.* 53, 334; *Ann. Pharm.* 109, 18.

First observed in 1841, by Gerhardt & Cahours (*N. Ann. Chim. Phys.* 1, 69.)

Formation. By the action of fuming nitric acid on cuminic acid. (Cahours.) — 2. If a solution of cuminic acid in cold nitro-sulphuric acid be mixed with water, nitro-cuminic acid separates from it after a short time. (Kraut, *N. Br. Arch.* 96, 274.)

Preparation. Cuminic acid is dissolved in warm concentrated nitric acid; the solution is heated to the boiling point, whereupon red vapours are evolved, but no violent action takes place; and after boiling for some minutes, it is precipitated with water. It then deposits a yellow, heavy, quickly solidifying oil, which must be washed two or three times with water and recrystallised from alcohol.

Properties. Yellowish white crystalline scales.

			Cahours. *mean.*
20 C	120	57·41	57·33
N	14	6·69	6·79
11 H	11	5·26	5·37
8 O	64	30·64	30·51
$C^{20}XH^{11}O^{4}$	209	100·00	100·00

Decompositions. 1. On treating the ammonia-salt with *sulphuretted hydrogen* (Cahours), or with iron-filings and acetic acid, (Boullay, *Compt. rend.* 43, 399), it is converted into amidocuminic acid. — 2. It is not altered by boiling with chromate of potash and sulphuric acid. (Hofmann, *Ann. Pharm.* 97, 206.)

Combinations. The acid is insoluble in *water.* It dissolves very readily in *ammonia,* potash and soda, forming crystallisable salts.

Nitrocuminate of Lime. Yellow needles grouped in stars. Becomes darker coloured by exposure to light. When dried at 100°, it contains 8·54 p.c. calcium, and is therefore $C^{20}CaXH^{10}O^{4}$ (calculation 8·77 p.c. Ca.) (Kraut, *N. Br. Arch.* 96, 274.)

Nitrocuminate of Silver. Obtained from the ammonia-salt by double decomposition. Beautifully white. Contains after drying in vacuo, 34·0 p.c. Ag. ($C^{20}AgXH^{10}O^{4}$ = 34·17 p.c. Ag.)

Nitrocuminic acid dissolves readily in *alcohol* and *ether.*

Nitro-nucleus $C^{20}X^2H^{10}$.

Binitrocuminic Acid.

$C^{20}H^{10}N^2O^{12} = C^{20}X^2H^{10},O^4$.

CAHOURS. (1849.) *N. Ann. Chim. Phys.* 25, 36; *J. pr. Chem.* 46, 346; *Ann. Pharm.* 69, 243.
BOULLEY. *Compt. rend.* 43, 309; *Chem. Centr.* 1856, 782.
KRAUT. *N. Br. Arch.* 96, 274; *Chem. Centr.* 1859, 85.

Formation and Preparation. Fused cuminic acid dissolves without evolution of gas in nitrosulphuric acid; and the solution on being heated to the boiling point, gives off red vapours, becomes turbid, and soon deposits crystalline laminæ, which may be washed with water and recrystallised from alcohol. (Cahours.) The solution of cuminic acid in nitrosulphuric acid is precipitated with water, after standing for 24 hours at a medium temperature; the precipitated brown powder is washed with water, and boiled with milk of lime; and the filtered solution is mixed with hydrochloric acid, which precipitates binitrocuminic acid, — to be purified by washing with water and recrystallisation from alcohol. (Kraut.)

Properties. Laminæ having a strong lustre. (Cahours.) Light yellow crystals of the doubly oblique prismatic system. Henhenohedrons (*Fig.* 121.) with the angles $u : y = 83° 32·1'$; $y : v = 82° 50'$; $u : v = 87° 4·5'$. The acute edge $y\ v$, is truncated by a dodecahedral face inclined to y at 118° 2·9′, and to v at 154° 47·1′; there is also to the left in front an octohedral face making with u an angle of 133° 2·1′, and to the left behind an octohedral face making with u an angle of 133° 4·2′. Disregarding the slight inequality of these last two angles, the face u, the two octohedral faces, and the dodecahedral face form together a rhombic prism with perpendicularly truncated edges, the faces y and v resting upon it in a doubly oblique direction. Cleavage parallel to u. (v. Dauber.)

Becomes darker in colour by exposure to light. (Kraut.)

			Cahours.	Kraut.
			mean.	*mean.*
20 C	120	47·24	47·27	47·31
2 N	28	11·02	10·83	
10 H	10	3·93	3·99	4·45
12 O	96	37·81	37·91	
$C^{20}X^2H^{10}O^4$	254	100·00	100·00	

Decompositions. 1. Not acted upon by fuming *nitric acid,* even at the boiling heat. (Cahours.) — 2. Treated with *iron filings* and *acetic acid,* it forms biamidocuminic acid. (Boullet.)

Combinations. According to Cahours, binitricuminic acid does not possess acid properties, being neither dissolved nor decomposed by warm ammonia, potash or soda-ley. According to Kraut, on the contrary, it does behave like an acid, and forms salts which acquire a darker yellowish red colour by exposure to light.

Binitrocuminate of Baryta. Obtained by dissolving the acid in baryta-water, precipitating the excess of baryta with carbonic acid, boiling, and evaporating the filtered solution. It first separates in films which become crystalline under the mother-liquor. After drying over oil of vitriol, it does not diminish in weight at 120°. It contains 20·48 p. c. Ba. and is therefore $C^{20}BaX^2H^9O^4$. (Calculation = 21·30 Ba.) (Kraut.)

Binitrocuminate of Lime. — Prepared like the baryta-salt. Yellowish red crystalline needles, which dissolve easily in water, with deep wine-red colour, do not diminish in weight at 120° after drying over oil of vitriol, and contain 7·01 p. c. Ca.; therefore = $C^{20}CaX^2H^9O^4$ (calculation = 7·33 Ca.) (Kraut.)

Binitrocuminate of Silver. — Obtained by precipitating the aqueous solution of the lime-salt with nitrate of silver, and recrystallising from hot water. Light yellow needles, which are scarcely altered by exposure to light. After drying over oil of vitriol, they give off 5·26 p. c. water at 100° (2 At. = 4·74 p. c.): and then contain 29·76 p. c. Ag. ($C^{20}AgX^2H^9O^4$ = 29·91 p. c.) (Kraut.)

Binitrocuminic acid is soluble in *alcohol,* and easily soluble in *ether.*

Binitrocuminate of Ethyl.

$C^{24}N^2H^{14}O^{12} = C^4H^5O,C^{20}X^2H^9O^3$.

KRAUT. *N. Br. Arch.* 96, 278.

Obtained by repeatedly passing hydrochloric acid into alcoholic binitrocuminic acid and precipitating by water, and purified by treatment with carbonate of soda, washing with water, and recrystallisation from alcohol.

Colourless, aggregated needles. Melts at 77·5°

			Kraut.
24 C	144	51·07	50·44
2 N	28	9·93	
14 H	14	4·97	5·56
12 O	96	34·03	
$C^4H^5O,C^{20}X^2H^9O^3$	282	100·00	

Ammonia converts it into binitrocuminamide, which crystallises in thick yellow prisms soluble in alcohol. — Treated with iron filings and acetic acid, it forms biamidocuminate of ethyl. (Boullet, *Compt. rend.* 43, 399.)

Binitrocuminic ether is soluble in *alcohol.*

Nitrochlorine-nucleus $C^{20}X^2Cl^2H^8$.

Nitrochloronicene.

$C^{20}N^2Cl^2H^8O^8 = C^{20}X^2Cl^2H^8$.

ST. EVRE. *N. Ann. Chim. Phys.* 25, 495; *J. pr. Chem.* 46, 458; *Ann. Pharm.* 70, 263.

Nitronicène monochloré = $C^{10}XClH^4$ (St. Evre). See page 142.

Formation and Preparation. (comp. p. 167.) Chloronicene is treated with fuming nitric acid, and the resulting mass is dissolved in alcohol of 36°. The less soluble resin is then first deposited, and afterwards nitrochloronicene crystallises out, which may be further purified by recrystallisation from alcohol.

Long, amber-yellow, silky needles.

			St. Evre. *mean.*
20 C	120·0	41·26	40·92
2 N	28·0	9·63	8.62
2 Cl	70·8	24·34	24·09
8 H	8·0	2·75	2·83
8 O	64·0	22·02	23·54
$C^{20}X^2Cl^2H^8$	290·8	100·00	100·00

An alcoholic solution of *hydrosulphate of ammonia* turns it brown, then dark violet, and yields chloronicin, with deposition of sulphur.

Soluble in *alcohol* and in *ether*.

Amidogen-nucleus $C^{20}AdH^{11}$.

Cuminamide.

$C^{20}NH^{13}O^2 = C^{20}AdH^{11},O^2$.

F. Field. (1847.) *Ann. Pharm.* 65, 45; *Mem. Chem. Soc.* 3, 404; *Phil. Mag. J.* 31, 459; *J. pr. Chem.* 44, 136.

Gerhardt. *Ann. Pharm.* 87, 79.

Gerhardt & Chiozza. *Ann. Pharm.* 87, 299; *N. Ann. Chim. Phys.* 46, 135.

Formation. 1. By heating cuminate of ammonia. (Field.) — 2. By the action of *ammonia* on cuminate of ethyl. (Dumas, *N. Ann. Chim. Phys.* 23, 349.) — 3. By the action of dry *ammonia gas* (Cahours, *N. Ann. Chim. Phys.* 23, 249), or of *carbonate of ammonia* (Gerhardt & Chiozza) on chlorocumyl. — 4. Cuminic anhydride is gradually converted into cuminamide by the action of aqueous ammonia. — Benzo-cuminic anhydride is converted by ammonia into a mixture of benzamide or benzoate of ammonia and cuminamide, to be separated by aqueous ammonia, which dissolves chiefly the benzamide. (Gerhardt.) — 5. Cumonitrile is slowly converted into cuminamide by alcoholic ammonia. (Field.)

Preparation. 1. Chloride of cumyl is triturated in a mortar with carbonate of ammonia, and the mixture gently heated; whereupon carbonic acid is evolved, and cuminamide is produced, to be separated from sal-ammoniac and excess of carbonate of ammonia by washing with water. (Gerhardt & Chiozza.) — 2. When cuminate of ammonia is heated in a sealed tube in the oil-bath to the boiling point of the oil, or continuously heated in a retort to incipient fusion, cuminamide is produced, and may be purified by recrystallisation from boiling dilute aqueous ammonia. (Field.)

Properties. Crystallises by rapid separation from its concentrated aqueous solution, in tables; by slow separation from a dilute solution, in long opaque needles. (Field.)

			Field. *mean.*	Gerhardt.
20 C	120	73·68	73·66	73·28
N	14	8·52	8·50	
13 H	13	7·99	8·13	8·00
2 O	16	9·81	9·71	
$C^{20}NH^{13}O^2$	163	100·00	100·00	

Field's cuminamide was obtained by formation 1 and 5; Gerhardt's by 4.

Decomposition. Cuminamide withstands the action of strong acids and alkalis more obstinately than other amides, and is converted by them into ammonia and cuminic acid, only after very long boiling. From solution in aqueous potash, it crystallises in large tables. (Field.) — When fused with potassium it does not form cyanide of potassium. (Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 600.)

Combinations. Cuminamide is insoluble in cold, but soluble in hot *water*. (Field.) It is insoluble in cold *ammonia* (Field), very sparingly soluble in boiling ammonia. (Gerhardt.) It dissolves in all proportions in *alcohol* and in *ether*, whether cold or hot. (Field.)

Amidocuminic Acid.

$C^{20}NH^{13}O^4 = C^{20}AdH^{11},O^4$.

Cahours. *Compt. rend.* 44, 567; *Ann. Pharm.* 103, 87; *J. pr. Chem.* 72, 112. — *Compt. rend.* 46, 1044; *Ann. Pharm.* 107, 147; *J. pr. Chem.* 74, 223. — In detail: *N. Ann. Chim. Phys.* 53, 322; *Ann. Pharm.* 109, 10; abstr. *Rep. Chim. pure.* 1, 29.

Cuminamic acid, Cuminaminsaüre.

Formation and Preparation. Nitrocuminate of ammonia is reduced by excess of hydrosulphuric acid; the liquid is evaporated at a gentle heat till all the ammonia is expelled and the excess of sulphur is separated; the concentrated solution is precipitated by a slight excess of acetic acid; and the resulting precipitate is collected, washed, dried, and recrystallised from alcohol. (Cahours.) — It is also obtained by treating nitrocuminic acid with iron filings and acetic acid (a brisk action then taking place attended with rise of temperature, after which the mixture must be heated for a while in the water-bath); digesting the mixture with aqueous carbonate of soda; filtering; neutralising the excess of carbonate of soda with acetic acid; precipitating with acetate of lead; and decomposing the precipitate with hydrosulphuric acid. (Boullet, *Compt. rend.* 43, 399.)

Properties. Colourless or light yellow crystals. By spontaneous evaporation of the solutions, it is obtained in tables.

			Cahours.
20 C	120	67·04	66·80
N	14	7·81	
13 H	13	7·26	7·13
O	32	17·89	
$C^{20}NH^{13}O^4$	179	100·00	

Decompositions. 1. In solution in *nitric acid,* it is converted by *nitric oxide gas* into oxycuminic acid. — 2. By treating *alcoholic* amidocuminic acid with *nitrous acid,* light yellow needles are obtained, consisting of a new bibasic acid $=C^{40}N^3H^{23}O^8$ (P. Griess, *Compt. rend.* 49·80);

$$2\,C^{20}NH^{13}O^4 + NO^3 = 3\,HO + C^{40}N^3H^{23}O^8.$$

3. Distilled with *caustic baryta* or *lumps of potash,* it yields an alkaline carbonate together with cumidine.

Combinations. Dissolves sparingly in cold, much more freely in boiling *water.*

Amidocuminic acid unites with *acids,* forming crystalline salts. It unites also with *bases.* (Boullet, *Compt. rend.* 43, 399.)

Sulphate of Amidocuminic acid. — Amidocuminic acid is mixed in slight excess with oil of vitriol diluted with an equal bulk of water, and the mixture is dissolved in warm alcohol. On cooling, thin, white, silky needles are deposited. The compound has a slightly sweet taste, dissolves sparingly in cold, easily in hot water.

			Cahours.
20 C	120	52·64	53·01
N	14	6·14	
14 H	14	6·14	6·22
5 O	40	17·54	
SO^3	40	17·54	17·28
$C^{20}NH^{13}O^4,HO,SO^3$	228	100·00	

Hydrochlorate of Amidocuminic acid. — Amidocuminic acid dissolves slightly in boiling hydrochloric acid, and the solution on cooling deposits thin needles. The compound may also be prepared by adding alcohol to a mixture of amidocuminic acid and hydrochloric acid, whereby a considerable quantity of amidocuminic acid is dissolved, and evaporating. Delicate shining prisms, which dissolve in water, and are partly precipitated on addition of hydrochloric acid.

			Cahours.
20 C	120·0	55·68	55·56
N	14·0	6·49	
14 H	14·0	6·49	6·56
Cl	35·5	16·47	16·28
4 O	32·0	14·87	
$C^{20}NH^{13}O^4,HCl$	215·5	100·00	

Nitrate of Amidocuminic acid forms beautiful prisms.

Chloroplatinate of Amidocuminic acid. — Obtained by adding alcohol to the mixed solutions of concentrated bichloride of platinum and hydrochlorate of amidocuminic acid, warming the mixture till it dissolves, then filtering and leaving the solution to evaporate.

Long reddish needles.

				Cahours.
20 C	120·0	....	31·21	31·00
N	14·0	....	3·64	
14 H	14·0	....	3·64	3·79
3 Cl	106·5	....	27·69	
Pt	98·0	....	25·48	25·52
4 O	32·0	....	8·34	
$C^{20}NH^{13}O^4,HCl,PtCl^2$	384·5	....	100·00	

Amidocuminic acid dissolves in *alcohol* and in *ether* more readily than in water.

Amidocuminate of Ethyl.

$C^{20}NH^{17}O^4 = C^4H^5O,C^{20}AdH^{10}O^3$.

Cahours. *N. Ann. Chim. Phys.* 53, 340; *Ann. Pharm.* 109, 21.

Cuminamate éthylique, Cuminamic ether, Amido-cuminvinester.

Formation and Preparation. By quickly reducing an alcoholic solution of nitrocuminate of ethyl with hydrosulphate of ammonia, or with iron filings and acetic acid. (Boullet, *Compt. rend.* 43, 399.) — On evaporating the solution, an abundant separation of sulphur takes place; and the concentrated filtrate deposits a dark heavy oil, which may be purified by repeated solution in alcohol and precipitation with water.

				Cahours.
24 C	144	....	69·56	69·36
N	14	....	6·76	
17 H	17	....	8·21	8·34
4 O	32	....	15·47	
$C^4H^5O,C^{20}NH^{12}O^3$	207	....	100·00	

By *ammonia*, it is slowly converted into an amide, probably homologous with phenyl-urea. It dissolves in *sulphuric, hydrobromic, hydrochloric* and *nitric acids,* forming crystallisable compounds.

Amidogen-nucleus $C^{20}Ad^2H^{10}$.

Biamidocuminic Acid.

$C^{20}N^2H^{14}O^4 = C^{20}Ad^2H^{10},O^4$.

Boullet. (1856.) *Compt. rend.* 43, 399; *Chem. Centr.* 1856, 782.

Produced from binitrocuminic acid by the action of iron filings and acetic acid in the same manner as amidocuminic acid from nitrocuminic acid (p. 174).

Crystallises. Combines with bases.

Conjugated Amides of the Cuminic series.

Cumanilide.

$$C^{32}NH^{17}O^{2} = C^{20}(NH.C^{12}H^{5})H^{11}O^{2} \text{ or } C^{12}(NH.C^{20}H^{11}O^{2})H^{5}.$$

Cahours. (1848.) *N. Ann. Chim. Phys.* 23, 349; *J. pr. Chem.* 45. 129; abstr. *Ann. Pharm.* 70, 46.

Phenyl-cuminamide.

Chloride of cumyl becomes heated in contact with aniline, and yields a product, which, after washing with aqueous potash and recrystallisation from alcohol, forms silky needles resembling benzoic acid.

			Cahours. *mean.*
32 C	192	80·28	80·33
N	14	5·92	
17 H	17	7·11	7·07
2 O	16	6·69	
$C^{32}NH^{17}O^{2}$	239	100·00	

When treated with *phosphoric anhydride*, it does not yield cumanilnitrile. (Cahours, *Ann. Pharm.* 74, 40.)

It dissolves sparingly in *alcohol.*

Cumyl-sulphophenylamide.

$$C^{32}NH^{17}S^{2}O^{6} = C^{12}(NH.C^{20}H^{11}O^{2})H^{5}S^{2}O^{4}.$$

Gerhardt & Chiozza. (1856.) *N. Ann. Chim. Phys.* 46, 151.

Azoture de sulfophényle et d'hydrogène.

Preparation. Sulphophenylamide is treated with chloride of cumyl in the oil-bath at a constant temperature; it is then rapidly attacked, and on cooling solidifies to an amorphous glassy mass, which may be crystallised from alcohol. If the temperature were allowed to rise too high, cumonitrile and sulphocarbolic acid would be produced.

Properties. Rectangular prisms, with shining, well-developed terminal faces. Melts at 161°.

			Gerhardt & Chiozza.
32 C	192	63·4	63·3
N	14	4·6	4·7
17 H	17	5·6	5·7
2 S	32	10·5	
6 O	48	15·9	
$C^{32}NH^{17}S^{2}O^{6}$	303	100·0	

When quickly *heated* in a test-tube, it yields cumonitrile. — Treated in a slightly ammoniacal solution with *nitrate of silver*, it yields cumyl-sulphophenylargentamide, and in presence of a larger quantity of ammonia, a sticky mass, probably amidocumylsulphophenate of silver.

It does not dissolve in boiling *water*. It dissolves readily in warm aqueous ammonia; also in cold, and still more in hot *alcohol*.

Cumyl-sulphophenylargentamide.

$C^{32}NH^{16}AgS^2O^6 = C^{12}(N.Ag.C^{20}H^{11}O^2)H^5S^2O^4$.

Gerhardt & Chiozza. (1854.) *Compt. rend.* 38, 457; *Ann. Pharm.* 90, 107; fully, *N. Ann. Chim. Phys.* 46, 153.

Azoture de sulfophényle, de cumyle et d'argent.

Preparation. Cumyl-sulphophenylamide suspended in boiling water is dissolved by addition of a few drops of ammonia, and the solution is precipitated by nitrate of silver.

Properties. Very light, slender needles.

			Gerhardt & Chiozza.
32 C	192	46·8	46·4
N	14	3·4	3·2
16 H	16	3·9	3·9
Ag	108	26·3	
2 S	32	7·8	
6 O	48	11·8	
$C^{32}NH^{16}AgS^2O^6$	410	100·0	

It decomposes quietly when *heated*, giving off cumonitrile. — It dissolves readily in *ammonia*, and the solution when evaporated yields cumyl-sulphophenyl-argent-hydrobiamide.

Scarcely soluble in boiling *water*.

Cumyl-sulphophenyl-argent-hydrobiamide.

$C^{32}N^2H^{19}S^2O^6 = C^{12}(N.Ag.C^{20}H^{11}O^2)H^5S^2O^4 + NH^3$.

Gerhardt & Chiozza. (1854.) *Compt. rend.* 38, 457; *Ann. Pharm.* 90, 107; *J. pr. Chem.* 62, 49.—In detail, *N. Ann. Chim. Phys.* 46, 154.

Diazoture de sulfophényle, de cumyle, d'argent, et d'hydrogène.

Preparation. By dissolving cumyl-sulphophenylargentamide in ammonia, and leaving the solution to evaporate. If evaporated by heat, it yields an oil.

Properties. Nacreous needles, grouped like a fan.

			Gerhardt & Chiozza.
32 C	192	45·0	45·0
2 N	28	6·5	6·2
19 H	19	4·5	4·7
Ag	108	25·3	
2 S	32	7·5	
6 O	48	11·2	
$C^{32}N^2H^{19}AgS^2O^6$	427	100·0	

By continued boiling with *water*, it gives off a little ammonia. Dissolves very sparingly in boiling *water*. Soluble in *alcohol.*

Cumyl-benzoyl-sulphophenylamide.

$C^{46}NH^{21}S^2O^8 = C^{12}(N.C^{20}H^{11}O^2.C^{14}H^5O^2)H^5S^2O^4.$

Gerhardt & Chiozza. (1853.) *Compt. rend.* 37, 86; *Ann. Pharm.* 87, 302. — In detail, *N. Ann. Chim. Phys.* 46, 149.

Azoture de sulfophényle, de benzoile et de cumyle.

Produced by the action of chloride of cumyl on benzoyl-sulphophenyl-argentamide, and obtained in confused prisms by dissolving the product in boiling ether and evaporating the ether.

Scarcely soluble in *water*. Dissolves with difficulty in *ammonia* ; the solution is precipitated by *acids* and by the salts of *lead* and *silver.*

Dissolves in *alcohol* more readily than benzoyl-salicylamide. Sparingly soluble in *ether.*

Cumyl-salicylamide.

$C^{34}NH^{17}O^6 = C^{20}(N.C^{14}H^6O^4)H^{11}O^2$?

Gerhardt & Chiozza. (1853.) *Compt. rend.* 37, 86; *Ann. Pharm.* 87, 301; *J. pr. Chem.* 60, 144. — In detail, *N. Ann. Chem. Phys.* 46, 141.

Azoture de salicyle, de cumyle et d'hydrogène.

Obtained by the action of chloride of cumyl on salicylamide (xii. 321), in a similar manner to benzoyl-salicylamide.

Properties. Very light, shining needles. Melts at about 200°, becomes pasty at a stronger heat, and remains so on cooling.

			Gerhardt & Chiozza. *mean.*
34 C	204	72·0	71·85
N	14	4·9	5·10
17 H	17	6·0	6·10
6 O	48	17·1	16·95
$C^{34}NH^{17}O^6$	283	100·0	100·00

Azo-nucleus $C^{20}NH^{11}$.

Cumonitrile $C^{20}NH^{11}$.

Fr. Field. (1847.) *Ann. Pharm.* 65, 51; *Mem. Chem. Soc.* 3, 408; *J. pr. Chem.* 44, 136; *Phil. Mag. J.* 31, 459.

Formation. 1. By the dry distillation of cuminate of ammonia, cuminamide being formed at the same time. — 2. By the action of bromide of cyanogen on cuminate of potash, carbonic acid being likewise evolved. (Cahours, *N. Ann. Chim. Phys.* 52, 201; *Ann. Pharm.* 108, 320,

$$C^{20}H^{11}KO^4 + C^2NBr = 2CO^2 + KBr + C^{20}NH^{11}.$$

3. By the action of heat on cumyl-sulphophenylamide and on cumyl-sulphophenylargentamide. If, in the preparation of cumyl-sulphophenylamide, the mixture of chloride of cumyl and sulphophenylamide be too strongly heated, cumonitrile and sulphocarbolic acid are produced. (Gerhardt & Chiozza, *N. Ann. Chim Phys.* 46, 157.)

Preparation. Cuminate of ammonia is heated in a retort to complete fusion and then maintained in violent ebullition, whereupon large drops of cumonitrile pass over together with water. As soon as the oil has completely passed over, it is separated with a pipette from the distillate, and the watery liquid is poured back into the cooled retort, and redistilled five or six times. The whole of the oil thus obtained is freed by washing with ammonia from traces of cuminic acid dissolved in the oil; it is then washed successively with hydrochloric acid and water, dried by leaving it for some days over chloride of calcium, and rectified. The portion which goes over last may contain water.

Properties. Transparent, colourless oil of sp. gr. 0·765 at 14°. Refracts light strongly. Boils constantly from platinum wire at 239°, under pressure of 0·7585 met. Has a very strong, but agreeable odour, and a burning taste.

			Field. *mean.*
20 C	120	82·76	82·83
N	14	9·66	9·34
11 H	11	7·58	7·77
$C^{20}NH^{11}$	145	100·00	99·94

Decompositions. 1. The vapour of cumonitrile is inflammable and *burns* with a brilliant flame. — 2. Cumonitrile is but slightly altered by strong *nitric acid* in the cold, but on boiling, cuminic or nitrocuminic acid is produced. — 3. Heated with *potassium,* it becomes darker and forms a large quantity of cyanide of potassium. — 4. Alcoholic *potash,* does not alter it immediately, but converts it, after a few days, into a crystalline pulp consisting of the oil turned yellow and cuminamide.

Cumonitrile dissolves but slightly in *water,* and renders it milky.

Paranicine.

$C^{20}NH^{13} = C^{20}NH^{11},H^2$.

St. Evre. *N. Ann. Chim. Phys.* 25, 506; *Ann. Pharm.* 70, 266; *J. pr. Chem.* 46, 468.

Compare page 142.

Formation and Preparation (comp. p. 169.) Sulphuretted hydrogen is passed through *alcoholic* solution of nitroparanicine saturated with ammonia; the liquid is evaporated; the residue is dissolved in weak hydrochloric acid; and the filtrate is left to crystallise, whereupon octohedrons of hydrochlorate of paranicine separate out. From this salt ammonia precipitates paranicine in pale yellow flocks.

			St. Evre.
20 C	120	81·63	81·34
N	14	9·53	9·51
13 H	13	8·84	8·82
$C^{20}NH^{13}$	147	100·00	99·67

If paranicine be dissolved in ether immediately after precipitation, and the ether then evaporated, there remains an amber-coloured oil, which dissolves in hydrochloric acid, and is precipitated by ammonia in snow-white flocks. These flocks dissolve in cold ether, and on evaporating remain as a solid mass, without passing through the liquid state.

Paranicine is insoluble in *water*.

Its solutions in dilute *nitric, acetic* and *oxalic acids,* yield crystallisable salts soluble in water.

Hydrochlorate of Paranicine. Octohedrons which redden litmus. Decomposes readily by contact with the air. Insoluble in cold water.

			St. Evre. *mean.*
20 C	120·0	65·57	65·59
N	14·0	7·65	7·86
14 H	14·0	7·65	7·73
Cl	35·9	19·13	
$C^{20}NH^{19},HCl$	183·5	100·00	

Chloroplatinate of Paranicine. Obtained by precipitating the hydrochlorate with bichloride of platinum. Crystalline precipitate which becomes liquid after a while, and is altered by light and air.

			St. Evre.
20 C	120·0	34·00	33·71
N	14·0	3·97	
14 H	14·0	3·97	4·31
Pt	98·7	27·96	27·77
3 Cl	106·2	30·10	29·00
$C^{20}NH^{13},HCl,PtCl^2$	352·9	100·00	

Paranicine is soluble in *acetic acid* and in *ether*.

Chlorazo-amidogen-nucleus $C^{20}Cl^2NAdH^8$.

Chloronicine.

$$C^{20}N^2Cl^2H^{12} = C^{20}Cl^2NAdH^8,H^2.$$

St. Evre. (1849.) *N. Ann. Chim. Phys.* 25, 499; *J. pr. Chem.* 46, 463; *Ann. Pharm.* 70, 265.

Formation and Preparation (comp. p. 173.) Into an alcoholic solution of nitrochloronicine, ammonia gas and hydrosulphuric acid are passed alternately, as long as sulphur continues to deposit; the liquid is boiled down; the residue exhausted with dilute hydrochloric acid, and the gold-yellow filtrate evaporated to the crystallising point. In this manner, hydrochlorate of chloronicine is obtained, the concentrated aqueous solution of which, on being mixed with ammonia, deposits brown flocks of chloronicine, which dissolve on addition of more water and are therefore difficult to purify.

			St. Evre.
20 C	120·0	51·99	51·54
2 N	28·0	12·13	13·39
2 Cl	70·8	30·67	29·58
12 H	12·0	5·21	5·61
$C^{20}N^2Cl^2H^{12}$	230·8	100·00	100·12

St. Evre supposed the atomic weight to be half this amount. Laurent & Gerhardt doubled his formula (*Compt. chim.* 1849, 163).

According to Gerhardt, the compound is perhaps identical with chloraniline (comp. p. 142).

Decompositions. 1. The solution of hydrochlorate of chloronicine neutralised with ammonia acquires an alkaline reaction after a while from decomposition. The solution of chloronicine in ether leaves on evaporation a pale brown oil which dissolves completely in cold hydrochloric acid, forming a solution from which ammonia throws down paranicine (p. 181.)

Hydrochlorate of Chloronicine. Light yellow, slender prisms, generally united in stars by threes. Reddens litmus strongly. Turns brown on the surface when exposed to the air. — Its concentrated solution mixed with a few drops of ammonia, immediately turns hyacinth-red and deposits chloronicine in brown flocks. Dissolves very easily even in cold water.

			St. Evre. *mean.*
20 C	120·0	39·52	40·32
2 N	28·0	9·22	9·91
4 Cl	141·6	46·62	45·52
14 H	14·0	4·64	5·48
$C^{20}N^2Cl^2H^{12},2HCl$	303·6	100·00	101·23

Chloride of mercury precipitates hydrochlorate of chloronicine.

Chloroplatinate of Chloronicine. Prepared by mixing aqueous hydrochlorate of chloronicine with bichloride of platinum, evaporating, and washing the deep yellow granular precipitate with ether.

			St. Evre.
20 C	120·0	18·67	18·83
2 N	28·0	4·35	5·38
8 Cl	283·2	44·07	43·64
14 H	14·0	2·18	1·93
2 Pt	197·4	30·73	30·22
$C^{20}N^2Cl^2H^{12},2HCl,2PtCl^2$	642·6	100·00	100·00

Acetate of Chloronicine. Chloronicine recently prepared and dried in vacuo, is dissolved in dilute acetic acid, and the solution is evaporated in vacuo.

Pale yellow, four-sided prisms, easily decomposible by light and air. Has an acid reaction, even after repeated recrystallisation.

			St. Evre.
28 C	168·0	47·88	47·56
2 N	28·0	7·98	8·41
2 Cl	70·8	20·18	19·88
20 H	20·0	5·70	6·32
8 O	64·0	18·26	17·83
$C^{20}N^2Cl^2H^{12},2C^4H^4O^4$	350·8	100·00	100·00

Primary Nucleus $C^{20}H^{14}$.

Cymene. $C^{20}H^{14}$.

Gerhardt & Cahours. (1841.) *N. Ann. Chim. Phys.* 1, 102; *Ann. Pharm.* 38, 101. *N. Ann. Chim. Phys.* 1, 372; *Ann. Pharm.* 38, 345.

Z. Delalande. (1841.) *N. Ann. Chim. Phys.* 1, 368; *Ann. Pharm.* 38, 342.

Noad. *Ann. Pharm.* 63, 281; *Mem. Chem. Soc.* 8, 421; *Phil. Mag. J.* 32, 15; abstr. *J. pr. Chem.* 44, 145.

Mansfield. *Ann. Pharm.* 69, 162; *Chem. Soc. Qu. J.* 1, 244.

Kraut. *Dessertation über Cuminol und Cymen.* Göttingen, 1854; abstr. *Ann. Pharm.* 92, 96; *J. pr. Chem.* 64, 159; *N. Ann. Chim. Phys.* 43, 347.

Church. *N. Phil. Mag. J.* 9, 256; *J. pr. Chem.* 65, 384.—*N. Phil. Mag. J.* 13, 415; *J. pr. Chem.* 72, 125; *Ann. Pharm.* 104, 111.

A. W. Hofmann. *Ann. Pharm.* 97, 206; *N. Ann. Chim. Phys.* 52, 104.

Barlow. *Ann. Pharm.* 98, 245.

Haines. *Chem. Soc. Qu. J.* 8, 289; *J. pr. Chem.* 68, 430; *Chem. Centr.* 1856, 593.

Lallemand. *N. Ann. Chim. Phys.* 49, 156; abstr. *Ann. Pharm.* 102, 119.

Sieveking. *Dissertation über Cuminol und Cymen.* Gött. 1857; abstr. *Ann. Pharm.* 106, 260.

J. Trapp. *Petersb. Acad. Bull.* 16, 296; *Ann. Pharm.* 108, 386; *J. pr. Chem.* 74, 428.

Cymen, Cymol, Camphogen (Delalande). *Camphene, Hydride of Thymyl, Thymylwasserstoff.*

Sources. In Roman oil of cumin, the volatile oil of *Cuminum Cyminum* (Gerhardt & Cahours. For the amount see p. 144.) — In the volatile oil of water-hemlock (*Cicuta virosa*). (Trapp, p. 145); in the volatile oil of *Ptychotis Ajowan*, according to Haines; but according to Stenhouse, it does not occur in that oil (see *Thymol.*) — In volatile oil of thyme (Lallemand.) Mixed with thymene, it forms the greater part of that which distils below 180°, and may be obtained by agitation with oil of vitriol, which dissolves the thymene, while cymene floats on the surface (Lallemand).

Formation. 1. In the dry distillation of coal, passing over into the lighter, but for the most part into the heavy oil of coal-tar (Mansfield.) — 2. By distilling camphor with phosphoric anhydride (Delaland); with chloride of zinc (Gerhardt.) — 3. In the action of moist carbonic acid gas on oil of turpentine at a low red heat, there is produced, with evolution of carbonic oxide, an oil having the composition of cymene (Deville *Ann. Chim. Phys.* 75, 66):

$$C^{20}H^{16} + 2CO^2 = C^{20}H^{14} + 2HO + 2CO.$$

4. By boiling cuminic alcohol with alcoholic potash (Kraut.) — 5. When purified oil of wormwood is repeatedly distilled over phosphoric anhydride, and finally over potassium, a compound is obtained similar to or identical with cymene (Leblanc, *N. Ann. Chim. Phys.* 16, 334.) — 6. Oil of wormseed (the volatile oil of the officinal *Semen Cynæ*) does not contain cymene ready formed; but from the cinæbene ($C^{10}H^8$ or $C^{20}H^{16}$) and cinæbene-camphor ($C^{10}H^9O$ or $C^{20}H^{18}O^2$) contained in it, cymene is produced, together with other oils, by heating with iodine or with dilute nitric acid. *a.* By distilling wormseed oil with iodine, agitating the product with potash-ley, then with mercury and lumps of potash, a mixture of cymene, cinæbene and cinæbene-camphor is obtained. — *b.* When wormseed oil is distilled with 2 vols. nitric acid of sp. gr. 1·16, nitrous fumes are evolved and volatile oils pass over. At the same time there is produced a resin, which, by continued boiling with an additional 2 vols. nitric acid, is converted into toluylic acid, nitrotoluylic acid and other products. Hence Hirzel supposes that cymene is first formed and immediately undergoes further alteration. (Hirzel, *Zeitschr. Pharm.* 1854, 23 and 67; 1855, 84 and 181; see also *infra.* Wormseed-oil.)

Preparation. From Roman Oil of Cumin. — 1. The portion which passes over in fractional distillation below 200° is rectified over caustic potash, the whole of the cuminol then remaining behind as cuminate of potash. (Gerhardt & Cahours.) The cymene thus obtained amounts to 41—44 per cent. of the Roman oil of cumin. (Noad.) — 2. The cuminol is separated in the manner described at page 145, and the cymene is dried and rectified. — 3. If it be not desired to obtain the cuminol, or only as cuminic acid, the Roman oil of cumin may be decomposed with alcoholic potash, as described at page 149. (Kraut.)

B. From *Coal-tar Oil.* (See xi, 135, 136.)

C. From *Camphor*. Camphor is repeatedly distilled with phosphoric anhydride (Delalande), or better with fused chloride of zinc, a few pieces of chloride of zinc being heated in a capacious tubulated retort to incipient fusion, and camphor added by small portions, whereupon the mixture froths up and blackens, and a distillate passes over still containing a large quantity of camphor. This distillate must be purified by repeated rectification over chloride of zinc. This process yields a large quantity of cymene with a comparatively small quantity of chloride of zinc. (Gerhardt, *Traité*, 3, 608.)

Properties. Colourless, strongly refracting oil. (Gerhardt & Cahours.) Boils at 170·7° (Church); 171° (Mansfield); 171·5° (Noad); 175° (Gerhardt & Cahours; Delalande; Lallemand); at 177·5°, correction being made for the lower temperatures of the column of mercury in the stem of the thermometer. (H. Kopp, *Ann. Pharm.* 94, 319.) Cymene prepared from Roman oil of cumin boils after rectification over sodium at 170·7°, but after treatment with oil of vitriol aided by heat, and separation with water, it boils at 175—176° like the camphor prepared with chloride of zinc. (Church.)

Sp. gr. = 0·845 at 26·7° (Haines); 0·857 at 16° (Noad); 0·860 at 13° (Delalande); 0·860 at 15° and 0·861 at 14° (Gerhardt & Cahours); 0·8678 at 12·6° = 0·8778 at 0°. (Kopp.) — Has an agreeable odour of lemons (Gerhardt & Cahours, Noad); when prepared from camphor it has a different odour (Gerhardt & Cahours) like that of camphor (Noad); but cymene prepared from Roman cumin-oil, if treated with oil of vitriol, and separated by water, smells like that prepared from camphor. (Gerhardt.) Cymene prepared from Ptychotis has a sweetish, smoky odour. (Haines.) Permanent in the air. (Gerhardt & Cahours). Vapour-density = 4·64 (Gerhardt & Cahours); 4·69 (Delalande.)

			Gerhardt & Cahours. *mean.*	Delalande.	Leblanc.	Kraut.	Haines.
20 C	120	89·56	89·07	88·75	88·9	88·95	89·87
14 H	14	10·44	10·83	10·38	10·6	10·81	10·66
$C^{20}H^{14}$	134	100·00	99·90	99·13	99·5	99·76	100·53

	Vol.	Density.
C-vapour	20	8·3200
H-gas	14	0·9702
Vapour of Cymene	2	9·2902
	1	4·6451

The cymene analysed by Gerhardt & Cahours, was prepared from Roman oil of cumin; Delalande's from camphor; Leblanc's from oil of wormwood; Haines's from oil of Ptychosis; Kraut's from cuminic alcohol.

Decompositions. 1. On passing air for several months through cymene prepared from oil of thyme and contaminated with thymene, it becomes viscid, assumes a dark red colour, and partly disappears; the mixture then yields thymene to aqueous potash. (Lallemand.) — 2. Cold *fuming sulphuric acid* dissolves cymene with dark red colour, without evolution of sulphurous acid, and forms sulphocymolic acid. (Gerhardt & Cahours; Delalande.) Ordinary oil of vitriol has no action upon cymene. (Gerhardt & Cahours.) Cymene exposed to the vapour of anhydrous sulphuric acid assumes a red and ultimately a black colour, becomes viscid, and forms with water a slightly coloured solution of sulphocymolic acid—dark-coloured if the sulphuric acid is in excess or brought into the liquid too quickly—which on standing deposits a thick oil still containing a large quantity of cymene. No product analogous to sulphide of benzene is formed in this reaction. (Sieveking.) — 3. *Bromine* and *chlorine*, in presence of water, unite with cymene directly and without evolution of hydrochloric or hydrobromic acid, and form bromide or chloride of cymene and hydrogen. (Sieveking.) Dry chlorine heats cymene, turns it brown and chars it. When cymene is repeatedly subjected to slow distillation in a stream of chlorine, a large quantity of hydrochloric acid is evolved, and finally between 170° and 230°, an oil passes over containing 10·7 per cent. of chlorine, similar to that which is produced by the action of alcoholic potash on chloride of hydrogen and cymene. (Sieveking.) — According to Gerhardt and Cahours, bromine or chlorine eliminates hydrobromic or hydrochloric acid gas, and forms a brominated or chlorinated product, which is decomposed by distillation. — Cymene does not absorb hydrochloric acid gas. — 4. Cymene carefully mixed with strongly cooled (fuming?) *nitric acid*, forms nitrocymene. (Barlow.) Moderately dilute nitric acid does not act upon it at mean temperature, but converts it, at the boiling heat, into a peculiar acid (Gerhardt & Cahours), into toluylic (xiii, 8) and nitrotoluylic acids (xiii, 22.) (Noad.) — 5. *Nitrosulphuric acid*, when strongly cooled, scarcely affects it, but at 50° converts it into an oil, from which after some time binitrocymene separates. (Kraut.) — 6. Cymene is not at all affected by caustic potash. (Gerhardt & Cahours.) — 7. Heated with *bichromate of potash and sulphuric acid*, it is converted into insolinic acid (xiii, 318.) (Hofmann.) It is violently attacked thereby and converted into an oil which is not altered by caustic potash. (Gerhardt and Cahours. It is not decomposed by continued digestion with chromic acid. (Noad.) — 8. It is not altered by digestion with *sulphuric acid and peroxide of manganese*. (Noad.) — With *permanganic acid*, it solidifies to a pulp of hydrated manganic oxide, without formation of a peculiar acid. (Noad.)

Combinations. Insoluble in *water*. Does not combine with alkaline bisulphites. (Bertagnini, *Ann. Pharm.* 85, 186.) Dissolves readily in *alcohol*, *ether* and *fat oils*. (Gerhardt & Cahours.)

Appendix to Cymene.

a Cymene. $C^{20}H^{14}$.

BARLOW. *Ann. Pharm.* 98, 245.

By treating nitrocymene with a pulp of acetic acid and iron filings, Barlow obtained, besides cymidine, an oil which was insoluble in hydrochloric acid, boiled at 175° after repeated rectification, and contained 89·21 per cent. C and 10·67 H. It had therefore the composition of cymene, but when treated with fuming nitric acid, it yielded nitrocymene lighter than water; hence Barlow distinguishes it as *a*-cymene.

Caryophyllin.

$C^{20}H^{16}O^2 = C^{20}H^{14},2HO$?

LODIBERT. (1825.) *J. Pharm.* 11, 101; *N. Tr.* 11, 1, 108; abstr. *Kastn. Arch.* 5, 463; *Repert*, 22, 134.
BONASTRE. *J. Pharm.* 11, 103; *N. Tr.* 11, 1, 112; abstr. *Kastn. Arch.* 5, 463; *Repert.* 25, 134; *J. Pharm.* 13, 519.
CHAZEREAU. *J. Pharm.* 12, 258.
DUMAS. *Ann. Chim. Phys.* 53, 169; *Ann. Pharm.* 9, 73; *Pogg.* 29, 90.
MYLIUS. *J. pr. Chem.* 22, 105.
JAHN. *Ann. Pharm.* 19, 333.
MUSPRATT. *Pharm. J. Trans.* 10, 343; *Liebig & Kopp's Jahresber.* 1850, 510.

Nelkelcampher, Stearoptene of oil of cloves. Discovered by Lodibert & Baget.

Sources. Occurs abundantly in East Indian cloves, in smaller quantity in those from Bourbon, not in those from Cayenne. (Lodibert, Bonastre.) It is not decidedly known whether the camphor which, according to Bizio (*Brugn. Giorn.* 19, 360), is deposited from oil of cloves in the cold, is identical with caryophyllin.

Preparation. Cloves immersed in cold alcohol are left to stand for about a fortnight till the crystalline deposit of caryophyllin no longer increases; the precipitate is then collected on a filter. (Lodibert.) The resin which adheres to them may be removed by washing with aqueous soda. (Bonastre.) Mylius washes the caryophyllin which separates spontaneously from oil of cloves with cold alcohol, and crystallises it from boiling alcohol. Muspratt exhausts cloves with ether, separates the caryophyllin by water, and purifies it by treatment with ammonia. The product amounts to about 3 per cent. of the cloves. (Bonastre.)

Properties. Spherules composed of radiating, white needles having a silky lustre, somewhat rough to the touch, not phosphorescent when rubbed. (Bonastre.) When heated it melts like a resin (Bonastre) sinters together somewhat at 320°, but does not melt till heated above 330°, forming a glass of faint yellow colour, which on cooling solidifies in crystalline nodules, melts again on renewed and stronger application of heat, and then solidifies on cooling to a mass exhibiting numerous fissures. This glass if again heated, becomes white and turbid, as if from incipient crystallisation, but melts again to a clear liquid, and flies to pieces suddenly on cooling. After stronger heating, it becomes much more easily soluble in alcohol, forming a yellow solution, and being at the same time converted into a bitter astringent substance. (Mylius.) At 280° it begins to volatilise (with an odour of resin according to Bonastre), without colouring or fusion, and may be completely sublimed in an air-bath between 280° and 290° (Mylius); at 285°. (Muspratt.) Tasteless and inodorous. Neutral. (Bonastre.)

			Dumas. *mean.*	Mylius. *mean.*
20 C	120	78·94	78·13	78·14
16 H	16	10·53	10·48	10·65
2 O	16	10·53	11·39	11·21
$C^{20}H^{16}O^2$	152	100·00	100·00	100·00

Ettling (*Liebig, Org. Chem.* 338) and Muspratt obtained numbers corresponding to the formula $C^{20}H^{16}O^2$.

Decompositions. Caryophyllin *burns* with a bright, white fuliginous flame. (Jahn.) — 2. It dissolves in *oil of vitriol* with rose-colour, changing to blood-red (Bonastre); it assumes with oil of vitriol an orange-colour, changing to blood-red, and when heated, to carmine-red, and then to brown with evolution of sulphurous acid. From the cold-prepared solution in oil of vitriol water throws down unaltered caryophyllin; and the portion which has not been dissolved by the oil of vitriol, but converted into a blood-red mass, swells up by contact with water and changes to a white, loose, semicrystalline tissue. (Mylius.) — 3. It is not altered by cold *nitric acid* (or even by the warm acid, according to Mylius); but by the boiling acid it is converted into a resin (with the fuming acid, a slight evolution of nitrous gas takes place), without formation of oxalic acid. (Bonastre.)

Combinations. Insoluble in *water,* even at the boiling heat. (Mylius, Jahn.)

Insoluble in dilute *mineral acids.* (Mylius.) According to Chazereau, it dissolves in water acidulated with sulphuric acid. Insoluble in *ammonia* and *potash,* whether caustic or carbonated. (Mylius.)

Sparingly soluble in aqueous *soda,* and somewhat more in aqueous *potash.* (Bonastre.)

Sparingly soluble in strong *acetic acid;* insoluble in cold, soluble in boiling *alcohol;* easily soluble in *ether;* in both these liquids, however, it dissolves less readily, in proportion as it is more free from resin. (Bonastre.) The alcoholic solution becomes milky on addition of water. (Jahn.) — Soluble in rectified *oil of turpentine,* less in *rock-oil.* (Jahn.)

Conjugated compounds of the Primary-nucleus, $C^{20}H^{14}$.

Sulphocymenic Acid.

$$C^{20}H^{14}S^{2}O^{6} = C^{20}H^{14},2SO^{3}.$$

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 106; *J. pr. Chem.* 23, 355; *Ann. Pharm.* 38, 101.
DELALANDE. *N. Ann. Chim. Phys.* 1, 368; *Ann. Pharm.* 38, 342.
CHURCH. *Phil. Mag. J.* 9, 256; *J. pr. Chem.* 65, 384.
SIEVEKING. *Dissertation über Cuminol und Cymen.* Gött. 1857, 17; abstr. *Ann. Pharm.* 106, 257; *J. pr. Chem.* 74, 505.

Sulphocymolic acid, Acide sulfo-cymenique (Gerhardt & Cahours). *Acide sulfo-camphique* (Delaland.) *Sulfocymylsäure* (Sieveking). *Acide thymyl-sulfureux* (Gerhardt). *Cymeschwefelsäure.*

Formation. (p. 185.) — It appears also to be produced by the action of fuming oil of vitriol on chloride of cymene and hydrogen (see below). (Sieveking.)

Preparation. Cymene is dissolved in a slight excess of fuming sulphuric acid (the mixture being cooled, according to Gerhardt & Cahours; heated in the water-bath, according to Delalande); the liquid is diluted with water, saturated with carbonate of lead, and filtered; and the solution of sulphocymenate of lead is evaporated to the crystallising point. — The aqueous solution of the crystals decomposed by sulphuretted hydrogen, and evaporated in vacuo after filtration, yields sulphocymenic acid. (Delalande.)

As the solution of the lead-salt is apt to decompose during evaporation, and leave a dark-brown mass, the solution of which is not decolorised by sulphuretted hydrogen, Sieveking decomposes the baryta-salt with dilute sulphuric acid, removes the excess of that acid by carbonate of lead, and the dissolved lead by sulphuretted hydrogen, and thus obtains aqueous sulphocymenic acid.

Properties. Small deliquescent crystals. (Delalande.)

Decompositions. 1. With fuming *nitric acid,* it easily forms nitrosulphocymenic acid, the salts of which detonate when heated. (Church.) — 2. The dry baryta-salt brought in contact with pentachloride of phosphorus, yields a yellowish distillate, which, when mixed with water, deposits a heavy brown oil. (Sieveking.)

Combinations. With *metallic oxides* it forms the *sulphocymenates.* These salts are all soluble; hence the solution of the baryta-salt does not precipitate metallic salts. (Gerhardt & Cahours.)

Sulphocymenate of Soda. — Obtained by precipitating the solution of sulphocymenate of baryta with an exactly equivalent quantity of carbonate of soda, and evaporating the filtrate over the open fire.

Slender needles or laminæ having a silky lustre. Dissolves very readily in water and alcohol. Contains 5 At. water of crystallisation, which go off at 170°. (Sieveking.)

			Sieveking. *mean.*
$C^{20}H^{13}S^{2}O^{6}$	213	75·80	
Na	23	8·18	8·22
5 HO	45	16·02	14·80
$C^{20}NaH^{13}S^{2}O^{6} + 5Aq$	281	100·00	

Sulphocymenate of Baryta. — The solution of cymene in fuming sulphuric acid (gently heated, according to Gerhardt & Cahours) is saturated with carbonate of baryta, and the filtrate is evaporated to the crystallising point.

The crystals heated to 100° (Gerhardt & Cahours), 130° (Trapp), 170° (Sieveking) yield the anhydrous salt.

	Dry.		Gerhardt & Cahours. *mean.*
20 C	120·0	42·61	42·15
13 H	13·0	4·62	4·70
Ba	68·6	24·36	24·10
2 S	32·0	11·36	11·60
6 O	48·0	17·05	17·45
$C^{20}BaH^{13}S^{2}O^{6}$	281·6	100·00	100·00

The salt prepared with cymene from cicuta-oil, contains 24·75 p. c. Ba (Trapp).

Compounds with Water. Sulphocymenate of baryta crystallises with 2 At. water (Gerhardt & Cahours), 3 At. (Sieveking) with 4 At. (Delalande).

a. Bi-hydrated. — Crystallises by cooling or evaporation in laminæ having a strong pearly lustre. (Gerhardt & Cahours.)

			Gerhardt & Cahours.
20 C	120.0	40·05	39·90
15 H	15.0	5·02	5·25
Ba	68·6	22·88	
2 S	32.0	10·66	
8 O	64.0	21·39	
$C^{20}BaH^{13}S^2O^6 + 2Aq$	299·6	100·00	

β. Ter-hydrated. — The solution evaporated till a crystalline film forms on its surface and cooled, yields the ter-hydrated salt in pearly laminæ having the form of Brookite. (Sieveking.)

			Sieveking.
20 C	120·0	38·9	
13 H	13·0	4·2	
Ba	68·5	22·2	22·30
2 S	32·0	10·4	10·03
6 O	48·0	15·6	
3 HO	27·0	8·7	8·67
$C^{20}BaH^{13}S^2O^6 + 3Aq$	308·5	100·0	

γ. Tetra-hydrated. — Laminæ obtained by evaporation and recrystallisation.

			Delalande.
20 C	120·0	37·78	35·41
17 H	17.0	5·35	5·57
Ba	68·6	21·59	
2 S	32·0	10·07	
10 O	80·0	25·21	
$C^{20}BaH^{11}S^2O^6 + 4Aq$	317·6	100·00	

Contains, according to Delalande (in accordance with his incorrect calculation of the tetra-hydrated salt) 26·1 p. c. of baryta, which however would come nearer to the quantity of baryta in the bi-hydrated salt (calculation, 25·5 BaO).

δ. Aqueous Solution. The baryta-salt dissolves readily in water, alcohol and ether. The aqueous solution decomposes when boiled; the hot-saturated solidifies on cooling. (Gerhardt & Cahours.) Tastes bitter, then disagreeably sweet; saccharine.

Interpolation. Sulphocymenate of Baryta containing the acid $C^{40}H^{28}S^2O^6$.

Gerhardt & Cahours, by neutralising crude sulphocymenic acid, *in the cold*, with carbonate of baryta, once obtained a confusedly crystalline mass, which dissolved in water much more readily than the ordinary (hot-prepared) salt, and contained 15·75 p. c. barium, whence they regarded it as $C^{40}H^{27}BaS^2O^6$ (calculation 16·4 Ba.) Sieveking did not succeed in preparing this salt.

Sulphocymenate of Lime. Obtained by neutralising crude sulphocymenic acid with marble. Thin colourless laminæ (having the taste of the baryta-salt, according to Delalande), very soluble in water and alcohol. Gives off 1 At. water (7·97 p. c.) at 150°, then 2 At. more (13·4 p. c. in all) at 170°, and then contains 7·98 p. c. alcum ($C^{20}H^{13}CaS^2O^6 =$ 8·5 Ca). (Sieveking.)

Sulphocymenate of Lead. — *Preparation* (p. 188). Pearly laminæ which, at 120°, give off 10·3 p. c. water (4 At. = 10·24 p. c.) without further alteration. (Delalande.)

	Laminæ.		Delalande.
20 C	120·0	34·02	33·75
PbO	111·8	31·69	31·80
17 H	17·0	4·82	4·60
2 S	32·0	9·07	9·40
9 O	72·0	20·40	20·45
$C^{20}PbH^{13}S^2O^6 + 4\,Aq$	352·8	100·00	100·00

When prepared with cymene obtained from oil of cicuta, it contains, after drying at 123°, 32·56 p. c. lead ($C^{20}H^{13}PbS^2O^6$ = 32·74), Trapp.

Cupric Sulphocymenate. Obtained by decomposing the baryta-salt with sulphate of copper. Light green laminæ with a silky lustre, easily soluble in water and alcohol. (Sieveking.)

Sulphocymenate of Silver. The solution of carbonate of silver in sulphocymenic acid becomes coloured when evaporated in vacuo or over the water-bath, and leaves a brown residue containing a few needle-shaped crystals. (Sieveking.)

Oxygen-nucleus $C^{20}H^{12}O^2$.

Anethol or Anise-camphor.

$C^{20}H^{12}O^2$.

GÜNTHER. *Alm.* 1783, 156.
SAUSSURI. *N. Ann. Chim. Phys.* 13, 280.
J. DUMAS. *Ann. Pharm.* 6, 253.
BLANCHET & SELL. *Ann. Pharm.* 6, 2873 (?)
CAHOURS. *Rev. scient.* 1840, 342; *J. pr. Chem.* 22, 58; in detail, *N. Ann. Chim. Phys.* 2, 274; *J. pr. Chem.* 24, 337; *Ann. Pharm.* 41, 56; *Compt. rend.* 19, 795; in detail, *N. Ann. Chim. Phys.* 14, 489; *J. pr. Chem.* 36, 421.
LAURENT. *Compt. rend.* 10, 531; 12, 764; *Rev. scient.* 10, 5 and 376; *J. pr. Chem.* 27, 232.
GERHARDT. *Ann. Chim. Phys.* 72, 167; *Compt. rend.* 15, 498; *N. Ann. Chim. Phys.* 7, 292; *Compt. chim.* 1845, 65; *J. pr. Chim.* 36, 267; abstr. *Compt. rend.* 20, 1440.

Investigated particularly by Cahours, Laurent and Gerhardt, the last of whom recognised the chemical identity of oil of tarragon with oil of anise and oil of fennel. The chief constituents, chemically similar but physically different, of the oils of anise, star-anise, fennel, and tarragon, are here united under the name *anethol*, which was formerly used provisionally by Gerhardt for anisoïn.

Sources. The volatile oils of anise (*Pimpinella Anisum*), fennel

(*Anethum Fœniculum*), tarragon (*Artemisia Dracunculus*), and star-anise (*Illicium anisatum*), consist almost wholly of anethol; and with the same mode of preparation, the oils of anise, fennel, and star-anise consist in some cases of a solid crystallisable variety of anethol, in other cases of liquid anethol; in the latter case, they generally contain also small quantities of a hydrocarbon isomeric with oil of turpentine. Anethol exists ready formed in the plants, and, according to Mohr, sometimes separates in the form of a flocculent wool, from bruised fennel seeds which have been left to themselves for a long time. (*Comment. zur Preuss. Pharmakopoe,* 2, 207.)

Separation: *a. Of solid Anethol* (*Anise* or *Fennel Camphor*) *from Oil of Anise, Fennel,* or *Star-anise* (see p. 191). The commercial oil is left to solidify at 0°, and pressed between filtering paper (Saussure) as long as the paper takes anything up, then crystallised two or three times from alcohol of sp. gr. 0·85 (Cahours), from warm alcohol of 90 p. c., and freed from adhering alcohol by fusion. (Blanchet & Sell.) The water which passes over with oil of fennel, deposits anethol, on keeping, in broad white laminæ. (Bizio, *Brugn. Giorn.* 19, 360.)

b. Of liquid Anethol from Oil of Fennel or Oil of Tarragon. Oil of fennel is subjected to fractional distillation, and the portion collected which passes over at 225° (Cahours); or the same process is applied to oil of tarragon, and the portion collected which passes over at 206° (Laurent); the last portions of the distillate are collected and rectified till a product of constant boiling point is obtained. (Gerhardt.)

Properties. Anethol exhibits totally different properties, according as it is obtained from one or other of the above-mentioned oils.

a. Solid Anethol from Anise, Fennel, or Star-anise oil. Anise-camphor, Stearoptene of Anise-oil. — White, granular mass. (Saussure). White shining laminæ. (Cahours.) Hard as white sugar (Saussure); friable, especially at 0°; melts at 16° (Blanchet & Sell), 18° (Cahours), 20° (Saussure); at 15° in the fresh state; at 20°, after keeping for a year. (Bizio.) Boils at 220° (Blanchet & Sell); at 222°, almost without decomposition (Cahours), and without alteration of the melting point. (Blanchet & Sell.) Sp. gr. of solid anethol at 12° = 1·044; in the liquid state at 25° = 0·9849; at 50° = 0·9669; at 94° = 0·9256, the sp. gr. of water at 12° being supposed = 1. (Saussure.) Has a fainter and more agreeable odour than anise-oil. Vapour-density = 5·19 at 338°, greater at lower temperatures. (Cahours, *Compt. rend.* 20, 51; *Pogg.* 65, 420; comp. vii, 54.) Permanent in the air. (Blanchet & Sell.) Less volatile at ordinary temperatures than common camphor.

b. Liquid Anethol from Oil of Fennel. Oil which does not solidify at 10°. Lighter than water. Boils at 225°. (Cahours, see p. 191.)

c. Liquid Anethol from Oil of Tarragon. Colourless mobile oil, having the taste and odour of oil of tarragon. (Laurent.) Smells like oil of anise. (Gerhardt.) Sp. gr. 0·945 at 15°. Boils at 206°. Vapour-density = 6·157 (Laurent), 5·34. (Gerhardt.) Permanent in the air. (Laurent.)

			Dumas.	Blanchet & Sell.
20 C	120	81·08	80·18	80·71
12 H	12	8·11	8·28	8·13
2 O	16	10·81	11·54	11·16
$C^{20}H^{12}O^2$	148	100·00	100·00	100·00

	Cahours.	Laurent.	Gerhardt.
20 C	80·96	81·00	80·81
12 H	8·12	8·85	8·46
2 O	10·92	10·15	10·73
$C^{20}H^{12}O^2$	100·00	100·00	100·00

	Vol.	Density.
C-vapour	20	8·3200
H-gas	12	0·8316
O-gas	1	1·1093
Vapour of anethol	2	10·2609 5·1305

Solid anethol from anise-oil (Dumas); liquid from tarragon-oil (Laurent, Gerhardt). Blanchet & Sell examined solid anethol from anise and fennel oil; Cahours, solid anethol from anise-oil, and liquid from fennel oil with like results. For the composition of tarragon-oil, Laurent formerly gave the formulæ $C^{24}H^{16}O^2$ and $C^{32}H^{31}O^3$.

Decompositions. 1. Anethol exposed to the air in the liquid state gradually loses the capability of crystallising (Cahours), and finally changes to a resin. (Saussure.) Melted anethol, but not the solid substance, absorbs oxygen from the air and thickens. (Blanchet & Sell, comp. p. 192.)

2. Anethol is inflammable, and *burns* easily with red, smoky flame. (Günther, Laurent.)

3. *Hydrated phosphoric* acid converts it into anisoïn. When distilled with *anhydrous phosphoric acid,* it does not give off any hydrocarbon, but is converted into anisoïn, part of which is decomposed during the distillation. (Cahours.)

4. Oil of anise mixed with small quantities of oil of vitriol, becomes heated, acquires a fine blood-red colour, and is converted into anisoïn. It dissolves completely in 3 or 4 pts. of oil of vitriol (even in the fuming acid), and after 24 hours, water separates part of it as unaltered oil, while the other portion remains dissolved, probably as sulphanetholic acid. (Cahours.) Tarragon oil is turned brown and resinised by fuming sulphuric acid, and on adding water, anisoïn is precipitated, while a portion remains dissolved in combination with sulphuric acid. (Laurent.)

5. Solid anethol in contact with *sulphurous* (or *hydrochloric,* comp. p. 195) *acid gas* becomes liquid, absorbs a quantity of gas increasing as the pressure is higher and temperature lower, then gradually gives off a small quantity of carbonic acid, and remains liquid even after the gas has been driven off, (Bineau, *N. Ann. Chim Phys.* 24, 335.)

6. Anethol dissolves *iodine* quickly at mean temperature, becoming thick after a few hours, and changing in a few days into a brown brittle resin. (Guizot, *J. Phys.* 5, 230). This is doubtless anisoïn. (Kraut.) Anethol, dropped into aqueous iodide of potassium saturated with iodine, solidifies to a hard friable mass of anisoïn. (Will & Rhodius, *Ann. Pharm.* 65, 230.) See page 197.

7. *Bromine*, dropped upon anise-camphor, causes much development of heat and evolution of hydrobromic acid gas, at the same time losing its colour and forming crystallisable terbromanethol. Oil of fennel forms a viscid liquid product with bromine. (Cahours.)

8. Dry *chlorine gas* is rapidly absorbed by oil of anise, with rise of temperature and evolution of hydrochloric acid gas. The resulting products, which are viscid and semifluid at mean temperature, are richer in chlorine in proportion as the action of that gas has been longer continued, so that at first terchloranethyl is produced, then, if the action be assisted by a gentle heat, the compound $C^{20}Cl^{4\frac{1}{2}}H^{7\frac{1}{2}}O^{2}$, into which, perhaps, it is still possible to introduce a further quantity of chlorine. (Cahours.) Tarragon oil immersed in chlorine gas, thickens, becomes hot, gives off acid vapours, and forms Laurent's *chlorure de dragonyle.*

9. Tarragon oil and star-anise oil, distilled with 8 pts. of chloride of lime and 24 pts. water, yield chloroform. (Chautard, *Compt. rend.* 34, 485; *J. pr. Chem.* 56, 238.)

9a. When anise oil is poured upon *chlorate of potash* and a few drops of oil of vitriol are added, inflammation takes place. (A. Vogel, jun., *Ann. Pharm.* 74, 114.)

10. *Pentachloride of phosphorus* acts violently on anethol, giving off hydrochloric acid, and forming oxychloride of phosphorus, together with a chlorinated oil which is precipitated by water, cannot be distilled without decomposition, and appears to be $C^{20}H^{12}Cl^{2}$. (Kraut.)

11. *Nitric acid* forms with anethol, according to the degree of concentration, temperature, and duration of action, either anisoic acid, or, together with oxalic and carbonic acids,—anisylous acid, anisic acid, and—finally nitranisic acid. By the action of *fuming nitric acid,* binitranisoïn is produced.

When star-anise oil is heated with nitric acid of sp. gr. 1·2, till the oil begins to sink to the bottom, anisoic acid (*vide inf.*) is produced. (Limpricht & Ritter, *Ann. Pharm.* 97, 364.) When anise oil is heated with dilute nitric acid (with 3 vols. nitric acid of 14° Bm., according to Cannizaro & Bertagnini) it sinks to the bottom, and is converted into anisylous acid (xiii, 120). By continued heating with nitric acid of 23° to 24°, it is converted, with violent action, into a brown resin (anisoïn? Kr.) and anisic acid (Cahours, xiii, 123). Nitric acid of 34° to 36° acts with great violence, first producing anisylous acid in the form of a heavy oil, which disappears after the action has been continued for some time, and if water be then added, nitranisic acid (xiii, 137) is thrown down in yellow flocks. (Cahours.) Fuming nitric acid acts with extreme violence, giving rise to abundant evolution of red vapours and forming binitranisoïn. (Cahours.) Nitric acid of ordinary strength does not act upon oil of tarragon in the cold, but on the application of heat, a violent evolution of gas takes place, and the oil thickens, swells up, and finally solidifies to a brown crystalline resin, a mixture of anisic acid, aniso-nitranisic acid (xiii, 140), nitranisic acid, and a brown resin, which may be converted into these acids by further treatment with nitric acid. (Laurent.)

12. Anethol is not at all altered by boiling with aqueous *potash* or by fusion with hydrate of potash (Gerhardt); not even by alcoholic potash. (Kraut.) Heated to 300° in a sealed tube with *soda-lime,* it is attacked, apparently with evolution of hydrogen, and yields a small quantity of an acid isomeric with cuminic acid. (Gerhardt.) When passed over soda-lime at a low red-heat, it is partly carbonised, partly volatilised without

alteration; no acid was found either in the aqueous solution of heated mass or in the residue. (Kraut.)

13. A mixture of *chromate of potash* and *sulphuric acid* converts anethol, with violent intumescence, into anisic acid, acetic acid passing over at the same time. (Persoz, Hempel: comp. xiii, 124.) Rochleder (*Ann. Pharm.* 37, 347) likewise observed the formation of a peculiar acid on heating fennel oil with sulphuric acid and bichromate of potash.

14. With *bichloride of tin* (or *terchloride of antimony*) anethol thickens to a stiff red mass in which a few needles are perceptible, and from which anisoïn is separated by water, alcohol or ether. (Gerhardt.)

By distillation over fused *chloride of zinc*, anethol is converted into a mixture of metanethol and metanethol-camphor. (Gerhardt.)

16. Anethol heated with *chloride of benzoyl* in a sealed glass tube to 120°—140°, becomes viscid and brown. On distilling the product, the greater part of the chloride of benzoyl passes over without evolution of hydrochloric acid, and on further heating, a decomposible residue is left which appears to be anisoïn. (Kraut.)

Combinations. Anethol dissolves slightly in *water*, the solid variety less easily than the liquid, imparting its smell and taste. The solid variety crystallises on cooling from the boiling solution in long needles. (Günther.)

With Hydrochloric acid. — Observed by Homberg (*Crell. N. Chem. Arch.* 3, 242) and by Saussure. — Anethol absorbs 19·83 per cent. of dry hydrochloric acid gas, and forms the compound $C^{20}H^{12}O^{2},HCl$. (Cahours.) Calculation = 19·78 HCl. Solid anethol is converted thereby into a limpid liquid, which, after a few hours, spontaneously assumes a fine red colour, and after a few days, gives off a third of the absorbed gas. Water removes the red colour, and yields a thick, white, opaque mixture. (Saussure.)

Anethol does not unite with alkaline bisulphites. (Bertagnini, *Ann. Pharm.* 85, 180.)

It dissolves in *alcohol* and in all proportions in *ether*. Solid anethol is less soluble in alcohol than the liquid variety. The solution is not precipitated by water. (Günther.) Anethol from tarragon oil dissolves in an equal volume of warm alcohol. (Laurent.) Solid anethol from anise oil dissolves at 10° in 4 parts, and at 15° in 0·6 pt. alcohol of sp. gr. 0·806 (Saussure), and crystallises by spontaneous evaporation of the alcohol at 5°. (Bizio.)

Anethol dissolves in 10 pts. of *oil of turpentine* and in an equal quantity of *oil of almonds* on heating, and crystallises on cooling. (Günther.)

Appendix to Anethol.

Oils almost wholly composed of Anethol.

a. Oil of Anise. Prepared from the bruised seeds of *Pimpinella Anisum* by distillation with a six-fold quantity of water. (*Pharm. boruss. ed.* 6.) — It is generally obtained from anise chaff, 100 lbs. of which yield 10¼ oz. of the oil. (Martius); 100 lbs. of anise seed yield 26¼ oz. (Van Hees, *N. Br. Arch.* 61, 18); 32½ (Zeller, *N. Jahresb. Pharm.* 1,148); 33⅓ oz. (Martius, *Repert.* 39, 238.)

Colourless or yellowish. (Saussure.) Yellow. (Blanchet & Sell.) Sp. gr. 0·977 to 0·98 at 20° (Van Hees), 0·9857 at 25° (Saussure), 0·991 at 17·5° (Tremlich), 1·075 at 25° (Chardin); of the recently prepared oil, 0·979; of the old oil, 0·9835 at 25° (Martius); different also according to the quantity of anise-camphor contained in it. (Blanchet & Sell.) It consists of $\frac{3}{4}$ liquid and $\frac{1}{4}$ solid matter (Saussure, Blanchet & Sell); of $\frac{4}{5}$ camphor which (not however, according to Blanchet & Sell, from every sample of the oil: comp. p. 192) crystallises out at 10° (Blanchet & Sell), at 12° to 14° (Tremlich), sometimes however only on opening and shaking the vessel, and then instantly. (Buchner.) Crystallises less easily the older it is. (Geoffroy, Buchner.) The oil obtained from the seeds is more fluid than that obtained from the chaff, which crystallises sooner, and contains more camphor. (Martius.) Melts at 17°. (Saussure.) When exposed to the air, it takes up oxygen and becomes viscid (Blanchet & Sell); resinises but does not turn sour, acetic acid being formed only towards the end of the process. (Bizio.) It dissolves at 24° in 2·4 pts. of alcohol of sp. gr. 0·84 and in all proportions in cold alcohol of sp. gr. 0·806. (Saussure.) It contains 80·25 p. c. carbon, 8·55 hydrogen, and 11·2 oxygen. (Blanchet & Sell.)

b. Oil of Fennel. Obtained from the seeds of *Anethum Fœniculum* in the same manner as oil of anise from anise seeds (p. 196). — 100 lbs. of the seeds yield 50 oz. of oil. (Van Hees, Zeller.) Colourless or yellowish. (Lewis.) Solidifies below 10° (Margueron, *J. Phys.* 45, 136), but often remains liquid even at lower temperatures. Sp. gr. 0·896 at 15° (Chardin), 0·968 at 20° (Van Hees), 0·997 (Lewis, Hasse). Smells like fennel seeds. (Blanchet & Sell.) Tastes mild, sweetish. Contains, according to Göbel, 75·4 per cent. C, 10·0 H, and 14·6 O; according to Blanchet & Sell, 76·14 p. c. C, 8·49 H, and 14·37 O. It consists almost entirely of two oils, a light oil volatile between 185° and 190°, isomeric with oil of turpentine, and anethol (sometimes solid, sometimes liquid). (Cahours.)

The *more volatile part* of fennel oil contains 87·86 p. c. carbon, 11·37 hydrogen, and 0·77 oxygen (Cahours), but it is difficult to purify it completely from anethol. It thickens and becomes turbid when nitric oxide gas is passed into it, and if alcohol of sp. gr. 0·8 be then added to the liquid, a peculiar white substance is deposited containing $C^{60}H^{48}N^8O^{16}$. This substance forms delicate white silky needles which turn yellow at 100°, and are completely decomposed at a stronger heat. (It dissolves in strong potash-ley and is precipitated therefrom by acids. It dissolves in ether, scarcely in alcohol of 0·80, and sparingly in absolute alcohol. [Cahours, *N. Ann. Chim. Phys.* 2, 303.]) Heated with hydrate of soda, it gives off ammonia, a gas which irritates the eyes, and an oil having the odour of rock-oil. It is not attacked by hyposulphite of soda. Treated at mean temperature with hydrosulphate of ammonia, and then with an acid, it yields a precipitate which detonates slightly when heated. Boiled with hydrosulphate of ammonia, it dissolves with brown colour, deposits sulphur, and emits a strong odour of bitter almonds. (Chiozza, *Gerhardt's Traité*, 3, 357.)

Calculation according to Cahours.			Cahours. *mean.*
60 C	360	55·55	55·41
48 H	48	7·40	7·41
8 N	112	17·28	17·19
16 O	128	19·77	19·99
$3C^{20}H^{16},NO^2$	648	100·00	100·00

c. Oil of Star-anise. From the seeds of *Illicium anisatum.* 100 lbs. of the seeds yield 40 oz. of oil (Van Hees), 35 oz. (Zeller). Mobile oil, transparent and colourless at first, but turning yellow after a few weeks. Does not solidify at 2·5°. (Meissner.) Deposits a camphor, like anise-camphor. (Cahours.) Sp. gr. 0·976 at 20°. (Van Hees.) Smells and tastes like anise. Dissolves readily in alcohol and ether. (Meissner, *Alman.* 1818, 63.)

d. Oil of Tarragon. Obtained by distilling with water the leaves of *Artemisia Dracunculus.* — Sp. gr. 0·9356. (Chardin-Hardancourt.) According to Laurent, it consists wholly of anethol, and boils between 200° and 206°. According to Gerhardt, it contains, together with anethol, extremely small quantities of a more volatile hydrocarbon.

Anisoïn. $C^{20}H^{12}O^{2}$.

Gerhardt. (1839.) *Ann. Chim. Phys.* 72, 167; in detail, *Compt. chim.* 1845, 65; *J. pr. Chem.* 36, 267; abstr. *Compt. rend.* 20, 1440.
Cahours. *Rev. scient.* 1840, 342; *J. pr. Chem.* 22, 59; in detail *N. Ann. Chem. Phys.* 2, 284; *J. pr. Chem.* 24, 344.
Laurent. *Rev. scient.* 10, 5; *J. pr. Chem.* 27, 232.
Will & Rhodius. *Ann. Pharm.* 65, 230; *Pharm. Centr.* 1848, 230.
Uelsmann & Kraut. *J. pr. Chem.* 77, 490.

Resinous variety of anethol (Gerhardt).

First observed in 1826, by Unverdorben (*Pogg.* 8, 484), afterwards re-discovered and investigated by Gerhardt. Uelsmann & Kraut showed that the product which Will & Rhodius obtained by the action of iodine on anise oil, was anisoïn, as Gerhardt (*N. J. Pharm.* 14, 130) had previously suggested.

Formation. By the action of bichloride of tin or terchloride of antimony (Gerhardt), of phosphoric acid or oil of vitriol (Cahours), of iodine dissolved in iodide of potassium (Will & Rhodius) on anethol.

Preparation. 1. Bichloride of tin is poured upon anethol (or upon crude oil of anise or tarragon); the thick red mass thus produced is precipitated with water; and the precipitated flakes are collected and purified by solution in ether and evaporation. (Gerhardt.) — 2. Anethol is treated with terchloride of antimony, till it turns red, and the mixture is diluted with water and boiled, whereupon the mass turns white and settles down. — The deposit is collected and washed, then pressed between bibulous paper, and purified by solution in a small quantity of ether and precipitation with weak alcohol. (Gerhardt.) — 3. Oil of vitriol is dropped upon oil of tarragon contained in a large basin, care being taken that the mass does not become too strongly heated. A hard, fissured mass is thereby formed, which must be well washed with hot water. (Gerhardt.) Cahours uses at most 1½ pt. oil of vitriol to 1 pt. anise oil, and distils carefully after washing with water, whereupon, according to his statement, a small quantity of anisoïn passes over, the greater part being however converted into a heavy oil (see page 200, 2). — 4. A cold-saturated solution of iodide of potassium is saturated with iodine; anise or fennel oil is then dropt into it, with strong agitation; and the thick gelatinous magma is diluted with 6 or 8 vols. alcohol. Anisoïn then separates as a white powder, which is to be washed with alcohol; its quantity amounts to more than half that of the oil used; in the case of fennel oil to 54·8 p. c. (Will & Rhodius).

To obtain the anisoïn pure, it must be repeatedly dissolved in ether and precipitated by alcohol. — Or the brittle product obtained by the action of iodine upon anethol may be pulverised; ether then poured upon it; the solution shaken up with excess of soda-ley; the decanted ethereal solution precipitated with alcohol; and the precipitated anisoïn washed repeatedly with water, then dried, pulverised, and purified by repeated solution in ether and precipitation by alcohol. (Kr.)

Properties. Yellow, transparent resin, or thin microscopic nodules. (Gerhardt.) White powder (Will & Rhodius), which, by spontaneous evaporation of its ethereal solution, may be obtained in small needles. (Cahours.) Extremely electrical. (Will & Rhodius.) Melts between 140° and 145° (Uelsmann & Kraut); at a heat considerably above 100°, and solidifies to a colourless glass. (Will & Rhodius.) At a higher temperature, it volatilises partly undecomposed. Heavier than water. Inodorous. (Cahours.)

			Gerhardt.	Cahours.	Wells & Rhodius.	Uelsmann & Kraut.
			mean.	*mean.*		*mean.*
20 C	120	81·08	80·75	80·97	77·84	80·69
22 H	12	8·11	8·20	8·09	8·34	8·09
2 O	16	10·81	11·05	10·94	13·82	11·22
$C^{20}H^{12}O^2$	148	100·00	100·00	100·00	100·00	100·00

Will & Rhodius gave the formula $C^{30}H^{18}O^4$.
Isomeric with anethol, metanethol, metanethol-camphor and cuminol.

Decompositions. 1. Anisoïn when heated in the air, *burns* like a resin, emitting an aromatic odour. (Cahours.) — 2. By *distillation*, it is converted into methanethol and metanethol-camphor, into the last, especially when pure anisoïn is used. (Gerhardt, comp. p. 199.)

3. In *chlorine gas*, at mean temperature, it turns violet, absorbs chlorine, gives off hydrochloric acid, and becomes heated without melting. When chlorine gas is passed over anisoïn at 100° as long as the substance continues to increase in weight, and the excess of chlorine is displaced by dry air, a chlorinated product is formed, without violet colouring, which contains 51·5 to 52·7 p. c. carbon, 4·5 to 4·8 hydrogen, and 31·9 to 32·7 chlorine, and, according to Will & Rhodius, is $C^{30}Cl^3H^{15}O^4$, more probably $C^{20}Cl^2H^{10}O^2$ = Bichloranisoïn. (Uelsmann & Kraut.) Calculation 55·3 p. c. C, 4·6 N and 32·7 Cl. — 4. Anisoïn is decomposed by strong nitric acid, only after continued boiling. (Will & Rhodius.) By *fuming nitric acid*, it is dissolved, with violent evolution of nitrous gas, and precipitated, on pouring the solution into water, as binitranisoïn. (Kraut.) — 8. *Potash-lime* attacks it at 300°, with evolution of hydrogen. Hydrochloric acid separates from the product yellow flakes which cake together to a brown resin. (Gerhardt.)

Anisoïn is insoluble in *water*. — It is not altered by dilute *acids*, or by *potash* or *ammonia*, even at the boiling heat.

It dissolves in *oil of vitriol* with red colour and is precipitated by water. (Cahours.)

It does not dissolve in *alcohol*, even with the aid of heat. It is soluble in *ether*, and is completely precipitated from the solution by alcohol: also in volatile oils.

Metanethol-camphor.

$C^{20}H^{12}O^2$.

GERHARDT. (Comp. page 197.)

Crystallised variety of Anethol (Gerhardt).

Formation and Preparation. — 1. Metanethol obtained by the dry distillation of anisoïn (especially if pure), as above described, deposits in the neck of the retort crystals of metanethol-camphor, which may be obtained in greater quantity by once rectifying the metanethol over chloride of zinc, and separated from the oil by washing with alcohol. — 2. In the preparation of metanethol by dropping anethol on chloride of zinc in the melted state (p. 200) crystals of metanethol-camphor are obtained, abundantly if oil of anise has been used, in small quantity if the preparation has been made with oil of tarragon.

Properties. Colourless crystals which do not melt at the heat of the water-bath after fusion, and distil without alteration at higher temperatures. Solidifies to a radiated warty mass. Inodorous.

	Crystals.		Gerhardt. *mean.*
20 C	120	81·08	81·45
12 H	12	8·11	8·15
2 O	16	10·81	10·40
$C^{20}H^{12}O^2$	148	100·00	100·00

Isomeric with anisoin, metanethol and cuminol.

By repeated rectification over *chloride of zinc*, it is converted into metanethol, with separation of charcoal. With *potash-lime* it behaves like anisoïn (p. 198).

Metanethol. $C^{10}H^{12}O^2$.

GERHARDT. *Compt. chim.* 1845, 65; *J. pr. Chem.* 36, 372; abstr. *Compt. rend.* 20, 1440.

Liquid variety, e, of anethol (Gerhardt).

Formation. By distilling anethol over chloride of zinc. — 2. By the dry distillation of anisoïn (p. 198). — 3. In the dry distillation of the sulphanethates, metanethol passes over and charcoal is separated.

Preparation. Anethol is dropped upon melted chloride of zinc contained in a tubulated retort; heat is applied as long as oil continues to pass over; and the metanethol-camphor produced at the same time is reconverted into metanethol by repeated rectification over chloride of zinc. Oil of tarragon yields more metanethol and less of the camphor than oil of anise.

Properties. Colourless oil, having a vinous odour somewhat resembling that of anise. Sp. gr. 0·954 at 25°. Boils at 206°. Vapour-density = 5·75 at 247°; 5·35 at 297°.

					Vol.	Density.
20 C	120	81·08	80·55	C-vapour	20	8·3200
12 H	12	8·11	8·30	H-gas	12	0·8316
2 O	16	10·81	11·15	O-gas	1	1·1093
$C^{20}H^{12}O^{2}$	148	100·00	100·00	Vapour of Metanethol	2	10·2609
					1	5·1305

Isomeric with anethol, metanethol-camphor, anisoïn and cuminol.

Sulphometanethic Acid.

$C^{20}H^{12}S^{2}O^{8} = C^{20}H^{12}O^{2},2SO^{3}$.

GERHARDT. (1845.) *Compt. chim.* 1845, 65; *J. pr. Chem.* 36, 275.

Sulphanethic acid, Sulphodraconic acid, Metanethschwefelsäure, Metanetholschwefelsäure.

Known only in combination with bases.

Formation. — 1. By dissolving anethol in oil of vitriol. (Gerhardt.) — 2. The solution of anethol (from anise oil, according to Cahours, from tarragon oil, according to Laurent), in at least 3 or 4 pts. of oil of vitriol, if mixed with water after standing for 24 hours, deposits only part of the oil in the form of anisoïn, the rest remaining dissolved in combination with the sulphuric acid, probably as sulphometanethic acid (p. 193). — 3. When thymol is heated with excess of oil of vitriol to 240°, sulphurous acid is evolved, and a viscid mixture perfectly soluble in water is obtained, which, after neutralisation with carbonate of baryta, yields a gummy very soluble salt, which behaves to ferric salts like sulphometanethate of baryta. (Lallemand, *N. Ann. Chim. Phys.* 49, 150.)

On diluting with water the solutions obtained by 1 or 2, neutralising with carbonate of baryta, filtering and evaporating, *sulphometanethate of baryta* is obtained as a yellow, amorphous, gummy mass, which has a very bitter taste, dissolves readily in water and alcohol, does not precipitate the nitrates of *calcium, lead,* or silver, and produces with aqueous *ferric* salts, a deep violet colouring, which is destroyed by ammonia and by acids. This, and the *lead-salt of sulphometanethic acid*, which is likewise amorphous, has the aspect of gum arabic, and is very soluble in water, yield by dry distillation, a distillate of metanethol with a residue of charcoal. (Gerhardt.)

Baryta-salt, salt at 100°.			Gerhardt.
20 C	120	39·40	38·4
12 H	12	3·94	4·3
$BaSO^4$	116·5	38·26	35·0
SO^5	56	18·40	
$C^{20}H^{11}BaO^2,2SO^3+HO$	304·5	100·00	

Lallemand found in sulphometanethate of baryta prepared from thymol, crystallised from weak alcohol and dried at 120°, 39·5 p. c. sulphate of baryta ($C^{20}H^{11}BaS^2O^8$ = 39·4 p. c- BaO).

Gerhardt's analysis does not agree with his formula, for which he erroneously calculates the amount of sulphate of baryta, at 34·6 p. c. (Kr.).

Eugenin.

$C^{20}H^{12}O^4 = C^{20}H^{12}O^2,O^2$?

Bonastre. (1833.) *J. Pharm.* 20, 565; *Ann. Pharm.* 13, 91.
Dumas. *Ann. Chim. Phys.* 53, 168; *Ann. Pharm.* 9, 71; *Pogg.* 29, 89.

Discovered by Bonastre, analysed by Dumas.

Separates after a while from the turbid water, loaded with volatile oil, which is distilled from cloves. (Bonastre.)

Delicate, white, transparent, pearly laminæ, becoming yellowish after some time. Smells fainter than cloves. Tasteless.

			Dumas.
20 C	120	73·17	71·21
12 H	12	7·32	7·65
4 O	32	19·51	21·14
$C^{20}H^{12}O^4$	164	100·00	100·00

Isomeric with cuminic and eugenic acids, to the latter of which it is related in the same manner as benzoïn to bitter almond oil.

With cold *nitric acid*, it acquires a bright blood-red colour as quickly as eugenic acid. (Bonastre.) Is but very slightly attacked by strong nitric acid. (Muspratt, *N. Phil. Mag.* 2, 297.)

Soluble in all proportions in *alcohol* and *ether*. (Bonastre.)

Eugenic Acid.

$C^{20}H^{12}O^4 = C^{20}H^{12}O^2,O^2$.

Bonastre. (1827.) *J. Pharm.* 13, 464 and 513; abstr. *Ann. Chim. Phys.* 35, 274; *Pogg.* 10, 611; *Mag. Pharm.* 20, 141.
Dumas. *Ann. Chim. Phys.* 53, 165; *Ann. Pharm.* 9, 65; *Pogg.* 29, 87; *Ann. Pharm.* 27, 151.
Ettling. *Ann. Pharm.* 9, 68; *Pogg.* 31, 526.
Böckmann. *Ann. Pharm.* 27, 155.
Stenhouse. *Ann. Pharm.* 95, 103; *Pharm. Centr.* 1855, 289.
Calvi & Chiozza. *Cimento* 3, 419; *Ann. Pharm.* 99, 242; *J. pr. Chem.* 70, 125; *Chem. Centr.* 1856, 829.

A. Brüning. *Ann. Pharm.* 104, 202; *J pr. Chem.* 73, 156.
C. Grev. Williams. *Chem. Gaz.* 1858, 170; *Ann. Pharm.* 107, 238; *N. Ann. Chim. Phys.* 54, 433.

Eugenol, Nelkensäure, Acid Oil of Cloves.

Bonastre discovered in 1827 the acid nature of oil of cloves, and investigated the remarkable compounds with alkalis and other salt-bases, which had already been observed by Philipp (*N. Tr.* 9, 1, 275) and Karls (*Pogg.* 10, 609).

Sources. Occurs in oil of cloves (Bonastre), together with a hydrocarbon isomeric with oil of turpentine (Ettling); in pimento-oil (Bonastre); in the so-called oil of cinnamon leaves from Ceylon (Stenhouse); in the oil of *Canella alba* (W. Meyer & v. Reiche); and probably in the volatile oil of Brazilian clove-cinnamon. (Comp. p. 209.)

Separation of Eugenic Acid from Oil of Cloves. The oil distilled from cloves which have been previously treated with alcohol to extract caryophyllin, consists solely of eugenic acid. (Dumas, *Ann. Pharm.* 27, 151.) 1. Crude commercial oil of cloves is mixed with strong potash-ley, and distilled as long as neutral oil of cloves passes over; the residue is then mixed with phosphoric or sulphuric acid; and the eugenic acid thus separated being distilled off, passes over as a clear colourless oil. (Ettling.)—2. Oil of cloves is decomposed by hydrate of potash; alcohol is added to the solidified mixture; and the salt thereby separated is collected and frequently pressed. The potash-salt is decomposed with dilute sulphuric acid, and the liberated eugenic acid is dried over chloride of calcium and rectified. (Brüning.) Dumas dehydrates eugenic acid by boiling and distilling, because, when treated with chloride of calcium, it readily becomes coloured or forms eugenate of lime.

Properties. Clear, colourless oil, having an unmistakeable odour and taste of cloves. Sp. gr. = 1·0684 at 14° (Williams), 1·076 (Stenhouse), 1·079 (Ettling). Boils at 242° (Stenhouse), 243° (Ettling), 248° (Brüning), 251° (Williams), between 153° and 154° (253° ? Williams), (Dumas). Vapour-density = 5·858 (Williams), 6·4; (this number is probably too high, since partial decomposition took place.) (Dumas, Calvi.) Reddens litmus-paper. (Ettling.) It neither affects blue litmus or turmeric-paper, nor even the aqueous, alcoholic, or ethereal solutions of these substances. (Bonastre.)

			Dumas. *mean.*	Ettling.	Böckmann.
20 C	120	73·17	69·01	71·63	71·7
12 H	12	7·32	7·40	7·44	7·4
4 O	32	19·51	23·59	20·93	20·9
$C^{20}H^{12}O^{4}$	164	100·00	100·00	100·00	100·0

	Stenhouse. *mean.*	Calvi. *mean.*	Brüning. *mean.*	Williams. *mean.*
20 C	72·13	72·6	72·61	73·10
12 H	7·31	7·1	7·33	7·65
4 O	20·56	20·3	20·06	19·25
$C^{20}H^{12}O^{4}$	100·00	100·0	100·00	100·00

	Vols.		Vapour-density.
C-vapour	20	....	8·3200
H-gas	12	....	0·8316
O-gas	2	....	2·2186
Eugenic acid-vapour	2	....	11·3702
	1	....	5·6851

Stenhouse analysed eugenic acid from oil of cinnamon leaves; Dumas gave the formula $C^{20}H^{12}O^5$, or the same doubled; Ettling, $C^{48}H^{20}O^{10}$. The formula $C^{20}H^{12}O^4$, which was previously proposed by Liebig (*Org. Chemie.* 337) and by Gerhardt (*Précis* 2, 171) was confirmed by Calvi, by Brüning, and finally by Williams.

Isomeric with cuminic acid and eugenin (p. 192).

Decompositions. The decompositions of crude oil of cloves are here inserted, as far as they may with probability be attributed to eugenic acid. — 1. Eugenic acid soon acquires a brown colour, even in perfectly full and hermetically sealed vessels. (Williams.) — 2. It becomes coloured after boiling for a certain time and leaves a brown residue; hence the vapour-density is found too high in vessels containing air. (Dumas, Williams.) — 3. Oil of cloves is turned dark-brown by *oil of vitriol* (Gaultier de Claubry), first clove-red, then of the colour of wine-lees. (Bonastre.) Comp. also Brandes (*N. Tr.* 21, 1, 37). — 4. *Chlorine-gas* causes cooled oil of cloves to thicken, colours it green, imparts to it a balsamic odour, and becomes converted in a few days into hydrochloric acid. On submitting the whole to distillation, undecomposed oil passes over, leaving a resin. (Bonastre.) Oil of cloves, gently heated with powdered *corrosive sublimate,* turns purple-red; and, on application of stronger heat, a purple-red oil containing hydrochloric acid passes over, together with acid vapours, leaving a black residue. The same purple-red oil is likewise obtained by acting on oil of cloves with hydrochloric acid gas or aqueous hydrochloric acid. (J. Davy.) — Oil of cloves, in contact with *chloride of lime,* becomes warm and emits vapours, without however taking fire. (R. Böttger, *J. pr. Ch.* 76, 241.) The less volatile oil of cloves is turned brown by small quantities of *iodine,* and in 24 hours acquires an olive-green colour; while the more volatile oil is turned first brown, then blue, and finally greenish blue. (Jahn, *N. Br. Arch.* 66, 141.) 5. *Pentachloride of phosphorus* decomposes eugenic acid, and yields, amongst other products, a gas burning with green flame like chloride of methyl. — 6. With *nitric acid,* eugenic acid forms oxalic acid and a brown resin. (Brüning.) Oil of cloves readily takes fire with fuming nitric acid. Heated with a large quantity of nitric acid, it yields oxalic acid (Karls, *Crell. Ann.* 1785, 1, 302; Bonastre); with $\frac{1}{4}$ of its bulk of nitric acid, it immediately turns dark red, with evolution of nitrous fumes, and then dissolves in water with dark yellow colour, which is rendered more intense by ammonia. (Bonastre.) — 7. Eugenic acid is converted by distillation over anhydrous *baryta* into a neutral oil, which is not affected by caustic potash, and, though possessing different properties, has the same composition and vapour-density as eugenic acid. (Calvi.) Eugenic acid distilled with an excess of baryta yields the hydrocarbon $C^{18}H^{12}$ (xiii, 341) (Church, *N. Phil. Mag. J.* 9, 256). — 8. Oil of cloves is not affected by dry *permanganate of potash.* (Böttger.) — 9. With *peroxide of lead* it develops heat, and smokes, without however taking fire. — 10. Oil of cloves is not affected by *mercuric oxide,* but it instantly takes fire, with emission of sparks and smoke, in contact with dry *oxide of silver,* with *peroxide of silver* prepared by electrolysis, or with *oxide of gold,* the oxides being thereby reduced to the metallic state. (Böttger, *J. pr. Ch.* 76, 241.) — 11. In contact with dry *nitroprusside of copper*, oil of cloves acquires a violet colour, varying to cherry-red, and yields a slate-gray deposit; $\frac{1}{2000}$ pt. nitroprusside of copper is sufficient to produce a rose-red coloration. Oil of turpentine prevents the reaction. (Heppe, *N. Br. Arch.* 89, 57.) — 12. Eugenic acid in the form of potash-salt gives with *iodide of ethyl*, eugenate of ethyl; with *chloride of benzoyl* (*toluyl* or *anisyl*) it forms benzo-eugenic anhydride (or the corresponding anhydrides). — (Cahours, *N. Ann. Chim. Phys.* 52, 189.)

Combinations. Eugenic acid dissolves sparingly in *water*, imparting its taste and odour.

With bases it forms the *eugenates*, the formula of which is $C^{20}H^{11}MO^{4}$ or $C^{20}H^{11}MO^{4},C^{20}H^{12}O^{4}$; according to Dumas, $C^{20}H^{42}O^{4}.MO$. They are for the most part crystallisable, and, with the exception of the baryta-salt, readily decomposible by water and alcohol. The solutions of the eugenates of the alkalis become alkaline by evaporation. (Ettling.) By nitric acid they are coloured various shades between yellow and red; they are decomposed by other acids (partially even by carbonic acid, Ettling) with liberation of eugenic acid. (Bonastre.)

Eugenate of Ammonia. Eugenic acid absorbs 9·73 p. c. of its weight of dry ammonia-gas (Dumas); when dry ammonia-gas is passed over it, it combines therewith, developing heat, but is not completely neutralized. (Ettling.) Oil of cloves in contact with ammonia-gas at 0°, thickens to a buttery, granular-laminaceous, yellow mass, which gradually becomes dark, and with more ammonia acquires the consistence of tallow. (Bonastre.) Small, very brilliant crystals. (Dumas.) Fragile, white laminæ (Bonastre, Brüning); heavier than water, of strong odour, and sharp, burning taste. (Bonastre.) In the air it immediately parts with ammonia (Dumas); melts a little above 0°, and gives off ammonia. (Brüning.) Though permanent below 12° in sealed tubes, it is converted in the air into a volatile and rather darker oil, owing to loss of ammonia. (Bonastre.) Eugenic acid over which ammonia-gas has been passed to saturation, parts with ammonia when melted, and is converted into an acid salt; and if ammonia be again passed over this product, it re-absorbs the gas to the amount of 4·14 p. c. of the weight of the acid. (Ettling.) — Dissolves in hot ammoniacal water, and on distilling the solution, passes over with the liquid, and crystallises from the cooled distillate as a white semi-solid mass, which gradually disappears even in stoppered bottles. (Bonastre.) Commercial oil of cloves yields with ammonia no crystals, but a pitch-like, buttery mass. (Dumas.)

			Dumas.
$C^{20}H^{12}O^{4}$	164	90·61	
NH^{3}	17	9·39	8·86
$C^{20}(NH^{4})H^{11}O^{4}$	181	100·00	

Eugenate of Potash. — Acid? — Oil of cloves is triturated with an equal weight of hydrate of potash, and the compound which is thus formed, with slight elevation of temperature, is dissolved in 5 pts. water (on boiling the solution a certain quantity of eugenic acid is driven off: *Bonastre, Calvi*), then filtered and evaporated, so that the liquid, when left to stand in the cold for 24 hours, crystallises. (Bonastre.) An excess of concentrated solution of caustic potash is added to eugenic acid, and, according to Brüning, the solution is precipitated with alcohol and the salt repeatedly pressed; according to Dumas, the mass is stirred up, the excess of potash poured off, and the salt pressed between blotting paper, and crystallised from alcohol.

Brilliant, white, fragile laminæ, having the burning taste, and somewhat of the odour of cloves. Reaction alkaline. (Bonastre.) Partly decomposed by recrystallisation from water. (Bonastre, Dumas.) According to Bonastre, it is also decomposed by alcohol and ether. Decomposes slightly at 100°, without perceptible alteration of weight. (Brüning.)

			Bonastre. *At* 100° C, *mean.*	Dumas. *mean.*	Brüning. *over oil of vitrol.*
$C^{40}H^{23}O^7$	319	87·08			
KO	47·2	12·92	11·69	12·0	12·22
$C^{20}H^{11}KO^4, C^{20}H^{12}O^4$	366·2	100·00			

According to Brüning, the formula is $C^{40}H^{23}KO^8, + 2Aq$, which requires 12·2 p. c. KO.

Eugenate of Soda. When oil of cloves is poured over an equal weight of hydrate of soda, it is gradually absorbed, forming a solid mass, which, on addition of a little cold water, is converted, in 24 hours, into fragile needles having a silky lustre. The excess of soda is removed by pressing the crystals between blotting paper. It tastes like cloves and strongly alkaline. On boiling the largely diluted aqueous solution, a small quantity of oil is evolved, but the liquid again yields crystals on evaporation. Dissolves in from 10 to 12 pts. cold, and in any quantity of hot water. Dissolves in alcohol and ether with decomposition. (Bonastre.)

	Needles.		Bonastre.
$C^{20}H^{11}O^3$	155	83·34	81·45
NaO	31	16·66	18·57
$C^{20}H^{11}NaO^4$	186	100·00	

Eugenate of Baryta is precipitated in crystalline spherules when baryta-water is shaken up with eugenic acid (or with its aqueous or alcoholic solution: Brüning), while only a small quantity remains in solution. The salt may be obtained in white nacreous needles by recrystallisation from hot water. (Bonastre.) The salt prepared from baryta-water and eugenic acid contains 27 p. c. BaO, but after recrystallisation from alcohol, it contains 32 p. c. BaO. (Ettling.) Smells and tastes of cloves. (Bonastre.) It is very stable, and may be recrystallised from water and from alcohol. (Williams.) When moist, it absorbs carbonic acid from the air (Ettling), and turns brown. (Brüning.) Dissolves sparingly in cold, and much more freely in hot water. (Bonastre.) For the decomposition of the baryta-salt by distillation, see page 203.

			Brüning. *mean.*
20 C	120	51·82	51·12
11 H	11	4·75	4·89
3 O	24	10·36	12·23
BaO	76·5	33·07	31·76
$C^{20}H^{11}BaO^4$	231·5	100·00	100·00

Bonastre found 32·81, Ettling 32·0, Calvi 32·8 (*Gerhardt's Traité*, 4, 1037), Williams, in the salt dried at 100°, 33·4 p. c. BaO.

Eugenate of Strontia. Obtained by boiling or agitating oil of cloves with strontia-water. White needles, less nacreous than the baryta-salt, with which they agree in other properties. (Bonastre.)

Eugenate of Lime. Quicklime combines with oil of cloves, forming a solid, amorphous compound, which is insoluble in cold and sparingly soluble in boiling water. — When oil of cloves is boiled with 2 pts. of lime and water, the filtered solution deposits on evaporation yellowish crusts, which have a faint odour of cloves, a very repulsive taste, and are turned wine-red, with lively effervescence, by oil of vitriol. Dissolves in 235 pts. water. (Bonastre.)

Eugenate of Magnesia. Obtained by the action of oil of cloves on calcined magnesia, as a very hard, white, non-crystalline compound, which is equally insoluble in cold and hot water. (Bonastre.)

Eugenate of Lead. Eugenic acid forms with oxide of lead, acid, basic, and hyperbasic salts. (Ettling.) By boiling oxide of lead with oil of cloves and water for three hours, a viscous, yellow, homogeneous mass, insoluble in water, is obtained. This when dried in the air becomes friable, and on addition of sulphuric acid, yields eugenic acid. Formed also by precipitating aqueous eugenate of potash (from oil of cloves, comp. Schindler, *N. Br. Arch.* 41, 140) with subacetate of lead, as a thick, yellow deposit. (Bonastre.) Hyperbasic eugenate of lead contains 62·61 p. c. PbO. (Bonastre.)

Ferrous Eugenate. Boiling aqueous solution of eugenate of potash or soda gives immediately with ferrous sulphate, a magma which instantly turns blue. (Bonastre.) Aqueous ferrous sulphate gives no reaction with oil of cloves; but with eugenate of ammonia, baryta, or strontia, it acquires a light lilac-colour; with eugenate of potash, from red to blue; and with eugenate of soda, a violet or greenish-blue colour. (Bonastre.) By standing over iron filings for 24 hours, oil of cloves acquires a purple tint, without dissolving any of the iron (? Kr.) — (Röttscher, *Br. Arch.* 14, 186.)

Cupric Eugenate. Solution of cupric sulphate precipitates aqueous eugenate of soda. The precipitate aggregates in a brown mass, which, when boiled for half an hour, changes from sky-blue to the colour of verdigris. (Bonastre.)

Oil of cloves is completely soluble in concentrated *acetic acid, alcohol,* and *ether.* (Bonastre.) It is insoluble in acetic acid of sp. gr. 1·05. (Jahn, *N. Br. Arch.* 66, 129.)

Appendix to Eugenic Acid.

1. Pyrolivilic Acid.

$$C^{20}H^{13}O^5 = C^{20}H^{12}O^4 + Aq\,(?).$$

Sobrero. *Ann. Pharm.* 54, 87.

Preparation. Pure dry olivil (the crystalline resin of the wild olive-tree) is slowly distilled in a retort, of which it occupies about one third, till the residual black mass begins to swell up. The pyrolivilic acid, which passes over as an oil together with water, is dissolved in ether, and the solution is distilled in a stream of dry carbonic acid, at a gradually increasing temperature. Ether, and all the water, first pass over, then the pure acid. (Chloride of calcium cannot be used for drying the acid, since it dissolves therein and cannot afterwards be separated.)

Properties. Colourless oil, heavier than water. Boils above 200°. It has an agreeable odour, and tastes and smells just like eugenic acid. Its aqueous solution reddens litmus.

			Sobrero. *mean.*
20 C	120	69·36	69·99
13 H	13	7·51	7·31
5 O	40	23·13	22·70
$C^{20}H^{13}O^{5}$	173	100·00	100·00

Sobrero's analysis agrees very closely with Dumas's analysis of eugenic acid, but not with those of Böckmann and Ettling.

Decompositions. 1. Turns brown on exposure to the *air,* and afterwards acquires a reddish-brown colour. — 2. The *potash*-solution blackens and becomes opaque in the *air,* owing to deposition of carbon. — 3. If the solution be now decomposed with an acid, and the precipitated pyrolivilic acid distilled, a large quantity of charcoal remains in the residue and the distillate has the mean composition : 68·92 p. c. C, 7·64 H, and 23·440. — 3. It is converted by *nitric acid* into resin and picric acid. — 4. Reduces aqueous *nitrate of silver.*

Pyrolivilic acid is very slightly soluble in *water.* It dissolves readily in solution of *caustic potash,* without yielding a crystallisable salt. (This distinguishes it from eugenic acid.) — It dissolves *chloride of calcium* and cannot again be separated therefrom.

Lead-salt. Subacetate of lead gives with alcoholic pyrolivilic acid, white curdy flakes, which become soft at 100°, and melt to a transparent, pulverisable, resinous mass ; they dissolve in alcohol but not in water, and are precipitated from the alcoholic solution by evaporation or by dilution with water. The salt appears to vary greatly in composition. Prepared from the alcoholic solution by evaporation, it contains 57·30 p. c. PbO ; precipitated from the same solution by water, 53·16 p. c. PbO.

Obtained by evaporation.			Sobrero.
20 C	120	30·99	30·59
12 H	12	3·09	2·89
4 O	32	8·29	8·89
2 PbO	224	57·63	57·63
$C^{20}H^{12}O^{4},2PbO$	388	100·00	100·00

Pyrolivilic acid dissolves readily in *alcohol* and in ether. Water precipitates the alcoholic solution. The ethereal solution, when left to evaporate, deposits the acid in oily drops.

2. Carmufellic Acid.

$C^{24}H^{20}O^{32}$ (?).

MUSPRATT & DANSON. (1851.) *N. Phil. Mag. J.* 2, 293; *J. pr. Chem.* 55, 25.

Formation and Preparation. About 20 lbs. of cloves are digested in a copper vessel with 36 lbs. water, and the whole is boiled for an hour. The dark-brown decoction is poured off, and the residue is repeatedly boiled with fresh quantities of water till the liquid is no longer coloured. The united extracts, amounting to about 270 lbs., are reduced by evaporation to 54 lbs., and divided into from 20 to 30 pts., each of which is mixed with cold nitric acid, and heated for several days in a covered vessel on a sand-bath. (If the extracts were evaporated to a syrup, a violent reaction would take place on treating them with nitric acid in the cold, and a blood-red liquid would be obtained.) A lively effervescence ensues, a suffocating gas which excites tears being evolved, together with carbonic acid and a few nitrous fumes, while the liquid, which contains a large quantity of oxalic acid, becomes pale yellow and deposits abundant white flakes. All the gas is completely expelled; the liquid filtered (this requires a long time); the residue washed with boiling water; and the filtrate evaporated, till it deposits yellow micaceous laminæ, which are dissolved in water and converted into a lead-salt by precipitation with acetate of lead. The washed lead-salt is decomposed by sulphuretted hydrogen, and the solution is decolorised with animal-charcoal and evaporated, whereupon dazzling white crystals of the acid are deposited. One pound of cloves yields about 2 grains of crude acid.

Properties. Brilliant, colourless, micaceous laminæ.

			Muspratt & Danson. *At* 100° (*mean.*)
24 C	144	34·29	34·25
20 H	20	4·76	4·81
32 O	256	60·95	60·94
$C^{24}H^{20}O^{32}$	420	100·00	100·00

Decompositions. 1. *Heated* in a test-tube, it melts, gives off vapours smelling like burnt sugar, and yields yellow drops of oil. — 2. It is not attacked by cold *oil of vitriol;* but chars on application of heat, with evolution of sulphurous acid.

Combinations. Insoluble in cold, sparingly soluble in boiling *water.*

Combines with bases, forming *salts.* Their formula, according to Muspratt and Danson, is $C^{24}H^{20}O^{32}$,MO, and therefore probably $C^{24}H^{19}MO^{32}$,HO. The acid dissolves in *ammonia* and in *caustic potash.* Its moderately dilute solution (in ammonia ? Kr.) produces with soluble salts of *baryta, strontia,* and *lime,* transparent gelatinous precipitates which cause the solutions to solidify. It gives with salts of *lead,* a white, transparent, gelatinous precipitate ; with *ferrous salts,* white; with *ferric salts,* bright yellow ; with *cupric salts,* green ; and with *silver salts,* white flakes. The precipitates occupy an exceedingly small space after they have been dried, and then resemble laminæ of mica. They dissolve with turbidity in dilute hydrochloric or nitric acid, except the lead-salt, which gives a clear liquid.

Carmufellate of Baryta. An equal number of atoms of carmufellic acid and acetate of baryta are dissolved in water; the mixed solutions are evaporated to dryness; and the residue is exhausted with water, and dried on a porous tile over oil of vitriol. — The precipitate obtained by throwing down nitrate of baryta with carmufellic acid, cannot after drying be separated from the filter.

Barely soluble in water, abundantly in hydrochloric and nitric acid.

Calculation according to Muspratt & Danson.			Musprratt & Danson.
$C^{24}H^{20}O^{32}$	420	84·59	
BaO	76·5	15·41	15·80
$C^{24}H^{20}O^{32},BaO$	496·5	100·00	

Carmufellate of Lead. Prepared like the baryta-salt. It is almost insoluble in water, but dissolves in nitric acid.

Calculation according to Muspratt & Danson.			Muspratt & Danson.
$C^{24}H^{20}O^{32}$	420	78·95	
PbO	112	21·05	20·61
$C^{24}H^{20}O^{32},PbO$	532	100·00	

Carmufellic acid is insoluble in *alcohol* and in *ether*.

3. Volatile Oils containing Eugenic Acid.

a. Oil of Cloves. (*Gewürznelkenöl.*) — From the buds or flower stalks of *Eugenia caryophyllata*. 100 pts. of cloves yield from 14·5 to 28 pts. of oil (Comp. Jahn, *N. Br. Arch.* 66, 129; Zeller, *N. Jahrb. Pharm.* 1, 93); while the same quantity of stalks gives only 4 pts. (Van Hees, *N. Br. Arch.* 69, 41.) The oil does not pass over completely till the distillation has been continued for a long time. Colourless and transparent; odour burning, peculiar; taste sharp, biting and warm. Does not solidify at — 25°. (Bonastre) Deposits camphor in the cold. (Bizio.) Sp. gr. = 1·034 (Lewis); of the commercial oil, 1·055, of that prepared by Bonastre, 1·061 (Bonastre); between 1·033 and 1·040 (Van Hees); between 1·046 and 1·058. The first portion of the distillate is lighter than the succeeding products, so that by fractional distillation oils of sp. gr. 0·95 and 1·076 may be obtained. (Jahn.) Prepared from clove-stalks it has a different odour, and a sp. gr. 1·049 (Van Hees, *Pharm. Centr.* 1847, 380); it then has a peculiar odour, like cabbage, and its sp. gr. is 1·051. (Jahn.) It is a mixture of neutral oil of cloves and eugenic acid (p. 202.) (Ettling), of the first of which the earlier portions of the distillate, as well as the oil from clove-stalks, contain a larger quantity. (Jahn.) Contains 73·6 p. c. C, 8·15 H, and 18·25 O. (Ettling.)

b. Oil of Cinnamon-leaves from Ceylon. Obtained according to Pereira, by macerating cinnamon leaves in sea-water, and submitting the whole to distillation. Closely resembles oil of cloves. Brown oil having a penetrating, aromatic odour, strong, biting taste and sp. gr. 1·053. Reaction acid. Converted by potash or ammonia into a buttery crystalline mass. It is a mixture of benzoic acid, eugenic acid, and a hydrocarbon $C^{20}H^{16}$. — (Stenhouse, *Ann. Pharm.* 95, 103.)

By treating oil of cinnamon-leaves with excess of aqueous potash, decanting the undissolved oil, treating it with fragments of caustic potash, then with chloride of calcium, and finally rectifying it over potassium, the hydrocarbon is obtained as a colourless oil which strongly refracts light, has a specific gravity 0·862, boils between 160° and 165°, and smells like cymene. Contains 88·14 p. c. C, and 11·68 p. c. H, corresponding to the formula $C^{20}H^{16}$. (By calculation, 88·24 p. c. C and 11·76 H.) — (Stenhouse.)

c. Pimento-oil. (*Nelkenpfefferöl.*) — Obtained from the fruit of *Myrtus pimenta.* The pods yield 10 p. c., the seeds 5 p. c. oil. (Bonastre, *J. Pharm.* 11, 187.) The whole fruit yields 1·9 p. c. oil (Braconnot), 2·34 p. c. of sp. gr. 1·03. (Jahn, *N. Br. Arch.* 66, 155.) Colourless or pale-yellow ; it has a more agreeable smell and taste than oil of cloves (Voigtel), less agreeable (Bonastre), and slightly repulsive, recalling that of *Myrtus communis.* It refracts light powerfully. When poured into water, it separates into two portions, one of which floats while the other sinks. (Jahn.) Becomes dark yellow by keeping. (Voigtel.) With ¼th its bulk of *nitric acid,* it immediately turns dark red, with effervescence, and forms a yellowish red solution, the colour of which is rendered more intense by ammonia. (Bonastre.) With *oil of vitriol, nitric acid,* and *iodine* it behaves like oil of cloves. Freshly distilled, it will not mix with *ammonia,* but after standing in contact with it for eight days, it is converted into a colourless crystalline mass. (Jahn.) According to Bonastre, it forms with *alkalis* the same solid compounds as oil of cloves. (*J. Pharm.* 13, 466.) It mixes with an equal quantity of caustic potash-ley, thereby developing heat and becoming turbid ; afterwards the liquid becomes quite clear and viscid, but on cooling it does not solidify in crystals, even on standing, and on addition of water is partly precipitated unchanged, while a resin remains in combination with the potash. (Jahn.) Dissolves completely in alcohol and ether. (Bonastre.)

d. Volatile oil of the Brazilian Clove-cinnamon. Obtained from *Persea caryophyllata.* (Martius.) Heavier than water, bright yellow, smells like oil of cloves, but less agreeably. Taste burning, like cloves. *Burns* with a bright flame, depositing much charcoal. It takes fire with *fuming nitric acid.* Forms with *bases,* compounds which are partly crystallisable, but can never be obtained neutral. Acids precipitate the oil unchanged. The compounds with *ammonia, potash,* and *soda* are crystallisable, but the *lime*-compound is not. Readily soluble in *alcohol,* from which it is precipitated by water.

e. Volatile oil of Canella alba. By distilling white cinnamon, the bark of *canella alba,* with water and cohobating the distillate, 0·94 p. c. of oil are obtained. This in contact with aqueous potash parts with eugenic acid, and on being distilled after several days, yields first a large quantity of oil which floats on water (*a* and *b*), then a small quantity of oil heavier than water (*c*), while half resinised oil floats on the potash-ley which contains eugenate of potash in solution. The lighter oil has a strong aromatic odour, like oil of cajeput, and boils between 180° and 245°; and by fractional distillation a first portion (*d*) is obtained at 180°, containing 75·25 p. c. C, 11·28 H, and 13·46 O. (If this be again fractionally and very slowly distilled, a portion boiling at 166° (*aa*) is obtained, yielding 79·11 p. c. C, 10·64 H, and 9·25 O. On further distilling the lighter oil, an oil (*b*) is finally obtained of sp. gr. 0·941, and boiling at 245°. It contains 80·54 p. c. C, 10·77 H, and 8·69 O. The oil (*c*) heavier than water does not combine with potash, and contains 73·7 p. c. C, 10·7 H, and 15·6 O. (W. Meyer & v. Reiche, *Ann. Pharm.* 47, 234.) Hence the oil of *canella alba* is a mixture of eugenic acid, cajeput oil, and an oxygenated oil. (Wöhler.)

Eugenate of Ethyl.

$C^{24}H^{16}O^{4} = C^{4}H^{5}O,C^{20}H^{11}O^{3}$.

CAHOURS. (1858.) *Compt. rend.* 46, 220; *Ann. Pharm.* 103, 265; *J. pr. Chem.* 73, 259; more detailed, *N. Ann. Chim. Phys.* 52, 189; *Ann. Pharm.* 108, 323.

Nelkenvinester, Eugenäthyl (Gm.). *Nelkensaures Aethyl. Eugenic ether.*

Formation and Preparation. By acting on eugenate of potash with iodide of ethyl in a sealed tube. The product is washed with dilute aqueous alkali, dried over chloride of calcium, and rectified.

Properties. Colourless oil, boiling at about 240°. It has an aromatic odour, slightly resembling that of cloves. Neutral.

			Cahours.
24 C	144	75·00	74·82
16 H	16	8·33	8·40
4 O	32	16·67	16·78
$C^{4}H^{5}O,C^{20}H^{11}O^{3}$	192	100·00	100·00

It is violently attacked by *bromine, chlorine,* or *fuming nitric acid,* yielding a viscid product.

Insoluble in *water.* Readily soluble in *alcohol* and *ether.*

Benzo-eugenic Anhydride.

$C^{34}H^{16}O^{6} = C^{14}H^{5}O^{3},C^{20}H^{11}O^{3}$.

CAHOURS. (1858.) *N. Ann. Chim. Phys.* 52, 189; *Ann. Pharm.* 108, 321.

Benzoate of Eugenyl, Eugenate of Benzoyl, Benzeugenyl, Benzoe-Nelkensäure-Anhydrid.

Preparation. Chloride of benzoyl is heated with eugenic acid as long as hydrochloric acid continues to be evolved, and until the mass, which at first was viscous and dark brown, has become bright brownish-yellow. It is then left to cool in a stoppered vessel. The next day concentrated solution of potash is added to the mass (which sometimes is still fluid, sometimes solidified in crystals), whereupon it solidifies, and is washed with water, pressed between blotting paper and crystallised from boiling alcohol.

Properties. Colourless needles, bright amber-coloured when not quite pure, melting between 50° and 55°, and boiling above 360°.

			Cahours. *mean.*
34 C	204	76·12	75·72
16 H	16	5·97	6·06
6 O	48	17·91	18·22
$C^{14}H^5O^3,C^{20}H^{11}O^3$	268	100·00	100·00

It is violently attacked by *bromine* and by *nitric acid.* It is not affected by cold or boiling aqueous *potash,* but is resolved by solid hydrate of potash into benzoate and eugenate of potash.

Insoluble in cold and boiling *water.* Dissolves in boiling *alcohol* and in *ether.*

Toluo-eugenic Anhydride.

$$C^{36}H^{18}O^6 = C^{16}H^7O^3,C^{20}H^{11}O^3.$$

Cahours. (1858.) *N. Ann. Chim. Phys.* 52, 189; *Ann. Pharm.* 108, 322.

Toluate of Eugenyl, Eugenate of Toluyl, Tolueugenyl Toluyl-Nelkensäure-Anhydrid.

Obtained and purified in the same way as benzo-eugenic acid, by the action of chloride of toluyl ($C^{16}ClH^7O^2$) on eugenic acid.

Needles resembling those of benzo-eugenic anhydride.

			Cahours. *mean.*
36 C	216	76·59	76·39
18 H	18	6·38	6·48
6 O	48	17·03	17·13
$C^{16}H^7O^3,C^{20}H^{11}O^3$	282	100·00	100·00

Heated with fragments of *caustic potash,* it is resolved into toluate and eugenate of potash.

Insoluble in *water.* Dissolves somewhat readily in boiling *alcohol,* still more in *ether.*

Aniso-eugenic Anhydride.

$C^{36}H^{18}O^{8} = C^{16}H^{7}O^{5},C^{20}N^{11}O^{3}$.

Cahours. (1858.) *N. Ann. Chim. Phys.* 52, 189; *Ann. Pharm.* 108, 323.

Anisate of Eugenyl, Eugenate of Anisyl, Aniseugenyl, Anis-Nelkensäure-Anhydrid.

Chloride of anisyl acts on eugenic acid in the same way as chloride of benzoyl, and yields a crystallisable product, insoluble in aqueous potash, and bearing the same relation to anisic acid, as benzo-eugenic anhydride to benzoïc acid.

Cumino-eugenic Anhydride.

$C^{40}H^{22}O^{6} = C^{20}H^{11}O^{3},C^{20}H^{11}O^{3}$.

Cahours. *Compt. rend.* 46, 220; *Ann. Pharm.* 105, 263; more detaile *N. Ann. Chim. Phys.* 52, 205; *Ann. Pharm.* 108, 323.

Cuminate of Eugenyl, Eugenate of Cumyl, Cumeugenyl, Cumin-Nelkensäure, Anhydrid.

Formation and Preparation Chloride of cumyl does not act upon eugenic acid in the cold, but on heating, abundant vapours of hydrochloric acid are evolved, while the mixture becomes coloured and thickens. When the evolution of hydrochloric acid has ceased, and the mixture has become light brown and liquid, it is left to cool, and the excess of eugenic acid or of chloride of cumyl is removed with concentrated potash-solution, whereupon the product solidifies in crystals. These are washed with water, pressed between blotting paper, and recrystallised from boiling alcohol.

Properties. Colourless, highly brilliant tablets, which melt at a gentle heat and volatilise when heated above 400°.

			Cahours.
40 C	240	77·42	77·11
22 H	22	7·09	7·14
6 O	48	15·49	15·75
$C^{20}H^{11}O^{3},C^{20}H^{11}O^{3}$	310	100·00	100·00

Isomeric with cuminic anhydride.

Decompositions. Decomposed by *oil of vitriol* in the same way as by caustic potash (*vid. inf.*). — 2. Not affected by boiling *hydrochloric acid.* — 3. It is violently attacked by *fuming nitric acid,* being converted into a viscid, reddish yellow resin and a crystalline body. — 4. It is not affected by boiling potash-solution, but *caustic potash in fusion* decomposes it into cuminate and eugenate of potash.

Bromine-nucleus $C^{20}BrH^{13}$.

Hydrobromate of Bromo-cymene.

$C^{20}Br^2H^{14} = C^{20}BrH^{13},HBr(?)$.

SIEVEKING. (1857.) *Dissert. über Cuminol and Cymen.* Gött, 1857; abstr. *Ann. Pharm.* 106, 261.

Bromide of Cymyl and Hydrogen, Cymylbromür.

Formation (p. 186).

Bromine is dropped into water, on which cymene floats, as long as the colour of the bromine continues to disappear, and the product is washed alternately with aqueous carbonate of soda and water, and then dried over oil of vitriol.

Colourless oil, heavier than water.

It cannot be distilled without decomposition. By prolonged boiling with alcoholic *potash*, it parts with all its bromine, being converted into an oil resembling cymene.

Chlorine-nucleus $C^{20}ClH^{13}$.

Hydrochlorate of Chlorocymene.

$C^{20}Cl^2H^{14} = C^{20}ClH^{13},HCl(?)$.

SIEVEKING. (1857.) *Dissert. über Cuminol and Cymen.* Gött. 1857; abstr. *Ann. Pharm.* 106, 261.

Chloride of Cymyl and Hydrogen, Cymylchlorür.

Formation (p. 186).

Chlorine is passed into water, upon which cymene floats, till the latter sinks. The product is washed with aqueous carbonate of soda and water and dried over oil of vitriol.

Limpid oil, containing 34, 41 p. c. Cl ($C^{20}H^{14}Cl^2 = 34{\cdot}34$ Cl).

It turns yellow by keeping and evolves hydrochloric acid. It cannot be distilled without decomposition. It is not further acted on by *chlorine.* Becomes hot with *fuming sulphuric acid,* evolves hydrochloric acid, turns brownish-red and forms sulphocymenic acid. Heated with alcoholic *ammonia,* it deposits chloride of ammonium. Boiled with alcoholic *potash,* it turns red, deposits chloride of potassium, and is converted into an oil, which is separable by water, and when distilled passes over colourless at first, then coloured, evolves hydrochloric acid, and leaves a residue of charcoal. The distillate, after standing over hydrate of lime, distils between 170° and 230°, still contains from 10 to 12·6 p. c. chlorine, and has an aromatic odour.

Hydrochlorate of chlorocymene does not dissolve in *water*, and but slightly in *alcohol.*

Oxybromine-nucleus $C^{20}Br^3H^9O^2$.

Terbromanethol.

$C^{20}Br^3H^9O^2$.

CAHOURS. (1840.) *Rev. scient.* 1840, 342; *J. pr. Chem.* 22, 58; more fully, *N. Ann. Chim. Phys.* 2, 279; *J. pr. Chem.* 24, 337; *Ann. Pharm.* 41, 56.

Bromanisol, Bromanisal.

Formation (p. 194).

Preparation. Bromine is gradually dropped upon anise-camphor, till a slight excess has been added, and the mixture is allowed to solidify. A brominated oil is then extracted by small quantities of ether, and the residue is dissolved in boiling ether, and left to crystallise. The crystals thus obtained are still contaminated with a small quantity of oil; they are therefore pressed between blotting-paper and recrystallised from ether.

Properties. Rather large, colourless, highly brilliant crystals, which crack between the teeth. Inodorous.

	Crystals.		Cahours. mean.
20 C	120	31·17	31·52
3 Br	240	62·33	
9 H	9	2·34	2·66
2 O	16	4·16	
$C^{20}BrH^9O^2$	385	100·00	

It is slightly decomposed by *heat* at 100°, and completely on distillation, with evolution of hydrobromic acid. It is not further acted upon by *bromine*.

Insoluble in *water*, slightly soluble in *alcohol*, more so in *ether*.

Oxychlorine-nucleus $C^{20}Cl^3H^9O^2$.

Terchloranethol.

$C^{20}Cl^3H^9O^2$.

CAHOURS. (1840.) *Rev. scient.* 1840, 342; *J. pr. Chem.* 22, 58. In detail. *N. Ann. Chim. Phys.* 2, 281; *J. pr. Chem.* 24, 337; *Ann. Pharm*, 41, 56.

Chloranisol, Chloranisal.

Formation (p. 194).

Only once obtained by the not too prolonged action of dry chlorine on anise-camphor.

In the cold it is a colourless syrup, which becomes more liquid when heated, and decomposes completely when distilled, evolving hydrochloric acid and leaving a residue of carbon.

			Cahours. *mean.*
20 C	120·0	47·71	47·72
3 Cl	106·5	42·34	41·92
9 H	9·0	3·57	3·66
2 O	16·0	6·38	6·70
$C^{20}Cl^3H^9O^2$	251·5	100·00	100·00

Appendix to Terchloranethol.

Chloride of Draconyl.

Cahours. *N. Ann. Chim. Phys.* 2, 282.
Laurent. *Rev. scient.* 1842, 5; *J. pr. Chem.* 27, 247.

Viereinhalbfachgechlortes Anethol. (Gm.)

Formation (p. 194).

Preparation. Anise-camphor (oil of tarragon, Laurent,) is acted upon at a moderate heat for a long time by chlorine gas, till all action has ceased. (Cahours.)

Colourless, semifluid, viscid and glutinous mass (Cahours) of the consistence of turpentine. (Laurent.)

			Cahours.	Laurent.
20 C	120·0	39·63	39·93	39·90
4½ Cl	159·7	52·61	52·14	
7½ H	7·5	2·47	2·75	3·50
2 O	16·0	5·29	5·18	
$C^{20}Cl^{4\frac{1}{2}}H^{7\frac{1}{2}}O^2$	303·2	100·00	100·00	

The compound from oil of tarragon investigated by Laurent, has according to him, the formula $C^{32}Cl^7H^{16}O^3$, according to Gerhardt, perhaps $C^{20}Cl^4H^{10}O^2$ (*Traité* 3,356)).

Decomposes by distillation (Cahours), and (when prepared from oil of tarragon) evolves hydrochloric acid and vapours of a very thick oil, while a small quantity of carbon is left. (Laurent.) It is attacked by boiling alcoholic potash. The oil thus changed, which is still very thick, contains 42·5 p. c. C, and 3·4 H; according to Laurent = $C^{32}Cl^6H^{15}O^3$; according to Gerhardt, it perhaps differs from the preceding by containing less hydrochloric acid.

Nitro-nucleus, $C^{20}XH^{13}$.

Nitrocymene.

$C^{20}NH^{13}O^4 = C^{20}XH^{13}$.

Barlow. (1855.) *Ann. Pharm.* 98, 247.

Nitrocymol, Nitrocyme.

Formation (p. 186).

Preparation. Cymene which has been cooled by a freezing mixture is dropped into fuming nitric acid, likewise carefully cooled, till the whole has become green and thick; it is then poured into cold water, and the nitrocymene, which is precipitated as a red oil, is washed first with water and then with aqueous carbonate of soda.

Properties. Reddish brown, transparent oil, heavier than water. Permanent in the air. Prepared from cymene *a* (= nitrocymene *a*) it is bright yellow and lighter than water.

Decompositions. 1. It is decomposed by distillation with water; on the water which distils over there floats a neutral oil which has the properties of cymene *a*, and is converted into *a*- nitrocymene by cooled fuming nitric acid. — 2. When nitrocymene is added to a paste of *iron filings* and *acetic acid*, heat is developed. If the whole be distilled, after the reaction has terminated, a distillate is obtained which, by treatment with hydrochloric acid, is resolved into cymidine, which dissolves, and an insoluble oil, *a*- cymene.

Nitro-nucleus, $C^{20}X^{2}H^{12}$.

Binitrocymene.

$$C^{20}H^{12}N^{2}O^{8} = C^{20}X^{2}H^{12}.$$

KRAUT. *Ann. Pharm.* 92, 70.

Dinitrocymol.

Cymene is cautiously dropped into nitrosulphuric acid as long as it continues to dissolve; the whole is then heated for some time to 50°, and, after standing for two days, is diluted with a large quantity of water, whereupon a brown, slowly solidifying oil is precipitated. On dissolving this oil in boiling alcohol, and leaving the solution to cool, drops of oil are first deposited, and on the removal of these, the liquid yields crystals of binitrocymene by evaporation.

Colourless, rhombic tables. Melts at 54°, and solidifies for the most part at 43°.

			Kraut. *mean.*
20 C	120	53·57	52·76
2 N	28	12·50	
12 H	12	5·36	5·66
8 O	64	28·57	
$C^{20}X^{2}H^{12}$	224	100·00	

Dissolves in *alcohol* and in *ether*, and is deposited from saturated solutions as an oil.

Oxynitro-nucleus, $C^{20}X^2H^{10}O^2$.

Binitranisoin.

$C^{20}H^{10}N^2O^{10} = C^{20}X^2H^{10}O^2$.

CAHOURS. (1841.) *N. Ann. Chim. Phys.* 2, 301.

Nitraniside.

Formation and Preparation. 1. Formed when anise-camphor is heated with fuming nitric acid, the reaction being attended with considerable development of heat, and evolution of nitrous fumes; the product, however, cannot be purified, since no solution of it can be made. — 2. Anisoïn is dissolved in fuming nitric acid, the solution is precipitated by pouring it into water, and the white pulverulent deposit is thoroughly washed. (Kraut.)

Snow-white, highly electric powder. (Kraut.) Yellow resin, melting at about 100°, and decomposing completely when distilled. Boiled with concentrated caustic alkali, it evolves a large quantity of ammonia, dissolves and forms a black, humus-like acid, viz., melanisic acid, which remains combined with the alkali.

			Cahours. *mean.*	Kraut. *at* 100°.
20 C	120	50·35	52·38	50·91
2 N	28	11·87	11·25	
10 H	10	4·19	4·54	4·49
10 O	80	33·59	31·83	
$C^{20}X^2H^{10}O^2$	238	100·00	100·00	

It gave too much carbon, because it contained anethol (Cahours).

Azo-nucleus, $C^{20}NH^{13}$.

Cymidine.

$C^{20}NH^{15} = C^{20}NH^{13},H^2$.

J. BARLOW. (1855.) *Ann. Pharm.* 98, 253. — Notice of results: *Phil. Mag. J.* 10, 454; *Chem. Gaz.* 1855, 319; *J. pr. Chem.* 66, 341; *Chem. Centr.* 1856, 48; *Instit.* 1856, 163.

Formation and Preparation. (Comp. p. 217.) Nitrocymene is added to a thick paste of acetic acid and iron filings, whereby heat is immediately developed. The whole is then distilled (after supersaturation with caustic soda, Kr. ?), and a very complicated product is obtained, from which the cymidine is extracted by hydrochloric acid. The cymidine, after the portion insoluble in hydrochloric acid has been removed, is precipitated from the solution by caustic soda, and extracted with ether. On distilling off the ether, the product remains in the retort as a brown oil, which is purified by distillation in a stream of hydrogen.

Properties. Yellow, inodorous oil, boiling about 250°. Neutral. Lighter than water.

Decompositions. It is not affected by *iodine,* and but very slightly by *bromine.* It is violently attacked and dissolved by *nitric acid;* soda separates from the solution a semi-solid substance. Becomes slightly warm with *chloride of cyanogen,* and forms a base, probably homologous with melaniline. This is precipitated by adding caustic soda to the solution obtained by boiling the mass with water. With chloride of benzoyl, it forms with evolution of heat, crystals, probably consisting of benzoylcymidide.

Combinations. Cymidine dissolves sparingly in *water,* and forms *salts* with acids.

Sulphate of Cymidine. White crystalline salt, soluble in water.

Hydrochlorate of Cymidine. Strong hydrochloric acid forms with cymidine white clouds and an oil lighter than water, which solidifies in crystals by evaporation or agitation. Turns pinewood yellow. Its solution dyes the skin red. It is not coloured by chloride of lime. Contains 19·68 p. c. HCl, corresponding to the formula $C^{28}NH^{15},HCl$ (by calculation = 19·72 p. c. HCl.

With *terchloride of gold,* cymidine forms a yellow, crystalline salt, sparingly soluble in water.

Chloroplatinate of Cymidine. Aqueous solution of hydrochlorate of cymidine yields with platinic chloride a yellow precipitate which dissolves sparingly in water, but abundantly in alcohol and especially in ether.

			Barlow.
20 C	120·0	33·78	33·77
N	14·0	3·94	
16 H	16·0	4·51	4·67
Pt	98·7	27·79	27·64
3 Cl	106·5	29·98	
$C^{20}NH^{16}Cl,PtCl^{2}$	355·2	100·00	

Prepared from α- nitrocymene (= chloroplatinate of α- cymidine), it contains 27·66 p. c. Pt.

Oxalate of Cymidine. White, crystalline salt, insoluble in water.
Cymidine dissolves readily in *alcohol* and in *ether.*

Azo-nucleus $C^{20}N^{2}H^{12}$.

Nicotine.

$$C^{20}N^{2}H^{14} = C^{20}N^{2}H^{12},H^{2}.$$

Posselt & Reimann. *Mag. Pharm.* 24, 3138; further, 15, 2, 57; presented as a prize essay to the Medical Faculty of Heidelberg, in 1828.

O. Henry & Boutron-Charlard, *J. Pharm.* 22, 689; *J. pr. Chem.* 10, 208.

Liebig & Gail. *Ann. Pharm.* 18, 66.

ORTIGOSA. *Ann. Pharm.* 41, 114.
BARRAL. *Compt. rend.* 14, 224; in detail, *N. Ann. Chim. Phys.* 7, 151; *J. pr. Chem.* 26, 49; *Ann. Pharm.* 44, 281. — *Compt. rend.* 24, 218; *J. pr. Chem.* 41, 466; more fully, *N. Ann. Chim. Phys.* 20, 345.
MELSENS. *N. Ann. Chim. Phys.* 9, 465; *Ann. Pharm.* 49, 353; *J. pr. Chem.* 32, 372.
v. PLANTA-REICHENAU. *Dissert. über das Verhalten der wichtigsten Alkaloide gegen Reagentien.* Heidelberg, 1846.
SCHLÖSSING. *Compt. rend.* 23, 1142; *J. pr. Chem.* 40, 184; more fully, *N. Ann. Chim. Phys.* 19, 230.
RAEWSKY. *N. Ann. Chim. Phys.* 25, 322; *J. pr. Chem.* 46, 470; abstr. *Ann. Pharm.* 70, 232.
J. BÖDEKER. *Ann. Pharm.* 73, 372.
v. PLANTA & KEKULÉ. *Ann. Pharm.* 87, 1.
STAHLSCHMIDT. *Ann. Pharm.* 90, 218; *J. pr. Chem.* 63, 89; *Pharm. Centr.* 1854, 680.
OTTO. *Anleitung zur Ausmittlung der Gifte.* Braunschweig, 1856, 87.

Vauquelin (*Ann. Chim.* 71, 139), in 1809, was the first to make experiments with the view of isolating the acrid principle of tobacco; he discovered the volatility of the nicotine compounds and their behaviour with potash, but did not succeed in isolating the alkaloïd. In this, Posselt and Reimann succeeded in 1828; Ortigosa, in 1842, analysed the compounds of nicotine, and Barral analysed nicotine itself. E. Davy (*Ann. Pharm.* 18, 63), described as aqueous nicotine the ammoniacal liquid obtained by the distillation of tobacco or tobacco-roots with solution of potash, being unacquainted with pure nicotine; his nicotine-salts were mixtures of these and ammonia-salts. (*Instit.* 1835, 137; *Ann. Pharm.* 18, 63; *J. pr. Chem.* 7, 90; *J. Pharm.* 22, 18.)

Formation. The dried substance of rotten potatoes distilled with caustic lime yields nicotine, recognisable by its odour. (? Kr.) (Winkler, *Jahrb. pr. Pharm.* 25, 82.)

Sources. In *Nicotiana Tabacum, rustica, macrophylla* and *glutinosa,* in combination with malic acid. (Posselt & Reimann.) — As a salt. (Schlössing.) — Nicotine exists ready formed in tobacco, and is not formed in its preparation. (Henry & Boutron, Schlössing.) It can be as effectually separated by magnesia as by alkalis (Henry & Boutron), also by lime, baryta and ammonia. (Schlössing.) Acrid vapours are evolved from a boiling infusion of tobacco by carbonate or bicarbonate of potash; the presence of nicotine in these vapours may be detected by mercuric chloride. Carbonate of lime produces the same effect, but to a less extent. (Schlössing.) — Also when tobacco is distilled without alkali, nicotine passes over, though in smaller quantity. (Henry & Boutron.) When an aqueous or alcoholic infusion of tobacco is too rapidly evaporated down, strong vapours of nicotine are evolved. (Schlössing.) When unfermented tobacco is extracted with ether, the solution evaporated, and the residue heated, an odour of nicotine is perceived. (Only a small portion, however, of the nicotine is thus extracted.) Alcohol entirely removes the acrid qualities of tobacco; the alcoholic extract precipitated with mercuric chloride gives the double salt of nicotine and mercury. (Schlössing.) If fresh tobacco-juice be precipitated with tannic acid, the precipitate decomposed at a gentle heat by excess of acetate of lead, the liquid then filtered, the filtrate freed from lead by dilute sulphuric acid, evaporated to dryness, mixed with carbonate of lime and perfectly dried, a large quantity of nicotine may be extracted from the residue by ether. (Henry & Boutron.) Melsens supposed that nicotine was a product of the fermentation or of the imperfect combustion of tobacco. (*N. Ann. Chim. Phys.* 9, 471.)

The following are the percentages of nicotine in different sorts of dry tobacco leaves, deprived of their ribs. *a. French tobaccos of the Departments:* — Lot, 7·96; Lot et Garonne, 7·34; Nord, 6·58; Ile et Vilaine, 6·29; Pas-de-Calais, 4·94; Alsace, 3·21 p. c. — *b. American tobaccos:* — Virginian, 6·87; Kentucky, 6·09; Maryland, 2·29; Havanna under 2 p. c. (Schlössing.) — Four kinds of Paraguay tobaccos contained 1·8; 2; 5·5 and 6 p. c. nicotine. (Lenoble, *N. J. Pharm.* 22, 30; *Lieb. Kopp. Jahresb.* 1852, 531.) When tobacco leaves are prepared for snuff, nicotine is lost in the fermentation (Henry & Boutron), to the amount of about ⅔rds, so that 100 pts. dry snuff still contain about 1·36 p. c. nicotine, chiefly as acetate which is soluble in ether. (Schlössing, *N. Ann. Chim. Phys.* 19, 246.) Tobacco-smoke contains nicotine which, when long porcelain pipes are smoked, is found in the juice collected in the bowl. (Melsens.) By the dry distillation of tobacco, Unverdorben obtained (*Pogg.* 8, 399), among other products, a base which, on being dissolved in water and boiled down with dilute sulphuric acid, was decomposed into ammonia, fuscine, and odorine (xi, 263). See also xiv, 234; *Empyreumatic oil of tobacco.*

Preparation. 1. Coarsely powdered tobacco is boiled with water; the liquid, after filtration through linen, is evaporated to the consistence of extract; and before it has completely cooled, it is shaken up with 2 vols. alcohol of 36°. On standing, the semi-fluid mass divides into two strata, the lower, which is black and almost solid, consisting chiefly of malate of lime, while the upper forms a black solution containing all the nicotine. This is decanted; the alcohol is distilled off; the residual extract again precipitated with alcohol; the alcoholic solution again evaporated; and the residue mixed, before it is quite cold, with concentrated potash-ley, whereupon heat is developed. After cooling, the whole is shaken with ether, which takes up nicotine and other substances, thereby acquiring a deep yellow colour. On distilling the ethereal solution, nicotine tolerably colourless passes over at 180°, but frequently contaminated with decomposition-products of the other substances; hence it is more advantageous to proceed as follows: To the ethereal solution, powdered oxalic acid is gradually added, the whole being continually shaken, whereby, when the ether is not too aqueous, a white precipitate of oxalate of nicotine is immediately produced, which afterwards deliquesces to a syrup at the bottom of the vessel. The liquid is decanted; the precipitated syrup washed with ether, and decomposed by potash; the liberated nicotine is taken up by ether; the ethereal solution heated on a water-bath to expel ether, water, and ammonia; and the temperature then gradually raised, and kept for a whole day at 140°, while a stream of hydrogen is passed through the liquid. The product is now heated to 180°, whereupon colourless nicotine passes over. 1000 grammes of tobacco from Lot yield from 50 to 60 grammes of nicotine. (Schlössing.) Posselt & Reimann adopted a similar process. (*Vid. infra.*)

2. Bad tobacco or tobacco-dust is macerated for 24 hours with water to which 1 p. c. of sulphuric or hydrochloric acid has been added; and

the expressed liquid is evaporated to the consistence of syrup, and distilled with about $\frac{1}{6}$th of its bulk of strong potash-solution, water being added as long as an alkaline distillate, containing ammonia and nicotine, is obtained. This is subjected to either of the following treatments.

a. The distillate is saturated with fragments of caustic potash, which dissolves, developing considerable heat, and expelling most of the ammonia, while the nicotine is separated as an oily stratum. This is decanted and freed by a gentle heat from adhering ammonia. (Liebig & Gail.)

b. The distillate is neutralised with oxalic acid and evaporated to dryness; the oxalate of nicotine is extracted from the residue by boiling alcohol; and the solution evaporated to the consistence of syrup, and shaken in stoppered bottles with fragments of potash and ether. By repeating this treatment, the whole of the nicotine is obtained dissolved in the ether. On distilling the ethereal solution in a water-bath, pure and aqueous ether, ether containing nicotine, and finally colourless oily nicotine (which is collected apart) pass over in succession. The nicotine still contains water. (Ortigosa.)

3. Finely cut Alsatian tobacco is digested with water containing sulphuric acid, pressed out after three days, and the residue submitted to the same treatment till it has entirely lost its acrid taste. The liquid is evaporated to half its bulk, and distilled with lime; the distillate is next shaken with ether, which takes up most of the nicotine, then poured back into the retort and again distilled. The distillate is again treated with ether; poured back into the retort, after the ethereal layer has been decanted, and so on, till the residue no longer has any acrid taste. The brown ethereal solution is gradually heated to 140° within 14 days, whereby ether, water, and other bodies more volatile than nicotine are driven off, then mixed with slaked lime, and heated to 190° in a stream of hydrogen; and the slightly coloured nicotine which passes over is collected as much as possible out of contact of air, and rectified. (Barral.)

4. From the so-called *Tobacco mordant* (*Tabaksbeize*). The brown liquid, mixed with a slight excess of sulphuric acid, is evaporated to a syrup, and mixed with a slight excess of potash-ley; the liberated nicotine is taken up by ether; the ethereal solution mixed with oxalic acid; and the resulting precipitate of oxalate of nicotine decomposed by potash-ley. By shaking up the potash-solution with ether, the nicotine is again dissolved, and may be obtained pure by distilling off the ether, and rectifying *per se.*

Melsens purifies the nicotine thus obtained by placing it in contact with potassium till the metal is no longer attacked even on heating the liquid, and then distils the brown liquid over caustic baryta in a stream of hydrogen; the purest portion passes over towards the middle of the distillation.

Older processes.— Tobacco is distilled with water and $\frac{1}{12}$ potash-hydrate ($\frac{2}{5}$ soda-hydrate and 12 pts. water, according to Henry & Boutron); the residue is mixed with thrice its bulk of water and redistilled; the united distillates containing tobacco-camphor (p. 232), nicotine, and carbonate of ammonia, are neutralised with sulphuric acid, and evaporated nearly to dryness; and the sulphate of nicotine is extracted from the residue by absolute alcohol. The alcoholic solution is evaporated;

the residue is shaken up with aqueous potash; and the liberated nicotine is taken up by ether; on distilling off the ether, the nicotine remains behind, amounting to $\frac{1}{960}$ of the tobacco. (Posselt & Reimann.) Henry & Boutron distil the sulphate of nicotine with hydrate of soda, and free it from ammonia by leaving it in vacuo. — Posselt & Reimann likewise exhaust the decoction prepared with water containing sulphuric acid and evaporated with alcohol of 90 per cent.; distil off the alcohol; decompose the residue with hydrate of lime or magnesia; and separate the nicotine from it by distillation and agitation with ether, like Schlössing. They dehydrate the ether containing nicotine with chloride of calcium, and expel the ether in the water-bath. The nicotine thus prepared contains a trace of chloride of calcium.

Estimation of Nicotine in Tobacco. — 10 grammes of tobacco containing a known amount of water are introduced into a glass tube, the lower end of which, contracted and bent at right angles, is inserted into the lateral aperture of a flask holding $\frac{1}{6}$ of a litre; the tobacco is moistened with a quantity of ammonia sufficient to liberate all the nicotine; ether is poured into the flask; and its neck is closed with a glass tube which conveys the vapours into a Liebig's condensing apparatus. The lower extremity of this condenser is bent, and fitted by means of a cork into the glass tube containing the tobacco, so that the ether volatilised by the boiling, and again condensed by the cooling apparatus, passes through the tobacco, drops into the flask loaded with nicotine, is again volatilised, and again made available for exhausting the tobacco. The apparatus thus arranged is heated for 2 to 4 hours, or till a few drops of the ether which run off from the tobacco no longer leave any nicotine when evaporated at a gentle heat; the tube containing the tobacco is then replaced by a receiver; the lateral tabulus of the flask is closed; and the liquid is distilled till the ethereal vapours, which at first are strongly ammoniacal, no longer contain any ammonia, and are likewise free from nicotine. The remainder of the ether is left to evaporate in the air, and the quantity of nicotine remaining (from which resin separates) is estimated by the amount of sulphuric acid of known strength required to neutralise it. — 49 pts. of oil of vitriol (SO^4H) correspond to 192 pts. of nicotine. (Schlössing.) Schiel (*Ann. Pharm.* 105, 257; *J. pr. Chem.* 74, 127).

Processes for the detection of nicotine in cases of poisoning are given by Stas (*Bull. de l'Acad. de Médecine de Belgique*, 9, 304; *Jahrb. pr. Pharm.* 24, 313; *Ann. Pharm.* 84, 379; *Liebig & Kopp's Jahresber.* 1851, 640); further: Orfila (*J. Chim. méd.* 27, 399). See also Lehmann (*Pharm. Centr.* 1853, 927); Melsens (*Bull. de l'Acad. de Médecine de Belgique* [2], 1, No. 9; *Rep. Chim. pure*, 1, 232).

Properties. Colourless, transparent oil which remains liquid at − 6° (Posselt & Reimann), at − 10° (Barral), and when heated, even to temperatures short of 100°, gives off white vapours having an intolerable odour. (Ortigosa.) — When nicotine is left in a vacuum for a few days, small crystals appear in it which resemble chlorate of potash, and deliquesce rapidly in the air. (Henry & Boutron.) It distils very slowly at 146°, begins to boil at 240° (towards 250°, according to Barral,) only a portion, however, distilling colourless and undecomposed, in heavy white fumes (Posselt & Reimann, *vid. inf.*) — Sp. gr. 1·048 (Henry & Boutron); 1·033 at 4°; 1·027 at 15°; 1·018 at 30°; 1·0006 at 50°; 0·9424 at 101·5°. (Barral.) It has a sharp odour, slightly resembling that of tobacco (Barral), unpleasantly pungent, like that of dry tobacco, especially when heated (Posselt & Reimann); has a strong odour, unpleasantly like that of tobacco (Ortigosa); slightly ethereal. (Otto.) — Taste burning. (Barral.) Even when diluted, it has an extremely sharp and caustic taste, producing choking in the throat. (Henry & Boutron.) — It is poisonous, $\frac{1}{4}$ of a drop being sufficient to kill a rabbit, and one drop being a fatal dose for a dog. (Posselt & Reimann.) — 5 milligrammes placed upon the tongue of a middle-sized dog kill it in 3 minutes. $\frac{1}{8}$ of a grain dropped into the eye of a full-grown cat produces contraction of the pupil and strong narcotic symptoms, which, however, pass off in the course of an hour. (Gergis & Hesse, *Ann. Pharm.* 7, 293.) Small birds are killed even by the approach of a glass rod moistened with nicotine. Very weak aqueous nicotine taken into the mouth, even for a second, produces heavy turpidity, lasting for 10 minutes, then a sensation of heaviness and headache lasting for several hours. (Henry & Boutron, comp. Melsens, *Ann. Chim. Phys.* 9, 468.)

Nicotine has a strong alkaline reaction. — Its vapour-density is 5·829; or, taking into account the 3 per cent. of residue left in the distillation, it is 5·607. (Barral.) It turns the plane of polarisation of a luminous ray strongly to the left. (Laurent, *Compt. rend.* 19, 926; Wilhelmy Pogg. 81, 527.) — Meat keeps for any length of time in nicotine vapour, merely assuming a brighter red colour. (Robin, *Compt. rend.* 32, 177.)

			Barral.	Melsens.	Schlössing.
20 C	120	74·08	73·69	74·3	73·59
2 N	28	17·28	17·04	17·3	17·11
14 H	14	8·64	8·86	8·8	8·70
$C^{20}N^2H^{14}$	162	100·00	99·59	100·4	99·4

	Vol.	Density.
C-vapour	20	8·3200
N-gas	2	1·9412
H-gas	14	0·9702
Nicotine-vapour	2	11·2314
	1	5·6157

Ortigosa, from his analysis of the platinum-salt, assigned to nicotine the formula $C^{10}NH^8$, which was adopted by Barral. Melsens proposed the formula $C^{10}NH^7$, and Barral, after recalculating his own analysis, showed that this formula was in accordance with it; he, moreover, doubled it to agree with the vapour-density, a conclusion to which Schlössing was also led by his determination of the saturating power of nicotine towards sulphuric acid.

Decompositions. 1. Nicotine quickly assumes a brownish yellow colour when exposed to light. (Henry & Bonastre.) — 2. When distilled, even in an atmosphere of carbonic acid, it always leaves a small residue amounting to about 3 per cent., this effect being reproduced every time distillation is repeated. No gas is evolved; and the residue, which is insoluble in water, but easily soluble in alcohol, appears to be an isomeric modification of nicotine. (Barral.) Nicotine when distilled leaves a resin soluble in alcohol and precipitable therefrom by water. (Ortigosa.) The same residue remains when nicotine is left to evaporate in the air. (Posselt & Reimann.) — 3. Nicotine exposed for some time to the *air*, turns brown, becomes more viscid, and is partly converted into a resin. (Posselt & Reimann, Burral and others.) 4. At ordinary temperatures, it is not set on fire by the approach of a flaming body, but burns in a wick with a bright smoky flame. (Posselt & Reimann.) The vapour which rises from nicotine heated in a crucible may be set on fire. (Henry & Boutron.)

5. Warm *oil of vitriol* does not act immediately on nicotine, but gradually acquires a red-brown colour by contact with it; the solution supersaturated with hydrate of soda, yields nicotine free from ammonia. (Henry & Boutron.) Boiling oil of vitriol decomposes nicotine completely (leaving a black thick mass, according to Stahlschmidt), so that the liquid neutralised with ammonia tastes no longer sharp but only bitter. (Posselt & Reimann.)

6. Aqueous nicotine mixed with *tincture of iodine*, (or with aqueous hydriodous acid or hydriodite of potash mixed with chlorine), becomes turbid, and yellowish at first, but afterwards crimson, even when diluted 1000 times (Posselt & Reimann); according to Planta, it produces with tincture of iodine, a kermes-brown precipitate. On mixing the ethereal solutions of *iodine* and nicotine, heat is evolved, and after a while the mixture solidifies to a crystalline pulp of teriodonicotine. (Wertheim, *Gerhardt's Traité*, 4, 193.)

7. When nicotine is dropped into a bottle filled with chlorine gas, a violent action takes place, sometimes attended with emission of light; hydrochloric acid gas is evolved; and the nicotine becomes blood-red, but loses its colour again by exposure to light for a few days, and then at a rather low temperature (below 8°) deposits long needles, which however melt at a slightly elevated temperature. The liquid, which has become colourless by exposure to light, deposits when mixed with water, a white sediment, which may be recrystallised from alcohol, the supernatant very acid liquid becoming red-brown when evaporated at a gentle heat. (Barral.) — When chlorine is passed over nicotine, a dark brown solid substance is obtained, which dissolves readily in alcohol but does not separate in the crystalline form on evaporation. (Stahlschmidt.) — Chlorine-water does not act on nicotine in the cold; if the liquid be heated at the same time, it turns yellow, without giving off nitrogen gas. (Henry & Boutron, Barral.) — Aqueous *hypochlorous acid* added to a concentrated aqueous solution of nicotine, produces a whitish turbidity, without evolution of nitrogen gas, which however takes place immediately on adding a small quantity of ammonia. (Henry & Boutron.) Nicotine is quickly decomposed by aqueous perchloric acid. (Bödeker, *Ann. Pharm.* 71, 64.) By the action of chlorine on hydrochlorate of nicotine, a beautifully crystallised compound is formed, easily soluble in water, insoluble in alcohol. (Geuther & Hofacker, *Ann. Pharm.* 108, 35.)

8. Nicotine heated with *nitric acid*, gives off copious red fumes, and if distilled with potash after the reaction is finished, yields a volatile base which appears to be ethylamine. (Anderson, *Ann. Pharm.* 75, 82.) — With hot nitric acid, it gives off nitrogen gas and yields a thick orange-coloured mass without any oxalic acid. (Henry & Boutron.) With nitric acid or *acid chromate of potash* and *sulphuric acid*, nicotine gives off a suffocating vapour and forms a brown liquid. (Stahlschmidt.) — Fuming nitric acid attacks it violently, even in the cold, but does not decompose it completely. (Posselt & Reimann.)

9. *Hydrate of soda* exerts a decomposing action upon nicotine, eliminating a small quantity of ammonia. (Henry & Boutron.) When nicotine containing water is left in contact with lumps of hydrate of potash, it dissolves potash, and yields by distillation a liquid which has an odour different from that of nicotine, contains 52 per cent. of carbon,

does not form chloroplatinate of nicotine when mixed with bichloride of platinum, but yields by evaporation of the mixed alcoholic solution, crystals easily soluble in alcohol. (Ortigosa, comp. p. 223.)

10. When *cyanogen gas* is passed over nicotine (Stahlschmidt), or into the alcoholic solution (Hofmann), a brown product is formed which does not crystallise from alcohol (Stahlschmidt) and does not exhibit basic properties. (Hofmann, *Ann. Pharm.* 66, 145.)

11. It acts upon *cyanate of ethyl* less quickly than aniline, forming a compound which crystallises in beautiful laminæ. (Wurtz, *Compt. rend.* 32, 418; *Ann. Pharm.* 80, 349.)

12. In contact with *iodide of methyl*, it deposits a heavy brown oil, and solidifies on cooling as crystalline hydriodate of methyl-nicotine. (Stahlschmidt, *Ann. Pharm.* 90, 222.) — In contact with *iodide of ethyl*, it is converted, even at ordinary temperatures, more quickly at 100°, into hydriodate of ethyl-nicotine. (v. Planta & Kekulé, *Ann. Pharm.* 87, 3.) When *iodide of amyl* is heated for several days with nicotine in a sealed tube, a brown syrup is obtained, which does not solidify, even when cooled and exposed to the air, or crystallise when its aqueous or alcoholic solution is left to evaporate, but when treated with water deposits the excess of iodide of amyl and yields a solution of hydriodate of amyl-nicotine. (Stahlschmidt.)

Combinations. With Water. A. *Hydrated Nicotine.* Nicotine exposed to moist air quickly takes up water, to the amount of 10 per cent. in a day, but gives it up again completely in a dry current of gas. (Schlössing.) In an air-space saturated with aqueous vapour, nicotine takes up, in the course of three weeks, 1·77 per cent. of water, which, however, is given off again when the hydrated nicotine is placed over hydrate of potash. Nicotine thus saturated with water solidifies completely in a freezing mixture of ice and salt. (Barral.)

B. *Aqueous Nicotine.* Nicotine dissolves in water in all proportions. (Posselt & Reimann, Barral and others.) With half its volume or less of water, it forms (when it contains resinous matter, according to Posselt & Reimann) a clear mixture which is rendered turbid by a larger addition of *water.* (Ortigosa.) Hydrate of potash separates nicotine from its aqueous solution. (Liebig & Gail.)

Nicotine at 100° dissolves 10·53 p. c. *sulphur,* the greater part of which crystallises out on cooling, the nicotine returning a dark brown colour. — It does not dissolve *phosphorus.* (Barral.) It absorbs *ammonia gas* but does not retain it more firmly than it retains water. (Schlössing.)

With Acids. Nicotine saturates acids completely. The *salts of nicotine* crystallise sometimes in laminar, sometimes in granular form. (Henry & Boutron.) The simple salts crystallise with difficulty, the double salts more easily. (Barral.) They have a very sharp taste. (Henry & Boutron.) Their aqueous solutions may be evaporated at a gentle heat without much loss of nicotine. (Posselt & Reimann.) They give off part of their nicotine when evaporated. (Henry & Boutron.) They emit the odour of nicotine when treated with potash-ley, and produce with iodine the kermes-colour of nicotine. (Posselt & Reimann.) They dissolve readily in alcohol of 40° (Henry & Boutron), but are insoluble in ether, with the exception of the acetate. (Schlössing.) Nicotine precipitates the salts of manganese, zinc, lead, iron, (*vide infr.*) and tartar-emetic, like the alkalis. (Henry & Boutron.) It precipitates the salts of manganese and iron in the cold, silver-salts when heated. (Schlössing.) It likewise precipitates acetate of lead, acetate of copper, and chloride of cobalt. (Otto.) It does not precipitate baryta or lime-salts, but when carbonic acid gas is passed into an aqueous mixture of nicotine mixed with excess of nitrate of lime or chloride of barium, a precipitate of carbonate of lime or carbonate of baryta is formed in the proportion of 1 at. to 1 at. of the nicotine used. (Schlössing.)

$$CaO,NO^5 + C^{20}N^2H^{14} + HO,CO^2 = C^{20}N^2H^{14},HO,NO^5 + CaO,CO^2.$$

Phosphate of Nicotine. The colourless syrup obtained by neutralising nicotine with aqueous phosphoric acid, yields by evaporation in sunshine, white crystals resembling cholesterin. (Posselt & Reimann.) — Nacreous laminæ. (Henry & Boutron.)

Sulphate of Nicotine. — 100 parts of oil of vitriol neutralise on the average 329·7 pts. of nicotine, forming neutral sulphate of nicotine, $C^{20}N^2H^{14},HO,SO^3$. (Schlössing.) (Calculation 330·6 pts.) The sulphate is a brown uncrystallisable syrup. (Posselt & Reimann.) Nacreous laminæ. (Henry & Boutron.)

Acid Iodate of Nicotine is nearly insoluble in alcohol. (Henry & Boutron.)

Hydrochlorate of Nicotine. — Nacreous laminæ. (Henry & Boutron.) Obtained by saturating nicotine with dry hydrochloric acid gas, and leaving the product in vacuo, in long deliquescent white threads, which are more volatile than nicotine, and dissolve readily in water and alcohol, not in ether. (Barral.) When dry *hydrochloric acid gas* is passed over gently heated nicotine, and the excess of hydrochloric acid is expelled by means of dry hydrogen gas, quantities of hydrochloric acid are taken up, varying from 1 to 2 At., but a considerable portion goes off on gently heating the product. The alcoholic solution of the salt deflects the plane of polarisation of a ray of light to the left. (*Pogg.* 81, 527.)

			Barral.
$C^{20}N^2H^{14}$	162	68·94	
2 HCl	73	31·06	29·74
$C^{20}N^2H^{14},2HCl$	235	100·00	

Nitrate of Nicotine crystallises with difficulty. (Henry & Boutron.)

Aqueous nicotine forms with *phosphate of magnesia* a gelatinous precipitate; with *acid sulphate of alumina,* needle-shaped crystals of a double salt. (Henry & Boutron.) With *phospho-molybdic acid,* it behaves like conine (xiii, 164; Sonnenschein, *Ann. Pharm.* 104, 47.) — *Phosphantimonic acid* (produced by dropping pentachloride of antimony into aqueous phosphoric acid) added to an aqueous solution containing $\frac{1}{250}$ pt. of nicotine, produces a slight turbidity. (F. Schulze, *Ann. Pharm.* 109, 179.)

Chloride of Cadmium with Hgdrochlorate of Nicotine. Nicotine forms with chloride of cadmium, a compound which is difficult to crystallise (G. Williams, *Chem. Gaz.* 1855, 450; *Chem. Centr.* 1856, 47), dissolves readily in water; does not give off any water at 100°, and corresponds to the formula $C^{20}N^2H^{14},2HCl,5CdCl$ (Galetly, *N. Edinb. n. Phil. J.* 4, 94; *Chem. Centr.* 1856, 606.)

By precipitating *bichloride of tin* with nicotine, a white double salt is obtained (Barral); with *ferric chloride,* a yellow-brown double salt (Barral); a brick-red precipitate (Henry & Boutron). With *sulphate of copper,* aqueous nicotine produces a greenish white precipitate, which is not turned blue or dissolved by excess of nicotine. (Henry & Boutron.)

Nicotine with Mercuric Iodide. $C^{20}N^2H^{14},2HgI$. Colourless laminæ, obtained by triturating nicotine with mercuric iodide (whereby heat is evolved, and a portion of the nicotine consequently volatilised) and boiling the mass with water. (Wertheim, *Gerhardt's Traité,* 4, 192.)

Iodomercurate of Nicotine. — A solution of mercuric iodide in hydriodic acid, is dropped into hydriodate of nicotine till the precipitate formed on each addition begins to be permanent; the double salt then crystallises from the solution after standing for some time. The mother-liquor is decomposed by evaporation. Small yellow prisms sparingly soluble in cold water and in alcohol. It is decomposed by hot water, depositing a reddish yellow resin insoluble in potash-ley. (Bödeker.) Hydrochlorate of nicotine added to potassio-mercuric iodide, produces a yellowish white precipitate insoluble in hydrochloric acid. (v. Planta.)

			Bödeker.
$C^{20}N^2H^{16}$	164	19·09	
4 I	508	57·84	58·33
2 Hg	200	23·07	22·71
$C^{20}N^2H^{14},2HI + 2HgI$	872	100·00	

Nicotine with Mercuric Chloride. — Pure nicotine and acetate of nicotine form with solution of mercuric chloride, white flocks, easily soluble in hydrochloric acid, insoluble in alcohol. (Posselt & Reimann.) Hydrochlorate of nicotine, throws down from corrosive sublimate, a white pulverulent precipitate easily soluble in hydrochloric acid and in sal-ammoniac. (v. Planta.)

a. With 2 *at. Mercuric Chloride.* — By precipitating a solution of corrosive sublimate with aqueous nicotine. White crystalline precipitate which melts and turns yellowish below 100°.

Insoluble in water and ether, sparingly soluble in alcohol. (Ortigosa.)

			Ortigosa.
20 C	120	27·72	27·70
2 N	28	6·46	
14 H	14	3·23	3·73
2 Cl	71	16·40	15·86
2 Hg	200	46·19	45·53
$C^{20}N^2H^{14},2HgCl$	433	100·00	

b. With 6 *At. Mercuric Chloride.* A solution of nicotine in dilute hydrochloric acid is dropped into a saturated solution of mercuric chloride, as long as the precipitate at first produced redissolves, and the solution is set aside for a few days, whereupon, if it is sufficiently diluted, the compound separates in crystals. If the solution is too strong, an oil is produced, which dissolves in hydrochloric acid, and may be converted into crystals by addition of mercuric chloride. Clear, colourless, or pale yellow crystals, sometimes an inch long. It crystallises in the right prismatic system. Combination of two vertical prisms *n* and *u*, and two pairs of basal faces *m*, *u*, *t*, (*Fig.* 77); in addition, a horizontal prism *l* (*Fig.* 78), $u : t = 148^\circ\ 55'\ 17''$; $n : t = 129^\circ\ 40'\ 33''$; therefore $n : u = 160^\circ\ 45'\ 16''$, observation gave $160^\circ\ 43'\ 28''$; $l : t = 123^\circ\ 57'\ 24''$. Cleavage parallel to *m*. (Dauber, *Ann. Pharm.* 74, 201.)

Dissolves sparingly in cold water and melts to a brown resin in hot water. Dissolves in acidulated water, sparingly in cold alcohol. (Bädeker.)

			Bödeker.
$C^{20}N^2H^{14}$	162	16·9	
6 Cl	213	21·7	21·6
6 Hg	600	61·4	61·9
$C^{20}N^2H^{14},6HgCl$	975	100·0	

Chloromercurate of Nicotine. With 8At. Mercuric Chloride. $C^{20}N^2H^{14},HCl,8HgCl$. — Obtained as a crystalline precipitate by treating a cold neutral solution of hydrochlorate of nicotine with a larger excess of aqueous chloride of mercury. Crystallises from hot water in stellate groups of needles. (Th. Wertheim, *Gerhardt's Traité*, 4, 191.)

Aqueous nicotine does not precipitate *cyanide of mercury*. (Henry & Boutron.)

Nicotine with Mercuric Chloride and Cyanide. A neutral solution of hydrochlorate of nicotine is mixed with an equal quantity of a saturated solution of cyanide of mercury. Colourless silky prisms grouped in tufts, dissolving easily and without decomposition in water and alcohol, both cold and hot. With hydrochloric acid, it evolves hydrocyanic acid Potash-ley does not precipitate the solution of the prisms, but colours the solid salt reddish yellow. Contains 60·85 p. c. mercury, 17·76 chlorine, and 2·46 cyanogen, and is therefore probably $C^{20}N^2H^{14},5HgCl,HgCy$ or $C^{20}N^2H^{14},4HgCl,2HgCy$. (Bödeker.)

Nicotine with Nitrate of Silver. — Aqueous nicotine does not precipitate nitrate of silver. (Henry & Boutron.) *a. With* $\frac{1}{2}$ *At. Nitrate of silver*, $2C^{20}N^2H^{14},AgO,NO^5$. When alcoholic nitrate of silver is mixed with excess of alcoholic nicotine, and the dilute solution left to evaporate, beautiful prisms are produced, which appear to belong to the oblique prismatic system. (Wertheim.)

b. With 1 *At. Nitrate of Silver*, $C^{20}N^2H^{14},AgO,NO^5$. Obtained like *a*, but with excess of nitrate of silver. Colourless prisms.

Nicotine with Terchloride of Gold — Aqueous nicotine forms with sodio-auric chloride a light orange-coloured precipitate. (Henry & Boutron.) Hydrochlorate of nicotine added to auric chloride, throws down light yellow flocks, insoluble or sparingly soluble in hydrochloric acid. (v. Planta.)

Chloroplatinite of Nicotine. — a. With 2 *At. Hydrochloric acid.* 1. Nicotine is gradually added to a luke-warm solution of protochloride of platinum in hydrochloric acid, stirring constantly and cooling the liquid, because it is apt to get heated. There is then produced a crystalline precipitate of orange-coloured chloroplatinite of nicotine with 4 At. hydrochloric acid, the quantity increasing as the stirring is continued; and the mother-liquor filtered from this precipitate yields by evaporation or cooling, red-coloured right prisms of chloroplatinite of nicotine with 2 At. hydrochloric acid. — 2. This salt is obtained in larger crystals, when the orange-coloured salt is redissolved in the mother-liquor by boiling, and the solution is left to cool and crystallise in vacuo. — 3. When the red prisms obtained by 1 or 2 are dissolved in a large quantity of hot water, the solution becomes turbid on cooling, from separation of yellow crystalline scales, isomeric with the red prisms obtained by 1 or 2. (Raewsky.)

Leaves platinum when ignited on platinum-foil. With hot nitric acid it gives off red vapours. It is turned brown by oil of vitriol, and when heated yields a brown precipitate and gives off sulphurous acid. It dissolves sparingly in cold water, more easily in hot water (if heated with too little water, it becomes gelatinous on the surface and less soluble), and separates on cooling in yellow crystalline scales, isomeric with the red prisms. It dissolves in cold nitric and hydrochloric acid, not in alcohol or in ether. (Raewsky.)

				Raewsky.
				mean.
	Red salt.		*a.*	*b.*
20 C	120·0	23·8	24·00	24·1
2 N	28·0	5·6	5·50	6·1
16 H	16·0	3·2	3·25	3·2
2 Pt	197·4	39·2	39·40	39·1
4 Cl	142·0	28·2	27·85	27·5
$C^{20}N^2H^{14},2HCl,2PtCl$	503·4	100·0	100·00	100·0

a. Red prisms. *b.* Yellow crystalline scales.

According to Raewsky, it is $PtCl,C^{10}NH^7,HCl$, that is to say, the hydrochlorate of a peculiar platinum base (the corresponding member to which among the ammoniacal platinum compounds (vi, 296) is not known; a view which is opposed by Gerhardt with respect to this and the following compound (*Compt. chim.* 1849, 206), inasmuch as the latter gives off nicotine when treated with potash.

b. With 4 *At. Hydrochloric acid.* — (*Preparation, vid. sup.*). Orange-yellow crystalline powder (*a*); separates by spontaneous evaporation from its solution in hydrochloric acid, in very large, regular, orange-coloured rhombic prisms (*b*); from its solution in nitric acid in small yellow crystals (*c*). When dissolved in (an insufficient quantity of?) boiling water, it leaves an amorphous residue (*d*), whilst the salt *a* crystallises from the solution. (Raewsky.)

Heated on platinum-foil, it swells up, gives off hydrochlorate of nicotine, burns like tinder, and leaves platinum. Cold oil of vitriol turns it white; hot oil of vitriol chars it, with evolution of sulphurous acid, and leaves a black residue of platinum. With potash, it evolves nicotine. (Raewsky.)

Insoluble in cold water, (*vide sup.*) Insoluble in alcohol and ether. Dissolves in nicotine, forming a red liquid, miscible without turbidity with cold water; and on evaporating this solution in vacuo, there remains a thick, glutinous, very deliquescent mass, resembling treacle, which dissolves in water, hydrochloric acid, nitric acid, alcohol and ether, and cannot in any way be made to crystallise. (Raewsky.) Perhaps $C^{20}N^2H^{14},2HCl,PtCl$ or $C^{20}N^2H^{14},HCl,PtCl$. (Gerhardt, *Compt. chim.* 1849, 206.)

			Raewsky.			
Orange-yellow salt.			*a.* *mean.*	*b.*	*c.*	*d.*
20 C	120·0	20·8	20·5	20·7	20·4	20·5
2 N	28·0	4·9	6·2	4·9	6·2	6·2
18 H	18·0	3·1	3·2	3·1	3·4	3·3
2 Pt	197·4	34·3	34·2	34·3	34·0	34·0
6 Cl	213·0	36·9	35·9	37·0	36·2	36·0
$C^{20}N^2H^{14},4HCl,2PtCl$	576·4	100·0	100·0	100·0	100·2	100·0

According to Raewsky, $PtClC^{10}NH^7,2HCl$ (comp. p. 230.)

Chloroplatinate of Nicotine. — *Nicotinplatinchlorid.* — On mixing the solutions of hydrochlorate of nicotine and bichloride of platinum, a yellow crystalline precipitate is formed if the solutions are concentrated, and if they are dilute, there are deposited, after a while, oblique four-sided prisms belonging to the right prismatic system. (Ortigosa.) Barral obtains the same compound as a granular powder by precipitating bichloride of platinum with nicotine. Liebig & Gail precipitate with bichloride of platinum the distillate containing nicotine and ammonia obtained in the preparation of nicotine, as described at page 222, whereupon the liquid filtered from the precipitate of chloroplatinate of ammonium deposits, after three or four days, large ruby-red crystals. — The salt has a bitter and very sharp taste. (Posselt & Reimann.)

When exposed to the air, it becomes dull, and cannot be recrystallised without decomposition. Distilled with potash-ley, it yields pure nicotine. (Liebig & Gail.) It dissolves with difficulty in water. (Ortigosa.) Soluble in boiling water. (Barral.) It dissolves in hot dilute hydrochloric acid (Ortigosa), somewhat in nitric acid. (Posselt & Reimann.) Insoluble in hydrochloric acid. (v. Planta.) Insoluble in alcohol and in ether (Ortigosa); very soluble in a slight excess of nicotine. (Barral.)

			Ortigosa.	Barral.
20 C	120·0	20·87	20·98	21·12
2 N	28·0	4·87	4·74	4·81
16 H	16·0	2·78	3·09	3·16
2 Pt	197·4	34·36	34·11	34·25
6 Cl	213·0	37·12		
$C^{20}N^2H^{14},2HCl,2PtCl^2$	574·4	100·00		

Acetate of Nicotine. — Nicotine supersaturated with glacial acetic acid and exposed to the air, forms after 8 days a neutral syrup. (Posselt & Reimann.) Acetate of nicotine crystallises with difficulty. (Henry & Boutron.) Strong acetic acid forms with the ethereal solution of nicotine a clear mixture, from which water extracts the acetate of nicotine. (Posselt & Reimann.) According to Schlössing also, acetate of nicotine is soluble in ether.

Oxalate of Nicotine. — Crystalline, easily soluble in water. (Posselt

& Reimann.) Insoluble in ether. (Schlössing.) Laminæ having a pearly lustre. (Henry & Boutron.)

Nicotine forms a crystallisable salt with *nicotic acid* (x, 229).

Tartrate of Nicotine is obtained by evaporating its solution in the air, as a crystalline granular mass easily soluble in water. (Posselt & Reimann.)

Purpurate of Nicotine. — Aqueous alloxan, to which a few drops of nicotine are added, assumes in a few seconds a dark purple colour, and, subsequently, there are formed in the red liquid, colourless rhombic tables, very similar to those of uric acid when the latter have acquired their obtuse angles; they may be freed from the mother-liquor by washing with a small quantity of water. The crystals dissolve in cold, moderately dilute potash-ley, with splendid purple blue-colour and the odour of nicotine. The purple mother-liquor may be evaporated over oil of vitriol to a blood-red viscid syrup, which dries up to an amorphous mass; it is decolorised by absolute alcohol, with precipitation of brick-red flakes which dissolve in alkalis with carmine colour, emitting at the same time an odour of nicotine. (Schwarzenbach.) — Hence Schwarzenbach supposes that the mother-liquor contains acid purpurate of nicotine, and that the crystals contain the neutral purpurate. (*Wittstein's Vierteljahrsschr.* 6, 424 and 8, 170.)

Picric acid added to hydrochlorate of nicotine throws down sulphur-yellow flocks. (v. Planta.)

Tincture of galls, added to aqueous nicotine, throws down a white curdy precipitate (Henry & Boutron); it forms, with hydrochlorate of nicotine, a whitish cloud, which disappears on addition of a few drops of hydrochloric acid, but is reproduced by a larger quantity. (v. Planta.)

Nicotine mixes in all proportions of *alcohol.* The mixture, when distilled, gives off first a comparatively pure alcohol, then spirit containing nicotine. (Posselt & Reimann.)

It mixes in all proportions with *ether,* and the solution when distilled gives off *pure* ether, with only a little nicotine towards the end. It gives up all its nicotine to acids. (Posselt & Reimann.) Ether entirely removes nicotine from its aqueous solution.

Nicotine dissolves in about 40 pts. of *oil of turpentine,* easily in *oil of almonds;* the latter solution has a very sharp taste, and gives up all its nicotine when shaken up with acetic acid. (Reimann.)

Appendix to Nicotine.

a. Nicotianine or Tobacco-camphor.

HERMBSTÄDT. *Schw.* 31, 442; abstr. *Berz. Jahresber*, 1823, 113.
POSSELT & REIMANN. *Mag. Pharm.* 24, 138; *Berz. Jahresber*, 1831, 193.
LUNDERER. *Repert.*, 53, 205.
BARRAL. *Compt. rend.* 21, 1376.

Obtained by Hermbstädt, in 1823, from *Nicotiana Tabacum.* — According to Landerer, it is produced in the drying of the tobacco, inasmuch as fresh tobacco-leaves do not yield it.

Preparation. The herb, either fresh or dry, is distilled with a small quantity of water, whereby a milky distillate is obtained, on the surface of which nicotianine separates after a few days in laminar crystals.

The remaining portion of the distillate is mixed with subacetate of lead, the precipitate decomposed by a not quite sufficient quantity of dilute sulphuric acid, and the liquid filtered from the sulphate of lead is left to evaporate. (Hermbstädt.) — According to Posselt & Reimann, this lead-precipitate is nothing but carbonate of lead, and does not yield any more nicotianine. These chemists pour 12 lbs. of water on 6 lbs. of tobacco-leaves; distil off 6 lbs; add to the residue 6 lbs. of fresh water; distil again; and repeat this treatment five times. The distillate deposits 11 grains of nicotianine, while nicotine remains in solution. Landerer extracts from the aqueous distillate of tobacco-leaves only a few drachms of water, from which the nicotianine separates on standing.

Properties. White, crystalline, laminar. Melts when heated, and then gradually evaporates (Hermbstädt); in some weeks, when exposed to the air in open vessels. (Posselt & Reimann.) Smells like fine tobacco (Hermbstädt); like tobacco-smoke and lilac-blossoms, more strongly when heated, but without exciting sneezing. (Hermbstädt.) On the tongue, or in the throat, it tastes like tobacco-vapour (Hermbstädt); not at all sharp, but warm and bitterly aromatic. (Posselt & Reimann.) When swallowed, it produces nausea and giddiness (Hermbstädt); a dose of 2 grains produces no particular effect. (Posselt & Reimann.) Neutral.

	Calculation according to Gerhardt. (*Traité* 4, 193.)		Barral.
46 C	276	71·87	71·52
2 N	28	7·30	7·12
32 H	32	8·33	8·23
6 O	48	12·50	13·13
$C^{46}N^{2}H^{32}O^{6}$	384	100·00	100·00

According to Buchner (Repert, 53, 209) it is, perhaps, a compound of nicotine with a volatile vegetable acid.

Decompositions. Nicotianine turns brown when exposed to the air. (Hermbstädt.) — It is insoluble in *nitric acid* when cold, but dissolves in it when hot, giving off nitrous gas. (Posselt & Reimann.) — It dissolves in potash-ley (Posselt & Reimann), and gives off nicotine when distilled therewith. (Barral.)

It is soluble in water. (Hermbstädt.) — It is not sensibly soluble in aqueous hydrochloric acid, and remains unaltered when evaporated by contact with it. — According to Hermbstädt, it precipitates lead and mercuric salts; but, according to Posselt & Reimann, these precipitations do not take place. — It forms a white precipitate with tincture of galls. (Hermbstädt.)

It dissolves in *alcohol* and in *ether.* — The alcoholic solution becomes milky on addition of water (Posselt & Reimann); according to Hermbstädt, it does not.

b. Empyreumatic Oil of Tobacco.

ZEISE. *J. pr. Chem.* 29, 388; *Ann. Pharm.* 47, 127; *Pogg*, 60, 278.

Compare p. 221.

Preparation. Dry tobacco is distilled, and the resulting tar is rectified. The oil thus obtained is several times shaken up with water; then dried over chloride of calcium, filtered, twice rectified, a certain quantity of tar remaining behind each time, but only a small quantity the second time, and the first half of the distillate is collected.

Slightly pale yellow, transparent. Sp. gr. 0·87. Boils at about 195°.

Calculation according to Zeise.			Zeise.
11 C	66	71·00	71·26
11 H	11	11·79	12·01
2 O	16 O and N	17·21	16·73
$C^{11}H^{11}O^{2}$	93	100·00	100·00

The oil contained about 3 per cent. of nitrogen which was not included in Zeise's calculation. As Melsens found nicotine in tobacco-smoke, which nicotine was not separated in Zeise's mode of preparation, the nitrogen of the nicotine appears to have been present in the oil, which would make the calculation altogether wrong. (Kr.)

The oil turns brown in contact with the *air.* — *Burns* with a strongly luminous, sooty flame. — *Potassium* acts on it slowly in the cold, and attacks it strongly when heated, converting it into a brown-red, viscid mass which yields by distillation a light yellow, somewhat viscid oil, having a strong aromatic odour, while a pitchy mass remains behind. — When the oil is boiled for five or six hours in a long-necked flask with lumps of *potash-hydrate,* and a little water, ammonia is evolved, and a yellow oil passes over, which boils at 220°, has a less unpleasant odour than the original oil, and does not act upon fused potassium. This oil contains 79·90 p. c. C, 10·01 H and 10·09 O. The alkaline residue dissolved in water, filtered from the separated charcoal, neutralised with sulphuric acid, and evaporated, gives up butyrate of potash to alcohol.

The oil is nearly insoluble in water. — It dissolves *iodine* quickly, and with brown colour. — It absorbs a small quantity of dry *hydrochloric acid gas,* becoming thereby more viscid and brown-red, and recovering its pale yellow colour on addition of ammonia.

It mixes in all proportions with *alcohol* and *ether*.

By slow combustion of tobacco in the pipe. Melsens (*N. Ann. Chim. Phys.* 9, 471) obtained nicotine (p. 221) and tar. The latter, distilled with water, yielded a brown oil having a sharp and peculiar empyreumatic odour, while a black, viscid mass was left soluble in alcohol. The oil is lighter than water; begins to boil at 140°, after drying over chloride of calcium, the temperature soon, however, rising to 200°, and ultimately to 300°; and passes over, light brown at first, but afterwards of darker colour.

Methyl-nicotine.

$C^{12}NH^9 = C^{10}(C^2H^3)NH^4,H^2$.

STAHLSCHMIDT. *Ann. Pharm.* 90, 222; *J. pr. Chem.* 63, 89; *Pharm. Centr.* 1854, 680.

Formenicotin. Known only as a hydrate and in salts.

Formation. p. 226.

Preparation. — Nicotine is mixed with iodide of methyl; the action, which soon begins, is allowed to come to an end; the dark-coloured hydriodate of methyl-nicotine, which solidifies in a crystalline mass on cooling (syrupy, if the quantity of iodide of methyl is insufficient, but becoming crystalline on the addition of a larger quantity), is washed with alcohol, crystallised from water, and the concentrated aqueous solution is decomposed with recently precipitated silver-oxide, whereby iodide of silver and an aqueous solution of methyl-nicotine are obtained. This solution, evaporated over oil of vitriol at 100°, leaves a dark, viscid, new crystalline residue, probably consisting of hydrate of methyl-nicotine.

Its aqueous solution has a bitter taste. It is inodorous, has a strong alkaline reaction, and dissolves the cuticle like caustic potash.

It remains unaltered, when the solution of its hydriodate is heated with *iodide of methyl.*

Methyl-nicotine is a strong base. It saturates acids completely, and forms salts, of which the *sulphate, hydrochlorate, nitrate,* and *hydrocyanate* crystallise with difficulty; the *hydrofluate, acetate, oxalate,* and *tartate* not at all. Aqueous methyl-nicotine precipitates other oxides from *copper* and *iron* salts. It dissolves recently precipitated *hydrate of alumina.*

Hydriodate of Methyl-nicotine. Soluble in water, less soluble in alcohol, and nearly insoluble in ether.

			Stahlschmidt.
12 C	72·0	32·28	32·86
N	14·0	6·27	
10 H	10·0	4·48	4·60
I	127·1	56·97	56·92
$C^{12}NH^9,HI$	223·1	100·00	

Chloromercurate of Methyl-nicotine. — Prepared on mixing mercuric chloride with aqueous hydrochlorate of methyl-nicotine, and may be crystallised in nodules from hot water. Contains 59·47 p. c. mercury, and is therefore $C^{12}NH^9,HCl,4HgCl$. (*Calculation,* 58·39 p. c. Hg.)

Chloro-aurate of Methyl-nicotine — Light yellow precipitate, produced by mixing the solutions of terchloride of gold and hydrochlorate of methyl-nicotine. It is nearly insoluble in cold water and alcohol. Dried at 100°, it contains 45·23 p. c. of gold, $C^{12}NH^9,HCl,AuCl^3 = 45·28$ p. c. Au.

Chloroplatinate of Methyl-nicotine. — Hydrochlorate of methyl-nicotine is precipitated with bichloride of platinum, and the precipitate is crystallised from boiling water. Crystalline product, sparingly soluble in cold water, insoluble in alcohol.

			Stahlschmidt.
12 C	72·0	23·92	23·85
N	14·0	4·64	
10 H	10·0	3·32	3·44
3 Cl	106·5	35·35	
Pt	98·7	32·77	33·03
$C^{12}NH^9,HCl,PtCl^2$	301·2	100·00	

Hydrochlorate of methyl-nicotine mixed with *chloride of palladium*, leaves on evaporation, a syrup which may be obtained on crystallisation from alcohol.

Ethyl-nicotine.

$C^{14}NH^{11} = C^{10}(C^4H^5)NH^4,H^2$.

v. Planta & Kekulé. *Ann. Pharm.* 87, 2; *J. pr. Chem.* 60, 237; *Pharm. Centr.* 1853, 890; *N. Ann. Chim. Phys.* 40, 230.

Aethyl-nicotin, Vinenicotin. — First observed by Hofmann (*Ann. Pharm.* 79, 31.) — Known only in combination with water and acids.

Formation. (Comp. p. 226.)

Preparation. Nicotine is mixed with excess of iodide of ethyl in a sealed tube, and heated for an hour in the water-bath, or till the mass solidifies in yellow crystals on cooling; the product is dissolved in water; the red resin which separates (it forms especially when the heat is too long continued) is removed by filtration, and the solution is left to evaporate; it then yields radiating crystals of hydriodate of ethyl-nicotine. On digesting the aqueous solution of these crystals with recently precipitated oxide of silver, iodide of silver is precipitated, and an aqueous solution of ethyl-nicotine is obtained, which is colourless (or slightly reddish yellow, if prepared with crude hydriodate of ethyl-nicotine), inodorous, has a very bitter taste, a strong alkaline reaction, and dissolves the cuticle like caustic potash.

Ethyl-nicotine is $C^{14}NH^{11}$ (which, by addition of 1HO, becomes $C^{14}NH^{12}O$, corresponding to NH^4O), if nicotine = $C^{10}NH^7$; or has the double formula, $C^{28}N^2H^{22}$, if nicotine is $C^{20}N^2H^{14}$. (v. Planta & Kekulé.) In the formation of ethyl-nicotine, the molecule of nicotine ($C^{20}N^2H^{14}$) is split up in such a manner, that from 1 At. nicotine and 2 At. iodide of ethyl, 2 At. hydriodate of ethyl-nicotine are produced. (Gerhardt's *Traité* 4, 185.) — Ethylnicotine, with addition of 1 H bears to nicotine the same relation that tetrethyl-ammonium bears to triethylamine.

Decompositions. 1. Aqueous ethyl-nicotine becomes turbid when heated, deposits a dark red-brown oil, and gives off when distilled, a brown oil and a strongly alkaline liquid, which exhibits a deep red colour by transmitted light, and a green iridescence by reflected light;

both these liquids colour the skin yellow, and have a pungent odour of stinking fish. Aqueous ethyl-nicotine undergoes a similar decomposition when left to stand in the air or in vacuo. — 2. Hydriodate and hydrobromate of ethyl-nicotine are not altered by *potash-ley* in the cold; but when heated with it, they yield the same products that are formed by the simple action of heat on aqueous ethyl-nicotine. — 3. Hydriodate of ethyl-nicotine melts when *heated*, turning slightly brown, and yields a distillate of nicotine and iodide of ethyl, which partly recombine in the receiver, forming hydriodate of ethyl-nicotine. — 4. A concentrated aqueous solution of ethyl-nicotine, heated with *iodide of ethyl*, is converted into hydriodate of ethyl-nicotine, without forming a base containing a larger proportion of ethyl.

Combinations. Ethyl-nicotine unites with *acids*, forming crystallisable and very soluble salts. It is a strong base, which expels ammonia from its salts, and behaves with saline solutions like the fixed alkalis, throwing down the heavy metallic oxides and the alkaline earths.

Aqueous ethyl-nicotine absorbs *carbonic acid* from the air. — *Sulphate of ethyl-nicotine* is a viscid syrup containing a few crystalline particles.

Hydriodate of Ethyl-nicotine. — Obtained by the action of alcoholic nicotine on iodide of ethyl, or by recrystallising from boiling alcohol the product prepared as described at page 236, in nodular groups of beautiful colourless prisms, which may be separated with some loss from the reddish yellow mother-liquor by absolute alcohol. It decomposes partially when its aqueous solution is evaporated, forming a red iodated resin. When heated, it decomposes in the manner above described (3). It is very soluble in water, sparingly soluble in alcohol and ether.

	From oil of vitriol.		v. Planta & Kekulé. mean.
$C^{14}NH^{12}$	110·0	46·39	
I	127·1	53·61	53·55
$C^{14}NH^{11},HI$	237·1	100·00	

Hydrobromate of Ethyl-nicotine. — When bromide of ethyl is brought in contact with nicotine, even in the cold, an oil is produced, which increases on heating the mixture in the water-bath, and finally solidifies in a crystalline mass. It is even more deliquescent than the hydriodate. It dissolves with moderate facility in absolute alcohol.

Hydrochlorate of Ethyl-nicotine is obtained as a radiated crystalline mass by evaporating its solution in vacuo.

Nitrate of Ethyl-nicotine. — Viscid syrup, containing a few crystalline particles.

Chloromurcurate of Ethyl-nicotine. — Mercuric chloride throws down from hydrochlorate of ethyl-nicotine, white flocks, sometimes caked together like a resin, which melt when heated, dissolve in boiling water, and separate in crystalline nodules on cooling. They may be washed with cold water.

			v. Planta & Kekulé.
14 C	84	15·22	15·39
N	14	2·54	
12 H	12	2·17	2·25
4 Cl	142	25·72	25·71
3 Hg	300	54·35	54·14
$C^{14}NH^{11},HCl,3HgCl$	552	100·00	

Chloroaurate of Ethyl-nicotine. — Terchloride of gold added to hydrochlorate of ethyl-nicotine, throws down a sulphur-yellow precipitate, which crystallises from its hot aqueous solution on cooling in splendid gold-yellow needles.

			v. Planta & Kekulé. *mean.*
$C^{14}NH^{12}Cl^4$	252	56·13	
Au	197	43·87	43·93
$C^{14}NH^{11},HCl,AuCl^3$	449	100·00	

Chloroplatinate of Ethyl-nicotine. — Hydrochlorate of ethyl-nicotine mixed with bichloride of platinum, throws down yellow flocks, which soon become orange-yellow and crystalline, and separate from boiling water in orange-red prisms, generally acuminated. It is nearly insoluble in boiling alcohol, insoluble in ether.

	From oil of vitriol, or at 100°.		v. Planta & Kekulé.
14 C	84·0	26·65	26·61
N	14·0	4·44	
12 H	12·0	3·81	3·24
3 Cl	106·5	33·79	
Pt	98·7	31·31	31·29
$C^{14}NH^{11},HCl,PtCl^2$	315·2	100·00	

Chloride of Palladium is not precipitated by hydrochlorate of ethyl-nicotine, but on evaporating the mixed solutions, a brown gum is obtained which, when its alcoholic solution is left to evaporate, leaves large brown rhombic tables.

With *oxalic* and *acetic acid,* ethyl-nicotine forms uncrystallisable salts.

Tannic acid does not precipitate aqueous ethyl-nicotine ; *picric acid* produces sulphur-yellow flocks.

Amyl-nicotine.

$$C^{20}NH^{17} = C^{10}(C^{10}H^{11})NH^4,H^2.$$

STAHLSCHMIDT. *Ann. Pharm.* 90, 226.

Mylinicotin. — Known only in aqueous solution and as a platinum-salt.

Formation (p. 226). — Nicotine is heated with iodide of amyl in a sealed tube to 100° for several days ; the product is dissolved in water ; the separated iodide of amyl is removed ; and the solution is digested with recently precipitated oxide of silver, whereby iodide of silver is separated, and an aqueous solution of amyl-nicotine is obtained.

This compound behaves with saline solutions like ethyl-nicotine; it saturates acids and forms salts, which cannot be obtained in the solid state, even by slow evaporation. The solution of amyl-nicotine, mixed with bichloride of platinum, throws down light yellow flocks, which, when dried at 100°, contain 28·25 p. c. platinum, and are therefore $C^{20}NH^{17},HCl,PtCl^2$ (calc. 27·63 p. c. platinum).

Primary Nucleus $C^{20}H^{16}$.

Oil of Turpentine.

$C^{20}H^{16}$.

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URE. *Phil. Trans.* (1818), 2, 338; *Schw.* 28, 329.
HOUTON-LABILLARDIÈRE. *J. Pharm.* 4, 5.
UNVERDORBEN. *Pogg.* 8, 485; further, 9, 516; further, 11, 34.
BOISSENOT & PERSOT. *J. Pharm.* 12, 214; *Ann. Chim. Phys.* 31, 442; *N. Tr.* 13, 1, 225.
HERMANN. *Pogg.* 18, 368.
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BLANCHET & SELL. *Ann. Pharm.* 6, 259; *Pogg.* 29, 133.
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Knop. *Pharm. Centralbl.* 1854, 321, 409 and 498.

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Geiger. *Mag. Pharm.* 16, 64.
Bernhardi & Trommsdorff. *N. Tr.* 16, 2, 46.
Brandes. *N. Br. Arch.* 11, 285.
Voget. *N. Br. Arch.* 23, 291.
Dumas & Peligot. *Ann. Chim. Phys.* 57, 334; *Ann. Pharm.* 14, 75; *J. pr. Chem.* 4, 386.
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Camphene (Deville); *Essence de térébenthine; Essence of turpentine; Terpenthinöl.* Described in the 8th century by Marcus Græcus.

Sources. In the root, stem, branches, leaves, and pericarps of several trees belonging to the coniferous family, and to the genera *Pinus, Picea, Abies, Larix;* hence also in *turpentine*, the resinous juice which exudes from incisions made for the purpose in the stems of these trees.

Extraction. 1. By distilling various kinds of turpentine either alone or with water. — Steam or air, heated to 107°, is passed either directly through turpentine or through a spiral tube coiled up in the turpentine covered with water, and serving to convey to it the heat required for the distillation of the volatile oil. (Kates, *Lond. J.* Sept. 1854, 172; Aug. 1855, 86.)

When turpentine is distilled *per se*, the oil passes over first, and towards the end of the distillation, succinic acid sublimes. (Lecanu & Serbat, *J. Pharm.* 8, 451.)

When Venice turpentine is distilled with water, the succinic acid remains dissolved in the water which passes over with the oil. Venice turpentine, distilled alone, yields first a more volatile, and afterwards a less volatile oil. (Unverdorben.)

Pine-resin, subjected to dry distillation, yields, together with the oil, a brown or yellowish, seldom colourless, turpentine-water, amounting to 1—1·5 per cent. of the resin, and containing acetic acid. (Grimm, *Ann. Pharm.* 107, 255.)

2. By distilling various parts of coniferous plants with water. — In this manner, oil of turpentine may be obtained: From the cones of the silver fir (*Abies pectinata,* Dec.) (Zeller, Flückiger), which contain the volatile oil in the pericarps, and a fixed oil in the seeds (Zeller); from the branches of the spruce fir (*Pinus abies,* L.) Gottschalk, *Ann. Pharm.* 47, 237); from the cones of the dwarf-pine (*Pinus Mughus,* Scop.) (Blanchet & Sell); from the cones of the Scotch fir (*Pinus sylvestris,* L.), which serve for the preparation of forest-wool. (Hagen.)

Purification. 1. By distilling crude oil of turpentine: (*a.*) *by itself;* (*b.*) *with water.* The oil which floats on the surface of the water in the distillate is skimmed off, and dehydrated by agitation with chloride of calcium. — When oil of turpentine is rectified with water, the oil at first passes over alone, and is not accompanied by water till towards the end of the distillation, probably because the formation of vapour of water requires 550° of heat, whereas, according to Despretz, that of oil of turpentine vapour requires only 76° (? Gm.) Aubergier. — (*c.*) With *aqueous alkalis* or *alkaline earths.* Oil of turpentine is distilled with milk of potash and lime (100 pts. of the oil with 100 pts. water, 1 pt. carbonate of potash, and 1 pt. quicklime. *Berl. Industriebl.* 1841), the resin dissolved in the oil then remaining with the lime. (Guthrie, *Sill. Am. J.* 21, 291.)

2. By agitation with *oil of vitriol.* — The oil of turpentine is shaken up with oil of vitriol diluted with an equal bulk of water, and then left at rest, whereupon the liquid separates into two layers, the lower of which takes up the brown resin; the supernatant oil may be further purified from resin by renewed agitation with the acid, till the latter no longer becomes coloured, and at last completely freed from it by water. (Guthrie.)

3. By treating crude oil of turpentine with a quantity of *alcohol* less than sufficient to dissolve it. — When 8 pts. of oil of turpentine are shaken up with 1 pt. of the strongest spirit (with slightly rectified spirit, according to Schultze, *N. Br. Arch.* 74, 114), and the mixture is left at rest, two layers of liquids are formed, the upper of which is a solution of the resin originally contained in the oil, while the lower consists of the purer oil, which may be completely purified by repeated agitation with fresh quantities of alcohol. (Nimmo, *Schw.* 36, 245; *J. of Science,* 13, 441.)

Modifications of Oil of Turpentine. — The volatile oil obtained from coniferæ (Dumas), even when prepared by distillation from one and the same species (Berthelot) is by no means a simple oil, but a mixture of isomeric oils, which, though identical in chemical composition, differ in boiling point, specific gravity, and optical properties, according to their origin and mode of preparation, and, according to Bouchardat, are probably formed from the oil originally contained in the turpentine by the action of the air at the moment of its separation, or, according to Berthelot, partly exist in the turpentine ready formed. Accordingly we have to distinguish—

1. *French oil of turpentine,* obtained from Bordeaux turpentine, the produce of *Pinus Maritima.* — When French oil of turpentine is mixed with carbonate of potash and carbonate of lime, the mixture left at rest for a day, and then distilled in vacuo, first on the water-bath, and then on the oil-bath, the receiver being cooled with ice, the oil distils between 80° and 180°, while the residual turpentine becomes thicker. The oil which distils between 80° and 180°, appear to consist of only one substance; but the latter portion of the distillate is a mixture of isomeric hydrocarbons and oxygenated oils, whose specific gravity, boiling point, and rotatory power vary between such narrow limits, that the isolation of a single definite product from them is impossible. Even the oil obtained by repeated fractional distillation, yields, when again distilled, a distillate of different properties, though identical in chemical composition. — The portions of the oil, which, when it is shaken up with a quantity of alcohol insufficient to dissolve it, either remain below the alcoholic solution, or are separated therefrom by water, likewise exhibit different properties, the alcohol dissolving especially those oils which have comparatively little rotatory power. (Berthelot.)

2. *English oil of turpentine* (*Camphene spirit*), from the Carolina turpentine of *Pinus tæda,* L. (Guibourt & Bouchardat), or that of *Pinus Australis,* Mich. (Berthelot.) — Turpentine from *Pinus Australis,* fractionally distilled four times in vacuo, yielded distillates of like composition but different rotatory power. (Berthelot.)

3. *German oil of turpentine,* from the turpentine of *Pinus sylvestris,* L, *P. nigra,* Link, *P. rotundata,* Link, *P. abies,* L.

4. *Templin oil,* from the cones of *Pinus Mughus* (Blanchet & Sell); from the cones of *Abies pectinata,* Dec., especially that obtained in the Emmenthal, Canton Bern, and in Aargau. (Flückiger.)

5. *Venetian oil of turpentine,* from the turpentine of *Larix Europœa,* Dec.

Properties. Colourless, mobile, transparent oil. Commercial oil of turpentine is yellowish, templin oil slightly coloured (Blanchet & Sell), the oil from the needles of the Scotch fir, yellowish-green (Hagen); templin oil becomes yellowish-green after some time. (Flückiger.) — Sp. gr. 0·86 at 22° (Saussure), 0·872 at 10° (Despretz), 0·86 at 31° (Brisson), 0·879 (Aubergier), 0·867 at 14° (Brix, *Pogg.* 55, 380), 0·872 (Biot), 0·86 (Soubeiran & Capitaine), 0·8902 at 0° (Frankenheim, *Pogg.* 72, 422).

French oil of turpentine has a density of 0·865 at 13° (Caillot, *J. Pharm.* 16, 440); 0·8806; — after rectification with water, 0·8736 to

0·8890; — after distillation without water, 0·8730; — oil ten years old distilled over potash, 0·87; — Strasburg oil of turpentine distilled with water, 0·863 (Guibourt & Bouchardat); — 0·8654 at 15°; — after distillation in vacuo between 80° and 100°, it is 0·864 at 15°; — when purified by shaking up with alcohol, 0·8616 to 0·8630, while the oil which distils between 280° and 290° has a density of 0·9203 at 16°. (Berthelot.) — English oil of turpentine: 0·863 (Guibourt & Bouchardat); 0·8665 at 15°; after fractional distillation, 0·886 to 0·878. (Berthelot.) — Oil of turpentine from the silver fir, 0·850 to 0·856 at 13° (Caillot), 0·85 (Zeller); templin-oil (Flückiger), 0·856 at 6° and 0·842 at 30°. (Berthelot.) — Oil from the Scotch fir, 0·865 at 13° (Caulliot); crude oil 0·8859 at 12°, rectified, 0·868 at 12°. (Hagen.) Oil from the spruce fir, 0·880 at 15° (Blanchet & Sell), oil from the branches treated with potassium (*vid. inf.*), 0·856 at 20°. (Wöhler.) Oil from *Abies Canadensis* and Venetian oil of turpentine, 0·863 at 13°.

Boiling point, 156·8° (Despretz); recently rectified, 152°, old, 158° (Ure), 150° (Blanchet & Sell), 157° (Aubergier), 159·2° (Brix, *Pogg.* 55, 380), 156° (Frankenheim, *Pogg.* 72, 422). — Oil from the spruce fir boils at 155° (Blanchet & Sell), that from the branches, after treatment with potassium, at 167° (Wöhler); templin-oil from *Pinus Mughus* at 165°, templin-oil (Flückiger) at 172°. (Berthelot.) — The first products of the distillation of French oil of turpentine, purified with alcohol, boil at 159·5° to 160° under a pressure of 750^{mm}; the later products between 161° and 162°, $\frac{1}{10}$ of the oil above 200°. (Berthelot.) — It does not solidify at − 20° (Cailliot), not even at − 110° (Faraday, *Pogg.* Ergänzungsband, 2, 216). At − 27° it deposits camphor, which melts at − 7° (Margueron, *J. Phys.* 45, 136). — Expansion at sp. gr. 0·879 from 0° to 100° = 0·106927; of oil boiled for 10 minutes and distilled = 0·103087 (Aubergier); at 0° and sp. gr. 0·8902, $= 1 + 0{\cdot}000874t + 0{\cdot}000001248t^2$ between 11 and 145°, or from 0 to 100° = 0·09722 (Frankenheim, *Pogg.* 72, 425); of templin-oil (Flückiger) from 30° to 130° = 0·112. (Berthelot.) — Compressibility for one atmosphere at 12·6° = 0·0000657. (Aimé, *Pogg.* Ergänz. Bd. 2, 237.) — Refracting power = 1·471 (Becquerel & A. Cahours, *Compt. rend.* 6·867; also *Pogg.* 51,427); 1·472, of the thickened oil = 1·4938, after being liquefied at 40° = 1·4938 (Deville, *Compt. rend.* 11·865; also *Pogg.* 51, 433); of templin-oil (Flückiger) = 1·467 (Berthelot).

The optical rotatory power of oil of turpentine is independent of that of the turpentine from which it has been prepared. French oil of turpentine rotates to the left like turpentine itself, but with different strength; English oil of turpentine to the right, whereas the turpentine (from *Pinus tæda*) used in its preparation rotates to the left; Venetian oil of turpentine rotates, according to Soubeiran, to the left, but Venice turpentine rotates to the right. (Guibourt & Bouchardat, Biot.) The French turpentine oil of commerce consists chiefly of lævo-rotatory oils, and contains but a small proportion of the dextro-rotatory. (Berthelot.)

Lævo-rotatory power of: French oil of turpentine, 39·95° (Biot), 43·38°, calculated for a sp. gr. of 1 (Soubeiran & Capitaine), 28·82° (Guibourt & Bouchardat), 35·4° (Berthelot). After rectification with water: first distillate, 31·657°, second distillate 22·327°; distilled without water, 33·23°; oil ten years old rectified over carbonate of potash, 33·95; Strasburg turpentine-oil distilled with water, 11·69° (Guibourt & Bouchardat); distilled between 80° and 100° in vacuo, 32·4°; fractionally distilled, between 33·7° and 32·25°; purified with water, 35·6° to 33·7;

that which distils from 240° to 280°, 6·5°. (Berthelot.) By distillation over the open fire, oil of turpentine gains in rotatory power from 28·33° to 33·23° (Bouchardat). — Of Swiss oil of turpentine, 11·2; of templin oil (Flückiger), 76·9° (Berthelot); of Venetian oil of turpentine, 5·24. (Guibourt & Bouchardat.)

Dextro-rotatory power of: English oil of turpentine from *Pinus tæda*, 18·6° (Guibourt & Bouchardat); from *Pinus Australis*, 18·6°. (Berthelot.) After fractional distillation: 1 = 18·9°; 2 = 18 8°; 3 = 16·4; 4 = 17·2. (Berthelot.)

Specific heat = 0·462 (Despretz), 0·488 (De la Rive & Marcet), 0·42593 (Regnault), 0·41 (Brix, *Pogg.* 55, 380), 0·416 at 2°. (Person, *Pogg*, 74, 422.) Heat of combustion evolved in the combination of 1 gramme of oil of turpentine with oxygen = 10496; of 1 litre of turpentine-oil vapour = 68349 heat-units. (Grassi, *N. J. Pharm.* 81, 177.)

Vapour-density = 5·01 (Despretz), 5·013 (Gay-Lussac), 4·763, (Dumas.) Latent heat of vapour = 76·8 (Despretz), 59·23 or 62·25 (Brix, *Pogg.* 55, 381); 68·7 (Frankenheim, *Pogg.* 72, 422). Specific heat of vapour 177·87. (Ure.)

The vapour, mixed with a large quantity of atmospheric air, produces a peculiar intoxicating effect when inhaled (Letellier, *Compt. rend.* 39, 243); in rooms recently painted with turpentine colours, it produces poisonous effects. (Favrat, *Compt. rend.* 45, 886.) It prevents the germination of seeds. (Ville, *Compt. rend.* 41, 757.) The smell of turpentine oil may be removed from vessels by shaking them up with a mixture of mustard and cold water. (Jourdan, *J. Chim. med.* 22, 727.)

Oil of turpentine is neutral to vegetable colours. The oil from the needles of the Scotch fir reddens litmus, because it contains formic acid. (Hagen.) Its taste and odour are strong and peculiar, like that of turpentine.

Strasburg oil of turpentine (Guibourt & Bouchardat), that from the spruce fir (Blanchet & Sell), has an agreeable odour like that of lemons. The oil from the branches of the spruce fir smells like fir-branches and fixed oil of laurel, but after treatment with potassium, it has an odour of lemons and sweet oranges (Wöhler); templin oil has a balsamic odour (Flückiger); templin oil from *Pinus Mughus* smells like orange-flowers (Blanchet & Sell); oil from the silver fir smells aromatic (Cailliat); like cumin, and has an aromatic, warming, slightly burning taste (Zeller); oil from the Scotch fir, has an aromatic odour like that of lavender. (Hagen.) The smell and taste of oil of turpentine depend upon the amount of ozone which it contains; strongly ozonised oil has a strong odour and taste of peppermint, and a few drops placed upon the tongue produce a peculiar persistent pain; the newly rectified oil does not produce this effect, and has a fainter odour. (Schönbein.)

			1. Houton Labillardière.	2. Saussure.	3. Oppermann.	4. Hermann.
20 C	120	88·23	87·6	87·788	84·59	88·88
16 H	16	11·77	12·3	11·646	11·73	11·12
$C^{20}H^{16}$	136	100·00	99·9	99·434	96·32	100·00

5. Blanchet & Sell.	6. Dumas.	7. Wöhler.	8. Hagen.	9. Berthelot. *a.*	9. Berthelot. *b.*
88·56	88·4	88·38	88·21	88·0	87·1
11·52	11·6	11·78	11·61	12·3	11·9
100·08	100·0	100·16	99·82	100·3	99·0

	Vol.	Density.
C-vapour	20	8·3200
H-gas	16	1·1088
Vapour of turpentine-oil	2	9·4288
	1	4·7144

2, according to Saussure, still contained 0·566 nitrogen; 4, according to Oppermann, contained 3·6728 oxygen; 5, oil from the spruce fir; 7, from the branches of the spruce fir, after treatment with potassium; 8, from the needles of the Scotch fir; 9, *a.* French; *b.* English oil of turpentine.

Oil of turpentine is a hydrocarbon, since its vapour passed, together with sulphur-vapour, through a red-hot tube, yields nothing but bisulphide of carbon and sulphuretted hydrogen. It contains 10 vols. carbon to 8 vols. hydrogen, and the condensation of 4 vols. hydrocarbon (hydrogène percarburé) with 2 vols. carbon-vapour, produces 1 vol. vapour of oil of turpentine. (Houton-Labillardière.) — Saussure found nitrogen in oil of turpentine, as well as carbon and hydrogen. Hermann found no nitrogen, but carbon and hydrogen in the ratio of 4 : 3. Oppermann found 4 per cent. of oxygen, together with carbon and hydrogen, and assigned to oil of turpentine the formula, $C^{30}H^{51}O$. Dumas concluded, from Oppermann's analysis, that oil of turpentine was a compound analogous to ether, and containing the radical camphogen (supposed by him to exist in camphor), in combination with ½ At. water; but from his own analysis he inferred that it is a compound corresponding to the formula $C^{10}H^{8}$, and that the oxygen found by Oppermann proceeded from impurities. The suggestion advanced by Thénard, that oil of turpentine is a mixture of several hydrocarbons, was thought by Blanchet & Sell to be corroborated by its behaviour with hydrochloric acid, these chemists supposing that oil of turpentine is a mixture of two isomeric oils of the formula $C^{10}H^{8}$, one of which, *dadyl*, forms a solid, the other, *peucyl*, a liquid compound with hydrochloric acid, and that the variations in the properties of oil of turpentine depend upon the relative quantities of these two compounds. Since, however, oil of turpentine has a constant boiling point, and its rotatory power remains unaltered in the solid hydrochlorate, whereas in the liquid compound it is very weak, Soubeiran & Capitaine suppose that it is a simple compound, but is resolved into two isomeric compounds under the influence of hydrochloric acid. The *dadyl* of Blanchet & Sell is identical with the *camphene* of Soubeiran & Capitaine and with the turpentine oil of Deville. The *peucyl* of Blanchet & Sell is identical with the *peucylene* of Soubeiran & Capitaine, and the *terebene* of Deville. According to Soubeiran & Capitaine, both these compounds are products of the decomposition of oil of turpentine; but according to Deville, this is the case with terebene only.

Decompositions. Oil of turpentine exposed to the air gradually becomes yellowish and viscid, resinises completely after a short time (Unverdorben, Blanchet & Sell, Zeller, Wöhler), and ultimately forms acetic acid (Boissenot & Persot; Bizio, *Brugn. Giorn,* 19, 360), formic acid (Laurent, *Rev. scient.* 1842, 119, Weppen), resins (Unverdorben, Weppen), and, in presence of water, it forms hydrate of turpentine-oil or turpentine-camphor. (Boissenot & Persot.) Oil of turpentine which has become thick by exposure to the air, contains a large quantity of resin partly soluble in potash, partly insoluble (this portion, however, being soluble in alcohol), and a compound of pyrocolophonic acid with a volatile oil, which latter is not soluble in potash, except in presence of the pyro-acid just mentioned, and can be distilled only with excess of potash and water. (Unverdorben). In oil of turpentine which had been long exposed to the air, hard crystals were found to have formed; on distilling it, aqueous acetic acid finally passed over, and from this distillate, after standing for some time at 7°, crystals again separated. (Boissenot & Persot.) On the covers of zinc boxes in which oil of turpentine had been kept, Laurent found white, granular crystals of formiate of zinc. The presence of formic acid in oil of turpentine may be recognized by the acid reaction of the oil and of the water which passes over on distilling it. It is produced by absorption of oxygen. (Weppen.)

$$C^{20}H^{16} + 40\,O = 4\,CO^2 + 8\,C^2H^2O^4.$$

Oil of turpentine, when exposed to the air, likewise forms an acid resin, which may be extracted by agitation with water and carbonate of magnesia. From the aqueous solution of the magnesia-compound, acids throw down a white precipitate, whose alcoholic solution precipitates most metallic salts, even in the cold, but corrosive sublimate only when heated. From the precipitate obtained with acetate of lead, and decomposed by sulphuretted hydrogen, alcohol extracts an acid resin, which remains when the solution is evaporated, partly as a brown viscid mass, partly in white crystalline scales. The lead-compound contains 45·99 p. c. carbon, 6·47 hydrogen, 18·36 oxygen, and 29·60 PbO; whence it is $C^{20}H^{21}O^9,PbO$.

2. *Electric sparks* passing between the terminal wires of a battery immersed in oil of turpentine and placed very close together but not quite in contact, excite luminosity on the oil in contact with the ends of the wires, and give rise to the evolution of a permanent gas. (Poggendorff, *Pogg*, 71, 227.)

3. Oil of turpentine is converted by *heat* into a less volatile oil. When heated in close vessels under a pressure of several atmospheres, it is partly converted into isomeric compounds of high boiling point (vid. *Isoterebene* and *Metaterebene.*) (Berthelot.) Heating over the open fire increases its power of dissolving caoutchouc and likewise its rotatory power. When it is distilled with brick-dust over the open fire, it turns yellowish, acquires the odour of thyme and rock-oil, boils at 154°, decreases in density from 0·8736 to 0·842, and likewise in rotatory power, which, in three experiments was found to diminish from 28·83° to the left to 8·68°, 13·82° and 19·03° to the left; but, its power of dissolving caoutchouc is augmented. (Bouchardat.) In general, the rotatory power of oil of turpentine is diminished by heating above its boiling point under pressure; that of the dextro-rotatory English oil is first diminished, and afterwards changed in direction, becoming lævo-rotatory. Its specific gravity is increased and its chemical properties are altered to a certain extent, according to the degree and duration of the heating. (Berthelot.)

From oil of turpentine which had been heated to 150° for three days, crystals sublimed, which likewise collected in the neck of the retort when the oil was distilled in the water-bath, and emitted a resinous odour when thrown on red-hot coals. (Cluzel, Chomet & Boullay, *Ann. Chim.* 51, 270.) — Oil of turpentine sealed up in thermometer-tubes, becomes suddenly coloured and contracts when heated above 200°. (Aubergier.) — The rotatory power of oil of turpentine is not altered by heating it in an atmosphere of carbonic acid, even for 60 hours; but French oil of turpentine, having a density of 0·8654 at 15° and a rotatory power of 35·4 to the left, after being heated in sealed tubes to 360° for five hours, exhibits a density of 0·9154 at 11°. Oil of turpentine dissolved in alcohol exhibited after heating for an hour and a-half to 360°, a rotatory power of 12° to the left. — English oil of turpentine of sp. gr. 0·8665 at 15°, and 18·6° dextro-rotatory power, exhibits after four hours heating to 250°, a density of 0·8657 at 15°, and dextro-rotatory power = 15·3°; after sixty hours heating to 250°—260°, a lævo-rotatory power = 8·55; after two hours heating to 300°, lævo-rotatory power = 9·9°

(isoterebenthene); and after five hours heating to 360°, a density of 0·9075 at 11°, and a lævo-rotatory power = 5·6, gas being also given off from it. Swiss oil of turpentine of sp. gr. 0·8618 at 15° and lævo-rotatory = 11·2°, exhibits after 74 hours heating to 300°, a sp. gr. = 0·8906 at 14°, a lævo-rotatory power = 1·55°, and gives off gas.

The products obtained by overheating oil of turpentine, exhibit in particular an increased power of absorbing oxygen. They are mixtures of several hydrocarbons isomeric and polymeric with oil of turpentine, some of them having boiling points near that of the original oil, while some boil at higher temperatures. (Berthelot.) In the same interval of time, 100 vols. French oil of turpentine absorbed 3·4 vol. oxygen, English 4·7, Swiss 4·9 vol.; after being heated to 300° for 42 hours, the French oil absorbed 5 vols, the English 9·7, and the Swiss 1·64 vol. oxygen. (Berthelot.)

4. By a *red-heat.* When oil of turpentine mixed with air is passed through a red-hot iron tube filled with coiled copper-foil, the products collected in the receiver are a large quantity of water, needle-shaped crystals, and yellow tar, which gradually unites with the crystals, an odour of oil of amber being at the same time evolved. (Richter, *Ann. Pharm*, 32, 125.)

5. Oil of turpentine is inflammable, and *burns* with a bright smoky flame. When crystals of anhydrous chromic acid are placed on an asbestos-wick moistened with oil of turpentine, and projecting $\frac{1}{4}$ of an inch from a spirit-lamp filled with oil of turpentine, the oil takes fire and reduces the chromic acid to chromic oxide, which continues to glow if the flame be carefully blown out, and forms a peculiar-smelling transparent liquid, not containing naphthalin. (R. Böttger, *Ann. Pharm.* 57, 134.)

Rectified oil of turpentine is used for illumination, either alone or mixed with other illuminating materials. A mixture of 4 vols. spirit of wine of 95 per cent., and 1 vol. oil of turpentine burns very clearly in lamps of peculiar construction; the illuminating power of the mixture is not increased by distillation. (Auduard, *J. Chim. méd.* 19, 717.) — A mixture prepared by heating together 5 pts. of alcohol, 10 pts. oil of turpentine, and 1 pt. oleic acid, burns with a white light, without smoke or odour of turpentine. (Rousseau, *J. Chim méd.* 22, 300.) — 4 pts. of rectified wood-spirit and 1 pt. of oil of turpentine rectified over lime burn in lamps of peculiar construction, without smoke and with a bright white flame. (Fabre, *Compt. rend.* 21, 161.)

6. *Oxygen gas* is abundantly absorbed by oil of turpentine. The oil in the course of fourteen days' exposure to the air, absorbs its own volume of oxygen, and does not subsequently give it off on boiling. (Brandes.) 1 vol. oil of turpentine takes up in four months, 20 vols. oxygen, and if previously saturated with carbonic acid, gives off 16 vols. of that gas; in eight months, it absorbs 24·3 vols. oxygen; in nine months more, 27·2 vols.; in the tenth month, at a temperature of 18° to 20°, somewhat more than 1 vol. daily; but in the following thirty-three months only 9 vols. more; making the quantity of oxygen absorbed in the whole 43 months, 128 volumes. It acquires at the same time a dark yellow-brown colour, deposits a few volatile crystals, but remains liquid, and, after it has absorbed 50 vols. oxygen, gives off carbonic acid and hydrogen; but after evaporation, or after exposure to the sun, it deposits a very acid watery liquid, so that the evolution of hydrogen is perhaps a consequence of the decomposition of this water

produced by the oxidation of the oil of turpentine. (Saussure, comp. p. 256.)

7. Oil of turpentine absorbs *chlorine gas,* with rise of temperature and evolution of hydrochloric acid. If the chlorine be passed into it, slowly at first, and in excess only at the end of the process, the oil of turpentine is converted into a viscid, colourless liquid, which smells like camphor, has a bitter-sweet taste, turns the plane of the polarization to the right, and is a mixture of chlorinated oil of turpentine and chloroterebene. (Deville.) Oil of turpentine is turned deep yellow by chlorine gas, becoming at the same time, thicker, but not opaque, and not forming any artificial camphor. (Cluzel.) When 6 pts. of oil of turpentine are heated to boiling with 25 pts. peroxide of manganese and 100 pts. hydrochloric acid, with frequent agitation at the beginning, acid water passes over, together with a viscid yellow liquid, which is heavier than water, has an aromatic odour, does not contain free chlorine, boils between 240° and 270°, giving off a large quantity of hydrochloric acid, and leaving a residue, which is yellow, green, blue, ultimately black and thick, and solidifies on cooling. This distillate is perhaps identical with the product formed by the direct action of chlorine upon oil of turpentine. (Chautard.)

8. *Bromine* decomposes oil of turpentine, eliminating hydrochloric acid and forming brominated oil of turpentine. (Deville.) On mixing oil of turpentine with a few drops of bromine, hydrobromic acid is evolved, the oil becomes heated, and is converted into a yellow viscid resin. (Balard, *Ann. Chim. Phys.* 32, 377.) Fresh oil of turpentine mixed with $\frac{1}{5}$ of its bulk of water, becomes heated when bromine is gradually added to it, destroys the colour of the bromine till that liquid has been added in the proportion of 228 pts. of bromine (4 At.) to 100 pts. of oil of turpentine, and is converted into a colourless aromatic oil. (G. Williams.) — When oil of turpentine is mixed with aqueous hydrobromic and dilute sulphuric acid, a large quantity of water and aqueous bromate of potash added to the mixture as long as the solution retains a slight orange colour after agitation, and the excess of bromine then removed by means of aqueous hyposulphite of soda, the oil of turpentine is found to have taken up a quantity of bromine, varying with the age and origin of the oil, viz., French oil of turpentine 260·2 p. c.; American 260·2 p. c.; German 227·1 p. c. once however in earlier experiments (probably with impure or peculiar oil 38·7 p. c. (Knop.)

9. *Iodine* dissolves in cold oil of turpentine, with dark green colour at first (Deville); but a violent explosion soon takes place (Walker's, *Pogg.* 6, 126; Blanchet & Sell; Guizot), yellow or violet vapours are evolved, and an acid resin is left behind. The vapours of iodine and oil of turpentine act on one another with great violence, forming a large quantity of hydriodic acid (Guizot); they decompose each other only after condensation, and without heat or explosion. Vapour of oil of turpentine is absorbed by iodine. (Winckler.)

When 1 pt. of iodine and 8 pts. of oil of turpentine are placed together under a bell-jar, the iodine is converted in the course of three days into a dark red resin, having a balsamic odour and an odour of iodine, and hydriodous acid which floats upon the resin; and after a week, if the glass be filled with the turpentine-oil, a brownish liquid having a balsamic odour separates from it. The resin thus obtained froths up when shaken with aqueous carbonate of potash, sinks to the bottom, and after washing with alcohol, yields by dry distillation, vapours of iodine and a thick oil like oil of mace, while charcoal and a small quantity of iodide of potassium remain behind. Its solution in ether gives with corrosive sublimate, red iodide of mercury, and with subacetate of lead, it yields after a few hours, iodide of lead. — After digestion with caustic potash, washing with alcohol, solution in 4 parts of ether, and evaporation of the solution at a moderate heat, it remains as a black, dry mass which has a balsamic and iodine-like odour,—burns when set on fire, with sparkling and a very smoky flame,—gives off, when heated, iodine and hydriodous acid in yellow needles,—is insoluble in water, and dissolves slowly with dark yellow colour in alcohol of 80 per cent., readily in ether. The dark brown ethereal solution is decolorised by agitation with potash-ley, and the decanted ether yields by evaporation a yellowish red, inodorous and tasteless resin not containing iodine, while the potash-ley takes up a quantity of iodine equal to 42·56 per cent. of the weight of the resin. (Winckler.)

When iodine is distilled with oil of turpentine, hydriodic acid is produced, together with a blackish viscid oil which is decolorised by agitation with aqueous potash (Deville); charcoal remains behind, and the distillate containing hydriodic acid deposits white flocks when shaken up with potash. (Guizot.) The brown solution of iodine in an equal quantity of oil of turpentine, the formation of which is attended with evolution of heat, gives off, when distilled to dryness, a large quantity of hydriodic acid, then a brown oil, and lastly a balsam which sinks to the bottom, while charcoal remains behind. The distillate when exposed to the air, gives off yellowish vapours, having a pungent odour like that of hydriodic acid, tastes very sour, gives off part of its hydriodic acid on exposure to the air, and the whole when placed near ammonia (the ammonia at the same time entering into the oil, *Gm.*), and then appears colourless, has a disagreeable taste and empyreumatic odour, and deposits the brown balsam which passed over with it, together with a small quantity of dissolved iodine. Oil of turpentine distilled with rather less than an equal quantity of iodine passes over nearly unaltered. (Guizot.)

10. *Nitric acid* acts on oil of turpentine in various ways, according to its strength and quantity and the duration of the action. Strong nitric acid acts on oil of turpentine with great violence, and often sets it on fire (Blanchet & Sell); an excess of the acid, diluted with an equal weight of water, forms, after continued boiling, carbonic acid, hydrocyanic acid, terephthalic acid (xiii, 13), terebenzic acid, acid resins, terebilic acid (xii, 467), oxalic acid, terechrysic acid (xi, 424) (Cailliot), together with acetic, propionic and butyric acids. (Schneider.) By the action of moderately dilute nitric acid, acetic acid is produced; by long continued boiling with very dilute nitric acid, nitrogen, carbonic acid, and carbonic oxide are evolved, whilst a resin remains, insoluble in water, and smelling of formic acid. (Deville.) — Nitric acid, mixed with ½ pt. alcohol, partially converts oil of turpentine into turpentine-camphor. (Wiggers, *Ann. Pharm.* 57, 247.)

Oil of turpentine, from turpentine produced in northern countries, is scarcely heated by nitric acid. (Bonastre, *J. Pharm.* 11, 529). When a small quantity of oil of turpentine is heated with excess of nitric acid diluted with an equal weight of water, as long as red vapours continue to escape, carbonic and hydrocyanic acids are evolved, and a quarter of the oil passes over with somewhat diminished rotatory power, while resins and an acid liquid remain behind. The resins consist of terephthalic acid, insoluble in alcohol, and three resins soluble therein (according to Chantard, *N. J. Pharm.* 24, 166, they consist of two substances containing hyponitric acid, one of which dissolves in ammonia with red colour, and is precipitated therefrom in yellow flocks by acids, while the other is insoluble in ammonia and in the fixed alkalis; both, however, yield toluidine when boiled with potash). The acid liquid mixed with water, after evaporation, deposits a yellow pitchy mass, consisting of resin, terephthalic acid and terebenzic acid (according to Svanberg & Ekman, *J. pr. Chem.* 66, 219. of an acid different from terephthalic acid), while the mother-liquor retains oxalic acid (quadroxalate of potash, according to Rabourdin), together with terebilic acid and a small quantity of terechrysic acid. (Cailliot.) — It is only chlorinated nitric acid that produces oxalic acid with oil of turpentine, and, on the other hand, less terebilic acid than is produced by pure nitric acid. (E. Kopp, *Compt. Chim.* 1849, 153.)

When 5 or 6 pts. of strong nitric acid diluted with an equal weight of water, are very gradually dropt into oil of turpentine very gently heated in a large tubulated retort, the portion which distils over being well cooled, a violent action soon takes place, the first portions of acid turning the oil brown, while the latter portions produce heating, ebullition and emission of red fumes. If the mixture be boiled for 24 hours after the action is over, the resin adhering to the sides of the retort disappears, a viscid scum forms for a while on the surface, and the nitric acid, on cooling, deposits a brown, bitter, acid resin. If the clear liquid in the retort be distilled down to one-third, and afterwards distilled off several times, with addition of water, a greenish yellow liquid, rendered turbid by drops of oil, passes over first, then a clear distillate, containing (besides nitric acid), acetic, propionic, and butyric acids. (Schneider.)

11. When oil of turpentine, saturated with *nitrous acid*, is distilled, a black resin is obtained, together with a red volatile oil, smelling like oil of turpentine and bitter almond oil. (Deville.)

12. *Oil of vitriol* decomposes oil of turpentine with rise of temperature, evolution of sulphurous acid, and formation of terebene and colophene. (Deville.) The mixture becomes heated, gives off sulphurous acid, and becomes brown and viscid. (Hatchett.) On gently heating the mixture, a viscid mass is formed, partly soluble in water, partly sinking therein, sparingly soluble also in alcohol (Link); an oil, smelling like strawberries, a slightly volatile acid, a large quantity of light brown resin, mobile at 100°, insoluble in potash, also extractive matters. (Unverdorben.) Oil of turpentine distilled with $\frac{1}{4}$ pt. of strong sulphuric acid, yields a red brown oil, which when freed from sulphuric acid by potash, has an aromatic odour like that of anise-oil (Perse), like rock-oil, oil of turpentine, and oil of rosemary. (Heldtmann, *Rep.* 14, 488.) When oil of turpentine is poured upon strong sulphuric acid, so that the two may not mix, the oil of turpentine floating on the top becomes thick after 6 or 8 days, dissolves readily in strong sulphuric acid, and may be separated therefrom by water. Oil of turpentine, poured in like manner upon sulphovinic acid, dissolves sparingly, gives off sulphurous acid when distilled, and yields a mobile oil containing sulphuric acid, whilst a thick oil, likewise containing that acid remains behind. By rectifying the distillate over antimonide of potassium, it becomes mobile, free from sulphuric acid, acquires an odour nearly the same as that of oil of turpentine, and resinises easily when exposed to the air. The viscid oil remaining in the residue may be extracted by ether, has an odour of camphor, and does not resinise in

the air. (Richter, *Ann. Pharm.* 32, 125.) When equal parts of oil of turpentine and strong sulphuric acid are distilled together, two volatile oils (terebene and colophene) pass over, while a tarry and a solid residue are left behind. The distillate yields sulphuric acid to water; the tarry residue is black, tasteless, difficult to burn, appears to volatilise undecomposed when heated; dissolves readily and in all proportions in ether and in oil of turpentine, partially only in nitric acid, the insoluble portion becoming hard, not at all soluble in weak acetic acid or in alcohol of 85 p. c.; sparingly in absolute alcohol; by dry distillation, it yields sulphuretted hydrogen, sulphur, and a volatile oil, which does not act upon potassium. The solid black residue possesses the same properties, excepting that it is richer in carbon and sulphur and less soluble. The distillate consists of two layers, the upper of which smells like peppermint, is very acid, and deposits sulphur after a while; after washing with soda, it is colourless, smells like thyme, is tasteless and neutral, burns like oil of turpentine, dissolves in all proportions in absolute alcohol, ether, and oil of turpentine, is not altered by nitric acid, turns greenish yellow, and gives off nitrous acid when heated with oil of vitriol and nitric acid, and is turned red by oil of vitriol. The lower layer of the distillate contains a very small quantity of a substance having an intolerable odour. (Boutigny.) When oil of turpentine is mixed by drops with a very large quantity of strong sulphuric acid, a red-brown solution is formed which deposits terebene when mixed with water; if, on the other hand, a very small quantity of sulphuric acid be poured into a larger quantity of oil of turpentine, the mixture becomes sensibly heated, blackens, and gives off a large quantity of sulphurous acid. (Gerhardt, *Compt. rend.* 17, 314.)

13. Oil of turpentine distilled with *phosphoric anhydride*, is resolved into terebene and colophene. Glacial phosphoric acid turns the oil red. (Deville.)

14. *Boracic acid*, heated with oil of turpentine to 100°, alters its rotatory power. French oil of turpentine, having a lævo-rotatory power of 35·4, exhibits, after being heated with boracic acid to 100° for 130 hours, a lævo-rotatory power of 23·0. (Berthelot.)

15. *Carbonic acid* does not decompose oil of turpentine in the cold; but when a mixture of the vapour with moist carbonic acid gas is passed through a tube heated nearly to redness, carbonic oxide and water are formed, together with a thin liquid, resembling acetone and isomeric with cymene. (Deville.)

$$C^{20}H^{16} + 2\,CO^2 = 2\,CO + 2\,HO + C^{20}H^{14}.$$

16. *Oxalic*, *tartaric*, *citric*, and *acetic acid* do not act upon oil of turpentine at ordinary temperatures, but, at 100°, they alter its specific gravity, rotatory power, odour, and boiling point, and some of its chemical properties, in various degrees, according to the duration of the action. (Berthelot.) French oil of turpentine of lævo-rotatory power 35·4°, exhibits, after being heated to 100° for 73 hours, with crystals of oxalic acid, a lævo-rotatory power of 15·2°; with crystals of tartaric acid, lævo-rotatory power=28·6°; with aqueous acetic acid, lævo-rotatory power=31·3°. English oil of turpentine, of lævo-rotatory power 18·6°, exhibits, after heating to 100° for 30 hours with crystals of oxalic acid, dextro-rotatory power = 16·2°; with glacial acetic acid, dextro-rotatory power = 14·7°. (Berthelot.) Berthelot, by heating oil of turpentine to 100° for 63 hours with oxalic acid, and subsequent distillation, obtained undecomposed oil of turpentine, a distillate smelling of terebene and exhibiting lævo-

rotatory power of 16·8° to 35·4°, and, lastly, a viscid, yellow, non-iridescent distillate, together with a solid residue. Oil of turpentine, altered by acetic acid at a high temperature, exhibits the boiling point of the original oil. (Berthelot.) When oil of turpentine is distilled with strong sulphuric acid and acetate of potash, the distillate consists of aqueous sulphurous acid, terebene, and colophene. (Deville.)

17. *Anhydrous hydrofluoric acid* imparts but a faint yellowish colour to oil of turpentine, even after long continued action, but throws down a greyish white tallowy substance, amounting to about $\frac{1}{554}$th of the oil, and imparts to the oil a very acid pungent odour, which is quickly destroyed by exposure to the air, the oil then becoming decolorised and depositing brown flocks. (Gehlen.) The rotatory power remains unaltered, and the product contains but little fluorine (3·05 p. c.), so that it cannot be regarded as a fluorated oil of turpentine. 1 pt. of oil of turpentine placed in the cooled leaden vessel rapidly absorbs the hydrofluoric acid evolved from 1½ pts. fluor-spar by 3 pts. oil of vitriol, becoming brown and viscid, and separating when left at rest into two layers, the upper of which is brown and fuming, while the lower is oily, and, after washing with water, dissolves in ether and in oil of turpentine completely, but in rock-oil, with separation of white flocks which quickly disappear. The solution in absolute alcohol, which is formed with difficulty, deposits on cooling, yellowish flocks which are not obtained from the other solutions, even after concentration and cooling to − 19°. On distilling the unaltered oil from leaden retorts, a fuming oil is obtained, which smells like camphor, while, by distillation from glass retorts, a thick, white, crystalline sublimate is obtained, having an aromatic sour taste, and consisting of a mixture of fluoride of silicium formed in the distillation, with the camphor-smelling oil just mentioned, which dissolves in ether, and remains, after evaporation of the ether, as a thick yellow resin free from fluorine. (Reinsch, *J. pr. Chem.* 19, 316.)

18. *Oil of turpentine* absorbs in the cold, 6·8 p. c. of *gaseous fluoride of boron*, and is thereby converted into an isomeric, iridescent, viscid liquid, which boils almost constantly at 300°, and has no rotatory power. — Oil of turpentine, sealed up in a glass tube with 2 vols. ($\frac{1}{160}$) of gaseous fluoride of boron, absorbs the gas, turns red, and becomes heated to the boiling point without evolution of gas; the heat thus developed is stronger than can be produced by the union of the oil with the fluoride of boron. Alcohol enclosed in the same tube is not converted into ether. (Berthelot.)

19. *Gaseous fluoride of silicium* does not act perceptibly on oil of turpentine. (Deville.)

20. Hydrochloric acid gas converts oil of turpentine partly into hydrochlorate of terebene, partly into artificial camphor. (Deville.) — Oil of turpentine is converted by hydrochloric acid into camphene and peucylene, which then unite with the hydrochloric acid. (Soubeiran & Capitaine.) According to Blanchet & Sell, hydrochloric acid gas does not decompose oil of turpentine, but unites with the dadyl and peucyl already contained in it.

21. *Hydrobromic and hydriodic acid* act in the same manner as hydrochloric acid gas. (Deville.)

22. An intimate mixture of 600 pts. water, 200 pts. *chloride of lime*, and 25 pts. oil of turpentine, emits, when distilled, a pleasant ethereal odour, gives off a large quantity of carbonic acid, froths up, and yields, even after the fire has been removed, a distillate which separates into

three layers, the uppermost of which is undecomposed oil of turpentine, the middle, an aqueous solution of chloroform, while the lowest consists of chloroform. (Chautard.) — *Hypobromous acid* distilled with oil of turpentine, yields bromoform. When bromine is dropped into a thin paste of lime, as long as it is thereby decolorised, the mass becomes heated and thickened. If it be then brought back to its original consistence by addition of water, carefully mixed, during agitation, with a quantity of oil of turpentine equal in weight to half of the lime employed, and heated, a brisk action begins, though less violent than with chloride of lime, carbonic acid escaping and aqueous bromoform distilling over.

23. *Liquid sulphide of phosphorus* converts oil of turpentine, after some months' contact, into a viscid, yellowish red resin which surrounds the sulphide of phosphorus, rendered very limpid and somewhat more mobile by the action. Sulphide of phosphorus takes fire under boiling oil of turpentine. (Böttger, *J. pr. Chem.* 12, 359.)

24. *Chlorochromic acid* sets fire to oil of turpentine. (Thomson, *Phil. Trans.* 1827; *Pogg.* 31, 607.)

25. *Potassium* does not act upon oil of turpentine in the cold. (Blanchet & Sell; Dumas.) It colours the oil brown and separates brown flocks without evolution of gas. (Deville, Hagen.) Potassium oxidises in oil of turpentine, gives off gas, and becomes surrounded with a thick resin. (Oppermann.) The oil of of the branches of the spruce fir, evolved hydrogen in a few minutes when treated with potassium, formed a light brown jelly, and was itself coloured brown because it contained an oxygenated oil. (Wöhler.)

26. *Fused hydrate of potash* colours ordinary oil of turpentine (with separation of brown flocks, according to Deville), but not Venetian oil of turpentine. (Scharling.) To the oil from the branches of the spruce-fir, it imparts, on distillation, the odour of ordinary oil of turpentine. (Wöhler.) — Common oil of turpentine is coloured by hydrate of potash, the more strongly the older it is, and may become heated to 60° at the same time. — Both ordinary and Venetian oil of turpentine, when shaken up with bisulphide of carbon and fused hydrate of potash, yield after a while, a white saline mass which behaves like xanthate of potash. (Scharling.)

Strong potash-ley does not alter oil of turpentine from the spruce-fir or Scotch fir (Wöhler, Hagen), or Venetian oil of turpentine, when distilled therewith, inasmuch as the distillate exhibits the same behaviour as before towards hydrate of potash and bisulphide of carbon. (Scharling.) It colours the common oil yellow and gradually brown. (Blanchet & Sell.) — A mixture of strong potash-ley and oil of turpentine separates into three layers; the uppermost of which is an oil, the lowest, potash-ley, while the middle layer is brown, thick, and soluble in potash-ley if weaker than the ley originally used From this milky solution, acids throw down a viscid resin which floats on the surface, and another which falls to the bottom in lumps and flakes, both being soluble in alcohol and having an acid reaction. The liquid resin becomes yellow and brittle after the adhering oil has evaporated. (Polex.)

27. Oil of turpentine absorbs 7¼ vols. *ammonia gas* at 16° (Saussure), acquiring a yellowish colour, but retaining its mobility. (Gehlen.) It forms a tallowy mass. (Saussure.) The milky liquid produced by agitating oil of turpentine with an equal quantity of aqueous ammonia separates, when left at rest, into three layers, the uppermost which is an oil, the lowest, a solution of sal-ammoniac, and the middle, a jelly like opodeldoc, which last, when separated from the liquid and pressed

between bibulous paper, forms a mass which melts between the fingers or when heated a few degrees above 0°.

28. Oil of turpentine takes fire with *chlorate of potash* and a few drops of oil of vitriol, burning with a tremulous, very smoky flame and leaving charcoal. (A. Vogel Jun., *Ann. Pharm.* 74, 114.)

29. *Quick lime* kept in contact for some time with crude oil of turpentine, deprives it of its unpleasant odour. (Blanchet & Sell.)

30. *Chloride of calcium, fluoride of calcium, chloride of barium, chloride of strontium, iodide of ammonium* and *chloride of ammonium* alter at 240°—250°, the rotatory power of oil of turpentine, and accelerate the very slow transformation which takes place at this temperature. (Berthelot.) — French oil of turpentine of lævo-rotatory power 35·4°, after being heated for 7 or 8 hours to 240°—250° with chloride of calcium, rotates 22·1° to the left; with fluoride of calcium, 5·9° to the left; with chloride of barium, 32·85° to the left; with chloride of strontium 18·4° to the left; — after being heated to 250° for two hours with chloride of calcium, 15·2° to the left; to 270° for two hours with chloride of calcium, 15·2° to the left; this last product is colourless and boils at 161°. English oil of turpentine, which rotates 18·6° to the right, exhibits after 7 or 8 hours heating to 240° — 250°, with fluoride of calcium, a rotatory power of 7·4° also to the right. (Berthelot.)

31. *Chloride of Zinc* does not act upon oil of turpentine at ordinary temperatures; but at 100°, it alters the rotatory power, retards the formation of turpentine-camphor, ultimately forms an oil containing $C^{20}H^{14}$ and gives off hydrogen, increasing in quantity with the duration of the action, so that in 130 hours, from 15 to 30 volumes are evolved: — ($C^{20}H^{16} = C^{20}H^{14} + 2H$). (Berthelot.) — French oil of turpentine having a lævo-rotatory power = 35·4°, exhibits, after 130 hours heating to 100° with chloride of zinc, a lævo-rotatory power of 15·5°; English oil of turpentine of dextro-rotatory power 18·6°, heated for four hours to 100° with chloride of zinc, exhibits dextro-rotatory power = 17·85°. Oil of turpentine heated to 270° with chloride of zinc, becomes coloured, smells of terebene, and increases in density from 0·8613 to 0·8698 at 11°. French oil of turpentine heated to between 100° and 270° with chloride of zinc, yields when distilled at 160°, at first a distillate of apparently unaltered oil of turpentine, of lævo-rotatory power 24·9° to 35·4°, then reddish coloured, and ultimately viscid oil having the boiling-point of colophene. (Berthelot.)

32. *Nitroprusside of copper* boiled with oil of turpentine produces a green or bluish green precipitate. By this reaction, oil of turpentine may be recognised in oxygenated oils, which colour nitroprusside of copper black-brown or green and themselves acquire a darker colour. (Heppe, *N. Br. Arch.* 89, 57.)

33. *Litharge* or *minium* does not alter cold oil of turpentine (Brandes, Müller), but, at a gentle heat, gives up oxygen to it, and converts it into terebentic and formic acids. (Weppen.) Hydrated oxide of lead colours an equal weight of oil of turpentine dark red after a short time; with a smaller quantity of the hydrated oxide of lead, it turns yellowish after some days, the lead-compound itself remaining white. (Brandes.) *Basic acetate of lead*, shaken up with an equal quantity of oil of turpentine, forms, after a few minutes, a thick mixture, which varies in colour from orange-yellow to wine-red, is insoluble in water, but dissolves partially in alcohol, leaving a yellowish, viscid, acid mass, containing lead; with

excess of subacetate of lead, the colouring takes place more slowly and is weaker. (Brandes, Müller; comp. also *Ozone with Oil of Turpentine,* p. 275.) The altered oil is a mixture of acid resin with oxide of lead, adhering subacetate, and oil of turpentine; the latter separates transparent and colourless, only the subjacent basic acetate of lead exhibiting a red colour; a yellow solid body separates between the two layers of liquid. The colouring is not due to an acid resin contained in the oil of turpentine, inasmuch as it is likewise produced by oil, which has been purified with potash-ley. (Polex.) A concentrated solution of bibasic acetate of lead imparts a dark red colour in a few minutes to oil of turpentine four years old; with fresher oil, the same effect is produced in two hours; the same oil acquires the same colour by boiling with lead-solution for a quarter of an hour. (Schindler, *N. Br. Arch.* 41, 40.) Bassic acetate of lead is coloured reddish after a while by crude oil of turpentine, but not by the rectified oil or by the vapour; the crude oil loses these properties by boiling and distillation; the rectified oil acquires them by three months exposure to the air. When oil of turpentine is shaken up with basic acetate of lead in a bottle containing air, it takes up oxygen, which does not escape when the oil is boiled alone or with water, but if previously red, it becomes decolorised and deposits yellow flocks and white hydrated oxide of lead. (Brandes.) The crude mixture of 1 pt. alcoholic sal-ammoniac, 8 pts spirit of camphor, and 8 pts. oil of turpentine, mixed with 2 pts. basic acetate of lead, acquires a kermes-brown colour in a few minutes, and solidifies to a jelly after some days. (Buchner, *Br. Arch.* 8, 133.)

Interpolation.

Terebentic Acid, $C^{18}H^{14}O^{10}$?

WEPPEN. *Ann. Pharm.* 41, 294.

Acide térébentinique. Terebentinsäure.

Formation. 1. By heating oil of turpentine with litharge. 2. By the action of the air on oil of turpentine mixed with oxide of lead, formic acid being produced at the same time:

$$C^{20}H^{16} + 14\,O = C^{18}H^{14}O^{10} + C^{2}H^{2}O^{4}.$$

Preparation. Oil of turpentine gently heated with oxide of lead, becomes coloured, absorbs oxygen with avidity, then again gradually loses its colour and deposits a copious yellow precipitate. This precipitate is boiled and washed with alcohol as long as the water runs off turbid, then decomposed by sulphuretted hydrogen, the terebentic acid dissolved out by alcohol, and the solution evaporated till it crystallises.

Properties. By slow evaporation it forms delicate white crystals; by quick evaporation, a brown tenacious mass. Its alcoholic solution reddens litmus.

			Kolbe.	
			a.	*b.*
18 C	108	53·46	55·14	54·00
14 H	14	6·93	6·97	6·93
10 O	80	39·61	37·89	39·07
$C^{18}H^{14}O^{10}$	202	100·00	100·00	100·00

The acid used for the first analysis contained resin, formed in consequence of the temperature rising too high.

Combinations. The alcoholic solution of terebentic acid precipitates most metallic salts; the precipitates are soluble in alcohol.

Terebentate of Lead. Obtained, together with formiate of lead, as above described, in the form of a yellow precipitate, which may be purified by washing with boiling water. If it be heated somewhat above 100°, while still moist from adhering alcohol, it burns away with a bright glimmering light, leaving a residue of metallic lead.

Terebentic acid dissolves in alcohol, and the solution is rendered turbid by water.

34. When oil of turpentine is distilled with *chromate of lead* and dilute sulphuric acid, carbonic acid escapes, a small quantity of aqueous formic acid distils over, and sulphate of chromium remains behind.

35. Oil of turpentine, mixed with *bichloride* of tin, thickens, and may become heated till it takes fire. (J. Davy.)

Combinations. 1. *With Oxygen.* — *a. Oxide of Turpentine-oil. Hydrated Oxide of Turpentine.* *Laurent's Oxide de camphène hydraté.* — $C^{20}H^{16}O^2,2HO$. — When a layer of oil of turpentine $\frac{1}{2}$ centim. thick is introduced into a glass bell-jar filled to $\frac{4}{5}$ with oxygen, and closed at bottom with water, the vessel then placed in sunshine and the oxygen-gas renewed as it is absorbed, the sides of the vessel below the oil become covered with small prisms, which may be collected, and purified by washing with water and oil of turpentine, and recrystallisation from alcohol.

Inodorous. Crystallises from boiling water in stellate groups of needles, which, when boiled with water containing sulphuric acid, yield a product smelling of oil of turpentine and camphor. It is soluble in water, alcohol, and ether, and crystallises from the hot solutions on cooling. (Sobrero, *Compt. rend.* 33, 66; *Ann. Pharm.* 80, 106.)

			Sobrero.
20 C	120	70·58	70·58
18 H	18	10·58	10·58
4 O	32	18·84	18·84
$C^{20}H^{16}O^2,2HO$	170	100·00	100·00

b. Oil of turpentine absorbs *oxygen gas*, acquiring new properties, and being converted into *ozonised oil of turpentine.* In this compound part of the absorbed oxygen appears to be more intimately, a second portion (amounting to 5·2 per cent. of the turpentine oil) less intimately combined, inasmuch as the latter may be transferred to other bodies, and still exhibits the properties of free ozone. (Schönbein.) — The formation of ozonised oil of turpentine takes place on agitating the oil with cold air in presence of light, the action going on the more quickly, the more numerous the points of contact of the oil and the air, the brighter the light, and the lower the temperature When, therefore, oil of turpentine is left for four months in a bottle $\frac{3}{4}$ filled with air, and exposed to diffused daylight, the air being renewed as it is used up, a mobile, acid, oxidising oil is obtained.

Ozonised oil of turpentine exerts an oxidising action on the following substances. It decolorises indigo-solution when agitated with it, especially if the solution be warmed (hence if a portion of the ozonised oil be introduced into a bottle, together with a strip of linen dyed blue with indigo-solution, the linen is bleached in a few hours). It converts aqueous sulphurous acid, with rise of temperature, into sulphuric acid; colours solution of iodide of potassium immediately yellow, the oil at the same time becoming reddish, and, when heated, brownish yellow from separation of iodine (hence, when it is placed upon paper soaked in a mixture of iodide of potassium and starch, the paper turns brown, or, if moistened with water, blue). It converts a hot solution of ferrous sulphate into ferric sulphate, which partly separates (basic salt) and partly remains in solution. Ozonised oil of turpentine colours white ferrous cyanide containing potassium, blue; yellow aqueous solution of ferrocyanide of potassium, deep yellow, especially on boiling; converts arsenic spots on a porcelain plate into arsenic acid, and causes them to disappear completely in the course of 10 or 15 minutes (it does not affect antimony spots, even after a long time); decolorises sulphide of arsenic suspended in water, when heated and agitated with it; likewise sulphide of lead and strips of paper coloured therewith, if these papers are suspended in a bottle containing the ozonised oil. (Schönbein.) — This property affords the means of detecting oil of turpentine in other oils which do not ozonise the air. (Williams, Overbeck, *N. Br. Arch.* 90, 138.) — Ozonised oil of turpentine boiled with phosphorus, not in contact with the air, forms phosphorous acid. Shaken up with finely divided silver and a small quantity of acetic acid, it forms acetate of silver. It dissolves guajac resin, forming a solution which is colourless at first, but afterwards turns blue, especially when heated, the ozone combining with the guajacum under the influence of heat. The oxidising action of ozonised oil of turpentine is intensified by the presence of blood-corpuscles and ferrous salts, the blood-corpuscles being thereby completely oxidised, and the protoxide of iron converted into sesquioxide. — A mixture of oil of turpentine, containing 2 per cent. of ozone with a solution of subacetate of lead, acquires, when shaken up at mean temperature, a lemon-yellow to red-yellow colour, and forms protoxide and bioxide of lead, the greater portion of these oxides separating at once, while a smaller portion remains and separates from the filtered oil after 24 hours, so that the oil is but slightly coloured by the peroxide of lead, but nevertheless continues to exert an oxidising action. The strongest colouring takes place in a mixture of 1 vol. solution of subacetate of lead (lead-vinegar, viii, 314,) and 2 vols. ozonised oil of turpentine; but peroxide of lead containing protoxide is likewise formed with every other proportion of the mixture.

Ozonised oil of turpentine sometimes also exerts a reducing action. — It abstracts part of the oxygen from peroxide of lead (oil of turpentine free from ozone has no action on that compound), losing its ozone at the same time, and giving off a gas not yet examined. It decolorises tincture of guajacum which has been coloured by peroxide of lead; also the aqueous solutions of permanganate of potash and of chromic acid mixed with sulphuric acid. — Hence even strongly ozonised oil of turpentine does not become coloured when shaken up with a few drops of lead-vinegar, inasmuch as the peroxide of lead formed in the first instance is quickly decomposed by the excess of ozone present.

Ozonised oil of turpentine is partially deprived of its peculiar properties by boiling. (Schönbein.) It recovers them again when exposed to the air, and the yellowish residue possesses twice as much bleaching power as the distillate, though no oxygen is given off. (Williams.)

Schönbein explains the simultaneous oxidising and reducing powers of ozonised oil of turpentine, by assuming that peroxide of lead contains a positive, and ozonised oil of turpentine a negative ozone, and that the union of these produces ordinary oxygen.

2. *With Water.* — Oil of turpentine forms with water three different compounds.

A. Turpentine-camphor. $C^{20}H^{20}O^4$.

Hydrate of Oil of Turpentine. Pyrocamphorium (Trautwein), *Terpenthinsalz* (Buchner), *Terpentinölcamphorid* (Trommsdorff), *Terpin* (Berzelius, List), *Trihydrate d'essence de térébenthine.* (Deville.) First observed in 1727, by Geoffroy, who, however, did not recognise it as a distinct compound; examined by Buchner, who regarded it as a salt formed by the union of succinic acid with a volatile base; recognised as hydrate of turpentine-oil by Dumas & Peligot, and by Wiggers.

Formation. 1. The compound forms after a considerable time in mixtures of oil of turpentine and water. (Hertz, Deville.) In the following cases, also, the formation of turpentine-camphor appears to depend upon the presence of water in the materials, or else the camphor existed ready formed in the oil of turpentine, and afterwards separated. (Kr.): — When oil of turpentine is left to itself for a considerable time (Dumas, Brandes), even in closed vessels (Häfner, Geign); when it is heated for some time to 50° (Cluzel; Blanchet & Sell); or distilled (Buchner); by distillation of oil of turpentine which has been previously exposed to the air. (Boissenot & Persot.) — Turpentine-camphor passes over, together with acetic acid, in the distillation of old oil of turpentine which has been long exposed to the air, and separates in the crystalline form from the aqueous distillate, not by evaporation, but by continued cooling to −7°. (Boissenot & Persot); — when oil of turpentine is left in contact with ether. (Trommsdorff.) — 2. By the action of alcoholic nitric acid on oil of turpentine, oil of lemons, oil of bergamot, oil of copaiba, &c. (Wiggers, Deville, Berthelot); on terpinol and isoterebenthene. (Berthelot.) — The alcohol serves merely as a solvent, and may be replaced by any substance that will dissolve both the oil and the acid, such as wood-spirit, acetone, ether, acetate of ethyl, butyric acid, or by such as dissolve only the oil, *e.g.*, benzene or fusel-oil; it may even be dispensed with altogether, but then the action is slower. The nitric acid, on the other hand, is essential to the formation of the turpentine-camphor, although it does not itself suffer decomposition, and retains for some time its power of saturating bases, and of forming turpentine-camphor with fresh quantities of oil of turpentine, losing this power only after it has given rise to the formation of secondary products; it cannot be replaced by any other substance except nitrous ether. — The formation of turpentine-camphor requires intimate contact of the acid with the oil. (Berthelot.) — 3. By the action of oil of vitriol, hydrochloric acid, or acetic acid on alcoholic oil of turpentine, but in smaller quantity and less quickly than when nitric acid is used (Wiggers); acetic acid does not produce it. (Deville.) — Glacial acetic acid does not dissolve oil of turpentine, or convert it into turpentine-camphor, even after several years' contact; but if a few drops of nitric acid be added, turpentine-camphor crystallises out in a few days. Neither does alcohol convert oil of turpentine into the camphor. (Deville.) — A mixture of oil of turpentine with hydrochloric acid, spirit of horse-radish, or spirit of caraway, deposits turpentine-camphor. (Rammelsberg, *Pogg.* 63, 570.) — When the liquid which remains after passing hydrochloric acid gas for some time through oil of turpentine, and separating the resulting crystalline compound, is mixed with water, turpentine-camphor separates from it. (Hertz.)

Preparation. 8 pts. of oil of turpentine are left in contact for 2 or 3 days with 2 pts. of nitric acid of sp. gr. 1·25 to 1·3, and 1 pt. of alcohol of 80 per cent., the mixture being frequently agitated, then for a considerable time without agitation at 20° to 25°, whereupon two layers of liquid form, the lower consisting of nitric acid and alcohol, and the upper containing oil of turpentine, which in time becomes darker, and ultimately brown and opaque, and smells like hyacinths. After a few days, crystals appear at the surface of contact of the two liquids, increasing very quickly during the first fourteen days, then uniting in crystalline crusts, finally sinking to the bottom, and attaining to a larger size the more the mixture is kept at rest. The yellowish brown crystalline crusts (contaminated with a brown substance), are collected, left for a few days on bibulous paper, then pressed and dissolved in hot water; the solution is boiled with animal charcoal and filtered; and the crystals, which separate on cooling, are left to dry in the air. (Wiggers.) — As a portion of the turpentine-camphor is very apt to be lost by volatilisation during the solution of the crystals in hot water and the boiling of the liquid, or by the decomposing action of the adhering acid, it is better to press the crystalline crusts between paper, pulverise them, and dissolve them in warm alcohol; the turpentine-camphor then separates on cooling, while the oil and acid remain in the mother-liquor. By repeated crystallisation, they may be obtained quite pure, and by spontaneous evaporation of the cold-saturated alcoholic solution, in well developed crystals. (List.)

2. A mixture of 4 vols. oil of turpentine, 3 vols. alcohol of 85 p. c., and 1 vol. nitric acid is left to itself for several months at mean temperature (Deville), in shallow vessels. (Berthelot.) — In deep vessels, the formation of the camphor is not completed for several years, whereas, if shallow vessels are used, crystals appear after an interval varying from 48 hours to a week, and in a few weeks their formation is completed. (Berthelot.)

3. Hydrochloric acid gas is passed into oil of turpentine till the solid hydrochlorate begins to separate; the passage of the gas is continued for some time; the liquid then cooled and left to stand for a night; sufficient water is then added to make it cover the bottom of the vessel about an inch deep; the mixture, after being shaken, is left to itself for a while; and the crystals, which separate after some time on the sides of the vessel, or float upon the oil, are collected and purified. (Hertz.)

4. Oil of turpentine, in quantities of about 10 grammes, is left in contact for some time with nitric acid and acetone or butyric acid. (Berthelot.) Under these circumstances, the oil is sometimes wholly converted into turpentine-camphor. (Berthelot.)

The quantity of turpentine-camphor obtained by these several methods varies with the constitution of the oil of turpentine used. Those kinds of turpentine-oil which yield much artificial camphor when treated with hydrochloric acid, likewise yield the largest amount of turpentine-camphor. (Wiggers.) By Wiggers' method, turpentine-oil yields 8·3 p. c. of turpentine-camphor; Fluckiger's templin-oil 15 p. c. (Fluckiger). By Deville's method, turpentine-oil yields in 4 to 6 weeks, 6·25 p. c., after longer standing, 25 p. c. (Deville); French oil of turpentine in 3 months, 27 p. c.; in two years 40 p. c.; American oil of turpentine in two months yields quantities which may amount to 45·4 p. c. (Berthelot.)

Vogel considered the presence of oil of amber as necessary to the formation of turpentine-camphor, and accordingly prepared it by mixing 1 pt. oil of turpentine with ⅛ pt. oil of amber and ½ pt. nitric acid of sp. gr. 1·25, and adding after 4 weeks ¼ pt. alcohol, whereby he obtained in 18 weeks 12·5 p. c. turpentine-camphor; by using equal parts of oil of turpentine, oil of amber, and nitric acid, and ¼ pt. alcohol, he obtained 5·8 p. c.; and with equal parts of oil of turpentine and nitric acid and ¼ pt. alcohol, 0·42 p. c. turpentine-camphor.

Crystallised turpentine-camphor is converted, by loss of water, into *anhydrous turpentine-camphor.* — *Bihydrate of oil of turpentine* (Deville), *Tetrahydrate of oil of turpentine.* (Berthelot.)

Properties. Milk-white, indistinctly crystalline mass (Wiggers), which volatilises undecomposed at 150° (103°, List), at 150° — 155° (Blanchet & Sell), and sublimes in acuminated crystals like benzoic acid (Buchner, Voget, Geiger), in slender needles having a silky lustre (Brandes), as a woolly mass (Trommsdorff.) — It sublimes only in a current of air, not when the air is excluded; when heated in a test-tube, it creeps up the sides. (List.) It is only when heated in considerable quantity, that it melts before subliming. (Brandes.) — Fused turpentine-camphor, suddenly cooled without access of moisture, remains for several days tough and amorphous, but solidifies in the crystalline form on being touched by a sharp body, or heated to 36°, or breathed upon, or brought in contact with water, alcohol, or ether. (List.)

Vapour-density 6·257. (Deville.) — Neutral. Inodorous. In the impure state it smells like turpentine. (Buchner, Trommsdorff.) The vapour smells like resin (Häfner); like old oil of turpentine. (Buchner.) — Tasteless. Its aqueous solution does not act on polarised light. (Deville, Berthelot.)

Anhydrous Turpentine-camphor.			Blanchet & Sell.	Wiggers.	Deville.
20 C	120	69·7	70·91	69·59	69·4
20 H	20	11·6	12·05	11·68	11·8
4 O	32	18·7	17·04	18·73	18·8
$C^{20}H^{10}O^4$	172	100·0	100·00	100·00	100·0

	Vol.	Density.
C-vapour	20	8·3200
H-gas	20	0·1386
O-gas	2	2·2186
Vapour of Turpentine-camphor	2	10·6772
	1	5·3386

Decompositions. 1. Turpentine-camphor *volatilises* on red-hot coals without taking fire. (Blanchet & Sell.) The vapour may be set on fire in the flame of a candle, and continues to burn (Geiger) with a very smoky flame (Trommsdorff); according to Buchner, the combustion does not continue. It leaves a small quantity of easily combustible charcoal. (Geiger.) — 2. Distilled with anhydrous phosphoric acid, it yields terebene and colophene. (Deville.) — The solution obtained by heating turpentine-camphor with an equal weight of deliquesced glacial phosphoric acid, yields by distillation an aqueous distillate probably containing acetic acid, on which a light yellow aromatic oil floats, and leaves a brown tumefied residue.

3. *Oil of vitriol* dissolves turpentine-camphor with red colour (Boissenot & Persot), without heating (Trommsdorff), water being separated and terpinol produced, which forms a yellowish red mass with the oil of vitriol. (List.) The solution has a balsamic odour, like that of artificial musk; gives off acid vapours (Buchner); becomes limpid after a few hours, and yields pointed crystals (Voget); and deposits resin on being mixed with water. (Boissenot & Persot.)

By boiling turpentine-camphor with *dilute sulphuric acid*, or with *aqueous bisulphite of potash*, or with *aqueous sulphurous acid*, terpinol is produced (List); likewise, though more slowly, by the action of aqueous oxalic acid, tartaric acid, bitartrate of soda, or benzoic acid. (List.)

4. *Hydrochloric acid gas* converts turpentine-camphor, with separation of water, into solid bihydrochlorate of turpentine-oil (Deville); into a liquid compound of hydrochloric acid and oil of turpentine, isomeric with hydrochlorate of terebene (Wiggers), which, however, according to List, is a solution of artificial camphor in terpinol. — Pulverised turpentine-camphor absorbs hydrochloric acid rapidly; deliquesces, with rise of temperature, to a brown liquid in which heavy drops first separate, and afterwards crystallise, so that it solidifies and must be warmed in order to pass hydrochloric acid gas through it; the liquid, after saturation, solidifies in the crystalline form, leaving only a small quantity of hydrochloric acid. (List.) — The solution of turpentine-camphor saturated while warm with hydrochloric acid gas, separates into two colourless layers, the lower of which is concentrated hydrochloric acid, and the upper a compound of oil of turpentine with hydrochloric acid. (Wiggers.) — Bihydrochlorate of turpentine-oil likewise forms in a mixture of turpentine-camphor and moderately strong hydrochloric acid. (List.)

5. *Hydriodic acid*, either gaseous or aqueous, converts turpentine-camphor into terpinol. The first product of the action is an iodated oil which, however, is completely decomposed by distillation, either alone or with water. (List.)

6. Turpentine-camphor dissolves without decomposition in cold *nitric acid*, the solution often beginning suddenly to boil (Trommsdorff); it gradually turns yellow when heated and gives off nitrous gas. (List.) — It deposits a yellow resin, and ultimately small yellowish crystals. (Trommsdorff); it smells like anise or fennel oil and rock-oil, and at higher temperatures, like camphor (Brandes); it emits an odour like that which is produced when a mixture of oil of turpentine and nitric acid takes fire. (Boissenot & Persot.)

7. When the vapours of fused turpentine-camphor are passed over *soda-lime* heated above 400°, terebentilic acid (xiii, 118) is obtained, together with marsh-gas and hydrogen:

$$C^{20}H^{20}O^{4} = C^{16}H^{10}O^{4} + 2C^{2}H^{4} + 2H.$$

(Personne, *Compt. rend.* 43, 553; *Ann. Pharm.* 100, 253.)

8. When turpentine-camphor is heated to 250° with *iodide of ammonium,* and the mixture is left at rest, two layers are formed, the lower consisting of aqueous iodide of ammonium with a few products of decomposition, and the upper of a brown oil which smells like terpinol and probably contains a hydrocarbon together with terpinol. (Berthelot.)

9. Turpentine-camphor is converted into terpinol by continued heating with *chloride of zinc* to 100°, or with *chloride of calcium, fluoride of calcium, chloride of strontium,* or *chloride of ammonium* to 160° – 180°. Chloride of barium and common salt do not act upon turpentine-camphor at this temperature. (Berthelot.)

Combinations. With *Water.* — *a. Crystallised Turpentine-camphor.* — Anhydrous turpentine-camphor is hygroscopic, and, when exposed to moist air, swells up and is converted into crystallised turpentine-camphor. (List.)

Transparent, colourless, shining rhombic prisms belonging to the oblique prismatic system. *Fig.* 73, without y, u, m; $u : u = 102^\circ\ 23'$; $u : u$ behind $= 77^\circ\ 37'$; $t : u = 133^\circ\ 48{\cdot}5'$; $t : i = 115^\circ\ 15{\cdot}5'$; $i : o$ (the octohedral face) $= 152^\circ\ 3{\cdot}5'$; $o : u = 126^\circ\ 58'$; $o : o$ on the non-truncated edges $= 135^\circ\ 43'$. The crystals are rhombic prisms with perpendicular truncation of the acute edges, and terminated by four-sided summits belonging to a rhombic octohedron, whose acute terminal edges are sometimes truncated by a pair of faces set upon the acute lateral edges of the prism (Rammelsberg, *Pogg.* 63, 570; see also Wiggers, *Ann. Pharm.* 57, 249; Hertz, *Pogg.* 44, 190; List, *Ann. Pharm.* 67, 364.) — The crystals obtained from a mixture of turpentine-oil with acetic acid and a small quantity of nitric acid, or of turpentine-oil and water, are different in form from those just described. (Deville.) The compound is therefore perhaps dimorphous, a supposition which is corroborated by Bernhardi's description. Crystallisation, augitic. *Fig.* 85 with i- and h- faces; $a : a = 75^\circ\ 25'$; $a : i = 127^\circ\ 42\frac{1}{2}'$; $a : u = 136^\circ\ 12\frac{3}{4}'$; $i : m$ behind $= 75^\circ\ 57\frac{3}{4}'$; $m : u = 126^\circ\ 52\frac{1}{4}'$; $u : u = 106^\circ\ 15\frac{1}{2}'$; $u : h = 151^\circ\ 13'$. Lamination parallel to i; cleavage parallel to i. (Bernhardi, *N. Tr.* 16, 2, 46.)

The crystals are half an inch long and 1 line broad (1 to 2‴ long and $\frac{1}{4}$‴′ broad, according to Buchner) united in tufts of five or six (Geiger, Boissenot & Persot); the lateral faces are longitudinally striated. (Buchner.) Harder than gypsum. (Trommsdorff.) — Sp. gr. 1·0994. (Trommsdorff.) In vacuo over oil of vitriol, they become dull, opaque, and give off 2 At. water (Deville); 9·423 p. c. Aq. (List.) (Calculation, $C^{20}H^{20}O^4 + 2Aq. = 9{\cdot}47$ Aq.), also when heated to 100°. (Deville.) This compound melts when heated, and gives off water above 75° (Häfner), below 100° (List), at 103°—105° (Deville), (according to List, the dehydrated turpentine-camphor does not melt till heated to 103°), forming a thin colourless oil, and solidifies on cooling to a milk-white, indistinctly crystalline mass of anhydrous turpentine-camphor. (Wiggers.) — Crystallised turpentine-camphor dissolves readily in heated *oils,* whether *fixed* or *volatile* (Trommsdorff, Buchner); from a warm solution in *turpentine-oil,* it does not separate on cooling (Häfner, Brandes), but from a solution in *poppy-oil* the separation takes place. (Häfner.) — According to Voget, it is insoluble in oil of turpentine and in oil of almonds.

			Dumas & Peligot.	Wiggers.	Deville.	Rammels.
20 C	120	63·16	63·8	63·31	63·2	64·05
22 H	22	11·58	11·4	11·55	11·7	10·61
6 O	48	25·26	24·8	25·14	25·1	25·34
$C^{20}H^{20}O^4 + 2Aq$	190	100·00	100·0	100·00	100·0	100·00

The turpentine-camphor analysed by Rammelsberg had not been recrystallised. According to Berzelius, it is the hydrated oxide of a radical $C^{20}H^{17}$.

b. Aqueous Turpentine-camphor. Crystallised turpentine-camphor dissolves in 200 pts. of cold water (250 pts. according to Voget) and in 22 pts. of boiling water (24 pts., Trommsdorff; 30 to 36 pts., Voget), and separates in the crystalline form from the hot solution on cooling. (Buchner, List.) Commercial turpentine-oils form turpentine-camphors of various degrees of solubility in water. (Berthelot, *N. Ann. Chim. Phys.* 40, 40.)

Turpentine-camphor dissolves in hot aqueous *ammonia* (Brandes); it dissolves in dilute aqueous *alkalis*, but when heated in concentrated aqueous alkalis, it melts without dissolving. (Trommsdorff.)

It dissolves in 8—10 pts. of *ether*. (Voget.)

It dissolves at 10° in 7 pts. of *alcohol* of 85 per cent., in 10 to 12 pts. of 86 p. c. alcohol, and in 5—6 pts. of boiling alcohol. The solution of anhydrous turpentine-camphor in alcohol yields crystals of the hydrated compound. (Deville.) According to some statements, the solution becomes turbid when mixed with water; according to others, it does not.

Turpentine-camphor dissolves in *acetic acid*. (Boissenot & Persot.) The solution is not rendered turbid by water (Brandes); when mixed with water, it deposits unaltered turpentine-camphor. (Trommsdorff.)

B. The so-called Liquid Turpentine-camphor.

$$C^{20}H^{18}O^2 = C^{20}H^{16},2HO.$$

Monohydrate d'essence de têrêbenthine. (Deville.) *Bihydrate d'essence de têrébenthine.* (Berthelot.)

A mixture of oil of turpentine and alcoholic nitric acid for the preparation of solid turpentine-camphor having been kept for three months excluded from the air, and then exposed to the air, did not deposit any solid turpentine-camphor, but on addition of water, yielded liquid turpentine-camphor in the form of an oil, which, after being distilled, was found to be $C^{20}H^{18}O^2$. (Berthelot.) The same liquid turpentine-camphor is constantly produced in the preparation of the solid camphor, as described at page 259, 2, the mother-liquor which remains after the separation of the solid compound, yielding by distillation, between 200° and 220°, a liquid product which turns the plane of polarisation to the left, and appears by analysis to be a solution of solid in liquid turpentine-camphor. (Berthelot.)

The liquid compound acts on polarised light like oil of turpentine. Rotatory power to the left = 42·4°. (Berthelot.)

			Deville.	Berthelot.
20 C	120	77·9	76·4	78·2
18 H	18	11·7	11·6	12·1
2 O	16	10·4	12·0	9·7
$C^{20}H^{18}O^2$	154	100·0	100·0	100·0

In presence of *water*, it appears to be capable of passing, under circumstances not precisely understood, into solid turpentine-camphor. Hydrochloric acid gas converts it into bihydrochlorate of turpentine-oil.

C. Terpinol.

$C^{20}H^{16},HO$ or $C^{40}H^{32},2HO$.

Monohydrate d'essence de térébenthine. (Berthelot, Gerhardt.) First prepared by Wiggers, examined and named by List.

Formation. 1. From turpentine-camphor (p. 258). *a.* By the action of hydriodic acid. (Wiggers.) — *b.* By continued boiling of the aqueous solution with the stronger acids, in smaller quantity also by the weaker acids, *e. g.*, tartaric, oxalic, benzoic, or sulphurous acid, acid sulphate of potash, or acid tartrate of soda. (List.) — *c.* By heating the camphor with *chloride of zinc* to 100°, with *chloride of calcium*, *fluoride of calcium*, *chloride of strontium*, or *chloride of ammonium*, to 160—180°, or with *iodide of ammonium* to 250°. (Berthelot.) — 2. From bihydrochlorate of turpentine-oil by boiling with water and alcohol (List), with alcoholic potash. (Berthelot.)

Preparation. Turpentine-camphor is heated for some time with concentrated hydriodic acid nearly to the boiling point; the supernatant oil which forms at 100° is distilled, washed and rectified with water, and dehydrated by agitation with chloride of calcium. (Wiggers.) — 2. A hot aqueous solution of turpentine-camphor is treated with a small quantity of hydrochloric acid (or with a drop of oil of vitriol to 11·5 grm. of the turpentine-camphor); the turbid mixture is distilled, and rectified with water containing hydrochloric acid if it contains unaltered oil of turpentine; the oil which has passed over is dehydrated with chloride of calcium; and the portion which in the rectification goes over at 168°, is decanted and collected. (List.)

Properties. Colourless, strongly refracting oil. (Wiggers.) Sp. gr. 0·852. Boiling point 168°. (List.) Has an agreeable odour of hyacinths, especially when much diluted. (List.)

			Wiggers.	List.	Berthelot.
20 C	120	82·7	82·95	82·98	82·5
17 H	17	11·7	11·64	11·76	11·9
O	8	5·6	5·41	5·26	5·6
$C^{20}H^{17}O$	145	100·0	100·00	100·00	100·0

According to Berzelius, it is the oxide of a radical $C^{20}H^{17}$.

Decompositions. 1. Distilled with *acid chromate of potash* and *sulphuric acid*, it yields acetic acid. 2. With *hydrochloric acid gas*, it assumes an amethyst-red colour, ultimately becoming darker; on continuing the passage of the gas, crystals of bihydrochlorate of turpentine-oil separate in such quantity that the liquid becomes nearly solid. The same reaction is produced by moderately concentrated aqueous hydrochloric acid. (List.)

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3. *With Hydrochloric Acid.* Oil of turpentine absorbs, with rise of temperature, 50 per cent. of hydrochloric acid gas (Thenard), 163 vols, at 22°, and 0·724 met. atmospheric pressure.

A. Monohydrochlorate of Turpentine-oil. Artificial Camphor. $C^{20}H^{16},HCl$.

Salzsaures Terpenthinöl; fester künstlicher Chlorcampher; salzsaures Dadyl (Blanchet & Sell); *salzsaures Camphen* (Soubeiran & Capitaine, and Deville); *Hydrochlorate de camphène* (Laurent); *Monohydrochlorate solide d'essence de térébenthene.* (Gerhardt.) Discovered in 1803 by Kindt, first described by Trommsdorff, investigated by Cluzel, Chomet & Boullay, afterwards by Dumas and others.

Formation. 1. By the action of hydrochloric acid gas an oil of turpentine (Kindt, Trommsdorff), or, on a solution of 1 vol. oil of turpentine in 2 vols. bisulphide of carbon. (Berthelot.) Hydrochlorate of terebene is formed at the same time. (Soubeiran & Capitaine.) — 2. When 1 pt. of the liquid product obtained by saturating with hydrochloric acid gas a mixture of 1 vol. oil of turpentine and 2 vols. chloroform or acetone, creosote, acetic acid, butyric acid, butylate of ethyl, olein, oleic acid, or fusel-oil (or by saturating with hydrochloric acid gas, oil of turpentine altered by oil of vitriol), is treated with 5 pts. of nitric acid, a violent action takes place, sometimes giving rise to explosion; and when it is ended, artificial camphor is found as a sublimate in the neck of the retort. (Berthelot.) — 3. By heating chlorinated oil of turpentine. (Deville.)

Preparation. 1. The gas evolved from 1 pt. of decrepitated common salt and $\frac{1}{2}$ pt. oil of vitriol, is passed through 1 pt. of oil of turpentine, which thereby becomes yellow and transiently turbid, deposits red drops of liquid, then becomes very hot (without rise of temperature, according to Kindt), acquiring a darker and ultimately a red-brown colour; it is to be set aside cold for 24 hours, and the resulting crystals separated from the acid mother-liquor. (Trommsdorff.) The oil must be well cooled; it increases in bulk by $\frac{1}{10}$th. (Cluzel.) — 2. Dry hydrochloric acid gas is passed to saturation into rectified oil of turpentine cooled from without, and the crystalline masses which separate after some hours are collected. (Oppermann.)

The portion of the oil which remains liquid is not converted into artificial camphor on continuing the passage of the gas (Trommsdorff, Oppermann), but deposits a small additional quantity of it when cooled to −10°. (Soubeiran & Capitaine.) The crystalline mass formed by the hydrochloric acid gas is dissolved or converted into a viscid oil by the portion which remains liquid, even at — 5°; the liquid must, therefore, be quickly decanted from the crystalline mass, and the latter left to drain at a low temperature. (Hertz.) The most abundant formation of artificial camphor by the action of hydrochloric acid gas, takes place between — 30° and + 35°; within these limits, the crystals, produced are always the same, though they vary in quantity; below — 30°, and at + 60° and + 100°, no crystals are produced. (Berthelot.)

Purification. 1. Artificial camphor is freed from adhering mother-liquor, first by draining, then by pressure (Trommsdorff), or it is exposed to the air (Thénard), or washed with water or aqueous potash (Cluzel); washed with alcohol and dried by exposure to the air. (Dumas.) — 2. It is sublimed: either alone, or repeatedly with 2 pts. of carbonate of lime (Trommsdorff), three times with hydrate of lime (Gehlen), or with an equal quantity of dry ash or porcelain clay, or charcoal powder (Cluzel); with chalk and chloride of calcium at 30—40. (Oppermann.) — It decomposes when sublimed either alone or mixed with chalk or quicklime. (Dumas.) — 3. By recrystallisation from alcohol. (Gehlen.) By drying the washed crystalline mass in the water-bath, and subliming it at 100° mixed with burnt lime (Blanchet & Sell), by melting the expressed crystalline mass in the oil-bath. (Dumas.) — 4. By precipitating its alcoholic solution with water, washing the precipitate and drying it in the oil-bath till it melts, or in vacuo. (Dumas.) — 5. By boiling its solution with oxide of silver till the adhering hydrochloric acid is removed, cooling the concentrated and filtered solution, and drying the separated crystals in vacuo. (Dumas.)

Artificial camphor is a mixture of isomeric bodies which differ only in their optical characters, and correspond to the different isomeric compounds used in their preparation, each of which produces only one artificial camphor distinguished by peculiar optical properties. (Berthelot.)

The quantity of artificial camphor obtained varies according to the origin of the turpentine-oil used in its preparation. — Oil from the Scotch fir yields but slowly a small quantity of artificial camphor (Hagen); that from the branches of the spruce fir, after treatment with potassium, yields none, even at 0°. (Wöhler.) Oil of turpentine heated with oxalic acid to 100° for 130 hours, still yields artificial camphor; but the last products of distillation of a French oil of turpentine which passed over between 240° and 280°, yielded none. (Berthelot.) — Trommsdorff obtained 26·5 p. c. artificial camphor; Cluzel 47; Oppermann more than 50; Berthelot obtained 51 p. c. at 0°, 67 at 35, Dumas 100°; Thénard, 110 per cent.

Properties. White, semi-transparent flocks (Trommsdorff), without crystalline form (Blanchet & Sell); when obtained by sublimation, it forms needles united in tufts (Cluzel), bright feathery, shining laminæ, which may be kneaded like wax. (Oppermann.) — Melts at 115°, boils at 165°, but not without decomposition. (Blanchet & Sell.) — Rotatory power right or left and of various strength, depending upon that of the oil of turpentine from which it has been prepared. (Berthelot.) The rotatory power calculated for a specific gravity = 1 is 34·07° to the left. (Soubeiran & Capitaine.) Prepared from a sample of French oil of turpentine distilled between 80° to 100° in vacuo, it had a rotatory power = 23·9° to the left; from the distillate of the same oil which passed over above 100°, it rotated 23·9° to the left; from the last distillate of the same oil, 22·3° to the left. The artificial camphor prepared from the most volatile portion of a sample of English oil of turpentine, had a rotatory power = 9·9° to the right; from the less volatile = 4·2 to the right; prepared from American oil of turpentine, 9° to the right. (Berthelot.) It smells like common camphor, sometimes also like turpentine; its odour is generally less powerful than that of camphor. Its taste is aromatic, but not so pungent and bitter as that of camphor. — It does not redden litmus.

			Dumas.	Blanchet & Sell.
20 C	120	69·6	70·35	70·2
17 H	17	9·9	9·95	10·0
Cl	35·5	20·5	19·85	19·5
$C^{20}H^{16},HCl$	172·5	100·0	100·15	99·7

The hydrocarbon which, in combination with hydrochloric acid, forms artificial camphor, is a peculiar constituent (called *dadyl* by Blanchet & Sell,) existing ready formed in the oil of turpentine (Thénard), having a composition different from that of common oil of turpentine (Oppermann), richer in hydrogen. (Gehlen.) Under the influence of hydrochloric acid upon oil of turpentine, camphene is produced, which unites with the hydrochloric acid to form artificial camphor. (Soubeiran & Capitaine.) Oil of turpentine unites with hydrochloric acid without previous alteration. (Deville.) Artificial camphor is $C^{20}H^{15}Cl,H^2$, the hydrogen-compound of chlorinated oil of turpentine. (Gm.)

Decompositions. 1. Artificial camphor when *heated*, partly sublimes unaltered, and is partly decomposed, with evolution of hydrochloric acid gas. (Gehlen, Thénard, Dumas.) It may be set on fire in a candle-flame (Saussure); it *burns*, even floating on water, with a green-edged flame, giving off hydrochloric acid. (Trommsdorff.) — When it is *distilled*, or when its vapour is passed through *red-hot tubes*, a large quantity of hydrochloric acid gas is evolved. (Gehlen, Thénard.) — 2. It decomposes but slightly with water or absolute alcohol at 170°, completely with a larger quantity of aqueous alcohol at 135°, or when repeatedly heated with 60 p. c. alcohol to 150—160°, forming hydrochloric acid, a small quantity of gas which burns with a greenish flame, and an oil precipitable by water. (Buttlerow, *Chem. Centr.* 1856, 406.) — 3. Heated with *oil of vitriol*, it is dissolved, with evolution of sulphurous acid. (Blanchet & Sell.) — 4. *Chlorine gas* converts it slowly, and with slight evolution of hydrochloric acid, into a liquid which is coloured yellow by chlorine, and easily decomposes, often with explosion, into hydrochloric acid and crystallised chlorinated oil of turpentine. (Deville.) — 5. *Ordinary nitric acid* neither dissolves nor decomposes artificial camphor (Cluzel); *concentrated nitric acid* dissolves it, forming a red-brown solution which gives off nitrous gas (Oppermann, Blanchet & Sell), as well as chlorine. (Thénard.) It is rendered turbid by water. (Cluzel.) — 6. Heated with *alcoholic potash* to 150—160°, it decomposes slightly, with formation of chloride of potassium. (Buttlerow.) Potash abstracts from its alcoholic solution a small quantity of hydrochloric acid. (Thénard, Oppermann.) — 7. When the vapour of artificial camphor, mixed with *ammonia gas*, is passed through red-hot tubes, a volatile oil is formed, together with charcoal. (Blanchet & Sell.) — 8. When it is distilled 5 or 6 times with *lime*, or when its vapour is passed over red-hot lime, the products are chloride of calcium, water, and volatile camphilene. (Oppermann, Dumas.) — Sublimed with chalk or white bole, it yields an oil smelling of turpentine, a brown acid water, and hydrochloric acid gas; when sublimed with hydrate of lime, it yields a limpid oil which crystallises on cooling, and an acid limpid liquid. (Gehlen.)

9. Alcoholic *sulphocyanide of potassium,* when repeatedly heated with the alcoholic solution of artificial camphor to 150—160°, converts it into a liquid, which, on addition of water, deposits an oil having a disagreeable alliaceous odour, and containing sulphur and nitrogen. *Sulphocyanide of silver* appears to act in like manner. (Buttlerow.) — 10. *Chloride of zinc* decomposes it at 100°, with evolution of a gas containing hydrochloric acid. (Berthelot.) — 11. Its aqueous solution is not altered by *nitrate of silver.*

12. Heated for 30—40 hours in sealed tubes with 8—10 pts. of *dry soap,* or 2 pts. *benzoate of soda,* to 240—250°, it yields camphene. (Berthelot, *Compt. rend.* 47, 26; abstr. *Ann. Pharm.* 110, 367; *Instit.* 1858, 52; *Cimento,* 7, 161.)

Combinations. Artificial camphor imparts its taste to water. (Cluzel.) — It dissolves in 3 pts. of *alcohol* of sp. gr. 0·806 at 14° (Saussure); the solution is rendered milky by water. (Trommsdorff. — It dissolves readily in *oil of turpentine* and *oil of almonds.* (Trommsdorff.)

B. Bihydrochlorate of Turpentine-oil. $C^{20}H^{16},2HQ$.

Citronencamphor (Deville), *Bihydrochlorate d'essence de térébenthine* (Berthelot), *Bihydrochlorate solide d'essence de térébenthine.* (Gerhardt.)

Formation. 1. By the action of fuming hydrochloric acid on oil of turpentine. (Berthelot.) — 2. By the action of hydrochloric acid gas or fuming hydrochloric acid upon crystallised or fused turpentine-camphor or terpinol. (Deville, List.)

Preparation. 1. A thin layer of oil of turpentine is poured upon fuming hydrochloric acid, the liquid left to stand, at first with frequent agitation, and the small crystals which separate after about a month are collected. The solution again exposed to the air deposits more crystals, and often likewise contains artificial camphor, which may be separated from it by nitric acid. (Berthelot.) — 2. A solution of oil of turpentine in alcohol, ether, or glacial acetic acid, is saturated with hydrochloric acid gas, mixed with water, and left to itself in a dish exposed to the air; and the crystals which separate after a few hours are collected and dried. — Another mode of preparation is to saturate with hydrochloric acid gas a solution of 1 vol. turpentine-oil in 6 vols. wood-spirit, or 2 vols. acetone chloroform, creosote, or butyric acid, and leave it to evaporate at the temperature of the air. (Berthelot.)

Properties. Bihydrochlorate of turpentine-oil possesses all the properties of the isomeric compound, lemon-camphor (Deville, Berthelot), excepting that the latter crystallises in small, rather elongated tables, and is less soluble in alcohol than bihydrochlorate of turpentine-oil, which crystallises in rhombic tables and dissolves with great facility in alcohol. (List.)

			1. Deville.	2. List.	3. Berthelot.
20 C	120	57·4	57·5	57·0	55·8
18 H	18	8·6	8·8	8·8	9·0
2 Cl	71	34·0	34·4	34·4	33·3
$C^{20}H^{16},2HCl$	209	100·0	100·7	100·2	98·1

1 and 2 prepared from turpentine-camphor; 3, from turpentine-oil, by the action of hydrochloric acid gas.

Decompositions. The compound gives off hydrochloric acid when *heated.* (Deville.) — *Boiled* with *water* or *alcohol* (List), with alcoholic potash (Berthelot), it is resolved into hydrochloric acid and oil of turpentine. — When treated with *potassium,* it yields an oil having the odour of lemons. (Deville.)

With Hydrobromic Acid. — Hydrobromate of Turpentine-oil, $C^{20}H^{16},HBr$. *Bromwasserstoff-saures Terpenthinol. Fester Bromcampher. Bromhydrate de camphène.* (Deville.) *Monobromhydrate solide d'essence de térébenthine.* (Gerhardt.)

Formation. When oil of turpentine is acted upon by hydrobromic acid, this compound separates in the crystalline form, while hydrochlorate of terebene remains in solution.

Preparation. Oil of turpentine is saturated with hydrobromic acid, and the mixture is exposed to the air so that the excess of acid may evaporate, and then cooled some degrees below 0°. The crystals which separate are collected, their quantity often exceeding that of the oil of turpentine used; the mother-liquor is left to drain at a low temperature, and the crystals are pressed between bibulous paper, recrystallised from alcohol, and again strongly pressed.

Properties. This compound exactly resembles artificial camphor in appearance, crystalline form, and odour.

			Deville. *mean.*
20 C	120	56·24	56·06
17 H	17	7·81	7·95
Br	80	35·95	35·95
$C^{20}H^{16},HBr$	217	100·00	99·96

It dissolves in *alcohol,* the solution, when exposed to the air, turning red from liberation of bromine. (Deville.)

With Hydriodic Acid. — Hydriodate of Turpentine-oil, $C^{20}H^{16},HI$. — *Iodwasserstoffsaures Terpenthinol.* (Löwig.) *Iodhydrate de Camphène.* (Deville.) *Monoiodhydrate d'essence de térébenthine.* (Gerhardt.)

Preparation. Hydriodic acid gas is passed into oil of turpentine, and the dark red, fuming, heavy liquid is freed from excess of acid by chalk, from excess of iodine by potash-ley, weak alcohol, or mercury, and from adhering water by chloride of calcium. (Deville.)

Properties. Colourless oil, which does not solidify even at several degrees below 0°, has a sp. gr. of 1·5097 at 15°, and turns the plane of polarisation to the left. The rotatory power cannot be exactly determined because the compound very soon loses its transparency. (Deville.)

			Deville.	
20 C	120	46·0	45·99	46·36
17 H	17	6·4	6·35	6·56
I	127	47·6	47·66	47·80
$C^{20}H^{16}$,HI	264	100·0	100·00	100·72

It is a mixture of hydriodate of turpentine-oil and hydriodate of terebene, both of which are liquid. (Deville.)

Decompositions. It decomposes quickly when exposed to the air, depositing iodine, absorbing oxygen, and turning black. When *heated*, it yields a heavy liquid distillate, together with iodine and hydriodic acid. (Deville.)

With *hydrocyanic acid*, oil of turpentine forms a heavy oil which sinks to the bottom, smells of hydrocyanic acid and camphor, may be freed from the excess of acid by washing with potash-ley, but not by washing with water, and afterwards recovers its original odour. (Ittner, *Beitr. z. G. d. Blausäure*, 1809.)

Phosphorus dissolves in warm oil of turpentine, and the solution solidifies completely to a spermaceti-like mass, consisting of a loose compound of phosphorus and oil of turpentine, which easily resinises on exposure to the air. (Jonas.) The smallest quantity of phosphorus in oil of turpentine may be easily recognized by the phosphorescence produced on adding oil of vitriol. (Jonas, *Ann. Pharm.* 34, 239.) Phosphorus does not shine in vapour of oil of turpentine, and may be boiled with the oil without taking fire. (J. Davy, *Phil. Mag. J.* 1833, July, 48; *Schw.* 68, 387.)

Oil of turpentine dissolves 5·87 p. c. of *sulphur* at 75°, about 1·35 p. c. remaining dissolved on cooling. (Payen, *Compt. rend.* 34, 456.) It readily dissolves *iodide of cyanogen* (Van Dyk, *Repert.* 21, 223), *chloride of arsenic, chloride of phosphorus*, and *chloride of sulphur*, with evolution of heat and formation of a colourless liquid; with *cupric oxide, cupric hydrate*, or *cupric acetate*, it forms at mean temperatures a green distillate, which is resolved by heat into a brown viscid oil and a precipitate of cuprous oxide. (A. Vogel.)

Sulphurous acid is absorbed by oil of turpentine with great rise of temperature, the oil turning light yellow, remaining mobile, and acquiring the odour of the acid. (Gehlen.) It absorbs 0·16—0·2 vols. *carbonic oxide gas*, 1·7 to 1·9 *carbonic acid*, 2·5 to 2·7 *nitrous oxide* (Saussure), 2·1 to 2·6 *olefiant gas* (Saussure, Faraday, *N. Bibl. Univ.* 59, 144), 5 vols. *cyanogen gas* (Gay-Lussac), 3·25 vols. *phosphuretted hydrogen*. (Graham.)

Oil of turpentine dissolves but a small quantity of *succinic acid*, even with aid of heat; but of *benzoic acid*, 100 pts. of oil of turpentine dissolve 0·4 pts., and at 100°, more than their own weight, the acid separating in the crystalline form on cooling. (Lecann & Serbut, *J. Pharm.* 9, 89.) *Suberic acid* dissolves at 5° in 19 pts. of oil of turpentine, at 20° in 16 pts., at 44·5° in 11·5 pts., at 120° in 2·1 pts., and at

170° in 1 pt.; the last-mentioned solution becomes, on cooling, tough, glutinous, and waxy. (Brandes, *Ann Pharm.* 9, 300.)

Oil of turpentine dissolves *resins* and *most volatile* oils. It dissolves $\frac{1}{20}$ of *stearic acid* (Braconnot), and, when mixed with alcohol, it dissolves almost any quantity of *oleic* and other *fatty acids* (Rousseau, *J. Chim. méd.* 22, 310); it mixes with *bisulphide of carbon* (Lampadius), and with *chloroform.* (Huraut & Larocque, *Compt. rend.* 26, 103.)

It dissolves in 7·4 pts. of *alcohol*, of sp. gr. 0·84, at 22° (Saussure); (according to Bouillon-Lagrange and Voget, the solution reddens litmus); in 12 pts. of alcohol, of 33° B. (sp. gr. 0·858), at 10°; in absolute alcohol it dissolves *in all proportions* (Blanchet & Sell); in 4 vols. alcohol of sp. gr. 0·83; in 5 vols. alcohol. (Auduard, *J. Chim. méd.* 19, 717). — 5 vols. oil of turpentine mix with 1 vol. alcohol; the mixture is not clouded by water, and is but slowly deprived of its alcohol when water is poured upon the mixture. (Vauquelin, *Berzel. Jahresbr.* 1824, 3, 181.) — It dissolves in *acetone* more readily than in aqueous alcohol. *Wood-spirit* or *alcohol,* diluted with so much water as to render it incapable of dissolving oil of turpentine, dissolves it after addition of a small quantity of *benzene.* (Mansfield, *Chem. Soc. Qu. J.* 1, 263.) — Oil of turpentine dissolves in *wood-spirit* in all proportions, and water added to the solution throws down the oil with milky turbidity. (Gmelin.)

Oils isomeric with Oil of Turpentine.

A. Products of the transformation of Oil of Turpentine.

1. Camphene.

BERTHELOT. (1858.) *Compt. rend.* 47, 266; abstr. *Ann. Pharm.* 110, 367. — *Inst.* 1858, 52; *Cimento,* 7, 161; *Liebig & Kopp's Jahresber.* 1858, 441.

Formation and Preparation. — Monohydrochlorate of turpentine-oil is heated with 8–10 parts of dry soap or 2 pts. benzoate of soda in sealed tubes to 240°—250° for 30 or 40 hours; and the product is distilled till white vapours appear, then rectified, the portion which passes over from 160° to 180° being collected and pressed between bibulous paper after solidification.

Properties. Crystalline, camphor-like mass, which melts at 46° and boils at about 160°.

Platinum-black converts it into camphor (or a substance very much like it). With hydrochloric acid, it forms a crystalline compound (monohydrochlorate of turpentine-oil?) (Berthelot.)

2. Isoterebenthene.

BERTHELOT. (1853.) *N. Ann. Chim. Phys.* 39, 16; abstr. *Compt. rend.* 26, 428; *Ann. Pharm.* 88, 347; *J. pr. Chem.* 59, 141.

Formation. By continued heating of oil of turpentine under pressure.

Preparation. English oil of turpentine (from *Pinus Australis*) is heated for three hours to 300° in a sealed tube; the portion which goes over below 250° is redistilled and rectified; and the distillate obtained between 176° and 178° is rectified.

Properties. Thin, colourless, strongly refracting liquid, of sp. gr. 0·8432 at 22°, boiling between 176° and 178°, and having a lævo-rotatory power = 10° (varying however with the duration and intensity of the heating, and the nature of the oil of turpentine used in the preparation). It smells like stale lemon-peel.

			Berthelot.
20 C	120	88·23	88·1
16 H	16	11·77	11·7
$C^{20}H^{16}$	136	100·00	99·8

The lævo-rotatory power of isoterebenthene is reduced from 8·8° to 7·0°, by heating the liquid to 100° for 30 hours with aqueous oxalic acid. — In 33 days it absorbs 16·8 p. c. *oxygen*, and gives off 1 p. c. carbonic acid.

Combinations. With *Water.* — When a mixture of 4 pts. isoterebenthene, 3 pts. alcohol, and 1 pt. nitric acid is left to evaporate in a shallow basin exposed to the air, crystals are formed in the course of a week, resembling turpentine-camphor in all their properties, while the mixture acquires the odour emitted in the formation of turpentine-camphor.

With Hydrochloric acid. — Isoterebenthene absorbs 34 p. c. hydrochloric acid gas at 24°, and forms a liquid mixture of hydrochlorate of terebene and bi-hydrochlorate of turpentine-oil:

$$3\,C^{20}H^{16} + 4\,HCl = 2\,(C^{20}H^{16},HCl) + C^{20}H^{16},2\,HCl.$$

In contact with fuming hydrochloric acid for four weeks, it forms crystals of bi-hydrochlorate of turpentine oil.

Isoterebenthene absorbs 14·3 p. c. *gaseous fluoride of boron* at 23°, assuming a darker colour and becoming tenacious. (Berthelot.)

3. Metaterebenthene.

Berthelot. (1853.) *N. Ann. Chim. Phys.* 39, 19.

Formation. By the prolonged action of heat on English oil of turpentine under pressure, the first product of the action being chiefly isoterebenthene.

Preparation. When the product obtained in the preparation of isoterebenthene, as above described, is distilled, and the liquid remaining after the portion which distils below 250° has passed off, is heated for several hours to 360°, and the portion which volatilises below 360° is distilled off, the residue consists of metaterebenthene, the quantity of it being greater in proportion to the time during which the oil of turpentine was heated.

Properties. Yellow, viscid oil, of sp. gr. 0·913 at 20°, and volatilising without decomposition above 360°. Has a strong and unpleasant odour, especially when heated.

Combinations. It absorbs in 33 days, 9·7 p. c. *oxygen,* gives off 0·3 p. c. carbonic acid, and assumes the consistence of colophony. — It absorbs only half as much *hydrochloric acid gas* as isoterebenthene, viz, 17·7 p. c. at 24° corresponding to the compound $3C^{20}H^{16},2HCl$.

4. Terebene.

Blanchet & Sell. (1833.) *Ann. Pharm.* 6, 259.
Deville. *Ann. Chim. Phys.* 75, 37; *J. pr. Chem.* 22, 82; *Ann. Pharm.* 37, 176; *J. Pharm.* 26, 655; abstr. *Compt. rend.* 12, 394; *N. Ann. Chim. Phys.* 27, 85.
Soubeiran & Capitaine. *J. Pharm.* 26, 1.
Berthelot. *N. Ann. Chim. Phys.* 38. 42; further 39, 14 and 21; further 40, 5.

Formation. — 1. By distilling oil of turpentine with oil of vitriol or anhydrous phosphoric acid; also, together with colophene, by distilling crystallised or fused turpentine-camphor with anhydrous phosphoric acid. (Deville.) — 2. By the action of hydrochloric acid gas, hydrobromic acid gas, chlorine, bromine, or iodine, upon oil of turpentine, uniting however immediately with the acids or salt-radicals. (Deville.) — Only a portion of the oil of turpentine is converted into terebene, which moreover cannot be separated without alteration from the compounds produced by the reaction. (Deville.) — No terebene is formed by the action of hydrochloric acid; for the hydrochlorate, which is formed in addition to the artificial camphor, possesses a rather strong rotatory power which pure terebene does not. (Berthelot.) This rotatory power is due to artificial camphor, which is always mixed with it. (Deville.)

Preparation. Oil of turpentine is mixed slowly and by drops with $\frac{1}{20}$ of oil of vitriol contained in a cooled vessel; the red viscid mixture is stirred and left to settle; the liquid is decanted, after 24 hours, from the black sediment produced at the same time by the acid, and distilled at a temperature not above 210°, whereupon sulphurous acid is evolved, and the colophene produced at the same time remains behind. To convert the still unaltered turpentine-oil in the distillate into terebene, it is repeatedly distilled with fresh quantities of oil of vitriol till the product has quite lost its rotatory power; and the distillate is washed with aqueous carbonate of soda, then with water, and dehydrated by chloride of calcium. (Deville.)

Properties. Colourless oil, resembling oil of turpentine, without rotatory power, and having a rather agreeable odour of thyme. (Deville.)

Sp. gr. 0·864 at 8°. Boiling point 156°. (Frankenheim, *Pogg.* 72, 422.) Latent heat for the unit of weight 67·2. (Frankenheim.) Refracting power 1·474 (Deville, *Pogg.* 51, 433), 1·479 (Becquerel & Cahours, *Pogg.* 51, 427). Vapour-density = 4·812 (by calculation 4·7144 comp. page).

			Deville. 1.	Deville. 2.
20 C	120	88·24	88·49	88·1
16 H	16	11·76	11·49	11·9
$C^{20}H^{16}$	136	100·00	99·98	100·0

1. Prepared from oil of turpentine with oil of vitriol.—2. From turpentine-camphor with anhydrous phosphoric acid.

Decompositions. The compound remains unaltered after two hours' *heating* to 300°. (Berthelot.) By chlorine it is converted, with evolution of hydrochloric acid, into *chloroterebene;* by bromine, with evolution of hydrobromic acid, into *bromoterebene.* (Deville.) — With a small quantity of *iodine,* it turns dark green, becomes heated, and loses its transparency, but does not deposit charcoal or give off hydriodic acid. When terebene is distilled with excess of iodine, hydriodic acid escapes, and an iodated viscid liquid distils over, which is easily decolorised by potash, and probably consists of iodoterebene. (Deville.) — When heated with *oil of vitriol,* it is converted into sulphoterebic acid. (Gerhardt, *Compt. rend.* 17, 314.)

Combinations. Terebene does not form a hydrate, even after half a year's contact with *water.* (Deville.) — It absorbs *gaseous fluoride of boron* without alteration. (Berthelot.)

With *Hydrochloric acid.* — *a. Bibasic Hydrochlorate of Terebene. Sous-chlorhydrate de térébène* (Gerhardt); *Monochlorhydrate de térébène.* (Deville.) — $2C^{20}H^{16},HCl$. — Produced when hydrochloric acid gas is passed into terebene. — Mobile oil of sp. gr. 0·902 at 20°, without rotatory power; smelling strongly of terebene, and slightly of hydrochlorate of terebene. (Deville.)

			Deville. *mean.*
40 C	240·0	78·16	78·28
33 H	33·0	10·53	10·68
Cl	35·5	11·31	11·04
$2C^{20}H^{16},HCl$	308·5	100·00	100·00

b. Hydrochlorate of Terebene. — *Flüssiger künstlicher Camphor; salzsaures Peucylen* (Soubeiran & Capitaine); *salzsaures Peucyl* (Blanchet & Sell); *Bichlorhydrate de Térébène.* (Deville.) *Monochlorhydrate liquide d'essence ds térébenthine.* $C^{20}H^{16},HCl$.

Preparation. From the liquid which remains in the treatment of oil of turpentine with hydrochloric acid gas, after the separation of the artificial camphor. — 1. By distillation *per se* (Blanchet & Sell), whereupon hydrochloric acid and a dark-coloured oil pass over, and charcoal remains. (Trommsdorff, *A. Tr.* 1, 2, 132,) — 2. The liquid is heated for a short time in the water-bath; the artificial camphor which separates on cooling is removed; the liquid is neutralised with chalk and cooled to — 10°, whereupon an additional quantity of artificial camphor separates, but not all. The liquid, which is syrupy in the cold, but very mobile at 15—18°, is decanted, mixed with 2 vol. alcohol, decolorised by boiling with animal charcoal, precipitated by water, and the oil which falls to the bottom is dehydrated by chloride of calcium. (Soubeiran & Capitaine.)

Properties. Colourless oil, of sp. gr. 1·017, boiling at 19·92° (Soubeiran & Capitaine), at 28°. (Berthelot.) Turns the plane of polarisation to the left. Refracting power = 1·4848. (Deville, *Pogg.* 51, 433.)

			Soubeiran & Capitaine.
20 C	120·0	69·6	70·3
17 H	17·0	9·9	9·9
Cl	35·5	20·5	19·8
$C^{20}H^{16},HCl$	172·5	100·0	100·0

Isomeric with mono-hydrochlorate of turpentine-oil.

Decompositions. 1. When *set on fire,* it burns with a green-edged flame and an odour like that of benzoic acid. (Blanchet & Sell.) — 2. When *chlorine gas* is passed into it, it gives off vapours of hydrochloric acid, and thickens like oil of turpentine treated with chlorine, but without depositing crystals like the latter. (Blanchet & Sell.) — 3. *Hydrochloric acid gas* does not convert it into artificial camphor. (Cluzel, *Ann. Chim.* 51, 270.) — 4. When hydrochlorate of terebene is distilled with *hydrate of lime,* hydrochloric acid and terebene are produced (Soubeiran & Capitaine); the product is a thin, aromatic oil. (Gehlen, *A. Gehl,* 6, 458.) No terebene is produced in this reaction, inasmuch as hydrochlorate of terebene cannot be freed from artificial camphor, even by repeated distillation and cooling; and moreover, the lime used in the reaction, or the temperature which it requires, exerts at the same time a decomposing action on the separated terebene. (Deville.) — 5. *Alcohol* decomposes hydrochlorate of terebene, especially when heated with it, forming an acid product and an oil which is precipitated by water. (Blanchet & Sell.)

c. Hydrochlorate of Terebene with Bihydrochlorate of Turpentine-oil. $C^{20}H^{16},2HCl + 2(C^{20}H^{16},HCl.)$ The liquid which remains after the separation of bihydrochlorate of turpentine-oil, from a solution of the oil in alcohol or glacial acetic acid saturated with hydrochloric acid gas (p. 268), and that which is produced by the action of hydrochloric acid gas on isoterebenthene (p. 271), contains 24·3 to 25·7 p.c. chlorine, and may accordingly be regarded as a compound of 2 At. hydrochlorate of terebene with 1 At. bihydrochlorate of turpentine-oil; or as a compound of bihydrochlorate of turpentine-oil with artificial camphor, inasmuch as the former separates when the liquid is exposed to the air, perhaps after the volatilisation of the latter, and moreover artificial camphor and bihydrochlorate of turpentine-oil liquefy on being mixed. But the liquid produced from French oil of turpentine and glacial acetic acid yields, when treated with nitric acid, a large quantity of turpentine-camphor, and is therefore not identical with a mixture of artificial camphor and bihydrochlorate of turpentine-oil, which under these circumstances does not produce artificial camphor. (Berthelot.)

Hydrochlorate of terebene dissolves in alcohol and ether, and is precipitated by water. (Cluzel.)

With Hydrobromic acid. — *a. Bibasic Hydrobromate of Terebene. Sous-bromhydrate de térébène* (Gerhardt); *Monobromhydrate de térébène.* (Deville.) — $2C^{20}H^{16},HBr$. — Formed by the action of hydrobromic acid upon terebene. — Terebene saturated with hydrobromic acid is shaken up with chalk to remove free acid, then decolorised with animal charcoal, and precipitated by chloride of calcium. — Colourless oil of sp. gr. 1·021 at 24°, without rotatory power, smelling like terebene, somewhat like camphor, and becoming coloured after a while by exposure to the air. (Deville.)

			Deville. *mean.*
40 C	240	67·99	68·63
33 H	33	9·35	9·53
Br	80	22·66	
$2C^{20}H^{16},HBr$	353	100·00	

b. Monohydrobromate of Terebene. — *Monobromhydrate liquide d'essence de térébenthene* (Gerhardt); *Bibromhydrate de térébène.* (Deville.) $C^{20}H^{16},HBr$.

Formation (p. 252). The mother-liquor, alterable by exposure to the air, which remains in the preparation of hydrobromate of turpentine-oil, as described at page 269, is a solution of hydrobromate of turpentine-oil in hydrobromate of terebene, and likewise contains bromoterebene, produced by the simultaneous liberation of bromine. The hydrobromate of terebene has not hitherto been separated from either of these liquids. — Oil of sp. gr. 1·279 at 21°, and solidifying completely at −5°. Rotatory power to the left, probably due only to hydrobromate of turpentine-oil dissolved in it. (Deville.)

			Deville.
20 C	120	56·15	54·04
17 H	17	7·78	7·53
Br	80	36·07	38·43
$C^{20}H^{16},HBr$	217	100·00	100·00

With Hydriodic acid. — *a. Bibasic Hydriodate of Terebene.* — *Sous-iodhydrate de térébène.* (Gerhardt.) *Mono-iodhydryate de térébène.* (Deville.) — $2C^{20}H^{16},HI$. — Formed by the action of hydriodic acid on oil of turpentine. — Hydriodic acid is absorbed by oil of turpentine with rise of temperature. The free acid is removed from the oil, which is dark-red after saturation, by shaking it up with chalk; dissolved iodine is removed by agitation with dilute potash-ley, weak spirit, or mercury; and admixed water by chloride of calcium. — Transparent, colourless liquid of sp. gr. 1·084 at 21 ; without rotatory power. — Has an agreeable camphorous odour, and quickly acquires a dark red colour by exposure to the air. (Deville.)

			Deville. *mean.*
40 C	240	60·59	60·87
33 H	33	8·14	8·14
I	127	31·27	30·49
$2C^{20}H^{16},HI$	400	100·00	99·50

b. Mono-hydriodate of Terebene. Monoiodhydrate liquide d'essence de têrébenthine. (Gerhardt.) *Bi-iodhydrate de térébène.* (Deville.) $C^{20}H^{16},HI$. Produced, together with hydriodate of turpentine-oil, by the action of hydriodic acid upon that oil, but cannot be separated therefrom, inasmuch as both compounds are liquid. (Deville.)

Appendix to Terebene.

Sulphoterebic Acid.

$C^{20}H^{16}S^2O^6$?

Terebenschwefelsäure, Terpenthinschwefelsäure. Formed by gently heating terebene with fuming oil of vitriol, or by dropping oil of turpentine, cubebs, pepper, lemons, or copaiba into a large quantity of oil of vitriol, but not so easily as terebene. (Gerhardt, *Compt. rend.* 17, 313; *Compt. chim.* 1845, 173.)

Sulphoterebate of Baryta. Prepared by heating terebene with oil of vitriol, saturating with carbonate of baryta, filtering, and leaving the solution to evaporate. (Gerhardt.)

			Gerhardt.
20 C	120·0	42·3	
15 H	15·0	5·3	
Ba	68·5	24·1	24·2
2 SO^3	80·0	28·3	
$C^{20}H^{15}BaS^2O^6$	283·5	100·0	

5. Camphilene.

Oppermann. (1831.) *Pogg.* 22, 199.
Dumas. *Ann. Chim. Phys.* 52, 400; *Pogg.* 20, 125; *Ann. Pharm.* 9, 56.
Blanchet & Sell. *Ann. Pharm.* 6, 276; *Pogg.* 29, 133.
Soubeiran & Capitaine. *J. Pharm.* 26, 1; *Ann. Pharm.* 34, 311.
Laurent. *Ann. Chim. Phys.* 66, 209.
Deville. *Ann. Chim. Phys.* 75, 74; *J. Pharm.* 26, 688.

Camphène (Dumas); *Dadyl* (Blanchet & Sell); *Térébène* (Soubeiran); *Camphilène* (Deville). — First prepared by Oppermann. — According to Dumas and Blanchet & Sell, it is the base of solid artificial camphor; according to Soubeiran & Capitaine and Deville, it is contained therein in combination with hydrochloric acid, but without alteration.

Formation and Preparation. 1. Artificial camphor mixed with 2—3 pts. of quicklime is distilled in the oil-bath; the distillate is again mixed with quicklime; the distillation is repeated five or six times in like manner (ten times, according to Oppermann, and Blanchet & Sell, or till the distillate no longer yields chlorine to potassium); and the resulting oil, amounting to $\frac{3}{4}$ths of the weight of the artificial camphor, is freed from adhering hydrochloric acid by rectification over antimonide of potassium, which, however, is apt to eliminate hydrogen (Dumas) and form colophene. (Deville.) — 2. Vapour of artificial camphor is passed through a tube heated in the oil-bath to 190°—195°, and filled with fragments of recently burnt lime; the same operation is repeated with the distillate as long as it retains hydrochloric acid; and the product is dried over chloride of calcium. (Soubeiran & Capitaine.)

Properties. Transparent, colourless, or slightly yellowish oil (Blanchet & Sell); somewhat viscid (Oppermann). Sp. gr. 0·87 at 15° (Blanchet & Sell), 0·86 (Soubeiran & Capitaine); boils at 145° (Blanchet & Sell), 156° (Dumas), 155° (Soubeiran & Capitaine). According to Oppermann, it solidifies below 12° to a transparent mass, which liquefies at the heat of the hand. (Oppermann.) — Vapour-density = 4·83. (Dumas.) It has no rotatory power. (Soubeiran & Capitaine, Deville.) Biot found that it had a lævo-rotatory power seven times less than that of oil of turpentine; but, according to Soubeiran & Capitaine, the camphilene which he examined contained undecomposed artificial camphor. It has a mild aromatic taste and odour. It resembles oil of turpentine in all its properties, but has a different odour, not however arising from decomposition by heat, since the vapour of oil of turpentine retains its odour after passing through a tube heated to 200°. (Soubeiran & Capitaine.)

			Oppermann.	Dumas.	Blanchet. & Sell. *mean.*
20 C	120	88·24	88·48	88·44	88·61
16 H	16	11·76	11·52	11·56	11·56
$C^{20}H^{16}$	136	100·00	100·00	100·00	100·17

Decompositions. *Chlorine* converts it, without evolution of hydrochloric acid, into hydrochlorate of chlorocamphilene:

$$C^{20}H^{16} + 2Cl = C^{20}H^{15}Cl,HCl.$$

which, when treated with alcoholic potash, yields chloride of potassium and chlorocamphilene. The latter, if again treated with chlorine gas, yields hydrochlorate of bichlorocamphilene, which may again be decomposed by alcoholic potash in the same manner as hydrochlorate of chlorocamphilene, yielding bichlorocamphilene, in which a further number of hydrogen-atoms may in like manner be replaced by chlorine. (Laurent.) — Camphilene, treated with *bromine*, becomes solid, and is probably converted into bromocamphilene. (Deville.) With *iodine*, it comports itself like oil of turpentine. (Blanchet & Sell.) By *oil of vitriol* and by heating with *potassium* in contact with the air, it is decomposed, with formation of a brown resin. (Oppermann.)

Combinations. Camphilene is not dissolved or altered by *fuming nitric acid* (Oppermann); *alcoholic nitric acid* converts it into a crystalline hydrate. (Gerhardt, *Traité* 3, 625.) It absorbs *hydrochloric acid gas* rapidly, especially when heated, forming a solid (Oppermann), and a somewhat liquid compound, both destitute of rotatory power. (Soubeiran & Capitaine.) — Fuming *hydrochloric acid*, in contact with camphilene, forms many solid and a few liquid compounds. With *hydriodic acid*, it forms a liquid compound. (Deville.)

Camphilene dissolves in *alcohol*, *ether*, and *bisulphide of carbon*, not in *acetic acid*. (Oppermann.)

Appendix to Camphilene.

a. **Colophene.** $C^{40}H^{32}$.

Deville. *Ann. Chim. Phys.* 75, 66; *J. pr. Chem.* 22, 158; *J. Pharm.* 26, 681; *Ann. Pharm.* 36, 102; abstr. *Compt. rend.* 12, 395. — *N. Ann. Chim. Phys.* 27, 85.

Formation. 1. In the distillation of oil of turpentine with oil of vitriol or anhydrous phosphoric acid, also of crystallised or fused turpentine-camphor with anhydrous phosphoric acid, terebene being formed at the same time. — 2. Goes off, together with water, in the rapid distillation of colophony, charcoal being separated at the same time.

Preparation. 1. By collecting apart the viscid yellow oil, which, in the preparation of terebene from oil of turpentine with oil of vitriol (p. 273), passes over after the terebene has been distilled off and the heat is raised, and repeatedly rectifying it, at last over antimonide of potassium, whereby it is freed from an impurity resembling colophony, and from sulphur. — 2. Colophony is distilled over a brisk fire, and the yellowish distillate is purified like that obtained by the first process. Colophene thus prepared is contaminated with a body richer in carbon, which is produced by the action of the antimonide of potassium, and cannot be separated from the colophene by distillation.

Properties. Oil, colourless by transmitted light, and exhibiting by reflected light a dark indigo-blue iridescence. Sp. gr. 0·940 at 9°, 0·9394 at 25°. Boiling point between 310° and 315°. Vapour-density = 11·13 (probably only twice as great as that of oil of turpentine, therefore = 9·526). Refracting power = 1·517 (Becquerel & Cahours, *Pogg.* 51, 427), 1·5212. (Deville, *Pogg.* 51, 433.) Without rotatory power. Smells like camphilene.

			Deville.	
			a.	*b.*
40 C	240	88·24	88·43	88·1
32 H	32	11·76	11·59	11·9
$C^{40}H^{32}$	272	100·00	100·02	100·0

a. Prepared from oil of turpentine by oil of vitriol; *b.* from turpentine-camphor by anhydrous phosphoric acid.

Colophene absorbs *chlorine gas*, without evolution of hydrochloric acid, becoming hot, and changing to a resin like colophony, which separates in yellow spherules from its solution in absolute alcohol. If, when the absorption of chlorine has ceased, the product be heated to fusion in the stream of chlorine, a large quantity of hydrochloric acid is evolved, and Deville's *chlorocolophene* = $C^{40}Cl^8H^{24}$ is formed, which however still contains a resin removable by alcohol, and when distilled, gives off hydrochloric acid, yields a distillate of colophene and hydrochlorate of colophene, and leaves charcoal.

Hydrochlorate of Colophene. Colophene absorbs hydrochloric acid gas, with rise of temperature, and acquires an indigo-colour. Hydrochlorate of colophene gives up nearly all its hydrochloric acid when treated with chalk, and when distilled with baryta, yields Deville's *colophilene* = $C^{40}H^{32}$, which does not exhibit the dichroism of colophene, and has a refracting power for light = 1·5175. (Deville; Becquerel & Cahours, *Pogg.* 51, 433 and 427.)

b. Colophene from Camphor.

Claus. *J. pr. Chem.* 25, 266.

Preparation. Camphor is distilled with an equal weight of iodine, whereupon hydriodic acid is evolved, camphine passes over at 180°, and charcoal, iodine, campho-creosote and colophene remain behind. On increasing the heat, the two latter substances distil over as a bluish-green oil, which is deprived of its creosote odour by agitation with potash, but cannot be obtained quite pure, even by distillation over lime, and finally over potassium.

Properties. Thick, yellowish oil, with violet iridescence, having a high boiling point, a mild taste, and an odour of violets.

Perhaps identical with colophene from oil of turpentine or from colophony.

Burns with a bright, very smoky flame.

Combinations. It is not soluble in *water* or in weak *alcohol,* but dissolves in strong *alcohol,* in *ether, oil of turpentine, rock-oil,* and *camphine.* When 2 drops of it are dissolved in 2 drachms of alcohol, the solution, after agitation with animal charcoal, exhibits a fine dark blue colour by reflected light.

6. Terebilene.

Blanchet & Sell. *Ann. Pharm.* 6, 259.
Subeiran & Capitaine. *J. Pharm.* 2, 61; *Ann. Pharm.* 34, 311.
Deville. *Ann. Chim. Phys.* 75, 74; *J. Pharm.* 26, 689.

Peucyl (Blanchet & Sell); *Térébilène* (Soubeiran & Capitaine; Deville). This according to Blanchet & Sell, is one of the isomeric hydrocarbons which those chemists discovered in oil of turpentine. According to Soubeiran & Capitaine, it is a decomposition-product of peucylene, a body which they suppose to be formed from oil of turpentine under the influence of hydrochloric acid; according to Deville, it is a product of the decomposition of terebene (*see page* 245).

Formation and Preparation. By distilling hydrochlorate of terebene over quicklime (Soubeiran & Capitaine), and finally over potassium (Blanchet & Sell), or by heating hydriodate of terebene with hydrate of potash, and rectifying the resulting oil over antimonide of potassium, in order to free it from iodine. (Deville.)

Properties. Colourless mobile oil (Blanchet & Sell), of sp. gr. 0·86 (Blanchet & Sell, Soubeiran & Capitaine), 0·843 at 21°. (Deville.) Boiling point 134°. (Blanchet & Sell.) Vapour-density = 4·767 (Soubeiran & Capitaine; Deville), by calculation 4·7144 (p. 245). Refracting power = 1·479 (Becquerel & Cahours, *Pogg.* 51, 427); 1·4735. (Deville, *Pogg.* 51, 433.) Without rotatory power. Smells like terebene. (Soubeiran & Capitaine.)

			Deville.
20 C	120	88·24	88·42
16 H	16	11·76	11·60
$C^{20}H^{16}$	136	100·00	100·02

With hydrochloric acid, it forms a brown liquid compound. (Soubeiran & Capitaine.)

B. *Natural Oils, or others related to them.*

(Arranged for the most part in alphabetical order.)

1. Oil of Bergamot.

VAUQUELIN. (1817.) *J. Pharm.* 3, 241.
OHME. *Ann. Pharm.* 31, 316.
SOUBEIRAN & CAPITAINE. *J. Pharm.* 26, 68; abstr. *Ann. Pharm.* 34, 321. — *J. Pharm.* 26, 509; *Ann. Pharm.* 35, 313.

Essence de Bergamot.

Source. In peculiar cells in the rind of *Citrus Bergamia.*

Preparation. The cellular tissue of the fresh rind is torn to pieces in a funnel having its inner surface like a rasp, or on a board covered with teeth, and the oil which exudes from the lacerated cells is collected.

Properties. Yellowish, or pale greenish to dark yellow: after rectification with water, it becomes transparent, colourless, and mobile. (Ohme; Zeller, *Studien über ätherische Oele,* Landau, 1850.) — Sp. gr. 0·87—0·888 (Lewis, Zeller), 0·856 (Ohme); after distillation with water, 0·869. (Soubeiran & Capitaine.) The first portion obtained by distillation with water, has a sp. gr. = 0·850, the last, 0·877. (Soubeiran & Capitaine.) Boiling point 183° (Ohme); of the first distillate obtained with water, 195°. (Soubeiran & Capitaine.) It solidifies at a few degrees below 0°. (Lewis.) Refracting power 1·468. (Deville, *Compt. rend.* 11, 865.) — Rotatory power of the oil rectified with water, 25° to the right (of the first distillate, 45° right; of the second, 38° right; of the third, 21° right; of the fourth, 0°; of the mixed distillate, 26° right). (Soubeiran & Capitaine.) Of the first distillate, 49°·396 right; of the last, 6°575 left. (Biot, *Compt. rend.* 11, 371. — Has an agreeable odour, less after distillation, and a bitter taste. (Ohme.) The oil is neutral. (Zeller.) Sour from admixed acetic acid; neutral after distillation withwater. (Ohme.) The vapour of the acid-reacting oil has also a strong acid reaction. (Ohme.)

	Ohme.	Soubeiran & Capitaine.			Wöhler.
		a.	*b.*	*c.*	*d.*
C	81·36	84.98	84·92	73.03	85·7
H	11·32	10·12	11·44	10·83	11·7
O	7·32	4·90	3·64	16·14	2·6
	100·00	100·00	100·00	100·00	100·0

a. First distillate: *b.* first distillate from *a*; *c.* last distillate; *d.* first distillate of the bergamot-oil with water.

Bergamot-oil is a hydrate of oil of lemon, $3C^{20}H^{16}+4HO$ (Ohme); a mixture of several oils (Soubeiran & Capitaine; Wöhler, *Ann. Pharm.* 37, 137); it contains one or two oils of the formula $C^{20}H^{16}$, a hydrate of the same, and an oxygenated oil produced by the action of the air. (Soubeiran & Capitaine.) It deposits bergaptene (p. 345) by keeping.

Decompositions. Bergamot-oil burns with a luminous flame.—2. It dissolves iodine with effervescence and evolution of vapours, varying in colour from yellowish-red to violet, and is converted into a soft mass. (Zeller.)—3. *Fuming nitric acid* colours it brown-yellow (Zeller); boiling nitric acid, bright green (Bonastre), and ultimately converts it into a brittle resin. (Zeller.)—4. *Oil of vitriol* turns it yellow without thickening it; afterwards, dark red to black, according to the quantity of the acid, and gives off sulphurous acid. (Brandes, *Mag. Pharm.* 32, 79.)—5. With *anhydrous phosphoric acid*, it becomes coloured and heated, and when distilled therewith, yields a colourless oil which smells like oil of turpentine,—rotates polarised light 4° to the right (40° to the right before distillation), combines with hydrochloric acid, contains 88·93 p. c. C and 11·52 H, and is isomeric with citrene. The phosphoric acid is at the same time partly converted into phosphobergamic acid. (Soubeiran & Capitaine.)—6. Bergamot-oil absorbs *hydrochloric acid* gas with evolution of heat, acquiring a brown colour and emitting fumes in the air, and if subsequently distilled with water, yields hydrochlorate of bergamot-oil. (Ohme.)—7. By distillation over *hydrate of potash*, it loses its agreeable odour.—8. Mixed with aqueous *acid chromate of potash and sulphuric acid*, it turns brown. (Zeller.)—9. With *iodide of potassium*, it turns brown, the salt at the same time acquiring a yellow colour. (Hübschmann, *N. Br. Arch.* 46, 250.)—10. With *chlorate of potash*, and a few drops of oil of vitriol, it burns with a smouldering very smoky flame, and leaves charcoal. (Vogel, Jun., *Ann. Pharm.* 74, 114.) 11. Distilled with 24 pts. water and 8 pts. *chloride of lime*, it gives off carbonic acid with effervescence and yields chloroform.—12. Distilled with *hypobromite of lime*, it yields bromoform. (Chautard, *Compt. rend.* 34, 485.)—13. With an equal quantity of concentrated aqueous solution of *bibasic acetate of lead*, it turns lemon-yellow, and yields a light-coloured precipitate. (Schindler, *N. Br. Arch.* 41, 140.)—14. *Nitroprusside of copper* colours it darker and forms a grey precipitate. (Heppe, *N. Br. Arch.* 89, 57.)

Combinations. 1. With *Water.*—*Hydrated Oil of Bergamot.*—$C^{20}H^{20}O^{4}$.—The crystals which separate after four or six weeks, when 4 pts. oil of bergamot are set aside with 3 pts. alcohol of sp. gr. 0·84 and 1 pt. of nitric acid, are identical with the turpentine-camphor (p. 265) produced by like treatment of oil of turpentine. (Deville, *N. Ann. Chim. Phys.* 27, 81; abstr. *Ann. Pharm.* 71, 348.)

Aqueous Oil of Bergamot. — Oil of bergamot does not take up water, even when boiled with it for a considerable time. (Soubeiran & Capitaine.)

2. With *Hydrochloric acid.* — *Hydrochlorate of Bergamot-oil.* — Produced by passing hydrochloric acid gas into bergamot-oil, and distilling the saturated oil with water, and passes over as a colourless, neutral, optically inactive oil, which smells like hydrochlorate of terebene. Sp. gr. 0·896. Boiling point 185°.

	Ohme.		Soubeiran & Capitaine.
C	78·91	....	63·00
H	10·87	....	9·19
Cl	8·34	....	27·81
O	1·88		
	100·00	....	100·00

According to Ohme, it is $3C^{20}H^{16},HCl + HO$; according to Soubeiran & Capitaine, it is isomeric with hydrochlorate of citrene.

The hydrochlorate when heated *burns* with a green-edged, smoky flame. — When repeatedly distilled over *hydrate of potash*, or *burnt marble*, it is converted into an oil having an odour of cajeput and still containing chlorine. Passed in the state of vapour over red-hot lime, it yields naphthalin, benzene, and charcoal. The alcoholic solution, added to aqueous nitrate of silver, throws down chloride of silver. (Ohme.)

Bergamot-oil dissolves in all proportions in *absolute alcohol;* in ½ pt. alcohol of sp. gr. 0·85 (Zeller), in 2 pts. of sp. gr. 0 951; ond in 28 pts. of sp. gr. 0·966; it takes up 8 p. c. alcohol of sp. gr. 0·966. (Vauquelin.)

2. Carvene.

VÖLKEL. (1843.) *Ann. Pharm.* 35, 308. — *Ann. Pharm.* 85, 246; abstr. *J. pr. Chem.* 60, 120.

SCHWEIZER. *J. pr. Chem.* 24, 267; *Ann. Pharm.* 40, 329; abstr. *Repert.* 80, 172.

Source. In oil of caraway, together with carvol. (Schweizer.)

Preparation. 1. The portion of oil of caraway, which passes over between 175° and 178°, is separated by repeated fractional distillation. (Völkel.) — Carvene cannot be separated from carvol by mere distillation of oil of caraway, either *per se* or with potash-ley. (Schweizer.) — 2. Oil of caraway is boiled with pulverised hydrate of potash, as long as it smells of caraway, then distilled with water, till all the oil has passed over, and rectified over hydrate of potash, till the potash is no longer coloured by it. (Schweizer.) — 3. Oil of caraway is boiled with fused glacial phosphoric acid in a flask, the liquid, which distils over, being constantly poured back, until the distillate no longer smells of oil of caraway; and to purify the distillate completely from undecomposed oil of caraway and from carvacrol produced at the same time, it is rectified over hydrate of potash, till that substance is no longer coloured by it. Oil of caraway thus treated yields more than a third of its weight of carvene. (Schweizer.) — 4. Oil of caraway is boiled with iodine, and the distillate continually poured back, as long as hydriodic acid continues to escape, and the oil which passes over is rectified, the first portion of the distillate being collected apart. (Schweizer.)

Properties. Transparent, colourless, mobile liquid. (Schweizer.) — Sp. gr. 0·861 at 15°. (Völkel.) — Boiling point 173°. — Vapour-density = 5·175 (by calculation, 4·7144, see page). — It has a faint, but agreeable taste and odour.

			Völkel.	Schweizer.	
20 C	120	88·23	88·08	86·52	87·03
16 H	16	11·77	11·81	11·77	11·74
$C^{20}H^{16}$	136	100·00	99·89	98·29	98·77

According to Völkel, its formula is $C^{30}H^{24}$.

Decompositions. 1. Carvene resinises when exposed in small quantities to the *air.* — 2. When *set on fire,* it burns with a bright-bordered smoky flame. — 3. With *chlorine,* it gives off hydrochloric acid, assumes a transient red-brown colour, and solidifies to impure chlorocarvene. — 4. *Nitric acid* converts it, with violent evolution of nitrous acid, into a reddish-yellow, bitter, easily fusible resin, somewhat soluble in hot water, easily soluble in hot alcohol, in ether, in potash, and in acids, insoluble in cold alcohol. — 5. By oil of *vitriol,* it is immediately resinised, with rise of temperature and evolution of sulphurous acid. (Schweizer.)

Combinations. — *With Hydrochloric acid. Hydrochlorate of Carvene.* $C^{20}H^{16},2HCl$. — Anhydrous carvene absorbs dry hydrochloric acid gas, at first with rise of temperature, acquiring a transient red colour, and after two days deposits solid crystalline masses. It is saturated completely with hydrochloric acid gas; the crystalline mass which separates is pressed between paper and dissolved in warm alcohol; and the crystals which separate as the solution cools, are again pressed.

Snow-white, shining scales, which melt at 50·5°, solidify again at 41·25°, and have a faint taste and odour.

			Schweizer.
20 C	120	57·4	57·72
18 H	18	8·6	8·50
2 Cl	71	34·0	33·78
$C^{20}H^{16},2HCl$	209	100·0	100·00

It decomposes when heated *per se.* Heated with *water,* it is very quickly resolved into hydrochloric acid, and an oil which is probably carvene. Heated with *potash,* it yields carvene, chloride of calcium, and water. — It dissolves readily in water, with some difficulty in cold alcohol, easily in hot alcohol. (Schweizer.)

Carvene dissolves slowly in *water,* easily in *alcohol* and *ether.* It does not dissolve chloride of calcium. (Schweizer.)

Appendix to Carvene.

Chlorocarvene $C^{20}H^{12}Cl^4$ (?)

SCHWEIZER. (1841.) *J. pr. Chem.* 24, 270.

Preparation. Carvene is completely saturated with dry chlorine; the oil, which assumes for a while a red-brown colour, and afterwards changes to a yellow greasy mass, is heated; and the viscid, yellow transparent mass which separates therefrom, is washed with water, then with potash-solution, digested with alcohol, and dried over oil of vitriol or hydrate of potash.

Properties. Yellowish, transparent, semifluid mass, which sinks in water, has a peculiar, but not unpleasant odour, and a sweetish taste.

Decompositions and Combinations. When *heated,* it gives off hydrochloric acid and a viscid volatile oil, and leaves a carbonaceous residue. — It *burns* with difficulty when heated in a glass tube. Exposed to the *air,* it quickly becomes moist, white and opaque.

3. Indifferent Oil of Cloves.

ETTLING. (1834.) *Ann. Pharm.* 9, 68; *Pogg.* 31, 526.
ERDMANN & MARCHAND. *J. pr. Chem.* 23, 176.
BRÜNING. *Ann. Pharm.* 104, 204; *J. pr. Chem.* 73, 156.
C. G. WILLIAMS. *Chem. Gaz.* 1858, 170; *Ann. Pharm.* 107, 242; *N. Ann. Chim. Phys.* 54, 433.

Camphene of Oil of Cloves.

Source. In oil of cloves. It is found chiefly in the first portions of liquid which pass over on distilling cloves with water, while the last portions consist almost wholly of eugenic acid.

Separation from Oil of Cloves. The oil which passes over on distilling oil of cloves, mixed with excess of potash, is again shaken up with aqueous potash, washed, dehydrated with chloride of calcium and rectified. (Brüning.)

Properties. Colourless, strongly refracting oil. (Ettling.) Sp. gr. 0·918 at 8° (Ettling); 0·9016 at 14°. (Williams.) Boils at 142°—143° (Ettling); at 251° (Williams); 255° (Brüning). — Smells like oil of turpentine, different from oil of cloves. (Brüning.) It is more viscid than oil of turpentine. (Williams.)

			Ettling.	Erdmann & Marchand.	Brüning.	Willliams.
20 C	120	88·24	87·17	88·16	87·38	87·7
16 H	16	11·76	11·76	11·77	11·90	11·8
$C^{20}H^{16}$	136	100·00	98·93	99·93	99·28	99·5

It is not altered by alkalis or by potassium. (Ettling.)

It absorbs *hydrochloric acid gas,* but does not form with it a crystalline compound. (Ettling.)

It is much less soluble in *alcohol* than oil of turpentine. (Williams.)

4. Oil of Copaiba.

Bonastre. (1825.) *J. Pharm.* 11, 529; *N. Tr.* 12, 1, 180.
Ader. *J. Pharm.* 15, 95; *Br. Arch.* 30, 311; *N. Tr.* 20, 1, 184.
Gerber. *Br. Arch.* 30, 157.
Blanchet. *Ann. Pharm.* 7, 156.
Soubeiran & Capitaine. *J. Pharm.* 26, 70; abstr. *Ann. Pharm.* 34, 321.

Capaiva-öl. Essence de Capahu.

Source and Extraction. — In balsam of copaiba, which exudes from incisions in various species of *Copaïfera.* — 1. The balsam is distilled with water (Soubeiran & Capitaine); *per se.* (Blanchet). — 2. A solution of 100 pts. balsam of copaiba in 100 pts. alcohol of sp. gr. 0·837 is shaken up with 37·5 pts., soda-ley of sp. gr. 1·33, and 150 pts. water, and the oil which rises to the surface after standing is collected. (Ader.)

Properties. Transparent, colourless, mobile (yellowish-green according to Blanchet). Sp. gr. 0·9 (Schönberg, *A. Gehl,* 6, 494, Ader); 0·91 (Gerber; Williams, *Ann. Pharm.* 107, 242); 0·878 at 22° (Blanchet); 0·881—0·885. (Soubeiran & Capitaine.) — Boiling point: 245° (Blanchet, Williams); 245—260°. (Soubeiran & Capitaine.) — Solidifies at —26°, partly in the crystalline state. (Gerber.) — Rotatory power, 34·18° left. (Soubeiran & Capitaine.) — Expansion from 0° to 100° = 0·83132; from 100° to 200° = 0·104034. (Aubergier, *J. Pharm.* 27, 278.) — Has an aromatic odour, like that of the balsam (according to Ader, it has a less agreeable odour when prepared by (2) than when obtained by distillation.) Tastes sharp, and persistently bitter. (Ader, Gerber.) Neutral (Blanchet); slightly acid. (Gerber.)

			Blanchet.	
20 C	120	88·24	88·74	88·55
16 H	16	11·76	11·66	11·75
$C^{20}H^{16}$	136	100·00	100·40	100·30

Decompositions. 1. By continued *boiling,* the oil becomes brown and viscid. — 2. *Chlorine* in sunshine makes it hot, colours it yellowish, blue, and then green, and separates white crystalline masses. (Blanchet.) — 3. *Iodine,* slowly added to it, unites without detonation (Blanchet), with reddish-yellow to brown-black colour; if the iodine be more quickly added, heating and frothing take place (Gerber); the product is a brown mass. (Stoltze, *Berl. Jahrb.* 27, 2, 200.) — 4. It explodes with *fuming nitric acid* in the cold (Blanchet), leaving a brown resin (Stoltze) insoluble in the hot oil. (Gerber.) With *nitric acid* of sp. gr. 1·32, it resinises only when heated (Blanchet); according to Bonastre, it assumes a violet tint at the beginning of the action. Weaker nitric acid forms with the oil a small quantity of yellow resin precipitable by water. (Gerber.) — 5. *Oil of vitriol* makes it hot and turns it red-brown. (Stoltze.) — With a few drops of oil of vitriol, it becomes hot and blackens; but when dropped into a larger quantity of oil of vitriol, it forms a red-brown solution of sulphoterebic acid. (Gerhardt, *Compt. rend.* 17, 314.) — The brown viscid mixture gives off a sulphurous acid when heated. (Gerber.)

6. With *hydrochloric acid gas*, it becomes hot and coloured (Blanchet); it becomes brown and viscid, and on cooling, slowly deposits solid bihydrochlorate of copaiba-oil. (Soubeiran & Capitaine.) — 7. It oxidises *potassium.* (Gerber.) — Potassium immersed in the oil becomes coated in three months with a thick soapy mass. (Gall, *Sill. Am.* p. 21, 63.) — 8. When shaken up with *aqueous potash* or *soda*, it becomes heated, acquires a brown colour, and yields to water a small quantity of resin, which does not pre-exist in the oil, but is produced from it by the action of the alkali. (Gerber.) — 9. Distilled with 24 pts. water and 8 pts. chloride of lime, it gives off carbonic acid and forms chloroform. — 10. Distilled with *hypobromite of potash*, it forms bromoform. (Chantard, *Compt. rend.* 34, 485.)

Combinations. With *Hydrochloric acid.* — *a. Bihydrochlorate of copaiba-oil*, $C^{20}H^{16},2HCl$. ***Camphre de copahu; salzsaures copahu.*** (Soubeiran & Capitaine.) ***Chlorhydrate de copahu.*** (Gerhardt.)

It is prepared by passing dry hydrochloric acid gas through dehydrated oil of copaiba, separating the crystalline mass which is deposited therefrom on cooling from the brown oil, pressing it between filtering paper, mixing its solution in ether with alcohol of sp. gr. 0·85, and washing the crystalline mass which separates with alcohol. (Blanchet.) — The crystals which separate from the oil when hydrochloric acid is passed through it are recrystallised from alcohol. (Soubeiran & Capitaine.)

Hydrochlorate of copaiba-oil forms short, transparent, right rectangular prisms (resembling chlorate of potash, according to Blanchet), which melt at 77°. (Soubeiran & Capitaine.) — They are inodorous (Blanchet; Soubeiran & Capitaine), have a faint camphorous odour, and an aromatic bitter taste. (Gerber.)

			Blanchet.	Soubeiran & Capitaine. *mean.*
20 C	120	57·4	57·95	57·85
18 H	18	8·6	8·73	8·58
2 Cl	71	34·0	33·04	33·41
$C^{20}H^{16},2HCl$	209	100·0	99·72	99·84

The hydrochlorate heated to 140—150° gives off a large quantity of hydrochloric acid gas. (Soubeiran & Capitaine.) When set on fire, it burns with a bright flame. (Gerber.) *Nitric acid*, heated with it, gives off nitrogen gas [? Gm.]. (Blanchet.) *Oil of vitriol* with aid of heat dissolves it, and deposits it again in the crystalline form on cooling; at a stronger heat, the solution gives off hydrochloric acid gas. (Blanchet.) Heated with *sulphide of lead*, it yields an oil having an alliaceous odour. Its alcoholic solution is precipitated by *nitrate of silver* or *mercurous nitrate.* (Blanchet.)

It is insoluble in water and in cold alcohol, sparingly soluble in hot alcohol, easily soluble in ether. (Blanchet.) The alcoholic solution leaves when evaporated a thick oil, which smells like balsam of copaiba, and appears to hold in solution undecomposed bihydrochlorate of copaiba-oil. (Soubeiran & Capitaine.)

b. Hydrochlorate of Copahilene. (Soubeiran & Capitaine.) The liquid portion of the product obtained by treating copaiba-oil with hydrochloric acid. It always contains in solution bihydrochlorate of copaiba-oil, which cannot be separated from it. (Soubeiran & Capitaine.)

It is a black, viscid oil, smelling like castoreum, and without action on polarised light. (Soubeiran & Capitaine.)

When distilled, it gives off hydrochloric acid gas, and yields a colourless oil which is a solution of bihydrochlorate of copaiba-oil. (Soubeiran & Capitaine.) It burns with a faint odour of hydrochloric acid. It gives up a portion of its hydrochloric acid when shaken up with water. (Gerber.) Soluble in alcohol and ether. (Gerber.)

Oil of copaiba dissolves *phosphorus* when heated with it, and deposits part of it on cooling; the solution shines in the dark. It dissolves *sulphur* with aid of heat, and deposits part of it in reddish crystals on cooling. (Gerber.)

It dissolves *glacial acetic acid*, and *hydrocyanic acid;* mixes with alcoholic *succinic acid* and *benzoic acid*, which remain combined with the oil after the evaporation of the solution. It mixes with solutions of *oxalic acid*, but not with *citric acid*. It absorbs *ammonia*, becoming milk-white and viscid. (Gerber.)

It dissolves in all proportions of *bisulphide of carbon*. (Gerber.) It dissolves in 2·5 pts. of *absolute alcohol* (in all proportions, according to Stoltze), in 30 pts. of alcohol of sp. gr. 0·85 at 25° (Blanchet), and in 8 pts. of the most highly rectified spirit. (Schönberg.) It dissolves in all proportions of *absolute ether* (Stoltze), in less than ½ pt. of common ether. (Blanchet.)

5. Para-copaiba Oil.

Soubeiran Capitaine (1840.) *J. Pharm.* 26, 70.
Posselt. *Ann. Pharm.* 69, 67.

Source and Extraction. In a variety of copaiba balsam from Brazil. It is distilled with water, and the oil is dehydrated with chloride of calcium. (Posselt.)

Properties. Transparent, colourless viscid oil, of sp. gr. 0 91 (0·893 according to Soubeiran & Capitaine), boiling at 250°. It smells like the balsam and has a sharp burning taste. (Posselt.) Rotatory power 28·553°. (Soubeiran & Capitaine.)

			Posselt.
20 C	120	88·24	88·13
16 H	16	19·76	11·77
$C^{20}H^{16}$	136	100·00	99·90

Decompositions. 1. Becomes yellowish when *boiled*, afterwards brown, thick, tenacious, and charred. (Posselt.) *Chlorine* converts the oil, with evolution of hydrochloric acid, into a yellow sticky mass. The oil dissolves *iodine* without detonation. — 3. With *fuming nitric acid*, it detonates even in the cold; but nitric acid of sp. gr. 1·32 resinises it only with aid of heat. Dilute nitric acid, heated with the oil, dissolves it completely after a few days, giving off nitrous acid, carbonic acid, and other volatile acids. From the solution of the oil in nitric acid, water throws down, after evaporation, a reddish-yellow acid resin, sparingly soluble in hot water, easily soluble in alcohol and ether, whilst a peculiar acid remains dissolved, which, when the solution is concentrated by evaporation, crystallises in slender, colourless, transparent, laminæ, easily soluble in water, alcohol, ether, and rock-oil, inodorous, having a bitter taste, and a slight acid reaction. (Posselt.) — 4. The oil absorbs *hydrochloric acid gas* with avidity, turning brown-red and fuming in the air, but not depositing any crystals on cooling.

The oil dissolves in all proportions in *ether*, less easily in *absolute alcohol*, still less in *common alcohol.*

6. Oil of Elemi.

Stenhouse. (1839.) *Phil. Mag. J.* 18, 184; *Ann. Pharm.* 35, 304.
Deville. *Ann. Chim. Phys.* 25, 80; *Compt. rend.* 12, 184; *N. Ann. Chim. Phys.* 27, 88; abstr. *Ann. Pharm.* 71, 352; *Pharm. Centralbl.* 1849, 691.

Essence d'elemi.

Source and Extraction. In elemi-resin, the resin of *Icica Icicariba*, Dec., and *Icica heptaphylla.* (Aublet.) Elemi-resin is distilled with water, and the oil, which passes over readily and floats on water, is separated from the watery distillate, and dehydrated by agitation with chloride of calcium. The process yields 3—5 pts. oil from 100 pts. resin (Stenhouse); good elemi-resin yields 13 p. c. (Deville.)

Properties. Limpid and mobile. Boils at 166° (Stenhouse); at 174° under 0·755 met. pressure. Sp. gr. 0·852 at 24° (Stenhouse); 0·849 at 11°. (Deville.) Refracting power 1·4719 at 14°. Rotatory power 90·3° to the left. Vapour-density 4·84. (Deville.) [Calculation = 4·7144 (p. 245).] Has a rather pleasant odour, like that of elemi-resin, and a sharp taste. (Deville, Stenhouse.)

			Stenhouse.	Deville.
20 C	120	88·24	87·83	88·05
16 H	16	11·76	11·71	11·90
$C^{20}H^{16}$	136	100·00	99·54	99·95

Decompositions. Oil of elemi when set on fire burns, with a bright fuliginous flame. — 2. With *iodine*, it becomes heated, gives off iodine-vapours, and solidifies to a thick red mass. — 3. *Nitric acid* colours it brownish yellow in the cold, and, when heated, converts it into a resin, with explosion and evolution of nitric oxide. — 4. *Oil of vitriol* gives it a fine red colour in the cold, and chars it when heated. (Stenhouse.) — 5. It absorbs hydrochloric acid gas, and is converted into solid and liquid hydrochlorate of elemi-oil. (Deville.) It is not altered by *potassium*, but *hydrate of potash*, with aid of heat, converts it into a brown resin. (Stenhouse.)

Combinations. — *With Hydrochloric Acid.* A. *Solid Bihydrochlorate of Elemi-oil,* $C^{20}H^{16},2HCl$. Dry hydrochloric acid gas is passed into oil of elemi, the stream of gas being kept up after complete saturation (100 pts. of the oil absorb 47·7 pts. of hydrochloric acid gas); the excess of hydrochloric acid is left to evaporate in the air, and the crystals which separate from the hitherto fluid mixture are collected. (Deville.)

Colourless crystals, optically inactive. (Deville.)

			Deville.
20 C	120	57·4	57·37
18 H	18	8·6	8·70
2 Cl	71	34·0	33·93
$C^{20}H^{16},2HCl$	209	100·0	100·00

B. *Liquid Bihydrochlorate of Elemi-oil.* (Gerhardt.) — The oil which remains liquid after the separation of the solid hydrochlorate above described. (Deville.)

Oil of elemi is insoluble in *water*, sparingly soluble in weak *alcohol*, easily in alcoholic *ether*. (Stenhouse.)

7. Gaultherylene.

Cahours. (1844.) *N. Ann. Chim. Phys.* 10, 358.

Source. In oil of winter-green (*Gaultheria procumbens*), to the amount of $\frac{1}{10}$, mixed with $\frac{9}{10}$ of methyl-salicylic acid (xii, 255).

Preparation. Winter-green oil is distilled with concentrated aqueous potash; the distillate, consisting of wood-spirit, water, and gaultherilene, is washed, first with water containing potash, then with pure water; and the undissolved oil is dehydrated with chloride of calcium and rectified over potassium.

Properties. Colourless, mobile, lighter than water; boils at 160°. Vapour-density 4·92 [by calculation, 4·7144 (p. 245)]. Has a rather agreeable peppery odour.

			Cahours.
20 C	120	88·23	87·85
16 H	16	11·77	12·25
$C^{20}H^{16}$	136	100·00	100·10

8. Oil of Gomart.

Deville. (1849.) *N. Ann. Chim. Phys.* 27, 90; abstr. *Ann. Pharm.* 71, 354; *Pharm. Centr.* 1849, 692; *J. pr. Chem.* 48, 64.

Bursera-oel.

Source and Extraction. In gomart resin, the thickened resinous juice of *Bursera gummifera.* (*L.*) It is obtained by distilling the resin with water. The produce is 4·7 p. c. of coloured oil, which is set aside with solid hydrate of potash, and then rectified over potassium.

Properties. Colourless, transparent oil, smelling like turpentine. Vapour-density = 4·70.

			Deville. *mean.*
20 C	120	88·24	88·10
16 H	16	11·76	11·85
$C^{20}H^{16}$	136	100·00	99·95

Combinations. When strongly cooled and saturated with hydrochloric acid gas, it yields silky needles, like those of bihydrochlorate of lemon-oil, and exhibiting a dazzling whiteness, after pressure between bibulous paper.

			Deville.
20 C	120	57·4	57·4
18 H	18	8·6	8·8
2 Cl	71	34·0	33·8
$C^{20}H^{16},2HCl$	209	100·0	100·0

9. Oil of Hops.

Payen & Chevallier. (1822.) *J. Pharm.* 8, 214 and 533.
R. Wagner. *J. pr. Chem.* 58, 351; *Dingl. pol. J.* 128, 217; abstr. *Chem. Centrbl.* 1853, 249.
Personne. *Compt. rend.* 38, 309; *N. J. Pharm.* 26, 241 and 329; 27, 22; *Instit.* 1854, 65; *Chem. Centrbl.* 1854, 228.

Hopfenöl, Essence de houblon.

Source and Extraction. In hops, the female cones of *Humulus Lupulus* (*L.*), and in lupulin, the dust contained therein. It is extracted by distilling lupulin (Payen & Chevallier), or fresh hop-cones (Wagner) with water. The product is 2 p. c. of oil (Payen & Chevallier), 0·8 p. c. (Wagner), together with valerianic acid, which remains dissolved in the water. (Personne.)

Properties. Transparent and colourless (Personne); greenish-yellow (yellow from old hops) (Payen & Chevallier); pale greenish-yellow (the distillate between 125° and 225° is colourless, from 225° to 235° yellowish) (Payen & Chevallier). Sp. gr. 0·91 (Payen & Chevallier); 0·908 at 16°.

(Wagner.) Boiling point between 125° and 235° (Wagner); from 140° to above 300°. (Personne.) It volatilises partially below 100°; $\frac{1}{6}$ of the oil boils at 175°; $\frac{1}{2}$ between 175° and 225°; $\frac{1}{6}$ between 225° and 135°; and $\frac{1}{6}$ remains behind. (Wagner.) It does not solidify at 17°. (Personne.) Rotation to the right. — Smells of hops, pungent and intoxicating (Payen & Chevallier); strong but not intoxicating (the portion which distils between 175° and 225°, has a faint odour of rosemary). (Wagner.) Tastes sharp (Payen & Chevallier); burning, slightly bitter, like thyme and origanum. (Wagner.) Neutral (Personne); when left for some time on litmus-paper in contact with the air, it reddens the litmus. (Wagner.)

			Wagner.				Wagner.
			a.				*b.*
20 C	120	88·23	88·9	20 C	120	77·92	78·19
16 H	16	11·77	11·9	18 H	18	11·69	12·00
				2 O	16	10·39	9·81
$C^{20}H^{16}$	136	100·00	100·8	$C^{20}H^{16}O^2$	154	100·00	100·00

a. Distilled with alcoholic potash: resembles the oil which boils between 125° and 175°. — *b.* Oil boiling at 210°. It corresponds to the formula $C^{20}H^{18}O^2$, and is a mixture of the hydrocarbon $C^{10}H^8$ and oil of valerian (Personne); consists of a hydrocarbon $C^{20}H^{16}$ and an oxygenated oil $C^{20}H^{18}O^2$, isomeric with Bornean camphor, oil of cajeput, oil of bergamot, and campholic aldehyde. It contains sulphur (Payen & Chevalier; Will, *Ann. Pharm.* 52, 2), it is free from sulphur. (Wagner.)

Decompositions. 1. The oil gradually resinises when exposed to the air (Payen & Chevallier), turns acid (Personne.) Dries up to a sticky mass. (Wagner.) — 2. *Bromine* and *iodine* turn it brown in the cold, and immediately resinise it, with violent action, when heated. (Wagner.) — 3. With *nitric acid* it forms a yellow resin and valerianic acid. (Personne.)

4. With *oil of vitriol* it turns red, and forms a conjugated sulphuric acid. (Personne.) — 5. The oil *a* absorbs dry *hydrochloric acid gas*, and turns brown, but does not solidify on cooling. — 6. With *melting potassium*, it thickens, turns brown, and gives off gas. (Wagner.) — 7. When dropt into *melting potash*, it forms a volatile hydrocarbon, $C^{10}H^8$, having an odour of thyme, together with carbonate and valerate of potash (Personne). Heated with *alcoholic potash*, it turns brown, and gives off the volatile oil *a*, which smells like rosemary, leaving carbonate and apparently also caprylate and pelargonate of potash. — 8. Distilled with *melting chloride of zinc*, it yields a colourless oil, apparently identical with *a*.

Combinations. It dissolves in 10,000 pts. of water, imparting its odour and taste, which however are easily removed by charcoal (Payen & Chevallier), in more than 600 pts. of water. (Wagner.)

10. Oil of Juniper-berries.

TROMMSDORFF. (1822.) *Taschenb.* 1822, 46.
BLANCHET. *Ann. Pharm.* 7, 165.
DUMAS. *Instit.* 97; *J. pr. Chem* 4, 344; *Ann. Pharm.* 15, 158.
ASCHOFF. *N. Br. Arch.* 40, 272.

SOUBEIRAN & CAPITAINE. *J. Pharm.* 26, 78; abstr. *Ann. Pharm.* 34, 325.
ZELLER. *Stud. über äther. Oele Landau,* 1850.
STEER. *Wien Akad. Ber.* 1856; *Chem. Centr.* 1856, 60.

Wachholderbeeröl, Wachholderbeeressenz, Essence de genièvre, Oleum baccarum juniperi.

Source and Extraction. In juniper-berries the fleshy scales of the female cones of *Juniperus communis* (*L.*). — The ripe but still green berries are bruised and distilled with water (Aschoff), with water and common salt (Blanchet), after previous exhaustion with cold water. (Steer.) The oil thus obtained is rectified with water (Soubeiran & Capitaine), or with quicklime, after washing with salt water and dehydrated by agitation with chloride of calcium. (Blanchet.) — By rectification it yields $\frac{4}{5}$ colourless oil, $\frac{1}{5}$ of oil which passes over coloured, and a small quantity of residual oil. (Soubeiran & Capitaine.)

Unripe juniper-berries yield by distillation a more volatile and a less volatile oil; the ripe berries only the latter. (Blanchet.) — The yield of oil is only 0·77 p. c. (Tremlich, *Repert.* 24, 434), 0·65 p. c. Martius, *Repert.* 39, 24); from the ripe berries of first year's plants, 0·39 p. c.; from green ripe berries, by distillation with water and common salt, 1·56 p. c. (Blanchet); from ripe berries with water, 0·32 p. c.; from fresh berries, 0·46 p. c.; from unripe berries, 0·35 p. c. (v. Hees, *Pharm. Centr.* 1847, 380); from berries mixed with a small quantity of water, coarsely bruised and exhausted with cold water, 0·75 p. c. (Steer.)

Properties. Mobile oil. (Blanchet.) Transparent, and colourless to slightly straw-coloured (Blanchet, Martius); greenish to brownish-yellow. (Zeller.) Boiling point of the most volatile oil from the unripe berries, 155°; of the less volatile oil and of that from the ripe berries, 205° (Blanchet); of the first distillate, 155°—163°; of the last, 155°—182°. (Soubeiran & Capitaine.) — Sp. gr. 0·862—0·870 (van Hees, *Pharm. Centr.* 1847, 380); 0·847—0·881 (Soubeiran & Capitaine); 0·853—0·870 (Zeller); 0·853 (Trommsdorff); of the most volatile oil, 0·839 at 25° (Zeller, Blanchet); 0·855 (Soubeiran & Capitaine); at 100° = 0·804 (Aubergier, *J. Pharm.* 27, 278); of the less volatile oil, 0·8784 at 25° (Blanchet); 0·881 (Soubeiran & Capitaine); of the fresh oil, 0·926; of older oil, 0·912. (Martius.) — Refracting power, 1·475 (Becquerel & Cahours, *Compt. rend.* 11, 867); 1·474 (Deville, *Compt. rend.* 11, 867); 1·474 (Deville, *Compt. rend.* 11, 865). — Rotatory power, 3·521° to the left. (Soubeiran & Capitaine,) — Vapour-density = 4·844 (Soubeiran & Capitaine), by calculation, 4·714 (comp. p. 245). — It has a strong odour of juniper, the volatile oil of the unripe berries smells also like fir-needles (Martius, Blanchet); has an aromatic odour and an aromatic resinous taste. (Trommsdorff.) Neutral. (Aschoff, Zeller.)

			Blanchet.		Dumas.
			a.	*b.*	
20 C	120	88·23	88·41	87.72	87·7
16 H	16	11·77	11·52	11·59	11·7
$C^{20}H^{16}$	136	100·00	99·93	99·31	99·4

a. The more volatile from the unripe berries. *b.* Oil from the ripe berries. It is a mixture of the two non-separable oils, which are perhaps formed from the original oil during the distillation. (Soubeiran & Capitaine.)

Decompositions. 1. The oil on *cooling* deposits juniper-camphor. (Bizio, *Brugn. Giorn.* 19, 360.) — 2. It oxidises in the *air* (Blanchet), and after a while, forms juniper-camphor (Zaubzer, *Repert.* 22, 415; Buchner, *Repert.* 22, 425); in contact with water, also a small quantity of formic acid, and then reddens litmus. (Aschoff.) The oil is partly converted into formic acid during the drying of the berries; for the water which distils over with the oil colours litmus, and reduces mercury and silver salts. (Aschoff.) — It absorbs *insolated oxygen gas,* thereby acquiring oxidising properties and turning sour. (Schönbein, *J. pr. chem.* 52, 187.) — 3. Heated with *water* to 40°, it deposits hydrated oil of juniper. (Blanchet.) — 4. It explodes violently with *iodine* (Guyot, *J. Chim. méd.* 12, 487; Tüchen), slightly with a small quantity of iodine (Schütze, *Br. Arch.* 23, 200); it becomes very hot and detonates slightly, giving off violet vapours, and leaving a mobile, brownish green residue having a balsamic odour like that of the oil. (Winckler, *Repert,* 32, 271; Flaschoff, *Br. Arch.* 33, 225.) — The fresh oil of unripe juniper-berries explodes very violently with iodine (Blanchet), giving off grey vapours, and becoming greenish-brown and viscid (Zeller); older oil from the unripe berries explodes less violently with iodine (Winckler); becomes yellowish-brown and viscid, and deposits a less coloured liquid (Zeller); the oil of ripe juniper-berries does not explode with iodine. — 5. On gradually adding *bromine* to the oil mixed with $\frac{1}{5}$ of its volume of water, the liquid becomes heated, and the colour of the bromine disappears, if 229 pts. of bromine are added to 100 pts. of the rectified oil, or 220 pts. bromine to 100 pts. of the crude oil,—that is to say, about 4 At. bromine. (Gr. Williams, *Chem. Gaz.* 263, 365; *J. pr. Chem.* 61, 20.) — 100 pts. of the oil take up 250 pts. of bromine. (Knop, *Chem. Centralbl.* 1854, 498.) — 6. With *fuming nitric acid,* it forms, with strong crackling, a viscid, yellow resin (Hasse); when heated with *nitric acid,* it assumes a yellowish colour, and gives off gas. (Zeller.) — 7. With *oil of vitriol,* it thickens, becomes brownish-red, balsamic, and resinous (Zeller), and gives off sulphurous acid. (Hasse.) — 8. With acid *chromate of potash* and *sulphuric acid,* it assumes a reddish, and then a yellowish-brown colour, which is not destroyed by heating. (Zeller.) — 9. With *hydrochloric acid gas,* it assumes a darker colour, and forms hydrochlorate of *juniper-oil.* (Soubeiran & Capitaine.) — 10. Mixed with *aqueous hydrate of potash,* it gradually deposits hydrated oil of juniper. (Blanchet.) — 11. Distilled with 24 pts. water, and 8 pts. *chloride of lime,* it gives off carbonic acid with effervescence, and forms chloroform. — 12. Distilled with *hypobromite of lime,* it yields bromoform. (Chautard, *Compt. rend.* 34, 485.)

Combinations. 1. *Hydrated Oil of Juniper.* (Blanchet.) — Formed from oil of juniper by prolonged contact with water at 40°, and is gradually deposited in slender needles from a mixture of hydrate of potash and the juniper-water obtained by distilling the berries with common salt. It exhibits the properties of hydrated oil of turpentine (p. 256).

2. *Hydrochlorate of Juniper-oil,* or *Hydrochlorate of Juniperilene.* (Soubeiran & Capitaine.) — Oil of juniper is saturated with dry hydrochloric acid gas; the mixture, which becomes coloured, but does not solidify, even at —20°, is saturated with chalk, then mixed with chloride of calcium, and filtered through a mixture of animal charcoal and chalk.

Colourless oil, of sp. gr. 1·029 and lævo-rotatory power = 2·866.

			Soubeiran & Capitaine.
30 C	180	64·99	65·31
26 H	26	9·38	9·03
2 Cl	71	25·63	25·66
$C^{20}H^{16},HCl + C^{10}H^{8},HCl$	277	100·00	100·00

Oil of juniper forms with ½ pt. *absolute alcohol* a clear solution, and with 1 — 10 pts. a turbid solution (Zeller); the more volatile oil of the unripe berries dissolves clearly in 1 pt., with turbidity in a larger quantity of absolute alcohol; the oil of the ripe berries in 8 pts. (Blanchet.) It dissolves sparingly in alcohol of sp. gr. 0·85 (Blanchet); with turbidity in 10 to 12 pts. (Zeller.)

In *absolute ether* it dissolves in all proportions. (Blanchet.)

Appendix to Oil of Juniper-berries.

Juniper-camphor.

Zaubzer. (1825.) *Repert.* 22, 415.
Buckner. *Repert.* 22, 425.

Obtained from oil of juniper-berries, which had been kept for 6 years in a half-filled loosely stoppered bottle; purified by washing with alcohol.

Colourless, transparent, rhomboidal tables grouped in tufts, heavier than water, melting when heated, and volatilising without decomposition, solidifying in the crystalline form on cooling. Nearly destitute of taste and odour. Neutral. (Zaubzer, Buchner.)

Burns like a volatile oil. (Zaubzer.) When distilled with phosphoric acid, it behaves like turpentine-camphor. (Buchner.)

With 200 pts. of cold water, it forms an incomplete solution, which becomes clear when heated, and remains clear on cooling. It is but slightly soluble in *aqueous ammonia.* Dissolves in *acetic acid* more readily than in water. (Buchner.) — From a hot solution in *alcohol* of sp. gr. 0·830, it separates on cooling in feathery crystals; dissolves more readily in *ether.* (Zaubzer.)

11. Laurel-oil of Guiana.

Hancock. (1824.) *Quart. J. of Sc.* 75, 47; *N. Tr.* 11, 171; *Br. Arch.* 13, 291; *J. Pharm.* 10, 547. — *N. Edinb. J. of Sc.* 3, 48; *Br. Arch.* 36, 333.
Brandes. *N. Br. Arch.* 21, 169.
Stenhouse. *Phil. Mag. J.* 20, 273; *J. pr. Chem.* 27, 251; *Mem. Chem. Soc.* 1, 43; *Phil. Mag. J.* 25, 200; *Ann. Pharm.* 50, 155; *Mem. Chem. Soc.* 2, 121.

Natural Oil of Laurel (Hancock); *Ocotea-öl* (Löwig, *Organ. Verb.* 2, 1027.)

Source. In the stem of a tree growing in Spanish Guiana, and belonging to the lauraceous order (Hancock), and to the species *Ocotea* (Christison), or *Pinus.* (Stenhouse.)

Extraction. By making incisions in the stem of the tree near the root, whereby the receptacles of oil saturated under the bark are opened, and collecting the oil which runs out.

Purification. By distilling the crude oil with water, dehydrating with chloride of calcium, and rectifying in the oil-bath. (Stenhouse.)

Properties. Transparent, colourless oil, yellowish in the crude state, of sp. gr. 0·864 at 13·3°. — Begins to boil at 149·5°, the boiling point gradually rising to 162·8°. (Stenhouse.) Smells like oil of turpentine and oil of lemon (Stenhouse); like oil of cajeput, and has a warm pungent taste. (Hancock.) The crude oil contains in solution a small quantity of resin and some formic acid, which reduces silver-solutions at the boiling heat. (Stenhouse.)

			Brandes.	Stenhouse.	
			a.	*b.*	*c.*
20 C	120	88·24	77·15	88·51	88·29
16 H	16	11·76	9·97	11·57	11·57
$C^{20}H^{16}$	136	100·00	87·12	100·08	99·86

a. Crude oil; *b.* rectified oil which passed over at 149·5°; *c.* at 162·8°. It conconsists of two oils isomeric with oil of turpentine.

Decompositions. 1. Laurel-oil thickens and absorbs oxygen when exposed to the air. (Brandes.) — 2. It burns with thick smoke when set on fire. (Hancock.) — Iodine added in small quantities imparts to the oil a transient red colour, producing also a hissing noise, evolution of heat, and a bituminous odour, but without appearance of fire; larger quantities of iodine convert the oil into a black tarry mass. (Hancock.) — 4. *Oil of vitriol* colours it brown for a while, but does not mix with it. (Hancock.)

Combinations. — With *Water.* — *Laurel-turpentine-camphor* $C^{20}H^{20}O^{4}$. 8 pts. of laurel-oil are mixed with 2 pts. of nitric acid of sp. gr. 1·25—1·3, and 1 pt. of alcohol of 80 p. c., the mixture being frequently agitated at first, then left to stand quietly for some months; and the deep yellow crystalline mass which separates is collected and purified by repeated crystallisation from alcohol, like turpentine-camphor (p. 259). (Stenhouse.)

Properties. White, rhombic, inodorous and tasteless prisms, which melt at 125°, and sublime at 130°.

			Stenhouse.
20 C	120	70·19	70·15
20 H	20	11·44	11·65
4 O	32	18·37	18·20
$C^{20}H^{16}, 4HO$	172	100·00	100·00

Isomeric or identical with turpentine-camphor. (Stenhouse.)

Decompositions. 1. Laurel-turpentine-camphor yields by distillation with *anhydrous phosphoric acid,* a colourless oil which floats on water, and has the taste and odour of Guiana laurel-oil. — 2. Gently heated with *oil of vitriol,* it forms a red solution, which at a stronger heat gives off acid vapours and forms a tough resin precipitable by water. (Stenhouse.)

Guiana laurel-oil is insoluble in *water*, soluble in *alcohol* and *ether*. A mixture of 1 pt. oil and 2 pts. alcohol floats on ether, although both the oil and the alcohol are heavier than ether. — When the oil is gradually mixed with rectified spirit of wine, the spirit floats for a long time on the oil in spherical drops.

Guiana laurel-oil dissolves *camphor*, *caoutchouc*, *pitch*, *resin* and *oils*, both *fat* and *volatile*. (Hancock.)

12. Oil of Lemon.

SAUSSURE. (1822.) *Ann. Chim. Phys.* 13, 262; *Pogg.* 25, 370; *Ann. Pharm.* 3, 157.
BOISSENOT. *J. Pharm.* 15, 325; *Ann. Chim. Phys.* 41, 434; *N. Tr.* 20, 2, 214.
DUMAS. *Pogg.* 26, 530; *Ann. Pharm.* 6, 255; *Ann. Chim. Phys.* 52, 405; *Pogg.* 29, 129; *Ann. Pharm.* 9, 61.
BLANCHET & SELL. *Ann. Pharm.* 6, 280.
LAURENT. *Ann. Chim. Phys.* 66, 212.
SOUBEIRAN & CAPITAINE. *J. Pharm.* 26, 1; *N. Br. Arch.* 22, 171; abstr. *Ann. Pharm.* 34, 317.
DEVILLE. *Ann. Chim. Phys.* 70, 81. — *N. Ann. Chim. Phys.* 25, 80. — *N. Ann. Chim. Phys.* 27, 86; *Ann. Pharm.* 71, 349.
GERHARDT. *Compt. rend.* 17, 314; *N. Ann. Chim. Phys.* 14, 113.
BERTHELOT. *N. Ann. Chim. Phys.* 37, 223; 38, 44; 39, 5; 40, 36; *Ann. Pharm.* 88, 346.
ZELLER. *Stud. über äther. Oele. Landau*, 1850.

Essence de Citron ; Citronen-oel.

Source and Extraction. — In the rind of the lemon (*Citrus limonum*). The fresh rind is torn to pieces and pressed ; the oil which runs out is filtered (Saussure) ; or the expressed oil is distilled ; or the fresh rind is distilled with water. (Berthelot.)

Properties. Transparent and colourless, or yellowish (Saussure) ; pale yellow or greenish yellow to dark yellow (Zeller) ; after rectification with water, it is colourless at first, but afterwards turns yellowish (Blanchet & Sell) ; mobile. (Saussure.) — Sp. gr. 0·8517 at 22° (Saussure) ; 0·8514 at 18° (Guibourt) ; 0·856 at 25° (Chardin) ; 0·790 at 100° (Aubergier, *J. Pharm.* 27, 278) ; 0·852 at 14·6 (Brix, *Pogg.* 55, 381) ; 0·838 at 0° (Frankenheim, *Pogg.* 72, 422) ; 0·84—0·86. (Zeller.) — Rectified : 0·847 at 22° (Saussure), 0·856 at 18° (Chardin) ; 0·848 (Soubeiran & Capitaine) ; distilled at 55° in vacuo : 0·8514 at 14° ; distilled at about 80° in vacuo, 0·8506 at 65° (Berthelot) ; distilled with water : first distillate, 0·877 ; last, 0·853. (Soubeiran & Capitaine.)

Boiling point 160°—170° (Soubeiran & Capitaine) ; 146° (Aubergier) ; 176·1°. (Brix.) Distilled with water : first distillate, 167° ; last, 173°. (Blanchet & Sell.) Expansion from 0° to 100° = 0·09821 ; from 0° to 135° = 0·138068. (Frankenheim, *Pogg.* 72, 422.) — Vapour-density = 4·73 (Soubeiran & Capitaine), by calculation 4·71 (comp. p. 245). — Specific heat (water = 1) = 0·45. Latent heat of vapour (vapour of water at 100° = 432) = 63·85. (Brix.) — Refracting power (water = 1·333) = 1·475 (Becquerel & A. Cahours, *Compt. rend.* 11, 867 ; *Pogg.* 51, 427) ;

1·472, of old oil of lemon, 1·4808. (Deville, *Compt. rend.* 11, 865; *Pogg.* 51, 433.) — Rotatory power, 80·484° to the right (Biot, *Ann. Chim. Phys.* 69, 22); 79·494° to the right (Soubeiran & Capitaine); 72·5 to the right. (Berthelot.) — Of the oil rectified with water: first distillate 15·34 right (Soubeiran & Capitaine); distilled at 55° in vacuo, 56·4° right. (Berthelot.) — Has an agreeable odour. Neutral. (Zeller.)

			Saussure.	Dumas.	Hermann.
			a.	*b.*	*c.*
20 C	120	88·23	86·899	88·45	88·5
16 H	16	11·77	12·326	11·46	11·5
$C^{20}H^{16}$	136	100·00	99·225	99·91	100 0

	Blanchet & Sell.	Berthelot.	
	d.	*e.*	*f.*
20 C	86·72	88·1	85·3
16 H	11·57	11·4	11·4
$C^{20}H^{16}$	98·29	99·5	96·7

a, contained 0·775 p. c. nitrogen. (Saussure.) *e*, distilled in vacuo (at to) 55°; *f*, up to 80°. (Berthelot.)

From its behaviour towards hydrochloric acid, oil of lemon must be regarded as a mixture of citronyl and citryl, two compounds isomeric with each other and with oil of turpentine. (Blanchet & Sell.) It is resolved, under the influence of hydrochloric acid, into two isomeric compounds, citrene and citrilene, which did not previously exist in it. (Soubeiran & Capitaine.) It is for the most part isomeric with oil of turpentine, but always contains in addition a small quantity of an oxygenated oil. (Gerhardt, Berthelot.)

Decompositions. 1. Lemon-oil absorbs *oxygen gas*, gradually assuming a brownish yellow colour, whilst carbonic acid, nitrogen, and hydrogen go off, together with the excess of oxygen. It absorbs in a week 0·8 vols., in the two following months, as a daily average, 1·07; after four weeks, at 23°, daily 1·7; within a year, 141·7; in the following thirty months, scarcely 2 vols. oxygen, and yields 16·6 vols. carbonic acid, 0·66 nitrogen, and 0·29 hydrogen. (Saussure.) In contact with insolated oxygen (Schönbein, *J. pr. Chem.* 52, 187), by very long contact with the air (Williams, *Chem. Gaz.* 261, 331; *J. pr. Chem.* 60, 254), it acquires a pungent odour and oxidising properties. — Lemon-oil turns acid when exposed to the air either by itself or in contact with water; the rectified oil, however, does not (Aschhoff, *N. Br. Arch.* 40, 273); it forms acetic acid and lemon-camphor, acquires a different odour, and yields by distillation, acid water and an oil, while resin remains behind. (Boissenot.) — 2. The oil may be heated to 300° for several hours without alteration, but at 360°, it begins to give off hydrogen and carbonic oxide. Its rotatory power begins to diminish when it is heated to 360°; after being heated for 34 hours to 200—240°, it exhibits a dextro-rotatory power of 72·70°; after heating to 300° for an hour, it rotates 73° to the right; to 360° for an hour, 65·6° to the right. The permanence of the rotatory power of oil of lemon when it is heated to 300°, distinguishes it from oil of turpentine; hence the presence of oil of turpentine in oil of lemon may be detected by the alteration of the rotatory power by a temperature of 300°. (Berthelot.) Lemon-oil, passed in the state of vapour through a heated porcelain tube, yields a non-inflammable gas, tar, and charcoal. (Saussure.) — 3. Cotton, saturated with oil of lemon, chars on the surface in dry *chlorine gas*, but does not take fire. (Böttger, *J. pr. Chem.* 73, 498.) In contact with 20 vols. water, it decolorises bromine gradually added to it, and forms hydrobromic acid. The rectified oil absorbs 227·8, the crude oil, 242·8—253·3 p. c. bromine. (Williams, *Chem. Gaz.* 263, 365; *J. pr. Chem.* 61, 18.) — 5. With *iodine*, it becomes heated, and gives off hydriodic acid, together with violet and yellow vapours. (Guyot, *J. Phys.* 5, 230; Walcker, *Pogg.* 6, 126); becomes reddish, yellow-green, and viscid. (Zeller.) — 6. With *fuming nitric acid*, it froths strongly, and forms a brownish-yellow resin (Hasse, *Crell. Ann.* 1785, 1, 422); with ordinary nitric acid, it assumes a slight brownish colour, and gives off gas when heated (Zeller); with alcoholic nitric acid, it forms hydrated oil of lemon. (Deville.) With *oil of vitriol*, it turns yellowish brown (Zeller), and is converted, like oil of turpentine, into terebene and colophene (pp. 257, 279) (Deville); dropt into a large quantity of oil of vitriol, it forms a red-brown solution of sulphoterebic acid. (Gerhardt, *Compt. rend.* 17, 314.) — 8. When distilled with *anhydrous phosphoric acid*, it yields terebene and colophene. (Deville.) With *hydrochloric acid gas*, it turns brown, (Thénard, *Mem. de la Soc. d'Arcueil*, 2, 32), yellow if heated, expanding by 16·6, p. c. and increasing in weight by 41 p. c. (Saussure), and solidifies to crystalline hydrochlorate of lemon-oil (Thénard), completely (Dumas), partially (Blanchet & Sell; Soubeiran & Capitaine.) Lemon-oil, distilled in vacuo at 55°, solidifies partially when saturated with hydrochloric acid gas; that which distils at 80°, solidifies completely. (Berthelot.) — 10. Lemon-oil remains unaltered when heated to 100° for three hours with anhydrous *boracic acid.* — 11. Heated to 100° for 30 hours with crystallised *tartaric* or *citric* acid, it remains unaltered, but when treated in like manner with *oxalic acid*, it decreases in rotatory power, and loses the property of crystallising with hydrochloric acid. — 12. With *potassium*, it gives off a small quantity of hydrogen in the cold, more when heated. — The oil, which is thereby coloured brown, ceases to be decomposed after repeated distillation over potassium, and acquires a very agreeable odour. — 13. When left in contact with *hydrate of potash*, it deposits brown flocks, which settle upon the solid potash. The oil thus treated does not turn brown, but acquires a stronger and more agreeable odour. (Gerhardt.) — 14. Distilled with 8 pts. *chloride of lime* and 24 pts. water, it yields chloroform. (Chautard, *Compt. rend*, 34, 485; *J. pr. Chem.* 56, 238.) Distilled with *hypobromite of lime* and water, it yields bromoform. (Chautard, *Compt. rend.* 34, 485; *J. pr. Chem.* 56, 238.) — 16. The rotatory power of lemon-oil oil is diminished by twenty hours heating to 100° with *chloride of zinc.* (Berthelot.) — 17. With a strong solution of *bibasic acetate of lead*, it forms a slight yellow precipitate. (Schindler, *N. Br. Arch.* 41, 140.) — 19. It is not altered by *nitroprusside of copper.* (Heppe, *N. Br. Arch.* 89, 57.)

Combinations. 1. *With Water. Hydrated Oil of Lemon; Hydrate of Lemon-oil.* — Isomeric and identical with turpentine-camphor. — It is produced by mixing 4 pts. of commercial oil of lemon, 3 pts. of alcohol of sp. gr. 0·85, and 1 pt. of commercial nitric acid, leaving the mixture to stand for 4 weeks, then collecting the resulting crystals and purifying them in the manner as those of turpentine-camphor. (Deville.)

2. *With Hydrochloric Acid. a. Monohydrochlorate of Lemon-oil.* (Deville.) $C^{20}H^{16},HCl$. Appears to be frequently present in small quantity in the portion of lemon-oil which remains liquid after saturation with hydrochloric acid gas (liquid lemon-camphor; Soubeiran & Capitaine).

It is produced by saturating with hydrochloric acid gas, a solution of lemon-oil in acetic acid or alcoholic oil of vitriol, and collecting the few crystals which separate, rarely however, and only under peculiar circumstances. It forms crystals like those of artificial camphor, which melt at 100°, and volatilise without decomposition at higher temperatures. (Deville.)

b. Bihydrochlorate of Lemon-oil. $C^{20}H^{16},HCl$. *Salzsaurer Citronencampher* (Dumas); *Salzsaures Citronyl* (Blanchet & Sell); *Muriate citré* (Saussure); *Hydrochlorate de Citrène* (Dumas, Laurent, Soubeiran & Capitaine); *Bichlorhydrate solide d'essence de citron.* (Deville.) First prepared by Thénard. (*Mem. de la Soc. d'Arc.* 2, 32.)

Formation. 1. By the action of dry hydrochloric acid gas on rectified oil of citron (Thénard); with evolution of heat. (Saussure; Blanchet & Sell.) — 2. By eight days contact and frequent agitation of aqueous hydrochloric acid with oil of lemon. — 3. By the action of dry hydrochloric acid gas on turpentine-camphor (p. 268), with separation of water. (Deville.) Lemon-oil, mixed with $\frac{1}{6}$ turpentine-oil, does not yield any solid hydrochlorate of lemon-oil when heated with hydrochloric acid gas. (Berthelot, *N. J. Pharm.* 29, 28.) — Rectified oil of lemon absorbs at 20°, and under a pressure of 0·724 met., 286 vols. hydrochloric acid gas, and forms a semi-fluid mixture of crystalline laminæ and liquid oil, which melts completely at 30°, and when pressed between filtering paper at 12°, yields 44·5 p. c. bihydrochlorate of lemon-oil.

Preparation. Rectified and dehydrated oil of lemon well cooled, is saturated with dry hydrochloric acid gas; the crystals which separate after a while are removed from the brown mother-liquor, pressed repeatedly between filtering paper, washed with cold alcohol, recrystallised from hot alcohol, dried in the air, then in vacuo or over oil of vitriol (Dumas), and once more crystallised from ether. (Blanchet & Sell.) — The mother-liquor which drains from the crystals (liquid lemon-camphor; [Soubeiran & Capitaine], hydrochlorate of citryl [Blanchet & Sell]), crystallises completely in the end if left to evaporate freely in the air. (Dumas.) — Only a part of the lemon-oil forms crystals with the hydrochloric acid; crude lemon-oil, saturated with hydrochloric acid gas, acquires a very dark colour, solidifies when cooled below 10°, does not yield half as great an amount of crystals as the rectified oil, and then likewise forms a black, very thick substance—a yellow substance (perhaps colouring matter of the lemon-peel), and a small quantity of a brown heavy liquid. (Saussure.) —Lemon-oil yields more than its own weight of the bihydrochlorate. (Dumas.)

Properties. Right four-sided prisms, often very much flattened (Saussure), white brittle laminæ. (Blanchet & Sell.) Heavier than water. (Saussure.) Melts at 41° (Saussure), at 43° (Blanchet & Sell), at 44°. (Deville.) — No longer volatile; solidifies in the crystalline form on cooling. (Saussure.) — Sublimes for the most part between 50° and 60° (Saussure); at 50° without any decomposition. (Blanchet & Sell.) — Boils with decomposition at 162° (Blanchet & Sell); 142°. (Cahours, *Ann. Chim. Phys.* 70, 101.) Optically inactive. (Soubeiran & Capitaine.) Smells like thyme (Saussure), like tuberoses. (Blanchet & Sell.)

			Dumas.	Blanchet & Sell.	Deville.
20 C	120	57·5	57·20	57·76	57·2
18 H	18	8·6	8·75	8·73	8·7
2 Cl	71	33·9	34·05	33·43	34·1
$C^{20}H^{16},HCl$	209	100·0	100·00	99·92	100·0

Decompositions. 1. When *heated,* it gives off hydrochloric acid gas (Saussure; Blanchet & Sell; Soubeiran & Capitaine; Deville); a volatile oil (Saussure); an oil which solidifies again at 20° (Blanchet & Sell), and distils partially without decomposition. (Saussure.) When quickly heated above 100°, it distils for the most part undecomposed, the distillate being merely covered with a trace of oil; when it is moderately heated to 50—60°, part of it sublimes in large laminæ, whilst the rest distils over as a limpid oil, containing hydrochloric acid and still holding crystals in solution. (Saussure.) — 2. When *set on fire*, it burns less easily than artificial camphor. (Saussure.) — 3. By distillation with *water*, it yields a watery liquid having an acid reaction. (Blanchet & Sell.) — 4. *Chlorine gas* acts upon fused bihydrochlorate of lemon-oil, partially converting it after a while, with evolution of hydrochloric acid, into chlorinated bihydrochlorate of lemon-oil. If this compound be gently heated to remove free chlorine and hydrochloric acid, an oil is obtained, consisting of 9 At. *hydrochlorate of chlorocitrenase* and 1 At. *hydrochlorate of citrene* = $9(C^{20}H^{14}Cl^2,2HCl) + C^{20}H^{16},2HCl$. (Laurent.) — 5. With *fuming nitric acid*, the compound froths up slightly, and dissolves in it after 14 days (Saussure); ordinary nitric acid does not attack it in the cold, but decomposes it completely when heated, giving off nitrous acid. (Blanchet & Sell.) — 6. *Oil of vitriol* poured upon the compound, eliminates hydrochloric acid gas. (Saussure.) — 7. Gently heated with *potassium*, it yields colourless oil of lemon, and by continued boiling with it at a higher temperature, it yields citrene. (Deville.) — 8. When treated with *potash*, it gives off part of its hydrochloric acid, and is converted into an oil from which no further quantity of acid can be extracted by potash. (Blanchet & Sell.) — 9. Heated with *lime* or *baryta*, it yields citrene. (Saussure and others.) — 10. It is decomposed by *nitrate of silver* and *mercuric nitrate*, even in the cold; but not by nitrate of lead, even with the aid of heat. (Blanchet & Sell.)

Combinations. Bihydrochlorate of lemon-oil is insoluble in *water*, soluble at 14° in 5·88 pts of *alcohol* of sp. gr. 0·806 (Saussure), soluble in *ether* (Blanchet & Sell), in *oil of lemon*. (Saussure.) The alcoholic solution deposits slender laminæ when mixed with water, and yields regular crystals by spontaneous evaporation (Saussure); it likewise decomposes partially when evaporating. (Soubeiran & Capitaine.)

c. *Liquid Lemon-camphor. Hydrochlorate of Citrylene.* (Soubeiran & Capitaine.) *Hydrochlorate of Citryl.* (Blanchet & Sell.) The compound which remains liquid after the saturation of lemon-oil with hydrochloric acid gas. The liquid is cooled to — 10°, to separate the solid bihydrochlorate which remains dissolved, and filtered through chalk and animal charcoal to remove colouring matter and free hydrochloric acid. (Soubeiran & Capitaine.) Volatile oil (Blanchet & Sell); without rotatory power. (Soubeiran & Capitaine.) It gives up hydrochloric acid when its alcoholic solution is precipitated by water, or when it is filtered through chalk and charcoal. (Soubeiran & Capitaine.) By saturation with dry hydrochloric acid gas, it is completely converted into a white crystalline mass, which, when dissolved in hot alcohol, does not yield any crystals on cooling, but a heavy oil and a specifically lighter acid, which remains dissolved in the alcohol, a few crystals of bihydrochlorate of lemon-oil likewise floating in the liquid. (Blanchet & Sell.)

Oil of lemon dissolves *phosphorus*, and then resinises quickly on exposure to the air. With a small quantity of phosphorus, it forms an oil smelling like oil of balm; with a larger quantity of phosphorus, a solid mass like spermaceti. (Jonas, *Ann. Pharm.* 34, 329.) — At 16° it absorbs 8·5 vols. of *ammonia-gas.* (Saussure.) — It dissolves in all proportions of *absolute alcohol* (Saussure, Zeller), in 7·14 pts. of alcohol of sp. gr. 0·837 at 16° (Saussure), and with turbidity in 10 pts. of alcohol of sp. gr. 0·85. (Zeller.)

Appendix to Oil of Lemon.

Lemon-camphor.

Boissenot. (1829.) *J. Pharm.* 15, 324; *Ann. Chim. Phys.* 41, 434; *N. Tr.* 20, 2, 214.
Blanchet & Sell. *Ann. Pharm.* 6, 280.
Mulder. *J. pr. Chem.* 17, 104; *Ann. Pharm.* 31, 69.
Berthelot. *N. Ann. Chim. Phys.* 40, 36.

Stearoptene of Lemon-oil. Citronen-camphor.

Source. In lemon-oil which has been long exposed to the air. (Boissenot.)

Preparation. 1. By leaving oil of lemon to itself for some time in a bottle not quite full and frequently opened; and: *a.* Collecting the crystals which form on the stopper; — *b.* Distilling the thickened oil, cooling the water containing acetic acid, which passes over with the oil, to —8°, and collecting the crystals which separate; — *c.* Mixing the alcoholic solution of the distilled oil with water, leaving the water separated from the oil to evaporate at 37°—40°, and collecting the crystals which separate on cooling. (Boissenot.) — 2. By distilling oil of lemon as long as the more volatile oil passes over, and collecting the crystals which separate from the residue on cooling. (Blanchet & Sell, Berthelot.)

Properties. Colourless, transparent, shining prisms. (Boissenot.) — Melting point 43°—45° (Boissenot); 46° (Mulder); above 100°. (Berthelot.) Boils above 100°, distilling over in drops which separate in the crystalline form on cooling (Boissenot); sublimes (Mulder). Odour faint (Boissenot); like that of lemon-oil. (Mulder.) Taste sharp and pungent. Neutral. (Boissenot.)

	Mulder.	Berthelot.
C	55·02	58·00
H	8·98	7·50
O	36·00	34·50
	100·00	100·00

Decompositions. 1. When thrown on red-hot coals, it volatilises, without *taking fire*, and is but partially decomposed in a red-hot crucible. — 2. Heated with *concentrated nitric acid*, it gives off nitrous acid without forming oxalic acid; in cold nitric acid it dissolves without decomposition. — 3. With *oil of vitriol*, it forms a red solution having a peculiar aromatic odour, from which water separates a resin insoluble in water and hydrochloric acid, and not melting at 100°. (Boissenot.)

Combinations. Lemon-camphor is insoluble in *cold,* but dissolves, abundantly in *boiling water.*—The solution solidifies in a crystalline mass on cooling (Boissenot); it is iridescent. (Berthelot.)

It does not absorb *hydrochloric acid gas,* but dissolves in *hydrochloric acid.*—The solution becomes turbid when heated above 100°, but clear again on cooling. (Boissenot.)—It dissolves in *acetic acid, alcohol,* and *ether,* is insoluble in pure oil of lemon, but soluble in the old oil containing acetic acid. (Boissenot.) The alcoholic solution partially solidifies on cooling in the crystalline form (Blanchet & Sell), gelatinous (Berthelot).

13. Citrene.

Saussure. (1820.) *Ann. Chim. Phys.* 13, 265.
Blanchet & Sell. *Ann. Pharm.* 6, 286.
Dumas. *Ann. Chim. Phys.* 52, 405; *Pogg.* 29, 129; *Ann. Pharm.* 9, 61.
Soubeiran & Capitaine. *J. Pharm.* 26, 1; *N. Br. Arch.* 22, 171; abstr. *Ann. Pharm.* 34, 318.
Deville. *N. Ann. Chim. Phys.* 27, 86.

Citrène (Dumas, Soubeiran & Capitaine); *Citronyl* (Blanchet & Sell.) First prepared in 1820 by Saussure (p. 301.)

Preparation. 1. Bihydrochlorate of citron-oil is distilled three times over lime, and the oil which passes over each time is redistilled six times over baryta. (Dumas.)—Saussure distilled it over 5 pts. of lime between 50° and 60°.—2. Bihydrochlorate of lemon-oil is first distilled by itself to remove part of the hydrochloric acid, then passed in the state of vapour over lime heated to 180° (Soubeiran & Capitaine), and the yellow oil which passes over is rectified over recently ignited lime, and finally over potassium. (Blanchet & Sell.)—Fused bihydrochlorate of lemon-oil is distilled over potassium, and the oil which passes over is collected. (Deville.)

Properties. Transparent and colourless. (Blanchet & Sell; Dumas.) Sp. gr. 0·8569 (Blanchet & Sell); 0·847. (Soubeiran & Capitaine.)—Boiling point 165°. (Blanchet & Sell; Soubeiran & Capitaine.)—Vapour-density 4·891 (Cahours, *Ann. Chim. Phys.* 70, 101); 473 (Soubeiran & Capitaine); by calculation = 4·71 (p. 245).—Optically inactive. (Soubeiran & Capitaine.)—Smells like oil of lemon (Dumas); less agreeably (Soubeiran & Capitaine); aromatic, like hydrochlorate of citron-oil. (Blanchet & Sell.

			Blanchet & Sell.	Dumas.	Deville.
20 C	120	88·24	88·45	88·32	88·04
16 H	16	11·76	11·64	11·77	11·82
$C^{20}H^{16}$	136	100·00	100·09	100·09	99·86

With *hydrochloric acid gas* it becomes coloured, without producing crystals (Saussure), forming a liquid and a solid hydrochlorate. (Soubeiran & Capitaine.)

14. Citrilene.

SOUBEIRAN & CAPITAINE. (1840.) *J. Pharm.* 26, 1; *N. Br. Arch*, 22, 171; abstr. *Ann. Pharm.* 34, 317.

Citryl. (Blanchet & Sell.)

Prepared by distilling liquid lemon-camphor over lime, and collecting the oil which passes over.

Properties. Sp. gr. 0·88. Boiling point 168°, gradually rising to 175°, and leaving a coloured residue. Vapour-density = 5·08. Optically inactive. (Soubeiran & Capitaine.)

15. Oil of Lime.

DUMAS. (1833.) *Instit. N.* 97; *J. pr. Chem.* 4, 434.
VOHL. *N. Br. Arch.* 74, 16; abstr. *Chem. Centr.* 1853, 318.

Limettöl. Huile de limette.

Source and Extraction. In the rind of the lime (*Citrus limetta*). — The rinds are torn and pressed, or distilled with water.

Properties. Like oil of lemon.

			Dumas.
20 C	120	88·24	87·6
16 H	16	11·76	11·4
$C^{20}H^{16}$	136	100·00	100·0

With a mixture of *chromate of potash* and *oil of vitriol*, it becomes strongly heated, and forms limettic acid, $C^{22}H^{8}O^{12}$. (Vohl.)

16. Oil of Mandarin.

LUCA. (1857.) *Compt. rend.* 45, 904; *J. pr. Chem.* 75, 187; *N. J. Pharm.* 33, 51; *Instit.* 1857, 393.

Mandarinol. Essence de Mandarin.

Source and Extraction. In peculiar cells of the rind of *Citrus bigaradia sinensis* and *myrtifolia*. The rinds are pressed, after their surface has been lacerated, and the oil which runs out is filtered.

Properties. Pale yellowish; after rectification, colourless, clear, and mobile. Sp. gr. 0·852 at 10°; 0·8517 at 12°. Boiling point 178°. Has an agreeable odour, different from the oils of lemon and orange, and a not unpleasant taste, like that of orange-oil. Rotatory power 85·5° to the right.

			Luca.
20 C	120	88·23	87·58
16 H	16	11·77	11·96
$C^{20}H^{16}$	136	100·00	99·54

Decompositions. 1. With *cold nitric acid,* it assumes a faint yellow colour, and is decomposed by *hot nitric acid,* with evolution of nitrous acid, the mixture, on addition of water, depositing a nearly solid mass. — 2. With *cold oil of vitriol,* it turns red, but is decolorised again when mixed with water; hot oil of vitriol chars it, and gives off sulphurous acid. — 3. With *hydrochloric acid,* it turns brown forming solid bihydrochlorate of mandarin-oil.

Combinations. 1. *With Water.* Mandarin oil, left in contact with alcoholic nitric acid, forms a crystalline mass, which is probably hydrated mandarin-oil.

2. *With Hydrochloric Acid.* — *Bihydrochlorate of Mandarin-oil.* The oil is saturated with dry hydrochloric acid gas, or shaken up with strong hydrochloric acid, and the crystalline mass which separates from the brown liquid after a few days, is collected, pressed between filtering paper and dried.

Small, solid, transparent laminæ, which melt when heated, volatilise without decomposition, have a peculiar odour, and are insoluble in water but soluble in alcohol and ether.

Mandarin-oil is insoluble in water, to which, however, it imparts its odour.

It dissolves in 10 pts. of *alcohol,* also in *ether* and in *glacial acetic acid,* and in every proportion of *bisulphide of carbon.*

It dissolves *iodine, bromine, phosphorus, sulphur, oils,* both *fixed* and *volatile, wax,* and *resins.* (Luca.)

17. Oil of Orange-peel.

Gaubius. *Adversaria.* 30.
Soubeiran & Capitaine. *J. Pharm.* 26, 65.
Zeller. *Stud. über. äther Oele. Landau,* 1850.

Essence d'orange, Orangenschalenöl, Pomeranzenschalenöl.

Source and Extraction. In orange-peel, the rind of *Citrus Aurantium (L.).* — The lacerated rind is pressed or distilled with water, or the expressed oil is distilled with water.

Properties. Pale yellow to greenish yellow, mobile. (Lewis, Zeller.) Sp. gr. 0.888 (Lewis), 0·835 — 0·837 (Soubeiran & Capitaine); 0·83 — 0·85; of older oil, 0·88 (Zeller). Boiling point 180°. Vapour-density 4·69. (Soubeiran & Capitaine.) Calculation = 4·714 (p. 245). Solidifies partially when cooled. (Bizio, *Brugn. Giorn.* 19, 360.) Rotatory power 125·59° — 127·43° right. It has an agreeable odour. Neutral. (Zeller.)

			Soubeiran & Capitaine.
20 C	120	88·23	88·44
16 H	16	11·77	11·65
$C^{20}H^{16}$	136	100·00	100·09

Decompositions. 1. When *kept* in closed vessels, it deposits crystalline, easily fusible, volatile clots, soluble in water and alcohol, and ultimately turns viscid and brown. (Gaubius.) With *iodine*, it gives off yellowish-red vapours with great violence, turning reddish yellow-brown, and assuming a resinous consistence. — 3. With *nitric acid,* it turns greenish-yellow, gives off gas when heated, and is converted into a brittle resin. — 4. *Oil of vitriol* colours it dark reddish yellow-brown. — 5. Mixed with an equal quantity of *bibasic acetate of lead,* it yields an orange-yellow precipitate, turning red in an hour, and becoming lighter after a week. (Schindler, *N. Br. Arch.* 41, 140.)

Combinations. With Hydrochloric Acid. — 1. *Monohydrochlorate of Orange-peel-oil.* The portion which remains liquid when the oil is saturated with hydrochloric acid gas. (Soubeiran & Capitaine.) — 2. *Bihydrochlorate of orange-peel oil* $C^{20}H^{18}CO^{2}$. *Solid Hydrochlorate of Orange-peel-camphor, Hydrochlorate of Hesperidene.* The portion which solidifies when the oil is saturated with hydrochloric acid gas. In crystalline form and odour it resembles bihydrochlorate of lemon-oil. Melts at 50°. Has no rotatory power. (Soubeiran & Capitaine.)

			Soubeiran & Capitaine.
20 C	120	57·5	57·95
18 H	18	8·6	8·61
2 Cl	71	33·9	33·44
$C^{20}H^{16},2HCl$	209	100·0	100·00

It decomposes as easily as bihydrochlorate of lemon-oil. (Soubeiran & Capitaine.)

Oil of orange-peel dissolves in *absolute alcohol,* and with turbidity in 7 — 10 pts. of alcohol of sp. gr. 0·85. (Zeller.)

18. Oil of China Orange.

Völkel. (1840.) *Ann. Pharm.* 39, 120; *Repert.* 80 164.

Apfelsinenöl.

Source and Extraction. In the rind of *Citrus aurantium sinensis.* It is obtained by pressing the fresh lacerated rind or distilling it with water.

			Völkel.
20 C	120	88·24	88·38
16 H	16	11·76	11·74
$C^{20}H^{16}$	136	100·00	100·12

19. Oil of Parsley.

Löwig & Weidmann. (1841.) *Pogg.* 46, 53; abstr. *Repert.* 70, 163.
Zeller. *Stud. über. äther. Oele; Landau,* 1850.

Petersilienöl, Essence de persil, Oleum petroselini.

Source and Extraction. In parsley-seeds, the fruit of *Apium petroselinum.* — The bruised seeds are distilled with water, and the more volatile oil which first passes over is collected. At the same time there passes over a less volatile oil, which solidifies to parsley-camphor. (Lowig & Wiedmann, *inf.*) The watery distillate must be kept for some time in the cold, in order to obtain the oil which then only separates from it. (Schutz, *Repert.* 15, 275.)

Properties. Greenish yellow oil; after rectification, colourless, transparent, and mobile. The crude oil boils above 210°, the rectified oil between 160° and 170°. (Löwig & Wiedmann.) It solidifies between 2° and 8°. Sp. gr. 1·015 — 1·144. (Zeller.) Smells like parsley. (Löwig & Wiedmann.) Neutral. (Zeller.)

			Löwig & Weidmann.
20 C	120	88·24	88·04
16 H	16	11·76	11·88
$C^{20}H^{16}$	136	100·00	99·92

Decompositions. 1. The crude oil thickens by boiling, finally becoming resinous, and when distilled *per se* or with water, is resolved into liquid oil which passes over and camphor which remains behind. (Löwig & Weidmann.) — 2. *Iodine* dissolves slowly in the heated oil, and colours it brown-red. (Flaschoff, *Br. Arch.* 33, 225.) It detonates with iodine, giving off yellow and violet vapours, and is converted into a dark red-brown resin. (Winkler, *Repert.* 32, 271.) — 3. *Nitric acid* colours it yellow or brown, and resinises it (Zeller); forms malic and oxalic acids. (Scheele, *Opusc.* 2, 206.) *Oil of vitriol* colours it violet to dark red, without thickening it (Zeller); the solution mixed with water deposits resin. (Bley.) It absorbs *hydrochloric acid gas,* with rise of temperature, and turns brown. (Löwig & Weidmann.)

Oil of parsley dissolves in 2·5 pts. *alcohol* of sp. gr. 0·85. (Zeller.)

20. Oil of Pepper.

Lucae. *Taschenbuch,* 1822, 81.
Dumas. *J. Chim. méd.* 11, 308; *Instit.* 97; *J. pr. Chem.* 4, 435.
Soubeiran & Capitaine. *J. Pharm.* 26, 75; abstr. *Ann. Pharm.* 34, 326.

Pfefferöl, Essence de poivre, Oleum piperis.

Source and Extraction In black pepper, the unripe berries, and in white pepper, the seed of *Piper nigrum,* (*L.*) Bruised black pepper is distilled with water; and the oil which passes over is rectified with salt-water, and dehydrated by agitation with chloride of calcium. (Soubeiran & Capitaine.) Black pepper yields 1·17, white pepper, 1·04 p. c. of oil. (Lecann.)

Properties. Limpid and mobile. Sp. gr. 0·993 (Lucae); 0·864. Boiling point 167·5°, ultimately rising to 170°. Vapour-density = 4·74. Calculated 4·714 (p. 245). (Soubeiran & Capitaine.) Has a strong smell of pepper and a mild taste. (Lucae.)

			Dumas.
20 C	120	88·23	87·9
16 H	16	11·77	11·7
$C^{20}H^{16}$	136	100·00	99·6

Decompositions. 1. By a few drops of *oil of vitriol,* it is heated and blackened; but when dropt into a large quantity of oil of vitriol, it forms a red brown solution of sulphoterebic acid. (Gerhardt, *Compt. rend.* 17, 314.) — 2. When saturated with dry *hydrochloric acid gas,* it turns brown, and forms hydrochlorate of pepper-oil. (Soubeiran & Capitaine.) — 3 When set aside or heated with *potassium,* it acquires an odour recalling that of pepper and of lemons. (Gerhardt, *Compt. rend.* 17, 315; *N. Ann. Chim. Phys.* 14, 114.)

Combinations. With Hydrochloric Acid. Hydrochlorate of Pepper-oil. — The oil is completely saturated with dry hydrochloric acid gas, and filtered through charcoal, which is completely covered with a layer of chalk. Colourless liquid, containing 62·69 p. c. C, 8·80 H, and 28·51 Cl, and therefore approximating in composition to the formula $C^{25}H^{20},2HCl$. (Soubeiran & Capitaine.)

21. Pepper-oil from Long Pepper.

DULONG. *J. Pharm.* 11, 59; *N. Tr.* 11, 1, 104.

In long pepper, the monospermic-berry-carrying flower-stalks of *Chaviea Roxburghii* and *Ch. officinarum.* (Dulong) They are bruised and distilled with water. — Limpid, lighter than water, with an unpleasant odour and sharp taste.

22. Oil of Peucedanum Oreoselinum.

SCHNEDERMANN & WINCKLER. *Ann. Pharm.* 51, 336.

Source and Extraction. By distilling the fresh herb of *Peucedanum Oreoselinum* with water.

Properties. Has a strong aromatic odour like that of juniper. Sp. gr. 0·840, and boiling point 163°.

			Schnedermann & Winckler. a.	b.
20 C	120	88·23	88·36	87·50
16 H	16	11·77	11·84	11·79
$C^{20}H^{16}$	136	100 00	100·20	99·29

a the first portion of the distillate; *b* the last.

Combinations With Hydrochloric Acid. The first portion of the distillate above-mentioned absorbs hydrochloric acid gas abundantly, and is thereby converted into a compound analogous to monohydrochlorate of turpentine-oil (p. 265). The oil cooled to 0° is saturated with hydrochloric acid gas; the resin which separates is removed, and the oil is shaken up with soda-solution, distilled with water, and dried over chloride of calcium.

Colourless liquid, gradually turning brown. Lighter than water; boils at about 190°; smells like turpentine.

			Schnedermann & Winckler.
20 C	120·0	69·6	69·54
17 H	17·0	9·9	9·71
Cl	35·5	20·5	20·86
$C^{20}H^{16},HCl$	172·5	100·0	100·11

23. Hydrocarbon from Oil of Chamomile.

GERHARDT. (1848.) *Compt. rend.* 26, 225; *N. J. Pharm.* 14, 52; *N. Ann. Chim. Phys.* 24, 96; *J. pr. Chem.* 45, 321; *Ann. Pharm.* 67, 235.

Oil of chamomile obtained by distilling the flowers of *Anthemis nobilis,* is a mixture of a non-oxygenated oil with angelic aldehyde and a small quantity of angelic acid (x, 413). When it is heated in a retort with pulverised hydrate of potash, and the oil which passes over is rectified over potassium, angelate of potash remains behind (easily resolved by excess of potash at a higher temperature into acetate and propionate of potash (Chiozza, *N. Ann. Chim. Phys.* 39, 435; *J. pr. Chem.* 61, 231; *Ann. Pharm.* 86, 261), and an oil is obtained, having an agreeable odour of lemons, boiling at 175°, and containing 87·8 p. c. C and 11·8 H, therefore isomeric with oil of turpentine. This oil does not form with oil of vitriol a compound analogous to sulphocymenic acid (p. 188), but it unites with chloride of calcium, forming crystals which are decomposed by water. The same oil is obtained by distilling oil of chamomile with alcoholic potash, mixing the alcoholic distillate with water, and syphoning off the oil which separates. (Gerhardt.)

Crude oil of chamomile is blue (Dehne, *Crell. chem. J.* 3, 25; Zeller), greenish, and distils to ⅘ between 180° and 190°, the remaining ⅕ passing over between 190° and 210°; the latter portion contains 76·06 p. c. C, 10·67 H, and 13·27 O. (Gerhardt.) The fresh flowers yield 0·31 p. c. oil (Hagen), 0·047 (Lecanu); the dry flowers, 0·08 p. c. (Lecanu), 0·61 p. c. (Hagen); and the water which passes over contains in solution, acetic, butyric, valerianic, and perhaps propionic acid. (Wunder, *J. pr. Chem.* 64, 499; Hautz, *J. pr. Chem.* 62, 317.)

24. Oil of Savin.

Dumas. (1835.) *J. Chim. méd.* 11, 307; *Ann. Pharm.* 15, 158; *J. pr. Chem.* 4, 435.
Laurent. *Rev. Scient.* 10, 127.
Zeller. *Stud. über äther. Oele; Landau,* 1850.

Sadebaumöl, Sevenbaumöl, Sabinaöl; Essence de Sabine; Oleum Sabinæ.

Source and Extraction. In the leaves, young branches, and twigs of *Juniperus sabina* (*L.*). They are cut to pieces while fresh, and distilled with water.

Properties. Pale to dark reddish yellow (Zeller); limpid after rectification. (Dumas.) Sp. gr. 0·89 — 0·94 (Zeller.) Boils at 155° — 161°. (Dumas.) Smells and tastes like the leaves and branches of the plant. Neutral. (Zeller.)

			Dumas.
20 C	120	88·23	88·6
16 H	16	11·77	11·7
$C^{20}H^{16}$	136	100·00	100·3

Decompositions. 1. When it is mixed with $\frac{1}{5}$ vol. water, and *bromine* is gradually added to it, the oil becomes heated, destroys the colour of the bromine, till 185 pts. of bromine have been added to 100 pts. of the crude oil, or 211·3 pts. bromine to 100 pts. of the rectified oil, and is converted into a colourless aromatic oil. (Williams, *Chem. Gaz.* 263, 365; *J. pr. Chem.* 61, 20.) — 2. With *iodine*, it becomes very strongly heated, detonates, gives off yellow and violet-red vapours, and forms a red-brown resinous mass, having the consistence of honey (Flaschoff, *Br. Arch.* 33, 225; Winckler, *Repert.* 32, 271; Zeller), and an empyreumatic odour. (Winckler.) Iodine dissolves, with rise of temperature, in an equal quantity of oil of savin, forming a red-brown solution which, when distilled to dryness, gives off a large quantity of hydriodic acid, and yields a distillate consisting of a brown oil, and finally of a balsam, which sinks to the bottom, while charcoal remains behind. (Guyot, *J. Phys.* 5, 230.) — 3. With *nitric acid*, it gives off gas with violence, becomes hot, and assumes a reddish-yellow to brownish-yellow colour. — 4. With *oil of vitriol*, it turns yellowish red (Hesse, Zeller); mixed with an equal quantity of oil of vitriol, and distilled with hydrate of potash, it yields 4 p. c. of an oil smelling like thyme. (Winckler, *Repert.* 92, 320) — 5. With *bichromate of potash* and *oil of vitriol* it assumes a pale brownish colour. (Zeller.) — 6. Distilled with 24 pts. of water and 8 pts. of *chloride of lime*, it gives off carbonic acid with effervescence, and yields *chloroform*. — 7. By distillation with *hypobromite of lime*, it yields bromoform. (Chautard, *Compt. rend.* 34, 485.)

Combinations. Oil of savin dissolves in all proportions of *absolute alcohol;* clearly in 2 pts. alcohol of sp. gr. 0·85; with opalescence in 3 pts. or more. (Zeller.)

25. Thymene.

DOVERI. *N. Ann. Chim. Phys.* 20, 174.
LALLEMANDE. (1853.) *Compt. rend.* 37, 433; *J. pr. Chem.* 60, 433; *N. Ann. Chim. Phys.* 49, 155; abstr. *Ann. Pharm.* 101, 119; 102, 119.
STENHOUSE. *Ann. Pharm.* 98, 308.

First observed by Doveri; obtained pure by Lallemand.

Source and Extraction. In volatile oil of thyme. It forms, together with cymene, the more volatile part of that oil. (Lallemand.)

Preparation. The portion of oil of thyme which passes over on fractional distillation between 166° and 185°, is repeatedly rectified over caustic potash, then *per se*, whereupon thymene passes over from 160° to 165°, and cymene at 175°. The process does not, however, afford a complete separation of the cymene, which has hitherto not been attained. (Lallemand.)

Properties. Colourless oil, having an agreeable odour of thyme, boiling at 160° — 165°, and of sp. gr. 0·868 at 20°. It deflects polarised light to the left, but less strongly after repeated rectification over caustic potash. (Lallemand.)

It dissolves in *oil of vitriol*, with rise of temperature, and yields by distillation the same products as oil of turpentine.

It absorbs *hydrochloric acid gas*, with slight rise of temperature, and forms a compound which remains liquid at — 20°, and, after purification with chalk and animal charcoal, contains 20 p. c. chlorine. (Lallemand.)

Doveri obtained by the fractional distillation of oil of thyme, a product boiling between 178° and 180°, which contained on the average 85·8 p. c. carbon, 10·9 hydrogen, and 3·3 oxygen, but had a vapour-density = 8·314, whence he regarded it as a mixture of a hydrocarbon with thymol. This substance was scarcely attacked by anhydrous phosphoric acid, merely becoming slightly heated, and after two distillations therewith, still contained 86 p. c. C, 11·4 H, and 3·6 O. It absorbed hydrochloric acid gas with avidity, becoming coloured and heated, and yielding, after the excess of hydrochloric acid had been driven out by a stream of dry carbonic acid, a thin red-brown liquid, which had an agreeable odour of camphor, solidified while immersed in a freezing mixture, and in which crystals made their appearance after the lapse of a month.

From the volatile oil of the seeds of *Ptychotis Ajowan,* Stenhouse obtained by fractional distillation, dehydration with chloride of calcium of the portion which passed over below 176°, distillation over caustic potash, treatment with sodium, and rectification, a colourless strongly refracting oil, having a pungent, aromatic odour, different from that of oil of thyme, of sp. gr. 0·854 at 12°, and boiling at 172°. It formed with hydrochloric acid gas, a brown, thin liquid. It contains 88·24 p. c. C, and 11·5 H, and is therefore $C^{20}H^{16}$ (and perhaps identical with Lallemand's thymene, Kr.) According to Haines, it is $C^{20}H^{14}$, therefore cymene (*Ann. Pharm.* 98, 315). See page 184.

26. Tolene.

DEVILLE. (1841.) *N. Ann. Chim. Phys.* 3, 154 ; *J. pr. Chem.* 25, 323.
E. KOPP. *Compt. chim.* 1849, 145 ; abstr. *Compt. rend.* 24, 614 ; *N. J. Pharm.* 11, 425.

Source. In balsam of tolu.

Preparation. 4 pts. of tolu-balsam are distilled with 3 pts. of water, and the distillate is repeatedly cohobated. The oil which passes over is a mixture of benzoic acid, cinnamein (xiii, 283), and tolene, which passes over when the crude oil is heated for some time to 160°, and may be obtained pure by frequent rectification over hydrate of potash (containing a sufficient quantity of water to keep it in the liquid state) and collecting the portion which first goes over (the latter portion which distils at 180° contains 84·90 p. c. carbon, 11·83 hydrogen, and 3·27 oxygen. (Deville.)

Properties. Colourless mobile oil, boiling from 154° to 160° (Kopp), at 170° (Deville), and of sp. gr. 0·858. (Kopp.) It has a sharp, pungent, peppery taste, and smells like elemi-resin, different from tolu-balsam. (Kopp.) Vapour-density somewhat below 5·71 (Deville) (by calculation 4·714 ; see page 245.)

			Deville. *mean.*	Kopp. *mean.*
20 C	120	88·23	88·60	88·40
16 H	16	11·77	11·33	11·45
$C^{20}H^{16}$	136	100·00	99·93	99·85

According to Deville, it is $C^{24}H^{18}$ (calculation 88·9 p. c. C, 11·11 H), which agrees better with the analysis, but not with the boiling point.

In vessels containing air, it becomes continually thicker, without colouring, and is finally converted into a soft oxidised resin, containing 75·2 p. c. carbon. (Kopp.)

27. Valerene or Borneene.

GERHARDT & CAHOURS. (1841.) *N. Ann. Chim. Phys.* 1, 62.
PELOUZE *Compt. rend.* 11, 365 ; abstr. *J. Pharm.* 26, 645 ; *J. pr. Chem.* 22, 379 ; *Ann. Pharm.* 40, 326.
GERHARDT. *N. Ann. Chim. Phys.* 7, 275 ; *Ann. Pharm.* 45, 29 ; abstr. *Compt. rend.* 14, 832 ; *J. pr. Chem.* 27, 124.
JEANJEAN. *Compt. rend.* 42, 857 ; *Instit.* 1856, 176 ; *J. pr. Chem.* 69, 204 ; *Ann. Pharm.* 101, 94 ; *Chem. Centralbl.* 1856, 575.
PIERLOT. *N. Ann. Chim. Phys.* 56, 291.

The non-oxygenated constituent of volatile oil of valerian, Gerhardt's Borneene, and Pierlot's Valerene, is, according to Gerhardt, identical with the hydrocarbon of the camphor-oil examined by Pelouze, and with the hyrocarbon which that chemist obtained from borneol by the action of anhydrous phosphoric acid ; according to Jeanjean, it is identical with the hydrocarbon of madder fusel-oil. The identity of these bodies being doubtful, we shall in the following distinguish as valerene the hydrocarbon from oil of valerian, as borneene that from oil of camphor, and as madder-borneene that from madder fusel-oil. (Kr.)

A. *Valerene from Oil of Valerian.* — Oil of valerian obtained by distillation with water, the root of *Valeriana off.* is a mixture of valerianic acid, valerol (xi, 396), valerene (borneene, according to Gerhardt), and borneol, gradually formed therefrom by the action of the air. If the portion which passes over first in the fractional distillation be rectified over fused hydrate of potash, whereby the valerol is converted into valerate of potash, a mixture of borneol and valerene is obtained, from which the borneol may be entirely removed by repeated fractional distillation, the product which passes over first being each time collected apart. (Gerhardt.) — Oil of valerian is a mixture of 5 pts. valerianic acid, 25 pts. valerene and 70 pts. valerol, which last (different from Gerhardt's valerol) contains $\frac{5}{70}$ water, $\frac{47}{70}$ resin, and $\frac{18}{70}$ valerian-camphor, or is resolved into these constituents by distillation. Valerian-oil when distilled gives off between 120° and 200° an acid yellow oil which, when rectified over fused hydrate of potash, yields valerene below 200°, while valerate of potash and Pierlot's valerol remain in the residue. (Pierlot.)

Properties of Valerene. Colourless oil, boiling at 160° under a pressure of 0·76 met. Vapour-density 4·60 (by calculation = 4·7144, p. 245). Lighter than water. Smells like oil of turpentine, but more agreeably. (Gerhardt, Pierlot.)

			Gerhardt.
20 C	120	88·23	88·08
16 H	16	11·77	11·86
$C^{20}H^{16}$	136	100·00	99·94

Decompositions. 1. It is not converted into camphor by dry *oxygen.* — 2. In contact with excess of *bromine,* it gives off hydrobromic acid, and becomes yellow and viscid. — 3. It absorbs *hydrochloric acid gas* and becomes crystalline. — 4. *Nitric acid* does not act upon it in the cold, but attacks it violently when heated. If the valerene is free from borneol, no common camphor is produced, though Gerhardt formerly obtained this substance by the action of nitric acid from valerene containing borneol, and supposed that it was produced from the borneol. — 5. It is not altered by melting *hydrate of potash,* but when set aside for some time with potash-ley and then distilled, it is converted, wholly or partially, into borneol, especially in presence of alcohol. (Gerhardt.)

B. *Borneene from the Camphor-oil of Dryabalanops Camphora.* — The younger stems of the camphor-tree (*Dryabalanops Camphora*), which grows in Borneo and Sumatra, contain oil of camphor, which exudes from incisions made in them, whereas the older stems are destitute of oil, but contain borneol in their cavities (Pelouze ; comp. also Martius, *Ann. Pharm.* 27, 63 ; Blanchet & Sell, *Ann. Pharm.* 6, 302). In the natural state, it contains a resin in solution, from which it may be freed by distillation. (Pelouze.)

Oil, of lower specific gravity than water, boiling at 165°, having an odour of turpentine-oil, and isomeric therewith. Rotatory power 39·8° to the left. (*Compt. rend.* 11, 371.) It absorbs oxygen gas with avidity, and is thereby converted into $C^{20}H^{16}O^4$, without forming carbonic acid. (Pelouze.) Pelouze does not state that he obtained common camphor in this manner, though Gerhardt (*N. Ann. Chim. Phys.* 7, 282), attributes this statement to him. Kr.) — It absorbs as much hydrochloric acid as oil of turpentine. (Pelouze, *Compt. rend.* 11, 367; abstr. *Ann. Pharm.* 40, 326.)

Camphor-oil from Laurus camphora. Martius (*Ann. Pharm.* 27, 63) examined camphor-oil imported from China, which, according to his later statements (*N. Repert.* 1, 541), was obtained from *Laurus camphora.* As this tree yields common camphor, but not borneol, the camphor-oil obtained from it was probably different from that of the *Dryabalanops camphora* examined by Pelouze, which is associated with borneol; and it is doubtful whether the camphor dissolved in the camphor-oil which Martius examined was common camphor, or borneol (as supposed by Gerhardt, *N. Ann. Chim. Phys.* 7, 284), since, in 1838, the distinctive characters of the two kinds of camphor were not known with certainty. Commercial, dark wine-yellow camphor-oil, of sp. gr. 0·945, is a mixture which deposits a large quantity of camphor by cooling or spontaneous evaporation. When subjected to fractional distillation, it leaves, after $\frac{1}{3}$ has passed over, a residue which contains a larger quantity of camphor and solidifies on cooling, while the distillate, on being redistilled till $\frac{1}{10}$ has passed over, yields rectified camphor-oil free from camphor. This oil is transparent, colourless, strongly refracting, mobile, smells like camphor and cajeput-oil, and has a density of about 0·91. It contains 82·03 p. c. C, 11·35 H, and 6·62 O, and according to Martius is $C^{20}H^{16}O$.

Rectified camphor-oil evaporated in a watch-glass leaves resin but no camphor. It does not appear to take up oxygen, but absorbs dry hydrochloric acid gas, with rise of temperature, forming a wax-yellow liquid, which fumes from excess of hydrochloric acid, and when cooled to — 8°, solidifies to a soft butter, without depositing crystals. When dry chlorine gas is passed through the rectified oil, it assumes a transient ruby-red colour, gives off hydrochloric acid, and forms, after washing with water, an oil similar to that produced by hydrochloric acid.

Rectified camphor-oil (probably that of Martius, Kr.) is $C^{20}H^{16}O$, and is converted into camphor by nitric acid. (Macfarlane, *Ann. Pharm.* 31, 72.)

In light yellow camphor-oil of unknown origin, which yielded no camphor when distilled alone, and only traces when distilled with water, Mulder (*J. pr. Chem.* 17, 106; *Ann. Pharm.* 31, 71) found, after drying over chloride of calcium, 80·41 p. c. C, 10·84 H, and 8·75 O, and accordingly regarded it as a mixture of common camphor and a non-oxygenated oil, $C^{20}H^{16}$.

C. *Madder Borneene from Madder Fusel-oil.* — The fusel-oil contained in the alcohol produced by the fermentation of madder-sugar yields liquid products when distilled at temperatures rising to 230°, while at higher temperatures lævo-rotatory borneol sublimes. From the former, by digestion with caustic potash, then with chloride of calcium, and repeated fractional distillation, a liquid may be separated which boils at 160°, contains 88·23 p. c. C, and 11·81 H, has a vapour-density of 4·85, and is probably therefore borneene $C^{20}H^{16}$. (Jeanjean.) — Lævo-rotatory borneol from madder fusel-oil yields by distillation with anhydrous phosphoric acid, a hydrocarbon smelling like oil of bergamot and oil of lemon (Jeanjean), which, according to Gerhardt's statements (p. 313), should be identical with madder borneene.

Appendix to Valerene.

1. *Crude Oil of Valerian.* Constituents (pp. 312, 313.) According to the (older) statements of Kraus, it is an oxide of oil of turpentine $C^{30}H^{24}O$; according to Ettling (*Ann. Pharm.* 9, 40) it is a mixture of oxygenated

and non-oxygenated oil. — According to Hurault (*N. J. Pharm.* 12, 96), the oil does not exist in the root ready-formed, inasmuch as ether does not extract any of it, but is produced from the root by the action of water. The same view is maintained by Bouchardat, but Pierlot considers it erroneous.

Properties of the crude oil. — Mobile oil, of pale yellow, or greenish to yellowish brown colour. (Trommsdorff, *N. Tr.* 18, 1, 3.) The root of the plant growing in woods yields a green oil, that which grows in marshes a yellow oil. (Pierlot.) Roots a year old yield 1·82 p. c. of oil (Bley, *Repert.* 48, 84). Sp. gr. 0·90 to 0·96 (Zeller); 0·936 at 10°. (Pierlot.) It does not solidify at −40°, but at −15° it deposits white flocks of valerianic acid. (Pierlot.) Its odour is fresh and agreeable, strong and pungent, like camphor, It is neutral, either in the fresh or in the rectified state (Gerhardt); acid (Zeller, Pierlot, and others). It is resolved into its constituents by distillation, as described at page 313.

Oil of valerian resinises when exposed to the *air*, acquiring an unpleasant odour, and forming valerianic acid, in consequence of its containing valerol. (Gerhardt.) After the ready-formed valerianic acid in the valerian-oil has been removed, it is not possible by any means to obtain an additional quantity of that acid from the oil. — When oil of valerian is exposed to the air, the greater part of the non-oxygenated oil, of the valerianic acid, and of the water escapes, and the oxygenated oil becomes resinised. (Pierlot.) — It dissolves *iodine* with evolution of heat, giving off a small quantity of greyish yellow vapours, and acquiring a dark red-brown colour. (Zeller.) — With $\frac{1}{6}$ pt. of *nitric acid* at 24°, it turns violet (Bonastre, *J. Pharm.* 12, 66); blue, afterwards yellow, acquires a viscid consistence (Rochleder), and forms oxalic acid. (Bonastre.) According to Rochleder, it does not form oxalic acid, but on distilling the mixture, it gives off nitrous acid, and forms common camphor precipitable by water, a volatile substance which attacks the eyes strongly, a less volatile body which reddens potash-ley, and a fixed yellow resin. — When oil of valerian is heated with nitric acid, a blue resin is formed, heavier than water, insoluble in alcohol and in potash-ley, and similar to that which exists in the root ready-formed. (Pierlot.)

With *oil of vitriol*, it turns dark brown-red to violet; with *bichromate of potash and oil of vitriol*, greenish. (Zeller, *Studien uber äther. Oele*, Landau, 1850.) Oil of valerian treated with potash-ley, yields a resin and a neutral oil which forms common camphor with nitric acid. (Rochleder, *Ann. Pharm.* 44, 1.) It does not form any compound with caustic potash or soda. (Pierlot.)

Oil of valerian dissolves in an equal quantity of *alcohol* of sp. gr. 0·85, and in every proportion of absolute alcohol. (Zeller.)

28. Xanthoxylene.

STENHOUSE. (1858.) *Pharm. J. Trans.* 17, 19; *Ann. Pharm.* 104, 236; *J. pr. Chem.* 73, 179; *Chem. Centralbl.* 1858, 237.

Source and Extraction. In the seed of Spanish pepper (*Xanthoxylum piperitum, Dec.*). — The bruised seeds are distilled with water; the oil, mixed with solid xanthoxylin, is collected and cooled, the separated xanthoxylin is removed by filtration, and the oil is dehydrated with chloride of calcium and rectified over potash, then over potassium.

Properties. Colourless, strongly refracting. Boils at 162°. Has an agreeably aromatic and persistent odour.

			Stenhouse.
20 C	120	88·23	88·08
16 H	16	11·77	11·60
$C^{20}H^{16}$	136	100·00	99·68

Xanthoxylene forms a liquid compound with hydrochloric acid. (Stenhouse.)

Appendix to Oils Isomeric with Oil of Turpentine.

(Oil of Wormseed and its Products of Decomposition.)

Oil of Wormseed.

Trommsdorff. (1819.) *N. Tr.* 3, 1, 312.
Völckel. *Ann. Pharm.* 38, 110; abstr. *Repert.* 80, 176. — *Ann. Pharm,* 87, 312; abstr. *J. pr. Chem.* 61, 515. — *Ann. Pharm.* 89, 358.
Zeller. *Stud. über äther. Oele,* Landau, 1850.
Hirzel. *Zeitschr. f. Pharm.* 1854, 3; 17; 65; 80. — Ibid. 1855, 2; 33; 49; 65; 81; 98; 114; 130; 144; 161; 179.

Wurmsamenoel, Oil or Essence of Semen contra, Oleum cinæ.

Source and Extraction. In Levant and Barbary wormseed, the unexpanded flower-buds of *Artemisia Vahliana Kosteletzky, Artemisia contra Vahl,* and *Artemisia Siberi.* — It is obtained by distilling the bruised wormseed with water. — The water which passes over with the oil contains acetic acid. (Wunder, *J. pr. Chem.* 64, 499.)

Properties. Transparent and colourless to pale yellow (Trommsdorff and others); pale yellow to brownish yellow. (Zeller.) The crude oil is brownish yellow; that which is obtained by distilling the seeds with milk of lime, and boils between 160° and 170°, is transparent and colourless (Hirzel); after distillation over hydrate of potash, it boils at 180°, and is transparent and colourless. (Völkel.) — Mobile (the crude oil is slightly viscid). (Hirzel.) — Sp. gr. 0·9258 at 11° (Wackenroder, *Kastn. Arch.* 11, 78; *N. Tr.* 14, 2, 3); 0·936 (Völkel); 0·92—0·93 (Zeller); 0·946 at 11°. (Hirzel.) — The oil rectified over hydrate of potash, and boiling between 175° and 180°, has a sp. gr. of 0·919 at 20° (Völkel); that which is obtained from the seeds by distillation with milk of lime has a sp. gr. of 0·945 at 8°. (Hirzel.) — Boiling point of the crude oil, 170°—220° (Völkel); 175°—180° (Hirzel); of the rectified oil, 175°. (Hirzel.) The oil treated with alcoholic potash and then distilled with water, boils at 175° (Völkel); that which is obtained from the seed by distillation with milk of lime, begins to boil at 160°, boils chiefly between 175° and 177°; after rectification, between 174° and 175. (Hirzel.) — It smells like the seeds (Hirzel); more like camphor than the seeds (Trommsdorff); wormseed oil from Baltimore smells more like chenopodium. (Buchner, *Repert*, 12, 438.) Its taste is sharp and somewhat bitter (Trommsdorff); burning and aromatic. (Wackenroder.) It reddens litmus (Zeller); is neutral. (Hirzel.)

			Völckel.			Hirzel.	
			a.	*b.*	*c.*	*d.*	*e.*
24 C	144	80·00	78·44	77·89	79·83	78·92	78·49
20 H	20	11·11	10·65	10·58	11·31	11·43	11·40
2 O	16	8·89	10·91	11·53	8·86	9·65	10·11
$C^{24}H^{20}O^2$	180	100·00	100·00	100·00	100·00	100·00	100·00

a the first; *b* the last distillate corresponding to the formula $C^{18}H^{15}O^2$ (Völkel); the first distillate corresponds to the formula $C^{10}H^7O$, according to which 3 At. oil = $C^{30}H^{21}O^3$, by giving up 3 At. H and taking up 3 At. O, forms santonin $C^{30}H^{18}O^6$ (Heldt, *Ann. Pharm.* 63, 55); *c*, the oil rectified over hydrate of potash, corresponds to the formula $C^{24}H^{20}O^2$; *d.* oil obtained from the seeds by distillation with water; *e.* with milk of lime; the former corresponds to the formula $C^{22}H^{19}O^2$, the latter to the formula $C^{20}H^{18}O^2$. (Hirzel.)

Wormseed oil is mixed with another oil which changes even by distillation (Völkel); it is a mixture of cinæbene, cinæbene-camphor, a small quantity of propionic acid, and oxide of propyl, the differences in its properties being due to the varying proportions of their constituents. (Hirzel.)

Decompositions. 1. When *set on fire*, it burns with a clear luminous flame. (Völkel, Hirzel.) — 2. It dissolves *iodine* quickly, without evolution of vapour or rise of temperature, forming a yellowish red-brown, viscid mass (Zeller); it dissolves $\frac{1}{6}$ to $\frac{1}{4}$ of iodine, with rise of temperature, and is converted into a dark brown-red, viscid, opaque, stinking liquid, which, on cooling, deposits black crystalline laminæ, apparently consisting of iodine and cinæbene. (Hirzel.) Water shaken up with the solution of iodine in wormseed-oil extracts from it acetic, propionic, and hydriodic acids, together with a substance smelling like opium, probably iodide of propyl. The solution of iodine in wormseed-oil gives off when distilled, aqueous propionic acid, hydriodic acid, iodoform, and especially a mobile, dark brown, peculiar-smelling oil, consisting chiefly of cinæbene-camphor, cinæbene and cymene, together with hydriodic acid both dissolved and chemically combined, also hydriodate of cinæbene, and small quantities of angelic acid and cinacrol, whilst there remains a solid, blue-black, easily inflammable body which burns, though very slowly, with a clear, luminous flame, and consists of cinæphene, cinæphone, and cinæphane. — 3. With *nitric acid*, it acquires a reddish yellow colour (Zeller), and when heated therewith gives off gas with violence, and is converted into a yellow resinous mass insoluble in water (Zeller, Völkel); with dilute nitric acid, it forms oxalic acid (Völkel); heated in small quantities with nitric acid, it forms toluylic acid, a small quantity of oxalic acid being formed only when strong nitric acid is used. (Hirzel.) — 4. With *oil of vitriol*, it acquires a red-brown colour (Zeller), becomes hot and viscid, and after some time gives off sulphurous acid. (Völkel.) — 5. It absorbs *hydrochloric acid gas*, and when saturated therewith forms a dark red oil, which on cooling deposits crystals of wormseed-oil camphor. (Völkel, Hirzel.) — 6. Heated with *anhydrous phosphoric acid*, it forms a black mass, which on boiling yields as, liquid products, aqueous propionic acid, cinæbene, cinæphene and cinacrol (Hirzel); it becomes partially resinised, viscid, and is converted into cynene. (Völkel.) — 7. Distilled with *hydrate of potash,* it yields a mobile, limpid oil having an agreeable odour (like oil of peppermint, according to Völkel), and a warm burning taste; easily inflammable, burning with a clear flame, having a sp. gr. of 0·93, consisting of an equal number of atoms of cinæbene, cinæbene-camphor and a compound containing $C^{10}H^8O$, with ½ At. propione, and boiling at 175°—176°·5. Hydrochloric acid gas colours this oil red, and forms with it, shining very deliquescent needles. Oil of vitriol renders it viscid and dark brown, and when heated with it, gives off sulphurous acid; nitric acid converts it into liquid volatile products and fixed resinous products; distilled with anhydrous phosphoric acid, it gives off propionic acid, an oil consisting of 4 At. cymene, 2 At. cinæbene, and 1 At. cinæbene-camphor, together with smaller quantities of cinæphene and cinacrol. (Hirzel.)

Combinations. With Hydrochloric Acid. Wormseed-oil camphor. — Obtained by passing dry hydrochloric acid gas into wormseed-oil, cooling the saturated red oil, and pressing the separating crystalline mass between filtering paper. — Colourless slender needles. Odour aromatic, like that of camphor; taste mild and warming. When exposed to the air, it deliquesces and takes up water (Volkel); without taking up water (Hirzel). When heated, it melts into a nearly colourless oil, which gives off hydrochloric acid by distillation. Deliquesces quickly when covered with *water.* (Volkel, Hirzel.)

Wormseed-oil dissolves in 1000 pts. of *water,* readily in *alcohol* and *ether* (Trommsdorff), in every proportion of *absolute alcohol,* and in an equal quantity of alcohol of sp. gr. 0·85. (Zeller.)

Cinæphane. $C^{20}H^8$.

HIRZEL. (1855.) *Zeitschr. J. Pharm.* 1855, 163, 182.

Formation. By distilling wormseed-oil with iodine (p. 317).

Preparation. The thick brown liquid produced by dissolving iodine in wormseed-oil is distilled, and the resulting brown oil is heated to above 360°, whereby a distillate is obtained, consisting chiefly of cinæbene-camphor, cinæbene, cinacrol, and cymol, while a mixture of cinæphane, cinæphene, and cinæphone remains behind. The residue well boiled with alcohol, gives up cinæphene to that solvent, and after the adhering alcohol has been evaporated, is itself soluble in chloroform. On mixing this solution with 20 pts. of alcohol of sp. gr. 0·84, it deposits a resin, which, after washing with hot alcohol and water, is a mixture of cinæphane and cinæphone. The latter is dissolved out by ether, and the residual cinæphane is purified by solution in chloroform, preparation with alcohol, and washing with ether. The cinæphone is precipitated from the ethereal solution by alochol.

Properties. Very soft, loose, nearly velvet-black powder, without taste or smell.

			Hirzel.
20 C	120	93·75	93·29
8 H	8	6·25	6·40
$C^{20}H^8$	128	100·00	99·69

Decompositions and Combinations. Cinæphene, when *heated*, burns away with a glimmering light, without melting or leaving any residue. It dissolves in *chloroform*, but not in *ether*. (Hirzel.)

Cinæphone. $C^{20}H^{12}$.

HIRZEL. (1855.) *Zeitschr. J. Pharm.* 1855, 163, 182.

Formation. By distilling wormseed-oil with iodine (p. 317).

Properties. Soft, loose, light, kermes-brown powder, which adheres strongly to glass, to paper, and to the fingers; tasteless and inodorous. It has not been obtained quite free from iodine.

Decompositions and Combinations. When *heated*, it melts to a black mass, gives off empyreumatic vapours, and leaves a light charcoal which burns away easily and completely. When *set on fire*, it burns with a yellow non-fuliginous flame, leaving a large quantity of pure charcoal. It dissolves readily in *chloroform*, *ether*, and *wormseed-oil*, but is insoluble in *water*, *alcohol*, and *aqueous alkalis*. (Hirzel.)

Cinæbene. $C^{20}H^{16}$.

HIRZEL. (1854.) *Zeitschr. f. Pharm.* 1854, 7, 67.—1855, 52; 68, 82; 147; 182.

Source. In wormseed-oil, together with cinæbene-camphor, and small quantities of propionic acid and oxide of propyl.

Formation. By distilling wormseed-oil with anhydrous phosphoric acid, whereby the cinæbene-camphor is dehydrated.

Preparation. By distilling wormseed-oil with anhydrous phosphoric acid in a retort, so long as, together with aqueous products, a light oil passes over with brisk but ultimately quiet ebullition, and till only a small quantity of oil remains mixed with the phosphoric acid; shaking up the oily distillate with water and carbonate of baryta; and rectifying it over anhydrous phosphoric acid after dehydration with chloride of calcium.

Properties. Transparent, colourless, slightly iridescent, refracting, mobile. Sp. gr. 0·878 at 16°. Boiling point 172°. Odour slightly aromatic, more like that of oil of amber when heated. Cinæbene from wormseed-oil, prepared by distilling wormseed with milk of lime, smells like oil of lemon. Taste slightly warming, afterwards burning.

			Hirzel.
20 C	120	88·23	88·27
16 H	16	11·77	11·71
$C^{20}H^{16}$	136	100·00	99·98

Isomeric with terebene. Probably identical with Völkel's cynene. (Schwanert.)

Decompositions 1. Cinæbene, when *set on fire,* burns with a clear flame — 2. Heated with an equal volume of nitric acid of sp. gr. 1·16, it gives off, with violent intumescence and evolution of nitrous acid,—first, water containing propionic or acetic acid, and floating thereon, a thin colourless oil which has a fruity odour, leaves when evaporated, flocks smelling like camphor, is very volatile, is easily set on fire, and burns with a clear flame,—and, ultimately, hydrocyanic acid with a small quantity of bitter almond-oil, while a viscid resin remains. This resin has a peculiar odour like anise and fennel, and yields, by renewed boiling with nitric acid of sp. gr. 1·16, a solution which, on cooling, deposits *toluylic* and *nitrotoluylic acids,* also an undissolved viscid oil which appears to be *anisylous acid.* No oxalic acid is formed. A small quantity of cinæbene added to *strong nitric acid* colours it dark red ; the mixture froths up strongly when heated, and contains a small quantity of oxalic acid. Cinæbene, heated with *oil of vitriol,* acquires a red-brown colour. — 3. Dry *hydrochloric acid gas* colours it wine-red without separating crystals ; on dissolving the cinæbene thus coloured in alcoholic potash, and adding water, a colourless oil separates, having a strong and agreeable odour of camphor, and decomposing when heated.

Combinations. 1. *With Water. Cinæbene-camphor, Hydrated Cinæbene,* $C^{20}H^{18}O^{2}$. Occurs in worm-seed-oil, together with propionic acid and oxide of propyl, but cannot be separated in the pure state. (Hirzel.)

2. *With Hydriodic Acid. Hydriodate of Cinæbene,* $2C^{20}H^{16},HI$. — Obtained by rectifying the oil which passes over when wormseed-oil is distilled with iodine ; collecting apart the last portion of the distillate, extracting the cinacrol from it by repeated agitation with aqueous potash; washing the residual oil with water, then distilling it with water, and collecting separately the last portion of the oily distillate, which must then be washed with water and dehydrated with chloride of calcium.

Limpid to pale yellow, tolerably viscid ; has an agreeable camphorous peristent odour. Neutral.

			Hirzel.
40 C	240	60·00	59·60
33 H	33	8·22	8·64
I	127	31·78	31·59
$2C^{20}H^{16},HI$	400	100·00	99·83

It becomes reddish by exposure to the air, and is decomposed by distillation, even with water. (Hirzel.)

Cinæbene is insoluble in water, but dissolves readily in alcohol and ether. (Hirzel.)

Cynene. $C^{24}H^{18}$.

VÖLKEL. *Ann. Pharm.* 89, 358.

Formation and Preparation. Wormseed-oil is repeatedly distilled with anhydrous phosphoric acid ; the oil, which resinises and becomes viscid, is mixed with oil of vitriol; and the layer of liquid which floats on the acid is removed, distilled with water after washing, and again *per se,* after dehydration with chloride of calcium.

Properties. Limpid and mobile. Sp. gr. 0·825 at 16°. Boils at 173° — 175°. Odour peculiar, like that of wormseed; taste faint, afterwards burning.

			Völkel.
24 C	144	88·89	88·74
18 H	18	11·11	11·14
$C^{24}H^{18}$	162	100·00	99·98

Formed from wormseed-oil, $C^{24}H^{20}O^2$, by separation of 2 At. water. (Völkel.) Probably identical with Hirzel's cinæbene. (Schwanert.)

Decompositions and Combinations. 1. Burns with a bright fuliginous flame when *set on fire.* — 2. With *cold strong nitric acid,* it becomes yellowish-brown; boiled with *strong nitric acid,* it forms, with violent action, a solution which deposits a heavy yellow oil when mixed with water; by warm *dilute nitric acid* it is not altered. It dissolves in *fuming oil of vitriol,* forming a conjugated acid. It is insoluble in *water,* easily soluble in *alcohol* and *ether.* (Völkel.)

Cinæphene. $C^{20}H^{16}$ or $C^{40}H^{32}$.

HIRZEL. *Zeitsch. f. Pharm.* 1854, 17, 182. — 1855, 162, 182.

Formation. By distilling wormseed-oil with anhydrous phosphoric acid or with iodine.

Preparation. 1. The oil which passes over on heating wormseed-oil with anhydrous phosphoric acid, is freed from admixed aqueous products, and the portion which goes over between 35° and 325°, when it is rectified *per se,* is collected and dried over chloride of calcium. — 2. The brown oil obtained by distilling wormseed-oil with iodine is rectified; the light brown viscid residue is extracted with strong aqueous potash, washed with water, and heated to 360° as long as oil continues to distil over; and this oil is freed from admixed cinacrol by agitation with warm dilute aqueous potash, then with water, afterwards dried with chloride of calcium, and rectified.

Properties. Transparent and colourless by transmitted light, but exhibits an indigo-blue iridescence by reflected light; viscid; lighter than water. Boils at 315°—325°. Nearly destitute of taste and smell.

			Hirzel.
20 C	120	88·24	88·03
16 H	16	11·76	11·63
$C^{20}H^{16}$	136	100·00	99·66

Probably isomeric with colophene. (Hirzel.)

Decompositions and Combinations. 1. When heated, it becomes mobile and gives off vapours smelling like amber; burns with a very smoky flame when set on fire. — 2. When heated with *strong sulphuric* *acid*, it is converted into a yellow resin, which has a peculiar musk-like odour, and when distilled with aqueous potash, yields, with frothing, a distillate smelling of ammonia.

Cinæphene is insoluble in *water*, sparingly soluble in cold *alcohol*, easily in hot *alcohol*, *ether*, and *volatile oils*.

Cinacrol. $C^{26}H^{18}O^4$.

Hirzel. *Zeitschr. f. Pharm.* 1855, 84; 98, 130.

Formation. From wormseed-oil: *a.* by heating with iodine; *b.* by distillation with anhydrous phosphoric acid; *c.* by heating with hydrate of potash.

Preparation. Wormseed-oil is distilled with $\frac{1}{4}$—$\frac{1}{6}$ iodine; the mobile, dark brown iodated oil which passes over is separated from the aqueous distillate, and rectified *per se;* the nearly black heavy oil which passes over towards the end of the distillation is collected and shaken up with strong aqueous potash; the potash-ley, which thereby acquires a dark brown-yellow colour, is heated till it becomes inodorous, then distilled with a slight excess of dilute sulphuric acid; and the oil which passes over is rectified over chalk, and dehydrated by agitation with chloride of calcium.

Properties. Colourless to pale yellow; viscid. Sp. gr. 1·05—1·15. Boiling point about 250°. — Has a faint, not unpleasant, smoky odour, a sharp, caustic taste, and produces white, painfully burning spots on the tongue. Mixed with hydrochloric acid, it does not colour fir-shavings. Permanent in the air.

			Hirzel.
26 C	156	75·73	75·45
18 H	18	8·74	9·12
4 O	32	15·53	15·43
$C^{20}H^{18}O^4$	206	100·00	100·00

It becomes mobile when heated, and burns quickly with a smoky flame when set on fire.

It dissolves sparingly in *water*, readily and in any quantity in aqueous *alkalis* and their carbonates, in aqueous *alkaline earths*, and in *ammonia*. — The aqueous solution forms with neutral acetate of lead, after addition of ammonia, a flocculent white precipitate (cinacrol with oxide of lead); with *basic acetate of lead*, an immediate precipitate, soluble in excess of the basic acetate. It colours *sesquichloride of iron* bluish green, affording a delicate reaction, but not in presence of alcohol. From *nitrate of silver* it throws down pale yellow flocks, reducing the silver when heated. — Cinacrol dissolves in *alcohol*, *ether*, and *acetic acid*. (Hirzel.)

C. Volatile Empyreumatic Oils.

1. Oil of Amber.

Anthon. (1835.) *Repert.* 54, 76.
Elsner. *J. pr. Chem.* 26, 101; *Pharm. Centr.* 1842, 454.
Pelletier & Walter. *N. Ann. Chim. Phys.* 9, 99; *J. pr. Chem.* 31, 114; *Pharm. Centr.* 1843, 910.
Döpping. *Ann. Pharm.* 54, 239; *N. Br. Arch.* 43, 147.
Marsson. *N. Br. Arch.* 62, 1; abstr. *Pharm. Centralbl.* 1850, 413.
Zeller. *Stud. über. äther. Oele.* Landau, 1850.

Huile de succin pyrogenée, Bernsteinol, Bernsteineupion.

Formation. The empyreumatic oil which passes over in the dry distillation of amber, either consists entirely of hydrocarbons having the composition of oil of turpentine, or contains such hydrocarbons mixed with other substances. — It is converted into rectified oil of amber by separation of the simultaneously formed succinic acid, and repeated rectification *per se* (Martius, *Repert*, 12,426), or with water (*Pharm. Boruss. Ed.* vi), whereupon, however, only a small quantity of the oil passes over (Marsson), or over pounded glass mixed with a small quantity of paste of chloride of lime. (Schütz. *Repert*, 15, 274). — Amber yields 25 to 31 p. c. of the crude oil. (Bley & Diesel, *N. Br. Arch.* 55, 171.)

Preparation of the Hydrocarbon from Oil of Amber. — 1. In the dry distillation of amber, two different oils are obtained, the first of which passes over below a red heat, the second at a dull red heat. In rectification, the first distils between 110° and 260°, the second between 140° and 300°, and at the end of the process, a solid substance like ozocerite remains; but even repeated rectification does not yield products of constant boiling point. The two oils are scarcely or not at all affected by hydrate of potash; but oil of vitriol attacks them violently, imparting a dark colour. If the two oils are repeatedly shaken up with strong sulphuric acid, decanted, distilled *per se*, again shaken up with sulphuric acid, and so on, they both yield the same colourless mobile oil, which is no longer coloured by strong sulphuric acid, and boils between 130° and 400°. This oil, after rectification over potassium and anhydrous phosphoric acid, or over anhydrous phosphoric acid alone, has the composition given below, and that which distils between 130° and 175°, has a vapour-density = 4·3; hence Pelletier and Walter assign to it the formula $C^{18}H^{14}$ (calc. vapour-density 4·23). (Pelletier and Walter.)

2. When oil of amber is shaken up with potash-ley, it yields to this liquid a brown-red substance, and nothing afterwards to oil of vitriol. The oil treated with potash-ley, dilute sulphuric acid, and lumps of potash, begins to boil at 140°, after standing over chloride of calcium, then distils over till the temperature rises to 170° or even higher, while a thic dark-coloured residue remains. The portion which distils between 160° and 170° is Döpping's oil *a*. Potassium separates a small quantity of gas from it, probably because it contains water; if this oil be left in contact with quicklime for a week, and then rectified, it boils between 170° and 190°, and then forms the oil *b*. When oil of amber purified by hydrate of potash is mixed carefully and without heating, with several volumes of oil of vitriol, and the mixture is left at rest, it separates into two layers, the upper of which, if removed and washed with caustic

potash (if repeatedly treated with oil of vitriol, it would ultimately dissolve altogether), then brought in contact with quicklime and rectified, boils partly between 190° and 200° (oil *c*), and differs from the oils *a* and *b*, in odour, specific gravity, boiling point, and refracting power. — Between 210° and 220°, an oil *d* passes over, yellow and smelling like poppy-oil, whilst a yellow residue is left, which after cooling is solid and inodorous. (Döpping.)

3. Marsson obtained the oil which he examined, by rectifying crude oil of amber, dehydrating and de-acidising the distillate with pulverised quicklime, and rectifying till $\frac{1}{8}$ had passed over.

4. For the preparation of his amber-eupione (which appears to be identical with the hydrocarbon obtained by method 1 or 2,) Elsner mixes rectified oil of amber, gradually, with agitation, and avoiding rise of temperature, with 18 vol. oil of vitriol, decants the layer which separates after standing for some time, washes it with water, dries out over chloride of calcium, and rectifies.

Properties. Transparent, colourless, or pale yellow, mobile or viscid oil, of no constant boiling point, and varying in specific gravity according to the temperature at which it has distilled; it alters partially in boiling point at each repetition of the distillation, and leaves a residue (on which account also its vapour-density cannot be determined.) (Döpping, vid. sup.)

Crude oil of amber varies in colour from yellow to brown-black. (Anthon.) Sp. gr. 0·87—0·93 (Anthon); 0·91—0·936 at 20° (von Hees, *N. Br. Arch.* 61, 18); 0·85—0·89. (Zeller.) Sp. gr. of the crude oil 0·9003 and 0·9219 at 15° (Marsson); of the rectified oil, 0·8795 at 16°; of the oil rectified with water, 0·8841 at 15°; of the most volatile distillate, 0·8403; of amber-eupione, 0·645 at 19° (Elsner); of that which passes over between 180° and 190°, 0·9928 (Döpping); of the most volatile distillate, 0·8798; of the later distillate, 0·9176. (Marsson.) Boiling point, 130° to 260° and higher; of amber-eupione, 280° (Elsner); 130°—270° and higher (Pelletier & Walter); 160°—166° and higher (Marsson); 140°—170° and higher. (Döpping.) — Taste and odour peculiarly unpleasant and pungent. — Amber-eupione smells like ripe fruit. (Elsner.) Neutral. (Döpping, Zeller.)

			Pelletier & Walter.		
20 C	120	88·24	87·39	to	89·19
16 H	16	11·76	11·30		10·10
$C^{20}H^{16}$	136	100·00	98·69		99·29

	Döpping. mean.				Marrson. mean.
	a.	*b.*	*c.*	*d.*	*e.*
C	87·03	87·97	87·48	87·32	86·67
H	11·54	11·53	12·06	11·98	11·70
	98·57	99·50	99·54	99·30	98·37

Elsner found in rectified oil of amber 84·0 p. c. C, 8·6 H and 7·4 O; in amber-eupione 84·55 p. c. C, 11·98 H and 3·47 O, whence he assigns to the latter, the formula $C^{32}H^{27}O$ or $C^{35}H^{26}O$. Döpping and Marrsson regard Elsner's analyses as incorrect. Pelletier and Walter's formula, $C^{18}H^{14}$, requires 88·53 p. c. C and 11·47 H, (comp. page 323.)

Decompositions. 1. Oil of amber, even after rectification, leaves when *distilled* a dark brown viscid residue (amber-colophony). (Elsner, Döpping.) — 2. It burns with a very smoky flame when set on fire. (Döpping.) — It does not absorb oxygen when exposed to the *air*. (Döpping.) — 3. Rectified oil of amber is coloured brown by *iodine*, but does not become heated (Elsner); it is partially resinised thereby. (Zeller.) — Amber-eupione dissolves iodine with red-brown colour. (Elsner.) — The volatile portions of rectified oil of amber, not yet treated with oil of vitriol, acquire a transient blue colour when treated with *chlorine*, and finally give off hydrochloric acid, become viscid, and heavier than water; the less volatile portions are scarcely altered thereby. (Pelletier & Walter.) — 4. Oil of amber absorbs a small quantity of *hydrochloric acid gas*, acquiring a dark colour, but becoming colourless again, on addition of water. (Döpping.) Oil of amber treated with hydrochloric acid gas is altered in colour and smell, but does not form an artificial camphor. (Pelletier and Walter.) — 5. Oil of amber prepared by method 1, imparts a reddish colour to *strong sulphuric acid*, but remains itself colourless. (Pelletier and Walter.) Oil of amber prepared by 2, dissolves when repeatedly treated with oil of vitriol, partially each time, and completely in the end. (Döpping.) (For the behaviour of the crude oil, and of the rectified oil not purified with oil of vitriol, see page 323.) — 6. In contact with *nitric acid*, oil of amber acquires an odour of musk, and becomes resinised. (Marggraf, *Ann. Chim.* 73, 182.) The resin thus produced is the so-called artificial musk. — Nitric acid of sp. gr. 1·36 colours oil of amber cherry-red, and afterwards brown (Anthon); acid of sp. gr. 1·28 colours it violet (Zeller); more dilute acid colours it yellowish brown. (Döpping.) Cold fuming nitric acid or hot dilute nitric acid yields artificial musk. (Foltz, *Repert*, 4, 226, and others.) Fuming nitric acid colours amber-eupione dark red-brown, whereupon water, after a few hours, throws down artificial musk. (Elsner.) Respecting artificial musk, see especially Elsner, *J. pr. Chem.* 26, 97; Foltz, *Repert*, 4, 226; Marsson, *N. Br. Arch.* 62, 8.) — When rectified oil of amber is boiled for 14 days with nitric acid of sp. gr. 1·3, an acid distillate is obtained containing acetic, propionic, and butyric acids, whilst a whitish yellow resin separates from the residue, and a larger quantity of it on addition of water. (Marsson.) It is to the presence of the volatile acids just mentioned, that artificial musk partially owes its odour. (Marsson.) — 7. Rectified oil of amber, and amber-eupione, do not act upon *potassium*. (Elsner; Pelletier and Walter.) Neither is purified oil of amber altered by aqueous potash or ammonia.

Combinations. Oil of amber dissolves at the heat of the hand in 50 pts. of *alcohol* of sp. gr. 0·855, likewise in 2 pts. of alcohol of sp. gr. 0·8 (Anthon), in 15 pts. alcohol of sp. gr. 0·85. (Zeller.) — The saturated solution, on cooling, deposits an oil which redissolves on the application of heat. (Anthon.) — Crude oil of amber yields to alcohol of 0·83, a dark yellow oil having a balsamic and penetrating odour (75·33 C, 14·04 H, 10·63 O); and from the residue, ether extracts a transparent kneadable resin (78·60 C, 12·82 H, 8·58 O), leaving a yellow crystalline residue (79·87 C, 14·92 H, 5·21 O), which burns without flame. (Drapiez, *Schw.* 30, 119.)

Oil of amber dissolves readily in *ether* (Elsner, Döpping), in 2 pts. of ether (Anthon), in *oils* both *fixed* and *volatile*. (Elsner.)

Oil of amber, when heated, dissolves a large quantity of *sulphur*, which crystallises out on cooling; it dissolves a large quantity of *caoutchouc*, and a very small quantity of *amber*. (Döpping.)

2. Empyreumatic Oil of Birch.

SOBRERE. (1842.) *N. J. Pharm.* 2, 207; *Ann. Pharm.* 44, 121. — *N. J. Pharm.* 3, 288.

Brenzliches Birkenöl. Essence de Bouleau.

Occurs in the tar obtained in Russia by the dry distillation of birch-bark. — When the tar is distilled by itself, and the acid oil which floats on the watery distillate is repeatedly treated with potash-ley and rectified in a stream of carbonic acid, a colourless oil passes over at 156°, having a sp. gr. of 0·847, containing 88·05 p. c. C, and 11·95 H, therefore $C^{29}H^{16}$ (calculation 88·23 p. c. C, 11·77 H); as the distillation proceeds and the boiling point rises, it becomes mixed with oxygenated oils containing less carbon and hydrogen.

The oil which passes over at 156° solidifies partially at 16°—17°; has a vapour-density of 4·975 (calculation = 4·7144, [p. 245]), smells like oil of turpentine, but fainter and disagreeably. — It takes up *oxygen* and resinises when exposed to the air; yields by distillation with *nitric acid* a green oil (which loses its colour and deposits resinous flocks at 100°), and 1—2 p. c. hydrocyanic acid; and when distilled with a mixture of 2 vol. nitric acid and 8 vol. water, becomes yellowish brown, thickens and sinks to the bottom of the distillate. It absorbs 32 p. c. hydrochloric acid gas, becoming black, but without forming artificial camphor, and dissolves sparingly in *water*, easily in *alcohol* and in *ether*.

3. Caoutchin.

HIMLY. (1835.) *Diss.* Götting. 1835, 47; *Ann. Pharm.* 27, 41; abstr. *Repert.* 60, 105,
C. GREVILLE WILLIAMS. *Proceedings of the Royal Society*, 10, 517.

Kautschin. Discovered and investigated by Himly; further by Williams.

Source and Extraction. Caoutchin occurs, together with many other substances in oil of caoutchouc. (Himly, *vid. inf.*) Obtained also from gutta percha. (Williams.) Oil of caoutchouc boiling at 140°—280°, obtained by fractional distillation, is repeatedly shaken up with dilute sulphuric acid, washed with water, then alternately with potash-ley and with water, and distilled with water several times. The liquid which passes over is dehydrated with chloride of calcium, and rectified *per se*, the portion which goes over between 160° and 175° being collected apart, and from this, by repeated rectification and removal of the portions which distil over below 166° and above 174°, caoutchin is obtained, boiling between 168° and 171°. By repeated fractional distillation, this product may be brought to boil at 171°; or the purification may be effected by passing dry hydrochloric acid gas into the cooled oil previously dried over chloride of calcium (whereupon it turns blackish green), whereby hydrochlorate of caoutchin is formed, decanting this liquid from the resin after it has stood for several days, dissolving it in absolute alcohol, and precipitating with water, The hydrochlorate of caoutchin again dehydrated and repeatedly distilled over caustic lime or baryta, then over potassium as long as the metal becomes coloured, yields pure caoutchin. (Himly.)

Properties. Transparent, colourless, mobile; makes grease-spots on paper which soon disappear, leaving a faint odour. Sp. gr. 0·8423 at 16°. Boiling point 171·5° at 0·75 met. pressure. Does not solidify at — 39°. Vapour-density 4·461 (Himly); 4·65 (Williams). Has but little electric conducting power. Smells like oil of China oranges (Apfelsinenöl p. 304), but less agreeably. Has a peculiar aromatic taste, burning but not bitter. (Neutral, Himly.)

			Himly.	Williams.
20 C	120	88·23	87·00	88·1
16 H	16	11·77	11·56	11·9
$C^{20}H^{16}$	136	100·00	98·56	100·0

	Vol.	Density.
C-vapour	20	8·3200
H-gas	16	1·1088
Caoutchin-vapour	2	9·4288
	1	4·7144

Williams's numbers are the mean of three analyses, two of which were made with caoutchin obtained from gutta percha.

Decompositions. 1. Caoutchin volatilises partially when exposed to the *air*, leaving a residue produced by *absorption of oxygen;* by prolonged contact with the air, it acquires a persistent bitter taste, and is finally converted into a yellow, tough, bitter resin (which appears to contain nitrogen). Caoutchin kept for a year in bottles containing air and not quite closed, does not deposit crystals, but becomes yellow, bitter, and less soluble in alcohol and ether than before; it gives off gas-bubbles with potassium, often with a rapidity amounting to ebullition; and is for the most part decolorised by agitation with aqueous potash, yielding to it a bitter substance. (Himly.) *Peroxide af hydrogen* converts caoutchin into a resin. (Himly.) — 2. With *chlorine* it turns brown, becomes heated to inflammation, gives off hydrochloric acid, and forms chlorocaoutchin. — 3. With *bromine,* it gives off hydrobromic acid, with effervesence, but remains colourless and transparent; it readily abstracts bromine from its solutions in water, alcohol, and ether, forming heavy drops of oil. Caoutchin mixed with $\frac{1}{5}$ vol. water decolorises bromine till 248 pts. bromine have been added to 100 pts. caoutchin (Williams, *Chem. Gaz.* 263, 365; *J. pr. Chem.* 61, 20); according to more recent determinations by Williams (*Proc. Roy. Soc.* 10, 517), 0·1091 grm. caoutchin decolorises 0·2527 grm. bromine (in 20 cub. cent. of water), which is in the ratio of 231·7 pts. bromine to 100 pts. caoutchin, or nearly 4 At. bromine to 1 At. caoutchin (calculation 235·3 bromine to 100 pts. caoutchin). [Oil of turpentine likewise decolorises bromine in the ratio of 1 At. to 4 At. bromine. (Williams.)] 4. By the alternate action of *bromine* and *sodium* on caoutchin [or oil of turpentine], 2 At. hydrogen are removed, and cymene, $C^{20}H^{14}$, is produced, having exactly the same odour as that obtained from oil of cumin (p. 184). (It gave as the mean of three analyses 89·4 p. c. C and 10·4 H.) At the same time there is produced an oil (paracymene) having the composition of cymene but boiling at 300°. (Williams, *Proc. Roy. Soc.* 10, 517.) — 5. With *iodine,* caoutchin acquires a black brown colour, especially when heated; and, if dropt upon iodine, gives off hydriodic acid with effervescence, but without taking fire. From aqueous alcoholic or ethereal solutions of iodine, it abstracts the iodine, forming iodocaoutchin, which is a black-brown oil, giving off hydriodic acid when distilled, easily decomposed by heating with oil of vitriol, bromine, chlorine, fuming nitric acid, or potash, nearly insoluble in water, but soluble in alcohol and ether. Caoutchin, distilled with excess of iodine, forms a colourless, fragrant oil, similar to that which is produced by the action of oil of vitriol on caoutchin, giving off at the same time a large quantity of hydriodic acid. (Himly.) — 6. With *nitric oxide*, caoutchin gradually turns yellowish; with *nitrous acid*, yellow and green, and is gradually converted into a very sharp and bitter-tasting yellow resin, soluble in alcohol and ether. — 7. It is not altered by *dilute nitric acid;* but *concentrated nitric acid* colours it rose-red, yellow, blue, then again yellow, with rise of temperature, evolution of nitric acid, and formation of a yellow resin; *fuming nitric acid* acts still more strongly. The yellow resin thus formed is brittle at 0°, tough and ductile when moderately heated, melts at a stronger heat, swelling up and giving off white, very offensive vapours, and ultimately takes fire, burning with flame, and leaving a large quantity of spongy charcoal; distilled with potash, lime, or baryta, it gives off ammonia having an empyreumatic odour; it dissolves very readily in aqueous potash, carbonate of potash, and ammonia, easily in alcohol both hot and cold, and is separated by water from the bitter solution in the form of a yellow powder; when repeatedly distilled with fuming nitric acid, it forms oxalic acid. — 8. Caoutchin gradually heated with *concentrated aqueous chloric acid*, becomes hot, and forms chlorocaoutchin and perchloric acid. — 9. It is decomposed by *iodic acid*. — 10. Boiled with *crystals of chromic acid*, it forms a yellow resin. — 11. When dropt into *oil of vitriol*, it becomes heated, eliminates sulphurous acid, and forms a brown unctuous acid, yielding with carbonate of baryta, a soluble baryta-salt, which, when decomposed by sulphates, forms non-crystalline salts, soluble in water. (Himly.) The formula of this acid is $C^{20}H^{16}S^2O^6$; its lime-salt gave by analysis 8·3 p. c. calcium, the formula $C^{20}H^{15}CaS^2O^6$, requiring 8·5 p. c. (Williams.) Caoutchin is coloured red-brown to black by oil of vitriol, becoming viscid, giving off sulphurous acid, and separating after 24 hours, a colourless oil floating on the surface which appears to be impure eupione. This oil, washed with water and dehydrated with chloride of calcium, has a specific gravity of 0·86, boils at 203°, smells like rock-oil, has an aromatic taste, volatilises without alteration, and is neutral; it is not decomposed by fuming nitric acid, absorbs only a small quantity of hydrochloric acid gas, is but slightly altered by boiling with oil of vitriol, and dissolves in alcohol in all proportions. When the thick acid liquid below this oil is mixed with water, and left at rest, an oil separates from it and collects on the surface of the acid water. This latter oil has an odour different from that of caoutchin, aromatic like that of rosemary; it is soluble in alcohol, still more in ether, and yields by distillation a strong-smelling oil, easily soluble in alcohol and ether, decomposed by fuming nitric acid and hot oil of vitriol,—also a resin, which separates from its ethereal solution on addition of alcohol, as a yellow, inodorous and tasteless powder, which melts below 100°. Dilute sulphuric acid does not act upon caoutchin. — 12. Caoutchin, boiled with *selenic acid* of sp. gr. 2·23 turns brown, and gradually decomposes. — 13. It is not decomposed by *phosphoric* or *phosphorous acid*. — 14. With dry *hydrochloric acid gas*, it becomes hot, acquires a brown colour, and is converted into hydrochlorate of caoutchin. — 15. *Hydriodic* and *hydrobromic acids* act in like manner. — 16. With *arsenic acid* it turns yellow, blackens on boiling, and leaves an insoluble residue. — 17. Distilled with *potassium*, it gives off a few gas-bubbles, covers the metal after a while with a grey film, then remains unaltered; it is likewise unaffected by *sodium, potash, soda, baryta,* or *lime*. — 18. It converts *cupric oxide* on boiling into cuprous oxide; *permanganate of potash*, on boiling, into peroxide of manganese; but exerts no de-oxidising action, even at the boiling heat, on *protoxide of lead, minium, peroxide of lead, mercuric oxide,* or *chromate of potash*. 19. Heated with *terchloride of gold* or *bichloride of* *platinum*, it gives off hydrochloric acid and forms chlorocaoutchin. — 20. With *terchloride of antimony*, it turns yellow, and on boiling, dark green, and forms impure hydrochlorate of caoutchin. Similarly when boiled with *mercuric chloride*, it forms hydrochlorate of caoutchin; with mercurous chloride, no action takes place. — 21. With *sesquichloride of iron*, it forms a black-brown mixture.

Combinations. Caoutchin absorbs in 14 days, 45 vols. oxygen, without becoming saturated; in 3 weeks, at 20°, it absorbs 2 vols. oxygen.

It dissolves in 2000 pts. of water. It takes up a small quantity of water in the cold, and at higher temperatures, a larger quantity, which separates on cooling. It may be dehydrated by agitation, but not by distillation with chloride of calcium.

It does not absorb *carbonic oxide, marsh gas,* or *olefiant gas*, but takes up 11 vols. *carbonic acid.* Caoutchin, saturated with carbonic acid, absorbs oxygen and evolves in 3 weeks 6 vols. carbonic acid.

Of *phosphorus*, it dissolves a small quantity in the cold, more when heated. The hot solution, which shines in the dark, deposits the greater part of the phosphorus on cooling, at first in fused globules, afterwards in small rhombohedrons.

Of *sulphur*, it dissolves a little in the cold, ½ pt. when heated. The hot solution deposits on cooling, slender shining needles, and at last octohedrons, still however retaining in solution a quantity of sulphur larger than that which caoutchin can take up in the the cold. Caoutchin does not absorb *sulphuretted hydrogen*, but dissolves *bisulphide of carbon* in all proportions. *Selenium* and *selenious acid* do not dissolve in caoutchin.

With Hydrochloric Acid. Hydrochlorate of Caoutchin. Monochlorhydrate de caoutchine liquide. (Gerhardt.) Caoutchin cooled with ice is completely saturated with dry hydrochloric acid gas, and the dark brown liquid, which is transparent only in thin layers and fumes strongly in the air, is shaken up with water, to remove free hydrochloric acid.

Brown. Sp. gr. 0·95 at 15°. Does not solidify at 39°. Odour strongly but repulsively aromatic, like that of thyme; persistent; taste, mild but disagreeable.

			Himly.
20 C	120·0	69·6	70·08
17 H	17·0	9·9	9·67
Cl	35·5	20·5	20·30
$C^{20}H^{16},HCl$	172·5	100·0	100·05

When *set on fire*, it burns with a red, strongly fuliginous flame, green at the edges. Gives off hydrochloric acid gas when *distilled.* Treated with *chlorine* or *bromine*, it gives off hydrochloric acid gas, and is converted into chloro- or bromo-caoutchin. It is not decomposed by aqueous *potash* or *soda*, but when distilled over lumps of potash, soda, lime, or baryta, it gives up its hydrochloric acid to the alkali.

It dissolves in *absolute alcohol*, in *ether*, and in *acetate of ethyl*, but on adding water or weak alcohol to either of these solutions, the whole of the caoutchin is precipitated.

With *Hydrobromic Acid*, caoutchin forms a compound analogous to the hydrochlorate; also, but less easily, with hydriodic acid.

Caoutchin dissolves in the cold a small quantity of *iodide of sulphur*; the solution, when boiled, gives off sulphuretted hydrogen, and leaves a black thick residue. It dissolves a small quantity of *iodide of phosphorus*, forming a brown solution which is decolorised by water. From an aqueous solution of *bromide of iodine*, it withdraws the whole of that compound, forming a bluish-green balsam, in which neither bromine nor iodine can be detected by metallic silver. It does not dissolve *mercuric iodide* in the cold; but with the aid of heat, it forms a yellow solution which, on cooling, deposits almost all the mercuric iodide in yellow scales, which after a while become red again.

It absorbs in five weeks 5 vols. *nitrogen*, a small quantity of *nitrous oxide*, and assumes a yellowish tint after some time by contact with *nitric oxide*. It absorbs 3 vols. *ammonia gas*. It does not unite with aqueous ammonia. It does not absorb *cyanogen gas*, but *hydrocyanic acid gas* is absorbed by it, and *chloride of cyanogen*, in almost any quantity.

It dissolves a small quantity of *iodide of carbon* when heated therewith, and deposits it in shining laminæ on cooling. When boiled with iodide of carbon, it turns brown. It dissolves with facility the *chlorides of carbon, sulphur*, and *phosphorus*. Mixes in all proportions with *xanthic acid*.

Caoutchin is slightly soluble in concentrated *formic* and *acetic acids*. The solutions prepared with aid of heat, deposit on cooling nearly the whole of the caoutchin in combination with formic and acetic acids. Caoutchin dissolves *malic acid* in very small quantity; *oxalic, citric*, and *tartaric acids*, not at all. All these acids, boiled for some time with caoutchin, produce a brown glutinous substance. Caoutchin, with aid of heat, dissolves a large quantity of *benzoic acid*, which partially separates in the crystalline state on cooling. It does not dissolve *tannic, mucic*, or *succinic acids*.

Caoutchin dissolves in all proportions in *absolute alcohol, ether*, and *acetate of ethyl*, but is not soluble in *chloride of ethyl*. The alcoholic solution deposits part of the caoutchin on addition of weak alcohol, and the whole when mixed with water. From the ethereal solution, water does not separate the caoutchin, unless alcohol is likewise added. The alcoholic solution burns, when set on fire, with a bright flame, which, if the right proportions have been chosen, does not deposit any soot.

Caoutchin dissolves in *oils* both *fixed* and *volatile*.

Appendix to Caoutchin.

1. Chlorocaoutchin.

HIMLY. (1835.) *Dissertation*, Göttingen, 1835, 79.

Chlorkautschin. Formed by the action of chlorine on caoutchin; also by boiling caoutchin with terchloride of gold or bichloride of platinum.

Preparation. Dry chlorine gas is passed into a flask having a layer of caoutchin at the bottom, the delivery-tube not however reaching to the surface of the liquid, but terminating a few lines above it, and the mixture being at first cooled with ice; and the resulting oil, — which is brown at first, but, when completely saturated with chlorine, becomes colourless and viscid, and gives off a larger quantity of hydrochloric acid gas, — is washed with a very weak soda solution, then with water, and finally dehydrated over oil of vitriol.

Properties. Transparent, colourless, viscid. Sp. gr. 1·433. Does not become crystalline on cooling. Has a peculiarly strong ethereal odour, and an intolerably and persistently sharp, burning taste. Neutral.

Decompositions. 1. When *distilled*, it gives off extremely irritating hydrochloric acid vapours. — 2. Boiled for some time with *oil of vitriol*, it gives off hydrochloric acid and becomes carbonised. — 3. By distillation with potash, lime, or baryta, it yields a variety of oily products.

Combinations. It dissolves in hot *nitric acid* and in hot *oil of vitriol*, separating out unchanged on cooling.

It dissolves sparingly in *water*, easily in *alcohol* and *ether*, and is precipitated from its alcoholic solution by water.

¶ 2. Isoprene. $C^{10}H^8$.

C. G. Williams. (1860.) *Proceedings of the Royal Society*, 10, 516.

Produced, together with caoutchin, by the dry distillation of cauotchouc and gutta percha; purified by repeated cohobation over sodium.

It is an exceedingly volatile liquid, of sp. gr. 0·6823 at 20°. Boils between 37° and 38°. Vapour-density 2·44.

			Williams.		Vol.	Density.
10 C	60	88·23	88·0	C-vapour	10	4·1600
8 H	8	11·77	12·1	H-gas	8	0·5544
$C^{10}H^8$	68	100·00	100·1	Vap. of Isoprene	2	4·7144
					1	2·3572

This experimental composition is the mean of five analyses, three of specimens from caoutchouc and two from gutta percha. Isoprene is polymeric with caoutchin being related to it in the same manner as amylene to paramylene. From the similarity of composition between isoprene, caoutchin, and pure caoutchouc, Williams is of opinion, that the decomposition of caoutchouc by heat is simply the disruption of a polymeric body into substances having simple relation to it.

Oxide of Isoprene, $C^{10}H^8O$. Isoprene exposed to the air for some months, thickens, and acquires bleaching properties, owing to the absorption of ozone. On distilling the ozonised liquid, a violent reaction takes place, the unaltered hydrocarbon distils off, and the residue solidifies to a pure white, amorphous mass, containing:

			Williams.
10 C	60	78·95	78·8
8 H	8	10·52	10·7
O	8	10·53	10·5
$C^{10}H^8O$	76	100·00	100·0

Borneol or Borneol-alcohol.

$$C^{20}H^{18}O^2 = C^{20}H^{16},2HO.$$

PELOUZE. (1841.) *Compt. rend.* 11, 365; *Ann. Pharm.* 40, 326; abstr. *J. pr. Chem.* 22, 379; *J. Pharm.* 26, 645; *Repert.* 72, 364.
GERHARDT. *N. Ann. Chim. Phys.* 7, 286; *Ann. Pharm.* 45, 38; abstr. *Compt. rend.* 14, 832; *J. pr. Chem.* 27, 124; further, 28, 46.
BERTHELOT. *N. Ann. Chim. Phys.* 56, 78; abstr. *Compt. rend.* 47, 265; *Ann. Pharm.* 110, 267; *Repertoire de Chimie pure,* 1, 64; *Ann. Pharm.* 112, 363.
Relating especially to the Modifications of Borneol:
JEANJEAN. *Compt. rend.* 42, 857; further, 43, 103; *J. pr. Chem.* 69, 204; *Ann. Pharm.* 101, 94; *Chem. Centralbl.* (1856.) 575 and 672.

Oxyde de Bornène. (Laurent.) *Camphol, Alcohol campholique.* (Berthelot.) *Fester Borneo-camphor, Camphre solide de Borneo; Baros-campher, Sumatra-campher, Dryobalanops-campher, Camphora Sumatrana, C. Borniensis, C. Malayana. Capuhr Barruhs* of the natives.

Source and Formation. 1. In the cavities of old stems of *Dryobalanops Camphora* (*Colebrooke*), a tree growing in Sumatra, especially in the province of Baros, more rarely in Borneo. (De Vriese, *Nederlandsch. Kruidkundig. Archiff*, 3, 1; *Hooker's Journal of Botany*, 1852, 33 and 68; abstr. *Pharm. J. Trans.* 12, 22; v. Kessel, *Wien. Akad. Ber.* 8, 418.) It is scooped out of fissures in the stems of hewn trees with small pieces of wood or nails. (De Vriese.) It occurs in the cavities of the stems generally mixed with camphor-oil (p. 314), and as a crystalline sublimate in the upper part of the cavities, when they are not quite filled with the oil. (Motley, *Pharm. J. Trans.* 12, 300.)

2. Oil of valerian contains borneol (and the other constituents mentioned at page 313), which, on rectifying the most volatile portions, sometimes, but not always, sublimes in the neck of the retort; hence it appears to be produced occasionally from valerene by the action of hydrate of potash, just as it is obtained (p. 313), sometimes abundantly, sometimes but sparingly, on setting aside a mixture of valerene and potash-ley, and subsequently distilling it. (Gerhardt.) The crystals thus obtained are not borneol, but valerian-camphor, $C^{24}H^{20}O^2$, either existing ready formed in the oil of valerian, or produced from the valerol by distillation. (Pierlot, *N. Ann. Chim. Phys.* 59, 291.) This view does not agree with Gerhardt's analyses; moreover, both Gerhardt and Rochleder obtained from oil of valerian, common camphor, which probably can be produced only from borneol. (Kr.)

3. From *common Camphor.* When camphor is heated with alcoholic potash, borneol is produced, either with evolution of oxygen:

$$C^{20}H^{16}O^2 + 2HO = C^{20}H^{18}O^2 + 2O;$$

or with simultaneous formation of camphic acid:

$$2C^{20}H^{16}O^2 + 2HO = C^{20}H^{18}O^2 + C^{20}H^{16}O^4,$$

slowly at 100°, more quickly at higher temperatures. (Berthelot.) When 2 pts. of common camphor are sealed up in a tube with 1 pt. hydrate of potash or soda and 5 — 6 pts. alcohol, and heated in the oil-bath to 180° — 200° for 8 or 10 hours, or to 100° for several weeks, a product is obtained from which water separates an oil, and a solid mixture of borneol and common camphor. The oil decanted and filtered, and submitted to fractional distillation, yields, below 240°, an additional quantity of this mixture, a viscid oil afterwards passing over, and a residue being left in the retort. This mixture may be purified from oil by pressure and sublimation, and then contains about 10 per cent. of common camphor with 90 per cent. of borneol. To remove the former, the mixture is heated with 2 pts. of stearic acid to 200° for several hours (or to 160°—180° for several days), whereby the common camphor is volatilised: the residual stearate of borneol is decomposed by heating it to 120° with ½ pt. finely pulverised soda-lime, and the borneol which sublimes in the neck of the retort, leaving a residue of stearate of lime, is collected: it amounts to about $\frac{1}{20}$ of the camphor employed.

Properties. Small, white, transparent, easily friable crystals (Pelouze, Gerhardt, Berthelot); six-sided rhombohedral prisms. (Pelouze.) Native borneol forms small lumps of round and oval shapes, flat, white, thin, and ¼ inch in diameter, mixed with very small dirty white granules. (v. Kessel.) Lighter than water. (Pelouze.) According to Christison, it is heavier than water. (*N. Br. Arch.* 48, 32.) Melts at 198° (Pelouze), less easily than common camphor. (Gerhardt.) Boils without decomposition at 212° (Pelouze), a little below 220° (Berthelot.) It is less volatile than common camphor. (Gerhardt, Mosley.) Sublimes even at common temperatures, and boils at a temperature not far from its melting point. (Berthelot.) Rotatory powe rof native borneol 33·4° to the right (Biot, *Compt. rend.* 11, 370), of the artificial, 44·9° to the right. (Berthelot.) Borneol, prepared with camphor obtained from oil of amber, exhibits 10 times less dextro-rotatory power than artificial borneol. (Berthelot.) Borneol smells like common camphor and at the same time like pepper (Pelouze, Gerhardt, Berthelot); its odour is more agreeable (Motley); it has a burning taste like a volatile oil. (Pelouze.)

			Gerhardt. *mean.*	Berthelot.
20 C	120	77·92	77·69	77·6
18 H	18	11·69	11·85	11·6
2 O	16	10·39	10·46	10·8
$C^{20}H^{18}O^2$	154	100·00	100·00	100·0

Gerhardt examined borneol from oil of valerian; Berthelot, that from common camphor. — Borneol is related to common camphor in the same manner as alcohol to aldehyde.

Decompositions. 1. Borneol heated with moderately *concentrated nitric acid,* gives off red vapours, and is converted into an oil which floats on the acid, and from which water separates common camphor. A similar decomposition takes place, slowly in the cold, more quickly and violently with strong nitric acid. (Pelouze, Berthelot):

$$C^{20}H^{18}O^2 = 2H + C^{20}H^{16}O^2.$$

2. By distillation with *anhydrous phosphoric acid,* it is resolved into water and a hydrocarbon $C^{20}H^{16}$ (Pelouze), which, according to Gerhardt, is identical with his borneene and that of Pelouze (p. 313). — 3. Heated with moderately strong hydrochloric acid, it forms hydrochlorate of

borneol. Slightly heated borneol, or its cold alcoholic solution, absorbs but a small quantity of hydrochloric acid gas. (Berthelot.) — 4. Heated for some time to 200° in a sealed tube with *benzoic acid*, it forms benzoate of borneol; with *stearic acid*, stearate of borneol. (Berthelot.)

Borneol dissolves sparingly in *water* (Pelouze); not at all. (Berthelot.) — It dissolves readily in *alcohol* and in *ether*. (Pelouze, Berthelot.) — From a solution of 2 pts. borneol in 10 pts. absolute alcohol, 100 pts. of water separate, after three days standing, 1·2 pts. of borneol, and on agitating the liquid with ether, the ether takes up an additional 0·6 pt. of borneol. (Berthelot.)

Compounds Isomeric with Borneol.

1. Lævo-rotatory Borneol.

Occurs in the alcohol produced by fermentation of madder-sugar, and is obtained by collecting the laminæ which crystallise out from the liquid on standing, or in the fractional distillation conducted as described at page 313. It is pressed between filtering paper, and then purified by washing with a large quantity of water and repeated crystallisation from ether. (Jeanjean.) — It appears to be produced from the borneene of madder fusel-oil. (Jeanjean.)

Properties. Crystalline laminæ resembling borneol, or white powder smelling like pepper and common camphor, It deflects polarised light to the left as much as ordinary borneol deflects it to the right.

		Jeanjean. *mean.*
20 C	77·92	77·76
18 H	11·69	12·05
2 O	10·39	10·19
$C^{20}H^{18}O^2$	100·00	100·00

Decompositions. 1. Lævo-borneol is converted by boiling *nitric acid* into lævo-rotatory camphor isomeric with common camphor. — 2. Distilled with *anhydrous phosphoric acid* or *chloride of zinc*, it yields a hydrocarbon resembling oil of lemon or oil of bergamot. (Jeanjean.) Comp. *Valerene* (p. 313).

Combinations. Sparingly soluble in *water.* — Rotates like common camphor when thrown on water. — Dissolves readily in *acetic acid,* in *alcohol,* and in *ether.* (Jeanjean.)

2. Oil of Cajeput.

PFUFF. *System de Mat. med.*
LEVERKÖHN. *Repert.* 34, 129
SCHÖNFELDER. *Repert.* 36, 132.

Guibourt. *J. Chim. méd.* 7, 586; *Repert,* 39, 261.
Döbereine. *Schw.* 63, 484.
Blanchet. *Ann. Pharm.* 19, 214.
Zeller. *Stud. über äther. Oele,* Landau, 1850.

Essence de Cajeput, Cajeputöl, Oleum cajeputi.

Source. In the leaves (also in the flower-buds, according to Lesson), of *Melaleuca trinervis, M. leucodendron* (*Dec.*), *M. Cajeputi* (*Boab.*)

Extraction. By distilling the leaves with water (after they have become heated by being left over night closely pressed in a sack : *Rump.*) The water which passes over with the oil reddens litmus. (Schönfelder.) — From the leaves of *Melaleuca hypericifolia,* Stickel obtained by distillation with water, 0·4 p. c. cajeput-oil.

Properties. Pale green (Gärtner, Blanchet, Stickel); grass-green (Döbereiner); greenish yellow to pale green (Zeller, *vid. inf.*); after rectification with water, the first $\frac{3}{4}$ are transparent and colourless, the last $\frac{1}{4}$ green (Schönfelder), the first $\frac{7}{8}$ transparent and colourless (Dobereiner, Blanchet), the last $\frac{1}{8}$ pale to dark olive-green (Guibourt), transparent and colourless (Döbereiner, Blanchet); after agitation with animal charcoal, it is transparent and colourless (Vasmer, *Br. Arch.* 37, 248); transparent (Döbereiner, Blanchet, Stickel); mobile. (Pfaff.) Sp. gr. 0·978 at 9° (Gärtner), 0·915 (Schönfelder), 0·9492 at 18° (Döbereiner), 0·9274 at 25° (Blanchet), 0·916—0·919 at 18°, 0·913 at 24° (Guibourt), 0·91—0·94 (Zeller); rectified with water: first distillate 0·907 (Schönfelder), 0·897 (Leverköhn), 0·9196 at 25° (Blanchet), last 0·917 (Schönfelder), 0·92 (Leverköhn). — Boiling point 175°. (Blanchet.) The first distillate boils at 173°, the last at 175° (Blanchet), the most volatile nearly at 100°. (Döbereiner.) — Odour pungent, like that of camphor (Pfaff); aromatic, fainter after rectification. (Blanchet.) — Cajeput-oil from Amboina smells like turpentine, camphor, peppermint, and roses; that from Paris, like rue and rosemary; after rectification with water, it has a pungent odour rather like turpentine than acid; the latter distillate is less pungent, more like that of rose-wood or aloe-wood. (Guibourt.) — Taste burning (Pfaff), warming. (Blanchet.) — Neutral to litmus. (Schönfelder, Zeller.)

			Blanchet.
20 C	120	77·92	78·00
18 H	18	11·69	11·48
2 O	16	10·39	10·52
$C^{20}H^{18}O^{2}$	154	100·00	100·00

Consists of two volatile oils (Leverköhn); of dadyl (p. 245) and water, in equal numbers of atoms $= C^{10}H^{8},HO$ (Blanchet.) Commercial cajeput-oil generally contains copper in solution, whereby its original green colour is deepened (Stickel); it exhibits a greenish colour, however, even when no copper is present. (Guibourt.) The copper which gets into the oil, when it is sent out in copper vessels, cannot according to Dobereiner, be always recognised by its usual character of imparting a blue colour to aqueous ammonia on agitation; it is also not easily precipitated from the oil by potassium, iron or zinc, but better by the electric current. When the polar wires of a voltaic battery are dipped into cajeput-oil mixed with water, the positive pole, if the oil contains copper, becomes covered with cuprous oxide, and the wire at the negative pole gives off hydrogen; if aqueous ammonia be added, gas is evolved at both poles, flakes of copper are likewise formed at the negative pole, and the oil turns yellow. — Copper dissolved in the oil may also be detected by shaking it up with aqueous ferrocyanide of potassium, which produces a red precipitate of ferrocyanide of copper. (Guibourt.)

Copper may be removed from the oil by distillation, inasmuch as it passes over only with the last portion of the distillate (Schönfelder and others); by agitation with animal charcoal (Vasmer, *Br. Arch.* 37, 348). — A sample of cajeput-oil from Paris contained according to Guibourt, 0·22 p. c. of copper.

Decompositions. 1. Crude cajeput-oil, when *heated,* yields a colourless distillate, and leaves a resin which colours ammonia blue, and burns away completely when set on fire (Blanchet); when distilled with water, it leaves a dark green syrupy mass which smells like aloe-wood or elemi, and is nearly as heavy as water. (Guibourt.) — 2. It dissolves *iodine* without explosion (Blanchet), giving off a small quantity of yellowish red vapours, and exhibiting a slight rise of temperature; the rectified oil forms with iodine, a greenish brown coagulum, which changes to a dry crumbling mass. (Zeller.)—3. Mixed with an equal quantity of *nitric acid,* it acquires a brown or black-brown colour without losing its odour (Bonastre, *J. Pharm.* 11, 129); becomes bluish-red if heated, and gives off gas with violence (Zeller); forms, with crackling noise, a soft yellow resin. (Hesse, *Crell. Ann.* 1785, 1, 422.) — Nitric acid has no action upon cajeput-oil. (Blanchet.) — 4. With cold *oil of vitriol,* it turns yellow (Blanchet), orange, then carmine-red, with evolution of sulphurous acid (Döbereiner), brown-red, forming a balsam which gradually becomes black-brown. (Pfaff.) — 5. It absorbs *hydrochloric acid gas,* acquiring a blue, violet, and finally an amethyst-red colour. — Cajeput-oil coloured amethyst-red by hydrochloric acid gas, turns violet in moist air, and when mixed with alcohol, deposits a heavy oil, and turns dingy yellow. (Döbereiner.) — 6. *Potassium* abstracts oxygen from cajeput-oil without turning it brown. (Blanchet) — It does not act on cajeput-oil more strongly than on oil of turpentine; the evolution of gas, which is weak even at first, soon ceases. (Döbereiner.) — 7. Green oil of cajeput becomes yellow by contact with aqueous *ammonia* (Döbereiner), sometimes quite colourless (Guibourt), the ammonia likewise remaining colourless (Döbereiner), assuming various shades from greenish blue to blue (if the oil contains copper?) (Guibourt.) — 8. When shaken up with aqueous *ferrocyanide of potassium,* it is decolorised, or acquires a greenish yellow colour, and deposits a red powder (in case it contains copper?) (Guibourt.) — 9. Boiled with nitroprusside of copper, it yields a black precipitate, and turns brown. (Heppe, *N. Br. Arch.* 89, 57.) — 10. When it is continuously agitated with $\frac{1}{12}$ of *corrosive sublimate,* calomel is separated, and the oil acquires a blue-brown colour, which afterwards continuously increases in depth. (Simon, *Pogg.* 37, 557.) — 11. When kept in copper vessels, it dissolves *copper* and turns green. (Guibourt.)

Cajeput-oil dissolves readily in *alcohol.* (Guibourt, Zeller.)

3. Oil of Coriander.

TROMMSDORFF. *N. Br. Arch.* 2, 14.
KAWALIER. *Wien. Akad. Ber.* 9, 313; *J. pr. Chem.* 58, 226; abstr. *Ann. Pharm.* 84, 351; *Chem. Centralbl.* 1852, 746; *N. J. Pharm.* 23, 479.

Source and Extraction. In coriander, the fruit of *Coriandrum sativum. L.* — The bruised fruits are distilled with water.

Properties. Colourless oil (Trommsdorff), pale yellowish. (Kawalier.) Sp. gr. 0·859 (Trommsdorff), 0·871 at 14°. (Kawalier.) Boiling point 150° (but not constant). (Kawalier.) — Smells like coriander, but more agreeably; tastes aromatic, but not burning (Trommsdorff), like coriander. (Kawalier.) Neutral. (Trommsdorff.)

			Kawalier.			
			a.	*b.*	*c.*	*d.*
20 C	120	77·92	77·82	77·73	85·67	85·47
18 C	18	11·69	11·67	11·63	11·58	11·59
2 O	16	10·39	10·51	10·64	2·75	2·94
$C^{20}H^{18}O^2$	154	100·00	100·00	100·00	100·00	100·00

a. Oil dried over chloride of calcium and rectified; *b.* Its most volatile part; both according to Kawalier, are isomeric with liquid turpentine-camphor. *c.* The most volatile product of an oil merely dehydrated with chloride of calcium, but not heated to the boiling point; *d.* The oil distilled therefrom at 200°; both *c* and *d*, according to Kawalier, are composed according to the formula $C^{80}H^{66}O^2 = 4\,C^{20}H^{16} + 2\,HO$ or $2\,C^{20}H^{16} + 2\,(C^{20}H^{16},HO)$.

Decompositions. 1. The oil explodes strongly with *iodine.* — 2. With 2 pts. of fuming *nitric acid,* it forms a yellow resin (Hesse, *Crell. Ann.* 1, 422), a greenish resin having a peculiar odour, and becomes very hot. (Trommsdorff.) — 3. Mixed with *oil of vitriol,* it yields a saffron-yellow liquid, which gradually becomes dark red and ultimately brown red, and chars rapidly when heated. (Trommsdorff.) — 4. When repeatedly distilled over *anhydrous phosphoric acid,* it is converted into a yellowish offensive-smelling oil isomeric with oil of turpentine (containing 88·28 p. c. C, and 11·78 H). (Kawalier.)

Combinations. With Hydrochloric Acid. $C^{20}H^{35}Cl^2O$. (Kawalier.) Dry hydrochloric acid gas is passed into coriander-oil cooled with ice; and the oil which remains liquid after saturation, is washed with aqueous soda, then with water, and dehydrated by agitation with chloride of calcium. (Kawalier.)

Calculation according to Kawalier.			Kawalier.
40 C	240	67·81	67·51
35 H	35	9·89	10·00
2 Cl	71	20·04	20·40
O	8	2·26	2·09
$(C^{20}H^{16},HO + HCl) + (C^{20}H^{16},HCl)$	354	100·00	100·00

Coriander-oil dissolves readily and abundantly in *glacial acetic acid, alcohol, ether,* and *fixed oils.* (Trommsdorff.)

4. Oil of Osmitopsis.

v. Gorup-Besanez. (1854.) *Ann. Pharm.* 89, 214; abstr. *J. pr. Chem.* 61, 513; *Chem. Centralbl.* 1854, 299.

Osmitesöl, Essence d'osmitopsis.

Source. In *Osmitopsis asteriscoïdes,* a South African plant.

Properties. Yellow or faintly greenish; that which distils between 178° and 188° is colourless, mobile, and feels rough between the fingers. Sp. gr. 0·931 at 16·2°; 0·921, rectified at 178°—188°. Boiling point not constant, but ranging chiefly between 176° and 188°. It begins to boil slightly at 130°, boils regularly at 176°, two-thirds distilling over rapidly at 178°. It does not solidify on cooling. Odour penetrating, unpleasantly like camphor and cajeput-oil; more delicate, after rectification between 178° and 188°. Has a burning taste, and produces a scratching sensation in the throat. Neutral.

			Gorup-Besanez.
20 C	120	77·92	77·36
18 H	18	11·69	11·53
2 O	16	10·39	11·11
$C^{20}H^{18}O^{2}$	154	100·00	100·00

Decompositions. 1. The crude oil when *distilled* finally gives off a yellowish liquid between 188° and 206°, afterwards camphor sublimes between 207° and 208°, and a dark-coloured resin remains. — 2. With *cold nitric acid,* it remains unaltered, but with the hot acid a violent evolution of nitrous gas takes place. — 3. It turns brown with *oil of vitriol.* — 4. With *potassium,* it gives off a small quantity of gas, the metal at the same time becoming oxidised. — It does not form a hydrocarbon by distillation with alcoholic potash. — 6. From *ammoniacal silver-solutions*, it reduces the metal only after long-continued boiling. — 7. It dissolves *iodine* without explosion.

Combinations. — It dissolves in all proportions of *alcohol* and *ether.* — It is nearly insoluble in *water*, but forms with it a turbid liquid having the odour of the oil.

Camphor.

$$C^{20}H^{16}O^{2} = C^{20}H^{16},O^{2}.$$

Hänel. (1703.) *Diss. de camph. Lugd. B.* 1703.
Demachy. *Dessen. Laborant in Grossen.* 1, 242.
Ferber. *Beiträge zur Mineralgeschichte,* 1, 370.
Kosegarten. *Diss. de camphora, &c.,* Gött. 1785.
Bouillon Lagrange. *Crell. Ann.* 1799, 2, 301.
Saussure. *Ann. Chim. Phys.* 13, 275; *Schw.* 28, 389; further, 29, 173; *N. Tr.* 5, 2, 112.
Dumas. *Ann. Chim. Phys.* 48, 430; further, 50, 225; *Pogg.* 26. 531; *Ann. Pharm.* 6, 259; *Schw.* 66, 89.
Liebig. *Pogg.* 20, 45; *Ann. Chim. Phys.* 47, 95.
Blanchet & Sell. *Ann. Pharm.* 6, 304.
Laurent. *Ann. Chim. Phys.* 63, 207; *Ann. Pharm.* 22, 135; *J. pr. Chem.* 11, 287. — *Compt. rend.* 10, 532; *J. pr. Chem.* 20, 498. — *Rev. scient.* 11, 263; *J. pr. Chem.* 28, 333. — *N. Ann. Chim. Phys.* 7, 291. — *Compt. chim.* 1845, 150 — *Compt. rend.* 20, 511. — *Rev. scient.* 19, 159.

Martius. *Ann. Pharm.* 25, 305; further, 27. 44. — *N. Repert,* 1, 541.
Dumas & Stas. *N. Ann. Chim. Phys.* 1, 48; *Ann. Pharm.* 38, 184.
Delalande. *N. Ann. Chim. Phys.* 1, 120; *J. pr. Chem.* 23, 387; *Ann. Pharm.* 38, 337.
Dutrochet. *Compt. rend.* 12, 2, and 29, and 126, and 598.
Claus. *Petersb. Acad. Bull.* 9, 229; *Rev. scient.* 9, 181; *J. pr. Chem.* 25, 257; *N. Br. Arch.* 30, 170.
Gerhardt. *N. Ann. Chim. Phys.* 7, 282; *J. pr. Chem.* 28, 46; *Ann. Pharm.* 45, 34.
Rochleder. *Ann. Pharm.* 44, 1 and 3 and 9.
Döpping. *Ann. Pharm.* 49, 353.
Bineau. *N. Ann. Chim. Phys.* 24, 337; *J. pr. Chem.* 46, 296; *Ann. Pharm.* 78, 276; abstr. *Repert,* 110, 176; *Pharm. Centralbl.* 1849, 56; *Compt. rend.* 27, 184.
Berthelot. *N. Ann. Chim. Phys.* 56, 78; abstr. *Compt. rend.* 47, 266; *Ann. Pharm.* 110, 367.

Memoirs relating especially to the Modifications of Camphor.

Dessaignes & Chautard. *N. J. Pharm.* 13, 241; *J. pr. Chem.* 45, 45; abstr. *Ann. Pharm.* 68, 342.
Chautard. *Compt. rend.* 37, 166; *N. J. Pharm.* 24, 168; *J. pr. Chem.* 60, 139; *Pogg.* 90, 622; abstr. *Chem. Centralbl.* 1853, 636; *N. Br. Arch.* 76, 168.
Jeanjean. *Compt. rend.* 42, 857; further, 43, 103; *Inst.* 1856, 176 and 260; *J. pr. Chem.* 69, 204; *Ann. Pharm.* 101, 94; *Chem. Centralbl.* 1856, 575 *and* 672.

Camphora, Camphre, Campher; Laurus campher; Dextro-camphor, Camphre droit; Kistencampher oder *chinesischer* oder *Formosae-campher: Tubbencampher,* or *Batavian, Dutch, Japanese Camphor. Oxyde de camphène* (Berthelot.) *Aldehyde campholique* (Berthelot.) Not known to the Greeks and Romans; first introduced into Europe by the Arabians; first noticed by Actius towards the end of the fifth century; regarded by Agricola (*de natura fossilis*) as fossil resin; by others, as a resin or a tree-gum.

Source and Extraction. In all parts of the camphor-tree (*Laurus Camphora, L.*), indigenous in China and Japan. It is obtained in those countries by boiling the comminuted parts of the plants with water in kettles, which are covered with rushes or rice-straw, and with an iron helm: crude camphor then sublimes into the straw, and is converted into refined camphor (generally in Europe) by sublimation, either *per se* or with chalk or lime. Camphor-trees raised in hot-houses, likewise yield camphor. (Göppert, *N. Br. Arch.* 20, 93.)

Formation. 1. By heating borneol with moderately strong nitric acid. (Pelouze, *Compt. rend.* 11, 365; *Ann. Pharm.* 40, 326; *J. Pharm.* 26, 645.) An oil forms on the surface of the acid, and from this oil camphor separates on addition of water. (Pelouze.) — 2. By the action of platinum-black on camphene (p. 271). (Berthelot, *Compt. rend.* 47, 266.) — 3. By distilling oil of valerian with fuming nitric acid (Rochleder); but, according to Pierlot (*N. Ann. Chim. Phys.* 56, 291), camphor is not formed in this manner (see page 322). — 4. When oil of sage is dropped into fuming nitric acid, a solution is formed, from which common camphor sublimes on distillation. (Rochleder.) — 5. By distilling oil of tansy with bichromate of potash and sulphuric acid. (Persoz, *Compt. rend.* 13, 433; Vohl, *N. Br. Arch.* 74, 16; *Pharm. Centr.* 1853, 319.) — 6. By the action of chlorine gas on oil of sassafras. (Faltin, *Ann. Pharm.* 87, 376.) — 7. Common camphor is formed by distilling amber with nitric acid, and may be separated by neutralising the distillate with potash and extracting with ether. (Döpping.) — 8. Macfarlane obtained common camphor by heating camphor-oil (p. 314) with nitric acid.

Properties. White, translucent, tough mass, generally with a crystallo-granular structure, made up of octohedrons or segments of octohedrons. When crystallised by slow spontaneous sublimation during a space of three years, it forms perfectly transparent, six-sided tables, some of which have a diameter of 7 or 8 millimetres, and a thickness of 2 millimetres, the greater number, however, being only $\frac{1}{4}$ to $\frac{1}{2}$ a millimetre thick. Crystalline system, the rhombohedral. Combination of the terminal face p (Fig. 133) with the pyramid r and the six-sided prism s (Fig. 135). $p : r = 118^\circ\ 9'$; whence follows $r : r$ at the base $= 123^\circ\ 42'$. Negatively double-refracting. (Descloizeaux.) May be impressed with the nail, cut with a knife, and pulverised, not *per se*, but when moistened with alcohol, and easily crumbled to small angular lumps. It forms dendritic crystals, the form of which is not influenced by light or by the solvent. (Reinige, *N. Br. Arch.* 48, 307.) A solution of a small quantity of camphor in a drop of alcohol leaves, when evaporated on a glass plate, crystals, which, when examined by the microscope with polarised light, exhibit beautiful colours (a property which distinguishes natural from artificial camphor). (Bailey, *Sill. Ann. J. Mai.* 1851; *Chem. Centralbl.* 1851, 592.)

Sp. gr. 0·9887 (Brisson), 0·9968 (Newton); 1·00 from 0° to 0·6°, 0·998 at 6·25, 0·992 from 10° to 12·5°. (Brisson, *N. Br. Arch.* 48, 327.) Camphor in small lumps floats on water at 15°, has a specific gravity equal to that of water at 6·25°, and floats on it again at 11°. (Brisson.) Camphor, at the temperature at which water possesses its maximum density, does not follow the same law of expansion as water, but contracts continuously as the temperature falls. (Muncke, *Repert.* 48, 246.)

Camphor melts at 150° (Venturi), 175° (Gay-Lussac), 142·2°. (Thomson, *Ann. Phil.* 1820, 392.) It boils at 204° (Gay-Lussac), 204·4° (Thomson), and may be sublimed without decomposition; it volatilises in the air even at ordinary temperatures. Vapour-density = 5·468. (Dumas.) Tension of the vapour at 15·5° = 0·004 met. of a column of mercury.

Rotatory power 37·4° to the right, diminishing however as the solution becomes more dilute. In solutions of camphor in acetic acid, the rotatory power varied with increased dilution from 36·2° to 30·6° to the right; in absolute alcohol, from 37·28° to 34·23° to the right. (Biot, *N. Ann. Chim. Phys.* 36, 257; *Compt. rend.* 35, 233; *Ann. Pharm.* 84, 160. The rotatory power of camphor increases with the refrangibility of the rays more than that of most other bodies. (Arntsen, *N. Ann. Chim. Phys.* 54, 417.) It is only camphor melted by heat, not solid crystallised camphor, that acts upon polarised light. (Descloizeaux, *N. Ann. Chim. Phys.* 56, 220.)

Camphor has a peculiar, aromatic, penetrating odour. The odour is disguised by addition of musk (Fleischmann, *Repert.* 104, 252; *Pharm. Centrabl.* 1850, 432); and completely destroyed by mixture with *Asafœtida, galbanum, sagapene, animé,* or *tolu-balsam;* partially by mixture of *dragon's blood, olibanum, mastic, benzoïn, opoponax, tacamahac, guaiac,* or *gum ammoniacum;* the odour is not destroyed by admixture of *jalap,* *resin, gamboge, euphorbium, bdellium, amber, myrrh, scammony, sandarach, pine-resin, colophony*, or *China-resin*. (Planche, *N. Br. Arch.* 22, 107.)

Camphor is not altered by exposure to light or air. Its taste is warming, bitter, and burning.

Small lumps of camphor thrown upon water, exhibit a rotatory motion. The cause of this movement has been supposed to be: 1. An electric current between the camphor and the sides of the vessel containing the water. (Romieu, *Mém. de l'Acad.* 1756.) — 2. An odoriferous elastic fluid, which, by surrounding the camphor, impedes the action of air and water upon it. (Prevost, *Ann. Chim.* 21, 255.) — 3. The attraction of camphor for air and water, and its simultaneous solution in the one and the other. — 4. The expansion of an oil, which, being given off from the camphor in the form of vapour, is attracted by the surface of the water and forms a thin layer thereon, this expansion being visible in the force with which all foreign particles floating on the water are repelled. (Ventury, *Ann. Chim.* 21, 262; Corradory, *Ann. Chim.* 37, 38.) — 5. The efflux of the camphor itself into the water and into the air. (Serullas, *J. Phys.* 91, 172.) — 6. The volatilisation of the camphor and its simultaneous solution in the nearest particles of water. (Matteucci, *Ann. Chim. Phys.* 53, 216.) — 7. The attraction of the water for the camphor, and the repulsive action exerted by the latter upon the water, two opposite directions of one and the same force, which acts in a curve, one extremity of whose major axis corresponds with the neighbouring bodies from which this force proceeds. (Dutrochet.)

			1. Saussure.	2. Göbel.	3. Thomson.	4. Ure.	5. Dumas.
20 C	120	78·94	74·38	74·67	73·8	77·38	78·03
16 H	16	10·53	10·67	11·24	14·4	11·14	10·39
2 O	16	10·53	14·61	14·09	11·8	11·48	11·58
$C^{20}H^{16}O^{2}$	152	100·00	99·66	100·00	100·0	100·00	100·00

	6. Liebig.	7. Blanchet & Sell.	8. Laurent.	9. Dumas & Stubs. *a.*	*b.*	10. Claus.
C	81·76	78·33	77·93	78·91	79·04	79·59
H	9·74	10·61	10·53	10·65	10·55	10·52
O	8·50	11·06	11·54	10·44	10·41	9·89
	100·00	100·00	100·00	100·00	100·00	100·00

	11. Gerhardt.	12. Rochleder. *a.*	*b.*	13. Vohl.
C	78·3	78·84	79·15	81·05
H	10·8	10·40	10·37	10·96
O	10·9	10·76	10·48	7·99
	100·0	100·00	100·00	100·00

	Vol.	Density.
C-vapour	20	8·2300
H-gas	16	1·1088
O-gas	1	1·1093
Camphor-vapour	2	10·4481
	1	5·2240

1 contains also 0·34 N; 2. *Schw.* 40, 356; 3. *Ann. Phil.* 1820, 392; 4. *Phil. Trans.* 1822, 11; *Schw.* 39, 335; 11. from borneol obtained from oil of valerian; 12. *a* from oil of valerian; *b* from oil of sage; 13. from oil of tansy.

According to Saussure, camphor is produced by the union of 1 at. carbonic oxide and 5 At. oil-gas; according to Liebig's first analysis, it corresponds to the formula $C^{12}H^9O$; according to Dumas, it agrees with the formula $C^{10}H^8O$, and consists of 1 vol. camphogen and ½ vol. oxygen, while Blanchet & Sell supposed it to contain a multiple of the radical C^4H^3, in combination with oxygen. Common camphor is related to borneol in the same manner as aldehyde to alcohol. (Berthelot.)

Decompositions. 1. Camphor-vapour, passed through a red-hot glass or porcelain tube, yields a combustible gas, which explodes with 2 vols. oxygen, producing 1·45 vol. carbonic acid (Cruikshank); a volatile oil containing camphor, easily soluble in alcohol; a combustible gas of sp. gr. 0·8397, 1 vol. of which absorbs by explosion 1·4554 oxygen, producing 0·955 vols. carbonic acid: no charcoal separates from the camphor vapours. (Saussure.)

2. Camphor loses its odour completely when an *electric current* is passed through it for some time; the camphor thus deprived of smell remains inodorous for a while, even when removed from the action of the current and in contact with the ground, and recovers its odour after a longer time. (Libri, *Ann. Chim. Phys.* 37, 100; *Schw.* 53, 175.)

3. Camphor, when *set on fire*, burns with a smoky flame, producing carbonic acid and water. A small quantity of camphoric acid (? Gm.) is formed at the same time, and charcoal remains behind. (Bouillon-Lagrange.) Spongy platinum laid on camphor begins to glow when the camphor is set on fire, continues glowing after the flame is blown out, and penetrates through the camphor, while the camphor-vapours in the neighbourhood form an arborescent crystalline sublimate. (Stratingh, *Repert.* 21, 410; Van Dyk, *Repert.* 21, 235.)

4. Moist *chlorine* converts camphor, with evolution of hydrochloric acid, into a liquid compound (hydrochlorate of camphor). (Claus.) Chlorine, passed into an alcoholic solution of camphor, decomposes the alcohol, and at last slowly decomposes the camphor. (Claus.) Camphor melts in chlorine gas to a liquid, which is scarcely heavier than water, rotates to the right, gives off chlorine in the air, leaves dextro-rotatory camphor, explodes readily in sunshine, and deposits camphor. (Deville, *Ann. Chim. Phys.* 75, 58.) Burning camphor goes out in chlorine gas, but burns away in it with a dark red flame and deposits charcoal, if it be wrapped up in tinfoil, and the tinfoil sprinkled with powdered sulphide of antimony. (Meerten & Stratingh, *Schw.* 3, 442; *N. Tr.* 16, 300.)

6. Heated with *iodine*, it gives off hydriodic acid gas (Colin & Gaulthier), only after long-continued action (Guyot, *J. Phys.* 5, 233); compare *Iodocamphor*.

7. By prolonged boiling with *nitric acid*, it is converted into camphoric acid. (Bouillon-Lagrange.)

8. Camphor, heated with *oil of vitriol* to 100° for 12 — 13 hours, is resolved into camphrene (p. xiii. 156), sulphurous acid gas, and charcoal. (Chautard, *Compt. rend.* 44, 66; *J. pr. Chem.* 71, 310.) Heated for an hour with excess of oil of vitriol, it is converted into a volatile oil, which has the chemical properties and composition of camphor, but less rotatory power, and, when heated with potash to nearly 200°, is converted into a solid camphor, whose rotatory power is less than that of the original camphor, but greater than that of the oily camphor. (Delalande, *Instit.* 307, 399.) According to Gerhardt (*Traité*, 3, 694), the oil obtained by Delalande is probably cymene; according to Chautard, it is camphrene containing camphor. Camphor, heated with oil of vitriol forms, with evolution of sulphurous acid gas, a brown mass, from which water

separates a brown substance; on continuing the heat, sulphurous acid gas goes off, together with water, a yellow oil smelling like peppermint, and camphor, and lastly, sulphuretted hydrogen, which decomposes with the sulphurous acid; and there remains a black-brown mass, of which 49 pts. dissolve in water or in alcohol, while 51 pts. remain undissolved. (Hatchett; Chevreul, *Ann. Chim.* 73, 68; *Gilb.* 44, 164.) When camphor is heated with water and a small quantity of sulphuric acid, the escaping vapours redden litmus. (Buchner, *Repert.* 9, 184.)

9. Camphor, distilled with *anhydrous phosphoric acid,* is resolved into water and cymene. (Delalande, *N. Ann. Chim. Phys.* 1, 368.) Heated with concentrated hydrated phosphoric acid, it volatilises for the most part undecomposed, the acid ultimately acquiring a black-brown colour. (Buchner, *Repert.* 22, 420.)

10. *Terchloride of phosphorus,* or *chlorine gas,* converts camphor into quadro- or sex-chlorinated camphor, according to the quantity of the chlorine passed in. (Claus.) Distilled with *penta-chloride of phosphorus,* it is converted into a crystalline substance, which has the appearance and odour of mono-hydrochlorate of turpentine oil, is sparingly soluble in alcohol, yields by repeated distillation a chlorinated oil smelling like turpentine and probably containing $C^{20}H^{15}Cl$, and is itself composed of $C^{20}H^{16}Cl^2$: it remains dissolved in the chlorophosphoric acid which passes over at the same time, is precipitated from this solution by water, and is not decomposed by alcoholic potash. (Gerhardt, *Traite,* 3, 694.)

$$C^{20}H^{16}O^2 + PCl^5 = PCl^3O^2 + C^{20}H^{16}Cl^2.$$

Camphor dissolved in *bromine,* is decomposed by terbromide of phosphorus, with rise of temperature and evolution of hydrobromic acid, yielding only bromocamphor. (Claus.)

11. Camphor is set on fire by *chlorochromic acid.* (Thomson, *Pogg.* 31, 607; *Phil. Trans.* 1827.)

12. By *pentachloride of antimony,* at 100°, camphor is converted, with violent intumescence and sudden evolution of hydrochloric acid, into a red-brown viscid mass. This mass, when shaken up with water, deposits powder of algaroth having a brown tint, while hydrochloric acid and a small quantity of chloride of antimony remain in solution. The alcoholic extract of the precipitated algaroth-powder leaves on evaporation a soft resin, having an agreeable odour, but not like that of camphor, and a sharp taste, producing a scratching sensation in the throat; this resin, when distilled, gives off hydrochloric acid gas and an oil, colourless at first, but afterwards becoming coloured, and having a pleasant taste, like that of peppermint, and leaves a bulky, shining charcoal. The algaroth-powder, after exhaustion with alcohol, still yields a black brown resin to ether. (Claus.)

13. When camphor-vapour is repeatedly passed, under pressure, over heated *potash-lime,* camphilate of potash is produced. (Delalande. *N. Ann. Chim. Phys.* 1, 120; *Ann. Pharm.* 38, 327.) Camphor, enclosed in a sealed tube with *alcoholic potash* or *soda,* and heated in the oil-bath to 180° — 200° for 8 or 10 hours, is converted into borneol (p. 332), with which a little camphor generally remains mixed. (Berthelot.)

14. Camphor continuously boiled with *aqueous permanganate of potash* reduces it, with formation of camphorate of potash. (Cloez & Guignet, *Compt. rend.* 46, 1110; *J. pr. Chem.* 75, 177.)

15. When camphor-vapour is passed through a red-hot tube filled with *fragments of lime,* a strongly coloured oil passes over, which has a

strong and peculiar odour, is lighter than water, boils at 75° after rectification, and dissolves in alcohol and in ether, but not in water. This is Fremy's camphrone = $C^{60}H^{44}O^2$, and contains 85·03 p. c. C, 16·25 H, and 4·72 O (calculation 85·71 p. c. C, 10·47 H, and 3·82 O). If the lime is raised to a very bright red heat, the camphrone is further resolved into carbonic oxide, carburetted hydrogen, and naphthalin. (Fremy, *Ann. Chim. Phys.* 59, 16; *J. pr. Chem.* 5, 355; *Ann. Pharm.* 15, 286.)

16. When camphor-vapour is slowly passed over *red-hot iron*, water and benzene (xi, 134) are produced, or an oil isomeric therewith, which boils at 140°, has a pale yellow colour, is lighter than water, and has a peculiar aromatic odour. (Composition, see xi., 137.) At a very high temperature, naphthalin is likewise produced. (D'Arcet, *Ann. Chim. Phys.* 66, 110; *J. pr. Chem* 13, 248; *Ann. Pharm.* 28, 83.)

17. Camphor, mixed with 2 pts. of alumina or clay, and distilled, is resolved into carbonic acid, carburetted hydrogen, empyreumatic oil, and a residue of charcoal. There is formed at the same time a small quantity of camphoric acid (? Gm.). (Bouillon-Lagrange.)

18. With melting *chloride of zinc*, it is resolved into water and cymene (Gerhardt, p. 183):

$$C^{20}H^{16}O^2 = 2\,HO + C^{20}H^{14}.$$

19. Heated with *corrosive sublimate*, it emits an odour like turpentine and gives off hydrochloric acid gas, leaving a black-brown mass, which, when exhausted with alcohol, leaves charcoal and calomel. (Claus.)

Combinations. With Water. — Camphor dissolves in 1000 pts. of water (Giese); the solution acquires the odour and taste of camphor, becomes turbid with aqueous potash, not with aqueous ammonia or soda. — Heated with water in a Papin's digester, it dissolves more abundantly, apparently with decomposition, without separating on cooling. (Pfaff, *Syst. d. Mat. med.*) — Its solubility in water is increased by the presence of the stronger acids, but not of carbonic acid. (Giese, Brandes.) — In boiling water, camphor volatilises for the most part with the aqueous vapour. (Buchner, *Repert*, 9, 284.)

Camphor melts with *phosphorus* when the two are heated together, the compound subliming without taking fire or shining. — The sublimate shines when rubbed, but not by the mere heat of the hand. — Phosphorus heated in camphor-vapour melts without shining. J. Davy, *N. Ed. Phil. J.* 15, 48; *Schw.* 68, 384.)

Camphor may be melted with *sulphur*. — At medium temperature and pressure, it absorbs sulphurous acid gas abundantly, and when saturated therewith, forms a colourless liquid, which is heavier than water, gives off sulphurous acid gas on exposure to the air and leaves camphor, and, on addition of water, deposits camphor, and dissolves iodine. — The quantity of sulphurous acid gas absorbed by camphor depends upon the pressure and temperature. (Bineau.)

100 pts. camphor absorb of sulphurous acid gas under a pressure of 0·70m.

at 4·0°	70·5 parts.
,, 8·0	58·6 ,,
,, 10·0	54·0 ,,
,, 12·5	48·9 ,,
,, 14·0	46·8 ,,
,, 15·5	44·3 ,,
,, 20·0	37·3 ,,
,, 24·0	33·1 ,,

Camphor dissolves in 0·36 pts. of cold, or in a small quantity of warm *oil of vitriol*, forming a compound which is liquid like pitch while warm, solidifies on cooling, and is soluble in alcohol (Wenzel); it dissolves in 4 pts. oil of vitriol at 100°, forming a dark yellow liquid (Chautard, *Compt. rend.* 44, 66, *J. pr. Chem.* 71, 310); from the solution when fresh, the camphor may be separated by water. (Chautard.) — Camphor, if well cooled, slowly unites with *anhydrous sulphuric acid*, almost without evolution of gas, to a soft brown mass, from which water separates the greater part of the camphor in its original state. (Bineau.) — Camphor does not absorb *sulphuretted hydrogen.* (Bineau.) — It dissolves in *bisulphide of carbon*, forming a liquid which mixes with alcohol, but not with water, and is not precipitated by water. (Lampadius.)

Equal parts of camphor and *iodine* triturated together form iodocamphor. (Claus.) — According to Guyot (*J. Phys.* 5, 233), equal parts of iodine and camphor do not unite at ordinary temperatures, but after some time, the mixture liquefies and gives off iodine without losing the odour of camphor. — Camphor dissolves a small quantity of iodine in the cold, and when heated with it, melts to a dark red-brown mass which solidifies on cooling and has the odour of its constituents (Winckler, *Repert*, 32, 273); triturated with $\frac{1}{10}$ of its weight of iodine, it forms a black-brown mass producing yellow stains. (Voget, *N. Br. Arch.* 16, 155.)

Camphor dissolves abundantly and without decomposition in *bromine* (Claus), forming a nearly inodorous mass which on cooling solidifies in a crystalline mass (Balard, *Ann. Chim. Phys*, 32, 377), consisting of beautifully crystalline bromocamphor. (Laurent.) — The solution of camphor in bromine is converted by phosphorus into liquid bromide of camphor, with formation of terbromide of phosphorus, evolution of hydrobromic acid, and great rise of temperature. (Claus.)

Camphor absorbs a small quantity of *dry chlorine* in sunshine, thereby acquiring a yellow colour in a few weeks.. (Claus.) — Camphor melted at 170° does not absorb chlorine, but volatilises undecomposed. (Claus.) — Camphor unites with *hydrochloric acid gas* in proportions varying according to temperature and pressure. (Bineau.)

100 pts. of camphor absorb of hydrochloric acid gas, according to Bineau:

at	3·0°	and under	0·738	met. pressure	26·0	parts.
,,	3·0	,,	0·232	,,	17·0	,,
,,	7·0	,,	0·740	,,	24·0	,,
,,	7·0	,,	0·230	,,	16·3	,,
,,	9·0	,,	0·288	,,	15·8	,,
,,	13·0	,,	0·322	,,	15·3	,,
,,	15·5	,,	0·744	,,	20·5	,,
,,	18·5	,,	0·735	,,	20·4	,,
,,	20·0	,,	0·740	,,	20·0	,,
,,	24·0	,,	0·747	,,	19·0	,,

Camphor no longer absorbs hydrochloric acid gas:

at	12·0°	and under	0·22	met. pressure.
,,	15·0	,,	0·34	,,
,,	20·0	,,	0·39	,,
,,	24·0	,,	0·42	,,

100 vol. camphor-vapour absorb 23·6 vol. hydrochloric acid gas. (Bineau.) Camphor at 10° and under pressure of 0·726 met. absorbs 144 vol. hydrochloric acid gas and deliquesces with it to a transparent colourless liquid (Saussure, Deville, *Ann. Chim. Phys.* 75, 58), having less rotatory power than camphor. (Deville.)

Camphor dissolves in 2·6 pts. of *concentrated hydrochloric acid*, and is precipitated from the solution by water. (Wenzel.)

Fluosilicic acid gas is not absorbed by camphor. (Bineau.)

Camphor does not absorb *nitrous gas.* (Bineau.) — With *nitrous gas* and *oxygen*, or with vapour of *hyponitric acid*, it forms a pale yellow liquid — greenish if it contains but a small quantity of nitrous acid — which, when exposed to dry air, gives off red fumes till it becomes covered with a crust of camphor, — is decomposed by water into camphor and decomposition-products of hyponitric acid—mixes with alcohol and ether, giving off gas, and similarly with hyponitric acid, — dissolves $\frac{1}{10}$ of iodine at ordinary temperatures, — and, when saturated at 18° contains 79 p. c. camphor and 21 p. c. hyponitric acid. — The hyponitric acid compound of camphor gives off hyponitric acid when immersed in sulphurous acid gas, and the sulphurous acid compound effervesces strongly when hyponitric acid is poured upon it ; in each case, a crystalline compound is produced, which soon turns yellow and gives off red vapours, deliquesces readily, and is resolved by water into camphor, sulphuric acid, nitric acid, and nitrous gas. — Camphor dissolves in *cold concentrated nitric acid*, forming with it a colourless or yellowish oil (nitrate of camphor-oil), which deposits camphor when mixed with water. — Camphor dissolves in $\frac{1}{6}$ pt. of cold fuming nitric acid. (Wenzel.) The camphor-oil which rises to the surface when 1 pt. camphor is heated with 16 pts. dilute nitric acid contains 72·3 p. c. camphor and 27·7 p. c. nitric acid. (Brandes.) The camphor-oil thus produced turns red and afterwards yellow when treated with hydrochloric acid (Bouillon-Lagrange) ; it scarcely dissolves any metal but mercury, because it immediately coats the metal with camphor; it is miscible with alcohol. (Wenzel.) — Camphor absorbs about 1 vol. *ammonia-gas.* (Saussure.)

Camphor is insoluble in aqueous *alkalis*, and does not combine with the other metallic oxides. — From an intimate mixture of camphor with carbonate of lime or carbonate of magnesia, water is said to take up three times as much camphor as it dissolves when shaken up with camphor alone.

Camphor is but sparingly soluble in *vinegar*, but it dissolves in $\frac{1}{12}$ pt. *concentrated acetic acid*, forming a thickish, sharp-tasting, easily volatile, perfectly combustible liquid. (Pfaff, *Syst. d. Mat. med.*) — When camphor dissolves in moderately strong acetic acid, the solution is effected only by the more concentrated portion of the acid, and a watery liquid separates containing a little acetic acid and a trace of camphor. (Vauquelin, *Schw.* 35, 437.) — It dissolves slowly, but abundantly in cold *valerianic acid ;* the colourless viscid solution may be distilled without decomposition, and, when mixed with 30 pts. of water, deposits camphor. (Trommsdorff.)

Camphor dissolves at 12° in $\frac{5}{6}$ pt. of *alcohol* of sp. gr. 0·806. (Saussure.) — The colourless solution (*spirit of camphor, Camphergeist, Spiritus vini camphoratus*), has a sharp taste, and when prepared warm, deposits part of the dissolved camphor on cooling ; when distilled, it gives off alcohol and leaves camphor, and deposits camphor when mixed with water. — 3 pts. alcohol, which, at ordinary temperatures, dissolve 1 pt. of corrosive sublimate, take up 2 pts. of that compound on addition of 1 pt. of camphor; 3 pts. on addition of 3 pts. camphor; 6 pts. on addition of 6 pts. camphor. (Karls, *Pogg.* 10, 608.) — 16 pts. alcohol of sp. gr. 0·865 dissolve 7 pts. of corrosive sublimate, and 9·6 pts. after addition of 4 pts. camphor; by agitation with finely pulverised corrosive sublimate, a solution is at length obtained, containing 25 pts. camphor and 16 pts. sublimate in 4 pts. alcohol. This solution is syrupy, has a sp. gr. of 1·326, and deposits a small quantity of calomel. When diluted with alcohol, it exhibits, with ammonia, potash, and iodide of potassium, the same reactions as corrosive sublimate. Mixed with water, it deposits camphor, and when covered with water and left to itself for a considerable time, it deposits camphor together with crystals of corrosive sublimate. When saturated with chlorine gas, it smells strongly of chloride of ethyl, and, if then left to evaporate, leaves a brown magma which deposits calomel on addition of alcohol, and whose alcoholic solution deposits brown camphor when mixed with water, yields on evaporation a brown resin containing corrosive sublimate, and turns brown when distilled, yielding a sublimate free from mercuric chloride—which smells of camphor and chloride of ethyl, and deposits camphor on addition of water—and leaving a black residue which contains calomel. (Simon, *Pogg*, 37, 553.)

Camphor dissolves in much less than its own weight of *wood-spirit.* (Gm.) — It dissolves abundantly in *acetone.* (Trommsdorff.) — In $\frac{1}{3}$ *chloroform.* (Smith, *N. J. Pharm.* 15, 441.)

Camphor dissolves abundantly in *ether*, and increases the solvent power of ether for corrosive sublimate. — 4 pts. of ether *per se* dissolve 1 pt. of corrosive sublimate; on addition of 1·33 pts. camphor, the same quantity of ether dissolves 1·33 pt.; with 4 pts. of camphor, it dissolves 2 pts.; with 8 pts. of camphor, 4 pts., and with 16 pts. of camphor, 8 pts. of corrosive sublimate. (Karls, *Pogg.* 10, 608.) — Camphor dissolves abundantly in *compound ethers.*

Camphor dissolves readily in *volatile oils:* from a hot solution part of the camphor crystallises on cooling. — It dissolves abundantly in *benzene.* (Mansfield, *Chem. Soc. Qu. J.* 1, 263.)

Camphor dissolves in *fixed oils* and *fats*, and in some *resins.* — Heated to 112° with a few drops of almond-oil and $\frac{1}{10}$ corrosive sublimate, it deliquesces after half an hour, turning brown and giving off hydrochloric acid; the product dissolves completely in a larger quantity of almond-oil, and in alcohol with a residue of calomel. (Simon, *Pogg.* 37, 553.)

Appendix to Camphor.

1. Iodocamphor.

CLAUS. (1842.) *J. pr. Chem.* 25, 264.

Formed by triturating together equal parts of iodine and camphor. — Brown, viscid mixture, which volatilises on exposure to the *air* more rapidly than either of its constituents alone. When *distilled*, it gives off hydriodic acid gas, and yields a brown, mobile distillate having a harsh disagreeable taste like that of turpentine (and, according to Guyot, *J. Phys.* 5, 223, an empyreumatic odour), and consisting of camphin, a small quantity of colophene (p. 279), camphocreosote (*vide inf.*), concentrated aqueous hydriodic acid, a little undecomposed camphor, and free iodine, whilst in the retort there remains a black campho-resin contaminated with charcoal, a little camphin, colophene, campho-creosote, and iodine ($2C^{20}H^{16}O^2 + I = 1$ at. camphin ($C^{18}H^{16}$), 3 at. water, 1 at. hydriodic acid, 1 at. camphoresin ($C^{20}H^{12}$), 2 at. carbon, and 1 at. oxygen, which is expended in the formation of camphocreosote)? — Aqueous *alkalis* decompose iodocamphor, separating the camphor in its original state.

Iodocamphor is insoluble in *water*, but dissolves easily, with hyacinth-red colour, in *alcohol* and *ether*. (Claus.)

2. Bromide of Camphor.

LAURENT. (1840.) *J. pr. Chem.* 20, 498. — *Rev. scient.* 11, 263; *J. pr. Chem.* 28, 333; *Compt. rend.* 10, 532.
CLAUS. *J. pr. Chem.* 25, 260.

Bromcamphor, Bromure de camphre, Camphre bromuré, oxyde de camphène bromuré. (Laurent.)

Formation. By dissolving camphor in bromine. (Laurent.) — When phosphorus is gradually added to a solution of camphor in bromine, oily bromide of camphor is formed, and may be separated from the solution by water. (Claus.)

Preparation. Camphor is dissolved in cold bromine, and the crystals which separate from the mother-liquor immediately or after a few hours (though not always) are quickly pressed between paper, and protected from the action of light. (Laurent.) — The warm solution of camphor in bromine deposits unaltered camphor on cooling. (Laurent.)

Properties. Red, right rhombic, or rectangular prisms.

			Laurent.
$C^{20}H^{16}O^2$	152	51·2	
2 Br	160	48·8	51·2
$C^{20}H^{16}O^2,Br^2$	312	100·0	

Claus considers Laurent's analysis incorrect, owing to the proneness of the bromide of camphor to decomposition.

Decompositions. — Bromide of camphor, when exposed to the *air*, deliquesces, gives off bromine, and leaves camphor. — When distilled, it yields bromine, camphor, a small quantity of hydrobromic acid, and a brominated oil. — In *aqueous potash* it deliquesces, and deposits camphor, after continued agitation.

It dissolves in *water*, the red solution gradually depositing camphor. (Laurent.)

3. Quadrichloro-camphor. $C^{20}H^{12}Cl^{4}O^{2}$.

Claus. (1842.) *J. pr. Chem.* 25, 259; *Rev. scient.* 9, 181.

Camphre quadrichloré, Vierfach-chlorcampher.

A solution of camphor in 3 pts. terchloride of phosphorus is completely saturated with chlorine; the solution which forms at first, with evolution of hydrochloric acid, is ultimately heated to 100°; the clear, pale yellow, balsam-thick product is washed with water and aqueous soda; and the hydrated chlorocamphor which then separates as a cream-like mass, is collected and freed completely from water by heating it in the water-bath, and passing a current of dry air through it. — In this manner, according to the quantity of the chlorine passed through, other chlorocamphors may be formed, containing 1—6 at. chlorine. (Claus.)

Properties. Greenish, nearly colourless, transparent, unctuous oil having at 100° the consistence of olive-oil. It has an agreeable aromatic odour, and a bitter camphorous taste, afterwards sharp and scratching.

			Claus.	
			a.	*b.*
20 C	120	41·38	44·52	
12 H	12	4·13	4·54	
4 Cl	142	48·97	45·12	51·0
2 O	16	5·52	5·82	
$C^{20}H^{12}Cl^{4}O^{2}$	290	100·00	100·00	

a. not completely saturated with chlorine, or a mixture of $C^{20}H^{13}Cl^{3}O^{2}$ and $C^{20}H^{12}Cl^{4}O^{2}$. *b.* obtained by completely saturating with chlorine, a solution of camphor in terchloride of phosphorus, ultimately heated to 100°. (Claus.)

Decompositions. Heated above 100°, it gives off hydrochloric acid gas, yields a chlorinated oil, colourless at first, afterwards pale rose-red, green, and ultimately black-brown, and leaves charcoal. A wick soaked in chlorocamphor *burns* as long as it is held in a flame, but is extinguished when taken out. *Chlorine* converts it, when heated, into sexchlorocamphor. A drop of *pentachloride of antimony* turns it purple-red, then indigo-blue, and frequently, on addition of water, green. (Claus.)

Combinations. Quadrichloro-camphor is insoluble in water, but forms therewith a cream-like mass; it dissolves readily in *alcohol* and *ether.*

4. Sexchloro-camphor. $C^{20}H^{10}Cl^{6}O^{2}$.

Claus. (1842.) *J. pr. Chem.* 25, 259; *Rev. Scient.* 9, 181.

Oxyde de chlocamphalose. (Laurent.)

Produced by passing chlorine gas for some time through quadrichlorocamphor heated to 100°. Colourless mass, of waxy consistence, otherwise resembling the quadrichlorinated compound.

			Claus.
20 C	120	33·42	34·80
10 H	10	2·79	3·10
6 Cl	213	59·47	57·74
2 O	16	4·32	4·36
$C^{20}H^{10}Cl^{6}O^{2}$	359	100·00	100·00

It is not altered by the continued action of a stream of *chlorine.* (Claus.)

Compounds Isomeric with Camphor.

1. Lævo-camphor.

Source. In the oil of *Matricaria Parthenium.* (Dessaignes & Chautard,)

Formation. By boiling lævo-borneol from madder-spirit with nitric acid. (Jeanjean.)

Preparation. The oil of *Matricaria Parthenium* is subjected to fractional distillation; the portion which goes over between 200° and 220 is cooled to — 5°; and the mass, which often solidifies completely, is pressed between paper. (Dessaignes & Chautard.)

Properties. Like those of ordinary camphor. It melts at 170°, boils at 204° (Dessaignes & Chautard), but possesses lævo-rotatory power. (Chautard.)

			Dessaignes & Chautard.
20 C	120	78·94	78·74
16 H	16	10·53	10·69
2 O	16	10·53	10·57
$C^{20}H^{16}O^{2}$	152	100·00	100·00

Decompositions. By prolonged boiling with *nitric acid,* it yields lævo-camphoric acid. (Chautard.)

2. Non-rotatory Camphor.

Separates from the volatile oils obtained from several plants belonging to the order *Labiatæ.* (Proust.) The camphor which separates from oil of lavender (78·14 C, 10·47 H, and 11·39 O, according to Dumas) is destitute of rotatory power. (Biot, *Compt. rend.* 15, 710.)

3. Oil of Wormwood.

Leblanc. *N. Ann. Chim. Phys.* 16, 333; abstr. *Compt. rend.* 21, 379.
Zeller. *Stud. über äther. Oele,* Landau, 1850.
Sasche. *Zeitsch. Pharm.* 5, 14.

Wermuthöl, Essence d'absinthe.

Source and Extraction. In wormwood, *Artemisia absinthum, L.*

The flowering plant, either fresh or dried, is distilled with water. It yields 0·312 p. c. of oil. (Buchner, Martius.)

Properties. Dark green (Leblanc), dirty green (Martius), dark yellow-brown (Zeller). It does not become colourless by repeated rectification. (Leblanc.) The green colour of the oil is due to a peculiar colouring matter; when wormwood-oil is distilled with oil of lemon and oil of cloves and water, colourless wormwood-oil passes over first, and at last green oil of cloves. (Sachse.) Sp. gr. 0·973 at 24° (Leblanc); 0·90—0·96; from the leaves, 0·92; from the flowers, 0·94. (Zeller.) Distils between 180° and 205°, and, after repeated rectification over lime, almost wholly at 205°. Rotatory power 20·67° to the right. Vapour-density = 5·3. (Leblanc.) Has a strong penetrating odour of wormwood and a burning taste (Leblanc); its taste is peculiarly ethereal, sharp, and bitterish. (Martius.) Neutral. (Zeller.)

			Leblanc.
20 C	120	78·9	78·9
16 H	16	10·5	10·6
2 O	16	10·6	10·5
$C^{20}H^{16}O^{2}$	152	100·0	100·0

	Vol.	Density.
C-vapour	20	8·3200
H-gas	16	1·1088
O-gas	1	1.1093
Vapour of Wormwood-oil	2	10·5381
	1	5·7691

Decompositions. 1. The oil becomes darker and more viscid by exposure to the *air*. — 2. With *iodine* it thickens, without fulmination or rise of temperature. Old wormwood-oil, or that which has been exposed to the air, becomes heated in contact with iodine, and gives off vapours up to the point of sublimation. Fresh oil from the leaves yields a grass-green syrupy residue; older oil leaves a brown thicker residue; and oil from the flowers leaves a tough mass which solidifies. (Zeller.) — 3. The oil takes up 2·156 pts. of bromine, and acquires a darker colour. (Knop, *Chem. Centr.* 1854, 498.) — 4. *Nitric acid* decomposes it with violence, forming a non-crystalline resin. (Leblanc.) With ¼ pt. nitric acid of sp. gr. 1·25, it assumes in a few minutes a green colour, changing to dark green and black brown. (Voget, *Br. Arch.* 19, 169; Zeller.) — 5. With *oil of vitriol* it becomes blackish (Leblanc), blue to deep violet (Zeller). — 6. When repeatedly distilled over *anhydrous phosphoric acid,* it gives off water, and yields volatile camphogen, $C^{20}H^{14}$. (Leblanc.) — 7. With *pentachloride of phosphorus* it gives up its oxygen, and exchanges 1 At. H for 1 At. Cl. (Cahours, *Compt. rend.* 25, 725.)

$$C^{20}H^{16}O^{2} + PCl^{5} = C^{20}H^{15}Cl + HCl + PO^{2}Cl^{3}.$$

8. It is not decomposed by *aqueous potash,* but partially by heated *potash* or *soda-lime,* inasmuch as it blackens and partially distils over without alteration. (Leblanc) — 9. *Bichromate of potash* and *sulphuric acid* immediately convert it into a dark flocculent resin. (Zeller.) — 10. When boiled with *nitroprusside of potassium,* it yields a brown black deposit. (Heppe, *N. Br. Arch.* 89, 57.)

Combinations. It dissolves in all proportions of *absolute alcohol,* and in alcohol of sp. gr. 0·85. (Zeller.)

4. Volatile Oil of Pulegium micranthum.

Buttlerow. (1854.) *Petersb. Acad. Bull.* 12, 241; abstr. *Pharm. Centralbl.* 1854, 359.

Source. In *Pulegium micranthum*, a plant growing on the southern steppes of Russia, especially round Sarepta and Astrachan.

Properties. Yellowish; after rectification, colourless or slightly yellowish, mobile. Sp. gr. 0·932 at 17°. Begins to boil at 202°, and boils with tolerable regularity at 227°. It does not solidify at — 17°. Smells and tastes like the oils of peppermint and sage.

			Buttlerow.	
20 C	120	78·94	78·45	79·16
16 H	16	10·53	10·63	10·69
2 O	16	10·53	10·92	10·15
$C^{20}H^{16}O^2$	152	100·00	100·00	100·00

Decompositions. 1. It absorbs oxygen from the air, becoming viscid, specifically heavier, and brownish yellow, without giving off carbonic acid. — 2. With *fuming nitric acid*, it forms chiefly acetic acid, together with small quantities of propionic acid and other fatty acids. — 3. With *hydrochloric acid gas*, it turns brown without solidifying. — 4. By boiling with strong *aqueous potash*, it is converted into a brown, amorphous, acid, brittle resin, insoluble in water, soluble in alkalis and in alcohol (77·96 C, 3·59 H, 13·15 O), and a volatile, altered oil, mixed with an acid liquid containing a fatty acid. When dropt into *melting potash*, it turns brown and decomposes partially, yielding acetic, valeric, and other fatty acids. Heated with *bichromate of potash* and *sulphuric acid*, it forms chiefly acetic acid and other fatty acids. Distilled with *hypochlorite of lime* and water, it yields chloroform.

Combinations. It dissolves readily in *alcohol*, *ether*, and *oils*.

5. Oil of Pennyroyal.

5. In pennyroyal, *Mentha pulegium, L.* The herb is distilled with water. Sp. gr. 0·9721; of the rectified oil, 0·9255. Boils between 183° and 188°.

			Kane. *mean.*
20 C	120	78·94	77·79
16 H	16	10·53	10·85
2 O	16	10·53	11·36
$C^{20}H^{16}O^2$	152	100·00	100·00

Occurs generally mixed with oil of turpentine. (Kane, *Lond. E. Mag. J.* 13, 440; *J. pr. Chem.* 15, 160.

Camphic Acid.

$C^{20}H^{16}O^{4} = C^{20}H^{16},O^{4}$?

Berthelot. (1858.) *N. Ann. Chim. Phys.* 56, 94; abstr. *Ann. Pharm.* 112, 367.

See p. 332. Formed, together with borneol, by heating common camphor for 8 or 10 hours with alcoholic potash to 180 — 200° in sealed tubes. The contents of the tubes are exhausted with water; the undecomposed camphor and the borneol are removed by filtration; the solution, containing potash and camphate of potash, is concentrated by evaporation after neutralisation with sulphuric acid; the mother-liquor is decanted from the sulphate of potash, which separates on cooling, and evaporated to dryness; the residue is exhausted with alcohol; the alcoholic solution is evaporated over the water-bath; the residue is again exhausted with alcohol; and the camphate of potash, which remains as a syrup after the evaporation of the alcoholic solution, is decomposed by dilute sulphuric acid.

The acid forms a nearly solid resin more or less coloured. It is difficult to obtain pure.

When *heated,* it yields an oil, a crystalline, not acid sublimate, and tar, leaving spongy charcoal. Heated with *nitric acid,* it forms a nitro-compound.

It is more or less soluble in *water*, and combines with *bases* to form salts.

Camphate of potash is an uncrystallisable deliquescent syrup; so likewise is *camphate of soda;* both these salts dissolve sparingly in concentrated aqueous alkalis, and separate from the solutions on evaporation, in the form of resinous soaps, easily soluble in pure water. The *camphates* of *zinc-oxide, lead-oxide, ferric oxide, cupric oxide, silver-oxide,* and *ferrous oxide* are thrown down from the aqueous solution of metallic salts by aqueous camphate of soda, as precipitates which are soluble in a large quantity of water and likewise in acetic acid.

Camphic acid is readily soluble in alcohol. (Berthelot.)

Hydrochlorate of Borneol.

$C^{20}ClH^{17} = C^{20}H^{16},HCl.$

Berthelot. *N. Ann. Chim. Phys.* 56, 78.

Camphol chlorhydrique, Chlorbornafer.

Borneol is sealed up in tubes with 8 to 10 pts. of aqueous concentrated hydrochloric acid, and heated to 100° for 8 or 10 hours; and the product is washed with dilute aqueous potash, then with water, and crystallised from alcohol. In most of its properties it resembles monohydrochlorate of turpentine-oil. Rotatory power to the right, but weaker than that of borneol, different from that of mono-hydrochlorate of turpentine-oil. (Berthelot.)

			Berthelot.
20 C	120·0	69·56	
17 H	17·0	9·85	
Cl	35·5	20·59	20·0
$C^{20}H^{16},HCl$	172·5	100·00	

Isomeric with monohydrochlorate of turpentine-oil (p. 265).

Melts and sublimes when *heated*, giving off a small quantity of hydrochloric acid. Ignited with *quicklime*, it gives off borneol, and leaves chloride of calcium.

It unites at ordinary temperatures with bihydrochlorate of turpentine-oil, forming a compound which melts at the heat of the hand.

Benzoate of Borneol.

$$C^{34}H^{22}O^{4} = C^{20}H^{5}O^{3},C^{20}H^{17}O.$$

BERTHELOT. *N. Ann. Chim. Phys.* 56, 78.

Camphol benzoique, Benzbornester.

Borneol and benzoic acid are heated together to 100° in sealed tubes for 8 or 10 hours; the product is washed with aqueous carbonate of potash and caustic potash to remove excess of benzoic acid, and the residual mixture of borneol and benzoate of borneol is heated to 150°, till it no longer has a camphorous odour.

Colourless, inodorous, neutral oil, soluble in alcohol and ether. Heated to 120° with *soda-lime*, it yields borneol and benzoate of soda. (Berthelot.)

¶ *Appendix to Borneene.* (p. 313.)

Oil of Dryabalanops Camphora.

LALLEMAND. *Étude sur la composition de quelques essences. N. Ann. Chim. Phys.* 57, 404; abstr. *Rep. chim. pure*, 2, 89; *N. J. Pharm.* 37, 287; *Ann. Pharm.* 114, 193; *Jahresber. d. Chem.* 1859, 502. — Short notice of results, *Compt. rend.* 49, 357.

This oil, which was originally brought from Sumatra, by Junghuhn, is there obtained by boiling the different parts of the tree, cut up into small pieces, with water, and collecting the oily layer which floats on the surface. — The oil thus produced appears to be essentially the same as that which runs out from incisions in the tree, although the properties of the latter, as described by Pelouze (p. 314), differ considerably from those assigned by Lallemand to the oil obtained by boiling the plant with water. Hence Lallemand concludes that the oil examined by Pelouze could not have been obtained from Dryabalanops camphora. — It is a viscid, reddish oil, having a strong balsamic odour, and turning the plane of polarisation of light to the right. It begins to boil at about 180°, but the boiling point quickly rises to about 255° and then to 300°, at which temperature the whole of the volatile portion has passed over, and there remains a resin, amounting to about half the weight of the original oil. The distilled oil is further resolved by repeated fractional distillation (mostly conducted under diminished pressure) into a more volatile and a less volatile oil, both having the composition $C^{20}H^{16}$.

a. More volatile oil. This oil, which constitutes the smaller portion of the distillate, begins to boil at 180°, the boiling point however quickly rising to 190°. The portion which first passes over (at 180°) has a lower specific gravity (0·86 at 15°), and greater dextro-rotatory power, than that which passes over at the higher temperature (towards 190°). — The oil becomes heated by contact with *oil of vitriol.* — With *hydrochloric acid,* it forms a compound which remains liquid at all temperatures, but which, when treated with strong nitric acid, yields a solid hydrochlorate $C^{20}H^{16},HCl$, resembling artificial camphor (p. 265) in all its properties, excepting that it possesses dextro-rotatory instead of lævo-rotatory power.

b. Less volatile oil. — Somewhat viscid, sparingly soluble in alcohol of ordinary strength, somewhat more in absolute alcohol. Begins to boil at 255°, the boiling point afterwards rising to 270°, and the greater portion distilling at 260°. The specific gravity of the distillate rises with the boiling point from 0·90 to 0·921 at 20°. The distillate is at first lævo-rotatory, then dextro-rotatory; the dextro-rotatory power increases till the boiling point rises to 260°, then diminishes, and the portion which distils at 270° is optically inactive.

The oil *b* gives by analysis 88·74 p. c. C and 11·76 H, agreeing nearly with the formula $C^{20}H^{16}$. — It becomes heated by contact with oil of vitriol.

Hydrochlorate of Oil b. $C^{30}H^{24},2HCl$. — The oil unites with hydrochloric acid, becoming heated at the same time, and forms a compound which is liquid at first, but solidifies partially after some days, and when recrystallised from ether-alcohol, forms colourless four-sided prisms. It turns the plane of polarisation to the left, whether prepared from lævo- or dextro-rotatory or optically inactive oil. Melts at 125°.

			Lallemand.	
30 C	180	64·98	64·80	64·66
26 H	26	9·38	9·45	9·59
2 Cl	71	25·64	25·55	25·92
$C^{30}H^{24},2HCl$	277	100·00	99·80	100·17

It decomposes at 175°, giving off hydrochloric acid. It is decomposed by oxide of lead or mercuric oxide at 100°, more readily by alcoholic potash-ley, with separation of the hydrocarbon (which then exhibits a sp. gr. of 0·90 at 25°, possesses lævo-rotatory power, boils at 260°, and unites with hydrochloric acid, reproducing the original compound).

The hydrochlorate is sparingly soluble in *ether,* moderately soluble in *alcohol.*

c. Resin. $C^{60}H^{46}O^4$? — The resin left in he first distillation of the oil of *Dryabalanops Camphora* is a neutral, dark red, brittle substance, which softens at 100°, and melts at a somewhat higher temperature. It turns the plane of polarisation strongly to the right. It is somewhat soluble in alcohol, more readily in ether. By solution in absolute alcohol, it may be rendered colourless, but cannot be obtained in the crystalline state. It is neutral, and does not unite with bases. It gave by analysis 81·32 p. c. C and 11·03 H, the formula requiring 82·19 C, 10·50 H and 7·31 O. Lallemand supposes it to be formed from the hydrocarbon $C^{30}H^{24}$, by assumption of 6 At. oxygen and elimination of 2 At. water ($C^{60}H^{46}O^4 = 2\,C^{30}H^{24} + O^6 - 2\,HO$).

The oil of Dryabalanops Camphora examined by Lallemand did not contain borneol.

Volatile of Laurus Camphora. — Mobile, nearly colourless, having a strong odour of common camphor and considerable dextro-rotatory power. By fractional distillation it is resolved into an oil boiling at 180°, and a portion boiling at 205°; the latter appears to be essentially the same as common camphor. — The oil boiling at 180° is very much like oil of lemons, possesses strong dextro-rotatory power, and forms with hydrochloric acid, a crystalline compound which melts at 42°, and gives by analysis, 57·34 p. c. C, 8·6 H and 33·83 Cl, agreeing with the formula $C^{20}H^{16},2HCl$ (calculation 57·42 C, 8·61 H, 33·97 Cl.).¶

Appendix to the Primary Nucleus $C^{20}H^{16}$.

Volatile Oils, not yet included in the System, together with the Camphors or Stearoptenes which separate from them.

(Arranged alphabetically.)

1. Oil of Acacia.

The ethereal extract of the flowers of *Acacia alba, L.*, leaves by spontaneous evaporation, a yellow, warty mass, which sticks to the fingers, and has a strong and persistent smell of acacia : it appears to be a product of the decomposition of the oil. — This mass yields by distillation an empyreumatic oil having an unpleasant odour; it is soluble in boiling alcohol, the solution on cooling depositing flocks which exhibit the characters of wax. (Favrot, 1838, *J. Chim. méd.* 14, 212,)

2. Volatile Oil. (*Aceite de amacéy.*)

In the branches of an unknown tree growing in the neighbourhood of Bogota. It exudes spontaneously when the branches are cut, and so plentifully that a litre of oil may be obtained in a few minutes. — Yellowish, mobile, not solidifying at a few degrees below 0°. — Smells like oil of neroli, or rather like oil of rose and *essence de cicari;* its taste is sweet at first, afterwards sharp and bitter. It is used in Bogota for adulterating balsam of copaiba. (Leroy, 1846, *N. J. Pharm.* 9, 107.)

3. Volatile Oil of Acorns.

Obtained by distilling bruised acorns, the fruit of *Quercus robur* and *Q. pedunculata* (*Willd.*), after maceration with water. — Buttery, lighter than water; has a strong peculiar odour. Appears to consist of an oil soluble in ether, and another oil soluble in alcohol of sp. gr. 0·85. (Bley, *N. Br. Arch.* 2, 124.)

4. Alyxia-camphor.

Separates from the inner surface of the bark of *Alyxia Reinwardii*, (*Blume*), a tree growing in Java and Amboyna. — White, neutral, capillary crystals, having an agreeable odour of Tonka beans and a slightly aromatic taste. — Sublimes without melting when heated to 75°—87°; melts and turns brown at a stronger heat. Distils partially with vapour of water. — Nitric acid of sp. gr. 1·2, colours it yellow without dissolving it. — Dissolves very sparingly in *cold*, more easily in *warm water*, and does not separate from the solution on cooling. — Dissolves readily in *aqueous potash, carbonate of potash, ammonia*, &c., without neutralising them; also readily in acetic acid, alcohol of sp. gr. 0·85, ether, and oil of turpentine. (Nees v. Esenbeck, *Br. Arch.* 28, 1.)

5. Oil of Angelica.

By exhausting with alcohol the comminuted roots of *Angelica sativa, M.*, concentrating the solution, precipitating with water, and distilling the separated balsam with hydrate of potash, a colourless oil is obtained, lighter than water, of penetrating odour and camphorous taste. — The same oil is obtained by distilling the comminuted roots with water, and rectifying the resulting oil over hydrate of potash, angelate of potash then remaining behind. — The oil obtained by either of these processes becomes coloured, and resinises on exposure to the air. (A. Buchner, *Repert.* 76, 161.) — Bucholz & Brandes (*N. Tr.* 1, 2, 128) obtained by distillation, 0·7 p. c. of oil; John (*Chem. Tab.* 4, 17), obtained 0·6 per cent.

6. Oil of Angustura.

Angustura-bark, the bark of *Galipea officinalis, Hanc*, yields by distillation with water, 0·75 p. c. of oil. — Light wine-yellow. Sp. gr. 0·934. — Boiling point 266°. — It cannot be rectified with water or solution of common salt. — Has a peculiar aromatic odour, and a mild taste with scratching after-taste. Contains 79·60 p. c. C, 12·31 H, and and 8·09 O, and is therefore perhaps $C^{13}H^{12}O = C^{5}H^{4} + C^{8}H^{8}O$, that is to say, a mixture of oxygenated and non-oxygenated oil. (Herzog, *N. Br. Arch.* 93, 146.) It is not apparently attacked by melting *hydrate of potash*. — Does not combine with *alkaline bisulphites.* (Kraut.)

7. Oil of Animé.

In *animé*, the resin of the locust-tree, *Hymenæa Courbaril, L.* — The resin is distilled *per se.* Colourless oil, with a strong not unpleasant odour and a burning taste. Volatilises without residue; is coloured deep orange-yellow by *oil of vitriol;* dissolves without turbidity in *alcohol.* (Paoli, *Brugn. Giorn.* 16, 326.)

8. Oil of Ants.

In the red ant, *Formica rufa, L.* (compare vii. 271) — The ants are distilled with water or alcohol, the distillate repeatedly cohobated (Marggraf, Nölle), and the oil which floats on the surface, collected. — The process yields 0·12 p. c. of oil (Nölle), 1 p. c. (Hermbstädt.) — Transparent and colourless, with an agreeable odour (Nölle); its taste is not burning (Marggraf, *Chym. Schriften,* 1, 342); sparingly soluble in *absolute alcohol.* (Marggraf; Nölle, *N. Br. Arch.* 31, 183.)

9. Oil of Arnica.

Wolverleiöl. — *a.* In the flowers of *Arnica montana, L.* — Obtained by distillation with water. — Blue (Heyer, *Crell. chem. J.* 3, 100), yellow to brownish green, with a peculiar odour (Zeller), like that of chamomile (Heyer); reacts slightly acid. (Zeller.) — In contact with *iodine,* it becomes slightly heated, reddish yellow-brown and viscid. With *nitric acid,* it assumes a brownish yellow colour, and if heated gives off a large quantity of gas, and forms a solid resin. — With *oil of vitriol,* it assumes a yellow to reddish brown colour. — It dissolves in 100 pts. of *alcohol* o sp. gr. 0·85, becoming turbid and flocculent; with 10—60 pts. of *absolute alcohol,* it forms a turbid liquid, becoming clear only when heated. (Zeller.)

b. In the roots of *Arnica montana, L.*, whence it is obtained by distillation with water. — Wine-yellow to brownish yellow. Sp. gr. 0·98—0·99. Reacts slightly acid. (Zeller.) — It dissolves *iodine,* without rise of temperature or evolution of gas, becoming red-brown and viscid. With *nitric acid,* it becomes hot, gives off gas, assumes a grass-green to yellow-brown colour, and after a while becomes viscid. — With *oil of vitriol,* it turns purple-red. — It dissolves in 2 pts. of *alcohol* of sp. gr. 0·85, and in all proportions of *absolute alcohol.* (Zeller, *Stud. über. äther. Oele,* Landau, 1850.)

10. Oil of Asarum.

GRÄGER. (1830.) *Diss. inaug. de asara europ.* Göttingen, 1830.
ZELLER. *Br. Arch.* 36, 266. — *Stud. über äther. Oele,* Landau, 1850.
SELL & BLANCHET. *Ann. Pharm.* 6, 296.

In asarabacca, the root of *Asarum europæum, L.* — It is exhausted with alcohol, the lower stratum of the extract, consisting of the oil and asarum camphor, is separated from the upper, and distilled ; the residual, oily, thick mass is rectified over hydrate of lime ; and the oil is decanted from the asarum-camphor which separates at the same time, and dehydrated over chloride of calcium. (Sell & Blanchet.)

Properties. Yellowish (Gräger), greenish yellow (Zeller), viscid, lighter than water. (Gräger.) Sp. gr. 1·018. (Zeller.) Smells like valerian, and has a sharp burning taste. (Gräger.) It is neutral. (Zeller.) Contains 75·41 p. c. C, 9·76 H, and 14·83 O, but still retains asarum-camphor in solution. (Sell & Blanchet.)

Asarum-oil, treated with *iodine,* gives off yellowish red vapours, and forms a yellow-brown resin. Heated with *nitric acid,* it gives off gas, and forms a yellow-brown solid resin. — By *oil of vitriol,* it is coloured brown to blood-red and resinised. (Zeller.) — It dissolves sparingly in *water,* more readily in *alcohol,* in *ether,* and in *oils* both *fixed* and *volatile.* (Gräger.)

11. Oil of Balm.

ZELLER. *Stud. über äther. Oele,* Landau, 1850.

In the herb of *Melissa officinalis, L.* at the flowering time. — Obtained by distilling the herb with water. — Colourless, pale yellow. Sp. gr. 0·85—0·82. Has a peculiar odour. Reddens litmus slightly. — According to Bizio (*Brugn. Giorn.* 19, 360), it contains a comphor in solution. — It dissolves *iodine,* with great rise of temperature and evolution of yellowish-red and grey vapours, and becomes viscid. With *nitric acid,* it turns brown, gives off a large quantity of gas when heated, and becomes resinised. — It dissolves in 5 to 6 pts. alcohol of sp. gr. 0·856.

12. Basil-camphor.

$$C^{20}H^{22}O^{6} = C^{20}H^{16},6HO\,?$$

BONASTRE. (1831.) *J. Pharm.* 17, 647.
DUMAS & PELIGOT. *Ann. Chim. Phys.* 57, 334; *J. pr. Chem.* 4, 386; *Ann. Pharm.* 14, 75.

Basilicum-camphor, Essence de basilic.

Basil, *Ocymum basilicum, L.,* distilled with water, yields about 1·56 per cent. of a yellowish green oil, lighter than water (Raybaud, *J. Pharm.*

20, 447), which when kept, solidifies almost wholly as crystalline basil-camphor. (Bonastre.)

Solid oil. Crystallised from alcohol: four-sided prisms having a faint smell and taste; crystallised from water, it forms white, transparent nearly tasteless tetrahedrons. (Bonastre.) Neutral.

			Dumas & Peligot.
20 C	120	63·15	63·8
22 H	22	11·58	11·5
6 O	48	25·27	24·7
$C^{20}H^{16},6HO$	190	100·00	100·0

Isomeric or identical with crystallised turpentine-camphor (p. 262, Dumas & Peligot.)

It burns with odour and flame when *set on fire;* reddens in contact with *oil of vitriol.* (Bonastre.)

Dissolves sparingly in *cold,* easily in *hot water,* in *nitric acid, acetic acid,* and *aqueous ammonia,* imperfectly in cold, perfectly in hot *alcohol,* scarcely at all in 6 pts. of *ether.* (Bonastre.)

13. Oil of Bay.

BONASTRE. (1824.) *J. Pharm.* 10, 36;—11, 3.
BRANDES. *N. Br. Arch.* 22, 160.

Oil of Laurel, Lorbeeröl.

Source and Extraction. In bay-berries, the fruit of *Laurus nobilis,* whence it is obtained by distillation with water, or by arranging the berries in alternate layers with straw, and distilling with steam. (Forcke, *N. Br. Arch.* 17, 177.) Or it is distilled with water and a little sulphuric acid, the latter serving to decompose starch and mucus. (Bonastre.) The yield of oil is 0·26 p. c. (Bley, *Repert.* 48, 96.)

Properties. Pale yellow (Bonastre, Brandes); the most volatile portion, or the oil rectified with water, is transparent and colourless, while the less volatile is yellowish. Lighter than water. (Bonastre.) Sp. gr. 0·914 at 150°; of the most volatile oil 0·857; of the less volatile, 0·885 (Brandes). Liquid at 31°, semi-solid at 12·5°; at low temperatures perfectly solid and dirty white. Smells like bay-berries; the most volatile portion, like oil of cajeput; the less volatile has a similar odour but less pure, and, after rectification with water, also like that of camphor (Brandes); the oil obtained by distilling bay-berries with sulphuric acid and water, has a less agreeable and empyreumatic odour. (Bonastre.) Tastes strong and bitter. (Bonastre.) It is neutral (the crude oil is slightly acid). (Bonastre.)

	Brandes.				
	a.	*b.*	*c.*	*d.*	*e.*
C	80·60	80·55	80·56	78·85	82·14
H	11·76	11·26	9·30	11·14	11·54
O	7·64	8·19	10·14	10·01	6·32
	100·00	100·00	100·00	100·00	100·00

a was obtained by rectifying the crude oil *per se* in the first instance; *b* that which passed over on rectifying the crude oil with water; *c* a portion boiling at a higher temperature; *d* that which has the highest boiling point; *e* obtained by rectifying the crude oil with concentrated aqueous potash. The latter has the composition of crude oil of camphor. (Brandes.)

Decompositions. 1. Bay-oil absorbs oxygen from the air (Brandes). — 2. With 2 pts. of *fuming nitric acid* it froths up, and forms a soft yellow resin, which separates on addition of water. (Hasse, *Crell. Ann.* 1785, 1, 422.) — 3. When agitated with *potash*, it forms after some time an oil, which floats on the surface, and a brown liquid, which, after saturation with hydrochloric acid, yields a white precipitate soluble in ammonia. Distilled with *aqueous potash*, it yields a neutral oil (*e*), having an odour of camphor and cajeput-oil, but not very pungent. (Brandes.)

Combinations. Mixed with *ammonia*, it yields a turbid liquid, and with *caustic baryta* a white viscid liquid. (Brandes.) It is easily soluble in *alcohol*. The least volatile portion of the oil dissolves but partially in *alcohol*, *aqueous potash*, and *ammonia*, leaving a brown oil, while the alcoholic solution contains a crystalline substance; the potash-solution, a substance which separates on supersaturating with hydrochloric acid, and is soluble in potash and in ammonia; and the ammoniacal solution contains a substance which forms a white precipitate with chloride of calcium.

Bay-oil dissolves readily in *ether* and in *oils*, both *fixed* and *volatile*; with the aid of heat, it dissolves *tallow* and *wax*. (Brandes.)

14. Volatile Oil of Beans.

Formed spontaneously in pulverised dry beans, *Phaseolus communis*: 1. On moistening the powder with water. — 2. On evaporating the alcoholic extract and mixing the residue with almond milk. Bean-flour, exhausted with alcohol, does not form any oil when moistened with water. (Ed. Simon, 1842, *N. Br. Arch.* 29, 186.)

15. Oil of Birch-leaves.

In the leaves of the birch, *Betula alba, L.* By distilling them with water, 0·36 p. c. of oil is obtained, floating on a milky distillate. Colourless, mobile; the last distillate is yellowish and viscid, lighter than water; becomes somewhat turbid and viscid at 0°, retains scarcely any fluidity at —5°; solidifies at — 10°, but not in the crystalline form; melts at the heat of the hand. Its odour is very agreeably balsamic, persistent and exciting, like that of young birch leaves and oil of roses. Its taste is at first mildly sweetish, afterwards peculiarly balsamic, sharp, and heating. The oil becomes pale yellow after some time, and when dropped upon paper makes a waxy spot, which may be extracted by boiling water, forming a solution which deposits white flocks on cooling. The oil appears to contain a waxy substance in solution (*Betulin*, Gm.).

It dissolves in 8 pts. alcohol of sp. gr. 0·85 at 12·5°, forming a clear liquid, which becomes turbid at 0°; it dissolves slowly in ether, separating out slowly at 0°. (Grassmann, *Repert.* 33, 337.)

16. Volatile Oil of Botany Bay Resin.

Obtained by distilling the resin of *Xanthorrœa arborea* (*R. Brown*) with 6 pts. water. Colourless; has an agreeable odour and very sharp aromatic taste. (Trommsdorff, *Taschenb.* 1826, 9.)

17. Camphor of *Buphthalmum maritimum.*

In the flowers of *Buphthalmum maritimum,* a plant growing on the shores of Greece. The flowers, which have an agreeable odour of roses, are distilled with water; the distillate is cohobated, and the crystals which separate from it at about 0° are collected. Yellow, pointed crystals, having a silky lustre, and melting at the heat of the hand to a yellowish oil, having an agreeable but not powerful odour. Reddens litmus slightly. Soluble in *alcohol;* the solution is rendered turbid by water. (Landerer, *Repert.* 79, 233.)

18. Oil of Cardamom.

In cardamoms, the seed of *Elettaria Cardamomum.* (*Whit. & Mat.*) They are distilled with water. The water likewise contains acetic acid. (Wunder, *J. pr. Chem.* 64, 499.) Pale yellow. (Neumann, Zeller.) Sp. gr. 1·92 — 0·94. Tastes and smells like the seeds. Neutral. (Zeller.) Probably a mixture of a liquid and a solid oil, inasmuch as Dumas & Peligot (*Ann. Chim. Phys.* 57, 334; *J. pr. Chem.* 4, 386; *Ann. Pharm.* 14, 75) found in it colourless prisms, which according to them contain 64·0 p. c. C, 11·4 H, and 24·6 O, a composition agreeing with the formula $C^{20}H^{16},6HO$. so that they are isomeric or identical with turpentine-camphor. Oil of cardamom, treated with *iodine,* gives off yellowish-red and grey vapours, and becomes reddish yellow-brown and viscid. With *nitric acid,* it yields a pale brownish-yellow resin. (Zeller, Hasse.) With *oil of vitriol,* it acquires a red-brown colour, with *chromate of potash* and *sulphuric acid,* greenish-brown. (Zeller.) It dissolves in *alcohol* of sp. gr. 0·85. (Zeller, *Stud. über. äther, Oele,* Landau, 1850.)

19. Oil of Carrot.

From the roots of *Daucus Carota, L.* They are cut up while fresh and distilled with water, whereby 0·0114 p. c. of oil is obtained. Colourless. Sp. gr. 0·8863 at 11·2. Has a peculiar strongly penetrating odour, and a taste of similar character, but at the same time warming and somewhat unpleasant. It dissolves sparingly in *water,* readily in *alcohol* and *ether.* (Wackenroder, *Mag. Pharm.* 33, 145.)

20. Oil of Cascarilla.

TROMMSDORFF. (1833.) *N. Tr.* 2, 136.
VÖLKEL. *Ann. Pharm.* 35, 306; *Repert*, 80, 169.

In cascarilla bark, the bark of *Croton Elateria* (*Schw.*) It is comminuted and distilled with water. The quantity of oil obtained amounts to 0·35 p. c. (Bley, *Repert.* 48, 97), to 0·87 p. c. (Trommsdorff.)

Properties. Dark yellow (Trommsdorff, Völkel) (sometimes of various shades from blue to yellow, or greenish: Trommsdorff): the first distillate is colourless, mobile, and refractive; the later portions yellowish and more viscid; the last very thick. (Völkel.) Sp. gr. 0·938 (Trommsdorff); 0·909; of the first distillate, 0·862. (Völkel.) Boiling point 180° and higher; of the first distillate 173°. Smells aromatic, like camphor, thyme, and lemons (Trommsdorff); its odour is agreeable; that of the last distillate less agreeable. (Völkel.) Taste aromatic, rather bitter. (Trommsdorff.)

	Völkel.	
	a.	*b.*
C	84·69	80·90
H	10·49	10·27
O	4·82	8·83
	100·00	100·00

a The first distillate obtained on rectifying with water; *b* the last distillate. The crude oil is a mixture of at least two oils, the most volatile of which is probably free from oxygen. (Völkel.)

Decompositions and Combinations. The oil is decomposed by the stronger *acids*, but not by *alkalis*. (Völkel.) With *fuming nitric acid*, it yields a yellow fragrant resin, without taking fire. (Trommsdorff.)

Dissolves readily in *alcohol;* the solution reddens litmus. (Trommsdorff.)

21. Oil of Convolvulus scoparius.

Rosenholzöl. In the wood of the root and stem of the plant. Pale yellow, mobile, lighter than water, with an odour of roses, cubebs, and balsam of copaiba, somewhat viscid, and a bitter aromatic taste. It becomes reddish after some time. It absorbs *iodine vapours* in a few hours, and becomes brown and black. With $\frac{1}{4}$ pt. *nitric acid*, it acquires a pale brown colour, without losing its odour. (Bonastre.) In *nitrous acid vapours* it acquires a dark yellow colour. Mixed with an equal number of drops of *oil of vitriol*, it forms a brown mixture, having an odour of cubebs. (Guibourt, *N. J. Pharm.* 15, 347.)

22. Oil of Culilawan.

Exists in the bark of *Cinnamomum Culilawan* (*Nees*), and is obtained therefrom by distillation with water. Colourless, heavier than water, smells like the oils of cajeput and cloves. With *fuming nitric acid* it becomes heated, without however taking fire, and forms a crimson liquid, which, on being mixed with water, deposits a brick-red resin (Schloss); heated with 5 pts. of fuming nitric acid, it swells up strongly, gives off nitrous gas, and, when repeatedly distilled, yields oxalic acid amounting to $\frac{1}{6}$ pt. of the oil. (Daryk.)

23. Oil of Castoreum.

Obtained by distilling castoreum repeatedly with water, and constantly pouring back the distillate (Bohn), or by exhausting with cold ether, evaporating the extract, and distilling the residue repeatedly with water, as long as oil passes over. (Brandes, *N. Br. Arch.* 1, 183). — Pale yellow (Bohn, Brandes); viscid (Bohn); heavier than water (Brandes); lighter than water (Bohn); has a strong odour of castoreum (Bohn, Brandes); and a sharp, bitter taste. (Bohn.) — If left for six weeks in contact with the water which has passed over with it, it is partially converted into an oil, which floats on the water, leaves resin when distilled, is completely resinised by contact with the air, especially if likewise exposed to light, but remains unaltered if protected from air and light. (Brandes.) — It dissolves sparingly in *water*, readily in *alcohol*. (Bohn.)

24. Camphor of Cat-thyme.

Amberkraut-camphor. — In all parts of cat-thyme, *Teucrium Marum, L.* — The dry herb is distilled with water, and the distillate repeatedly cohobated over fresh quantities of the green herb. — White, crystalline, transparent, brittle mass, consisting of thin laminæ, and sinking in water. Has an unpleasant odour and aromatic taste. (Bley, 1827, *N. Tr.* 14, 2, 87.)

25. Oil of Celery.

Sellerei-öl. — In the seeds (Tietzmann), the herb (Vogel) of celery, *Apium graveolens,* L. — It is obtained by distillation with water. — Transparent and colourless (Vogel), pale yellow (Tietzmann), lighter than water (Vogel), of sp. gr. 0·881; has a pungent, sweetish heating odour. Dissolves sparingly in *water*, readily in *alcohol* and *ether*. (Vogel, *Schw.* 37, 365; Tietzmann, *Taschenbuch*, 1821, 45.)

26. Oil of Wild Chamomile.

Zeller. (1827.) *Repert,* 25, 467.—*Stud. über äther. Oele,* Landau, 1850.
Steer. *Repert,* 61, 85.
Bornträger. *Ann. Pharm.* 49, 244; abstr. *Repert,* 90, 215.

Kamillenöl, Essence de camomille bleue.

Source and Extraction. In the flowers of wild chamomile, *Matricaria Chamomilla, L.*—The herb recently dried is distilled with water or with steam.—Tin receivers are used for collecting the distillate, because all the oil then collects on the surface of the water which passes over with it, whereas in glass receivers, a portion of the oil adheres obstinately to the sides of the vessel.—Distillation with steam is preferable to distillation with water, because it obviates the risk of burning the chamomile-flowers, which swell up considerably; the steam must however be passed through without interruption, to prevent the chamomiles from adhering in lumps, which would interfere with the passage of the vapour. (Steer.)—The water which passes over contains a colourless oil, having a different odour from the oil which floats on the surface; this oil may be extracted from the water by agitation with ether, and it remains behind after the evaporation of the ether. (Bornträger.) The water which passes over with the oil contains acetic acid. (Hautz, *J. pr. Chem.* 62, 317.)

The yield of chamomile-oil is less as the flowers are older; dry chamomiles yield 0·113 p.c., (Gumprecht, *Br. Arch.* 7, 108); chamomiles four years old yield in four distillations 0·04 p.c.; recently dried chamomiles yield by two distillations with steam the distillate being collected in tin vessels, 0·416 p.c. of oil. (Steer.)

Properties. Dark blue, azure-blue, nearly opaque; perfectly fluid at 12°, viscid at 5° (Zeller); of the consistence of honey at −4°, solid at −6° (Bizio, *Brugn. Giorn.* 19, 360); solid from −10° to −12°; melting again at −5°. (Zeller.) According to Bornträger, it merely becomes thick below 0°, but does not solidify.—Sp. gr. 0·92 — 0·94.—Has a strong odour of chamomile, and an aromatic warming taste. (Zeller.)

	Bornträger.		
	a.	*b.*	*c.*
C	79·83	79·56	78·26
H	10·64	10·83	
O	9·53	9·61	
	100·00	100·00	

a, crude oil; *b* rectified; *c* the last distillate. Its composition is nearly the same as that of common camphor. (Gerhardt, *Traité*, 4, 353.)

Decompositions. 1. When exposed to *air* and *light,* it assumes various shades of colour from green to brown, and finally becomes greasy. The fresher the chamomiles used in the preparation, the longer does the oil retain its colour on exposure to air and light. (Zeller.)—2. When distilled, it leaves a small quantity of brown resin; distilled with water, it passes over blue from first to last, while the water which goes over at the same time is colourless. (Bornträger.)—3. With *iodine,* it becomes heated without detonating; gives off a few yellowish red vapours becomes greenish to yellowish brown, viscid, and at last solid and friable. (Zeller.) — 4. With *fuming nitric acid* it assumes a dark brown colour, and then yields with water a yellow-brown resin smelling like musk (Hasse, *Crell. Ann.* 1785, 1, 422); with nitric acid of sp. gr. 1·28 it turns green, then dark red-brown, gives off gas with violence when heated, and leaves a brittle, friable resin. (Zeller.) — 5. With *oil of vitriol*, it assumes a dark red-brown colour, and forms a soft resin (Zeller); on adding water to the mixture, it takes fire with explosion. (Hasse, *Crell. Ann.* 1786, 2, 36.) — 6. With *bichromate of potash* and *sulphuric acid*, it becomes yellow-brown and thickens. (Zeller.) It dissolves in 8 to 10 pts. of alcohol of sp. gr. 08·5 easily and with blue colour in *ether*. (Zeller.)

27. Oil of Chenopodium Ambrosioïdes.

M. Martini. (1737.) *Diss. de Chenop. ambrosioïd.*
Bley. *N. Tr.* 2, 32. — *Repert.* 48, 96.
Becker & Hirzel. *Pharm. Zeitschr.* 1854, 8.

Mexicanisches Traubenkrautöl.

Source and Extraction. In *Chenopodium ambrosioïdes, L.*, a plant growing in Mexico. The plant, distilled with water, yields 0·31 p. c. oil (Martini), 0 319 p. c. (Bley), 0·78 — 1·17 (Becker.)

Properties. Pale yellow or pale greenish yellow (Bley); transparent and colourless after rectification (Hirzel); very mobile (Bley); strongly refractive after rectification (Hirzel). Sp. gr. of the rectified oil, 0·902; boiling point 179° — 181°. (Hirzel.) When floating on water at low temperatures, it solidifies with the consistence of tallow or wax. (Martini.) Has a strong odour like that of the plant (Becker), and at the same time like that of onions. (Bley.) Tastes stongly aromatic, somewhat bitter and burning (Bley); cooling like oil of peppermint. (Beckel.)

Decompositions. 1. The oil easily *takes fire* (Hirzel), and burns with a very smoky flame. (Bley, Hirzel.) It is violently attacked by *fuming nitric acid.* — 3. With *oil of vitriol* it turns red and resinises. (Bley.)

Combinations. With aqueous *ammonia* it forms a permanent liniment. (Bley.)

It dissolves sparingly in *water*, easily in *alcohol, ether,* and *oils* both *fixed* and *volatile* (Bley); in 3 pts. of alcohol and in 30 pts. of water. (Becker.)

28. Oil of Coffee.

Occurs in roasted coffee. To obtain it, coffee roasted at a gentle heat is covered with 10 pts. of water, and left to stand for two hours, and the whole is then distilled from a retort, which is connected with four receivers joined together by tubes; the contents of the third receiver, which consists of solid inodorous oil and a watery distillate smelling strongly of coffee, are collected, and the latter is agitated four times in succession with ½ of its volume of ether, the ether being each time decanted after standing for a quarter of an hour, and then left to evaporate. It is advantageous to fill the third and fourth receivers with lumps of chloride of calcium, connect them with the fourth by means of a chloride of calcium tube; cool the fourth receiver to 20° — 30° during the distillation; extract its contents as before with ether; and leave the ether to evaporate. A volatile empyreumatic hydrocarbon distils over at the same time, and collects in the last receiver in greater quantity in proportion as the coffee has been roasted at a stronger heat.

Oil of coffee is orange-yellow, and has a strong odour of coffee. It consists of two oils, one of which is less volatile and liquid than the other, and appears to be produced by alteration of the other which possesses the fragrant odour. (Payen, *Compt. rend.* 23, 244; *J. pr. Chem.* 38, 478; *N. Ann. Chim. Phys.* 26, 116; abstr. *N. J. Pharm.* 10, 270.)

29. Oil of Curcuma.

In the root of *Curcuma longa, L.* The comminuted root is distilled with water, and the distillate is cohobated several times. Lemon-yellow, mobile, with a penetrating odour and burning taste. (Vogel & Pelletier, 1815; *J. Pharm.* 1, 291.)

30. Oil of Curcuma Zerubet.

Zitterwurzöl. — In the tubers of *Curcuma Zerubet* (*Roxbourgh*), from which it is extracted by distillation with water. Pale yellow, turbid, viscid, heavier than water; has a peculiar, strongly camphorous odour, and a rather bitter, fiery, camphorous taste. (Buckholy, 1817; Alman, 1817, 45.)

31. Oil of Dahlia.

In the roots of several species of *Dahlia.* They are bruised to a pulp and distilled with water. The oil is lighter than water, has a strong odour like the roots, and a sweetish taste, with slightly acrid after-taste in the throat. It changes after a while into a reddish resin insoluble in alcohol. In *water,* it gradually sinks to the bottom, becomes buttery and indistinctly crystalline; melts when heated, and forms on cooling long prisms of benzoic acid, whilst the oil separated therefrom does not crystallise. It forms with *water* a permanently turbid emulsion, which runs through the filter. It dissolves in *alcohol,* and is left with amber-yellow colour when the alcohol evaporates. (Payen, 1824, *J. Pharm.* 9, 384; 10, 239; abstr. *Repert.* 20, 337.)

32. East Indian Grass Oil.

This oil appears to be identical with *Oil from Namur*, though the latter, according to Royle, is obtained from *Calamus aromaticus.* It occurs in *Andropogon Ivarancusa*, a grass growing in the East Indies. It is yellow, but becomes transparent and colourless after distillation with water; floats on water; boils between 147° and 160°, or partly at higher temperatures. Has a pungent aromatic odour, similar to, but fainter than that of rose-oil, less agreeable after distillation with water. Tastes sharp like lemon-oil. Contains 83·51 p. c. C, 11·46 H, and 5·03 O. In contact with *sodium*, it quickly gives off hydrogen, deposits a reddish resin, and if then distilled, yields an oil which quickly resinises, contains 88·37 p. c. C, and 11·56 H, and is therefore isomeric with oil of turpentine. (Stenhouse, 1844, *Phil. Mag. J.* 25, 201; *Ann. Pharm.* 50, 157; *Mem. Chem. Soc.* 2, 122; *Chem. Gaz.* 1844, 294.)

33. Oil of Elder-flowers.

Fliederblüthenöl, Hollunberblüthenöl. — In the flowers of the elder, *Sambucus nigra.* The dried flowers are distilled with water, and the distillate is several times redistilled over fresh quantities of the flowers; or very concentrated elder-water is agitated with ether and the ether left to evaporate. The flowers yield scarcely 0·32 p. c. of oil. (Pagenstecher.) Buttery (Lewis); crystalline and of waxy consistence, greenish-white (Eliason), light yellow, mobile, floats on water, smells strongly of the flowers (Pagenstecher); has a rather bitter burning taste, with cooling after taste. (Eliason, Pagenstecher.) The oil becomes dark brown and viscid when exposed to the *air.* — *Chlorine gas*, passed into elder-water, at first produces thick fumes, and afterwards imparts a dark yellow colour to the drops of oil which float on the water, and finally sink to the bottom, whilst the water acquires a strong odour of radish, contains but little hydrochloric acid after saturation, and, when evaporated at a gentle heat, leaves a chlorinated oil having a sharp biting taste, mixed with crystals. *Bromine* acts like chlorine, yielding a brown brominated oil, which sinks in water. — Elder-water mixed with *hydrochloric acid*, yields a small quantity of sal-ammoniac when evaporated; the ammonia which it contains results from the decomposition of a constituent of the flowers; the oil is free from ammonia. (Pagenstecher, *Repert.* 73, 35.) — The oil dissolves in absolute *alcohol* and *ether*, sparingly in alcohol of sp. gr. 0·85, in *oil of rosemary* and in *water;* the aqueous solution is neutral. (Eliason, *N. Tr.* 9, 1, 246.) Fr. Müller (*N. Br. Arch.* 45, 153), by distilling recently dried elder-flowers with water, obtained a yellow water, which, when treated with alkalis, became darker in colour, gradually deposited yellowish non-crystalline flocks, which when dissolved in ether, coloured it yellow, and remained when the ether was evaporated in the form of yellowish transparent scales, soluble with yellow colour in carbonate of potash, and precipitated by acetic acid.

34. Oil of Feverfew.

Obtained by distilling common feverfew, *Pyrethrum Parthenium* while in the flowering state, with water. Greenish; passes over between 165° and 220°; the largest portion between 205° and 220°, leaving a coloured residue. Deposits camphor on standing, this deposit being formed most abundantly in the oil which passes over between 212° and 220°, on cooling. Oil prepared in 1845, did not yield any camphor on standing.

	Dessaignes & Chautard.					
	a.	*b.*	*c.*	*d.*	*e.*	*f.*
C	77·60	77·96	76·92	77·02	85·77	86·46
H	10·37	10·60	10·37	10·24	11·22	11·58
	87·97	88·56	87·29	87·26	96·99	98·04

a, Oil separated from the deposited camphor; *b*, oil containing only a small quantity of camphor; *c*, oil boiling at 216° — 220°; *d*, at 212° — 216°; *e*, at 170° — 180°; *f*, at 160° — 167°, repeatedly rectified over potash. The oil contains camphor, a hydrocarbon, and an oil richer in oxygen than camphor. (Dessaignes & Chautard, *N. J. Pharm*, 13, 251; *J. pr. Chem.* 45, 45.) — The camphor contained in oil of feverfew is lævo-camphor. (Chautard, *Compt. rend.* 37, 166.)

35. Oil of Galanga.

Galgantöl. — In the root-stocks of *Alpinia Galanga* (*Schwartz*). They are pulverised and distilled with water. The water which passes over with the oil has the odour and taste of the roots, and contains carbonate of ammonia. Yellowish white, transparent and colourless after rectification (Vogel); brownish yellow (Raybaud, *J. Pharm.* 20, 455); lighter than water (Vogel, Raybaud); not very volatile; smells like oil of cajeput. Contains 73·91 p. c. C, 11·67 H, and 14·42 O, and has therefore the composition of cajeput-oil (p. 335). Loses its odour and becomes viscid on exposure to the *air*. Dissolves partially in *aqueous potash*, completely and readily in *alcohol* and *ether*. (A. Vogel, jun., *Repert.* 83, 22.)

36. Oil of Gale.

Obtained from sweet gale, *Myrica Gale, L.*, by distilling the fresh leaves with water and cohobating the distillate several times. The yield of oil amounts to 0·65 per cent. — Brownish yellow. Sp. gr. 0·876. Solidifies partially at 17·5°, and changes at 12·5° into a thickish, slightly crystalline mass, mixed with tough, transparent, yellowish laminæ. Odour peculiar, balsamic, and agreeable; taste, mild at first, then transiently burning and permanently astringent. Neutral. — Contains about 70 p. c. camphor, and consists of 81·75 p. c. C, 3·00 H and 15·05 O. — It dissolves *iodine* without explosion, becoming viscid and olive-green. By *fuming nitric acid* at mean temperature, and by ordinary *nitric* acid at 100°, it is converted, with evolution of nitrous acid, into a gold-coloured thickish liquid, which becomes turbid on cooling, and does not form a clear solution in water. — With *oil of vitriol,* it forms a dark brown mixture. — It dissolves in 40 pts. of *alcohol* of sp. gr. 0·875 at 15°, more abundantly in *ether.* (Rabenhorst, *Berl. Jahrb.* 35, 2, 220; *Repert.* 60, 214.)

37. Oil of Geum urbanum.

Nelkenwurzöl. — In the root of wood avens, *Geum urbanum, L.*, whence it is obtained by distillation with water, the yield being 0·04 p. c. — Greenish yellow, buttery. (Trommsdorff.) Smells like cloves. Consists of an acid oil, which unites with alkalis and separates from the solution on addition of acids. (Buchner, *Repert.* 85, 19.) — Dissolves readily in *alcohol* and *ether.* (Trommsdorff, 1818, *N. Tr.* 2, 1, 55.)

38. Oil of Ginger.

Buchholz. (1817.) *Almanach,* 1817, 111.
Morin. *J. Pharm.* 9, 253; *Repert.* 20, 376.
Papousek. *Wien. akad. Ber.* 9, 315; *J. pr. Chem.* 581, 228; abstr. *Ann. Pharm.* 84, 252.

Ingweröl, Essence de gingembre.

Source and Extraction. In ginger, the roots of *Zinziber officinale* (*Rosc.*), whence it is obtained by distillation with water.

Properties. — Yellowish (red, according to Neumann, greenish blue, according to Morin), very mobile. (Buchholz.) Sp. gr. 0·893. — Boiling point 246°. Has a strong odour of ginger, and a burning aromatic taste (Papousek); rather mild, with somewhat biting and bitter aftertaste. (Buchholz.)

Dehydrated.			Papousek.
80 C	480	81·49	81·03
69 H	69	11·72	11·58
5 O	40	6·79	7·39
$C^{80}H^{64} + 5HO$	589	100·00	100·00

Such according to Papousek, is its composition when slowly distilled at a heat below 150°.

Decompositions. 1. When strongly heated, it becomes darker and gives up water. — 2. By repeated distillation over *anhydrous phosphoric acid,* it is converted into a yellowish oil isomeric with oil of turpentine (87·99 C and 11·88 H).

Combinations. With Hydrochloric acid. $C^{80}H^{67}Cl^3 = 3(C^{20}H^{16},HCl) + C^{20}H^{16}$? — Obtained by passing hydrochloric acid gas to saturation into oil of ginger, washing and distilling the brown product with water, and dehydrating over chloride of calcium.

			Papousek.
80 C	480·0	73·45	73·39
67 H	67·0	10·25	10·36
3 Cl	106·5	16·30	16·25
$3(C^{20}H^{16},HCl) + C^{20}H^{16}$	653·5	100·00	100·00

This is the formula assigned to it by Papousek.

39. Oil of Hedwigia.

In the balsam of *Hedwigia balsamifera* or *Bursera balsamifera.* — Obtained by distillation with water. Yellow, transparent oil, which floats on water, has an agreeable odour of turpentine, and a burning taste. — With ¼ pt. *nitric acid,* it becomes first flesh-coloured, then crimson, then dark amaranth-coloured, and after 24 hours, brown, but colourless again on being mixed with water; when boiled with 2 pts. of nitric acid, it assumes a yellow colour and becomes resinised. — With *oil of vitriol,* it turns first yellow, then yellowish red, soon acquiring an empyreumatic taste and odour. — With *hydrochloric acid,* it assumes first a rose-, then an amaranth-red colour. — It dissolves completely at first in more than 4 pts. of *alcohol,* and in all proportions of *ether.* (Bonastre, 1826, *J. Pharm.* 12, 488.)

40. Volatile Oil of Hemp.

In hemp (*Cannabis sativa.*) — The fresh herb, just after flowering, is distilled, and the oil-drops which float on the milky distillate containing carbonic acid, are collected. — The yield of oil is 0·3 per cent. — Pale yellow, lighter than water, smells like the fresh herb, tastes aromatic, not burning but strong; its vapour, when inhaled, produces head-ache and slight delirium; a few drops taken internally produce warmth in the throat and stomach, heaviness in the head, and giddiness, but no abdominal derangement. (Bohlig, *Jahrb. pr. Pharm.* 3, 4. — *Repert.* 80, 308.)

41. Oil of Hyssop.

STENHOUSE. (1842.) *Phil. Mag.* 20, 274; *J. pr. Chem.* 27, 255; *Mem. Chem. Soc.* 1, 43.
ZELLER. *Stud. über äther. Oele,* Landau, 1850.

Hyssopöl, Ysopöl, Essence d'hysope.

Source and Extraction. In hyssop, *Hyssopus officinalis, L.* It is obtained by distilling the fresh herb or the fresh leaves with water. — The yield of oil is very large. (Stenhouse.)

Properties. Transparent and colourless (Stenhouse), greenish yellow. (Zeller.) — Sp. gr. 0·88—0·98. (Zeller.) — Passes over between 142° and 162·8°, the last portions being coloured. — Has a peculiar odour and a sharp camphorous taste. (Stenhouse.) Neutral. (Stenhouse, Zeller.)

	Stenhouse.		
	a.	*b.*	*c.*
C	84·18	81·29	80·31
H	11·00	10·95	10·45
O	4·82	7·76	9·24
	100·00	100·00	100·00

a distilled at 142°; *b* at 148·3°; *c* at 168·3°. It is a mixture of several, or at least of two oils. (Stenhouse.)

Decompositions. 1. The oil when exposed to the *air* gradually becomes yellowish and resinous. (Stenhouse.) — 2. With *iodine* it becomes hot, gives off yellowish red vapours, turns reddish yellow-brown and thickens. (Zeller.) — 3. Heated with *nitric acid*, it yields a yellow resin (Zeller); with 2 pts. of *fuming nitric acid*, it crackles and forms an unctuous resin. (Hasse, *Crell. Ann.* 1785, 1, 422.) — 4. With *oil of vitriol*, it turns dark yellow-brown, and becomes thick like a balsam. (Zeller.) — 5. Dropped upon melting *hydrate of potash*, it is for the most part converted into a brownish resin, and a volatile oil, which does not smell like hyssop, and is not completely deoxygenated by repeated distillation over hydrate of potash (86·65 p. c. C, 11·41 H, and 1·94 O). (Stenhouse.)

Combinations. Dissolves easily in *absolute alcohol*, forms a clear solution in 1—4 pts. of alcohol of sp. gr. 0·85, and a slightly opalescent solution with a larger quantity of alcohol of sp. gr. 0·85. (Zeller.)

42. Camphor of Iris florentina.

A. VOGEL. *J. Pharm.* 1, 483.
DUMAS. *J. Pharm.* 21, 191; *J. pr. Chem.* 4, 434; *Ann. Pharm.* 15, 158.

When iris root is distilled with water, camphor in white scales floats on the distillate (Vogel), and may be separated by filtration. (Dumas.) Nacreous crystalline laminæ. (Dumas.)

Calculation according to Dumas.			Dumas.
16 C	96	66·67	67·2
16 H	16	11·11	11·5
4 O	32	22·22	21·3
$C^{16}H^{16}O^4$	144	100·00	100·0

It is insoluble in water. (Dumas.) Dissolves readily in alcohol; the solution has an agreeable odour of violets, and is rendered milky by water.

43. Jasmin-camphor.

Separates in the crystalline form from oil of jasmin when exposed to cold, and may be purified by pressure between paper, solution in alcohol and recrystallisation. Transparent, colourless, shining laminæ, or white translucent granules, of tallowy whiteness, lighter than water; melts at 12° — 15°; has a faint agreeable odour, and a heating camphorous taste. When *set on fire*, it burns with a bright flame, like rose-camphor. Heated with *iodine*, it forms a liquid, varying in colour from brown to dark red, and becoming grass green when more strongly heated. With *strong nitric acid*, it volatilises without evolution of gas, colouring, or formation of oxalic acid. With *strong hydrochloric acid*, it becomes slightly yellow, forming bubbles and partly dissolving. It does not oxidise *potassium*. It dissolves sparingly in water, imparting its odour; is quite insoluble in acetic acid, but dissolves with moderate facility in *alcohol*, in *ether*, and in *oils*, both *fixed* and *volatile*. (Herberger, *Repert.* 48, 1081.) As jasmin-oil generally contains a fixed oil, jasmin camphor is perhaps a fixed fatty acid. (Gm.)

44. Oil of Jonquil.

From *Narcissus Jonquilla, L.* Fresh, recently opened jonquil flowers are introduced into a displacement apparatus, and exhausted by ether made to pass slowly through them; the yellow ethereal solution which runs through and floats on the top of a greenish watery liquid, containing a little salt, is separated from the latter, and distilled in the water-bath; the residual solution is separated by pressure from the jonquil-camphor, which crystallises in warty masses during the distillation and cooling of the liquid; and the ether is left to evaporate spontaneously. Full-blown jonquil-flowers yield jonquil-camphor in yellowish, odourless, sublimable nodules. The oil is yellowish, buttery, melts at the heat of the hand, and has a strong odour of the flowers. Boiling point above 100°. By *keeping*, it gradually becomes opaque, does not melt even at 100°, and becomes mixed with yellow, granular jonquil-camphor, which separates when the oil is dissolved in ether. Blackens metallic *iron* when in immediate contact with it.

Brown Jonquil-oil. Contained in peculiar cells of jonquil-flowers, which are not penetrated by the ether. To obtain it the flowers, after having been exhausted with ether, are treated with alcohol, and the alcohol is distilled off from the extract. It is a brown viscid oil, which has an unpleasant odour like that of train-oil, and deposits a few yellow crystals: it is soluble in ether. It unites with alkalis, acquiring at the same time a darker colour. (Robiquet, 1835, *J. Pharm.* 21, 334.)

45. Volatile Oil of Lançon Balsam.

Obtained by distilling the balsam with water. Pale amber-yellow, colourless after rectification, transparent, lighter than water; solidifies at — 12°; has a peculiar odour like that of tar; tastes sharp, but less so than oil of turpentine and somewhat bitter. Mixed at 20° with $\frac{1}{4}$ pt. *nitric acid*, it becomes rose-red in 5 minutes, wine-red in 10 — 12 minutes, dark violet in 20 — 25 minutes, and finally blue. Dissolves in 10 — 12 pts. *alcohol* of sp. gr. 0·85, forming a somewhat turbid liquid, and in all proportions of *ether*, forming a clear solution. (Bonastre, *J. Pharm.* 15, 668.)

46. Oil of Lavender.

THÉNARD. (1811.) *Mém de la Soc. d'Arc.* 2, 32.
SAUSSURE. *Ann. Chim. Phys.* 4, 318; 13, 273; *Schw.* 29, 172; *Pogg.* 25, 370; *Bibl. univ.* 49, 159; *Ann. Pharm.* 3, 163; *Ann. Chim. Phys.* 49, 159.
VAUQUELIN. *Ann. Chim. Phys.* 19, 279; *Schw.* 35, 435; *N. Tr.* 7, 1, 286.
KANE. *Lond. Ed. Mag. J.* 13, 444; *J. pr. Chem.* 15, 163; *Ann. Pharm.* 32, 287.
BELL. *Pharm. J. Trans.* 8, 276; *J. Chim. méd.* 25, 487; *Pharm. Centrbl.* 1849, 191.
ZELLER. *Stud. über äther. Oele,* Landau, 1850.
LALLEMAND. *N. Ann. Chim. Phys.* 57, 404; abstr. *Ann. Pharm.* 114, 197.

Essence de lavande. Lavandelöl, Lavandelessenz.

Source. In the flowers and leaves of the lavender, *Lavandula angustifolia* (*Ehrhardt*). There are two kinds, viz.: *a. Lavender-oil,* in the leaves and flowers of *Lavandula augustifolia* (*Ehrhardt*), and *b. Spike-oil, Huile d'aspic,* in the leaves and flowers of *Lavandula latifolia.* (*Ehrhardt.*)

Extraction. Fresh or dried lavender flowers stripped from the stalks are distilled with water or with steam, the lavender-water which passes over with the oil being used for the subsequent distillations. The yield of oil varies with the state of the flowers, and the amount of water distilled from them, as well as with the quantities used; with small quantities of the flowers, the loss of oil is comparatively greater than with larger quantities. The quality of the oil is considerably better, when the flowers are distilled without the stalks: for the disagreeable odour sometimes perceptible in the commercial oil, proceeds from the stalks, which when distilled alone, yield an oil possessing this bad odour in a high degree. (Bell.) Dry lavender-flowers yield 1 p. c. oil (Van Hees, *Pharm. Centr.* 1847, 380), 1·4 p. c. (Bell.)

Properties. *a.* Of *Oil of Lavender:* Pale yellow, very mobile. Sp. gr. 0·87 — 0·94 (Zeller); 0·893 (Pfaff, *Syst. d. Mat. med.*); 0·936 (Lewis, *Thomson's Syst.*); 0·898 at 20°; when rectified, the first part of the distillate has a sp. gr. of 0·877 (Saussure); 0·9174; that which distils between 185° and 188° has a sp. gr. = 0·8865 to 0·8745 (Kane); the commercial oil, 0·917; oil prepared by van Hees, 0·892 (van Hees). Boiling point 185° — 188°. (Kane.) Tension of vapour: $7 \cdot 3^{mm}$ of mercury at 13·75° (Saussure). Has an agreeable odour like that of the flowers; less agreeable if the flowers and stalks have been distilled together. (Bell.) Its taste is burning, somewhat bitter, sharp, and aromatic. Neutral to vegetable colours. (Zeller.) Deposits camphor on cooling. (Bizio, *Brugn. Giorn.* 19, 369.)

b. Of *Oil of Spike:* Yellow, mobile; sp. gr. 0·87 — 0·89. (Zeller.) Its odour is less agreeable than that of oil of lavender; more like turpentine.

	Saussure. *a.*		Kane. *b.*		*c.*
C	75·50	....	75·77	....	79·45
H	11·07	....	11·73	....	11·30
O	13·07	....	12·50	....	9·25
	99·64	....	100·00	....	100·00

a is said to contain 0·36 p. c. N; *b* distilled at 185°; *c*, at 188°.

Oil of lavender is a mixture of volatile oil and camphor, corresponding to the formula $C^{15}H^{14}O^2$, of which the specifically heavier oil contains a comparatively larger quantity. Oil of lavender, from Murcia, contains $\frac{1}{2}$ pt., English oil of lavender $\frac{1}{4}$ pt., Spanish also $\frac{1}{4}$ pt. camphor. (Proust.) The camphor of lavender-oil is identical with common camphor. (Dumas, *Ann. Chim. Phys.* 50, 225.)

¶ Both oil of lavender and oil of spike are resolved by distillation into a hydrocarbon, isomeric with oil of turpentine, and a camphor similar to or identical with common camphor. The hydrocarbon from oil of lavender, appears to be the same in molecular condition as the hydrocarbons which are produced from all the oils, $C^{20}H^{16}$, by the action of oil of vitriol on fluoride of boron. It boils at 200° — 210°, and turns the plane of polarisation to the right. The hydrocarbon from oil of spike, boils at 175°, and turns the plane of polarisation to the left. Both these hydrocarbons form liquid compounds with hydrochloric acid. The portion of oil of spike which distils between 200° and 210° contains a large quantity of camphor, which may be isolated by nitric acid, and acts on polarised light in the same manner and in the same degree as common camphor. (Lallemand.)¶

Decompositions. 1. Oil of lavender, *heated* for some time above its boiling point, forms a small quantity of acetic acid. (Gay-Lussac, *Compt. rend.* 1841, 21; *Instit.* 369, 21.) — 2. It absorbs large quantities of *oxygen gas* at ordinary temperatures, and gives off carbonic acid. At 24° it absorbs the following quantities of oxygen: In the first 12 hours, none; in the two following days, 1·39 vols. daily; in the following week, 6·17 vols. daily; altogether in $4\frac{1}{2}$ months, 111 vols.; in the following 30 months, 8 vols.; therefore, in $34\frac{1}{2}$ months, 119 vols.; in the same interval it forms 22·1 vols. carbonic acid, and becomes somewhat yellowish. Kept over mercury in the shade during four winter-months, below 12°, it absorbs 52 vols. oxygen, and forms 2 vols. carbonic acid. (Saussure.) It absorbs *insolated oxygen,* thereby acquiring oxidising properties and the power of reddening litmus. (Schönbein, *J. pr. Chem.* 52, 187.) — 3. When *bromine* is slowly added to the oil mixed with $\frac{1}{5}$ of its volume of water, heat is produced, and the colour of the bromine disappears till 217 pts. = 4 At. bromine have been added to every 100 pts. of the rectified oil. (G. Williams, *J. pr. Chem.* 61, 20.) With *iodine*, it rapidly gives off yellowish-red vapours, becomes reddish yellow-brown and viscid, and acquires a balsamic, somewhat acid odour. (Zeller.) It decomposes but slowly with iodine in the cold (Guyot, *J. Chim. med.* 12, 487), and after an hour or two, forms a thick mixture which dissolves easily in the rest of the oil. (Guyot, *J. Phys.* 5, 230.) It becomes heated with iodine and explodes, the iodine volatilising.

(Walcker, *Pogg.* 6, 126.) Oil of spike reacts with iodine like oil of lavender, but with less violent detonation. (Zeller.) — 5. With *nitric acid* it assumes a brownish to reddish-brown colour, and on heating the mixture, strong evolution of gas takes place and a soft yellow resin is formed (Zeller), together with oxalic acid. (v. Grotthuss, *N. Gehl.* 8, 709.) Spike-oil, mixed with nitric acid, turns pale yellow to yellow, and, when heated, gives off gas and acquires the consistence of balsam. (Zeller.) With strong sulphuric acid, oil of lavender thickens and assumes a dark red-brown colour. (Zeller.) — 8. With *hydrochloric acid gas,* it becomes blackish (Thénard), reddish-black to black, and specifically heavier but not solid. (Saussure.) It absorbs 68·7 vols. hydrochloric acid gas (Thénard); 210 vols. without being saturated. (Saussure.) — 9. With *ammonia-gas* it becomes turbid, and at 20° absorbs 47 vols. of the gas. (Saussure.) — 10. Distilled with 24 pts. water and 8 pts. *chloride of lime,* it gives off carbonic acid gas with effervescence and yields chloroform. (Chautard, *Compt. rend.* 34, 485.) Distilled with *hypobromite of lime,* it yields bromoform. (Chautard, *Compt. rend.* 34, 487.) — 12. With *bichromate of potash* and *sulphuric acid,* it assumes a greenish to brown-yellow colour, and partly resinises. (Zeller.) — 13. When boiled with dry *nitroprusside of copper,* it yields a slate-grey deposit, the depth of colour varying with the quantity of oil. (Heppe, *N. Br. Arch.* 89, 57.) — 14. It decolorises very thin films of *sulphide of lead,* converting that compound into sulphate of lead. (Williams, *J. pr. Chem.* 59, 504.) — 15. When shaken up with $\frac{1}{6}$ of *corrosive sublimate,* it quickly turns brown, without dissolving much of the salt. (Simon, *Pogg.* 37, 857.)

Combinations. ¶ The hydrocarbon ($C^{20}H^{16}$) contained in oil of lavender (p. 373), combines with *hydrochloric acid,* forming an instable compound which has the composition of hydrochlorate of lemon-oil, $C^{20}H^{16},2HCl$, remains liquid at all temperatures, and does not yield any solid compound when treated with fuming nitric acid. (Lallemand.) The hydrocarbon, $C^{20}H^{16}$, contained in oil of spike, forms with *hydrochloric acid* a liquid compound from which nitric acid separates a small quantity of a solid hydrochlorate, which turns the plane of polarisation to the right, but in other respects exhibits the properties of hydrochlorate of oil of turpentine.¶

Oil of lavender dissolves in *acetic acid;* according to Lallemand, it always, even when recently prepared, contains acetic acid, both free and combined, probably also, valerianic acid. — 80 vols. of the oil shaken up with 80 vols. acetic acid of sp. gr. 1·075, take up 45 vols. of the acid, and leave a weaker acid containing oil, which, if shaken up with 80 vols. of fresh oil, produces 110 vols. of oil containing acetic acid, while 5 vols. of still weaker acetic acid remain, containing a large quantity of oil separable by water. The oil charged with acetic acid gives up the greater part of that acid when agitated with an equal volume of water, and the whole when agitated with four times the quantity of water, a certain quantity of the oil dissolving in the water at the same time. (Vauquelin.)

Oil of lavender dissolves in all proportions of *absolute alcohol* and of alcohol of sp. gr. 0·85 (Zeller), of sp. gr. 0·83 (Saussure). It dissolves in 2·5 pts. of alcohol of sp. gr. 0·887 at 20°. (Saussure.) Oil of spike dissolves in alcohol like oil of lavender. (Zeller.)

47. Ledum-camphor.

Rauchfuss. (1796.) *A. Tr.* 3, 1, 189.
Meissner. *Berl. Jahrb.* 13, 170.
Grassmann. *Repert.* 38, 53.
Buchner. *Repert.* 38, 57; *N. Repert.* 5, 1; *Chem. Centralbl.* 1856, 400; *N. J. Pharm.* 29, 318; *Instit.* 1857, 82.
Willigk. *Wien. akad. Ber.* 9, 302.

Camphor of Marsh Wild Rosemary, Porsch-campher. First observed by Grassmann, 1833.

Source and Extraction. In the volatile oil of marsh wild rosemary *Ledum palustre, L.* This oil consists for the most part of a hydrocarbon isomeric with oil of turpentine, and of an oxygenated oil, and when recently prepared corresponds to the formula $C^{80}H^{63}O^{5}$. (Willigk.) It consists of 2 pts. camphor to 1 pt. volatile oil, the camphor existing in it ready formed, and not being produced from the oil by the action of the air. (Grassmann.) The flowering plant or the leaves are comminuted and very quickly distilled with water; the oil which floats on the distillate is removed and pressed between paper after solidification (Grassmann); and the solidified oil is washed with cold *alcohol*, and purified by pressure between paper, solution in ether, and recrystallisation. (Buchner.) By slower distillation, the volatile oil passes over first, and afterwards the camphor. (Grassmann.)

Properties. Colourless, slender, transparent prisms ($\frac{1}{4}$ inch long, according to Grassmann); when crystallised from alcohol: very delicate silky prisms and efflorescent crystals. (Buchner.) Melts at a gentle heat, sublimes at a stronger heat (Buchner), diffusing a pungent odour which produces headache and giddiness. (Grassmann.) Smells slightly of the herb (somewhat like oil of roses and oil of turpentine), and has a warming aromatic taste. (Buchner.) Neutral. (Grassman.)

Calculation according to Buchner.			Buchner.
50 C	300	81·74	81·25
43 H	43	11·71	12·28
3 O	24	6·55	6·47
$C^{50}H^{43}O^{3}$	367	100·00	100·00

It contains a hydrocarbon isomeric with oil of turpentine, and a hydrate of that hydrocarbon; $5(C^{10}H^{8}) + 3HO$. (Buchner.)

Heated on platinum foil, it takes fire, and burns with a highly luminous, sooty flame. (Buchner.) It is nearly insoluble in water. (Grassmann, Buchner.) Dissolves sparingly in *hydrochloric acid*, still less in *acetic acid*, not at all in *aqueous ammonia*, readily in *alcohol* and *ether*. (Buchner.)

48. Oil of Lilac.

In the flowers of the lilac, *Syringa vulgaris*. The fresh flowers are exhausted with ether in a displacement apparatus; the yellow ethereal solution which runs through and floats on the surface of the watery liquid, is removed; the greater part of the ether distilled off; the residue left to evaporate; and the oil which remains mixed with a solid mass is separated by filtration. Amber-yellow, with an odour like that of the flowers. Deposits solid masses (*Syringa-campher, Schw.*), when left to itself. Scarcely blackens iron (an effect produced in a greater degree by oil of jonquil, p. 373). (Favrot, 1838, *J. Chim. med.* 14, 212.)

49. Camphor of Lily of the Valley.

Campher der Maiblumen. — The fresh flowers of lily of the valley, *Convallaria majalis, L.*, are suspended in the capital of a still and distilled with six times their weight of water, and the camphor which floats on the watery distillate is collected. This watery liquid is slightly turbid and has no acid reaction; its odour is fragrant after a few days, but is disagreeable and producing headache if smelt too closely. The camphor is a radio-crystalline mass. (Herberger, *Repert.* 52, 397.)

50. Oil of Lime-flower.

Brossat. (1820.) *J. Pharm.* 6, 396; abstr. *Repert.* 58, 105.
Landerer. *Repert.* 58, 103.
Buchner. *N. Br. Arch.* 8, 70.
Winckler. *Pharm. Centralbl.* 1837, 781; abstr. *Repert.* 70, 16.

Source and Extraction. In the flowers of the lime, *Tilia Europæa, L.* The fresh, just opened flowers are distilled with water, and the milky distillate is cohobated over fresh quantities of fresh flowers (Brossat, Landerer), or the distillate is mixed with common salt and shaken up with ether; the ethereal layer is removed and left to evaporate, and the residual oil is rectified over chloride of calcium. (Winckler.) When fresh lime-flowers are exhausted with ether in the displacement apparatus, the ethereal solution dehydrated with chloride of calcium, and the ether distilled off, there remains a greenish-yellow aromatic residue, which solidifies on cooling, and is deprived by ether of its odour of lime-flowers; the ethereal solution leaves when evaporated a small quantity of wax and chlorophyll, but scarcely any oil. (Buchner.) The amount of oil obtained is 0·1 p. c. (Herberger, *Repert.* 66, 1); 0·042 p. c. (Winckler.)

Properties. Colourless, mobile (Landerer, Winckler), yellowish (Brossat); lighter than water, very volatile (Landerer); has a strong odour of fresh lime-flowers (Winckler); extremely pleasant odour and sweetish taste. (Landerer.)

Decompositions. 1. Reddens on exposure to *light.* (Landerer.) — 2. Alters slightly on exposure to the light. (Winckler.) — 3. It dissolves *iodine* without rise of temperature, forming a brown liquid, soluble in all proportions of alcohol and ether. (Winckler.)

Soluble in *alcohol.* (Landerer.)

51. Oil of Marjoram.

KANE. (1838.) *Lond. Ed. Mag. J.* 13, 439; *J. pr. Chem.* 15, 157; *Ann. Pharm.* 32, 285.
ZELLER. *Stud. über. äther. Oele,* Landau, 1850.

Majoranöl, Essence de marjolaine.

Source and Extraction. In marjoram, *Origanum majorana, L.*, whence it is obtained by distillation with water. It must be freed from dissolved camphor by repeated distillation. (Kane.) The water which passes over with the oil contains acetic acid. (Hautz, *J. pr. Chem.* 62, 317.)

Properties. Yellow-green to pale-green (Zeller); sp. gr. 0·8901; rectified, 0·8673 (Kane), 0·89 (Zeller). Boiling point nearly constant at 163°. (Kane.) Has an extremely pungent odour like that of the herb, and a warming acrid, somewhat bitter taste. Slightly acid. (Zeller.)

	Kane. *a.*	Kane. *b.*
C	86·32	84·48
H	11·41	10·80
O	2·27	4·72
	100·00	100·00

a rectified; *b* distilled at 173·3°.

Decompositions. 1. Deposits camphor when cooled to — 15°. (Trommsdorff, *N. Tr.* 20, 2, 24.) With *iodine,* it becomes heated and gives off yellow-red vapours without fulmination, acquires a reddish yellow-brown colour, the consistence of a balsam, and a rather acid balsam-like-odour. With *nitric acid,* it becomes reddish-brown colour, quickly gives off gas, and acquires the consistence of balsam when heated. — 4. With *oil of vitriol,* it acquires a slight bluish-red tint. — 5. With bichromate of potash and sulphuric acid, it becomes greenish brown-yellow, and deposits resinous flocks. (Zeller.)

Combinations. It dissolves without turbidity in 1 pt. alcohol of sp. gr. 0·85, and with opalescence in 2 or more pts. (Zeller.)

52. Marjoram-camphor.

GÜNTHER. (1783.) *Alm.* 1783, 134.
MULDER. *J. pr. Chem.* 17, 103; *Ann. Pharm.* 31, 69.

Observed in old oil of marjoram as early as 1686, by Krüger (*Miscell. Nat. Cur. Germ. Dec.* 2, *Ann.* 5, *Obs.* 38), Neumann (*Chymia Medica,* 2, 1, 182) and Dehne (*Crell. chem. J.* 1, 41).

Formation. When oil of marjoram is kept in loosely closed vessels. (Günther, Mulder.)

Properties. White hard crystals (Mulder), brittle (Günther), heavier than water (Mulder), melts and volatilises completely (Mulder), subliming in laminæ like benzoic acid. (Günther.) Smells and tastes like the oil. (Günther.)

	Mulder.
C	60·07
H	10·70
O	29·23
	100·00

According to Mulder, its composition may be expressed by the formula $C^{14}H^{15}O^5$.

Decompositions. 1. Heated to 112°, it gives off 1·42 p. c. water without becoming turbid (Mulder); does not volatilise so readily as common camphor. (Günther.) — 2. When set on fire it burns with flame, which however does not deposit soot. (Günther.) — 3. It is coloured red by oil of vitriol. (Mulder.)

Combinations. It dissolves in boiling *water*. (Günther, Mulder.) Absorbs 12·95 p. c. hydrochloric acid gas, producing a very acid compound, from whose alcoholic solution nitrate of silver throws down chloride of silver. (Mulder.) It dissolves in 10 pts. of concentrated *nitric acid.* (Günther.) It dissolves in *aqueous potash.* Does not absorb ammonia-gas. (Mulder.) Dissolves in *alcohol* and in *ether* (Mulder), in 10 pts. of alcohol, forming a solution which is not rendered turbid by water. (Günther.) It dissolves in 10 pts. of *oil of turpentine,* in 10 pts. of boiling *oil of almonds,* crystallising from the latter solution after a while. (Günther.)

Oil of Wild Marjoram—see *Oil of Origanum* (p. 391).

53. Oil of Massoy.

In massoy-bark, the bark of *Cinnamomum Kiamis, Nees.* The comminuted bark is distilled with water, and the milky distillate is separated from an oil which floats on the surface, and another oil which sinks to the bottom, together with a camphor.

a. Light oil. Nearly colourless, mobile, transparent, with an aromatic odour like that of sassafras-oil, and a sharp pungent taste. — With *strong nitric acid,* it becomes flesh-red and ultimately cherry-red. — It dissolves readily in *alcohol*, *ether*, and *strong acetic acid*, and is separated from the latter solution by the addition of 3 pts. of water.

b. Heavy oil. More viscid and less volatile than the former. Smells and tastes like sassafras-oil, the odour being fainter than that of the light oil, but the taste equally strong; becomes turbid and thickens at —10°, but does not crystallise. — With *cold nitric acid*, it becomes flesh-coloured, and when heated therewith, forms a mixture which deposits a small quantity of oxalic acid, and has no bitter taste. — The heavy oil dissolves in all proportions of *alcohol, ether*, and *strong acetic acid,* from which last solution it is precipitated by water. Mixes imperfectly with aqueous *potash, soda, ammonia, baryta,* and *strontia,* and when shaken up with the two latter, becomes white, thick and turbid, but separates again when left at rest.

c. Massoy-camphor. — White powder, heavier than water, less soft to the touch than fatty substances. — It does not become electrical by friction, is inodorous and nearly tasteless. — It is related to laurin and caryophyllin. — *Nitric acid* colours it pale yellow, perhaps only in consequence of the presence of a small portion of oil. — Dissolves in hot *alcohol* and in *ether.* (Bonastre, 1829, *J. Pharm.* 15, 204.)

54. Oil of Masterwort.

WACKENRODER. (1831.) *Br. Arch.* 37, 341.
HIRZEL. *J. pr. Chem.* 46, 292; *Chem. Centralbl.* 1849, 37; *Mitth. d. Zürich. naturforsch. Gesellsch.* 1848, 27.

Meisterwurzöl, Essence d'imperatoire.

Source and Extraction. In the root of *Imperatoria Ostruthium, L.* — The comminuted root is distilled with water; the oil which floats on the distillate is removed; the water is shaken up with ether; the ethereal solution evaporated; the residual oil, together with the portion previously removed, is rectified with a small quantity of water; and the distilled oil is dehydrated by agitation with chloride of calcium. (Hirzel.) — The yield of oil is 0·78 p. c. (Bartels), 0·18 p. c. (Lecanu.)

Properties. Transparent and colourless (Hirzel), pale yellow (Wackenroder), mobile (the portion which distils between 200° and 220° is more viscid). Boils between 170° and 220°; has an aromatic odour (somewhat empyreumatic between 200° and 220° (Hirzel); penetrating (Wackenroder); its taste is strongly heating (Hirzel); camphorous like that of poppy-oil. (Wackenroder.)

	Hirzel.			
	a.	*b.*	*c.*	*d.*
C	85·57	84·40	81·43	81·74
H	11·45	11·38	11·32	11·27
O	2·98	3·22	7·25	6·99
	100·00	100·00	100·00	100·00

a and *b* distilled from 170° to 180°; *c* from 200° to 220°. The oil is a mixture of several hydrates of a hydrocarbon isomeric with oil of turpentine, corresponding to the formulæ $4(C^{10}H^8) + HO$ and $3(C^{10}H^8) + 2HO$. (Hirzel.)

Decompositions. 1. Burns when *set on fire* with a bright fuliginous flame. — 2. It absorbs *chlorine,* with rise of temperature and evolution of hydrochloric acid gas, being thereby converted into a yellow, viscid oil, which sinks in water, has a peculiar odour, and a biting taste. — 3. It is decomposed in like manner by *bromine,* with evolution of hydrobromic acid. — 4. By distillation with *anhydrous phosphoric acid,* it yields a transparent, colourless oil, which has an odour of rosemary and an aromatic taste, agrees in composition (87·76 p. c. C, 11·76 H) with the formula $C^{20}H^{16}$, and is therefore isomeric with oil of turpentine. — This oil absorbs hydrochloric acid gas, assuming a reddish yellow colour, and forming, after complete saturation, rectification with water, and dehydration with chloride of calcium, an oil which has an agreeable odour, an aromatic taste and a composition (74·98 C, 10·86 H, 13·28 Cl) agreeing with the formula $3(C^{20}H^{8}) + HCl$. (Hirzel.)

55. Oil of Matico.

In the leaves of *Piper asperifolium*, a plant growing in *Guiana*. (*Ruiz. and Pav.*) — The leaves are distilled with water, and the oil which slowly sinks to the bottom of the milky distillate is collected. — Pale green, thickish; has a strong and persistent odour, and a persistent camphorous taste. — By keeping, it becomes thicker, and ultimately crystalline; by *nitric acid*, it is coloured amber-yellow and resinised. — It dissolves in *oil of vitriol*, forming a carmine-coloured liquid which becomes milky on addition of water. It dissolves readily in *alcohol* and *ether*, not in *aqueous potash* or *ammonia*. (Hodges, 1844, *Phil. Mag. J.* 25, 204; *Mem. Chem. Soc.* 1, 123.)

56. Neutral Oil of Meadow-sweet.

LOWIG & WEIDMANN. (1839.) *Pogg.* 46, 57; *Pharm. Centr.* 1839, 129.

ETTLING. *Ann. Pharm.* 35, 241; *Pharm. Centr.* 1840, 837.

Neutral oil of Spiræa.

Source. In the flowers of meadow-sweet, *Spiræa ulmaria*, together with salicylous acid and crystalline camphor. (Ettling, *comp.* xii, 235.)

Preparation. 1. The watery liquid which passes over on distilling the flowers with water, is shaken up with ether; the ethereal solution is separated from the water and shaken up with potash-ley to remove salicylous acid; and the residual ethereal liquid is evaporated at a gentle heat. (Löwig & Weidmann.) — 2. The oil obtained by distilling the flowers is shaken up with potash-ley of sp. gr. 1·28, redistilled either alone or with water, and rectified after dehydration with chloride of calcium. The yield of oil is $\frac{1}{30}$. (Ettling.)

Properties. Transparent, colourless oil, which floats on water, boils more readily than crude oil of meadow-sweet; is neutral; has a strong odour somewhat like that of salicylous acid, and a slightly burning taste. (Ettling.) — It solidifies partially in the cold. (Löwig & Weidmann.) Löwig & Weidmann found in the oil 71·21 p. c. C, 10·35 H, and 18·44 O: hence it is perhaps $C^{20}H^{18}O^{4}$. (Gm.)

Decompositions. 1. When exposed to the *air*, it turns first yellow, then darker-coloured, without taking up oxygen. — The oil which last passes over in rectification gradually turns brown and deposits small colourless spicular crystals. (Ettling.) — 2. It is violently attacked by chlorine, with evolution of hydrochloric acid, becoming viscid but not solid. (Löwig & Weidmann; Ettling.) — 3. *Oil of vitriol* colours it brown-red, the solution on addition of water becoming milky white and depositing a small quantity of apparently unaltered oil. — 4. It leaves *potassium* unaltered and does not redden solutions of *ferric salts*. (Ettling.)

It dissolves readily in *ether* and in *alcohol*. (Ettling.)

57. Oil of Mecca Balsam.

Obtained from *Balsamodendron gileadense* (*Kunth.*) by distillation with water, the quantity amounting to 10 per cent. (Bonastre), 30 p. c. (Trommsdorff, *N. Tr.* 16, 1, 72.) — Transparent, colourless, mobile. (Bonastre, Trommsdorff.) Sp. gr. 0·876. Does not solidify at —12°. Has a strong odour of turpentine (Bonastre); agreeable like that of the balsam (Trommsdorff); has a strong taste, somewhat pungent, not bitter but cooling. (Bonastre.) Neutral. Contains 80·03 p. c. C, 11·50 H, 8·42 O. (Trommsdorff.) — Burns with a bright flame when *set on fire.* Dissolves *iodine* with a brown colour and without explosion. (Trommsdorff.) It is scarcely coloured by *strong nitric acid* (Bonastre), but mixes with it quietly, the mixture becoming warm after a while, giving off nitrous acid, and depositing, on addition of water, a brittle pale yellow resin which has an agreeable odour like that of musk. (Trommsdorff.) — With *oil of vitriol,* it becomes saffron-red (Bonastre), dark red without rise of temperature; the mixture, on addition of water, deposits a fragrant pale yellow resin. (Trommsdorff.) — It dissolves with turbidity in 12 pts. of *alcohol* (Bonastre); clearly and in all proportions in *ether,* easily in *rock-oil, fixed oils, strong acetic acid* (Trommsdorff), not at all in *aqueous potash* (Trommsdorff), *soda* and *ammonia.* (Bonastre, *J. Pharm.* 18, 97.)

58. Volatile Oil of Mentha viridis.

Obtained by distilling spear mint, *Mentha viridis, L.* with water. Sp. gr. 0·939 (Brandes); 0·9142, after separation of the dissolved camphor by rectification, 0·876. (Kane.) Boils with tolerable regularity at 160°. Contains 84·21 p. c. C, 11·23 H, and 4·56 O, and is therefore $7C^5H^4 + O$. (Kane, *Lond. Ed. Mag.* 13, 440; *J. pr. Chem.* 15, 163.)

59. Oil of Mercurialis annua.

Obtained by distilling the dry herb with water (the fresh herb does not yield any oil). — It contains numerous white crystals; becomes coloured and thickens by keeping. (Raybaud, 1834, *J. Pharm.,* 20, 461.)

60. Oil of Mignonette.

In the flowers of mignonette, *Reseda odorata, L.* They lose their odour when dry, but yield by distillation with water, an aqueous liquid, having an odour of mignonette, but at the same time a disagreeable grassy odour, and with alcohol, a distillate of not very agreeable odour. — To prepare the oil, the flowers are exhausted with ether; the green ethereal layer of the extract is separated from the lower watery layer, and left to evaporate spontaneously. — Soft dark green mass, smelling strongly of mignonette, and consisting of chlorophyll, wax and oil; the oil cannot be separated from it. (Buchner, *N. Br. Arch.* 8, 70.)

61. Oil of Millefoil.

BLEY. (1828.) *N. Tr.* 16, 1, 247; further, 16, 2, 96. — *Repert.* 48, 95.
FORCKE. *N. Br. Arch.* 17, 177.
ZELLER. *Stud. über äther. Oele,* Landau, 1850.

Schafgarbenöl.

Source and Extraction. In millefoil, *Achillea millefoliam, L.* Obtained by distilling with water the flowers, herb, roots, or seeds. — Water distilled over the flowers contains propionic acid together with the oil (Kramer, *N. Br. Arch.* 54, 9); water distilled over the roots contains acetic acid together with the oil (Bley). — The roots yield 0·032 p. c.; the dry herb, 0·065; the fresh dried flowers, 0·114; the air-dried seeds, 0·052 p. c. oil (Bley).

Properties. 1. *From the flowers:* Dark blue (Zeller); from *Achillea millefolium var. dilatata,* yellow to green; from *var. contracta;* blue (Forcke). Sp. gr. 0·92 to 0·928. Has a slight acid reaction. — (Zeller.) — 2. *From the herb:* Blue, darker than oil of wild chamomile; viscid, nearly buttery in the cold, lighter than water; from the plant while flowering, 0·852 — 0·917. Has a strong smell and tastes like the herb, producing a slight scratching sensation in the throat. (Bley, Zeller.) — 3. *From the roots:* Colourless, slightly yellowish, lighter than water, with a peculiarly unpleasant odour, somewhat like that of valerian, and a disagreeable taste, but neither strong nor burning. (Bley.) — 4. *From the seeds:* Greenish. (Bley.)

Decompositions. 1. By exposure to the *air,* it becomes brown, strongly acid and resinous. — 2. Stirred up with *iodine,* it becomes heated, without detonating, and gives off yellowish-red vapours, at the same time acquiring the consistence of a balsam. (Zeller.) — 3. With *nitric acid,* it acquires a reddish-brown colour; with *fuming nitric acid,* greenish-brown; when heated therewith, it quickly gives off gas (Zeller), and leaves a soft resin. (Bley, Zeller.) — 4. *Oil of vitriol* colours it brown and thickens it to the consistence of a balsam, giving off a peach-like odour. (Bley, Zeller.) With *bichromate of potash* and *sulphuric acid,* it becomes turbid and thickens. (Zeller.)

Combinations. — With *aqueous potash* or *ammonia,* it forms a soapy compound. (Bley.) — It dissolves readily in *alcohol* and *ether* (Bley); without turbidity in 1 pt. of alcohol of sp. gr. 0·85; with a larger quantity, even with 40 pts., it forms a turbid solution, holding flocks in suspension; *absolute alcohol* dissolves it in all proportions. (Zeller.)

62. Oil of Noble Millefoil.

From *Achillea nobilis, L.* — Obtained by distilling the flowering plant, or the flowers, herb, or seeds with water. — The dry flowers yield 0·24 p. c.; the dry herb, 0·26; the seeds, 0·09 p. c. oil. — Pale yellow, viscid;

of sp. gr. 0·983; if obtained from the herb, 0·970; has a very powerful odour, finer than that of the oil obtained from common millefoil, but resembling it, and also like that of camphor. Tastes aromatic, like camphor, somewhat bitter. — With *iodine,* it forms, without explosion or rise of temperature, a solution, which, on addition of water, deposits a brown resin having a burning taste. — With *fuming nitric acid,* it becomes hot and yellow, thickens, and on addition of water, yields a soft, floating resin. — With *oil of vitriol,* it becomes red-brown and viscid; on addition of water, the mixture deposits a dirty-yellow soft resin. — The oil dissolves in *ether, alcohol,* and *oils,* both *fixed* and *volatile.* (Bley, *N. Br. Arch.* 2, 124.

63. Oil of Mugwort.

Beifussöl. In the root of mugwort, *Artemisia vulgaris, L.* — The root is comminuted and distilled with water. — Pale greenish-yellow, buttery, crystalline, lighter than water; boils above 100°, has a peculiar pungent odour, and an unpleasant, somewhat bitter taste, burning at first, afterwards cooling. Neutral. — It is not easily inflammable, but when once *set on fire,* burns with a light yellow, sooty flame, which diffuses an offensive odour. — It is quickly thickened by dilute *nitric acid,* giving off nitrous acid, and yielding a tough brown resin, soluble in alcohol. — The oil dissolves readily in alcohol, ether, oil of rosemary, oil of turpentine and poppy-oil. (Bretz & Eliason, 1826, *Taschenbuch,* 1826, 61.)

64. Oil of Myrtle.

In the leaves, flowers, and fresh fruit of *Myrtus communis.* — Obtained by distillation with water. — Yellow to greenish yellow, lighter than water. (Raybaud, 1834, *J. Pharm.* 20, 463.)

65. Oil of Nasturtium.

MÜLLER. (1838.) *Ann. Pharm.* 25, 209; *N. Br. Arch.* 14, 265; *Repert.* 70, 286.
BERANGS. *Repert.* 88, 382.
CLOEZ. *Recueil de trav. de la Soc. d'emul. p. l. sciences pharm.* 1847, 41; abstr. *N. J. Pharm.* 12, 69.

Kapuzinerkressenöl, Huile essentielle de capucine.

In the garden nasturtium, *Tropæolum majus. L.* — The plant (especially the seeds, according to Bernays) yields by distillation with water 2·17 p. c. of oil. (Müller.) — The water which passes over with the oil, gives off a large quantity of sulphuretted hydrogen when heated with zinc and oil of vitriol. (Bernays.)

Yellow (Müller, Bernays); heavier than water. (Bernays, Cloez.) Boiling point between 120° and 130°. (Cloez.) Has a peculiar, strongly aromatic odour, which irritates the eyes and nose (Müller), like oil of garlic (Bernays). Taste acrid and burning (Müller), pungent (Bernays). It irritates the skin much more strongly than oil of mustard. (Müller.) — It contains *sulphur* (Bernays, Cloez), but not *phosphorus*, as Bracounot supposed. (Bernays.) — **It should have been treated as described at page 56, vol. x.**

66. Oil of Neroli.

Bonastre. (1825.) *J. Pharm.* 11, 529; *N. Tr.* 12, 1, 180.
Boullay. *J. Pharm.* 14, 496.
Zeller. *Stud. über äther. Oele,* Landau, 1850.

Relating especially to Orange-flower water.

Ader. (1830.) *J. Pharm.* 16, 412.
Le Roy. *J. Chim. med.* 6, 313.
Wahart Dunesmal. *J. Pharm.* 16, 410; *N. Tr.* 23, 1, 307.
Soubeiran. *J. Pharm.* 17, 619; *N. Tr.* 23, 1, 307.
Boullay. *Bull. Pharm.* 1, 337.
Guisney. *J. Chim. méd.* 22, 352.

Oil of Orange-flower, Pomeranzenblüthenöl, Orangenblüthenöl, Essence de Néroli.

Source and Extraction. In the flowers of the orange, *Citrus Aurantium, L.* — They are distilled in the fresh state with water. The oil which passes over is a mixture of two oils, one easily soluble in water and very fragrant; the other, sparingly soluble, of less agreeable odour; the latter floats upon the watery distillate, and is easily separated. (Soubeiran.)

Properties. Transparent, colourless (Bonastre), yellow to brownish yellow. (Zeller.) Sp. gr. 0·85 to 0·90. (Zeller.) — Has a very fragrant odour. (Bonastre.) Neutral. (Zeller.) Contains neroli-camphor in solution.

Decompositions 1. Becomes reddish yellow by keeping. (Bonastre.) — 2. With *iodine,* it froths up, gives off violet and yellowish red vapours, and is converted into a soft yellowish brown mass. (Zeller.) — 3. With *nitric acid,* it assumes a yellow colour gradually changing to that of iron-rust, and becoming red-brown after six hours, and ultimately loses its odour (Bonastre); on applying heat, the mixture rapidly gives off gas and acquires a resinous consistence. (Zeller.) — 4. With *oil of vitriol,* it acquires a dark orange-yellow colour (Paoli), dark red-brown, and becomes viscid. (Zeller.) — 5. *Bichromate of potash* colours it red-brown and separates resin from it. (Zeller.) — 6. In contact with *platinum-black,* it produces a peculiar acid. (Döbereiner.)

Combinations. It dissolves clearly in 1–3 parts of *alcohol* of sp. gr. 0·85, and with turbidity in a larger quantity. (Zeller.)

Appendix; Orange-flower water. *Aqua naphæ.* — This is the aqueous distillate which passes over on distilling fresh orange-flowers with water,—freed from the oil of neroli which floats on the surface.—It contains especially the more fragrant and more volatile oil of the flowers, which dissolves most readily in water (Soubeiran), and cannot therefore be prepared by agitating the neroli-oil with water (Le Roy), or by agitating with water neroli-oil triturated with magnesia (Cottereau), or by distilling a mixture of neroli-oil and water. (Soubeiran.)

Fresh orange-flowers, which have expanded in warm weather, are distilled with water, till the distillate amounts to three times their weight.—Neutral water then passes over first, afterwards water containing acetic acid; if flowers freed from the flower-leaves are distilled, the distillate is neutral to the end, but has a less agreeable odour.—Water, free from acetic acid, is obtained by distilling orange-flowers with water mixed with about 0·75 p. c. of calcined magnesia.—Transparent, colourless, with a pleasant odour of orange-flowers, more or less powerful,—fragant in the highest degree when prepared with orange-flowers which have expanded in warm weather. (Boullay.)—By keeping, it readily turns sour, from formation of acetic acid, but does not lose its odour. (Journeil, *J. Chim. méd.* 18, 752).—With *nitric acid*, it acquires in a few minutes a rose-red colour (Ader and others),—or crimson with a larger quantity of acid, or if the mixture is heated. (Ader.) The colour of a mixture of nitric acid and orange-flower water in equal volumes remains unaltered for a long time, and is especially lasting in a mixture of nitric acid with orange-flower water containing aqueous potash, ammonia, or baryta; it disappears in this mixture on addition of potash, but re-appears on supersaturating the liquid with nitric acid. (Ader, Wahart, Dunesmal.)—With *oil of vitriol* it becomes rose-coloured (Le Roy); not, however, with pure oil of vitriol, but only with the commercial acid containing nitric acid. (Ader.)—It is not coloured by phosphoric or hydrochloric acid. (Ader.)

Ether, *almond-oil*, and *castor-oil* abstract from orange-flower water the whole of the volatile oil; the ether solution, mixed with nitric acid, immediately assumes a rose-colour, and leaves on evaporation a fragrant volatile oil. (Ader, Soubeiran.)—*Artificial orange-flower water*, prepared by agitating with water, either oil of neroli, or the same triturated with magnesia, or by distilling a mixture of neroli-oil and water, differs from real orange-flower water by its stronger, but less agreeable, odour, which soon disappears when the oil is exposed to the air,—as well as by being not at all, or but slightly, reddened by nitric acid. (Ader, Soubeiran, Gaisney.)

67. Neroli-camphor.

Boullay. (1828.) *J. Pharm.* 14, 496.
Plisson. *J. Pharm.* 15, 152; *N. Tr.* 20, 1, 189; abstr. *Ann. Pharm.* 40, 83; *J. Pharm.* 20, 63.
Landerer. *Repert*, 56, 84.

Aurade, Auradine. (Plisson.)

Source and Extraction. Contained in solution in fresh oil of neroli.—Separates from the oil when kept for some time (Landerer) from the alcoholic oil by slow evaporation. (Plisson.) — To prepare it, oil of neroli is mixed with alcohol of sp. gr. 0·85, as long as a white precipitate is thereby produced; the liquid is filtered after a while, and the precipitate washed with cold alcohol (Boullay), then dissolved in ether, and the solution either precipitated by alcohol or left to evaporate in the air. Fresh oil of neroli yields 4 p. c. of the camphor; oil a year old, yields less and older oil, none. (Plisson.)

Properties. White crystals, having a pearly lustre (Plisson); slender needles (Boullay); rhombic prisms (Landerer); resembling spermaceti. (Plisson.) Sp. gr. 0·913 at 17·5°. Becomes soft at 50°, melts at 55°; solidifies on cooling to a waxy, translucent mass; volatilises and sublimes at a stronger heat. (Plisson.) — Melts at 100°. (Boullay.) — Without taste or odour. (Plisson.) Smells like neroli-oil, and has a sharp taste. (Landerer.) Neutral. (Plisson.)

C	83·76
H	15·08
O	1·16
	100·00

Decompositions. 1. Unaltered by exposure to the *air*, volatilises partially when heated in vessels containing air, and leaves a brown residue. (Plisson.) — 2. Boiled with *nitric acid*, it volatilises partially and partly remains undecomposed. Impure crystals thus treated give off vapours smelling like musk and ambergris. (Plisson.) The nitric acid solution deposits wax when mixed with water. (Landerer.) — 3. Heated with *oil of vitriol*, it chars and evolves sulphurous acid. (Plisson.) It is not decomposed by *hydrochloric acid*. — 5. *Potash* does not saponify it. (Plisson, Boullay.)

Combinations. Neroli-camphor is insoluble in *water* (Blisson, Boullay); sparingly in *cold*, readily in *hot alcohol* (Boullay, Landerer); in 60 pts. alcohol of sp. gr. 0·9, separating in indistinct scales on cooling. It dissolves abundantly in *ether*, and is precipitated from the solution by addition of water or alcohol. (Boullay, Plisson.) It dissolves in *hot acetic acid* (Landerer), very easily in *hot oil of turpentine*, separating completely in transparent laminæ on cooling. (Plisson.)

68. Oil of Nigella.

Schwarzkümmelöl. In the seed of *Nigella sativa, L.* Prepared by distilling the bruised seeds with water. Transparent, colourless, exhibiting a bluish iridiscence by reflected light; lighter than water; smells like a mixture of oil of fennel and bitter almond-oil. Distilled with *aqueous potash*, it gives off a non-iridescent oil having a faint odour, while there remains a strong-smelling residue, which, after supersaturation with sulphuric acid, smells like camphor and deposits an abundance of white flocks. On washing these white flocks with ether, and evaporating the adhering ether, they change into a buttery oil smelling like camphor, which exists ready-formed in the original oil (is probably produced therefrom by the action of hydrate of potash: Gm.). It dissolves in *alcohol* and *ether*, the solution exhibiting a bluish iridescence by reflected light. (Reinsch, *Jahrb. pr. Pharm.* 4, 387.)

69. Oil of Nutmeg.

Bley. *N. Tr.* 14, 1, 34. — *Repert.* 48, 94.
Mulder. *J. pr. Chem.* 17, 108; abstr. *Ann. Pharm.* 31, 71.

Muscatnussöl.

In nutmeg, the seed of *Myristica aromatica, Lam.* The seeds distilled with water yield 6 p. c. of oil. (Bley.)

Properties. Transparent, colourless, mobile (Hasse, *Crell. Ann.* 1785, 1, 422), nearly colourless (Bley). Sp. gr. 0·948 (Lewis), 0·920 (Bley). Smells of nutmeg and camphor, and has an aromatic burning taste. (Bley.) It contains 81·13 p. c. C, 10·83 H, 8·04 O, and is a mixture of oil and camphor. (Mulder.) Consists of two oils, one lighter than water, the other heavier. (Hasse.)

Decompositions and Combinations. 1. The oil gradually turns yellowish when exposed to the air. (Hasse.) — 2. With *fuming nitric acid*, it becomes very hot, and forms a yellow fatty mass (Bley), a brown solid resin (Hasse). — 3. With *oil of vitriol*, it forms a red-brown resinous mixture. — 4. Heated with *mercuric chloride*, it first turns brown, then black, giving off a large quantity of acid vapours. (J. Davy, *Phil. Trans.* 1822, 360.) It unites with aqueous *alkalis*, forming a soapy mass. (Bley.) It dissolves readily in *alcohol*, forming a solution which becomes milky on addition of water. (Hasse.)

70. Nutmeg-camphor.

John. (1821.) *Dessen chem. Schriften*, 6, 61; *Schw.* 33, 249.
Bley. *N. Tr.* 1, 56.
Mulder. *J. pr. Chem.* 17, 102; *Ann. Pharm.* 31, 62.

Myristicin, Muscatcamphor.

Deposited from nutmeg-oil; purified by recrystallisation from water.

Transparent, colourless, long, very thin prismatic tables, with dihedral summits; by rapid crystallisation: stellate groups of needles (John), friable, white hemispheres, heavier than water (Mulder), lighter than water (Bley). Melts above 100°, and evaporates, leaving charcoal (Bley); sublimes completely at a higher temperature in white very slender needles. (Mulder.) Has an aromatic taste and odour (John), like oil of nutmeg (Mulder).

	Mulder.
C	62·1
H	10·6
O	27·3
	100·0

Agrees with the formula $C^{16}H^{16}O^{5}$ (Mulder); $C^{20}H^{20}O^{6}$ (Gm.)

It yields by distillation, first a transparent and colourless, then a yellow volatile oil, and an alkaline water, having an aromatic burning taste and smell. (John.) *Heated* in a glass tube, it gives off vapours, having at first an agreeable, afterwards a fatty odour. Heated on platinum-foil, it *burns away* completely without deposition of soot (Mulder), leaves charcoal (Bley). With *fuming nitric acid*, it turns brown and acquires an odour of musk. (Bley.)

It is sparingly soluble in cold water, but dissolves in 19 pts. of boiling water; the hot solution, which is sometimes acid, sometimes alkaline, solidifies in the crystalline form on cooling. (John.)

It absorbs 11·83 p. c. *hydrochloric acid gas*, melting to a transparent mass, the aqueous solution of which has a strong acid reaction, and is precipitated by nitrate of silver.

Nutmeg-camphor dissolves in *cold nitric acid* and *aqueous potash* (Mulder), easily in *alcohol* and *ether* (John, Mulder), in warm *oils*, both *fixed* and *volatile* (Bley).

71. Oil of Nutmeg-flower.

In the arillus of the nutmeg, which, when comminuted and distilled with water, yields a turbid aromatic water, with films of oil floating on its surface. (Henry, *Repert.* 18, 105.) By cohobating four times, 4·7 p. c. oil is obtained (Hoffmann, *Repert.* 43, 296); from old nutmeg-flowers, 4·1 p. c. (Bley, *N. Tr.* 14, 1, 61; *Repert.* 48, 94). — Transparent, colourless. Sp. gr. 0·931. Smells strongly of nutmeg-flower, and has a burning aromatic taste. With aqueous *soda* it yields a soapy compound (? Gm.); with *ammonia*, a liquid, permanent liniment.

72. Oil of Olibanum.

In frankincense, the gum-resin of *Boswelia floribunda*, (*Royle*,) and *B. serrata* (*Stockh.*). Pulverised frankincense is distilled with water, and the oil which floats on the distillate is dehydrated by agitation with chloride of calcium. The product is 0·4 p. c. of limpid oil of sp. gr. 0·866 at 24°, and boiling point 162°. It smells like turpentine but more agreeably.

C	83·83
H	11·27
O	4·90
	100·00

It is isomeric with the oil of *Mentha viridis*, and agrees with the formula $C^{35}H^{28}O$ (Stenhouse); it contains an oxygenated and a non-oxygenated oil. (Löwig, *Org. Verb.* 2, 1027.) Burns when *set on fire* with strongly luminous, sooty flame. Mixed with *nitric acid*, it assumes a dark brown colour, and, when heated therewith, detonates and acquires a resinous consistence. *Oil of vitriol* colours it red in the cold and chars it when heated. Heated with caustic potash, it is converted into a brown resin. It dissolves in all proportions in *absolute alcohol* and *ether*, less in weaker alcohol. (Stenhouse, 1840, *Phil. Mag. J.* 18, 185; *Ann. Pharm.* 35, 306.)

73. Oil of Origanum.

Kane. *Lond. Ed. Mag. J.* 13, 439; *J. pr. Chem.* 15, 157; *Ann. Pharm.* 32, 285.
Zeller. *Stud. über äther. Oele,* Landau, 1852.

Dostenöl, Essence d'Origan, Oil of Wild Marjoram.

Source and Extraction. In wild marjoram, *Origanum vulgare, L.* Obtained by distilling the plant in the flowering state with water.

Properties. Pale to brownish-yellow. (Zeller.) Sp. gr. 0·909 (Brand); 0·8901 — 0·909, rectified, 0·8673 (Kane); 0·87 — 0·97 (Zeller). Boils almost constantly at 161°. (Kane.) Smells strongly of the plant, and has a sharp aromatic taste. Neutral.

	Kane.			
C	86·71	86·08	86·33	86·18
H	11·11	11·44	11·44	11·64
O	2·18	2·48	2·23	2·18
	100·00	100·00	100·00	100·00

It is a mixture of oil and camphor, corresponding to the formula $C^{50}H^{40}O$.

Decompositions. 1. Deposits camphor after long standing. — 2. With *iodine*, it becomes strongly heated and detonates, giving off violet and yellow-red vapours and becoming viscid. (Zeller.) — 3. With *nitric acid*, it becomes brownish-red to yellow-brown, giving off gas with violence when heated, and leaving a solid yellow resin. (Hasse, Zeller.) — 4. With *oil of vitriol*, it becomes dark blood-red. — 5. With *bichromate of potash* and *sulphuric acid*, it becomes dark brown. (Zeller.) — 6. Heated with a concentrated aqueous solution of *bisulphite of ammonia* or *soda*, it is resolved into a permanently liquid hydrocarbon belonging to the camphenes, and a white solid mass which, when washed with alcohol, ether, and water, presents the appearance of a white amorphous powder not containing either sulphur, or ammonia, or soda. (Rochleder, *Wien. Akad. Ber.* 13, 169; *J. pr. Chem.* 64, 29; *Chem. Centr.* 1854, 723.)

Combinations. Dissolves in 12 — 16 pts. alcohol of sp. gr. 0·85, forming a turbid liquid. (Zeller.)

74. Oil of *Parmelia parietina* (*Achard.*)

The lichen is distilled with water, 20 lbs. of it yielding 5 grains of the oil. Light green (colourless, according to Hinterberger (*Repert.* 47, 199), of buttery consistence, lighter than water. It has a musty smell and taste, producing an after-sensation of scratching in the throat. (Gumprecht, 1824, *N. Tr.* 1, 1, 62; *Repert.* 18, 241.)

75. Oil of Pelargonium.

Recluz. (1829.) *J. Pharm.* 13, 529.
C. and P. Simonnet. *N. J. Pharm.* 13, 43.
Guibourt. *N. J. Pharm.*. 15, 346.

Source and Extraction. In *Pelargonium odoratis-simum, P. roseum, Willd.*, and *P. capitatum, Art.* The fresh flowers and leaves are distilled with water, and the distillate is repeatedly cohobated over new portions.

Properties. Transparent, colourless, viscid like palm-oil (Simonnet), pale-yellow, mobile (Guibourt); solidifies in a white crystalline mass below 18° (Recluz), becomes turbid, without solidifying, when cooled to 0° (Guibourt); smells like roses (Simonnet) and lemons (Guibourt), and has a warming taste (Guibourt). It contains pelargonic acid (xiii, 369) and a neutral oil. (Pless, *Ann. Pharm.* 59, 54.)

In iodine-vapour it becomes brown after a few seconds, then black. In *nitrous acid vapours* it turns apple-green. Mixed with *oil of vitriol*, it yields a brown oil, having a strong and unpleasant odour. (Guibourt.) It dissolves readily in *alcohol* of sp. gr. 0·85. (Simonnet.)

76. Oil of Pimpinella.

a. From the root of the common Burnet-saxifrage, *Pimpinella Saxifraga, L.* The root is distilled with water; the yellow oil-drops which pass over with the water are collected; and the water is partly redistilled to obtain the oil. Gold-yellow, mobile oil, which floats on water, has a strong penetrating odour like parsley seeds, and a disagreeably bitter taste with scratching after-sensation. — *Fuming nitric acid* colours the oil red, and converts it into a brown, balsamic, resinous mass. — It dissolves slightly in water, easily in *alcohol* and *ether*, imparting to those liquids its strong taste and odour. (Bley, *N. Tr.* 12, 2, 62.)

b. From the root of *Pimpinella nigra, Willd.* — The root contains 0·38 p. c. of the oil, which is obtained from it by distillation with water. — Light blue oil which floats on water. Its odour, like that of the root, is less penetrating than that of the preceding oil; its taste, also like that of the root, is burning, and afterwards scratching. — In *sunshine*, it turns green after a few weeks, even in closed vessels. — *Fuming nitric acid* converts it into an odourless crystalline resin. — *Oil of vitriol* forms with it a brown odorous resin.—It dissolves slightly in *water*, easily in *alcohol, ether*, and *oils*, both *fixed* and *volatile*.

77. Oil of Poplar-buds.

In the buds of the black poplar, *Populus nigra*, whence it is obtained by distillation with water. — Colourless, fragrant oil, which floats on water. It makes stains on paper which are completely dissipated by heat; burns with black smoke when set on fire; is sparingly soluble in *alcohol*, very soluble in *ether*. (Pellerin, 1822, *J. Pharm.* 8, 428; abstr. 15, 237.)

Oil of Pyrethrum—see *Oil of Feverfew* (p. 369).

78. Raspberry-camphor.

Expressed raspberries are distilled with water; the flocks which separate after a while from the distillate are collected and dissolved in ether; and the solution is left to evaporate. — Small laminæ, some of which float on water, while others sink. — Volatilises readily when *heated.* With cold *oil of vitriol*, it assumes a yellowish colour, without losing its odour; with hot oil of vitriol, it turns violet-brown, giving off a large quantity of sulphurous acid. — It dissolves in *water*, in aqueous *ammonia*, and in *aqueous potash*, with the odour of violets when heated. — It dissolves in *alcohol* and in *ether*. (Bley, 1837, *N. Br. Arch.* 132, 48.)

79. Oil of Roses.

SAUSSURE. (1828.) *Ann. Chim. Phys.* 13, 337.
BLANCHET. *Ann. Pharm.* 7, 154; *Repert.* 50, 134.
GÖBEL. *Schw.* 58, 473.
GUIBOURT. *N. J. Pharm.* 15, 345.
ZELLER. *Stud. über äther. Oele,* Landau, 1850.

Rosenöl, Essence de rose.

Source and Extraction. In the flowers of *Rosa centifolia, L., R. moschata, Gesn. R. sempervirens, L.*, and *R. damascina, Mill.* — The fresh rose-leaves are distilled with water, the solidifying oil which floats on the watery distillate is removed; and the water is cohobated several times over fresh quantities of roses. — In India, the oil which floats on the water is collected by dipping into it sticks covered with cotton, and then pressing the cotton. (Chéreau, *J. Pharm.* 1826, 436.) — A larger quantity of rose-oil is obtained, by leaving the roses freed from their calices, in contact with water for some days before distillation, till they begin to ferment and acquire a vinous odour. (Cenedella, *Gazz. eclet. di Chim. med. Agosto,* 34.) — In Arabia, roses are distilled with solution of common salt without cooling; the distillate is poured into earthen vessels buried in the ground, and the solidified oil which rises to the surface is removed. (Landerer, *Repert,* 77, 378.) — In Macedonia, the expressed juice is exposed to the sun for 5 or 6 days (Landerer, *Repert,* 96, 401), in Bengal, roses steeped in water are thus exposed, and the oil which then floats on the surface is soaked up with cotton. (Monro, *Bull. Pharm.* 3, 177.)

Properties. Transparent, colourless (Saussure), slightly coloured (Göbel, Blanchet), greenish yellow (Guibourt), brownish yellow. (Zeller.) Sp. gr. at 33° = 0·832 (Saussure); at 25°, 0·867 — 0·872 (Chardin, *Ann. Pharm.* 7, 154); German rose-oil, 0·814; Persian, 0·832. (Zeller.) — Solidifies above 0° to a buttery mass (Saussure), to a white, transparent, laminated mass (Göbel), at 26° (Blanchet), at various temperatures (Guibourt), at 25°. (Zeller.) — When slowly cooled, it remains transparent, and appears traversed by slender, shining, iridescent laminæ (when adulterated with spermaceti, it becomes opaque); by rapid cooling it becomes turbid and cloudy.) (Guibourt.) Melts at 29°—30°. (Saussure), at 22·5° (Göbel), at 37·5°. (Zeller.) — Tension of the vapour at 14·5° = 2^{mm} of mercury. (Saussure.) — Has a penetrating odour of roses (Saussure); strong, pleasant only when diluted with alcohol; very persistent. (Göbel.) — Taste, mild, rather sweetish. (Saussure.) — Has a strong acid reaction. (Zeller.)

	Saussure. *a.*	Blanchet. *b.*	Göbel. *c.*
C	82·05	74·08	69·66
H	13·13	12·14	16·06
O	3·95	13·78	14·28
	99·13	100·00	100·00

a contains 0·87 p. c. nitrogen. It is a mixture of volatile oil and camphor (Saussure); contains ½ pt. camphor in solution (Blanchet).

Decompositions: 1. *Iodine* imparts to oil of roses a faint crimson colour (Zeller); in vapour of iodine the oil remains colourless. (Guibourt.) — 2. With 2 pts. of *fuming nitric acid,* it froths up, and, after addition of water, deposits white, tallowy, kneadable laminæ (Hasse, *Crell. Ann.* 1785, 1, 422); assumes a pale brownish yellow colour and becomes somewhat more tenacious. (Zeller.) — 3. In *nitrous acid gas,* it acquires a deep yellow colour. (Guibourt.) — 4. With an equal volume of *oil of vitriol,* it turns brown, and acquires a more agreeable but fainter odour. (Guibourt.) — 5. With *bichromate of potash* and *sulphuric acid,* it becomes brownish and, after a time, violet. (Zeller.)

Combinations. The oil dissolves sparingly in water. — At 18·7°, it dissolves in 160 pts. of alcohol of sp. gr. 0·815 (Göbel); at 14° in 143 pts., at 22° in 33 pts. alcohol of sp. gr. 0·806. (Saussure.) — The oil is not separated from its alcoholic solution by water (Blanchet); but from its aqueous solution it is taken up by platinum-black and platinic oxide, which thereby acquire the property of glowing when dried and heated to 100°. (Döbereiner, *Schw.* 66, 298.)

80. Rose-camphor.

SAUSSURE. (1820.) *Ann. Chim. Phys.* 13, 337.
BLANCHET. *Ann. Pharm.* 7, 154.
HERBERGER. *Repert.* 48, 102.

Solid Rose-oil. Stearoptene of Rose-oil.

Source and Extraction. In rose-oil. — Separates from rose-water in the cold. — 1. The oil is cooled and pressed between bibulous paper when solid. (Saussure.) — 2. Rose-oil is mixed with 3 pts. alcohol of sp. gr. 0·875; and the crystalline mass which then separates is dissolved in ether, precipitated therefrom by addition of alcohol, and freed from adhering oil by repeated washing with alcohol. (Blanchet.)

Properties. Transparent, colourless, shining laminæ (Saussure); six- to eight-sided crystals (Herberger), which exhibit the colours of the rainbow. (Guibourt, *N. J. Pharm.* 15, 345.) — It has the consistence of wax (Saussure); when separated from rose-water, it is a white, buttery, crystalline mass (Blanchet); from concentrated rose-water it crystallises in six-sided laminæ. (Steinacher.) — Lighter than water, lighter also than rose-oil containing the camphor (Saussure, Herberger); heavier than alcohol. (Herberger.) — It is buttery and crystalline at 25°, melts at 35°, boils without decomposition at 280°—300° (Blanchet); melts at 33°—34° (Saussure); melts to a colourless oil at 15°, and at a higher temperature solidifies in the crystalline form, leaving a small quantity of charcoal (Herberger); after being kept for a year, its melting point rises from 15° to 20°. (Bizio.) Solidifies again at 35°. (Blanchet.) Tension of vapour = 0·0005 met. at 14·5°. (Saussure.) — Has a faint odour of roses. (Blanchet, Herberger.) Smells of roses, even after being three times sublimed over ignited charcoal, or after its alcoholic solution has been treated with animal charcoal. (Herberger.) Has a somewhat warming aromatic taste. (Herberger.)

C	86·74	81·09
H	14·89	14·39
	101·63	95·48

Agrees with the formula $C^{16}H^{16}$. (Blanchet.)

Decompositions. — 1. When *set on fire,* it burns with a bright non-fuliginous flame. (Blanchet.) — 2. *Chlorine* passed into an alcoholic solution of rose-camphor, produces a white odourless precipitate. — 3. With *nitric acid,* it turns yellow, dissolves with slight evolution of gas, loses its odour, and forms oxalic acid. — 4. It is dissolved and turned brown by *oil of vitriol.* — 5. It is not altered by *potassium.* (Herberger.)

Combinations. Very sparingly soluble in *water.* (Herberger.) After being moistened with alcohol, it unites with *iodine,* without rise of temperature or detonation; the compound partly volatilises undecomposed when heated. It dissolves very sparingly in *hydrochloric* acid, with difficulty in *aqueous potash,* more easily in *aqueous ammonia.* — The solution of rose-camphor in *alkalis* and *alkaline carbonates* does not possess any odour of roses, or even acquire it after supersaturation with acids. (Herberger.)

Rose-camphor is soluble in *acetic acid.* (Herberger.)

It dissolves sparingly in *alcohol,* readily in *ether.* (Blanchet.) — It dissolves in 500 pts. alcohol of sp. gr. 0·85 at 14° (Saussure), in 490 pts. of alcohol of sp. gr. 0·85 at 15°; more easily in absolute alcohol; the alcoholic solution is clouded by water, and yields crystalline laminæ when evaporated. (Herberger.)

It dissolves in *volatile oils.* (Herberger.)

81. Oil of Rosemary.

Saussure. (1820.) *Ann. Chim. Phys.* 13, 278.
Kane. *Lond. Ed. Mag. J.* 13, 437; *J. pr. Chem.* 15, 156; *Ann. Pharm.* 32, 284; abstr. *Repert.* 70, 161.
Zeller. *Stud. über. äther. Oele,* Landau, 1850.
Volh. *N. Br. Arch.* 74, 16.

Rosmarinöl, Essence de rosmarin or romarin, Oleum Anthos.

Source and Extraction. In *Rosmarinus officinalis, L.* — It is obtained by distilling the fresh leaves and flowers with water.

Properties. Transparent, colourless (Saussure), yellowish to yellow. (Zeller.) Sp. gr. 0·933 at 15°; rectified 0·886 (Saussure); 0·897; after repeated rectification, 0·8854—0·8875 (Kane), 0·88—0·91. (Zeller. — Boiling point 166·5 to 168° (Kane); of the fresh oil, below 100°; of old oil, 132° (Kane); of the rectified oil, 165°. (Saussure.) — Tension of vapour at 16°=0·0095 met. of mercury. (Saussure.) It has a camphorous taste and smells like the plant. It is neutral. (Zeller.) Turns the plane of polarisation of light to the right. (Lallemand.)

	Saussure.		Kane.
	a.		*b.*
C	82·21	....	83·40
H	9·42	....	11·66
O	7·73	....	4·94
	99·36	....	100·00

a contains 0·64 p. c. nitrogen; *b* may be represented by the formula $C^{15}H^{38}O^2 = 9(C^5H^4) + 2HO$. It is probaby a mixture of a hydrocarbon isomeric with oil of turpentine and an oxygenated oil. (Kane.) See next page.

Decompositions. 1. Spanish oil of rosemary leaves on evaporation $\frac{1}{10}$ of camphor. (Proust.) — 2. When cooled to between — 27° and — 30°, it deposits camphor. (Trommdsorff, *N. Trs.* 20, 2, 24.) — 3. With *iodine* it becomes hot, but does not explode, gives off a small quantity of yellow-red vapours, and thickens without alteration of odour. (Zeller.) — It becomes heated by contact with iodine, sufficiently to volatilise the iodine with explosive violence. (Walcker, *Pogg.* 6, 126.) — 4. With *nitric acid,* it assumes a pale yellow to yellow colour, becomes heated, and gives off gas with violence, without thickening. (Zeller.) — With fuming nitric acid, it emits a crackling noise and forms a brown-red balsam. (Hasse, *Crell. Ann.* 1785, 1, 422.) — 5. With *oil of vitriol,* it becomes black (Kane), reddish-brown (Zeller): the mixture saturated with lime contains the lime-salt, soluble in water, of a peculiar acid (Unverdorben, *Pogg.* 8, 484), — of a sulphuretted acid, and yields by distillation Kane's *rosmarine,* an oil isomeric with oil of turpentine, having an alliaceous odour, of sp. 0·8678, and boiling point 173·8°. — Oil of rosemary yields with oil of vitriol, a brown mass of the consistence of a balsam (Hasse, *Crell. Ann.* 1786, 2, 36), an easily fusible resin, soluble only in hot oil of vitriol, and an oily acid. (Unverdorben, *Pogg.* 8, 484.) — 6. With *hydrochloric acid gas,* it blackens and forms a heavy oil, but no solid compound. (Cluzel, *Ann. Chim.* 52, 270.) — At 22° it absorbs 218 vol. hydrochloric acid gas, becoming black and turbid. Saussure.) — 7. With *bichromate of potash* and *sulphuric acid,* it becomes strongly heated, assumes a yellowish brown colour (Zeller), and forms limettic acid. (Vohl.) — 8. Distilled over *hydrate of potash* or *lime,* it yields rosemary-camphor, which sublimes. (Meyer, *Chem. Vers. über ungelöschtem Kalk.* 1764, 81.) — 9. Heated with *hypochlorite of lime,* it yields carbonic acid and chloroform. — 10. Distilled with *hypobromite of lime,* it yields, in like manner, carbonic acid and bromoform. (Chautard, *Compt. rend.* 34, 485.) — 11. Finely divided *sulphide of lead* is converted by oil of rosemary — through the action of the ozone contained therein — into sulphate of lead. (Overbeck, *N. Br. Arch.* 79, 138.)

Combinations. Oil of rosemary at 29° absorbs 9·75 vol. *ammonia-gas.* (Saussure.) — It dissolves in every proportion of *alcohol* of sp. gr. 0·85 (Zeller), at 18° in 40 pts. alcohol of sp. gr. 0·887. (Saussure.) — It dissolves abundantly *copal* and *caoutchouc.*

¶ According to Lallemand (*N. Ann. Chim. Phys.* 57, 404), oil of rosemary may be separated by fractional distillation into two oils, one boiling at 165°, the other between 200° and 210°. — *a.* The former is a mobile hydrocarbon which turns the plane of polarisation to the left: it unites with *hydrochloric acid,* the combination being attended with rise of temperature, and forms a compound which remains liquid if left to itself, but, when treated with nitric acid, yields a considerable quantity of a crystalline hydrochlorate apparently identical with artificial camphor (p. 265). The same oil quickly absorbs moist oxygen in sunshine, forming crystals which are similar to those produced in like manner from oil of turpentine, but disappear if subjected to the further action of oxygen, yielding a brown acid soluble in water.

b. The portion boiling between 200° and 210°, deposits at low temperatures a large quantity of camphor, resembling common camphor in all respects, excepting that it has rather less dextro-rotatory power. An additional quantity of it may be obtained by treating the mother-liquor with dilute nitric acid. ¶

Camphor of Marsh Wild Rosemary—see *Ledum-camphor* (p. 377).

82. Oil of Saffron.

Aschoff (1818.) *Berl. Jahrb.* 1818, 51.
Dehne. *Crell. Chem. J.* 3, 11.
Henry. *J. Pharm.* 7, 400.
Bouillon-Lagrange & Vogel. *Ann. Chim.* 80, 195.
Quadrat. *Wien. Akad. Ber.* 6, 546; further, *J. pr. Chem.* 56, 68.

Safranöl, Essence de safron.

Source and Extraction. In saffron, the stigmata of *Crocus sativus, L.* — 1. Obtained by distillation with water. (Bouillon & Vogel, Quadrat.) — 2. Saffron distilled over a quick fire, with 8 pts. of saturated solution of common salt and 4 pts. of aqueous potash of sp. gr. 1·24, yields 9·4 p. c. of oil. (Henry.)

Properties. Yellow, mobile, heavier than water (Henry, Bouillon & Vogel), lighter than water (Quadrat). Smells like saffron, and has a burning, sharp, rather bitter and caustic taste. (Henry, Bouillon & Vogel.)

It gradually changes into a solid mass, which makes its appearance, even during the distillation of saffron with water (Bouillon, Dehne), and sinks in water. (Henry, Quadrat.) — Easily soluble in *water.* (Bouillon.)

83. Oil of Sage.

ILISCH. (1811.) *A. Tr.* 20, 2, 7.
HERBERGER. *Repert.* 34, 131.
ROCHLEDER. *Ann. Pharm.* 44, 4; abstr. *Repert.* 79, 310.
ZELLER. *Stud. über äther. Oele,* Landau, 1850.

Salveiöl, Salbeiol, Essence de sauge.

Formation. By boiling oil of mustard with aqueous soda. (Hlasiwetz, *Wien. Akad. Ber.* 5, 189):

$$10\,C^6H^5CyS^2 + 12\,NaO = 4\,C^{12}H^{10}O + 2\,C^6H^5NaO^4 + 10\,NaCyS^2.$$

Source and Extraction. In *Salvia officinalis, L.* — Obtained by distilling the fresh herb with water.

Properties. Greenish to brownish yellow (Zeller); from young plants: green, soon turning brown; from old plants in autumn: yellow (Cartheuser); distilled from oil 8 years old at 128° — 130°, or from oil 2 years old at 150°: colourless; from the least volatile part of a two years old oil, by distillation with water: pale yellow. (Rochleder.) — Sp. gr. 0·864 (Ilisch); 0 86 — 0·92. (Zeller.) — Boils between 130° and 160°. but not at a constant temperature. (Rochleder.) Smells and tastes like the plant, when distilled from oil 8 years old oil at 128° to 130°; burning and camphorous, from oil 2 years old at 150°; disagreeably like rum. — Neutral. (Zeller.)

	Rochleder.				Hlasiwetz.
	a.	*b.*	*c.*	*d.*	*e.*
C	80·25	77·97	78·33	80·64	80·63
H	10·91	10·69	10·64	10·95	11·70
O	8·84	11·34	11·03	8·41	7·67
	100·00	100·00	100·00	100·00	100·00

a. The first tenth, distilled at 135°, of a sample of sage-oil 8 years old, redistilled *per se* in the oil-bath between 128° and 130° till ¾ had passed over. — *b.* The distillate from 8 years old oil, between 130° and 140°, redistilled over chloride of calcium between 96° and 105°. — *c.* The distillate from 2 years old oil below 160°, distilled at 150° *per se* over chloride of calcium. — *d.* The product obtained by distilling with water at 130° — 145°, the least volatile of a 2 years old oil, rectified *per se* over chloride of calcium. — *e.* Prepared from oil of mustard. — Sage-oil is a mixture of several oils, of which *a* and *d* correspond to the formula $C^{12}H^{10}O$, *b* and *c* to the formula $C^{13}H^{15}O^2$. (Rochleder.)

Decompositions. 1. Sage-oil when exposed to the air for some time, deposits camphor (Herberger), and becomes slightly acid. (Zeller.) — 2. The Spanish oil when *evaporated,* leaves ½ pt. camphor (Proust); German-oil becomes resinous without leaving camphor. (Ilisch.) — 3. With *iodine,* it gives off yellowish red and grey vapours without fulmination, and forms a soft, extractive mass. (Zeller.) — It forms with iodine, without losing its odour, a thick magma easily soluble in the rest of the oil. (Guyot, *J. Phys.* 5, 230.) — 4. With *cold concentrated nitric acid,* or with *weaker nitric acid,* if warmed, it acquires a brown-red colour (Rochleder), reddish brown (Zeller), and deposits a red resin, with rise of temperature and brisk evolution of gas. — This resin consists of unaltered oil; a yellow resin soluble with red colour in aqueous potash; and nitrate of camphor, which, when distilled with water, yields a volatile oil having a peculiar odour, and a residual, yellowish red, brittle resin. — The mixture dropped into *fuming nitric acid,* becomes heated, gives off carbonic acid and nitric oxide, and forms common camphor. — On distilling the nitric acid solution of this mixture with 4 pts. of water, common camphor sublimes. (Rochleder.) — 5. *Oil of vitriol* colours it brownish red to crimson. (Zeller.) — 6. Distilled with *hydrate of potash,* it yields volatile oils, with evolution of hydrogen at last, then turns brown, and leaves carbonate of potash. — Sage-oil two years old distilled with a small quantity of hydrate of potash, yields — at first without evolution of gas — a colourless oil smelling of oil of turpentine (84·40 C, 11·87 H, 3·73 O), then another oil (83·17 C, 11·26 H, 5·57 O = $C^{65}H^{50}O^3$), and at last, with evolution of hydrogen, an oil having a strong burning odour of sage and peppermint (76·87 p. c. C, 11·50 H, 9·83 O = $C^{22}H^{20}O^2$); sage oil 8 years old, distilled after digestion at a gentle heat with a large quantity of hydrate of potash, yields a colourless oil having an empyreumatic odour (82·65 C, 12·52 H, 4·83 O = $C^{22}H^{20}O$) and leaves carbonate and hydrate of potash tinged with brown. (Rochleder.) — 7. With *bichromate of potash* and *sulphuric acid,* it acquires a dark brown colour, afterwards becoming greenish. (Zeller.) — 8. Boiled with *nitroprusside of copper,* it yields a slate-grey deposit and acquires a darker colour. (Heppe, *N. Br. Arch.* 89, 57.)

It dissolves in every proportion of *alcohol* of sp. gr. 0·85. (Zeller.)

84. Sage-camphor.

This substance was found in sage-oil which had been kept for a long time in a badly-closed vessel, and was purified by pressure between slightly warmed filtering paper. — Yellowish white mass, lighter than water, melting at 31—37°, having an odour like that of turpentine-camphor and slightly like that of sage-oil, and a persistently sharp and bitterish cooling taste. Neutral. — When strongly *heated,* it swells up, diffusing a smoke which produces a scratching sensation in the throat, and a strong odour of turpentine-camphor, and yielding a slight sublimate. — When set on fire, it burns with a bright flame, leaving shining charcoal. — With *nitric acid* of sp. gr. 1·27, it becomes slightly heated, and yields a yellow resin but no oxalic acid. — With *oil of vitriol* it becomes brown-red and acquires a resinous consistence. — With *hot hydrochloric acid,* it forms a resinous mass. — With *caustic alkalis,* it forms a yellow-brown resin. — Sage-camphor dissolves in 450 pts. of cold and 300 pts. of hot *water;* the solution yields crystalline films when evaporated, but does not deposit crystals on cooling. — It dissolves without alteration in *dilute sulphuric acid.* — It dissolves in 5 pts. alcohol of sp. gr. 0·82, in all proportions of *ether,* easily in *oil of turpentine,* less easily in *rock-oil,* easily in *fixed oils.* (Herberger, *Repert,* 34. 131.)

85. Oil of Sweet Sedge.

TROMMSDORFF. (1809.) *Ann. Chim.* 81, 332; *A. Tr.* 18, 2, 122.
SCHNEDERMANN. *Ann. Pharm.* 41, 374.
ZELLER. *Stud. über äther. Oele*, Landau, 1850.

Kalmusöl, Essence d'acore.

Source and Extraction. In the root-stocks of the sweet sedge, *Acorus calamus, L.* — The roots fresh or at least not too old, yield when comminuted and distilled with water, 1 p. c. of oil (Martius, *Repert.* 39, 240), 1·09 p. c. (Bley *Repert.* 48·96) ; dry roots a year old yield 1·36 p. c. ; fresh, slightly dried roots, 0·73 p. c. (van Hees, *Pharm. Centralbl.* 1847, 380.)

Properties. Pale yellow to dark yellow (Trommsdorff, Martius) ; light brownish yellow (Bley); pale to reddish yellow and brown. (Zeller.) According to Schnedermann, the most volatile portion of the oil is colourless. — Sp. gr. 0·899 at 25° (Trommsdorff), 0·89—0·94 (Zeller), 0·950—0·984. (van Hees.) — Boiling point 195° (after the most volatile portion has been distilled off). (Schnedermann. — Has a strong pungent odour, like that of the roots, and an aromatically bitter, burning, slightly camphorous taste. (Trommsdorff.) — Neutral. (Zeller.)

	Schnedermann. *a.*	 *b.*
C	80·82	79·53
H	10·89	10·28
O	8·29	10·19
	100·00	100·00

a, distilled at 195°; *b*, at 260°. It is a mixture of several non-separable oils; the most volatile, containing 1½ p. c. oxygen, is in the pure state, most probably $C^{20}H^{16}$; the less volatile, boiling at 260°, is a mixture of resin and oil, the latter passing off when the mixture is heated, and the resin remaining. (Schnedermann.)

Decompositions. 1. It becomes darker in colour by exposure to *light.* (Trommsdorff.) — 2. When exposed to the *air*, it thickens and turns slightly acid, but does not yield any camphor. (Hasse, *Crell. Ann.* 1785, 1, 422.) — 3. Gently heated with *iodine*, it gives off a small quantity of greyish yellow vapours without explosion, and is converted into a tough, reddish yellow-brown mass. (Zeller.) — It takes up 1·52 pts. of *bromine*, and acquires a blackish green colour. (Knop, *Chem. Centralbl.* 1854, 498.) — 5. With *nitric acid*, it acquires a yellowish red-brown colour, and is converted into a solid resin (Hasse), crumbling. (Zeller.) — With *oil of vitriol*, it resinises. — 7. *Alcoholic potash* turns it reddish yellow-brown. — 8. With *bichromate of potash* and *sulphuric acid*, it forms a dark brown, thickish, turbid mass. (Zeller.)

It dissolves without turbidity in *absolute alcohol* and in 1 pt. of alcohol of sp. gr. 0·85.

86. Oil of Serpentaria.

In Virginian snake-root, *Aristolochia Serpentaria, L.* — It is obtained by distilling the comminuted root with water. — The root contains 0·5 p. c. of oil. (Buchholz.) — Light brown; in single drops, brownish yellow. Lighter than water. Smells and tastes like valerian and camphor. (Grassmann, *Repert.* 35, 463.)

Neutral Oil of Spiræa, see *Neutral Oil of Meadow-sweet* (p. 382.)

87. Oil of Squill.

Meerzwiebelöl. — From *Scillus maritimus, L.* — Obtained by crushing the fresh plant and distilling it with water. — Greenish yellow, viscid; has a disagreeable and persistent odour, sharp, but not so penetrating as that of mustard-oil; produces burns on the skin. — Soluble in *alcohol;* the solution irritates the skin. — The oil is different from that which is obtained by distilling fermented squills with water. (Landerer, *N. Br. Arch.* 95, 260.)

88. Oil of Syringa.

Unachtes Jasminöl. — In the flowers of the syringa, *Philadelphus coronarius, L.* — The flowers lose their odour when dry, and, on being distilled with water, yield an aqueous distillate having rather a repulsive than a pleasant odour, but acquiring after some time an odour of roses. — To obtain the oil, the fresh flowers are exhausted with ether in a displacement-apparatus; the upper ethereal layer is separated from the lower gummy watery liquid; the ether is carefully distilled off, and the residue is collected in a basin and filtered when cold. There then remains on the filter a yellow buttery mass, which loses its odour by washing with cold alcohol; and a watery liquid smelling strongly of the flowers runs off. The latter is shaken up with ether, and the ether is removed, shaken up with chloride of calcium, and left to evaporate. — Golden-yellow oil, having an intoxicating odour in the mass, fragrant in the dilute state. (Buchner, *N. Br. Arch.* 8170.)

Oil of Syringa vulgaris, see *Oil of Lilac,* p. 377.

9. Volatile Oil of Tagetes glandulosa.

Light yellow, strongly anthelmintic. (Fr. Eisenbeck, *Br. Arch.* 3, 421.)

90. Oil of Tansy.

Fromherz. *Mag. Pharm.* 8, 35.
Persoz. *Compt. rend.* 13, 433; *J. pr. Chem.* 25, 60; *Ann. Pharm.* 44, 31.
Zeller. *Stud. über äther. Oele.* Landau, 1850.
Wohl. *N. Br. Arch.* 74, 16; *abstr. Pharm. Centralbl.* 1853, 318.

Rainfarrenöl, Essence de tanaisie, oleum tanaceti.

Source and Extraction. In the herb and flowers of the tansy, *Tanacetum vulgare, L.* — Obtained by distilling either the fresh or the dried plant with water.

Properties. Pale yellow from the leaves, gold-yellow from the flowers (Fromherz); the plant grown on a damp soil yields yellow oil; that grown on a dry soil yields green oil. (Geoffroy.) Sp. gr. 0·946 (Lewis); 0·952 at 20° (Fromherz); from the flowers, 0·921; from the herb, 0·918. (Zeller.) Smells like the herb; tastes burning and bitter. (Fromherz.) Neutral. (Zeller.)

Decompositions. 1. It dissolves *iodine*, becoming viscid and brown-red (Flaschoff, *Br. Arch.* 33, 225), slightly warm and acid at the same time (Winckler, *Repert.* 33, 185); without rise of temperature or formation of vapour. (Zeller.) — Heated with *nitric acid*, it gives off gas with violence, acquires a reddish brown to reddish yellow colour and becomes resinous. — 3. With *oil of vitriol*, it becomes reddish yellow. (Zeller.) — 4. Heated with 5 pts. *bichromate of potash*, 11 pts. *oil of vitriol*, and 40 pts. water, it yields common camphor. (Persoz, Vohl.) — 5. With nitroprusside of copper, it yields a brown-black precipitate. (Heppe, *N. Br. Arch.* 89, 57.)

Dissolves readily in *alcohol*.

Oil of Tropæolum, see *Oil of Nasturtium*, p. 385.

91. Oil of Tea.

Mulder. (1838.) *Pogg.* 43, 163.

Source and Preparation. In tea, the dried leaves of various species of *Thea.* — 1. A hundred grammes of tea are digested for 48 hours with 1 litre of ether; the ether is then poured off, and distilled till only 3 oz. are left; the residue is mixed with 1 oz. water; the mixture is distilled to dryness, in the sand-bath; the upper ethereal layer of the distillate is separated from the lower and shaken up with chloride of calcium; and the ether decanted therefrom is left to evaporate. — Chinese Hyson yields 0·79 p. c., Congo 0·60 p. c., Java Hyson 0·98 p. c. of oil. — 2. One part of tea is distilled with 1 pt. of common salt and 6 pts. of water; the milky distillate, which has an intoxicating smell of tea, is shaken up with ether; the ethereal solution which floats on the liquid when left at rest is dehydrated with chloride of calcium and distilled to a small residue, and the ether is left to evaporate spontaneously therefrom. — No oil is obtained by repeatedly distilling the watery distillate over common salt.—Tea distilled with dilute sulphuric acid, yields a distillate having a faint odour, but no oil.

Properties. Lemon-yellow; lighter than water; solidifies easily when cold (because it contains camphor in solution); smells strongly of tea, and so intoxicating that it acts like a narcotic; tastes of tea, but not astringent. — The oil prepared by the second method resinises quickly when exposed to the air.

92. Oil of Wild Thyme.

HERBERGER. (1830.) *Repert.* 34, 41.
ZELLER. *Stud. über. äther. Oele,* Landau, 1850.

Quendelöl.

Source and Extraction. In wild thyme, *Thymus Serphyllum, L.* — Obtained by distilling the herb with water. — The aqueous distillate from old herb contains acetic acid as well as oil. (Trommsdorff, *N. Tr.* 25, 2, 149.) — The yield of oil amounts 0·08 to 0·09 p. c.

Properties. Gold-yellow (Herberger); wine-yellow to brown. (Zeller.) Sp. gr. 0·89 to 0·91. (Zeller.) Has an agreeable odour of lemons and thyme, and an aromatic bitter taste. (Herberger.)

Decompositions. 1. It is not decomposed by *iodine* in the cold, but when heated with it to 75°, forms, without violent explosion, a mixture which gives off iodine-vapours, takes fire, and after the combustion leaves a resin. (Herberger.) It quickly evolves yellowish red vapours with iodine,—especially the oil obtained from the dried herb,—thickening at the same time and acquiring a reddish yellow-brown colour. (Zeller.) — 2. With *nitric acid,* it acquires a dark yellow-brown colour, gives off gas when heated, and leaves a soft resin. (Zeller.) Nitric acid of sp. gr. 1·28 does not act upon the oil at 22·5°, but when the mixture is heated to the boiling point, it explodes, gives off nitrous acid, and leaves a resin. (Herberger.) — 3. With *oil of vitriol,* it acquires a dark brown-red colour and the thickness of a balsam. (Zeller.) — 4. *Strong hydrochloric acid* does not act upon the oil below 75°; but at that temperature, it produces ebullition, the mixture becoming viscid on cooling, and appearing to be mixed with blackish green oil-drops. (Herberger.) — 5. With *bichromate of potash* and *sulphuric acid,* it assumes a greenish brown-yellow colour. (Zeller.)

Combinations. The oil dissolves in all proportions in *alcohol* of sp. gr. 0·85. (Herberger, Zeller.)

93. Oil of Vitiveria.

In the root of a grass which grows in India. — The grass is cut up and distilled with water; the oil which passes over is collected; the milky water which goes over towards the end of the distillation is exhausted with ether, and the ether is left to evaporate spontaneously from the solution. — The more volatile portion of the oil is yellowish, transparent, lighter than water; the less volatile is turbid, viscid, heavier than water, and sticks to the receiver. This latter is probably a mixture of oil and resin; on treating the oil with aqueous soda, the resin unites with the soda, and may be separated from the solution by supersaturation with nitric acid. (Cap, 1833, *J. Pharm.* 19, 48; *Ann. Pharm.* 7, 83.)

94. Oil of Fine-leaved Waterdrop.

In the seeds of *Phellandrium aquaticum, L.* — They are bruised and distilled with water, yielding, according to Remler, 0·8 p. c. of oil. The plant distilled with $\frac{1}{6}$ pt. carbonate of potash, $\frac{1}{4}$ pt. lime, and 6 pts. water, yields a milky, ammoniacal, aqueous distillate having a strong taste and smell: on this distillate there floats about 0·67 p. c. of oil. (Frickhinger.) — Pale yellow, lighter than water (Pfaff); viscid, heavier than water (Rayhaud, *J. Pharm.* 20, 453); when obtained by distilling the seed with potash, it is brownish yellow, viscid, of sp. gr. 0·8526 at 19°. (Frickhinger.) Has a penetrating odour and a persistent aromatic taste, like that of the seed. (Pfaff, Frickhinger.) Neutral. It does not exert any narcotic action on animals, unless administered in rather large quantities (Frickhinger, *Repert.* 68, 1.) — It fulminates with *iodine,* giving off violet vapours and leaving a brittle resin. With *fuming nitric acid,* it becomes dark brown, then colourless and tenacious.

95. Oil of Water Horehound.

In the fresh herb of water horehound, *Lycopus Europæus, L.,* whence it is obtained by distillation with water. — Green, buttery oil, which smells like the plant and has a sharp taste. (Geiger, 1823, *Repert.* 15, 2.)

Second Appendix.

Ferment Oils.

(Arranged alphabetically.)

Fermentolea.

These are volatile oils, produced by the fermentation of various plants, not originally contained therein, and essentially different from the oils which are extracted from unfermented plants by distillation with water. According to Becker (*N. Br. Arch.* 55, 161), they were known to the alchemists, and by them designated *quintessences.* The number of them known to exist has increased, since Büchner (*Repert.* 53, 299) in 1835, first separated an oil of this nature from the fermented herb of *Erythræa Centaurium Pers.* by distillation. — Ferment-oils are for the most part much more soluble in water than ordinary volatile oils.

— According to Berzelius (*Jahresber.* 27, 541), they are perhaps peculiar alcohols, related to fusel-oil, and forming compound ethers with salt-radicals and acids.

1. *Ferment-oil of Chærophyllum sylvestre.*—The flowering plant is left to ferment in water; the liquid distilled when the fermentation is ended; the distillate mixed with common salt, and shaken up with ether; and the ether removed from the aqueous solution and left to evaporate: the ferment-oil dissolved in it is then left behind. — Brown, lighter than water, with a strong and peculiar pungent odour, and an aromatic taste, not bitter, but slightly scratching. — Evaporates quickly even at 18°; burns when *set on fire*, with a clear, luminous flame, diffusing a vapour which excites coughing. — *Chlorine-water* converts it into yellow flocks retaining the odour of the oil. It dissolves iodine. It is decomposed with violence by *nitric acid*. By *oil of vitriol* it is coloured brown, without losing its odour; the solution is rendered milky by water. It forms an emulsion with *aqueous ammonia*, dissolves sparingly in *water*, easily in *alcohol, ether*, and *oils*, both *fixed* and *volatile*. It dissolves resin. (Bley, *N. Br. Arch.* 45, 50.)

2. *Ferment-oil of Chelidonium majus, L.*— Obtained from the roots, in the same manner as the ferment-oil of *Chærophyllum sylvestre*. — Lighter than water; has an agreeable odour like the bouquet of wine, and a persistent biting taste. It is not very volatile. — With *iodine* it forms a violet solution. With *nitric acid* it evolves nitrous gas, and with *oil of vitriol* it forms a slightly coloured solution, which is scarcely clouded by water. — It dissolves sparingly in *water*, readily in *alcohol, ether*, and *oils*, both *fixed* and *volatile*. (Bley, *N. Br. Arch.* 48, 156.)

3. *Ferment-oil of Conium maculatum.* — Obtained from fresh hemlock in the same manner as the ferment-oil of *Chærophyllum sylvestre*. — Colourless; has a peculiar odour, not like that of hemlock, and a sharp burning taste; it is not poisonous. — Dissolves with facility in *alcohol, ether*, and *oils* both *fixed* and *volatile*. (Landerer, *Repert.* 94, 237.)

4. *Ferment-oil of Erythræa Centaurium, Pers.* — The plant, after maceration in water for 12 hours, gives off a perceptible odour, which increases up to 60 hours maceration and then ceases. (Büchner.) — The aqueous distillate is pale yellow, with white turbidity; has a persistent enlivening, aromatic odour, which is not pleasant when close, and irritates the eyes and nose; its taste is excessively burning, like that of creosote, but not persistent. It reddens litmus, but not permanently (Büchner, *Repert*, 53, 303), and when heated with ammonia and nitrate of silver, reduces the solution to the metallic state. (Büchner.) — To prepare the oil, fresh herb is macerated in water for 48 hours, the whole distilled, the odoriferous distillate redistilled, and this process continued as long as drops of oil pass over with the watery vapour. — Thin greenish oil, having a peculiar, but not disagreeable, odour: it is not poisonous. (Büchner, *Repert.* 53, 299.)

5. *Ferment-oil of Echium vulgare, L.*—The plant in the flowering state is distilled with water after maceration; the distillate is shaken up with ether, and mixed with common salt; and the ether decanted therefrom is distilled off. — Pale yellow oil lighter than water, and smelling like other ferment-oils. — Easily soluble in *alcohol* and in *ether*. (Bley, *N. Br. Arch.* 30, 167.)

6. *Ferment-oil of Erica vulgaris.* — The fresh herb is distilled after maceration with water; the distillate is cohobated and repeatedly distilled after addition of common salt, then shaken up with ether as long as the ether acquires any odour; and the ether is carefully distilled off from the dissolved oil. The oil obtained amounts to 0.023 per cent. — Greenish yellow, mobile, lighter than water, with a peculiar odour, and a sweetish, aromatic, burning taste; reddens litmus. — When *set on fire*, it burns with a clear, blue-edged flame, without leaving any residue. — It is not deodorised by *chlorine-water*. — It dissolves *iodine* without detonation. — With *fuming nitric acid*, it froths up, and the solution mixed with water deposits resinous flakes. — With *oil of vitriol*, it becomes darker, without losing its odour. (Bley, *N. Br. Arch.* 21, 302.)

7. *Ferment-oil of Tussilago farfara, L.* — The fresh bruised herb is macerated in water for 10 or 12 days, during which it turns light green and acquires the odour of pickled girkins; the whole is then distilled; the distillate, which has a vinous odour, is saturated with common salt and redistilled; this second distillate is shaken up with a large quantity of ether; and the ether is taken off and evaporated, the dissolved oil then remaining behind. — Yellowish, lighter than water, very volatile, with a peculiar, strongly aromatic, penetrating odour, and an aromatic taste, neither burning nor cooling. — It easily takes fire, and burns at first with a whitish, afterwards with a reddish, sooty flame. — It dissolves *iodine* abundantly, dissolves in oil of vitriol with yellowish colour, without losing its odour, and turns brown when heated with it. — With *potash*, it forms a whitish, soapy compound (Qy. Gm.). — It dissolves sparingly in *water*, readily in *alcohol* and *ether*. (Bley, *Repert.* 62, 406, *N. Br. Arch.* 13, 38.)

8. *Ferment-oil of Marrubium vulgare, L.* — The comminuted herb is soaked in water and exposed to the sun, whereby it acquires an offensive odour; the liquid is then distilled; the distillate saturated with common salt; the flocks thereby separated, are collected on a filter and dissolved in ether; and the ether is left to evaporate slowly. — The distillate saturated with common salt yields when heated, a second aqueous distillate, from which oil may be extracted by agitation with ether. — Lighter than water; has a peculiar, sweet, ethereal odour, and an aromatic, slightly biting taste. — When *set on fire*, it burns with flame, without leaving charcoal. It dissolves in *dilute nitric acid*, and yields a bitter substance with *strong nitric acid*. With *oil of vitriol*, it becomes heated and acquires a peculiar odour. — With *chlorine-water*, it emits an odour of roses and forms a film of resin. — It dissolves in *aqueous alkali* and in *water*. (Bley, *N. Br. Arch.* 10, 67.)

9. *Ferment-oil of Achillea Millefolium, L.*—The fresh flowering plant is macerated in water and left to ferment; the whole is distilled, with cohobation; the blue oil which floats on the distillate is removed; the residual water, after addition of common salt, is agitated with ether; and the ether which separates is left to evaporate. — Yellow-brown oil, having a slightly aromatic odour, and an aromatically bitterish, rather sharp taste. It dissolves in alcohol, ether, and oils, both fixed and volatile. (Bley, *N. Br. Arch.* 30, 167.)

10. *Ferment-oil of various species of Plantago.* — Obtained from plantain-leaves by fermentation, distillation, and agitation of the distillate with ether, in the same manner as the ferment-oil of *Achillea Millefolium.* — Yellow, transparent; has an ethereal odour slightly resembling that of mustard-oil, and an aromatic, sweet, burning taste. — Very volatile. — With *fuming nitric acid,* it turns brown, with rise of temperature and intumescence; the solution first becomes greenish yellow, with milky turbidity, then clear, smells like artificial musk, and has a disgustingly bitter taste. — With *oil of vitriol,* it forms a dark brown-red mixture, from which water separates resinous flocks smelling of resin and ferment-oil. — It dissolves in *alcohol, ether,* and *oils.* (Bley, *N. Br. Arch.* 40, 130.)

11. *Ferment-oil of Quercus Robur, Willd.* — Obtained from fresh oak-leaves by fermentation, distillation, and treatment of the distillate with ether, in the same manner as the ferment-oil of *Achillea Millefolium.* — Pale green; sp. gr. 0·695, has an agreeably enlivening odour, a sweet, burning taste, and reddens litmus. — It is easily inflammable, and burns, with penetrating odour, and with a first bluish, then whitish, non-fuliginous flame. — With *fuming nitric acid* it froths up and becomes very hot, but does not lose its odour. — With *oil of vitriol,* it becomes hot and assumes a dark red-brown colour. — It dissolves sparingly in *water,* readily in *alcohol, ether,* and *oils,* both *fixed* and *volatile.* (Bley, *N. Br. Arch.* 26, 48.)

12. *Ferment-oil of Salix pentandra, L.* — Obtained from fresh willow-leaves in the same manner as the ferment-oil of *Achillea Millefolium.* — Yellow, lighter than water; has an aromatic odour, like that of castoreum, and at the same time like that of willow-leaves; reddens litmus. — Smells strongly when *heated,* and burns, when set on fire, with a very smoky flame, leaving a small quantity of charcoal. Dissolves *iodine* abundantly. — With *fuming nitric acid,* it froths up and thickens, but does not take fire, and if water be then added, deposits light yellow, bitter, resinous flocks. With *oil of vitriol,* it becomes slightly warm, brown, and viscid, and on subsequent addition of water, deposits resinous flocks smelling of the ferment-oil. It dissolves sparingly in water, easily and in all proportions in *alcohol, ether, volatile* and *fixed oils,* and *creosote.* (Bley, *N. Br. Arch.* 40, 129.)

13. *Ferment-oil of Salvia pratensis, L.* — Obtained from the fresh herb, like the ferment-oil of *Achillea Millefolium.* — Dark red-brown, with a repulsive, ethereal, sweetish odour, and an aromatic taste. — It dissolves sparingly in water, easily, and in all proportions, in *alcohol, ether,* and *oils,* both *fixed* and *volatile.* It forms a liniment with *aqueous ammonia,* and is very sparingly dissolved by *aqueous potash.* (Bley, *N. Br. Arch.* 51, 257.)

14. *Ferment-oil of Trifolium fibrinum, L.* — Obtained like the ferment-oil of *Achillea Millefolium,* from the dried plant, even after it has been well boiled with water and no longer has a bitter smell, by fermentation, distillation, saturating the distillate with common salt, and shaking it up with ether.—Pale yellow, lighter than water, smells strongly aromatic, like the ferment-oil of *Tussilago farfara;* its taste is at first burning and sweetish, afterwards aromatic. When *set on fire,* it burns with a blue, slightly fuliginous flame, giving off

strong-smelling vapours which excite coughing, and leaves a small quantity of charcoal. It dissolves sparingly in *water*, easily in *alcohol* and *ether*. (Bley, *Jahrb. pr. Pharm.* 2, 207.)

15. *Ferment-oil of Urtica urens, L.* — Obtained like the ferment-oil of *Achillea Millefolium*, from the flowering plant, which, during fermentation, emits, first a vinous, then a sharp and intoxicating odour. Resembles the ferment-oil of *Echium vulgare*. (Bley, *N. Br. Arch.* 30, 167.)

16. *Ferment-oil of Vitis vinifera, L.* — Fermented vine-leaves are distilled; the distillate is cohobated and shaken up with ether; the ethereal solution is distilled; and the ethereal, peculiar-smelling distillate is rectified: the ferment-oil dissolved in it then remains behind. Pale yellow, lighter than water; has a peculiar vinous odour, like vine-flowers and mignonette, and a burning, sweetish, aromatic taste. It reddens litmus slightly but permanently. It evaporates in the *air*, diffusing a strong odour. Heated with *fuming nitric acid*, it resinises and assumes a grass-green colour. With *oil of vitriol*, it forms first a white, then a light-red, and ultimately a brown mixture, without losing its odour. It is not deodorised by agitation with *chlorine-water*. With *aqueous potash*, it forms a clear mixture, from which the oil afterwards separates, with red-brown colour, but with its original odour. It dissolves sparingly in *water*, without alteration in *hydrochloric* and *acetic acid*. With *sulphide of carbon*, it forms a milky liquid, from which it afterwards separates unaltered; with *carbonate of potash*, a liniment from which it also separates unaltered; with *aqueous ammonia*, a soapy mixture. It dissolves abundantly in *alcohol*, *ether*, and *fixed oils*; in *oil of turpentine* and *oil of lemon*, it forms at first a milky solution, which afterwards becomes clear. (Bley, *Repert.* 68, 301.)

An oil, different from that just described, may be obtained from wine, by leaving it to freeze, distilling off the volatile part of the remaining liquid, and shaking up the residue with ether. (Bley.)

17. *Ferment-oil of diseased Apples.* — *Maloïl, Oil of Apples.* — Produced in cellulostasis, a disease of the apple, which imparts a musky odour to that fruit. It is obtained from the diseased apples by distillation with water. Yellowish grey, lighter than water; boils at 109°. Smells of musk, tastes rough and sharp. Contains 64·15 p. c, C, 20·65 H, 15·15 O, and 0·05 N. It volatilises completely when *heated*, and burns, when set on fire. with a feeble flame, diffusing a small quantity of smoke. *Chlorine* decomposes it, with elimination of hydrochloric acid. With dry *hydrochloric acid gas*, it forms a crystalline compound (*Chlorhydrate de maloïle*). It dissolves readily in *alcohol* and *ether*, and imparts a musk-like odour to *water*. (Rossignon, *J. Pharm.* 27, 158; *J. pr. Chem.* 23, 398; *Ann. Pharm.* 39, 121.)

Oxygen-nucleus $C^{20}H^{14}O^2$.

Thymol.

$C^{20}H^{14}O^2$.

A. E. ARPPE. (1846.) *Ann. Pharm.* 58, 42; abstr. *Berz. Jahresber.* 27, 451.

DOVERI. *N. Ann. Chim. Phys.* 20, 174; *Ann. Pharm.* 64, 374; *Compt. rend.* 24, 390.

A. LALLEMAND. *Compt. rend.* 37, 498; *J. pr. Chem.* 60, 431; *Pharm. Centralbl.* 1853, 754. — *Compt. rend.* 38, 1022; *J. pr. Chem.* 62, 295; *Pharm. Centr.* 1854, 513. Report. by Dumas & Bussy, *Compt. rend.* 39, 723. — *Compt. rend.* 43, 375. Report, 43, 459. — Abstract of the preceding Memoirs; *Ann. Pharm.* 101, 122. — Fully, and with Emendations, *N. Ann. Chim. Phys.* 49, 148; abstr. *Ann. Pharm.* 102, 119.

STENHOUSE. *Ann. Pharm.* 93, 269; 98, 307.

R. HAINES. *Chem. Soc. Qu. J.* 8, 289; *J. pr. Chem.* 68, 430; *Chem. Centralbl.* 1856, 593.

Thymian-campher. Ajwakaphul of the Hindoos. — First observed by Neumann (*Chymia medica*, 21, 282), Brown & Forcke (*N. Br. Arch.* 17, 178), investigated by Doveri and Lallemand. The stearoptene of monarda-oil examined by Arppe, was recognised by Gerhardt, (*Traité*, 3, 610) and by Stenhouse, as identical with thymol. The (partly differing) statements of Stenhouse relate to the camphor or stearoptene of Ptychotis-oil, which has not yet been completely proved to be identical with thymol, and has been twice investigated by Stenhouse, with varying results.

Source. In oil of thyme. — In the volatile oil of *Monarda punctata* (Arppe). In the volatile oil obtained from the seed of *Ptychotis Ajowan* (or *Ajwan*), an East Indian umbelliferous plant. (Stenhouse, Haines.)

Formation. By the oxidation of thymene or cymene. A mixture of thymene and cymene through which 1500 litres of dry air were passed for four months, became viscid and dark red, and yielded to caustic alkali a large quantity of thymol. (Lallemand.)

Preparation. *a.* Of *crude Oil of Thyme.* — Bruised thyme is distilled with water in a large still. — 1 lb. of the dry herb yields on the average 38 grains; I lb. of the fresh herb, 45·7 grains. (Zeller, *N. Jahrb. Pharm.* 2, 78.) — By repeatedly distilling the seeds of *Ptychotis Ajowan* with water, a volatile oil is obtained amounting to 5 or 6 p. c. of the seeds, having a light brown colour, an agreeable aromatic odour, and sp. gr. = 0·896 at 12°. (Stenhouse.)

b. Preparation of Thymol. — Oil of thyme is subjected to fractional distillation, whereupon it begins to boil at 150°, and if the boiling point be raised quickly to 175°, then slowly to 180°, thymene and cymene pass over together. While the temperature of the liquid rises quickly from 180° to 230°, a mixture of thymene and thymol passes over; then between 230° and 235°, thymol, which must be collected apart. (Doveri.) By this process, only an imperfect separation of the two constituents is effected, the distillate obtained below 225°, still containing a considerable quantity of thymol; this distillate is therefore shaken up with strong soda-ley to dissolve the thymol, and the liquid is separated from the undissolved thymene, which floats on the surface, and mixed with dilute hydrochloric acid, which precipitates the thymol. After this portion of thymol has solidified, and the distillate which passed over between 230° and 235° has been caused to solidify by the introduction of a few crystals of thymol, the whole of the crystals are repeatedly pressed between bibulous paper and recrystallised from alcohol. (Lallemand.) — Arppe presses between filtering paper the thymol which separates from monarda-oil on standing, and distils it either *per se* or with water. — Stenhouse leaves the oil of *Ptychotis Ajowan* to evaporate spontaneously, whereupon thymol gradually crystallises out at low temperatures; or subjects the oil to fractional distillation, collects separately the portion which distils between 218° and 222°, brings it to the solidifying point by agitation or by immersion in a frigorific mixture, and crystallises it from thymene or from alcohol. Haines decomposes the same oil by fractional distillation into cymene (p. 184), boiling at 175°, and thymol boiling at 230°, and promotes the solidification of the latter by introducing a crystal of thymol.

Properties. Thin, rhombic tables, probably belonging to the right prismatic system. (Arppe.) Angles 82° 30′ and 97° 30′, with cleavage parallel to the edges of the tables. (Arppe.) Miller, in Stenhouse's Memoir (*Ann. Pharm.* 93, 269), describes the ¼″ long crystals as belonging to the oblique prismatic system. In a later Memoir by Stenhouse (*Ann. Pharm.* 98, 310), two crystalline forms of thymol are described as determined by Miller. From the crude oil, thymol crystallises in the rhombohedral system. (Fig. 143.) Rhombohedrons, having the terminal edges replaced by *c*-faces. Moreover the middle edges of the rhombohedron $r' : r^3$, $r' : r^5$, &c., are truncated by a six-sided prism (*s* in *Fig.* 145). The faces *c* and *s* are very narrow, $s : s = 120°$; $r : c = 130° \ 39'$; $r : r = 81° \ 22'$; $r : a = 139° \ 19'$. From alcohol it crystallises in forms belonging to the oblique prismatic system. Thin rhombic tables (somewhat like Fig. 112), having their edges bevelled by the unequally inclined faces *n* and *h*, and their acute summits bevelled by the unequally inclined faces *t* and *f*; the four-edged summits of *h* and *n* are replaced by a pair of *m*-faces; — *f*, *i*, *m* are hexaïd-faces; *u* and *n* a posterior augite-pair; *t*, a posterior oblique terminal face; *h* and *h* the second pair; $m : i = 90°$; $t : f = 76° \ 37'$; $f : m = 90°$; $t : f = 137° \ 43'$; $t : i = 118° \ 54'$; $h : f = 130° \ 39'$; $h : m = 139° \ 21'$; $h : i = 81° \ 20'$; $u : i = 130° 42'$; $u : h = 130° \ 38'$; $t : h = 118° \ 49'$; $u : t = 137° \ 47'$; $h : h = 98° \ 42'$. In the crystals separated from the oil, the directions of cleavage are parallel to the rhombohedral faces *r*, and therefore intersect one another at angles of 81° 22′; the crystals separated from alcohol cleave parallel to *i* and *h*; but as the angles $i : h$ and $l : h$ are nearly equal to the former angles, Miller is of opinion that the two kinds of crystals may, in all essential points, be referred to the same form.

Thymol in the solid state is somewhat heavier than water; in the liquid state lighter. (Lallemand.) Sp. gr. 0·932 at 25·6° (Haines), of the solid thymol, 1·0285 (Stenhouse). It melts at 44° (Lallemand, Stenhouse), at 48° (Arppe), at 52·7° (Haines), forming a colourless oil, which may remain liquid for a long time at ordinary temperatures, but solidifies when a crystal of thymol is thrown into it (Lallemand) or when it is cooled or shaken (Stenhouse), the temperature then remaining stationary at 44°. After being melted, it solidifies at 38°; but if it be heated somewhat above its melting point, the solidifying point falls, so that after heating to 70°, 105°, 140°, and 170°, solidification takes place at 34°, 33°, 31⅓°, and 31°, the temperature of the thymol rising at the same time to 38°, 37°, 35½°, and 35°. (Arppe.) It solidifies after distillation *per se* (Arppe), or after the decomposition of its potash-solution by hydrochloric acid (Lallemand), immediately on cooling. It appears to volatilise at ordinary temperatures. (Miller.) Thymol boils at 220° (Arppe), at 222° (Stenhouse), at 230° (Doveri, Lallemand). It does not deflect the plane of polarised light. (Lallemand.) Smells like thyme (Arppe, Haines), has a strong peculiar odour (Stenhouse), faint, different from that of thyme-oil (Lallemand). Its taste is sharp and burning (Arppe), pungent and aromatic (Lallemand). Neutral to vegetable colours. (Lallemand, Stenhouse.) It has an acid reaction. (Doveri). Vapour-density at 275° = 5·53 (Doveri), 5·42 (Lallemand).

			Arppe. *mean.*	Doveri. *mean.*	Lallemand. *mean.*
20 C	120	80·00	78·88	78·7	79·94
14 H	14	9·33	9·42	10·0	9·46
2 O	16	10·67	11·70	11·3	10·60
$C^{20}H^{14}O^{2}$	150	100·00	100·00	100·0	100·00

	Stenhouse. *mean.*	Haines. *mean.*
C	79·73	79·59
H	9·24	9·55
O	11·03	10·86
	100·00	100·00

	Vol.	Density.
C-vapour	20	8·3200
H-gas	14	0·9702
O-gas	1	1·1093
Thymol-vapour	2	10·3995
	1	5·1997

Arppe examined thymol from oil of monarda. Doveri and Lallemand, that from oil of thymene; Stenhouse and Haines that from the oil of Ptychotis Ajowan. Stenhouse formerly examined crystals from Ptychotis-oil, which contained 69·17 p. c. C, and 9·51 H ($C^{44}H^{34}O^{10}$ = 69·84 C and 8·99 H, *Stenhouse*), and formed a peculiar compound with chlorine (p. 442); but he afterwards regarded these crystals as identical with thymol from *Ptychotis*.

Isomeric with cuminic alcohol, carvol, and carvacrol.

Decompositions. 1. Thymol is somewhat altered by repeated distillation, the liquid which passes over containing less carbon. (Stenhouse.) It decomposes when heated considerably above its boiling point, and consequently the determination of its vapour-density comes out too high. — 2. When mixed with *anhydrous phosphoric acid*, it becomes hot, assumes a wine-red colour, and forms a syrup which yields oil by distillation. On rectifying the distillate once or twice over anhydrous phosphoric acid, then with water, a light, colourless, mobile oil is obtained, which boils at 175°, contains 84·1 p. c. C and 10·15 H (whence Doveri deduces the formula $C^{20}H^{14}O$, requiring 84·5 C and 9·8 H), and, after being again repeatedly rectified over anhydrous phosphoric acid, finally yields a hydrocarbon which boils at 180°, contains 89·2 p. c. C and 10·0 H, and is therefore perhaps $C^{20}H^{13}$, this formula requiring 90·3 C and 9·7 H. (Doveri.) By the action of anhydrous phosphoric acid, thymol is converted into a green substance, which dissolves in alcohol, and is precipitated from the solution by water as a thick, dark green, acid liquid, but cannot be crystallised either alone or in combination with potash. (Stenhouse.) — 3. By *oil of vitriol*, at 50° — 60°, it is converted into sulphothymic acid; heated with excess of oil of vitriol to 240°, it yields *sulphodraconic acid.* (Lallemand.) — 4. *Chlorine* in diffused daylight acts with great violence on thymol, with rise of temperature, and elimination of hydrochloric acid gas, the thymol remaining liquid and assuming a wine-red colour at the beginning of the action. If too great heat be avoided, the product consists of terchlorothymol (which, when the quantity of chlorine absorbed amounts to $\frac{2}{3}$ the weight of the thymol, sometimes separates in needles); then, if the passage of the chlorine be continued in bright daylight, a very viscid oil is formed from which quintichlorthymol gradually crystallises. (Lallemand.) Thymol from ptychotis-oil absorbs chlorine quickly, becomes hot, and forms a peculiar chlorine-compound (p. 442), then, when more chlorine is passed through it, an uncrystallisable resin. (Stenhouse.) Oil of thyme, distilled with 8 pts. chloride of lime and 24 pts. water, yields chloroform. (Chautard, *Compt. rend.* 34, 485; *J. pr. Chem.* 56, 238.) — 5. *Bromine*, in sunshine, converts thymol into white, solid, earthy quintibromthymol, which melts at a stronger heat, decomposing at the same time and giving off hydrobromic acid, and may be crystallised from ether. (Lallemand.) On thymol from ptychotis-oil bromine acts quickly, forming an uncrystallisable substance. (Stenhouse.) — 6. Thymol is not altered by *hydrochloric acid.* (Stenhouse.) When hydrochloric acid gas is passed over thymol, it quickly assumes a brown and, after removal of the excess of hydrochloric acid, a purple-brown colour, but does not increase in weight by more than 2 to 3 p. c. even when heated; on distilling the product, unaltered thymol is first obtained, then a red substance. The latter turns blue when treated with alkalis in the cold, green when heated therewith, and recovers its red colour by exposure to the air. It dissolves with blue colour in baryta-water, and may be precipitated from this solution by carbonic acid, together with carbonate of baryta, then extracted from the precipitate by alcohol, and remains, after the evaporation of the alcohol, as an amorphous, dark violet, chlorinated mass, which may be distilled and forms red vapours when heated. (Arppe.) — 7. Thymol is violently attacked by *nitric acid*, giving off nitrous and carbonic acid gases, and forming a soft, brown-yellow, offensive-smelling resin (Doveri), and a large quantity of oxalic acid. (Lallemand.) Nitric acid slowly dissolves thymol, and forms a peculiar, colourless, crystallisable acid, which does not form chloropicrin when heated with chloride of lime. (Stenhouse.) Respecting the formation of binitrothymol, see page 419. — 8. Thymol is decomposed by boiling with strong *acids* or *alkalis*. (Stenhouse, *vide inf.*) — 9. Aqueous sulphothymic acid (the solution of thymol in oil of vitriol, according to Stenhouse), becomes heated by contact with *peroxide of manganese* or *bichromate of potash* and sulphuric acid, and yields a distillate of thymol and aqueous formic acid, whilst a brown acid remains, which is solid and friable at mean temperature, and dissolves in alcohol with dark-red colour. (Lallemand.) — 10. Thymol dissolves in *glacial acetic acid*, and on subsequent addition of oil of vitriol, forms sulphacetothymic acid. (Lallemand.)

Combinations. Thymol dissolves in about 333 pts. of *water*. (Lallemand.) It is not altered by aqueous *ammonia*, but takes up a large quantity of gaseous ammonia, and resolidifies after the ammonia has escaped. (Lallemand.) Oil of thyme digested with aqueous ammonia, first turns yellow, then red, then dark brown. (Lewis, *Alm.* 1780, 32.)

Thymol dissolves in aqueous alkalis and combines with them. (Lallemand.) Thymol from ptychotis-oil is liquefied by aqueous alkalis, but does not dissolve in them. (Stenhouse.) The compounds are decomposed by the carbonic acid of the air or by aqueous alkalis, with separation of thymol.

Thymol-soda. — When thymol in the state of vapour is passed over soda-lime heated to dull redness, no gas is evolved, but a crystallisable substance is formed, which has the composition $C^{20}H^{13}NaO^2$, melts when heated, and, when dissolved in water, precipitates the solutions of mercuric nitrate and nitrate of silver. The mercury-compound is greyish violet, is not decomposed at mean temperature by dilute sulphuric acid or nitric acid, but is decomposed by hydrochloric acid, with separation of thymol, and, after prolonged washing with acetic acid and alcohol, contains 56·8 p. c. mercury, and is therefore $C^{20}H^{13}HgO^2,HgO$ (calculation = 56·07 Hg). (Lallemand.) Alcoholic thymol does not precipitate alcoholic solution of *neutral acetate of lead*. It does not precipitate *nitrate of silver*, even after addition of ammonia. (Stenhouse.)

Thymol dissolves very readily in *alcohol*, *ether*, and *glacial acetic acid*. (Lallemand.) It is precipitated from the alcoholic sotution by water in drops, according to Stenhouse, not at all according to Lallemand.

Oil of Myrrh.

$C^{20}H^{14}O^2$

Ruickholdt. *N. Br. Arch.* 41, 10.

The volatile oil of myrrh, the gum-resin of *Balsamodendron Myrrha* and *B. Kalaf*. The alcoholic extract of myrrh yields by distillation a quantity of the oil amounting to 2·2 p. c. of the myrrh. Bley & Diesel (*N. Br. Arch.* 43, 304), by distilling myrrh with water, obtained 1·6 to 3·1 p. c. of volatile oil, the quantity being smallest from myrrh which had an acid reaction, and the watery distillate then containing formic acid; this acid is likewise produced, together with a soft resin, when oil of myrrh oxidates in contact with air and water. Pfaff (*Mater med.?*) mentions a volatile oil of myrrh heavier than water and not distillable therewith. Brandes (*Almanach*, 1819, 125) describes a mobile, colourless oil of myrrh, likewise heavier than water, and distillable with water but not with alcohol. The last-mentioned oil resinises when exposed to the air, and forms with nitric acid a turbid mixture, with oil of vitriol a dark red mixture, from which water throws down white flocks. It dissolves in alcohol, ether, and fixed oils, and is extracted from the ethereal solution by hydrochloric acid, imparting to that liquid a dark purple-red colour. — Braconnot (*J. Pharm.* 15, 288; *Repert.* 34, 398) obtained from (perhaps impure) myrrh, 3 p. c. of a pale yellow, volatile oil, which turned red when mixed with an equal quantity of cold nitric acid, dissolved in 2 — 3 pts. of alcohol or glacial acetic acid, readily in ether.

Properties. Light wine-yellow, viscid oil, having the taste and smell of myrrh, lighter than water and heavier than alcohol. It has an acid reaction and becomes viscid and darker-coloured by exposure to the air.

			Ruickholdt. *mean.*
20 C	120	80·00	79·34
14 H	14	9·33	10·16
2 O	16	10·67	10·50
$C^{20}H^{14}O^2$	150	100·00	100·00

Ruickholdt gives the formula $C^{22}H^{16\frac{1}{2}}O^2$; Heldt, (*Ann. Pharm.* 63, 59) gives $C^{44}H^{32}O^4$; but Ruickholdt's analyses when recalculated, one of them giving 9·88 p. c. H, agree better with the above formula (Kr.)

Oil of myrrh is soluble in *alcohol* and in *ether*.

Carvol. $C^{20}H^{14}O^{2}$.

VÖLKEL. (1840.) *Ann. Pharm.* 305, 308; *Ann. Pharm.* 85, 246; abstr. *J. pr. Chem.* 60, 120.
SCHWEIZER. *J. pr. Chem.* 24, 257.
VARRENTRAPP. *Liebig, Poggendorff & Wöhler, Handworterb. d. Chem.* 4, 686.

Source. In oil of caraway, together with carvene (p. 283). (Völkel.)

Preparation. The portion of oil of caraway which passes over between 225° and 230° is separated by repeated fractional distillation. (Völkel.) When hydrosulphate of carvol is digested with dilute alcoholic potash, and the filtrate is treated with water, carvol separates out, and may be dried and rectified with chloride of calcium; it then passes over at 250°. (Varrentrapp.)

Properties. Transparent, colourless, mobile. Sp. gr. 0·953 at 15°. (Völkel.) Boiling point above 250°. (Varrentrapp.) Smells like carvene. (Völkel.)

			Völkel.	Varrentrapp.
20 C	120	80·00	80·17	79·80
14 H	14	9·33	9·47	9·31
2 O	16	10·67	10·36	10·89
$C^{20}H^{14}O^{2}$	150	100·00	100·00	100·00

According to Völkel, it is $C^{30}H^{21}O^{3}$, and therefore = carvene ($C^{20}H^{24}$) *minus* 3 At. H and *plus* 3 At. O. Isomeric with cuminic alcohol, thymol and carvacrol.

Decompositions. 1. Carvol when *heated* appears to be transformed into carvacrol, and yields by distillation a strongly coloured, viscid oil. (Völkel.) — 2. By *nitric acid* and *oil of vitriol*, it is violently attacked and resinised. — 3. By distillation with *glacial phosphoric acid*, it is converted into carvacrol. — 4. It likewise yields carvacrol when distilled with *hydrate of potash*. (Schweizer.) — 5. With alcoholic *hydrosulphate of ammonia*, it forms hydrosulphate of carvacrol. (Varrentrapp.) — 6. When *hydrochloric acid* and air are passed successively through carvol, hydrochlorate of carvol is formed, which contains 18·79 p. c. HCl, and is therefore $C^{20}H^{14}O^{2}$, HCl (calculation 19·55 p. c. HCl). (Varrentrapp.)

Carvol absorbs *hydrocyanic acid* abundantly, and gives it off again completely when air is passed through it for some time. (Varrentrapp.)

Carvacrol. $C^{20}H^{14}O^{2}$.

SCHWEIZER. *J. pr. Chem.* 24, 271; further, 26, 118.
CLAUS. *J. pr. Chem.* 25, 266.

Camphokreosot. (Claus.)

Formation. Together with carvene, when oil of caraway is distilled with glacial phosphoric acid; together with resin, when the same oil is distilled with pulverised hydrate of potash; and with evolution of hydrogen, when it is distilled with potassium; also, mixed with carvene, when oil of caraway is repeatedly distilled with iodine, as long as hydriodic acid is evolved, and the distillate then decomposed by aqueous potash. (Schweizer.) — Produced also by distilling camphor with an equal weight of iodine, the other products of the reaction being camphin, colophene, and camphoresin (Claus); also by heating carvol with fused phosphoric acid or pulverised hydrate of potash. (Völkel, *J. pr. Chem.* 30, 376.) — By distilling oil of thuja with iodine, being then accompanied by thujone and colophene;—or, together with resin, by distilling the same oil with pulverised hydrate of potash. (Schweizer, *J. pr. Chem.* 30, 376.)

Preparation. 1. Oil of caraway is distilled over glacial phosphoric acid, till all the carvene has passed over and the difficultly volatile oil which remains is decanted from the hydrated phosphoric acid and distilled *per se.* — 2. Oil of caraway is distilled with pulverised hydrate of potash, carvene then passing over; the residue is dissolved in water, poured off from the resin which separates, and mixed with dilute sulphuric acid; and the thick mixture of resin and carvacrol which separates is distilled *per se.* (Schweizer.) — 3. Common camphor is distilled with an equal weight of iodine, whereupon camphin first passes over, and when the residue is more strongly heated, a distillate mixed with colophene is obtained. This distillate is dissolved in potash-ley and separated from the solution by an acid; and the resulting oil is distilled over lime. (Claus.)

Properties. Transparent, colourless or yellowish, viscid oil. Heavier than water (Schweizer), lighter than water. (Claus.) — Boiling point almost exactly 232°. (Schweizer.) — Has an odour like that of creosote (Völkel, Claus); peculiarly disagreeable; the vapour is pungent and excites coughing; the taste is persistent, strong and biting (Schweizer), like that of creosote, sweetish at first, afterwards scratching. (Claus.)

			Schweizer.	
			a.	*b.*
20 C	120	80·00	80·73	80·35
14 H	14	9·33	9·66	9·42
2 O	16	10·67	9·61	10·23
$C^{20}H^{14}O^2$	150	100·00	100·00	100·00

a, prepared with phosphoric acid; *b* with hydrate of potash. Its formula is $C^{40}H^{28}O^3$ (Schweizer); it is carvol ($C^{30}H^{21}O^3$) — HO = $C^{30}H^{20}O^2$ (Völkel); isomeric with thymol (Cahours, Gerhardt, *Traité*, 3, 615.) Claus's campho-creosote is identical with carvacrol. (Schweizer.)

Decompositions. 1. Carvacrol when *set on fire* burns with a bright, very smoky flame. — 2. With *nitric acid*, it forms, with evolution of nitrous acid, a yellow resin (which is more soluble in water than the resin obtained with carvene (p. 284); its alcoholic solution produces deep reddish yellow stains, and is not precipitated by neutral acetate of lead. — 3. Heated with *potassium*, it gives off hydrogen, becomes dark brown, more viscid, and finally hard, and, if water be then added, carvacrol separates, contaminated with a small quantity of a brown resin insoluble in aqueous potash.

Acids added to the solution, separate an additional quantity of carvacrol and a resin soluble in potash. These resins are produced by the action of the resulting hydrate of potash on the carvacrol. — 4. With *hydrate of potash,* it becomes warm and immediately assumes a dark brown colour, thickens when heated, and on addition of water, deposits a resin insoluble in potash-ley, while the solution, after addition of acids, yields a resin soluble in potash-ley. — Both these resins are identical with those which are produced by the action of hydrate of potash on oil of caraway. — 5. It absorbs *ammonia,* becoming more mobile and red-brown, but gives off all the ammonia when heated, leaving a quantity of red-brown resin.

Alcoholic carvacrol does not precipitate *neutral acetate* of lead. (Schweizor.) It coagulates white of egg. (Claus.) — Carvacrol is somewhat soluble in water, and dissolves with facility in aqueous *potash,* in *alcohol,* and in *ether.*

Appendix to Carvol.

Crude Oil of Caraway.

The volatile oil obtained by distilling with water the seeds of *Carum Carvi,* is a mixture of carvene (p. 283) and carvol. (Schweizer, Völkel.) — Dry seeds yield 4·37 p. c. (Trommsdorff), 4·17 (Martius, *Repert.* 39, 242), 3·12 (Rayhaud), 5·12 (Hopff, *Jahrb. pr. Pharm.* 12·99), 4 p. c.; Saxon seeds, 3 p. c. (van Hees, *Pharm. Centr.* 1847, 380.) To obtain the whole of the oil, the caraway-seeds must be distilled with water several times. (Martius.)

Crude oil of caraway varies from pale-yellow to colourless; it is mobile, of sp. gr. 0·94 (Lewis), 0·938 (Völkel), 0·913—0·926 (van Hees), 0·91 to 0·97. (Zeller.) It begins to boil at 175°, giving off chiefly carvene at first, then carvol, as the temperature rises to 232°, and leaves a slight viscid residue. (Völkel.) According to Bizio (*Brugn. Giorn.* 19, 360), it solidifies partially on cooling. Smells of caraway, and has a burning, sharply bitterish taste, less powerful than that of the first portion of the distillate. (Schweizer.) According to Völkel, it contains from 86·10 to 76·80 p. c. carbon and 11·09 to 9·22 p. c. hydrogen, according as it consists in greater part of carvene or of carvol. Similar results were obtained by Schweizer, *J. pr. Chem.* 24, 257; *Ann. Pharm.* 40, 329; *Rev, scient.* 8, 195.)

By exposure to *light* and *air,* it becomes darker: the same change takes place spontaneously by keeping, in consequence of the formation of a volatile substance (which may be separated by heating the altered oil with half its volume of aqueous potash, precipitating the oil with water, and distilling. (Völkel.) — Every time that the crude oil is distilled, there remains, according to Völkel, a thick coloured residue (probably from partial decomposition of the carvol), or, according to Schweizer, a reddish yellow, brittle resin, soluble in absolute alcohol and ether, and containing 75·15 p. c. C, 8·98 H, and 25·87 O. — It dissolves when heated, a mixture of *sulphur* and *phosphorus,* forming an offensive-smelling oil volatile after boiling with potash, and probably also spontaneously inflammable phosphoretted hydrogen. (Schweizer.) — It dissolves *iodine* with dark brown-red colour, rise of temperature and slight detonation (Flaschhoff, *Br. Arch.* 33, 225), becoming thick and resinous. (Winckler, *Repert.* 33, 185.) When the dark brown solution of iodine in oil of caraway is repeatedly distilled, it gives off hydriodic acid, assumes first a yellow, afterwards on cooling, a red colour, and, if then distilled, yields carvene and a residue of carvacrol. (Schweizer.) — Only old oil of caraway becomes hot and detonates with iodine. (Zeller, *Stud. über. äther. Oele,* Landau, 1850.) — With *fuming nitric acid,* oil of caraway yields a black greasy resin (Hasse, *Crell. Ann.* 1785, 1, 422), oxalic acid (Gren, *Crell. Ann.* 1786, 2, 151; Grotthuss, *N. Gehl.* 8, 709.) With *oil of vitriol,* caraway-oil forms a black mass, with rise of temperature and evolution of sulphurous acid. (Schweizer.) — With pulverised *hydrate of potash,* it immediately assumes a deep brown colour; the mixture when repeatedly distilled yields colourless carvene, and leaves a thick, strongly intumescent mass, consisting of carvacrol, a resin soluble in aqueous potash, and another insoluble therein. The resin which is left behind on treating the residue with aqueous potash, is dark brown, brittle, melts at 90°, dissolves in alcohol and ether, and, contains 80·90 p. c. C, 9·23 H, and 9·87 O; the resin which separates, together with the carvacrol, from the potash-solution on addition of oil of vitriol, is dark-brown, transparent, melts at 100°, is not precipitated from its alcoholic solution by neutral acetate of lead, and contains 77·88 p. c. C, 8·56 H, and 13·56 O. (Schweizer.) — Oil of caraway heated with *alcoholic potash,* leaves a soft, coloured resin, only partially soluble in aqueous potash. (Völkel, *Ann. Pharm.* 35, 308 and 85, 246.) — It is not altered by distillation over *lime* and *hydrate* of potash. (Schweizer.) — Distilled with *aqueous chromate of potash* and sulphuric acid, it yields acetic acid and a peculiar acid, the greater part of which is however decomposed by the chromic acid. (Persoz, *Compt. rend.* 13, 433; *J. pr. Chem.* 25, 59.) — Heated with finely divided *corrosive sublimate,* it turns brown and afterwards black, giving off a large quantity of acid vapours. (J. Davy, *Phil. Trans.* 1822, 360.)

Crude oil of caraway absorbs a large quantity of *sulphuretted hydrogen gas,* acquiring an offensive odour, and depositing after a few days a small quantity of sulphur. (Planche, *J. Pharm.* 8, 372.) It dissolves *sulphur* abundantly when heated, depositing it again on cooling; likewise *phosphorus;* it does not dissolve chloride of calcium. It is somewhat soluble in *water,* to which it imparts its odour and taste; it dissolves with facility in *alcohol* and *ether.* (Schweizer.)

Hydrosulphate of Carvol.

$$C^{20}H^{15}O^{2}S = C^{20}H^{14}O^{2},HS.$$

VARRENTRAPP. *Liebig, Poggendorff & Wöhler, Hand. d. Chem.* 4, 686.

Sulfhydrate de carvol. (Gerhardt.)

When the portion of oil of caraway (principally carvol), which distils above 190°, is covered with an equal volume of alcoholic hydrosulphate of ammonia, and left to stand for half an hour, it yields crystals of hydrosulphate of carvol, which, after the mother-liquor has been drained off, may be washed with alcohol and recrystallised from hot alcohol.

White silky needles, often more than an inch long and half a line broad, melting when heated, and for the most part volatile without decomposition.

			Varrentrapp.
20 C	120	71·86	71·9
15 H	15	8·98	9·0
2 O	16	9·58	9·4
S	16	9·58	9·7
$C^{20}H^{14}O^{2},HS$	167	100·00	100·0

Burns, when set on fire, with a bright, fuliginous flame, giving off sulphuric acid. — In alcoholic solution it is converted by *sulphuretted hydrogen* into hydrosulphate of sulphocarvol. — Treated in the fused state with *hydrochloric acid gas*, it gives off sulphuretted hydrogen and is converted into a brown oil. — Digested with dilute *alcoholic potash*, it gives off sulphur and is converted into carvol, which is precipitable by water. — Mixed with *peroxide of lead* and heated to 153°, it is for the most part resinised, and when raised to a higher temperature, suddenly takes fire.

It dissolves in *alcohol*, especially after prolonged boiling, and crystallises on cooling. (Varrentrapp.)

Appendix to Hydrosulphate of Carvol.

Hydrosulphate of Sulphocarvol.

$C^{20}H^{14}S^{2},HS$.

VARRENTRAPP. (1849.) *Liebig, Poggendorff & Wöhler, Handwört. d. Chem.* 4, 686.

Preparation. 1. Sulphuretted hydrogen is passed for a long time into hydrosulphate of carvol dissolved or suspended in alcohol; the viscid, slightly yellowish oil, which sinks to the bottom, is dissolved in 3–4 vol. ether; the solution is mixed with 18–24 vol. of strong alcohol, whereupon, after standing for some time, it deposits white flocks which cake together into resinous lumps; the whole is heated to the boiling point, and the resin which then becomes soft, is boiled once or twice more, with fresh alcohol, the liquid being all the while strongly agitated. — 2. Sulphuretted hydrogen is passed for 10 to 20 hours through the decanted mother-liquor of hydrosulphate of carvol, which still contains oil and hydrosulphate of ammonia (p. 417); the viscid oil which separates is dissolved in ether, and precipitated from the solution by alcohol; and the solution in ether and precipitation by alcohol are repeated two or three times.

Properties. White, brittle, easily friable resin, which melts to a colourless oil at 70°, and at 40° may be stirred and drawn out into satiny threads.

			Varrentrapp.
20 C	120	65·58	65·68
15 H	15	8·19	8·22
3 S	48	26·23	26·76
$C^{20}H^{14}S^2,HS$	183	100·00	100·66

Its ethereal solution forms with an ethereal solution of *mercuric chloride*, a white precipitate containing variable quantities of mercury (18·5 to 70·5 p. c.) and of chlorine (5·6 to 11·1 p. c.), according as one or the other solution has been added in excess; the precipitate gives off *hydrochloric acid* in drying, but without alteration of external appearance. — Dissolved in a large quantity of ether, it forms with *bichloride of platinum* precipitates of variable composition.

Sulphothymic Acid.

$$C^{20}H^{14}S^2O^8 = C^{20}H^{14}O^2,2SO^3.$$

A. Lallemand. (1853.) *Compt. rend.* 37, 498; *J. pr. Chem.* 60, 432; abstr. *Ann. Pharm.* 101, 120. — *N. Ann. Chim. Phys.* 49, 150; abstr. *Ann. Pharm.* 102, 119.

Thymolschwefelsäure, Sulfothyminsäure.

Formation and Preparation. Thymol dissolves abundantly in oil of vitriol at 50—60°, and solidifies on cooling to a crystalline mass, having only a faint red colour. By dissolving this mass in water, and saturating the solution with carbonate of baryta or carbonate of lead, sulphothymate of baryta or lead is obtained, from which the sulphothymic acid may be separated, and crystallised by evaporating its aqueous solution in vacuo. — Thymol from ptychotis-oil dissolves in moderately warm oil of vitriol, forming a red liquid which solidifies on cooling, and when treated with hot water, yields a colourless solution (only a few red oil-drops remaining undissolved), which crystallises on cooling. The crystals consist of a conjugated sulphuric acid, which forms crystallisable salts with baryta and oxide of lead; but the quantity obtained was too small for analysis. (Stenhouse.)

Properties. Translucent, pearly tables or prisms. Does not deliquesce on exposure to the air. Contains 2 At. water of crystallisation, and is therefore $C^{20}H^{14}S^2O^8 + 2Aq$.

Its aqueous solution, treated with *nitric acid*, forms binitrothymol; with sulphuric acid and *peroxide of manganese* or *bichromate of potash*, it forms thymoïl.

Very soluble in *water*.

With salifiable bases it forms the *sulphothymates* $C^{20}H^{13}MS^2O^8$, which crystallise in forms of the oblique prismatic system. They decompose at 120°, with violet-red colouring and volatilisation of thymol. The *ammonia-salt*, which separates from its aqueous solution in well-developed crystals, and the *potash* and *soda-salts*, leave, when thus treated, anhydrous bisulphates. [As however they contain only 13 At. H and 8 At. O, the quantity of HO is too small by 1 At. for this transformation: $C^{20}H^{13}MS^2O^8 = [(C^{20}H^{14}O^2 - HO) + MO,2SO^3$. (Kr.)] — The sulphothymates dissolve very easily in water and in absolute alcohol, somewhat less in ether.

Sulphacetothymic Acid.

$$C^{24}H^{16}S^2O^{10} = C^4H^3O^3,C^{20}H^{13}O,2SO^3.$$

LALLEMAND. (1857.) *N. Ann. Chim. Phys.* 49, 150; abstr. *Ann. Pharm.* 102, 120.

When thymol is dissolved in glacial acetic acid, and oil of vitriol containing a little anhydrous sulphuric acid is added to the mixture, combination takes place at a gentle heat, and the liquid, on cooling, deposits a crystalline mass, which must be dried on porous earthenware, and freed from excess of acetic acid by leaving it over quicklime in vacuo.

The acid is soluble in *water*. With bases, it forms crystallisable salts, which become anhydrous without decomposition at 110°, but are decomposed, with liberation of acetic acid, when their aqueous solutions are boiled or quickly evaporated. The salts are soluble in water and in alcohol.

Sulphacetothymate of Baryta, $C^{24}H^{15}S^2O^9,BaO$, is obtained by saturating the acid with carbonate of baryta.

Oxygen-nucleus $C^{20}H^{12}O^4$.

Quassiin.

$$C^{20}H^{12}O^6 = C^{20}H^{12}O^4,O^2 ?$$

WINCKLER. *Repert,* 54, 85; further, 65, 74.
WIGGERS. *Ann. Pharm.* 21, 40.

Discovered by Winckler in 1835, after Thomson (*System of Chemistry*, 4, 47), Pfaff, (*Syst. d. Mat. med.* 2, 11) and Buchner (*Repert*, 24, 257), had described the behaviour to re-agents of the quassia-bitter which they had obtained as an extract.—Keller, (*Repert*, 52, 197) by precipitating with basic acetate of lead, the aqueous solution of old quassia-extract, which had become crystalline by standing, evaporating the filtrate to an extract after removing the lead by sulphuretted hydrogen, exhausting the extract with alcohol, and evaporating the alcoholic solution to an extract — obtained crystals which he regarded as quassia-bitter, though Wiggers regarded them as nitre or common salt.

Quassia-bitter, *Quassite*, *Quassin.*—The bitter principle of the wood of *Quassia amara* and *Q. excelsa,* perhaps also of the bark of *Quassia Simaruba,* inasmuch as the alcoholic extract of this bark freed from malic and gallic acids by neutral acetate of lead, and from excess of lead by sulphuretted hydrogen, agrees in character with the quassia-bitter of the older authors (Morin, *J. Pharm,* 8, 57.)—By distilling quassia-wood with water, Bennerscheidt, (*Br. Arch.* 36, 255), obtained a white tabular mass, his *quassia-camphor*, having a peculiar odour of quassia.

Preparation. 1. Three ounces of pulverised quassia-wood are exhausted with 2 lb. of 80 p. c. alcohol; the tincture is evaporated in a water-bath; the residue dissolved in water; and the filtered solution evaporated to an extract. This extract is repeatedly treated with small quantities of absolute alcohol, as long as the alcohol acquires the bitter taste of quassia; the filtrate is evaporated nearly to dryness; and the residue is exhausted with hot water, whereupon a small quantity of dark-brown resin remains, while the light yellow solution, which must be decolorised by animal charcoal, yields crystals of quassia by gentle evaporation. (Winckler.) From aqueous extract of quassia prepared by himself, Winckler was not able by any process whatever to obtain quassiin, perhaps because the extract had already undergone some alteration. — 2. Eight pounds of quassia-wood are boiled with water; the decoction is evaporated to 6 lbs.; the cooled residue is mixed with slaked lime, whereby pectin is chiefly separated; then left to stand, with frequent agitation; filtered; and the filtrate is evaporated nearly to dryness and boiled with alcohol of 80 to 90 p. c., which leaves gum, common salt, and nitre undissolved, and dissolves quassiin, together with brown colouring matter and small quantities of common salt and nitre. The alcohol is distilled off; and the residue is evaporated to dryness, dissolved in the smallest possible quantity of absolute alcohol, and mixed with a small quantity of ether, which throws down brown colouring matter. The filtrate evaporated to dryness is redissolved in absolute alcohol, precipitated by ether, and this treatment is repeated till a nearly colourless residue is obtained by evaporation no longer containing crystals of quassiin. Lastly, the ether-alcoholic solution is poured upon a small quantity of water, and left to evaporate spontaneously, whereupon quassiin crystallises out. If the substances precipitated by ether are repeatedly treated with alcohol and ether as above, they yield a little more quassiin. (Wiggers.)

Properties. Crystallises by spontaneous evaporation from the ether-alcoholic solution mixed with water, or, on cooling from the hot aqueous or slightly alcoholic solution, in white opaque, shining prisms, which lose 1·3 p. c. in weight at 100° in a current of air, and 0·37 p. c. more when heated to fusion. (Wiggers.) Very delicate slender needles, having a silky lustre. (Winckler.) — Melts somewhat less easily than colophony and solidifies to a transparent, yellowish, somewhat brittle mass. From solutions in absolute alcohol or ether, it is obtained as a transparent varnish, which becomes white and opaque when water is poured upon it, but does not crystallise. — Permanent in the air, inodorous, neutral. Its taste is extremely bitter, like that of quassia-wood, but much more intense. (Wiggers.) According to Winckler, it has a slight alkaline reaction.

			Wiggers. *mean.*
20 C	120	66·67	65·75
12 H	12	6·67	6·89
6 O	48	26·66	27·36
$C^{20}H^{12}O^{6}$	180	100·00	100·00

So, according to Gerhardt (*Traité,* 4, 330); according to Wiggers it is $C^{20}H^{12\frac{1}{2}}O^{6}$.

Decompositions. Quassiin, *heated* in a tube above its melting point, becomes more fluid, acquires a brown colour, chars, and gives off vapours which have an empyreumatic, rather acid odour, a slightly bitter taste, and redden litmus. (Wiggers.) In the open fire, it burns like a resin, with a bright very smoky flame, and leaves a loose, easily combustible charcoal. (Wiggers.) — *Nitric acid* of sp. gr. 1·25 dissolves quassiin, apparently without alteration, and, with the aid of heat, converts it into oxalic acid, with evolution of nitrous gas. (Wiggers.) — *Oil of vitriol* dissolves quassiin at mean temperature, forming a colourless solution, from which water separates the quassiin, apparently unaltered; on heating the solution, carbonisation takes place. (Wiggers.)

Quassiin does not dissolve very readily in *water* (Winckler); it dissolves slowly in 222 pts. of water at 12°, more easily in water containing foreign substances. (Wiggers.)

It does not neutralise *acids*. The solution in hydrochloric acid leaves when evaporated quassiin free from hydrochloric acid. (Wiggers.) According to Winckler, quassiin neutralises acids but slightly.

The aqueous solution of quassiin is not precipitated by *iodine, chlorine, neutral* or *basic acetate of lead*, or *iron-salts*. (Wiggers.) According to Winckler, it is precipitated by *mercuric chloride;* but, according to Wiggers, it is not.

Tannin precipitates quassiin from its alcoholic solution in thick white flocks. (Winckler.)

Quassiin dissolves easily in *alcohol*, especially in hot absolute alcohol. The saturated solution in alcohol of 90 p. c. is rendered turbid by water, but becomes clear again on adding a large quantity of water. (Wiggers.)

It is but sparingly soluble in *ether*.

Oxygen-nucleus $C^{20}H^{10}O^{6}$.

Opianyl.

$$C^{20}H^{10}O^{8} = C^{20}H^{10}O^{6},O^{2}.$$

DUBLANC. (1832.) *Ann. Chim. Phys.* 49, 17.
COUERBE. (1832.) *Ann. Chim. Phys.* 49, 44.—50, 337.—59, 148.
REGNAULT. *Ann. Chim. Phys.* 68, 157.
ANDERSON. *R. Soc. Edinb. Transact.* 20, 347; *Ann. Pharm.* 86, 190; *R. Soc. Edinb. Transact.* 21, 204; *Ann. Pharm.* 98, 44.

Couerbe's Meconine.

First observed by Dublanc; prepared in the pure state by Couerbe.

Source. In opium. (Dublanc, Couerbe.)

Formation. 1. By the slow action of dilute nitric acid on opian (narcotine), together with teropiammone, cotarnine, opianic acid, and hemipinic acid; but it cannot be obtained with certainty. (Anderson.) — 2. By the action of strong caustic potash upon opianic acid, which is thereby resolved into opianyl and hemipinic acid. (Matthiessen & Foster, p. 429.)

Preparation. A. *From Opium.* 1. Finely-cut Smyrna opium is exhausted with cold water; the filtrate is evaporated to 8° B.; and the morphium and opian are precipitated by dilute ammonia. The filtrate evaporated to a syrup and then left for several weeks in a cool place, deposits brown crystals, which must be pressed and then dried at a gentle heat. The brown crystalline mass contains opianyl, meconates, and other substances. It is exhausted with boiling alcohol of 36°, and the extracts are concentrated to one-third by distilling off the alcohol: the liquid then on cooling deposits crystals, which are purified by recrystallisation from boiling water, with addition of animal charcoal, then from hot ether. The mother-liquor from which the crystals have separated, yields an additional quantity of opianyl by concentration. (Couerbe.)

2. Aqueous extract of opium dissolved in water, is precipitated at the

boiling heat with ammonia and then left to cool, whereupon morphine separates, together with small quantities of opianyl and crystals of opian. The filtrate is evaporated down; the meconic acid precipitated with baryta-water; the excess of baryta removed from the filtrate by carbonate of ammonia; the clear solution evaporated to a syrup; the mother-liquor decanted after some days from the crystals of narceine which separate, then concentrated to a certain extent and treated with absolute ether, which takes up opianyl together with smaller quantities of opian and oil. The ether is evaporated; the opianyl separated from the residue by water; the hot aqueous solution decolorised by animal charcoal; the filtrate brought to the crystallising point; and the opianyl which separates, is purified by repeated crystallisation from water. (Pelletier, *Ann. Chim. Phys.* 50, 252.) — The opianyl precipitated by ammonia may also be extracted by absolute ether and purified like the rest.

3. The aqueous extract of opium is precipitated by chloride of calcium; the precipitated meconate of lime is filtered; the filtrate evaporated to the crystallising point, and separated from the deposited hydrochlorate of morphine; and the dark mother-liquor is diluted with water, filtered from the flocks which separate, and treated with ammonia, which precipitates opian, thebaine, and a large quantity of resin. The filtrate is mixed with acetate of lead; the excess of lead is removed from the filtered liquid by dilute sulphuric acid; and the filtrate is neutralised with ammonia and evaporated to the crystallising point at a moderate heat, whereupon narceine separates out, and then sal-ammoniac by further concentration. The mother-liquor is repeatedly digested with $\frac{1}{5}$ vol. ether at 26°, and the ether is distilled off from the extracts, a brown syrup then remaining. On treating this syrup with dilute hydrochloric acid, papaverine dissolves, and opianyl remains, in the form of a dark grey, crystalline powder, which, to free it from resin and purify it completely, must be several times crystallised from boiling water, with addition of animal charcoal. (Anderson.)

B. *From Opian.* Opian is heated in the water-bath to 49° with 2·8 pts. of nitric acid of sp. gr. 1·4, and 8 pts. water, whereupon it melts into a yellowish mass, dissolves slowly without evolution of gas, if constantly stirred, and then gradually deposits crystalline terapiammone. The liquid is filtered through asbestos; the filtrate saturated with potash-ley; the solution again filtered from the precipitated cotarnine, and concentrated to a small bulk; crystallised nitre is removed, and the mother-liquor freed from carbonate of potash by precipitation with alcohol; the alcohol distilled off; and the cooled residue treated with hydrochloric acid, which precipitates opianic acid, hemipinic acid, and opianyl. If this precipitate be dissolved in a large quantity of boiling water, opianyl crystallises out on cooling (mixed with a little opianic acid, if the quantity of water added was insufficient), and may be purified by recrystallisation from water or alcohol. (Anderson.)

Properties. Slender, colourless, six-sided prisms, acuminated with two faces. (Couerbe.) White shining needles. (Anderson.) Melts at 90°, and solidifies again in an unctuous mass at 75°. It does not lose weight by prolonged fusion. Distils without alteration at 155° (Couerbe), not even at 270°. (Regnault, *Ann. Chim. Phys.* 68, 158.) Melts under water at 77°, *per se* at 110°, and solidifies at 104·5°. When cautiously raised to a high temperature, it volatilises, and sublimes in beautiful crystals. (Anderson.) Inodorous. Tasteless at first, but with sharp aftertaste. (Couerbe.) Its taste is bitter. (Anderson.)

			Couerbe.	Regnault.	Anderson.	
			mean.	*mean.*	*mean.*	
					a.	*b.*
6 C	120	61·85	61·01	61·39	61·45	61·64
10 H	10	5·15	5·13	5·34	5·12	5·26
8 O	64	33·00	33·86	33·27	33·43	33·10
$C^{20}H^{10}O^8$	194	100·00	100·00	100·00	100·00	100·00

Couerbe, Regnault and Anderson (*a*) analysed opianyl obtained from opium; Anderson (*b*) that from opian. Couerbe first gave for opianyl the formula $C^9H^9O^4$, then $C^{10}H^5O^4$, then $C^{20}H^{10}O^8$, which last is confirmed by the experiments of Regnault and of Anderson.

Decompositions. 1. Opianyl dissolves without colour in *dilute sulphuric acid,* becomes dark green when heated with it, rose-red on addition of alcohol, and green again after dilution of the alcohol. Water added to the green solution throws down brown flocks, which dissolve in sulphuric acid with green, in alcohol and ether with red colour: the alcoholic solution of these flocks is precipitated by the salts of oxide of lead, binoxide of tin, and alumina. (Couerbe.) — With *strong sulphuric acid,* it forms a colourless solution, which becomes purple when heated, brown on addition of water, depositing at the same time a brown precipitate which dissolves with red colour in alkalis. (Anderson.) — 2. With *chlorine,* it forms *chloropianyl.* (Anderson.) Chlorine acts but slightly on opianyl at ordinary temperatures, but is rapidly absorbed by melting opianyl, forming a red and then a dark brown mass, which melts at a higher temperature than opianyl, and solidifies in the crystalline form on cooling. It contains mechloic acid, meconin-resin, and 25·54 p. c. chlorine. (Couerbe.) — 3. Opianyl is not altered by *iodine,* but when treated with *chloride of iodine,* it forms iodopianyl; with *bromine-water,* it forms bromopianyl. (Anderson.) — 4. *Nitric acid,* either dilute or concentrated, converts opianyl into meconin-hyponitric acid (Couerbe); into nitropianyl, with evolution of red vapours (Anderson). — 5. With *peroxide of lead* and dilute sulphuric acid, it gives off carbonic acid, and forms an amorphous substance, which remains dissolved. (Anderson.)

Combinations. With Water. — A. *Hydrate of Opianyl,* $C^{20}H^{10}O^8 + Aq.$, was once accidentally obtained in the decomposition of opianyl by nitric acid. Resembles anhydrous opianyl, but is lighter and melts at 96·1°. (Anderson.)

		At 100°	Anderson.
20 C	120	59·11	58·84
11 H	11	5·41	5·29
9 O	72	35·48	35·87
$C^{20}H^{10}O^8 + Aq$	203	100·00	100·00

B. *Aqueous Opianyl.* — Opianyl dissolves in 265·7 pts. of cold water (Couerbe); in 700 pts. at 15·5 (Anderson). It dissolves in 18·56 pts. (Couerbe); in 22 pts. (Anderson) of boiling water.

Opianyl dissolves without alteration in *hydrochloric acid;* it is insoluble in *ammonia,* but dissolves in *potash* and in *soda-ley,* and is precipitated therefrom by carbonate of ammonia or by acids (Couerbe). It appears not to dissolve more readily in alkalis than in water; does not unite with metallic oxides, and is not precipitated by *basic acetate of lead.* (Anderson.) It is not precipitated by solution of neutral acetate of lead, but the basic acid precipitates it, forming with it a crystalline compound of very variable composition, containing 8 to 39 p. c. oxide of lead. (Couerbe.)

Opianyl dissolves in *alcohol, ether, acetic acid* (Couerbe, Anderson), and *volatile oils.* (Couerbe.)

Other combinations. With stearic acid.

Appendix to Opianyl.

Mechloic Acid.

Couerbe. *Ann. Chim. Phys.* 50, 343; further, 59, 148.

Mechlorsaure, Acide méchloïque.

Formation and Preparation. When chlorine is passed into melting opianyl, the mass becomes red, then dark brown, and solidifies in the crystalline form on cooling. The mass which is nearly insoluble in water, and sparingly soluble in ether, is treated with boiling alcohol of sp. gr. 0·833, whereby a solution is formed which yields crystalline granules by spontaneous evaporation. The yellow acid mother-liquor contains the greater part of the absorbed chlorine. The crystalline granules are colourless, melt at 125°, volatilise at 190° — 192° with an odour of jasmin, decomposing partially at the same time, and yielding drops of a yellow oil which solidifies on cooling and contains 5·43 p. c. chlorine. This is dissolved in potash-ley and the boiling solution is saturated with nitric acid, whereupon the mechloic acid crystallises in prisms on cooling. The chlorinated crystalline granules may likewise be dissolved in weak alcohol, and the solution treated with oxide of silver, the acid crystallising as the filtrate evaporates, in pearly scales which are converted by crystallisation into four-sided prisms.

Long four-sided needles, which melt at 160°, and have an acid reaction.

Calculation according to Couerbe.			Couerbe.
14 C	84	49·12	48·63
7 H	7	4·09	4·06
10 O	80	46·79	47·31
$C^{14}H^7O^{10}$	171	100·00	100·00

Volatilises at 165, leaving a small quantity of charcoal. It is not decomposed by *oil of vitriol* or *hydrochloric acid*, but *nitric acid* decomposes it, apparently without formation of oxalic acid.

It dissolves sparingly in cold, more freely in boiling *water*. Precipitates *lead-salts* but not those of *lime*, *iron*, *copper*, *mercury*, or *silver*.

Dissolves in boiling *alcohol* and in *ether*.

Meconin-resin.

Couerbe. *Ann. Chim. Phys.* 53, 352; further, 59, 150.

When the chlorinated mother-liquor from which mechloic acid has separated (*vid. sup.*) is mixed with water, a brown chlorinated resin is deposited, from which the chlorine may be extracted by boiling with aqueous carbonate of soda.

			Couerbe. *mean.*
10 C	60	46·51	46·65
5 H	5	3·87	3·79
8 O	64	49·62	49·56
$C^{10}H^5O^8$	129	100·00	100·00

According to Anderson, (*Ann. Pharm.* 98, 68), it is perhaps bichloropianyl.

Insoluble in *water*, soluble in *ether*.

Opiansulphurous Acid.

? $C^{20}H^{10}S^{2}O^{12} = C^{20}H^{10}O^{8},2SO^{2}$.

WÖHLER. *Ann. Pharm.* 50, 10.

Formation and Preparation. Hot aqueous opianic acid absorbs a large quantity of sulphurous acid gas, and, when the solution cools, no opianic acid crystallises out, provided the quantity present is not too great, and a sufficient degree of heat has been applied. The solution evaporated at a gentle heat leaves opiansulphurous acid, generally somewhat moist from adhering sulphuric acid. The sulphuric acid is not present in the recently prepared liquid, and is merely an accidental product. (Wöhler.) Perhaps it is produced by the reduction of the opianic acid to opianyl, which then unites with the sulphurous acid: $C^{20}H^{10}O^{10} + 4SO^{2} + 2HO = C^{20}H^{10}O^{8},2SO^{2} + 2(SO^{3},HO)$. (Gerhardt, *Traité* 4, 86.)

Properties. Inodorous, finely-crystalline mass. Has a peculiar bitter taste, with sweetish aftertaste.

Opiansulphurous acid, is, according to Wöhler $C^{20}H^{7}O^{8},2SO^{2}$; according to Gerhardt, either $C^{20}H^{8}O^{8},2SO^{2}$ or $C^{20}H^{10}O^{8},2SO^{2}$, in the latter case, comparable with the acid (and its analogues) whose ammonia-salt may be supposed to be formed by the combination of bitter almond oil with bisulphite of ammonia (xii, 27.) The latter formula (perhaps in itself the most probable) does not however explain the resolution of opiansulphurous acid into opianic acid and sulphurous acid, and is reconcilable with Wöhler's determination of the water in the lead-salt, only on the supposition that the salt was decomposed at the temperature employed to drive off the water. (Kr.)

Decompositions. When *water* is poured upon opiansulphurous acid, it becomes milk-white, and dissolves partly undecomposed, whilst another portion is resolved into opianic acid which separates, and sulphurous acid which dissolves.—It reduces *selenious acid,* after addition of hydrochloric acid. — With *terchloride of gold,* it forms metallic gold and opianic acid.

Combinations. The carbonates of barium and lead dissolve in a solution of opianic acid in sulphurous acid, forming crystallisable salts which are not decomposed by nitric acid, and only partially by chlorine.

Opiansulphite of Baryta. — Colourless, shining, rhombohedral tables, which become milk-white at 140°, giving off their water of crystallisation and then decomposing. It is sparingly soluble in water. According to Wöhler, it is $C^{20}H^{6}BaO^{8},2SO^{2}+3Aq$, according to Gerhardt, $C^{20}H^{9}BaO^{8}, 2SO^{2}+3Aq$.

Opiansulphite of Lead. — Colourless, strongly shining, four-sided prisms, with two very broad lateral faces, and acuminated with two faces, whereby six-sided tables are produced. Permanent in the air.

At 100° it becomes milk-white, then yellow by exposure to light. It gives off 6·5 p. c. water at 130°, and the rest at 170°, in all 13·68 p. c. ($C^{20}H^{7}PbO^{8},2SO^{2} + 6Aq. = 13{\cdot}07$ p. c. Aq.), assuming a yellow colour and emitting an odour of sulphurous acid.

Calculation according to Gerhardt.				Wöhler.
a.		*b.*		
20 C	29·05	20 C	30·23	29·23
13 H	3·15	13 H	3·27	3·00
17 O	32·93	15 O	30·23	33·00
2 S	7·75	2 S	8·06	8·10
PbO	27·12	PbO	28·21	26·67
$C^{20}H^7PbO^8,2SO^2 + 6Aq$	100·00	$C^{20}H^9PbO^8,2SO^2 + 4Aq$	100·00	100·00

According to Wöhler, it is $C^{20}H^6PbO^8,2SO^2 + 6Aq$. (p. 426). The 4 At. water of formula *b* correspond to 9·07 p. c.

Opianic Acid.

$$C^{20}H^{10}O^{10} = C^{20}H^{10}O^6,O^4.$$

LIEBIG & WÖHLER. (1842.) *Ann. Pharm.* 44, 126.
WÖHLER. *Ann. Pharm.* 50, 1.
J. BLYTH. *Ann. Pharm.* 50, 36.
LAURENT. *Compt. rend.* 20, 1118; *N. Ann. Chim. Phys.* 19, 372; *J. pr. Chem.* 40, 408; *Ann. Pharm.* 62, 105; *Compt. rend.* 21, 1118; further, 24, 219; *N. Ann. Chim. Phys.* 19, 370; *Pharm. Centr.* 1847, 381.
ANDERSON. *R. Soc. Edinb. Trans.* 20, 347; *Ann. Pharm.* 86, 179; *J. pr. Chem.* 57, 358. — *R. Soc. Edinb. Transact.* 21, 204; abstr. *Ann. Pharm.* 98, 44; *N. Ann. Chim. Phys.* 46, 105; *Chem. Centr.* 1856, 450.

Formation. 1. In the oxidation of opian (narcotine) by peroxide of manganese and sulphuric acid (Liebig & Wöhler), by peroxide of lead and sulphuric acid. (Marchand.) — 2. By boiling hydrochlorate of opian with excess of bichloride of platinum and water. (Blyth.) — 3. By the action of dilute boiling nitric acid upon opian. (Anderson.) — 4. By boiling teropiammone with potash-ley. (Anderson.)

Preparation. 1. Opian is dissolved in excess of dilute sulphuric acid; finely pulverised peroxide of manganese is added; and the liquid is heated to the boiling point, whereupon it turns yellow and gives off carbonic acid; the boiling is continued, with frequent addition of peroxide of manganese and sulphuric acid, so as to keep both in excess, as long as carbonic acid continues to escape; and the liquid is filtered at the boiling heat,—the straw-yellow filtrate then depositing yellow crystals of opianic acid as it cools. — These crystals are triturated and thrown upon a filter, then pressed, washed several times with cold water, again strongly pressed, heated to boiling with hypochlorite of soda till they become quite colourless, and gradually mixed with excess of hydrochloric acid: the liquid then on cooling deposits crystals of opianic acid, which are washed with water, strongly pressed, and purified by recrystallisation from boiling water. The mother-liquor yields a little more acid by evaporation. — 2. Opian dissolved in dilute hydrochloric acid is boiled with excess of bichloride of platinum and water for half an hour, whereupon the liquid first assumes an orange then a dark red colour, and the platinum-salt, which has also become dark-coloured, melts. The liquid is filtered hot, and the impure opianic acid, which crystallises from the filtrate on cooling, is purified by recrystallisation. (Blyth.) The mother-liquor yields more opianic acid by evaporation. — The mother-liquor of the preparation of opianyl (p. 423, B) likewise yields a little opianic acid by evaporation. (Anderson.)

Properties. Colourless, thin narrow prisms, grouped in radiating masses. The presence of an extremely small quantity of xanthopenic acid colours them uranium-yellow. The acid has a slightly bitter taste and a weak acid reaction. At 140° it melts, without giving off water. It is not volatile, but creeps up the sides of hot glass vessels, so that it appears to distil over. (Wöhler.) Fused opianic acid remains soft, transparent, and of the consistence of turpentine for several hours after cooling, then begins to exhibit a milky whiteness from the surface inwards, and slowly hardens in the course of a few days, without however exhibiting any crystalline structure under the microscope. If water or alcohol be poured upon this amorphous opianic acid, while still transparent, it becomes milk-white, and if boiled with the liquid, is converted into a white earthy mass, a small quantity of which dissolves, and separates on cooling in white, apparently amorphous flocks. The latter, when examined by the microscope, present the appearance of a mixture of long threads and small four-sided crystals. Fused opianic acid is not dissolved by aqueous ammonia and only after prolonged boiling by aqueous potash.

			Wöhler.		Blyth.
			a.	*b.*	
20 C	120	57·14	57·04	57·23	57·02
10 H	10	4·76	4·89	4·64	4·86
10 O	80	38·10	38·07	38·13	38·12
$C^{20}H^{10}O^{10}$	210	100·00	100·00	100·00	100·00

	Laurent.	Anderson.	
		c.	*d.*
C	57·10	57·05	56·96
H	4·88	5·00	4·98
O	38·02	37·95	38·06
	100·00	100·00	100·00

Wöhler analysed (*a*) opianic acid dried at 120°; (*b*) fused opianic acid; Anderson (*d*) opianic acid obtained by decomposition of teropiammone.

Wöhler originally gave the formula $C^{20}H^{9}O^{10}$; but from his analyses, Gerhardt (*Compt. chim.* 1, 61) calculated the formula above given, which was adopted by Berzelius (*Jahresb.* 24, 419), and has been confirmed by the analyses of Laurent and Anderson.

Decompositions. 1. Opianic acid when heated in the air, fumes, volatilises with an odour of vanille, and burns with a bright, smoky flame. — 2. In its boiling aqueous solution it is not apparently altered by *sulphuretted hydrogen*, but when the temperature falls to 70°, it is converted into sulphopianic acid, without the formation of any other product. — 3. With *sulphurous acid*, it forms opiansulphurous acid. — 4. *Oil of vitriol* converts it into a colouring matter, which produces all the madder-colours with iron and alum mordants, and is perhaps alizarin. (Anderson.) — 5. When melted in dry *chlorine gas*, it forms a reddish yellow resin. (Wöhler.) — 6. Boiled with *peroxide of lead* and dilute sulphuric acid, it is converted into hemipinic acid. (Wöhler.)

$$C^{20}H^{10}O^{10} + 2O = C^{20}H^{10}O^{12}.$$

7. It is partially converted into hemipinic acid by boiling with aqueous

bichloride of platinum. (Blyth.) — ¶ 8. Evaporated nearly to dryness with an excess of strong *potash*, it is converted into opianyl and hemipinic acid. (Matthiessen & Foster. *Proc. Roy. Soc.* 11, 57.)

$$2\,C^{20}H^{10}O^{10} = C^{20}H^{10}O^{8} + C^{20}H^{10}O^{12}.$$

9. Distilled with concentrated *hydriodic acid*, it yields iodide of methyl and a non-volatile substance, which is easily decomposed by heat, and oxidises readily in the air, especially in contact with alkalis. (Matthiessen & Foster.)¶

Combinations. Opianic acid is slightly soluble in cold *water*, much more soluble in hot water, so that the solution solidifies completely on cooling. (Wöhler.) — With bases, it forms the *Opianates*, all of which are soluble in water. — Hot aqueous opianic acid decomposes the carbonates of barium, lead, and silver, with effervescence.

Opianate of Ammonia. — Opianic acid absorbs ammonia gas, with rise of temperature, and deliquesces instantly in aqueous ammonia. — The saturated solution of opianic acid in ammonia, mixed with alcohol, and left to evaporate, yields large tables. If the solution be evaporated even at a very gentle heat, a transparent amorphous mass is obtained, which when covered with water, becomes milk-white and dissolves but partially, leaving opiammone in the form of a white powder. (Wöhler.)

Opianate of Baryta. Prisms united in radiating groups, which effloresce when heated, giving off 6 p. c. water (2 At. = 6·09 p. c. Aq.), and dissolve very readily in water. (Wöhler.)

Opianate of Lead. Obtained either in very brilliant transparent crystals apparently of the form of sphene, or in anhydrous, slender prisms united in tufts. The former crystals contain 5·4 p. c. water (2 At. = 5·44 p. c. Aq.), part of which they give off at 130°, and the rest at 150°, melting at the same time. Begins to decompose at 180°. — Dissolves with some difficulty in water, more readily in alcohol. (Wöhler.)

Crystals.			Wöhler. *at* 100°.
20 C	120·0	36·27	36·23
11 H	11·0	3·32	3·34
11 O	88·0	26·61	26·81
PbO	111·8	33·80	33·62
$C^{20}H^{9}PbO^{10} + 2\,HO$	330·8	100·00	100·00

Opianate of Silver. — Short, translucent prisms, with a tinge of yellow, which however appears to be produced in the first instance by the action of light, the colour being afterwards unaffected by light. Gives off its water of crystallisation towards 100°, and at 200° becomes opaque and melts into a liquid of fine dark green colour and metallic lustre, afterwards acquiring a red metallic colour and ultimately leaving metallic silver. (Wöhler.)

Dred at 100°.			Wöhler.
20 C	120	37·86	37·85
9 H	9	2·84	3·10
9 O	72	22·71	22·36
AgO	116	36·59	36·69
$C^{20}H^{9}AgO^{10}$	317	100·00	100·00

Opianic acid dissolves in *alcohol* and *ether*.

Hemipinic Acid.

$C^{20}H^{10}O^{12} = C^{20}H^{10}O^6,O^6$.

Wöhler. (1844.) *Ann. Pharm.* 50, 17.
J. Blyth. *Ann. Pharm.* 50, 36, and 43.
Anderson. *Ann. Pharm.* 86, 194.

Formation. 1. In the oxidation of opian (narcotine) by nitric acid (Anderson); by peroxide of lead and sulphuric acid, or peroxide of manganese and hydrochloric acid. (Wöhler.) — 2. By boiling chloroplatinate of opian with aqueous bichloride of platinum. (Blyth.) — 3. In the oxidation of opianic acid by peroxide of lead and sulphuric acid (Wöhler); by bichloride of platinum. (Blyth.) — 4. By the action of potash on opianic acid. (Matthiessen & Foster, p. 429.)

Preparation. 1. Opianic acid is heated to the boiling point with water and peroxide of lead; dilute sulphuric acid added by drops till carbonic acid begins to escape; the liquid left to cool partially; a quantity of sulphuric acid dropt in sufficient to precipitate the whole of the dissolved lead; and the filtrate evaporated to the crystallising point. (Wöhler.) Unaltered opianic acid often crystallises out first, and the liquid filtered therefrom yields crystals of hemipinic acid, which are easily purified by recrystallisation from the boiling saturated solution. (Wöhler.) — 2. The mother-liquor obtained in the precipitation of opianic acid as described at p. 427, 2, is slowly evaporated, after the whole of the opianic acid has separated from it. The liquid then assumes a deep yellow colour, gives off a large quantity of hydrochloric acid gas, and yields by spontaneous evaporation, large, flat rhombohedrons of hemipinic acid, which, by quick recrystallisation from water, are converted into rhombic prisms. (Blyth.) — 3. The solution obtained as described at p. 423, B, from which opianic acid has separated, is precipitated with acetate of lead, and the precipitate is washed and decomposed by sulphuretted hydrogen. (Anderson.)

Properties. Colourless, oblique rhombic prisms (Wöhler), or large flat rhombohedrons. (Blyth.) Has a slightly sour, somewhat astringent taste, and a strong acid reaction. (Wöhler, Blyth.) Effloresces in the air. (Blyth.) Gives off 13·73 p. c. water (4 At. = 13·74 p. c. Aq.) below 100°; melts at 180° and solidifies in a highly crystalline state on cooling. May be sublimed between two dishes, in shining laminæ, like benzoic acid. (Wöhler.)

Effloresced.			Wöhler.	Blyth.	Anderson.
20 C	120	53·14	52·94	51·93	53·17
10 H	10	4·42	4·65	4·85	4·64
12 O	96	42·44	42·41	42·49	42.19
$C^{20}H^{10}O^{12}$	226	100·00	100·00	99·27	100·00

Wöhler formerly regarded hemipinic acid as $C^{10}H^5O^6$; it was first recognised as a bibasic acid by Laurent (*Compt. rend.* 20, 1118.)

Decompositions. Hemipinic acid burns with a luminous flame. (Wöhler.) — Heated with *peroxide* of lead and dilute sulphuric acid, it appears to be completely resolved into carbonic acid and water. (Wöhler.) — Distilled with excess of concentrated *hydriodic acid,* it is completely resolved into carbonic acid, iodide of methyl, and an acid having the composition $C^{14}H^6O^8$. (Matthiessen & Foster, *vid inf.*)

$$C^{20}H^{10}O^{12} + 2\,HI = C^{14}H^6O^8 + 2C^2H^3I + 2CO^2.$$

Combinations. Hemipinic acid dissolves with difficulty in cold water (Wöhler); more readily than opianic acid. (Blyth.)

Hemipinic acid is *bibasic.* (Laurent.) It forms *bibasic* (*neutral*) *salts* $C^{20}H^8M^2O^{12}$ and *mono-basic* (*acid*) salts $C^{20}H^9MO^{12}$. (Anderson.) The lead, silver, and ferric salts are insoluble. The last has a fine orange-yellow colour. (Blyth.)

Hemipinate of Ammonia. — Crystals permanent in the air. (Wöhler.)

Hemipinate of Potash. — *a. Bibasic.* — Easily soluble; crystallises with difficulty. (Anderson.) — *b. Monobasic.* — Obtained by half saturating aqueous hemipinic acid with potash, and evaporating. — Forms thick, six-sided tables. Has a strong acid reaction. Contains 14·3 p. c. water of crystallisation (5 At. = 14·55 p. c. Aq.), which it gives off at 100°. Easily soluble in water and alcohol. (Anderson.)

			Anderson.
20 C	120·0	45·42	45·04
9 H	9·0	3·40	3·46
11 O	88·0	33·32	33·62
KO	47·2	17·86	17·88
$C^{20}H^9KO^{12}$	264·2	100·00	100·00

Hemipinate of Lead. — White precipitate insoluble in water. It dissolves in aqueous acetate of lead and afterwards separates in transparent crystalline nodules. (Wöhler.)

Hemipinate of Silver. — *Bibasic.* — White precipitate insoluble in water.

			Wöhler.	Blyth.
20 C	120	27·28	27·19	27·98
8 H	8	1·81	1·83	2·00
10 O	80	18·18	18·10	17·27
2 AgO	232	52·73	52·88	52·75
$C^{20}H^8Ag^2O^{12}$	440	100·00	100·00	100·00

Contains 53·05 p. c. AgO. (Anderson.)

Hemipinic acid dissolves more readily in *alcohol* than in *water.* (Wöhler.) It is easily soluble in *ether.* (Blyth.)

¶ *Appendix to Hemipinic Acid.*

Acid produced by the decomposition of Hemipinic Acid.

$C^{14}H^6O^8$.

A. Matthiessen & G. C. Foster. *Proceedings of the Royal Society,* 11, 58.

Obtained by distilling hemipinic acid with concentrated aqueous hydriodic acid (*vid sup.*) and evaporating the residue on the water-bath: purified by crystallisation from water. It forms colourless, needle-shaped crystals. Its aqueous solution has a strong acid reaction to test-paper. At 100°, the crystals lose 14·80 p. c. water (3 HO = 14·92 p. c.), and slowly sublime.

Dried at 100°.			Matthiessen & Foster. *mean.*
14 C	84	54·54	54·39
6 H	6	3·90	3·91
8 O	64	41·56	41·70
$C^{14}H^{6}O^{8}$	154	100·00	100·00

The composition of this acid assigns it a place in the following series.

$C^{14}H^{6}O^{2}$	Oil of bitter almonds.
$C^{14}H^{6}O^{4}$	Benzoic acid.
$C^{14}H^{6}O^{6}$	Salicylic acid.
$C^{14}H^{6}O^{8}$	Acid from hemipinic acid (M. & F.)
$C^{14}H^{6}O^{10}$	Gallic acid.
? $C^{14}H^{6}O^{12}$	Tannoxylic acid.

Its behaviour with ferric chloride (*inf.*) connects it with salicylic and gallic acid.

Heated for some time to a little above 100°, it gradually becomes brown; the same change takes place when a *pure* aqueous solution is evaporated on the water-bath, but appears to be prevented by the presence of a trace of hydriodic acid.

It is moderately soluble in cold *water;* very soluble in hot water.

It has decided acid properties, but none of its salts have yet been obtained pure. Its *alkaline* and *alkaline-earthy salts* are very quickly coloured brown in the air. The *lead-salt* is a yellowish white, curdy precipitate; the *silver-salt* decomposes almost instantaneously, even in the cold, with separation of metallic silver; the *copper-salt* is decomposed at 100°, with separation of suboxide of copper. With *sesquichloride of iron,* the acid or its ammonia-salt gives an intense indigo-blue coloration, which is destroyed by strong acids, and changed to blood-red by ammonia. In a clear *mixture of sesquichloride of iron with red prussiate of potash,* it causes an immediate precipitate of prussian blue.

The acid dissolves very readily in hot *alcohol* and *ether.* ¶

Sulphopianic Acid.

$$C^{20}H^{10}S^{2}O^{8} = C^{20}H^{10}O^{6},S^{2}O^{2}.$$

WÖHLER. *Ann. Pharm.* 50, 12.

Comp. page 428. When washed sulphuretted hydrogen gas is passed into aqueous opianic acid heated to 70°, the solution becomes turbid and deposits sulphopianic acid, the formation of which does not cease till after the sulphuretted hydrogen has been passed through the solution for a day.

Yellowish powder, which, if heated while still immersed in the mother-liquor, melts to a pale yellow, clear oil which solidifies on cooling. The alcoholic solution yields slender, pale yellow transparent prisms, which soften below 100°, melt completely below 100°, and cannot afterwards be obtained in the crystalline form by spontaneous evaporation of their alcoholic solution.

	Amorphous.		Wöhler.
20 C	120	53·10	53·15
10 H	10	4·42	4·19
2 S	32	14·16	14·32
8 O	64	28·32	28·34
$C^{20}H^{10}S^2O^8$	226	100·00	100·00

It is therefore opianic acid having 2 At. O replaced by 2S, or 2HO by 2HS. Wöhler originally gave the formula $C^{20}H^9S^2O^8$, which was altered by Gerhardt (*Compt. chim.* 1, 61), and Laurent (*Compt. rend.* 20, 1118, 21, 1418.)

Decompositions. When *heated* above its melting point, it emits a strong sulphur-yellow vapour, which thickens to fine yellow crystalline needles, insoluble in water, easily soluble in alcohol. — It *burns* with flame and the odour of sulphurous acid. — In *alkaline* solution, it decomposes after a while, with formation of metallic sulphide.

Combinations. It dissolves in *alkalis,* forming a yellow solution which, when recently prepared, may be precipitated by acids without evolution of sulphuretted hydrogen.

Sulphopianate of Lead. — Ammoniacal sulphopianic acid added to neutral acetate of lead, throws down a copious brown-yellow precipitate which becomes brown-black after a while, under the liquid, and at the boiling heat is immediately converted into black sulphide of lead.

Sulphopianate of Silver. — A solution of sulphopianic acid in ammonia forms with nitrate of silver, a brown-yellow precipitate, which, if left under the liquid, changes after a while to black-brown sulphide of silver. If quickly filtered and dried in vacuo, the precipitate may be melted on paper without loss of weight. When burnt, it leaves black sulphide of silver. It contains quantities of silver varying from 28 to 37 per cent. ($C^{20}H^9AgS^2O^8 = 32{\cdot}43$ p. c. Ag.).

The same precipitates are obtained with lead and silver-salts, by dissolving the sulphopianic acid in boiling mono-hydrosulphate of ammonia, volatilising the excess of the base, and then adding the metallic salts. Sulphopianic acid is therefore not a sulphide, since it combines, not with sulphur-bases, but with oxides.

Sulphopianic dissolves readily in *alcohol,* forming a yellow solution.

Conjugated Compounds of the Opian-series.

Opianate of Ethyl.

$$C^{24}H^{14}O^{10} = C^4H^5O,C^{20}H^9O^9.$$

WÖHLER. *Ann. Pharm.* 50, 5.
ANDERSON. *Ann. Pharm.* 86, 193.

Opianic ether, Opiannaphtha, Opiansäure-äther, Opian-vinester.

Formation and Preparation. — When a warm alcoholic solution of opianic acid is saturated with sulphurous acid, and the liquid somewhat concentrated, opianic ether crystallises out on cooling. (Wöhler.) — It was once accidentally obtained by mixing alcoholic opianate of potash with hydrochloric acid. (Anderson.) It is not produced by saturating alcoholic opianic acid with hydrochloric acid gas. (Wöhler.)

Properties. Slender, white prisms united in tufts and spherical masses. (Wöhler.) Colourless needles melting at 92·2° (Anderson), without loss of weight. (Wöhler.) Under water it melts at 92·2° (Anderson), near 100° (Wöhler), forming a transparent oil which sinks to the bottom, and on cooling immediately solidifies, with great contraction of volume, in white radiating masses, like wavellite,—but if heated above the melting point, remains soft and amorphous for a long time, even after cooling, and does not solidify for some time after. When heated between two basins, it sublimes without alteration. It is inodorous, has a slightly bitter taste, probably from decomposition. (Wöhler.)

			Wöhler.	Anderson.
24 C	144	60·50	60·50	59·86
14 H	14	5·88	5·77	5·90
10 O	80	33·62	33·73	34·24
$C^4H^5O,C^{20}H^9O^9$	238	100·00	100·00	100·00

This is Anderson's formula. Wöhler formerly supposed it to be $C^4H^5O,C^{20}H^8O^9$.

When heated *per se*, it requires a very high temperature to decompose it; but it is resolved into opianic acid and alcohol by boiling with *water*, and by distillation with *potash-ley*. (Wöhler.)

It is insoluble in *water*, but dissolves readily in *alcohol* and in *ether*.

Ethyl-hemipinic Acid.

$$C^{24}H^{14}O^{12} = C^4H^6O^2,C^{20}H^8O^{10}.$$

ANDERSON. *Ann. Pharm.* 86, 195.

Acid Hemipinic ether; Aetherhemipinsäure, Weinhemipinsäure.

Produced by passing hydrochloric acid gas into a solution of hemipinic acid in absolute alcohol.

Properties. Needles grouped in tufts, which melt to a transparent liquid at 132·2° when heated alone, and at the boiling point under water. It has a strong acid reaction. Gives off 9·93 p. c. water at 100° (calculation 3 Aq.=3·60 p. c.).

			Anderson.
24 C	144	56·69	56·45
14 H	14	5·51	5·67
12 O	96	37·80	37·88
$C^4H^5O,HO,C^{20}H^8O^{10}$	254	100·00	100·00

Yields alcohol when boiled with *potash*.

It dissolves sparingly in cold, somewhat more freely in boiling *water*.

The ethyl-hemipinates are difficult to obtain pure. Aqueous hemipinic acid does not precipitate *lead* or *silver* salts, but forms a bulky, brown-yellow precipitate with *sesquichloride of iron*.

Ethyl-hemipinate of Baryta. — Obtained by digesting the acid with carbonate of baryta. Small tufts of needles which appear to decompose with great facility.

Opiammone.

$C^{40}H^{19}NO^{16} = C^{40}H^{17}AdC^{14},O^{2}.$

WÖHLER. *Ann. Pharm.* 50, 6.

Binopiammone (Anderson, *Ann. Pharm.* 86, 189.)

Formation. In the decomposition of opianate of ammonia by heat. (Comp. xiv, 429.)

Preparation. A solution of opianic acid in ammonia is evaporated to dryness at a gentle heat; the transparent amorphous residue is kept at a heat somewhat above 100° and constantly stirred as long as it smells of ammonia; and the mass, which has now become pale yellow and insoluble in water, is freed by boiling with water from any opianate of ammonia that may have escaped decomposition.

Properties. Pale yellow powder consisting of microscopic, translucent, crystalline lumps; in the perfectly pure state, it would probably be colourless. Melts easily when heated, and creeps up the side of the vessel, without subliming.

			Wöhler. *mean.*
40 C	240	59·85	59·86
19 H	19	4·74	4·88
N	14	3·48	3·75
16 O	128	31·93	31·51
$C^{40}H^{19}NO^{16}$	401	100·00	100·00

Wöhler formerly supposed it to be $C^{40}H^{17}NO^{6}$.—Opiammone = 2 At. $C^{20}H^{10}O^{10}$ + 1 At. NH^{3} — 4 At. HO

Decompositions. 1. Opiammone somewhat strongly *heated* in contact with the air, smells like melting opianic acid, and gives off a yellow vapour. — 2. When it is boiled for some time with *water*, a small portion dissolves, probably in consequence of decomposition. Heated with water to 150° in a sealed tube, it dissolves completely, forming a clear pale yellow liquid, which on cooling deposits crystals of opianic acid, while opianate of ammonia remains in solution. — 3. It dissolves in cold *oil of vitriol*, forming an orange-yellow solution, which is rendered milky by water, but becomes clear again when heated, and deposits crystals of opianic acid on cooling, an ammoniacal salt being formed at the same time. — It is not altered by hot dilute acids. — 4. An aqueous solution of pure *potash* or *carbonate of potash* dissolves opiammone after a few seconds, with evolution of ammonia, forming a uranium-yellow solution. On boiling the solution, $\frac{3}{4}$ of the ammonia belonging to the opiammone escapes, and hydrochloric acid then precipitates yellow flocks of xanthopenic acid, whilst the filtrate on cooling yields crystals of opianic acid mixed with xanthopenic acid.

Opiammone is insoluble in cold *water*. In boiling *alcohol*, it dissolves slowly but abundantly, forming a certain quantity of opianic acid, which crystallises by spontaneous evaporation. (Wöhler.)

Appendix to Opiammone.

Xanthopenic Acid.

WÖHLER. *Ann. Pharm.* 50, 9.

Prepared by boiling opiammone with potash-ley (*vid. sup.*).

Beautiful yellow flocks, forming when dry, a lemon-yellow powder, which appears crystalline under the microscope. Fusible. Gives off ammonia when heated with *soda-lime*. Dissolves in *alkalis* with fine yellow colour.

Teropiammone.

$$C^{60}H^{29}NO^{26} = C^{40}H^{17}AdO^{16},C^{20}H^{10}O^{10}.$$

ANDERSON. *Ann. Pharm.* 86, 187.

Produced in variable, but always very small quantity, together with many other products, when opian is decomposed by dilute nitric acid (p. 423, B); purified by washing with alcohol and recrystallisation from boiling alcohol.

Small colourless needles.

	At 100°.		Anderson. *mean.*
60 C	360	58·91	59·20
29 H	29	4·74	4·98
N	14	2·29	2·12
26 O	208	34·06	33·70
$C^{60}H^{29}NO^{26}$	611	100·00	100·00

Decompositions. Cold *oil of vitriol* dissolves teropiammone with yellow, or, when heated, with fine crimson colour. — Teropiammone is not decomposed by *hydrochloric acid* or *ammonia*, but *nitric acid* decomposes it; it is also decomposed by *potash* into ammonia and opianic acid.

It dissolves sparingly in cold, somewhat more in boiling *alcohol* and in *ether*. (Anderson.)

Oxyiodo-nucleus $C^{20}IH^9O^6$.

Iodopianyl.

$$C^{20}IH^9O^8 = C^{20}IH^9O^6,O^2.$$

ANDERSON. *Ann. Pharm.* 98, 48.

Iodomeconin, Hydrure d'iodopianyle. (Gerhardt, *Traité*, 4, 1049.)

Formation and Preparation. When chloride of iodine is added to aqueous opianyl, and the mixture left to itself for several days in a warm place, long crystals form in it, contaminated by free iodine. They are purified by recrystallisation from boiling alcohol.

Properties. Colourless needles, which melt at 112° to a colourless liquid.

			Anderson.
20 C	120·0	37·48	37·16
9 H	9·0	2·81	2·96
I	127·1	39·70	39·48
8 O	64·0	20·01	20·40
$C^{20}IH^9O^8$	320·1	100·00	100·00

Decompositions. Melts at a temperature above 100° to a brown liquid, which decomposes at a stronger heat, with volatilisation of iodine. — It dissolves in *oil of vitriol*, forming a dark-coloured liquid when heated. — It is decomposed by *nitric acid*, with separation of iodine.

It is nearly insoluble in *water*, more soluble in *alcohol* and *ether*.

Bromine-nucleus $C^{20}Br^4H^{12}$.

Brominated Oil of Turpentine.

$$C^{20}Br^4H^{12}.$$

DEVILLE. *Ann. Chim. Phys.* 75, 63; *J. Pharm.* 26, 678.

Bromterpenthinöl, Terpenthinolbromür. (Löwig.) *Bromure d'essence de térébenthine.* (Deville.) *Essence de térébenthine quadribromé.*

Formation and Preparation. Oil of turpentine is gradually mixed with small quantities of bromine, till a dark red, fuming, viscid, heavy liquid is produced; this liquid is partially decolorised by animal charcoal; and the free hydrobromic acid and water contained in it are removed by agitation with chalk and chloride of calcium.

Properties. Sp. gr. 1·975 at 20°. — Dextro-rotatory.

			Deville. *mean.*
20 C	120	26·55	27·43
4 Br	320	70·79	
12 H	12	2·66	3·00
$C^{20}Br^4H^{12}$	452	100·00	

Isomeric with bromoterebene.

Bromoterebene.

$C^{20}Br^4H^{12}$.

DEVILLE. *Ann. Chim. Phys.* 75, 51; *J. pr. Chem.* 22, 92; *J. Pharm.* 26, 666.

When bromine is slowly dropped into well-cooled terebene, till the liquid acquires a deep red colour, a large quantity of hydrobromic acid is given off, and bromoterebene is formed, which may be decolorised, though not completely, by treatment with animal charcoal.

Reddish, viscid liquid, of sp. gr. 1·978 at 20°.

			Deville. *mean.*
20 C	120	26·55	27·43
4 Br	320	70·79	
12 H	12	2·66	2·95
$C^{20}Br^4H^{12}$	452	100·00	

Isomeric with brominated oil of turpentine.

When *heated*, it gives off hydrobromic acid (which yields free bromine, in contact with the air) and leaves a residue of charcoal.

Oxybromine-nucleus $C^{20}BrH^9O^6$.

Bromopianyl.

$C^{20}H^9BrO^8 = C^{20}BrH^9O^6,O^2$.

ANDERSON. *Ann Phar* . 98, 48.

Bromomeconin, Hydrure de bromopianyle. (Gerhardt, *Traité*, 4, 1049.)

Formation and Preparation. When bromine-water is gradually added to aqueous opianyl, crystals of bromopianyl separate out, and may be purified by recrystallisation from boiling alcohol.

Properties. Colourless needles, which melt at 167°, and behave in other respects like chloropianyl.

			Anderson.
20 C	120	43·95	43·81
9 H	9	3·29	3·40
Br	80	29·30	29·21
8 O	64	23·46	23·58
$C^{20}H^9BrO^8$	273	100·00	100·00

Dissolves sparingly in *water*, more readily in *alcohol* and *ether*.

Chlorine-nucleus $C^{20}Cl^{2}H^{14}$.

Bichloroterebene.

$C^{20}Cl^{2}H^{14}$.

DEVILLE. *Ann. Chim. Phys.* 75, 49; *J. pr. Chem.* 22, 91; *J. Pharm.* 26, 665; *Pogg.* 51, 433.

Monochlortérébène.

When the product obtained, together with hydrochloric acid and hydrochlorate of terebene, by the distillation of quadrichloroterebene, is heated with a quantity of potash-ley sufficient to saturate the hydrochloric acid which is set free, bichloroterebene is produced, and may be dehydrated by rectification over chloride of calcium:

$$3C^{20}Cl^{4}H^{12} = 20\,C + 2\,C^{20}Cl^{2}H^{14} + 8\,HCl. \quad \text{(Deville.)}$$

Colourless oil, of sp. gr. 1·137 at 20°; refracting power 1·5186 (Deville), 1·531. (Becquerel & Cahours, *Pogg.* 51, 427.)

			Deville. *mean.*
20 C	120	58·53	58·27
2 Cl	71	34·63	
14 H	14	6·84	6·83
$C^{20}Cl^{2}H^{14}$	205	100·00	

It is resolved by *heat* into hydrochlorate of terebene (p. 274), and a residue of charcoal.

Chlorine-nucleus $C^{20}Cl^{4}H^{12}$.

Chlorinated Oil of Turpentine.

$C^{20}Cl^{4}H^{12}$.

DEVILLE. *Ann. Chim. Phys.* 75, 57; *J. Pharm.* 26, 672; *J. pr. Chem.* 22, 97.—*Pogg.* 51, 433.

Chlorterpenthinöl, Terpentinölchlorür. (Löwig.) *Chlorocamphène.* (Deville.) *Chlorocamphose.* (Laurent.) *Essence de térébenthine quadrichloré.* (Gerhardt.)

Formation and Preparation.—When chlorine gas is very slowly passed over artificial camphor (p. 265), a small quantity of hydrochloric acid gas is evolved, and there is formed a liquid coloured yellow by chlorine ($C^{20}H^{12}Cl^{4}$,HCl, according to Deville), which decomposes with explosion, even in the atmosphere of chlorine, but still more in contact with the air, giving off hydrochloric acid gas and chlorine, and solidifying to crystalline chlorinated oil of turpentine.—It is also produced, mixed with quadrichloroterebene, by passing chlorine into oil of turpentine (p. 248).

Properties. Crystalline mass of sp. gr. 1·5 at 8°, and refracting power = 1·5448. Melts without volatilising between 110° and 115°. Has no optical rotatory power.

			Deville. *mean.*
20 C	120	43·79	43·54
4 Cl	142	51·83	
12 H	12	4·38	4·80
$C^{20}Cl^{4}H^{12}$	274	100·00	

Isomeric with quadrichloroterebene.

Decompositions. When slowly heated, it gives off a large quantity of hydrochloric acid gas, with separation of charcoal, and yields a distillate consisting of chlorinated oil of turpentine, artificial camphor, a body containing less chlorine, probably $C^{20}H^{14}Cl^{2}$, and a large quantity of hydrochlorate of terebene.

Quadrichloroterebene.

$C^{20}Cl^{4}H^{12}$.

DEVILLE. *Ann. Chim. Phys.* 75, 48; *J. pr. Chem.* 22, 90; *J. Pharm.* 26, 664. — *Pogg.* 51, 433.

Chloroférébène.

Formation and Preparation. Chlorine gas is passed through terebene well cooled and exposed to diffused day-light, as long as any of it is absorbed, whereupon hydrochloric acid gas is abundantly evolved, so that the bottle containing the terebene is liable to burst, unless it be frequently opened. — The compound is also obtained, together with chlorinated oil of turpentine, when chlorine gas is passed into oil of turpentine (p. 248).

Colourless viscid oil of sp. gr. 1·36 at 156°, refracting power = 1·5294, and no rotatory power. Has a peculiar camphorous odour.

			Deville. *mean.*
20 C	120	43·79	43·67
4 Cl	142	51·83	
12 H	12	4·38	4·73
$C^{20}Cl^{4}H^{12}$	274	100·00	

Isomeric with chlorinated oil of turpentine.

Quadrichloroterebene blackens when heated, gives off a large quantity of hydrochloric acid gas, and yields a colourless distillate consisting of aqueous hydrochloric acid gas, bichloroterebene, hydrochlorate of terebene, and undecomposed quadrichloroterebene, while charcoal remains behind. If the heat be quickly applied, the distillate is red, blue, and ultimately black, and contains a large quantity of hydrochlorate of terebene: $2C^{20}Cl^{4}H^{12} = 20C + C^{20}H^{16},HCl - 7HCl$. (Deville.)

Oxychlorine-nucleus $C^{20}ClH^9O^6$.

Chloropianyl.

$C^{20}ClH^9O^8 = C^{20}ClH^9O^6,O^2$.

ANDERSON. *Ann. Pharm.* 98, 47.

Chloromeconin, Hydrure de chloropianyle. (Gerhardt, *Traité*, 4, 1049.)

Formation and Preparation. When chlorine gas is passed into a cold-saturated aqueous solution of opianyl, an abundant crop of crystals quickly separates, consisting of chloropianyl, which may be purified by recrystallisation from alcohol. — It is likewise produced when dry chlorine gas is passed over melted opianyl.

Properties. Colourless needles, which melt at 175° and sublime undecomposed at higher temperatures.

			Anderson.
20 C	120·0	52·51	52·45
9 H	9·0	3·93	4·24
Cl	35·5	15·53	15·17
8 O	64·0	28·03	28·14
$C^{20}ClH^9O^8$	228·5	100·00	100·00

Decompositions. Dissolves in cold *oil of vitriol*, assumes a greenish blue colour when heated therewith, and on subsequent addition of water deposits brown flocks which dissolve with red colour in alkalis. — It dissolves with red colour in *nitric acid*, and is decomposed by heating.

Combinations. It dissolves sparingly in cold, somewhat more freely in boiling *water*,—in *alkalis* to about the same amount as in water, and without decomposition.

It is soluble in *alcohol* and in *ether*.

Oxychlorine-nucleus $C^{20}Cl^3H^{11}O^2$.

Terchlorothymol.

$C^{20}Cl^3H^{11}O^2$.

LALLEMAND. (1856.) *Compt. rend.* 43, 376; *N. Ann. Chim. Phys.* 49, 158; *Ann. Pharm.* 101, 123, and 102, 122.

Thymoltrichloré.

Formation (p. 411).

Preparation. Chlorine gas is passed into thymol in diffused daylight—care being taken to avoid too much heating—till the thymol has absorbed a quantity of chlorine equal to $\frac{2}{3}$ of its weight. On leaving the product to stand, long yellow needles are formed, which ultimately cause it to solidify: they may be purified by expressing the remaining liquid and recrystallising from ether-alcohol.

Lemon-yellow, oblique rhombic prisms, which melt at 61° and have an intoxicating odour.

The compound decomposes at 180°. — Heated with *oil of vitriol* to 100°, it is converted into a colourless liquid, which floats on the oil of vitriol, solidifies on cooling, and, after solution in aqueous potash, precipitation with hydrochloric acid, and drying, forms silky, talc-like flocks. This substance has at first an agreeable odour of benzoin, melts at 45°, and distils without decomposition at 250°; it dissolves in ammonia and forms a salt, crystallising in slender needles,—whence it is probably terchlorocarbolic acid; (xi, 181) with which it appears to agree in composition.

Oxychlorine-nucleus $C^{20}Cl^5H^9O^2$.

Quintichlorothymol.

$C^{20}Cl^5H^9O^2$.

LALLEMAND. (1856.) *Compt. rend.* 43. 376; *N. Ann. Chim. Phys.* 49, 158; *Ann. Pharm.* 10, 123, and 102, 123.

Thymol pentachloré ou quintichloré.

Formation (p. 411).

Preparation. When thymol is exposed for a considerable time to the action of dry chlorine gas in bright daylight, a reddish yellow glutinous oil is formed, in which, after a while, crystals of quintichlorothymol make their appearance: they may be purified by recrystallisation from ether.

Properties. Colourless, very hard crystals, having the form of terchlorothymol (according to another statement of Lallemand, it has the form of thymol), melting at 98°, and containing 55 p. c. chlorine (calculation = 55·03 Cl).

Decomposes at 200°, giving off hydrochloric acid gas and propylene gas (C^6H^6), while a solid product (terchlorotoluenol) collects in the neck of the retort, and charcoal remains behind:

$$2\,C^{20}H^9Cl^5O^2 = C^{14}H^5Cl^3O^2 + C^6H^6 + 7HCl + 2CO + 18C.$$

In one experiment, in which very pure quintichlorothymol was heated, the carbonic oxide evolved towards the end of the process was mixed with marsh-gas, and the solid distillate, melting at 150°, and crystallising from alcohol in needles, had the composition $C^{14}H^4Cl^4O^2$, and was therefore quadrichlorotoluenol: $2C^{20}H^9Cl^5O^2 = C^{14}H^4Cl^4O^2 + C^6H^6 + 6HCl + CH^2 + 2CO + 17C$. Impure quintichlorothymol yielded also by distillation a large quantity of liquid product, which, after the solid products had been removed by weak potash-ley, boiled at 265° (or, according to Lallemand's first statement, at 365°), and had the composition of bichlorocumol (xiii, 346). — Stenhouse, by passing chlorine-gas over the crystals from ptychotis-oil (p. 411) previously examined by him (*Ann. Pharm.* 93, 269), obtained dark yellow crystals, which were less soluble in cold alcohol and ether than thymol, and after recrystallisation from hot alcohol, pressing and drying in vacuo, contained 40·26 p. c. C, 3·99 H, 43·09 Cl, and 12·66 O, whence Stenhouse deduced the formula $C^{44}Cl^8H^{26}O^{10}$.

Oxynitro-nucleus $C^{20}XH^9O^6$.

Nitropianyl.

$$C^{20}H^9NO^{12} = C^{20}XH^9O^6,O^2.$$

ANDERSON. *R. Soc. Edinburgh Transact.* 21, 204; *Ann. Pharm.* 98, 46.

Nitromeconin. Hydrure de nitropianyle. (Gerhardt, *Traité* 4, 1049.)

Formation and Preparation. Opianyl dissolves abundantly in cold concentrated nitric acid, the solution giving off red fumes when heated. On diluting with water, bulky crystals separate, which may be obtained pure by washing and recrystallisation from boiling alcohol.

Properties. White needles and prisms, melting at 160° to a transparent liquid, which solidifies in the crystalline form on cooling. Neutral.

			Anderson.
20 C	120	50·20	50·11
9 H	9	3·76	3·92
N	14	5·85	
12 O	96	40·19	
$C^{20}XH^9O^8$	239	100·00	

Decompositions. 1. Heated in small quantities on platinum-foil, it volatilises almost without decomposition, leaving only a small quantity of charcoal; but, if heated in a test-tube, it decomposes suddenly and leaves a large quantity of porous charcoal. — 2. With *oil of vitriol,* it turns yellow, and dissolves to a red liquid when heated. — 3. Boiled with *ammonia* or *potash,* it forms, without decomposition, a yellow solution which does not deposit anything on cooling or on addition of acids.

Combinations. Nitropianyl dissolves sparingly in cold, somewhat more freely in boiling *water:* it is insoluble in *hydrochloric acid,* but dissolves in cold strong *nitric acid,* separating in flocks when the solution is diluted. In cold *ammonia* and *potash,* it is not more soluble than in water. It is not precipitated by *metallic salts.*

It dissolves in boiling *alcohol* and *ether.*

Appendix to Nitropianyl.

Meconin-hyponitric Acid.

$$C^{20}H^9NO^{12}.$$

COUERBE. *Ann. Chim. Phys.* 50,347, and 59, 141.

Acid hyponitromeconique, Meconinuntersalpetersäure, Meconinsalpetersaure, Nitromeconinsaure.

Formation and Preparation. When the solution of opianyl in nitric acid is exposed to dryness in the water-bath, a fused mass remains, which solidifies in the crystalline form on cooling. It is purified by recrystallisation from water and alcohol. — Anderson (*Ann. Pharm.* 98, 47) did not obtain it by this process.

Properties. Colourless or slightly yellow, long, thin, four-sided prisms with rectangular base. Has a strong acid reaction. Melts at 150°.

			Couerbe.
20 C	120	50·20	50·24
9 H	9	3·76	3·98
N	14	5·85	6·36
12 O	96	40·19	39·42
$C^{20}H^9NO^{12}$	239	100·00	100·00

It is perhaps identical with Anderson's nitropianyl, to which, however, Anderson ascribes other properties.

Decompositions. Sublimes at 190°, with partial decomposition and the odour of bitter almonds. — When thrown on red-hot coals, it takes fire and burns away.

Combinations. The compound dissolves in *water*, with light yellow colour.

In concentrated *acids*, it dissolves when heated, and crystallises, without alteration, on cooling, or when the solution is diluted with water, the liquid then becoming colourless. — It dissolves readily in *alkalis*, with red colour, and is precipitated unaltered by acids. — With *potash*, it forms a very soluble salt. — It precipitates *iron*-salts reddish yellow, *copper*-salts *green*, but forms no precipitate with the salts of *lime*, *magnesia*, *lead*, *mercury*, or *gold*.

It dissolves in alcohol with *yellow* colour, and forms a colourless solution in *ether*.

Oxynitro-nucleus $C^{20}X^2H^{12}O^2$.

Binitrothymol.

$$C^{20}H^{12}N^2O^{10} = C^{20}X^2H^{12}O^2.$$

LALLEMAND. (1856.) *Compt. rend.* 43, 376; abstr. *Ann. Pharm.* 101, 122; *N. Ann. Chim. Phys.* 49, 152.

Thymol binitré, Acide binitrothymique, Dinitrothyminsäure.

When nitric acid is slowly dropped into sulphothymolic acid, or into a solution of a sulphothymate, the liquid becomes slightly warm and deposits a reddish oil which soon solidifies.

Crystals which melt at 55°.

Nitrosulphuric acid converts it into ternitrothymol. — When heated with *alcohol* and *oil of vitriol*, it is easily converted into solid binitrothymolate of ethyl.

It dissolves sparingly in *water*.

With *bases*, it forms salts which crystallise in silky needles, detonate at 150°, and dissolve sparingly in water, to which however they impart a strong colour.

Binitrothymate of Potash. — Orange-yellow in the anhydrous, ruby-red in the hydrated, state. Very little soluble in water.

Binitrothymate of Lead. — Contains 32·7 p. c. oxide of lead, and is therefore $C^{20}H^{11}X^2PbO^2$ (calculation = 32·65 PbO). Dissolves very sparingly in water.

Binitrothymate of Silver is very sparingly soluble in water.

In *alcohol* and *ether*, binitrothymol dissolves in all proportions, separating as an oil when the solvent evaporates.

Oxynitro-nucleus $C^{20}X^3H^{11}O^2$.

Ternitrothymol.

$C^{20}H^{11}N^3O^{14} = C^{20}X^3H^{11}O^2$.

Lallemand. (1856.) *Compt. rend.* 43, 376; *N. Ann. Chim. Phys.* 49, 152; *Ann. Pharm.* 101, 123.

Thymol trinitré, Acid trinitrothymiqué, Trinitrothyminsäure.

Formation and Preparation. Binitrothymol is dissolved in oil of vitriol, and a small quantity of nitric acid is gradually added, without allowing the mixture to get hot. On diluting with water, yellowish flocks of ternitrothymol are precipitated, which may be recrystallised from boiling water.

Beautiful yellow needles, which melt at 100°, and decompose suddenly at a higher temperature.

A mixture of *oil of vitriol* and *alcohol* readily converts it into solid ternitrothymic ether.

Ternitrothymol dissolves sparingly in cold *water*.

It unites with *bases*, forming yellow or orange-yellow salts, which detonate at 150°, and dissolve in water more readily than the binitrothymates. The aqueous solution of ternitrothymate of potash precipitates the salts of the heavy metals.

Ternitrothymate of Lead contains 28·83 p. c. lead oxide, and is therefore $C^{20}X^3H^{10}PbO^2$ (calculation = 28·86 PbO).

Ternitrothymol dissolves readily in *alcohol* and in *ether*.

Primary Nucleus $C^{20}H^{18}$.

Menthene.

$C^{20}H^{18}$.

Walter. (1839.) *Compt. rend.* 8, 913; *Ann. Chim. Phys.* 72, 87; *Pogg.* 51, 1, 336; *J. pr. Chem.* 14, 104; *Ann. Pharm.* 32, 288.

Discovered by Walter in 1838.

Formation. By distilling peppermint-camphor with anhydrous phosphoric acid or oil of vitriol. — Probably also by heating peppermint-camphor with potassium. (Walter.)

Preparation. Small lumps of anhydrous phosphoric acid are gradually added to peppermint-camphor, as long as heat is thereby produced; the mixture, which separates into two layers, is distilled; and the colourless distillate is twice rectified over anhydrous phosphoric acid ($C^{20}H^{20}O^2 = 2HO + C^{20}H^{18}$).

Properties. Transparent, colourless, thin liquid of sp. gr. 0·851; boiling between 161° and 163°. Has an agreeable peculiar odour (which it appears to lose when it contains water, and to recover by boiling with potash), and a refreshing taste. Vapour-density = 4·94.

					Vol.	Density.
20 C	120	86·96	86·4	C-vapour	20	8·3200
18 H	18	13·04	12·9	H-gas	18	1·2474
$C^{20}H^{18}$	138	100·00	99·3	Menthene-vapour	2	9·5674
					1	4·7837

According to Kane (*Phil. Mag. J.* 16, 418; *J. pr. Chem.* 20, 439), it is $C^{21}H^{18}$. — Isomeric with camphin and sebacin.

Decompositions. 1. Menthene, when *set on fire*, burns with a bright, smoky flame. — 2. Dry *chlorine* colours it green, with rise of temperature and evolution of hydrochloric acid, finally yellow, and converts it into pentachloromenthene. — 3. With *bromine*, it acquires a violet, with *iodine*, a red colour. — 4. It is not decomposed by *cold concentrated nitric acid;* with the *hot concentrated* acid, it turns green, with evolution of nitrous and carbonic acids, then red, floats at first upon the acid, but ultimately mixes with it, forming a peculiar acid ($C^{20}H^{18}O^{18}$) together with flocks insoluble in water, and a small quantity of an oil slightly soluble in water. — When menthene is heated with strong nitric acid 10 or 15 times, or as long as nitrous acid continues to escape, the liquid then diluted with water, the precipitated white flocks separated by filtration, the concentrated filtrate repeatedly heated with alcohol to remove undecomposed nitric acid, then dissolved in water, and again evaporated in vacuo, the acid remains in the form of a yellow oil, which contains 42·77 p. c. C, 6·61 H, and 50·62 O (therefore $C^{20}H^{18}O^{18}$), decomposes by distillation, and is soluble in water and in alcohol. — 5. Menthene is not altered by cold *oil of vitriol* or by *potassium.* (Walter.)

Combinations. With *Hydrochloric Acid.* — *Hydrochlorate of Menthene,* $C^{20}H^{19}Cl$. — *Chlormenthose* (Laurent, *Rev. Scient.* 14, 341). — *Chloromenthène* (Walter). *a. Chlormenthen* (Löwig.) — Fused peppermint-camphor is distilled from a tubulated retort with pentachloride of phosphorus added gradually and in slight excess; the chlorophosphoric acid (terchloride of phosphorus, according to Walter), which first passes over, is removed; and then the yellow oil which passes over at a higher temperature is collected: this oil is washed with cold water, and rectified several times over pentachloride of phosphorus, washed with solution of carbonate of soda and with water, shaken up with chloride of calcium, and dried in vacuo (Gerhardt, *N. J. Pharm.* 14, 224):

$$C^{20}H^{20}O^2 + PCl^5 = PCl^3O^2 + HCl + C^{20}H^{19}Cl.$$

It is a very pale yellow oil, lighter than water, boiling at 204°, not however constantly, and with blackening and evolution of hydrochloric acid; has a peculiar odour, like that of nutmeg-flowers, and a refreshing taste.

			Walter.
20 C	120·0	68·7	68·9
19 H	19·0	10·8	10·5
Cl	35·5	20·5	20·9
$C^{20}H^{18},HCl$	174·5	100·0	100·3

According to Walter, it is chloromethene, $C^{20}H^{17}Cl$; according to Kane (*Phil. Mag. J.* 16, 418), $C^{21}H^{19}Cl$; according to Gerhardt (*N. J. Pharm.* 14, 224), $C^{20}H^{19}Cl$. — It is not yet, however, absolutely proved to be hydrochlorate of menthene, (Schwanert.)

The chlorine-compound when *set on fire,* burns with a smoky green-edged flame. With cold *oil of vitriol* it acquires a blood-red colour. Heated with *potassium,* it is violently decomposed, with formation of chloride of potassium; if the action takes place in the cold, the metal becomes covered with a brown crust. It is not altered by *alcoholic potash* even at the boiling heat.

The chlorine-compound dissolves sparingly in water, easily in alcohol and wood-spirit, very easily in ether and in oil of turpentine.

Menthene is insoluble in *water*. With a small quantity of *alcohol* or *ether*, it forms a turbid mixture; with large quantities, a clear mixture. It dissolves with moderate facility in *wood-spirit,* very easily in *oil of turpentine.*

Sebacin.

$C^{20}H^{18}$.

T. Petersen. (1857.) *Ann. Pharm.* 103, 187; abstr. *Chem. Centr.* 1857, 907; *J. pr. Chem.* 73, 72.

Formation. By dry distillation of sebate of lime mixed with excess of lime.

Preparation. Sebate of lime, mixed with excess of lime is subjected to dry distillation, whereupon a mixture of propionic aldehyde, œnanthol, and a small quantity of benzene passes over, and finally solid sebacin, which adheres to the sides of the receiver and the neck of the retort: more of it is obtained on leaving the liquid products of the distillation at rest. The product is purified by solution in oil of vitriol, precipitation by water, and recrystallisation from alcohol.

Properties. Solid fatty mass; crystallises from alcohol in nearly colourless laminæ which easily cake together. Melts at 55°; volatilises above 300°. Lighter than water. Inodorous. Tasteless.

Dried over oil of vitriol.			Petersen.
20 C	120	86·9	86·70
18 H	18	13·1	13·28
$C^{20}H^{18}$	138	100·0	99·98

Dissolves in *oil of vitriol* with red colour, and is precipitated in its original state by water. Scarcely altered by *nitric acid* or *caustic potash.*

Insoluble in *water,* easily soluble in *alcohol* and *ether.*

Camphin.

$C^{20}H^{18}$.

Claus. *J. pr. Chem.* 25, 264.

Formation. By distilling common camphor with iodine.

Preparation. The impure camphin obtained in the preparation of colophene from camphor (p. 280), is agitated with mercury to remove iodine, then distilled *per se* to remove colophene, camphor, and camphocreosote, then shaken up with potash-ley, and repeatedly rectified over potash-lime, as long as the distillate retains iodine. The last trace of iodine may also be removed by setting it aside over potassium, and rectifying.

Properties. Thin colourless oil of sp. gr. 0·827 at 25°. Boils at 167° — 170° under an atmospheric pressure of 28 inches. Odour agreeable, like that of mace, but at the same time recalling that of turpentine.

						Claus. *mean.*
20 C	120	86·96	18 C	108	87·10	86·06
18 H	18	13·04	16 H	16	12·90	12·79
$C^{20}H^{18}$	138	100·00	$C^{20}H^{16}$	124	100·00	99·85

Claus is undecided between these two formulæ. According to the first, camphin is isomeric with menthene (p. 445); according to the second, with campholene (xiii, 365). — According to Gerhardt (*Traité* 3, 694), camphin is perhaps impure cymene: the formula of cymene requires however 89·5 p. c. C and 10·5 H.

Decompositions. 1. Camphin, when set on fire, burns with bright, very smoky flame. — 2. It absorbs dry *chlorine*, with rise of temperature and evolution of hydrochloric acid gas, and forms chlorinated products, which are thicker in proportion as they contain more chlorine.

When chlorine gas evolved from 4 ounces of common salt is passed through 10 grammes of camphin, and the excess of chlorine is removed by a current of air, a transparent, colourless oil is obtained, of the thickness of olive-oil, sp. gr. 1·19 at 21°, containing 47·25 p. c. C, 5·6 H, and 46·7 Cl (press-errors in the memoir render it impossible to recalculate these numbers with the new atomic weights: Kr.); and, according to Claus, it is $C^{18}Cl^3H^{13}$. This oil is resolved by heat, like quadrichloroterebene (p. 440), into hydrochloric acid and chlorinated oils; heated with alcoholic potash, it yields chloride of potassium and a chlorinated oil. In sunshine it absorbs an additional quantity of chlorine gas, forming chlorinated chlorocamphin, which is a colourless, viscid, neutral mass, having the thickness of turpentine, and containing 33·1 p. c. C, 3·0 H, and 63·9 Cl, whence Claus calculates the formula $C^{18}Cl^6H^{10}$.

3. By *bromine*, camphin is attacked more violently than by chlorine, and is converted, with effervescence, evolution of hydrobromic acid, and brown colour, which soon disappears, into a brominated oil. — 4. It dissolves *iodine* with rose-red to brown colour, and resinises after a while, with evolution of hydriodic acid. — 5. Dilute *nitric acid* acts slightly on

camphin; the concentrated acid colours it dark red at ordinary temperatures, with effervescence and evolution of red vapours, and forms after a while, with decolorisation, an azotised oil having an odour of cinnamon. Fuming nitric acid converts camphin into a thick red oil, soluble in potash. — 6. Camphin, shaken up with *oil of vitriol*, colours it yellow, but otherwise remains unaltered. — Heated with *fuming sulphuric acid*, it turns brown and thickens, gives off sulphurous acid, and distils partly unaltered. — 7. Resinises in contact with *pentachloride of antimony*.

Combinations. Camphin dissolves in *alcohol, ether, oil of turpentine*, and *rock-oil;* not in *water*, weak *alcohol, potash-ley*, or *dilute acids*, not even in *strong hydrochloric acid*. It absorbs a small quantity of hydrochloric acid gas. (Claus.)

Appendix to Camphin.

Camphoresin $C^{20}H^{12}$?

Claus. *J. pr. Chem.* 25, 264.

The residue left on distilling camphor with an equal quantity of iodine (p. 280), consists of camphoresin with small quantities of charcoal camphin, colophene, camphocreosote, and iodine.

Properties. Solid, black, very brittle resin, resembling asphalt, and having a glassy lustre, easily rubbed to a black powder; fracture conchoïdal. Melts easily. Tasteless and inodorous.

According to Claus, it contains, when not quite pure, 88·88 p. c. C, 8·39 H, and 2·0 I, and is therefore $C^{22}H^{12}$. (Claus.) It probably likewise contains oxygen, and, as it was produced from camphor, it is more probably $C^{20}H^{12}$. (Gm.)

Decompositions: Camphoresin when *boiled*, gives off white vapours smelling of creosote. — It takes fire when heated, and burns with a bright flame, leaving a tumefied charcoal, which colours an alcohol-flame green when ignited therein. — By dry distillation, it yields small quantities of camphin, camphocreosote, colophene, and lastly oil-gas and resin, and leaves a residue of charcoal.

Combinations. Camphoresin is insoluble in *water* and in *aqueous alcohol;* but *absolute alcohol* and *ether*, oil of turpentine and camphor, dissolve it, leaving however a residue of charcoal: the solutions, after agitation with animal charcoal, exhibit a light green iridescence; the solution in *rock-oil* has a blue iridescence after agitation with animal charcoal.

Peppermint-camphor.

$$C^{20}H^{20}O^2 = C^{20}H^{18},2HO.$$

Gmelin. (1829.) *Handb.* Aufl. iii, 2, 408.
Dumas. *Ann. Chim. Phys.* 50, 232; abstr. *Ann. Pharm.* 6, 252.
Blanchet & Sell. *Ann. Pharm.* 6, 293.

WALTER. *Ann. Chim. Phys.* 72, 83; *Pogg.* 51, 1, 334; *J. pr. Chem.* 14, 103; *Ann. Pharm.* 32, 288.
KANE. *Phil. Mag. J.* 16, 418; *J. pr. Chem.* 20, 439.
LAURENT. *Rev. scient.* 14, 341.

Pfefferminzcampher, Menthencampher, Stearoptene of Peppermint-oil, solid Peppermint-oil, Oxide de menthène hydraté. (Laurent.)

Oil of peppermint obtained by distilling *Mentha piperita* with water, deposits on standing (Blanchet & Sell), or when cooled to —20° (Bizio, *Brugn. Giorn.* 19, 360), to —27° (Margueron, *J. Phys.* 45, 136), crystals of peppermint-camphor. American peppermint-oil solidifies at 0° (Dumas); when it is subjected to fractional distillation, the last third of the distillate, if collected apart, deposits crystals on standing. (Walter.)

Properties. Transparent, colourless, shining prisms, which melt at 36·5° (Dumas), (at 25° Dumas, 27° Blanchet & Sell, 34° Walter), and volatilise without decomposition. (Gmelin.) Solidifies at 24°. (Blanchet & Sell.) Boiling point, 208° (Blanchet & Sell), 213°. (Walter.) Vapour-density=5·62. (Walter.) Smells and tastes like oil of peppermint (Blanchet & Sell, Walter), less burning, less agreeably, more bitter, very cooling. (Gmelin.) Neutral. (Gmelin.)

			Dumas.	Blanchet & Sell.	Walter.
20 C	120	76·9	76·5	76·4	76·3
20 H	20	12·8	13·1	12·5	12·7
2 O	16	10·3	10·4	11·1	11·0
$C^{20}H^{20}O^2$	156	100·0	100·0	100·0	100·0

	Vols.	Density.
C-vapour	20	8·3200
H-gas	20	1·3860
O-gas	1	1·1093
Vapour of Peppermint-camphor	2	10·8153 5·4076

According to Kane, it is $C^{21}H^{20}O^2$.

Decompositions. 1. Peppermint-camphor boiled in contact with the air acquires a yellowish colour (Blanchet & Sell), brown-yellow. (Walter.) — 2. When *set on fire,* it burns with a smoky flame. (Gmelin, Walter.) — 3. *Chlorine* decomposes fused peppermint-camphor, with evolution of hydrochloric acid, converting it into chlorinated peppermint-camphor. (Walter.) — 4. With *bromine,* it acquires a fine red colour, and evolves hydrobromic acid; *iodine* does not decompose it. — 5. It absorbs *hydrochloric acid gas* abundantly, and becomes viscid. (Walter, Bineau, *N. Ann. Chim. Phys.* 21, 335.) — The solution, which is red by transmitted light, deposits nearly unaltered peppermint-camphor, when shaken up with water. (Walter.) — 6. Cold *nitric acid* colours it red, without giving off gas; with hot nitric acid, it gives off nitrous acid, and forms an acid whose solution quickly changes on exposure to light. (Walter.) — Fuming nitric acid dissolves peppermint-camphor, without evolution of gas, forming a layer of oil which floats on the aqueous nitric acid, and when shaken up with water yields peppermint-camphor in drops which gradually solidify. (Gmelin.) — 7. Triturated with 2 pts. of *oil of vitriol*, it forms a semi-fluid mass of fine blood-red colour, from which nearly all the peppermint-camphor separates again on saturation with alkali; the blood-red mixture heated on the water-bath yields menthene floating on a thick red liquid. On saturating this liquid with potash, and precipitating the resulting sulphate of potash with alcohol, the solution yields by spontaneous evaporation, an oil, which, after washing with water, solution in ether, and evaporation of the ethereal solution, contains 81·3 p. c. C, 11·1 H, and 7.6 O (corresponding to the formula $C^{20}H^{19}O$, according to Walter, and to the formula $C^{20}H^{17}O$, according to Laurent, who called it *menthase*),—also a shining salt containing 37 p. c. C and 6·8 H. (Walter.)—When strongly heated with oil of vitriol, it gives off sulphurous acid, first with brown colouring, afterwards with carbonisation. (Gmelin, Walter.) — 8. Heated with *anhydrous phosphoric* acid, it is resolved into water and menthene (p. 445). — 9. *Pentachloride of phosphorus* added to fused peppermint-camphor, produces great heat and evolution of hydrochloric acid, and colours the camphor blue, rose-red, and finally dark red: the mixture yields by distillation, chloromenthene and terchloride of phosphorus (Walter), chlorophosphoric acid and hydrochlorate of menthene. (Gerhardt, *N. J. Pharm.* 14, 224.) — 10. *Potassium* oxidises slowly in fused peppermint-camphor, the mixture acquiring a doughy consistence when heated. — The doughy mass separates, on addition of water, into two layers, the upper consisting of aqueous potash having a red colour, the lower probably of menthene mixed with peppermint-camphor. — 11. It is not altered by *hydrate of potash*. (Walter.)

Peppermint-camphor dissolves sparingly in *water*. — The solution in boiling water becomes turbid on cooling. (Gmelin.) — It dissolves readily in *alcohol* and *ether* (Dumas, Walter); easily in *volatile* oils (Dumas), less easily in *oil of turpentine* (Walter), in *wood-spirit* and *bisulphide of carbon*. (Walter.) — It does not crystallise from a hot solution in alcohol or ether-alcohol. (Blanchet & Sell.)

Appendix to Peppermint-camphor.

1. *Crude Oil of Peppermint.* — *Essence de menthe poivrée.* — The oil obtained by distilling peppermint, *Mentha piperita*, with water, is a mixture of peppermint-camphor with a liquid oil not well examined. — The crude oil has generally an acid reaction. (Zeller.) — The dry flowering plant yields 1·25 p. c. oil. (Martius, *Repert.* 39, 243.) The fresh plant yields the same quantity of oil and of the same properties, whether distilled with steam or over the open fire; but the dry plant yields 1½ times more oil by distillation over the open fire than by steam distillation, and the oil obtained by the latter process is specifically lighter and less coloured than that yielded by the former. When the oil obtained from the dried plant by distillation over the open fire, is rectified with steam, oil of sp. gr. 0·91 passes over, and there remains a portion, which, after rectification over the open fire, exhibits a sp. gr. of 0·93; hence the specifically lighter oil contained in the fresh plant appears to be changed into the heavier oil by drying. (Geiseler, *N. Br. Arch.* 86, 151.)

Oil of peppermint is limpid, pale yellow, yellow-green to brownish (Pfaff; Zeller, *Stud. über. äther. Oele*, Landau, 1850); it has a peculiar odour, and a strong burning taste, but at the same time cooling, like that of camphor (Pfaff); the American oil is less burning. (Bley, *Br. Arch.* 39, 51.) Sp. gr. 0·92 (Pfaff); 0·89 to 0·92 (Zeller); of the American oil, 0·84 (Bley); 0·907 (Brandes); 0·9083 (Kane); of the oil separated from peppermint-camphor by rectification, 0·8998 (Kane); of English oil, 0·9068 at 18° (Chardin); French, 0·914 at 25° (Chardin); German, 0·9098; rectified, 0·9024 (Martius); 0·86 (Bley); 0·908 at 20° (van Hees, *N. Br. Arch.* 61, 18.). Boiling point between 188° and 193°. (Kane.) — Contains 75·1 p. c. C, 13·4 H, and 11·5 O (Göbel); mean, 78·5 p. c. C, 11·0 H, and 10·5 O (Blanchet & Sell, *Ann. Pharm.* 6, 293); mean, 76·66 p. c. C, 12·15 H, and 11·19 O; the first tenth which passes over in rectification, perhaps containing oil of turpentine, contains 78·42 p. c. C, 11·86 H, and 9·72 O (Kane, *Lond. Ed. Mag. J.* 13, 440; *J. pr. Chem.* 15, 159), whence Blanchet & Sell deduce the formula $C^{12}H^{10}O$, and Kane deduces the formula $C^{21}H^{20}O^2$.

Oil of peppermint treated with *chlorine* acquires a turbid, whitish aspect. (Bley.) It dissolves *iodine*, without evolution of vapour or rise of temperature, acquiring a yellowish to red-brown colour and viscid consistence. (Zeller.) The darker colour disappears on addition of water. The oil does not undergo any alteration of odour. (Flaschoff, *Br. Arch.* 33, 225; Winckler, *Repert.* 32, 271.) It forms with *iodine*, a thick magma (Guyot *J. Hist. phys.* 5, 230); with iodine dissolved in iodide of potassium, it does not form any solid product corresponding to the anisoin of oil of anise. (Will. *Ann. Pharm.* 65, 230.) With *bromine*, it assumes a lemon-yellow colour, becoming lighter on addition of water. (Bley.) — With *concentrated nitric acid*, it forms, with great hissing and rise of temperature, an unctuous mass having an odour of pitch, and depositing a brown resin on addition of water (Bley); ordinary nitric acid colours it purple-red to reddish brown, and thickens it, when heated, at the same time giving off a large quantity of gas. (Zeller.) — With *oil of vitriol*, it turns brown and acquires the thickness of a balsam (Zeller), without losing its odour. (Bley.) — By *chromate of potash* and *sulphuric acid*, it is partially thickened, and coloured yellowish brown, ultimately greenish brown. (Zeller.) — When *hydrochloric acid gas* is passed into it, or when it is treated with the aqueous acid, it acquires a purple-red colour. (Davy.) — Mixed with *ammonia* (alcoholic, aqueous, or gaseous? Gm.) it gradually loses the odour of peppermint and of ammonia, and becomes turbid, depositing indistinct flocks. (Boullay, *N. J. Pharm.* 5, 336.) — Distilled with *chloride of lime*, it yields chloroform; with *hypobromite of lime*, bromoform. (Chautard, *Compt. rend.* 33, 671 and 34, 485.) — It decolorises finely divided *sulphide of lead*, and by the action of the ozone contained in it, converts that compound into sulphate. (Williams, *N. Phil. Mag. J.* 5, 536; *J. pr. Chem.* 59, 504.) — Boiled with *nitroprusside of copper*, it yields a dark deposit and acquires a dark colour. (Heppe, *N. Br. Arch.* 89, 57.) With finely divided *mercuric chloride*, it turns yellow, and blackens immediately when heated, whereupon a somewhat purple-coloured oil distils over, together with acid vapours, while calomel and a little charcoal remain behind. (J. Davy, *Phil. Trans.* 1822, 360.)

Oil of peppermint is slightly soluble in *water*. — Fresh peppermint-water, and fresh elder-flower-water mixed in equal parts, form a mixture which soon acquires a blood-red colour, and after two months, deposits a red substance somewhat soluble in alcohol and ether. If the waters are more than a month old, they do not become coloured. (Recluz, *J. Chim. méd.* 14, 470.)

It dissolves in 1—3 pts. of alcohol of sp. gr. 0·85, forming a clear solution; with a larger quantity, an opalescent solution. (Zeller.) It dissolves in all proportions of alcohol of sp. gr. 0·815, in 10 pts. of alcohol of sp. gr. 0·868. (Bley.) — It dissolves with turbidity in *bisulphide* of carbon. (Bley.)

2. Chlorinated Peppermint-camphor.

WALTER. (1839.) *Ann. Chim. Phys.* 72, 99; *Compt. rend.* 8, 914; *Pogg.* 51, 1, 344; *Ann. Pharm.* 32, 294.

A. *Oxide of Chloromenthene.* (Laurent, *Rev. scient.* 12, 341), $C^{20}H^{15.5}Cl^{2.5}O^2$. — Chlorine gas washed and dried, is passed in the dark through fused peppermint-camphor as long as hydrochloric acid gas continues to escape; the liquid is then heated on the water-bath to expel free chlorine, then washed several times with water and solution of carbonate of soda, and dried in vacuo, after being shaken up with chloride of calcium. — Yellow oil, heavier than water, not crystallisable, having a peculiar odour, and a taste refreshing at first, afterwards bitter and exciting. — It contains 49·16 p. c. C, 6·52 H, 37·80 Cl, and 6·52 O (Walter); it is probably $C^{20}H^{15}Cl^3O^2$. (Gm.) — When *set on fire*, it burns with a smoky green-edged flame. It is decomposed by heat, giving off a large quantity of hydrochloric acid gas, and leaving charcoal. — It is not altered by *chlorine* in the dark, but in sunshine it is transformed into the following chlorinated peppermint-camphor. With cold *oil of vitriol*, it immediately turns red. — It dissolves slightly in *water*, and in *aqueous carbonate of soda*, easily in *alcohol*, *wood-spirit*, *ether*, and *oil of turpentine*. (Walter.)

B. *Oxide of Chloromenthelane.* (Laurent.) $C^{20}H^{12.5}Cl^{5.5}O^2$. — Produced by exposing the compound A to direct sunshine in a bottle filled with chlorine, and purified in the same manner as the preceding. — Green-yellow, viscid oil, containing 35·38 p. c. C, 3·88 H, 56·85 Cl, and 3·89 O. — *Oil of vitriol* colours it after long contact. — It is slightly soluble in cold *alcohol*. (Walter.)

Campholic Acid.

$$C^{20}H^{18}O^4 = C^{20}H^{18},O^4.$$

DELALANDE. (1841.) *N. Ann. Chim. Phys.* 1, 120; *J. pr. Chem.* 23, 390; *Ann. Pharm.* 38, 337; *Repert.* 80, 159.

BARTH. *Ann. Pharm.* 107, 249; abstr. *J. pr. Chem.* 76, 125; *Chem. Centr.* 1858, 784.

Campholsäure, Acide campholique; Acide bornénique. (Laurent, *Rev. scient.* 14, 366.) Discovered by Delalande.

Formation and Preparation. Camphor-vapour is repeatedly passed to and fro, under pressure, over heated potash-lime; the whole is then dissolved in boiling water; the filtrate saturated with acid; and the white, acid, crystalline mass which separates from it, is washed and dried, and recrystallised from alcohol and ether-alcohol. — No gas is evolved when camphor-vapour is passed over potash-lime. (Delalande.)

Properties. White crystals. Melts at 80°, boils at 250°. Vapour-density=6·058. Slightly reddens litmus. (Delalande.)

			Delalande.
20 C	120	70·58	69·76
18 H	18	10·58	10·66
4 O	32	18·84	19·58
$C^{20}H^{18}O^4$	170	100·00	100·00

	Vols.	Density.
C-vapour	20	8·3200
N-gas	18	1·2474
O-gas	2	2·2186
Vapour of campholic acid	2	11·7860
	1	5·8930

$C^{20}H^{18}O^4 = C^{20}H^{16}O^2 + 2\,HO$. (Delalande.)

Decompositions. 1. Distilled with *anhydrous phosphoric acid*, it yields campholene (xiii, 265, in which place, read *campholic* instead of *camphoric acid*), carbonic acid gas being probably evolved at the same time (Delalande):

$C^{20}H^{15}O^4 = 2\,CO + 2\,HO + C^{18}H^{16}$. (Gerhardt, *Traité* 3, 697.)

2. Fused with excess of *hydrate of potash*, it forms a frothy, viscid mass of campholate of potash, which no longer melts with the excess of potash, but at a higher temperature gives off an aromatic smoke, without forming acetic or caprylic acid. (Barth.) — 3. By the dry distillation of its lime-salt, it is resolved into carbonate of lime and campholene, which, after rectification, contains 81·60 p. c. C, 11·61 H, and 6·79 O; therefore $C^{38}H^{34}O^2$. (Delalande.) — Calculation 82·01 p. c. C, 12·23 H, and 5·76 O.

Combinations. Campholic acid is insoluble in *water*, but imparts to it a slight aromatic odour. (Delalande.) With bases, it forms the *Campholates.*

Campholate of Lime. — Aqueous campholic acid is supersaturated with ammonia, the boiling solution is mixed with aqueous chloride of calcium, and the white crystalline powder which precipitates is dried. For the decomposition by dry distillation, *vid sup.*

			Delalande.
20 C	120	60·61	59·97
18 H	18	9·09	9·08
5 O	40	20·20	20·82
Ca	20	10·10	10·13
$C^{20}H^{17}CaO^4,HO$	198	100·00	100·00

Campholate of Silver. — Aqueous campholate of ammonia is mixed with nitrate of silver, and the resulting precipitate is washed and dried. White, curdy flocks.

			Delalande.
20 C	120	43·32	43·00
17 H	17	6·13	6·23
4 O	32	11·56	12·17
Ag	108	38·99	38·60
$C^{20}H^{17}AgO^{4}$	277	100·00	100·00

Campholic acid is soluble in *alcohol* and *ether*. (Delalande.)

Oxygen-nucleus $C^{20}H^{16}O^{2}$.

Camphoric Acid.

$$C^{20}H^{16}O^{8} = C^{20}H^{16}O^{2},O^{6}.$$

Kosegarten. (1785.) *Diss. de camphora et partibus quæ constituunt*, Göttingen, 1785.
Dörffurt. *Abhandl. über den Campher.* Wittenberg u. Zerbst. 1793.
Bouillon-Lagrange. *Ann. Chim.* 23, 123; 27, 19, and 221; *Crell. Ann.* 1799. 2, 221, and 313.
Buchholz. *N. Gehl.* 9, 332.
Brandes. *Schw.* 38, 269; *Repert.* 15, 431; 20, 324; *Br. Arch.* 9, 167.
Liebig. *Pogg.* 20, 41; *Repert.* 37, 470. — *Ann. Pharm.* 22, 50; *Repert.* 40, 131.
Laurent. *Ann. Chim. Phys.* 63, 207; *Ann. Pharm.* 22, 135; *J. pr. Chem.* 11, 287. — *Compt. rend.* 20, 511; *J. pr. Chem.* 35, 501.
Malaguti. *Ann. Chim. Phys.* 64, 157; *Ann. Pharm.* 22, 38; *J. pr. Chem.* 11, 294; *J. Chim. méd.* 13, 107; abstr. *J. Pharm.* 23, 74 and 513. — *Compt. rend.* 41, 625; *J. pr. Chem.* 67, 277; abstr. *Chem. Centralbl.* 1855, 874.
Walter. *Ann. Chim. Phys.* 74, 38; *Ann. Pharm.* 36, 59; *J. pr. Chem.* 21, 241; abstr. *Repert.* 80, 113; *Ann. Chim. Phys.* 75, 212. — *N. Ann. Chim. Phys.* 5, 187; 9, 177; *Ann. Pharm.* 48, 248; abstr. *N. Br. Arch.* 39, 75.

Relating especially to the Isomeric Modifications of Camphoric Acid:

Chautard. *Compt. rend.* 37, 166; *N. J. Pharm.* 24, 168; *J pr. Chem.* 60, 139; *Pogg.* 90, 622; *N. Repert.* 2, 565; abstr. *Chem. Centralbl.* 1853, 636; *N. Br. Arch.* 76, 168.

Dextro-camphoric acid, Camphersäure, Camphorsäure, Rechts-Camphersäure, Camphylsäure, Acid camphorique, Acid camphique. (Laurent.) — Observed and regarded as camphor by Lemery in 1675 (*Cours de Chemie*): discovered by Kosegarten in 1785; regarded as benzoic acid by Dörffurt, a view which was shown to be erroneous by Bouillon-Lagrange and Buchholz.

Formation. By prolonged boiling of common camphor with nitric acid. — It was found in an anatomical preparation preserved in oil of turpentine. (Henry, *Thoms. Ann.* 15, 117; *Schw.* 31, 361.)

Preparation. 1 pt. of camphor is distilled from a retort with 10—11 pts. of strong nitric acid (Dörffurt); (with 25 pts. of nitric acid of sp. gr. 0·33; Lagrange; 12 pts. of sp. gr. 1·25; 4 pts. of fuming nitric acid of sp. gr. 1·55; Buchholz, 7 pts. of nitric acid: Löwig, *Org. Verb.* 2, 611); the distillate is poured back into the retort ten times (Laurent), or till the camphor is completely dissolved and no more nitrous gas is evolved, fresh quantities of nitric acid being added from time to time, if necessary; the acid solution is somewhat concentrated; and the crystals which separate after cooling are collected and purified by repeated crystallisation from water, or by solution in aqueous potash and precipitation with hydrochloric acid (Brandes), and recrystallisation from water or alcohol.

Camphor boiled with nitric acid is at first converted, without evolution of carbonic acid, into a yellow oil which afterwards disappears: the turbid solution, if not boiled long enough, deposits camphoric acid containing camphor, which, by further boiling, is completely converted into camphoric acid. (Liebig.) — The mother-liquor contains free nitric acid and a small quantity of camphoric acid; it becomes syrupy when evaporated, gives a precipitate with aqueous acetate of lead, after neutralisation with ammonia, and yields by distillation a peculiar oil, together with camphoric anhydride. (Laurent.) — When the nitric acid solution of camphoric acid is heated in a porcelain dish, till white fumes escape from it, there remains, if the liquid be slowly cooled, a viscid mass, whose hot aqueous solution yields white crystalline grains on cooling. These crystals are not altered by further boiling; they are difficult to melt, but sublime undecomposed, not however in the crystalline form. They have a slightly sour taste, and dissolve sparingly in water, forming a solution which has an acid reaction,—decomposes alkaline carbonates,—gives a slight precipitate with solution of neutral acetate of lead,—copious with basic acetate of lead, sesquichloride of iron, and mercurous nitrate,—crystalline with copper-salts,—and produces no alteration in solutions of nitrate or ammonio-nitrate of silver, nitrate of lime, chloride of barium and lime-water. (Blumenau, *Ann. Pharm.* 67, 119.) It is perhaps resinous inactive camphoric acid. (Gerhardt, *Traité*, 3, 701.)

Properties. White four-sided laminæ, rectangular and arranged like steps (Kosegarten); small, six-sided pyramids united in plumose groups. (Buchholz.) Belongs to the right prismatic system. — Rhombic prisms *u* (Fig. 55), having the obtuse edges truncated by *i*-faces, and the summits with four-sided acuminations formed by the faces *i* and *u* (Fig. 53). Laurent.) — Melts at 62·5°, solidifies in the crystalline form on cooling, sublimes at a higher temperature (Brandes), with loss of water (Laurent), as camphoric anhydride. (Bouillon.) — Rotatory power 38·873° to the right; weaker after saturation with soda, but increases again on decomposing the soda-salt with hydrochloric acid. (Bouchardt, *Compt. rend.* 28, 319.) — Camphoric acid dissolved in acetic acid exhibits a rotatory power of 38° to the right; dissolved in absolute alcohol, 38·6° to 38·9° to the right. (Biot, *Compt. rend.* 35, 233; *Ann. Pharm.* 84, 160.)

Camphoric acid is inodorous (Brandes); has an odour of saffron (Kosegarten); when heated to 37°, it smells like camphor and fat, likewise sour; at 100° very pungent. (Brandes.) Its taste is bitter, inclining to acid (Kosegarten and others), sweetish, scarcely acid. (Dörffurt.) When taken internally, it passes unaltered into the urine. (Bertagnini, *Cimento*, 1, 363; *Ann. Pharm.* 97, 248.) Reddens litmus. (Kosegarten.)

			Brandes.	Malaguti.	Liebig.	Laurent.
20 C	120	60	61·34	59·49	59·73	59·43
16 H	16	8	5·62	8·03	8·09	7·96
8 O	64	32	33·04	32·48	32·18	32·61
$C^{20}H^{16}O^{8}$	200	100	100·00	100·00	100·00	100·00

Decompositions. — 1. *Heated* in a retort, it is resolved into water and camphoric anhydride, leaving a small quantity of charcoal. (Laurent.) When heated above its melting point, it turns brown and froths, and at a higher temperature leaves a small residue of charcoal, and gives off a small quantity of acid empyreumatic water, empyreumatic oil, and a white opaque sublimate of unaltered camphoric acid (Buchholz), of altered camphoric acid, which no longer reddens litmus and is insoluble in water. (Bouillon.) The acid browned by fusion solidifies on cooling into a brown, transparent, non-crystalline, resinous mass. (Brandes.) When thrown on red-hot coals, it volatilises completely, diffusing a dense aromatic vapour. (Bouillon.) — 2. When heated in the air, it *burns* with a bright flame, leaving a small quantity of charcoal. (Brandes.) — 3. By repeated distillation with *peroxide of manganese* and *sulphuric acid*, it yields acetic acid. (Dörffurt.) — 4. It dissolves in cold *oil of vitriol*, forming a limpid solution from which water precipitates camphoric anhydride; the solution heated in the water bath to 45°, gives off a small quantity of carbonic oxide, and at 60° a larger quantity, with violent effervescence, and is converted into sulphocamphoric acid (xiii, 379). In *fuming oil of vitriol*, it dissolves with yellow to brown colour, likewise forming sulphocamphoric acid. (Walter.) — Distilled with *alcohol* and *oil of vitriol*, it yields ethyl-camphoric acid (Malaguti); with *wood-spirit* and *oil of vitriol*, methyl-camphoric acid. (Loir, *N. Ann. Chim. Phys.* 37, 196; *N. J. Pharm.* 22, 288.) — 5. Heated with syrupy *phosphoric acid* to 195°, it is resolved into: (1), carbonic oxide; (2), a colourless oil, boiling at 121°, having an agreeable odour with somewhat of a turpentine character, of sp. gr. 0·793 at 25°, vapour-density 4·29, and corresponding to the formula $C^{18}H^{16}$; and (3), a pale yellow oil boiling at 250°, having an agreeably aromatic odour, of sp. gr. 0·889 at 21°, of composition not yet determined. (Galle, *Epist. Communication.*) — 6. Distilled with *pentachloride of phosphorus*, it yields camphoric anhydride, hydrochloric acid, and chlorophosphoric acid. (Gerhardt & Chiozza, *Compt. rend.* 36, 1050; *Ann. Pharm.* 87, 290; *J. pr. Chem.* 59, 452; *Instit.* 1853, 255.) — 7. *Potassium* and *sodium* decompose camphoric acid at temperatures far below its melting point, without emission of light, leaving a residue of alkali and charcoal. (Gay-Lussac & Thénard.) — 8. The *lime-salt* when distilled yields phorone (xiii, 342). (Gerhardt & Liès-Bodart, *Compt. rend.* 28, 506; *Ann. Pharm.* 72, 293.) According to Fittig (*Ann. Pharm.* cxii, 309), the oil which passes over in the distillation of camphorate of lime, begins to boil at 60°, the greater portion distilling between this temperature and 270°, leaving however a residue. The portion which passes over in fractional distillation between 200° and 205° has the composition of phorone ($C^{18}H^{14}O^{2}$). The portions boiling at lower temperatures did not yield any definite compound. — 9. The soda and potash-salts distilled with an equal weight of *perchlorovinic ether* (ix, 26), yield a distillate of camphoric anhydride, water, sesquichloride of carbon, carbonic acid, and combustible gases, leaving a residue of hydrochlorate and carbonate of the alkali. (Malaguti.) — 10. Camphoric acid heated for some time to 200° in a sealed tube with *glycerin*, forms camphorin, which may be extracted by ether from the mass, after cooling and mixing with excess of aqueous carbonate of potash, and remains, after evaporation of the ether, as a viscid neutral mass, soluble in ether, and resolved by oxide of lead into camphoric acid and glycerin. (Berthelot, *Compt. rend.* 37, 398; *N. J. Pharm.* 24, 266; *Ann. Pharm.* 88, 311.)

Combinations. With *Water.* — *Aqueous Camphoric acid.* — Camphoric acid dissolves in 400 pts. of cold water (Dörffurt), 200 (Kosegarten), 100 (Buchholz), 80 (Lagrange), and in 24 pts. of boiling water (Dörffurt), 12 (Kosegarten), 11 (Buchholz), 10 (Bouillon). — It dissolves in 88·8 pts. of water at 12·5°; in 70 pts. at 25°; in 61·5 pts. at 37·5°; in 40·7 pts. at 50°; in 23·4 pts. at 62·5°; and 7·2 pts. at 82·5°; in 8·9 pts. at 90°; in 8·6 pts. at 96·25°;—under the ordinary atmospheric pressure, the saturated solution cannot be heated above 96·25°. (Brandes.)

It dissolves without alteration in *nitric acid*. (Laurent.)

Camphorates. — Camphoric acid forms with bases, *bibasic* (*neutral*) salts = $C^{20}H^{14}M^2O^8$, and *mono-basic* (*acid*) salts = $C^{20}H^{15}MO^8$. — The neutral salts are the most easily prepared. — The camphorates are inodorous, have generally a rather bitter taste; yield when heated, an empyreumatic oil, with a residue of charcoal (the lime-salt yielding phorone, the lead-salt camphoric anhydride), and burn in the air with a blue, or sometimes with a red flame. They are decomposed by sulphuric, hydrochloric, nitric and acetic acid, and are but slightly soluble in water. Camphoric anhydride boiled with bases, yields peculiar salts isomeric with the camphorates (*vid. inf.*)

Camphorate of Ammonia. — *Bibasic.* — Dry ammonia-gas is passed over camphoric acid, and the excess of ammonia is expelled by passing dry air over the product at 100°. (Malaguti.) Separates from its solution by evaporation as a saline film composed of slender needles. (Bouillon.) Tasteless and inodorous. (Malaguti.) Has a rather bitter taste (Bouillon), sharply saline. (Brandes.) Reacts slightly acid. Melts when heated, giving off ammonia with intumescence, and volatilises partly undecomposed, leaving a little charcoal (Bouillon, Brandes); yields water, ammonia, and camphoric anhydride. (Laurent.) Dissolves readily in water (Malaguti); in 100 pts. of cold water (in a much smaller quantity, according to Brandes), in 3 pts. of boiling water; the solution gives off ammonia when heated. (Bouillon.) Easily soluble in alcohol. (Bouillon.)

			Malaguti.
2 NH^4O	52	22·22	22·34
$C^{20}H^{14}O^6$	182	77·78	77·66
$C^{20}H^{14}(NH^4)^2O^8$	234	100·00	100·00

b. Four-thirds basic. — By saturating aqueous camphoric acid with bicarbonate of ammonia, small, very white prisms are obtained, which melt somewhat above 100°, have a slightly sour taste, and redden litmus. Dissolves readily in cold water. Dried at 100°, it gives off 19 p. c. water. (Malaguti.) — (18 At. HO = 19·5 p. c.)

Dried at 100°.			Malaguti.
60 C	360	53·89	52·84
60 H	60	8·98	8·98
4 N	56	8·38	8·51
24 O	192	28·75	29·67
$3C^{20}H^{16}O^8 + 4NH^3$	668	100·00	100·00

According to Gerhardt, it is perhaps monocamphorate of ammonia, $C^{20}H^{15}(NH^4)O^8$ (containing in the crystallised state 6 At. water, by calculation 19·9 p. c. Aq.), on which hypothesis, the formula of the dry salt requires 55·3 p. c. C, 8·7 H, and 6·6 N. (*Traité* 3, 702.)

Camphorate of Potash. — *Bibasic.* — Obtained by neutralising aqueous camphoric acid with potash a carbonate of potash. — Small six-sided prisms (Bouillon, Buchholz); needles grouped in tufts. (Brandes.) — The salt prepared with camphoric anhydride and potash forms broad pearly laminæ. (Malaguti, p. 458.) Tastes faint saline, aromatically bitter. Melts when heated, turns brown, and at higher temperatures hardens to a white mass having a sharp taste. (Buchholz, Bouillon.) — It dissolves in 100 pts. of cold, and in 4 pts. of boiling water; also in alcohol (Buchholz, Bouillon); deliquesces slowly on exposure to the air and dissolves in a very small quantity of water. (Brandes.) The less soluble salt is perhaps the monopotassic and the more soluble the bipotassic camphorate. (Gerhardt, *Traité*, 3, 703.)

			Brandes.
2 KO	94·1	34·4	32·5
$C^{20}H^{14}O^6$	182·0	65·9	
$C^{20}H^{14}K^2O^8$	276·4	100·0	

Camphorate of Soda. — *Bibasic.* — Aqueous carbonate of soda is saturated at the boiling heat with camphoric acid; the solution is evaporated to dryness; the residue dissolved in alcohol; and the crystals which separate from the syrupy solution after standing for a long time, are collected and dried over oil of vitriol. (Kemper, *Epist. communication.*) — Limpid indistinct crystals. (Bouillon.) Needles and cauliflower-like masses. (Brandes.) Swells up when heated, melts, blackens, and gives off vapours which burn with deposition of soot. It deliquesces in the air (Brandes, Kemper); dissolves in 200 pts. of cold, and 8 pts. of boiling water (Bouillon); in 80 pts. of cold alcohol. (Brandes.)

			Brandes.	Kemp.
2 NaO	62	25·11	24·32	24·88
$C^{20}H^{14}O^6$	182	74·59		
$C^{20}H^{14}Na^2O^8$	244	100·00		

Camphorate of Baryta. — *Bibasic.* — Obtained by boiling camphoric acid with baryta-water. — Thin laminæ or needles. Taste, rather acid, bitter (Bouillon), saline. (Brandes.) Gives off 11·87 p. c. water when heated (Brandes) (by calculation, 6 At. = 12·5 p. c. Aq). Dissolves in 1·8 pt. water at 19°, and in 600 pts. of boiling water. (Bouillon.)

Dried at 100°.			Brandes.
2 BaO	153	45·67	42·66
$C^{20}H^{14}O^6$	182	54·33	
$C^{20}H^{14}Ba^2O^8$	335	100·00	

Camphorate of Strontia. — White, translucent, crystalline laminæ having a rather bitter saline taste, and still more soluble in water than the baryta-salt. (Brandes.)

Camphorate of Lime. — ***a. Polybasic?*** — White, non-crystalline, slightly bitter, perfectly neutral laminæ, which crumble when exposed to the air, are nearly insoluble in cold water, soluble in 200 pts. of boiling water, insoluble in alcohol, and contain 43·6

p. c. CaO (or CaO,CO^2?), 50 pts. camphoric acid (hyp. anhydrous ?), and 7 p. c. water. (Bouillon.) — The first two determinations cannot be reduced to any probable calculation; the amount of water would correspond to 2 At. for bibasic camphorate of lime. (Kr.)

b. Bibasic. — 100 pts. of camphoric acid dissolve 56 pts of carbonate of lime (2 At. $CaO,CO^2=50$ pts.), and yield the following salt, even when neutralised with lime-water. (Brandes.) Rhombic prisms. (Bernhardi.) Has a slightly saline, bitterish taste; with astringent after-taste; reddens litmus; and when heated, makes a hissing noise, becomes opaque and brown, giving off water and empyreumatic oil. (Buchholz.) For the decomposition by dry distillation, see page 458.

	Anhydrous.		Brandes.
2 CaO	56	23·53	20·24
$C^{20}H^{14}O^6$	182	76·47	79·76
$C^{20}H^{14}Ca^2O^8$	238	100·00	100·00

	Crystals.		Brandes.
2 CaO	56	14·67	14·54
$C^{20}H^{14}O^6$	182	47·64	47·96
16 HO	144	37·69	37·50
$C^{20}H^{14}Ca^2O^8$ + 16 Aq	382	100·00	100·00

Camphorate of Magnesia. — *Bibasic.* — Translucent bitter prisms, which contain 17 p. c. MgO ($C^{20}H^{14}Mg^2O^8$=18·0 p. c. MgO), become moist on exposure to the air and dissolve in 6·5 pts. of water at 2·5°. Brandes.) — When camphoric acid is heated with water and excess of magnesia alba, the filtrate yields by evaporation, under apparently similar circumstances, crystals varying in their amount of water, whilst another part of the salt effloresces. — The crystals effloresce in the air, and give off their water of crystallisation below 120°, without suffering any further alteration at 200°. Those which contain 15 At. water, dissolve in 2·5 pts. water at 20°. (Kemper, *Epist. comm.*) — Camphorate of magnesia dissolves in 54 pts. of absolute alcohol at 3·7° (Brandes); it is insoluble in cold alcohol, and dissolves with decomposition in hot alcohol. (Bouillon.)

	Crystals.		Kemper. *mean.*
2 MgO	40	11·20	11·21
$C^{20}H^{14}O^6$	182	50·98	
15 HO	135	37·82	38·04
$C^{20}H^{14}Mg^2O^8$ + 15HO	357	100·00	

	Crystals.		Kemper.
2 MgO	40	9·13	9·04
$C^{20}H^{14}O^6$	182	41·55	
24 HO	216	49·32	49·82
$C^{20}H^{14}Mg^2O^8$ + 24 HO	438	100·00	

	Crystals and effloresced salt.		Kemper.	
2 MgO	40	8·60	8·58	8·91
$C^{20}H^{14}O^6$	182	39·14		
27 HO	243	52·26	52·48	53·58
$C^{20}H^{14}Mg^2O^8$ + 27 HO	465	100·00		

b. Monobasic? When the aqueous solution of the bibasic salt is heated, the camphoric acid separated from an equal quantity of it, and the solution left to cool, it deposits camphoric acid, but does not form a monobasic salt. (Kemper.)

Camphorate of Alumina. — Obtained by boiling hydrate of alumina with camphoric acid and water, and evaporating the filtered solution. — White powder, having a harsh, sour, rather bitter taste, capable of reddening litmus, permanent in the air, soluble in 200 pts. of cold, and in a smaller quantity of hot water, sparingly soluble in cold, easily in hot alcohol. (Bouillon.)

Uranic Camphorate. — Aqueous uranic salts form a yellowish precipitate with camphorate of potash. (Brandes.)

Camphorate of Manganese. — By boiling carbonate of manganese with camphoric acid and water, a solution is produced, which, when left to evaporate, yields crystalline laminæ very soluble in water. (Brandes.) Alkaline camphorates do not precipitate manganous salts. (Brandes.)

Camphorate of Zinc. — Obtained by decomposing the aqueous solutions of the alkaline camphorates with zinc-salts. White precipitate. (Brandes.)

Stannous Camphorate. — White precipitate produced by decomposing the aqueous solution of an alkaline camphorate with protochloride of tin. (Brandes.) The aqueous solution of neutral camphorate of magnesia forms with protochloride of tin, a precipitate which disappears at first, but afterwards becomes permanent. (Kemper.)

Camphorate of Lead. — *Bibasic.* — Obtained by precipitating aqueous nitrate of lead with camphorate of potash (Brandes); or by boiling the aqueous solution of camphoric acid with neutral acetate of lead, and washing the resulting precipitate with hot water. (Liebig, Boucsein.) — White precipitate insoluble in water. (Brandes.) When subjected to dry distillation, it gives off camphoric anhydride, together with a small quantity of phorone, and leaves oxide of lead, coloured grey or black by separated charcoal. (Boucsein, *N. Br. Arch.* 83, 277.)

Al 100°.			Boucsein.
20 C	120·0	29·60	29·29
14 H	14·0	3·45	3·48
6 O	48·0	11·85	12·55
2 PbO	223·4	55·10	54·68
$C^{20}H^{14}Pb^2O^8$	405·4	100·00	100·00

Contains 54·5 p. c. oxide of lead.

Ferric Camphorate. — Obtained by precipitating aqueous ferric salts with aqueous camphorate of potash. — Light brown, bulky precipitate insoluble in water. (Brandes.)

Camphorate of magnesia does not precipitate nitrate of *cobalt.* (Kemper.)

Camphorate of Nickel. — By precipitating aqueous nickel-salts with aqueous camphorate of potash. Greenish white precipitate, sparingly soluble in water. (Brandes.)

Camphorate of Copper. — *Bibasic.* — Produced by precipitating aqueous sulphate of copper with camphorate of potash (Brandes); with neutral camphorate of ammonia (Malaguti). — Light green precipitate, which, when carefully heated, becomes sky-blue, and at a higher temperature, dark green, then white, and suddenly black, burns with bright flame and waxy odour, and leaves cupric oxide. It is nearly insoluble in water, and forms a crystalline compound with ammonia.

			Brandes.	Malaguti.
2 CuO	79·4	30·3	29·6	30·01
$C^{20}H^{14}O^{6}$	182·0	69·7		
$C^{20}H^{14}Cu^{2}O^{8}$	261·4	100·0		

Mercurous Camphorate. — *Bibasic ?* — By precipitating aqueous mercurous nitrate with camphorate of soda (Brandes), with camphorate of potash (Harff, *N. Br. Arch.* 5, 300). — White powder, greyish white after drying (Brandes); has a bitterish taste (Harff). Turns grey in sunshine. When heated in a tube, it sublimes with very slight alteration, leaving a residue of charcoal. It is not sensibly altered by cold oil of vitriol; but hot oil of vitriol decomposes it, with separation of camphoric acid. Potash separates black mercurous oxide. (Harff.) — It is insoluble in cold water (nearly insoluble, according to Brandes). — By boiling water or cold alcohol, it is partly converted into mercuric camphorate. — It unites with ammonia, forming basic ammonio-mercurous camphorate. Dissolves in 1666 pts. of ether. (Harff.)

			Harff.
2 $Hg^{2}O$	416	69·5	63·9
$C^{20}H^{14}O^{6}$	182	30·5	
$C^{20}H^{14}Hg^{4}O^{8}$?	598	100·0	

Basic Ammonio-mercurous Camphorate. — Produced by passing ammonia-gas into water in which mercurous camphorate is suspended, — black, nearly tasteless powder, containing 81·76 p. c. $Hg^{2}O$. The moist salt rubbed in the hand yields metallic mercury. Leaves charcoal when ignited. When dissolved in nitric acid, it leaves a white powder; dissolved in glacial acetic acid, it leaves mercury; gives off ammonia when heated with potash. — Insoluble in water, alcohol, and ether. (Harff.)

Mercuric Camphorate. — *Bibasic ?* — By precipitating aqueous mercuric nitrate with camphorate of potash. — White precipitate, having a rather bitter taste. — Heated in a tube, it sublimes partly without decomposition, leaving a residue of charcoal. — It is not sensibly altered by cold oil of vitriol, but is decomposed by hot oil of vitriol, with separation of camphoric acid, and by potash, with separation of mercuric oxide. — It is nearly insoluble in cold, more soluble in boiling, water; dissolves in nitric and hydrochloric acid, and unites with ammonia, forming basic ammonio-mercuric camphorate. Insoluble in alcohol, but soluble in 1666 pts. of ether. (Harff.)

			Harff.
2 HgO	216	54·2	48·8
$C^{20}H^{14}O^{6}$	182	45·8	
$C^{20}H^{14}Hg^{2}O^{8}$	398	100·0	

Basic Ammonio-mercuric Camphorate. — Obtained by passing ammonia-gas into water in which mercuric camphorate is suspended. — White, nearly tasteless powder, containing 70·0 p. c. HgO, and leaving charcoal when ignited. Dissolves in nitric acid, leaving a white powder; similarly in hydrochloric acid. With potash it turns yellow and gives off ammonia. Insoluble in water and alcohol; soluble in 1000 pts. of ether. (Harff)

Camphorate of Silver. — *Bibasic.* — Obtained by precipitating aqueous nitrate of silver with camphorate of potash (Brandes), with camphorate of ammonia (Laurent). — White precipitate (Brandes), electric (Laurent). — Turns bluish when exposed to light. Melts when heated and burns away, leaving metallic silver. (Brandes.)

			Brandes.	Laurent.
2 AgO	232	56·0	55·1	55·4
$C^{20}H^{14}O^{6}$	182	44·0		
$C^{20}H^{14}Ag^{2}O^{8}$	414	100·0		

Camphorate of Platinum. — Aqueous camphorate of soda forms with bichloride of platinum a white precipitate, sparingly soluble in water. (Brandes.) Camphorate of magnesia does not precipitate bichloride of platinum. (Kemper.)

Camphoric acid dissolves in *alcohol*, in *ether*, and in *oils*, both *fixed* and *volatile*. — It dissolves in ½ pt. boiling, and 1 pt. cold alcohol (Buchholz); in 0·94 pts. alcohol at 8·7°, in 0·89 pts. at 12·5°, in 0·79 pts. at 25°, in 0·59 pts. at 37·5°, and in 0·68 pts. at 62·5°. (Brandes.)

Appendix to Camphoric Acid.

Isomeric Modifications of Camphoric Acid.

1. *Lævo-camphoric acid.* — Obtained from the lævo-rotatory camphor of *Matricaria Parthenium, L.* (p. 350), by boiling with nitric acid, in the same manner as ordinary camphoric acid from ordinary camphor. — The acid thus obtained possesses lævo-rotatory power equal in amount to the dextro-rotatory power of ordinary camphoric acid, with which it agrees in all other properties. (Chautard.)

2. *Paracamphoric acid.* *Acide racémique camphorique.* — By evaporating an aqueous mixture of equal quantities of ordinary camphoric and lævo-camphoric acid, crystals are obtained, destitute of rotatory power, but agreeing in other respects with camphoric acid. (Chautard.)

Methyl-camphoric Acid.

$$C^{22}H^{18}O^{8} = C^{2}H^{4}O^{2},C^{20}H^{14}O^{6}.$$

Loir. (1853.) *N. Ann. Chim. Phys.* 37, 196; *N. J. Pharm.* 22, 288; *N. Ann. Chim. Phys.* 38, 483.

Methylcamphersäure, Methylencamphersäure, Camphermethylensäure, Acide camphomethylique, Acid methyl-camphorique.

Formation and Preparation. By distilling 2 pts. of camphoric acid with 4 pts. wood-spirit and 1 pt. oil of vitriol, cohobating the distillate twice over the residue, mixing the alcoholic solution of the viscid, brown distillate with water, washing the viscid oil thereby separated wit water, and leaving it to stand exposed to the air or under water till it solidifies in the crystalline form. The collected crystalline masses are pressed between filtering paper and boiled with water, set aside till they have again solidified in the crystalline form, then collected and dried over oil of vitriol.

Properties. Rhombic prisms belonging to the right prismatic system, having the acute lateral edges truncated, and with 4-sided summits formed by the faces of a rhombic octohedron. *Fig.* 67 without *p.* — $u : u = 106^\circ\ 30'$; $u : t = 126^\circ\ 45'$; $a : u = 135^\circ\ 50'$; $a : t = 115^\circ\ 25'$; $a : a =$ over the obtuse lateral edge of the rhombic prism $= 129^\circ\ 10'$; $a : a$ over the acute lateral edge of the rhombic prism $= 109^\circ\ 50'$. — By rapid evaporation of the ethereal solution, hemihedral crystals are obtained: in that case only the faces *a* and *t* appear, and, by the predominance of the *t*-faces, the crystals acquire the appearance of four-sided tables. Cleavage at right angles to *t*.

Melting point 68°. — Rotatory power 51·4° to the right. The alcoholic solution reddens litmus.

			Loir.
22 C	132	61·60	61·37
18 H	18	8·41	8·48
8 O	64	29·99	30·15
$C^{2}H^{4}O^{2},C^{20}H^{14}O^{6}$	214	100·00	100·00

Decompositions. 1. When *heated,* it forms without loss of weight a viscid oil, which becomes opaque some hours after cooling; if heated above the melting point, it is resolved into camphoric anhydride, a small quantity of viscid liquid (perhaps camphorate of methyl), and a small quantity of charcoal. — Burns, *when set on fire,* with a bright fuliginous flame. — 3. By distillation with hydrate of potash, it is resolved into wood-spirit and camphorate of potash.

Combinations. Methylcamphoric acid is slightly soluble in *water.* — Aqueous or alcoholic methylcamphoric acid is not altered by *lime-water* or dissolved *baryta-salts;* it is clouded by baryta-water, but becomes clear again on the addition of a small quantity of nitric acid; with aqueous *acetate of lead,* it forms a white crystalline precipitate, soluble in excess of the precipitant; with *cupric acetate,* a crystalline greenish precipitate; it is but slightly clouded by *nitrate of silver,* but reduces *oxide of silver.*

Methylcamphoric acid dissolves readily in *alcohol, ether,* or *chloroform,* and crystallises by evaporation of the solvent.

Camphorate of Ethyl.

$$C^{28}H^{24}O^{8} = 2C^{4}H^{5}O,C^{20}H^{14}O^{6}.$$

MALAGUTI. (1837.) *Ann. Chim. Phys.* 64, 152; *J. pr. Chem.* 11, 294; *Ann. Pharm.* 22, 32; abstr. *J. Pharm.* 23, 75, and 513; *Repert.* 61, 123.

Camphoric ether, Camphernaphtha, camphersäures Aethyloxyd, Campherformester, Camphorate d'éthyle, Ether camphorique.

Formation and Preparation. Ethyl-camphoric acid is subjected to dry distillation; the distillate, which solidifies in the crystalline form, is dissolved in hot alcohol; the solution is left to itself till it has deposited camphoric anhydride; the mother-liquor is precipitated by water; the oil which separates and gradually becomes thicker, is boiled with weak aqueous potash, washed with water, dried in vacuo, and distilled *per se*; and the distillate is again washed with water, and dried in vacuo.

Properties. Amber-yellow oil, of sp. gr. 1·029 at 16°, and boiling at 285° — 287°. Has a strong, unpleasant odour, and a bitter, very disagreeable taste. Neutral.

			Malaguti.
28 C	168	65·6	64·1
24 H	24	8·9	9·4
8 O	64	25·5	26·5
$2C^4H^5O,C^{20}H^{14}O^6$	256	100·0	100·0

Decompositions. 1. Turns brown when heated above its boiling point, and leaves a black residue, yielding, however, a distillate of pure camphoric ether. — 2. It requires to be heated before it can be set on fire by a flaming body, and then burns with a quiet, white, strongly fuliginous flame. — 3. With dry *chlorine gas*, it turns yellow, becomes heated, increases in volume, gives off hydrochloric acid, and forms chlorinated camphoric ether. (Malaguti, *Ann. Chim. Phys.* 70, 360.) Acetic acid is formed at the same time. — 4. It dissolves in hot *oil of vitriol* without evolution of sulphurous acid, but does not separate on addition of water: the solution smells like oil of lavender. — 5. It is not decomposed by *nitric* or *hydrochloric acid*, even with aid of heat. — 6. When boiled for a very long time with strong aqueous *potash*, it forms alcohol and camphorate of potash. — 7. It is not decomposed by *ammonia*.

Combinations. Insoluble in *water*. — It dissolves in cold *oil of vitriol*, and is precipitated in its original state by water. — It dissolves *iodine*, which can afterwards be only partially separated by heat, without decomposing the camphoric ether. It dissolves *bromine*, and that substance may be completely expelled from it by heat.

It dissolves in *alcohol* and in *ether*. (Malaguti.)

Ethylcamphoric Acid.

$$C^{24}H^{20}O^8 = C^4H^6O^2,C^{20}H^{14}O^6.$$

MALAGUTI. (1837.) *Ann. Chim. Phys.* 64, 152; *J. pr. Chem.* 11, 294; *Ann. Pharm.* 22, 45; abstr. *J. Pharm.* 23, 75, and 513; *Repert.* 61; 123.

Camphovinic acid, Weincamphersäure, Aethyl-camphersäure, Acide camphovinique, Acide camphoéthylique, Acide ethylcamphorique.

Formation and Preparation. 2 pts. of camphoric acid or camphoric anhydride are distilled with 4 pts. of absolute alcohol and 1 pt. of oil of vitriol; the distillate amounting to about half the mixture is cohobated; the residue in the retort is mixed with water; the oil which then separates is washed with water, dissolved in aqueous potash, precipitated by hydrochloric acid, and dissolved in alcohol after washing with water; the solution is left to evaporate; and the residue is dried at 130°.

Properties. Limpid, syrupy liquid, of sp. gr. 1·095 at 20·5°. Begins to boil at 196°, but the boiling point soon rises, in consequence of decomposition. Has a rather peculiar odour, disagreeably bitter but not acid. Reddens litmus after some time only.

			Malaguti.
24 C	144	63·15	62·55
20 C	20	8·77	8·87
8 O	64	28·08	28·58
$C^4H^6O^2,C^{20}H^{14}O^6$	228	100·00	100·00

Ethyl-camphoric acid is resolved by *heat* into camphoric anhydride, camphoric ether, water, a small quantity of alcohol, and carburetted hydrogen gas; by prolonged contact with *water*, or by boiling therewith, it yields camphoric acid and camphoric ether, and by continued boiling with aqueous *alkali*, it is converted into camphoric ether and an alkaline camphorate.

Combinations. Ethylcamphoric acid unites with bases, forming the *ethylcamphorates.* These salts dissolve in aqueous *alkalis* and are precipitated therefrom by acids. The *lime, baryta, strontia, magnesia,* and *manganous* salts are soluble in water; the *alumina, iron, zinc, lead, copper* and *mercury* salts are insoluble or sparingly soluble in water.

Ethylcamphorate of Ammonia. — An alcoholic solution of ethylcamphoric acid is not quite saturated with ammonia, the unneutralised portion of the acid is separated by water, and the filtrate is evaporated. — The salt has an alkaline reaction, but does not contain free ammonia.

Ethylcamphorate of Silver. — Aqueous ethylcamphorate of ammonia is precipitated by nitrate of silver, and the precipitate is dried at 100°. When heated, it blackens, melts, gives off a fragrant odour, and leaves 31·9 p. c. silver ($C^{24}H^{19}AgO^8 = 32{\cdot}2$ p. c. Ag).

Ethylcamphorate of Copper. — By decomposing ethylcamphorate of ammonia with sulphate of copper, a sesquibasic salt is produced, containing 4 At. water.

Ethylcamphoric acid is slightly soluble in *alcohol* and in *ether.* (Malaguti.)

Chlorinated Camphoric Ether.

$$C^{28}H^{20}Cl^4O^8 = 2C^4H^3Cl^2O,C^{20}H^{14}O^6.$$

Malaguti. (1839.) *Ann. Chim. Phys.* 70, 360; *J. pr. Chem.* 18, 45; *Ann. Pharm.* 32, 33; *N. Br. Arch.* 12, 150; *Repert.* 70, 134.

Chlorcamphernaphtha, Campher-Chlorvinester, Ether camphorique chloruré, Camphorate d'ethyle bichloré (comp. vii, 309).

Preparation. Camphorate of ethyl is saturated with dry chlorine; the excess of chlorine is removed by heating the yellow liquid; and the cooled thickish mass is washed, first with weak aqueous potash, then repeatedly with weak alcohol, dissolved in absolute alcohol, and evaporated in vacuo.

Properties. Limpid, viscid oil of sp. gr. 1·386 at 14°. Has an agreeable odour, and a strong, persistently bitter taste.

			Malaguti.
28 C	168	42·6	42·1
20 H	20	5·1	5·4
4 Cl	142	36·0	35·3
8 O	64	16·3	17·2
$2C^4H^3Cl^2O,C^{20}H^{14}O^6$	394	100·0	100·0

Decompositions. 1. When *heated,* it becomes viscid and then decomposes. — 2. *Aqueous potash* acts upon it very slowly, if at all; by *alcoholic potash,* it is converted into camphorate and acetate of potash and chloride of potassium:

$$C^{28}H^{20}Cl^4O^8 + 8(KO,HO) = C^{20}H^{14}K^2O^8 + 2C^4H^3KO^4 + 4KCl + 8HO.$$

Combinations It dissolves in 8 pts. of *alcohol* and in an equal quantity of *ether.* (Malaguti.)

Oxygen-nucleus $C^{20}H^{14}O^4$.

Camphoric Anhydride.

$$C^{20}H^{14}O^6 = C^{20}H^{14}O^4,O^2.$$

BOUILLON-LAGRANGE. (1799.) *Ann. Chim.* 23, 153; *Crell. Ann.* 1799, 2, 221.

LAURENT. *Ann. Chim. Phys.* 63, 207; *Ann. Pharm.* 22, 41, and 135; abstr. *J. Pharm.* 23, 513.

MALAGUTI. *Ann. Chim. Phys.* 64, 152; *J. pr. Chem.* 11, 294; *Ann. Pharm.* 22, 41; *J. Chim. méd.* 13, 107.

Anhydrous Camphoric acid, Oxyde de Camphèse. (Laurent.)

Formation. By the action of heat on camphoric acid. (Bouillon, Laurent.) Also on ethyl-camphoric acid (Malaguti), methyl-camphoric acid (Loir. *N. Ann. Chim. Phys.* 37, 196), camphoranilic acid (Laurent & Gerhardt, *N. Ann. Chim. Phys.* 24, 191), camphorate of lead (Boucsein, *N. Br. Arch.* 83, 773), and by heating alkaline camphorates with an equal quantity of perchlorovinic ether. (Malaguti, *Compt. rend.* 41, 625; *J. pr. Chem.* 67, 277; *Chem. Centr.* 1855, 874.) — 2. By the action of pentachloride of phosphorus on camphoric acid. (Gerhardt & Chiozza, *Compt. rend.* 36, 1050; *Ann. Pharm.* 87, 290; *J. pr. Chem.* 59, 452.) — 3. By dissolving camphoric acid in oil of vitriol, and precipitating the solution with water. (Walter, *N. Ann. Chim. Phys.* 59, 177.)

Preparation. 1. Camphoric acid is distilled *per se,* and the white sublimate which settles on the neck of the retort is collected. (Bouillon, Lagrange.) — 2. Ethyl-camphoric acid is distilled; the solidifying distillate is dissolved in boiling alcohol; and the crystals of camphoric anhydride which separate after the cooling and further evaporation of the solution, are separated from the camphoric ether which remains dissolved in the mother-liquor, and purified by recrystallisation from alcohol. (Malaguti.)

Properties. Long white prisms. (Malaguti.) — Crystallises from alcohol in long, upright, six-sided, very flat prisms, with rhombic base and broad faces on the two obtuse vertical lateral edges; the terminal faces are replaced by acumination-faces, two of which are rhombic and rest upon the acute vertical lateral edges, and two triangular, resting on the two vertical faces which replace the obtuse lateral edges of the prism. (Laurent.) Sp. gr. 1·194 at 20·5°; begins to sublime in long needles at 130°; melts at 217° (Malaguti); at about 220° (Boucscin); distils completely at 270°. — Tasteless at first, but after a while produces irritation in the throat. Neutral. Electric when rubbed. (Malaguti.)

			Malaguti.
20 C	120	65·93	66·24
14 H	14	7·69	7·90
6 O	48	26·38	25·86
$C^{20}H^{14}O^{6}$	182	100·00	100·00

	Liebig.	Laurent.	Walter.	Boucsein.
20 C	65·71	64·87	65·55	65·70
14 H	7·85	7·87	7·91	7·76
6 O	26·44	27·26	26·54	26·54
$C^{20}H^{14}O^{6}$	100·00	100·00	100·00	100·00

The colourless solution of camphoric anhydride in cold *oil of vitriol* gives off carbonic oxide when heated to 45°—50°, abundantly at 60°, and forms sulphocamphoric acid (xiii, 379, Walter, *N. Ann. Chim. Phys.* 9, 177). Camphoric anhydride dissolves in anhydrous or in fuming sulphuric acid, with evolution of sulphurous acid, forming a dark-coloured liquid. — Distilled with *oil of vitriol* and *absolute alcohol*, it yields ethylcamphoric acid. (Malaguti.) — 2. When carefully distilled with *anhydrous phosphoric acid*, it gives off a gaseous mixture consisting of 1 vol. carbonic acid and 4 vols. carbonic oxide, yields a yellowish oil having a penetrating, but not disagreeable odour, and isomeric with oil of turpentine or with naphtha (88·30 p. c. C, 11·27 H), and leaves a black acid residue. (Walter, *Ann. Chim. Phys.* 75, 212.) — 3. Alcoholic camphoric anhydride saturated at the boiling heat with *ammonia-gas* (or with ammonia or bicarbonate of ammonia, according to Malaguti), yields camphoramate of ammonia (Laurent, *Compt. chim.* 1845, 141; *Ann. Pharm.* 60, 326), and probably also camphoramide. (Laurent, *Rev. scient.* 10, 123; *J. pr. Chem.* 27, 314.) — 4. It is not acted upon by aniline in the cold, but when heated with it, yields camphoranilic acid and camphoranil. (Laurent & Gerhardt, *N. Ann. Chim. Phys.* 24, 191.)

Combinations. Camphoric anhydride dissolves sparingly in *cold water*, somewhat more abundantly in *boiling water* (Malaguti), though with difficulty, and by prolonged boiling with water, is completely converted into camphoric acid. (Laurent, Boucsein.) According to Malaguti, the hot aqueous solution deposits unaltered camphoric anhydride, even after two hours' boiling.

Camphoric anhydride does not absorb *ammonia* in the cold. (Malaguti, Laurent, *Compt. chim.* 1845, 141.) — When ammonia-gas is passed over melting camphoric anhydride, a yellowish liquid distils over, which on cooling solidifies in a transparent mass, easily soluble in alcohol and water, and not giving off ammonia when boiled with aqueous potash.

Salts of Camphoric anhydride. Alcoholic camphoric anhydride does not precipitate metallic salts. (Boucsein.) — Camphoric anhydride appears to be capable of forming peculiar salts with bases (Laurent, *Compt. chim.* 1845, 141): it first unites with water, and then forms with bases, salts which have the same composition as the ordinary camphorates, but exhibit different properties. (Malaguti.) — Camphoric anhydride boiled with aqueous *potash* forms a camphorate of potash which crystallises, not in needles like the ordinary camphorate, but in broad pearly laminæ. (Malaguti.) — The solution produced by boiling camphoric anhydride for some time with *milk of lime,* deposits by evaporation, films, which require long boiling with water to dissolve them: alcohol added to the solution throws down small white needles containing 14 p. c. Ca, agreeing approximately with the formula $C^{20}H^{27}Ca^{3}O^{14}$ (calculation = 13·67 p. c. Ca). Laurent (*Compt. chim.* 1845, 141; *Ann. Pharm.* 60, 330). — The aqueous solution of the potash-salt added to aqueous *sulphate of copper,* forms a precipitate containing 30·14 p. c. cupric oxide. — The aqueous solution of camphoric anhydride is not precipitated by *neutral acetate of lead.* (Malaguti.)

Camphoric anhydride dissolves in *cold,* and abundantly in *hot alcohol* (Malaguti), less easily than camphoric acid. (Laurent.) — It dissolves in cold *ether,* more readily than in alcohol. (Malaguti.)

Oxygen-nucleus $C^{20}H^{12}O^{6}$.

Cantharidin.

$$C^{20}H^{12}O^{8} = C^{20}H^{12}O^{6},O^{2}\,?$$

Robiquet. (1812.) *Ann. Chim.* 76, 302; *Schw.* 4, 198; *J. Pharm.* 14, 363; *J. Pharm.* 21, 123.

Thierry. *J. Pharm.* 21, 44; *Ann. Pharm.* 15, 314; *J. Chim. méd.* 11, 139; *J. pr. Chem.* 8, 54.

Regnault. *Ann. Chim. Phys.* 68, 159; *Ann. Pharm.* 29, 314; *J. pr. Chem.* 16, 316.

Lavini & Sobrero. *N. J. Pharm.* 7, 467; abstr. *Repert.* 100, 562.

W. Procter, Jun. *Pharm. J. Trans.* 12, 287; *Viertelj. J. Pharm.* 2, 322.

Vesicating principle of Cantharides, Canthariden-campher. Discovered by Robiquet in 1812.

Source. In Spanish flies or cantharides (*Lytta vesicatoria, Fabric.*); in *Lytta vittata* (Dana, *Schw.* 30, 247); *Mylabris Cichorii* (Bretonneau, *J. Pharm.* 14, 67); in *Meloë violaceus, M. autumnalis, M. fucia, M. punctatus, M. variegatus, M. Scabrosus, M. majalis.* (Lavini & Sobrero.)

Preparation. From *Cantharides* or *Mylabris Cichorii,* both of which contain about 0·4 p. c. of cantharidin (Warner, *Viertelj. pr. Pharm.* 6, 86), more easily from the latter, as they contain less oil. (Robiquet.) — 1. Aqueous extract of cantharides is evaporated to dryness; the residue is exhausted with hot strong alcohol; the solution evaporated to an extract; this extract is exhausted with warm ether; and the solution left to evaporate in the air. The residue is treated with cold alcohol to remove a yellow substance, and the residual cantharidin is dried. (Robiquet.) — Lavini & Sobrero boil powdered meloë with water, evaporate the decoction, exhaust the residue with warm ether, and leave the ether to evaporate. — Direct exhaustion with alcohol yields a very oily extract, which does not deposit cantharidin. (Lavini & Sobrero.) — 2. Powder of cantharides is exhausted in a displacement apparatus, with ether made to run through it very slowly; the nearly pure oil which first passes through is collected apart; and only the following tinctures are treated for cantharidin, by distilling off the ether, and purifying the crystals which separate from the residue, by pressure and recrystallisation from alcohol. (Robiquet.) — Thierry likewise uses ether-alcohol of sp. gr. 0·82, or alcohol of sp. gr. 0·85, and macerates the cantharides therewith for a few days, before introducing them into the displacement apparatus. He distils off the ether and alcohol from the extracts, separates the oil from the residue, and obtains cantharidin from the aqueous solution by crystallisation, pressure, and recrystallisation with the aid of animal charcoal.

Properties. Colourless, rectangular four-sided prisms belonging to the right prismatic system, with four-sided summits resting on the faces of the prism. Faces p, m, i and u of Fig. 53. — $i : i = 107^\circ\ 30'$; $i : p$ — $121^\circ\ 15'$; $u : u = 123^\circ\ 28'$; $u : m = 118^\circ\ 15'$; $i : u = 138^\circ\ 55'$. The crystals exhibit a tabular form from predominance of the p- or m- face. Cleavage parallel to p and m. (Marignac, *Recherches sur les formes crystallines*, Geneva. 1855.) — Rhombic prisms or micaceous laminæ. (Robiquet, Thierry.) Generally, four-sided flat prisms, grooved so as to give them a step-like appearance. Separates from ether or acetic acid, in flat, oblique, four-sided prisms with dihedral summits, and belonging to the rectangular system. (Procter.) — Cantharidin does not volatilise with vapour of water, nor sensibly in a test-tube at 104°; at 121° it volatilises slowly, at 182° somewhat more quickly; it melts at 208°—210° (at 210°, according to Robiquet and others), and then volatilises quickly in white fumes, which condense in fine needles (Robiquet and others), in rectangular prisms having a strong lustre and sometimes iridescent. (Procter.)—Inodorous. Neutral. Sinks in nitric acid of sp. gr. 1·38. (Procter.) Placed on the skin, even in extremely small quantities, it raises blisters (Robiquet and others);—not by itself in the dry state, but quickly when moistened with oil. (Procter.)

			Regnault.	Lavini & Sobrero.
20 C	120	61·22	60·36	61·17
12 H	12	6·12	6·22	6·30
8 O	64	32·66	33·42	32·53
$C^{20}H^{12}O^{8}$	196	100·00	100·00	100·00

According to most authors, it is $C^{10}H^{6}O^{4}$, but Gmelin placed it among compounds containing 20 At. C. (Kr.) — Isomeric with picrotoxin.

Decompositions. 1. Heated on platinum foil, it *burns* with a white flame, leaving an easily combustible charcoal. (Lavini & Sobrero.) — 2. When cantharidin moistened with oil of vitriol is heated on a watch-glass to commencing ebullition, and *chromate of potash* is then added, brisk effervescence takes place, a splendid green mass is formed, and after some hours, a solution which ultimately becomes turbid and of a leaf-green colour. (Eboli, *Messagero de Lima; N. Br. Arch.* 87, 187.)

Combinations. Cantharidin is insoluble in *water*, whether cold or boiling. It is however rendered soluble in water by the yellow matter of cantharides, so that hot water extracts therefrom the whole of the cantharidin. (Robiquet and others.) — It dissolves without colour in hot *oil of vitriol*, and is precipitated by water. — It is nearly insoluble in cold *hydrochloric acid* of sp. gr. 1·18, and in cold *phosphoric acid;* a little more soluble in those acids when hot. — It dissolves abundantly in boiling *nitric acid*, scarcely at all in hot *formic acid*, slightly in cold, more easily in hot *acetic acid* of sp. gr. 1·041; 40 pts. of glacial acetic acid dissolve completely with the aid of heat, 1 pt. of cantharidin. According to Robiquet, it is insoluble in acetic acid. From all these liquids, the cantharidin crystallises on cooling. (Procter and others.)

It is insoluble in aqueous *ammonia* (Thierry), slightly soluble in the hot liquid (Procter). — It dissolves in potash and soda-ley, and is precipitated therefrom by acetic acid. (Thierry.)

Slightly soluble in *alcohol* and *acetate of ethyl* when cold, more soluble when heated; less in *wood-spirit*, more in *ether* (in 34 pts. of cold ether, according to Warner); its best solvents are *acetone* and *chloroform*, which latter abstracts cantharadin from its aqueous solutions. — It dissolves in hot *oil of turpentine*, in the *oils of cinnamon*, *cloves*, and *sassafras*, also in *almond-oil*, *olive-oil*, and *lard*, and crystallises on cooling. (Thierry and others.)—According to Procter, Cantharadin is extracted from cantharides by glacial acetic acid, oil of turpentine, and olive-oil, but only the last-mentioned retains any considerable quantity of it in solution after cooling.

Appendix to Cantharidin.

Volatile Acrid Principles.

The irritating action of certain plants on the organs of sensation, is in all probability due to peculiar substances contained in them but not separable, and perhaps allied to the volatile oils or camphors. They were first distinguished as peculiar substances (*Principia acra plantarum*) existing in certain plants by Gren (*Syst. Handb. d. Chem.* 1794, 2, 229); they are very volatile, are lost in the drying of the plants, generally pass over in the distillate when the plants are distilled with water, and impart to the distillate their acrid burning taste; in some cases, however they are decomposed during distillation. They are often found in the alcoholic extract of plants, and are the cause of the exciting action of such extracts on the organs of sensation: they are especially distinguished by their easy destructibility. The most important of these volatile acrid principles are the following:

Volatile acrid principle in Aconitum Napellus. (Braconnot, *Ann. Chim. Phys.* 8, 139; Geiger, *Mag. Pharm.* 34, 62.) In the leaves before flowering, in the seeds after flowering; adheres to the chlorophyll in the leaves. It is not completely extracted by repeatedly pressing the plant with water, but alcohol extracts the whole of it. The fresh herb distilled with water in the chloride of calcium bath, diffuses a peculiar odour, irritating to the eyes, but not very acrid, and soon ceasing, and yields at first a distillate having a very acrid taste and odour, while the residue is quite destitute of acridity. The distillate loses by rectification more and more of its odour, which is destroyed at 100°, *Volatile acrid principle in Arum Dracunculus.* (Landerer, *Repert.* 57, 199.) Occurs in the fresh roots, and in the inner blue part of the flower, but especially in the spadix. The fresh roots, which have a sharp, burning taste, lose it by boiling or roasting; the bruised spadices redden the skin when rubbed into it, but without raising blisters, and yield by distillation with water, an aqueous distillate, having a sharp, tear-exciting odour, and a faint herb-like taste. The fresh spadices and the blue parts of the flowers yield, after digestion with alcohol, a very sharp-tasting extract, the most volatile distillate of which produces reddening and burning of the skin, while the less volatile residue contains, in addition to wax and blue colouring matter, a sharp-tasting resin soluble in ether and in volatile oils.

Volatile acrid principle in Arum maculatum. (Stendel, *Diss. inaug. de acred. novell. veget.* Tubing. 1805; J. Dulong, *J. Pharm.* 12, 156; *Taschenb.* 1827; 65.) In the fresh roots, which have a sharp pungent taste, if pressed during mastication against the sides of the mouth, but otherwise only a slight burning taste: the juice has scarcely any taste. They yield a neutral distillate which has not an acid but a sickly taste, and an empyreumatic odour; they yield non-acrid extracts with water, alcohol, acetic acid, and olive-oil, but nevertheless lose their acridity, which is quite destroyed by the action of those liquids.

Volatile acrid principle in Clematis viticella. — The fresh plant yields by distillation with water, a small quantity of yellow oil which floats on the water, and has a burning taste.

Volatile acrid principle in Clematis flammula. (Braconnot, *Ann. Chim. Phys.* 6, 134.) The fresh plant yields an aqueous distillate, without oil-drops, which has a sharp caustic taste, reddens the skin, and causes pain, but is not acid.—The volatile acrid principle may be extracted from the plant by fixed oils, but is lost when the plant is boiled with water.

Volatile acrid principle in Helleborus fœtidus. (Braconnot, *Ann. Chim. Phys.* 6, 138.) The stems and leaves distilled in the fresh state, yield a distillate having a very acrid taste and odour.

Volatile acrid principle in Daphne Mezereum. (Landerer, *Repert.* 58, 114.) The bark yields by distillation with water, a neutral liquid, having a sharp burning taste, and, by exhaustion with alcohol, a deep green solution having a very acrid taste, and yielding by evaporation a thick extract, from which ether removes all the acridity. The alcoholic extract, mixed with neutral acetate of lead, filtered, and freed from excess of lead by sulphuretted hydrogen, leaves by evaporation an extract together with a small quantity of an oil, which has a sharp burning taste, reddens the skin, dissolves in aqueous potash, and, when separated from the potash-solution by distillation with phosphoric acid, is transparent and colourless, and has an acid, acrid, and pungent odour. — The volatile acrid principle is not extracted from the bark by digestion with pure water, or with water containing hydròchloric acid.

Volatile acrid principle in Polygonum hydropiper. (John, *dessen. chem. Schwift.* 3, 14.) The plant yields by distillation in non-luted vessels, a tasteless water, but in luted vessels, a water having a burning taste: the residue, in either case, is destitute of acridity.

Volatile acrid principle in Ranunculus bulbosus, R. flammula, R. lingua, and R. acris. (Braconnot, *Ann. Chim. Phys.* 6, 138.) The stalks, and more especially the roots of these plants, yield by distillation with water a distillate which has an acrid taste and an odour of radish, becomes turbid after two months, and deposits white flocks, together with small shining micaceous scales, without losing its taste or odour. The residue of the distillation is free from acridity. — *Ranunculus lanuginosus, R. auricomus, R. phyhonolis, R. repens,* and *R. ficaria,* do not yield an acrid-tasting distillate by distillation with water. — The volatile acrid principle in *Ranunculus sceleratus* will be described with *Anemonin* $C^{30}H^{12}O^{12}$.

The *volatile acrid principle of certain Sponges* (Letellier, *Mag. Pharm.* 16, 137,) is destroyed by distilling them with water, or by digesting them with vinegar, alcohol, or aqueous potash.

Picrotoxin.

$$C^{20}H^{12}O^{8} = C^{20}H^{12}O^{6},O^{2}\ ?$$

BOULLAY. Fully, *Bull. Pharm.* 4, 5; *Ann. Chim.* 80, 209; *Schw.* 7, 365; further, *J. Pharm.* 5, 1; *Taschenbuch,* 1820, 122; *Repert.* 7, 76; abstr. *Gilb.* 63, 319; further, *J. Pharm.* 11, 505; abstr. *Repert.* 23, 166; *Kastn. Arch.* 7, 374; further, *J. Pharm.* 12, 106.
MERCK. *N. Tr.* 20, 1, 134.
DUFLOS, *Schw.* 64, 222.
PELLETIER & COUERBE. *Ann. Chim. Phys.* 54, 181; *Ann. Pharm.* 10, 183.

Menispermin (but different from the menispermin of Pelletier). (Couerbe.) *Cocculin. Picrotoxic acid.* — Discovered by Boullay in the seeds of *Menispermum Cocculus.*

Preparation. 1. The seeds separated from their husks are boiled with water; the decoction is evaporated; the residue exhausted with boiling alcohol of 38° B; the filtrate left to itself in a cool place for several days, any fat that separates being removed, and then evaporated to dryness; the residue comminuted with a small quantity of water and $\frac{1}{6}$ of its weight of magnesia, which forms insoluble compounds with any acid that may be present and with the fat; the mixture completely dried, and repeatedly boiled with alcohol of 30°; and the solution evaporated to the crystallising point, after decolorisation with animal charcoal. (Boullay.) The picrotoxin thus obtained may be purified by solution in boiling alcohol of 20° B. and spontaneous evaporation. (Boullay.)

The aqueous decoction merely freed from fat deposits, by evaporation, nodules, which, when treated, first with cold and then with hot water, leave colourless picrotoxin, to be purified by recrystallisation. (Meissner, *Berl. Jahrb.* 1827, 1, 132.) — Casaseca (*J. Pharm.* 12, 99; abstr. *Kastn. Arch.* 7, 376) likewise exhausts the watery extract with alcohol; evaporates; removes the fat; sets aside the remaining extract in contact with magnesia; and boils it for 24 hours with absolute alcohol, whereupon picrotoxin crystallises from the filtrate on evaporation. — If the aqueous decoction evaporated to a thick syrup be set aside for 24 hours with $\frac{1}{20}$ of baryta or magnesia, then repeatedly boiled with absolute alcohol, the tincture evaporated to dryness, and the residue again treated with alcohol,—the alcoholic solution, after being decolorised by animal charcoal, yields crystals of picrotoxin by evaporation and cooling. (Boullay.)

2. The decoction is precipitated with subacetate of lead; the dissolved lead removed from the filtrate by sulphuretted hydrogen; the residue exhausted with alcohol; the solution filtered and evaporated;

the residue again exhausted with alcohol; and the solution in alcohol, filtering, and evaporation are repeated till the extract becomes completely soluble in alcohol. The alcoholic solution evaporated to a syrup is then mixed with carbonate of potash, which, by removing the acetic acid, separates the picrotoxin after a while in the crystalline form; an additional quantity of picrotoxin is obtained by evaporation from the mother-liquor, which likewise contains sugar and colouring matter; and the entire product is washed with cold water and crystallised from water containing alcohol. (Boullay.) — Crystals of picrotoxin are likewise obtained from the aqueous decoction merely precipitated with subacetate of lead and freed from lead. (Boullay; Schrader, *Br. Arch.* 8, 147.)

3. Bruised grains of cocculus are exhausted by boiling with alcohol of sp. gr. 0·85; the filtrate is distilled till the residue amounts to about $\frac{1}{3}$ of the weight of the grains; the fat is removed after cooling; the residue boiled with half its weight of water; the solution filtered at the boiling heat; and the filtrate (after addition of a small quantity of acid, according to Pelletier & Couerbe), brought to the crystallizing point. (Vogel, *Br. Arch.* 20, 250.) The portion of the extract insoluble in water contains menispermin, paramenispermin, and a brown acid mentioned below. (Pelletier & Couerbe.) The extract of shelled grains of cocculus prepared with weak alcohol yields by evaporation, brown picrotoxin, which may be purified by washing with cold alcohol and repeated solution in water. By further evaporation, an additional quantity of picrotoxin is obtained, but in slender needles of different aspect. (Gmelin.)

4. Kukle evaporates the aqueous decoction of cocculus grains nearly to the consistence of honey; cools; removes the separated oil; evaporates to an extract; heats the extract in a distillatory apparatus with alcohol of sp. gr. 0·84 till half the alcohol has passed over; pours off the solution; and treats the residue repeatedly with alcohol, as long as any bitter substance is thereby extracted. The tincture evaporated to the consistence of honey after the distillation of the alcohol, and shaken up with fresh quantities of ether, yields to this solvent, picrotoxin and menispermin, which latter is immediately extracted from the solution, together with the colouring matter, by agitation with hydrochloric or nitric acid. (*Zeitschr. Ph. v. W.* 5, 339.) — When grains of cocculus are treated with alcohol and tartaric acid, the solution evaporated, the residue exhausted with water, and the solution shaken up with ether, the ethereal solution yields crystals of picrotoxin by evaporation. (G. Günkel, *N. Br. Arch.* 94, 14.)

5. Wittstock (*Berz. Jahrb.* 3 Aufl., 3, 289) frees the shelled grains from fat by pressure; boils the residue several times with alcohol; distils off the alcohol; boils the solidified residue with water; separates the oil, and leaves the picrotoxin to crystallize.

Properties. White shining four-sided prisms. (Boullay.) Sometimes slender needles, sometimes flexible silky threads, and transparent plates, sometimes radio-nodular and hard granular masses, varying in character according to the concentration and temperature of the solution and the presence of foreign bodies. (Pelletier & Couerbe.) Without action on vegetable colours. (Oppermann, Duflos.) According to the earlier statements of Boullay, it has an alkaline reaction. It has a very bitter taste and poisonous action. Ten grains killed young dogs, with convulsions and vertigo. (Boullay.) Does not contain any water of crystallisation. (Pelletier & Couerbe.) The alcoholic solution turns the plane of polarisation to the left, Lævo-rotatory power = 28·1 (Bouchardat & Boudet, *N. J. Pharm.* 23, 288, *J. pr. Chem.* 60, 118. *Liebig u. Kopp's Jahresber.* 1853, 194).

		a.			*b.*		Oppermann. *mean.*
20 C	120	61·22	24 C	144	60·50	60·21
12 H	12	6·12	14 H	14	5·88	5·86
8 O	64	32·66	10 O	80	33·62	33·93
$C^{20}H^{12}O^{8}$	196	100·00	$C^{24}H^{14}O^{10}$	238	100·00	100·00

	Pelletier & Couerbe. *mean.*	Regnault. *mean.*	Francis. *mean.*
C	59·77	59·52	60·26
H	6·00	5·86	5·70
O	34·23	34·62	32·74
	100·00	100·00	98·70

Isomeric with cantharidin. — According to Oppermann (*Mag. Pharm.* 35, 237; *Pogg.* 23, 446), it is $C^5H^3O^2 = \frac{1}{4} C^{24}H^{12}O^8$; according to Pelletier & Couerbe, $C^{12}H^7O^5$. Gerhardt (*Traité* 4, 227) adopts the first formula doubled = $C^{10}H^6O^4$. — It is perfectly free from nitrogen. (Oppermann, Erdmann & Marchand, *J. pr. Chem.* 37, 146, and others.) According to Francis (*Lieb. Organ. Chem.* 335), it contains 0·75 — 1·30 p. c. nitrogen.

Decompositions. 1. By *dry distillation,* it yields carbonic acid and combustible gas, a small quantity of acid water, a very large quantity of acid brownish yellow, empyreumatic oil, but no ammonia, and leaves charcoal. (Boullay.) When heated, it melts like wax, takes fire and leaves charcoal. (Merck.) Melts to a brown liquid and gives off aromatic acid vapours. (Gmelin.) Decomposes when heated on red-hot coals, without melting or taking fire. (Boullay.) — 2. It is not altered by boiling with *iodine* and water, and crystallizes by evaporation, free from iodine and hydriodic acid. (Pelletier & Couerbe.) Triturated with $\frac{1}{10}$ part of iodine, it forms a red-brown mass which yields a reddish solution on addition of water. (Vogel, *Br. Arch,* 16, 155.) It is not altered by *sulphurous acid,* or *chlorine* (Boullay), or by *iodic acid* (Duflos), and is not coloured by vapour of *bromine, iodine,* or *chloride of iodine.* (Douné.) — 3. Cold *oil of vitriol* dissolves it with yellow colour (without colouring, according to Merck); warmed oil of vitriol chars it. (Boullay.) — 4. It dissolves without decomposition in cold *nitric acid,* forming a greenish yellow solution (the colour of which gradually disappears, according to Duflos); but warm nitric acid converts it into oxalic acid. (Boullay.) With *aqua regia* it likewise yields oxalic acid. (Pelletier & Couerbe.) It is reddened by nitric acid (Pettenkofer, *Repert.,* 7, 91); not coloured (Merck). — 5. It does not give off ammonia when treated with *hydrate of potash.* (Boullay.) By strong *ammonia, potash,* or *soda,* it is completely decomposed, especially if gently heated, and from the resulting orange-coloured solution, acids throw down a brown powder similar to that which is produced from many organic bodies by the action of potash. (Pelletier & Couerbe; see also *Combinations.*) — Aqueous picrotoxin changes the colour of *bichromate of potash* to a fine green. (Duflos.) In alkaline solution, it reduces *protoxide of copper* to di-oxide. (G. Beckers, *N. Br. Arch,* 85, 22; G. Günkel.) Hence Ludwig (*N. Br. Arch.,* 82, 139), who examined it only after boiling with acids, was led to regard it as a conjugated sugar-compound. — Solutions of *gold, silver*, and *copper-salts* are not altered by aqueous picrotoxin for several hours, provided light be excluded : *ferric sulphate* is very slowly reduced to ferrous sulphate. (Duflos.)

Combinations. It dissolves in 150 pints of *water* at 14°, in 25 pts. of boiling water (Pelletier & Couerbe, Boullay), in 180 pts. of boiling water (Merck), in 162 pts. of cold, 54 pts. of boiling water (Duflos), in 160 pts. of water at 18¾° Abl. (*Oesterreich. Zeitschr. Pharm.* 8, 201).

With Acids. — According to Boullay, picrotoxin unites with acids to form salts, which, however, is denied by Oppermann and others. — It does not neutralise the smallest quantity of acid. (Oppermann.) Even a very large excess of picrotoxin does not remove the acid reaction from water containing traces of hydrochloric acid. It crystallises free from hydrochloric acid from a solution containing that acid. (Pelletier & Couerbe ; Regnault, *Ann. Pharm.* 29, 214 ; *J. pr. Chem.* 16, 289 ; Duflos.) Similarly with iodic acid. (Serullas.) Hence the picrotoxin-salts, described by Boullay, are probably merely picrotoxin with adhering acid. — Picrotoxin dissolves in dilute acids (Boullay) ; not more than in pure water, more abundantly only in acetic acid. (Pelletier & Couerbe.)

With Alkalis. — Aqueous *ammonia, potash,* and *soda* dissolve picrotoxin very abundantly. (Boullay.) Acids, even carbonic acid, separate it unaltered from the solution. (Pelletier & Couerbe.) Hence it is regarded by Pelletier & Couerbe (not by Liebig, *Ann. Pharm.* 10, 204), as an acid : *picrotoxic acid.* If the alkali is saturated, while hot, with picrotoxin, that substance separates on cooling, and, after washing with cold water, is free from alkali. When a solution of picrotoxin in potash is placed in the voltaic circle, picrotoxin is deposited in slender needles at the positive pole, while the liquid at the negative pole becomes richer in potash and is no longer bitter. (Pelletier & Couerbe.) — *Baryta, strontia, lime,* and *magnesia,* prevent the crystallisation of picrotoxin in needles. *Lime* causes it to crystallise in plates or granules, and needles are produced on addition of acids.

Picrotoxin with Oxide of Lead. — Oxide of lead forms, with picrotoxin, a very soluble uncrystallisable salt, which may be obtained by prolonged boiling of picrotoxin with excess of oxide of lead and a small quantity of water, and evaporating the filtrate in vacuo. Contains 45 or 48 p. c. oxide of lead. (Pelletier & Couerbe.)

With Organic bodies. — It dissolves in 3 pts. of hot *alcohol* of sp. gr. 0·81. The solution on cooling solidifies in a silky mass. It is precipitated by a small quantity of water. The finest crystals are obtained from a mixture of equal parts of alcohol and water. (Boullay.)

It dissolves with difficulty in cold *ether* (Merck), in 250 pts. of ether of sp. gr. 0·7. (Boullay.) Picrotoxin is not extracted from its aqueous solution by ether, or from the alcoholic solution mixed with caustic potash, but ether abstracts it from the alcoholic solution mixed with hydrochloric acid. (G. Günkel, *N. Br. Arch.* 94, 14.)

Picrotoxin dissolves completely in concentrated *acetic acid,* but requires 2400 pts. of distilled vinegar to dissolve it, and does not dissolve perceptibly in a mixture of equal parts of distilled vinegar and water. (Merck.) Acetic acid facilitates the solution of picrotoxin in water. (Pelletier & Couerbe.) The easily produced solution of picrotoxin in acetic acid, which is precipitated by concentrated carbonate of potash, yields by evaporation, according to Boullay, needles of acetate of picrotoxin, which give off acetic acid when treated with nitric acid, but not with sulphuric acid, and when washed with water, lose their acid reaction, but not the whole of the acetic acid.

Aqueous picrotoxin is not precipitated by *tincture of galls*. (Duflos.)

Picrotoxin (containing acid) does not dissolve in *oils*, either *fixed* or *volatile*. (Boullay.)

Other Compounds. Picrotoxin forms with *quinine, cinchonine, morphine, strychnine,* and *brucine,* compounds, which are more soluble than these bodies in the separate state; they are crystallisable, and are decomposed in the voltaic circuit, the picrotoxin going to the positive, and the alkaloid to the negative pole. (Pelletier & Couerbe.)

Appendix to Picrotoxin.

Brown Acid from the Husks of Cocculus-grains.

PELLETIER & COUERBE. *Ann. Chim. Phys.* 54, 196; *Ann. Pharm.* 10, 195.

Acide hypopicrotoxique.

Preparation. The coarsely pulverised husks of cocculus-grains are exhausted in a Papin's digester with alcohol; the wax which separates as the tincture cools is removed by filtration; the solution is evaporated; and the residual extract is exhausted, first with cold water, then with boiling acidulated water, and finally with ether, which when evaporated leaves a brown extract, a mixture of the chlorophyll and the brown acid. The part of the extract which is insoluble in ether, dissolves in boiling alcohol (or in aqueous potash), forming a solution which deposits wax on cooling, and the filtrate separated therefrom leaves on evaporation a brown mass, from which ether extracts fat and chlorophyll, leaving the brown acid.

Properties. Solid, amorphous brown mass, which softens at 100°.

			Pelletier & Couerbe. *mean.*
22 C	132	63·1	64·14
13 H	13	6·2	6·09
8 O	64	30·7	29·77
$C^{22}H^{13}O^{8}$	209	100·0	100·00

So according to Pelletier and Couerbe. — The analysis gives ½ p. c. too much carbon, the contrary of that which generally takes place; and as the capacity of saturation was not determined, the formula is altogether inadmissible. Liebig, *Ann. Pharm.* 10, 297. — It is perhaps picrotoxin, contaminated with the brown acid into which that substance is converted by alkalis. (Gm.)

It is insoluble in *water*, even at the boiling heat.

It dissolves readily in *alkalis*, forming a dark-coloured solution, whence it is precipitated by acids in brown flocks. Insoluble in *ether*.

Oxygen-nucleus $C^{20}H^{10}O^8$.

Oenolin.

$$C^{20}H^{10}O^{10} = C^{20}H^{10}O^8,O^2.$$

MULDER. *Chemie des Weins.* Leipzig, 1856, S. 44, u. 228.
GLÉNARD. *Compt. rend.* 47, 468; *J. pr. Chem.* 75, 316; fully, *N. Ann. Chim. Phys.* 54, 366.

Oenolic acid. The colouring matter of the skins of red grapes and of red wine. — A. Vogel (*Schw.* 20, 417) and Ficinus (*Br. Arch.* 2, 309) were acquainted with the behaviour of red wine to acids, alkalis and lead-salts. — Batilliat's *Rosite* is, according to Mulder, a mixture containing oenolin (*vide inf.*) Fauré (*Analyse chimique et comparée des vins de la Gironde*, 1844; abstr. *Mulder's Chemie des Weins*, 245,) distinguishes a blue and a yellow colouring matter of wine, both of which, according to Mulder, were impure or products of decomposition.

Preparation. A. From Grape-skins. The skins, after being well washed with water, are exhausted with water containing acetic acid; the solution is precipitated by neutral acetate of lead; and the washed precipitate is suspended in water and decomposed by sulphuretted hydrogen. The sulphide of lead, purified by boiling with water, gives up the colouring matter to acetic acid, and the solution when evaporated leaves the colouring matter, which may be purified from adhering fat by boiling with ether. (Mulder.)

B. From Red Wine. 1. Bordeaux wine is precipitated with neutral acetate of lead; the dirty blue precipitate is collected and washed, as long as the water runs off coloured, then decomposed under water by sulphuretted hydrogen; the precipitated sulphide of lead is freed from apothema by boiling with water; and the colouring matter is extracted from it by alcoholic acetic acid. The solution when evaporated leaves the colouring matter, which may be freed from fat by ether, and from adhering lead-oxide by acetic acid. (Mulder.) — 2. Red wine is precipitated by basic acetate of lead; and the blue precipitate is washed by decantation, then on the filter, afterwards dried between 100° and 110°, and treated in the state of fine powder in the displacement apparatus, with such a quantity of anhydrous ether into which hydrochloric acid gas has been previously passed, that the hydrochloric acid contained in it may not completely saturate the lead-oxide in the precipitate. After the ether containing hydrochloric acid has run off, the precipitate is washed with pure ether as long as anything is taken up,—tartaric acid, tannic acid, a peculiar crystallisable and volatile acid, fat and wax being thereby removed; and the washed precipitate is dried by exposure to the air, and exhausted with ether, as long as colouring matter continues to dissolve. The alcoholic tincture freed from the greater part of the alcohol by distillation, and mixed when cold with 4 or 5 vols. water, deposits red flocks which must be completely washed with water and dried. (Glénard.)

Properties. Nearly black mass, yielding by trituration a powder of a fine violet-red colour, or red-brown if the mass has been dried between 100° and 120°. (Glénard.) Bluish black mass, resembling plumbago.

(Mulder.) In the moist state it has the dark colour of wine-lees, without lustre. Under the microscope, it appears to be composed of roundish groups of granules. Permanent in the air. (Glénard.)

	At 120°.		Glénard. *mean.*
20 C	120	57·14	57·02
10 H	10	4·76	4·89
10 O	80	38·10	38·09
$C^{20}H^{10}O^{10}$	210	100·00	100·00

Decompositions. 1. Swells up when *heated*, giving off a peculiar odour and leaving charcoal. (Glénard.) — 2. *Burns* on platinum-foil. (Glénard.) — 3. When its solution in weak alcohol is boiled for a long time with *water*, it becomes insoluble in alcohol, and iridescent films form on the surface of the water. (Glénard.) — 4. The alcoholic solution of oenolin is decomposed by hot, but not by cold *oil of vitriol*. (Glénard, *vid. inf.*) — 5. A small quantity of weak *nitric acid* imparts a brighter colour to the alcoholic solution of oenolin; but a larger quantity gradually decolorises it, more quickly if heated (Mulder), with formation of a brown detonating resin. — 6. Oenolin dissolved in alcohol is converted by *chlorine* into a yellow soluble compound (Glénard); when dissolved in a mixture of alcohol and tartaric acid, it is first coloured brown by chlorine, and yellow by a larger quantity. (Mulder.) — With *chloride of lime*, a yellow-brown precipitate is formed, together with a yellow solution. (Glénard.) — 7. In contact with *potash-ley* or *carbonate of soda*, it absorbs oxygen, and turns brown. (Glénard.) — Its solution in alcoholic tartaric acid acquires the colour of chrome-alum on addition of a small quantity of *ammonia*; a somewhat larger quantity colours it blue; an excess, green, and after a few seconds brown. The green, but not the brown solution, is coloured red by acids. Potash, soda and lime act like ammonia.

Oenolin is insoluble in *water* (Mulder), very sparingly soluble in cold water, somewhat more in hot. (Glénard.)

Oil of vitriol colours the solution of oenolin in alcoholic tartaric acid bright light red, and in excess, violet, the pure red colour being however restored by addition of water. (Mulder.) — *Hydrochloric acid* does not alter the weak alcoholic solution, even at the boiling heat.

Oenolin dissolves more readily in water containing *tartaric* or *acetic acid*. It dissolves in *wood-spirit*, not in *sulphide of carbon* or *chloroform*. (Glénard.)

According to Mulder, oenolin is quite insoluble in *alcohol*; according to Glénard, it dissolves readily, with fine crimson colour, and remains as a varnish when the alcohol evaporates. — According to Mulder, it dissolves in alcohol containing a trace of acetic acid, with pure blue colour, and if more acetic acid is present, with red colour. (Mulder.) In alcohol containing tartaric acid, it dissolves slowly but completely, with pure red colour. (Mulder.)

The alcoholic solution exhibits the following reactions: *Bicarbonate of soda* colours it blue; *chloride of calcium* forms a blue precipitate; *alum* brightens its colour, and on addition of carbonate of soda, forms a lilac lake. — With neutral *acetate of lead*, it yields a pure blue precipitate, which, after drying at 120°, contains 35·67 PbO, and after subtraction thereof, contains in 100 pts. 59·67 p. c. C, 4·49 H, and 35·84 O, and is therefore $C^{20}H^{9}PbO^{10}$ (calculation 35·74 PbO, and 59·71 C, 4·47 H, 35·82 O). With *nitrate of lead,* it forms after a few seconds a violet precipitate, and with the *basic acetate,* blue inclining to brown. It colours *ferrous sulphate* violet, and then forms a bluish violet precipitate. It precipitates *ferric sulphate* dark chestnut-brown, *ferric chloride* yellowish, *cupric acetate* chestnut-brown, *protochloride of tin* violet-red, *mercurous nitrate* colour of wine-lees, *mercuric nitrate* light-brown, *nitrate of silver* brown-red after a while. It does not precipitate *mercuric chloride.* (Glénard.)

The solution in alcoholic tartaric acid is not altered by *alum;* with *acetate of alumina* (acetate and phosphate of soda), and a small quantity of acetic acid, it forms a violet precipitate; with *nitrate of lead,* light red; with *neutral* and *basic acetate of lead,* blue, the precipitate being soluble with red colour in alcoholic acetic acid. It is coloured darker red to violet by *bichloride of tin,* not altered by *mercurous nitrate,* coloured lighter red by *mercuric chloride,* darker red by *nitrate of silver.* (Mulder.)

Oenolin is insoluble in *ether, benzene, olive-oil,* and *oil of turpentine.*

Batilliat (*Traité sur les vins de la France;* abstr. *Bull. Soc. d'encour.* 1848, 451; *Dingl. pol. Journ.* 110, 66) distinguishes two colouring matters of wine, *Rosite* and *Pourprite.*

Rosite. — Occurs especially in the sediment of new wines. — The sediment, which remains after the first drawing off of the wine, is collected upon linen, and suspended in alcohol of 85 p. c.; the liquid is filtered and evaporated; the residue exhausted with water, which leaves pourprite undissolved; the liquid precipitated with solution of gelatin; and the filtrate evaporated.

Colour rose-red. When heated, it leaves slowly burning charcoal and a small quantity of alkaline ash.

Dissolves in *water,* and without decomposition in *oil of vitriol* of 66°; soluble in *alcohol,* not in *ether.* Not precipitated by *white of egg* or *solution of jelly.*

Pourprite. — Found chiefly in the sediment of old wines, which indeed consists almost entirely of it. Dark blackish red. Has a rough, astringent taste. Leaves, when burnt, an ash consisting of lime, potash, and iron. — Insoluble in *water.* — Dissolves in *oil of vitriol,* and is precipitated by water. — Soluble in 150 pts. of *alcohol* of 80 p. c.; less soluble in stronger alcohol, and quite insoluble in *ether.* With *jelly,* it forms a compound insoluble in water and in alcohol.

Chlorine-nucleus $C^{20}Cl^5H^{13}$.

Quintichloromenthene.

$C^{20}Cl^5H^{13}$.

WALTER. *Compt. rend.* 8, 913; *Ann. Chm. Phys.* 72, 106; *Pogg.* 51, 1, 349; *Ann. Pharm.* 32, 296.

Chlormenthen (Löwig); *Chloromenthase* (Laurent, *Rev. scient.* 14, 341); *Quintichloromenthène* (Gerhardt, *Traité* 4, 359).

Dry chlorine is passed into menthene (p. 445) as long as hydrochloric acid gas continues to go off, and the product is washed, first with water and then with carbonate of soda, again subjected to the action of chlorine, washed as before, and dried over chloride of calcium, then in vacuo.

Yellow syrupy liquid, heavier than water.

			Walter.
20 C	120·0	38·64	38·24
13 H	13·0	4·18	4·68
5 Cl	177·5	57·18	57·30
$C^{20}Cl^5H^{13}$	310·5	100·00	100·22

Burns, when set on fire, with a smoky, green-edged flame *Oil of vitriol* colours it deep red.

Soluble in cold *alcohol* and *wood-spirit,* more readily in ether and in oil of turpentine. (Walter.)

Oxyamidogen-nucleus $C^{20}AdH^{15}O^2$.

Camphoramic Acid.

$C^{20}NH^{17}O^6 = C^{20}AdH^{15}O^2,O^4$.

LAURENT. (1845.) *Compt. chim.* 1845, 141; abstr. *J. pr. Chem.* 35, 501; *Ann. Pharm.* 60, 326; *Repert.* 100, 89.

Camphoraminsäure, Camphoramsäure, Acide camphoramique. — The crystals which form on saturating camphoric anhydride with ammonia were regarded by Malaguti (*Ann Chim. Phys.* 64, 162) as a peculiar camphorate of ammonia: their true nature was recognised by Laurent.

Formation and Preparation (p. 468). A boiling solution of camphoric anhydride in absolute alcohol, concentrated as much as possible, is saturated with ammonia-gas; the crystals of camphoramate of ammonia which separate on cooling (and of which the mother-liquor yields a larger quantity by gentle evaporation), are dissolved in a larger quantity of water and decomposed by hydrochloric acid; and the acid which separates by cooling or by evaporation at a gentle heat, is purified by recrystallisation from cold alcohol. — When hot concentrated solutions of camphoramate of ammonia are decomposed by hydrochloric acid, the camphoramic acid separates as a syrup, a small quantity only remaining dissolved in the supernatant liquid. (Malaguti, Laurent.)

Properties. Colourless, transparent, rectangular prisms. Fig. 56 with *p*-face. $u : u$ behind $= 114° \ 30'$; $u : t = 122° \ 45'$; $a : u = 155°$; $i : t = 138° \ 20'$. — Melts when heated and solidifies on cooling, partly crystalline, partly as a transparent vitreous mass, which is no longer camphoramic acid.

			Laurent.
20 C	120	60·30	60·0
N	14	7·03	7·4
17 H	17	8·50	8·4
6 O	48	24·17	24·2
$C^{20}AdH^{15}O^6$	199	100·00	100·0

By heating to 150° — 160°, or by distillation, camphoramic acid is converted, with loss of water, into camphorimide.

The acid dissolves sparingly in *water.* — With *bases,* it forms the *Camphoramates,* which are crystallisable and all soluble in water. —

Aqueous camphoramate of ammonia does not precipitate lead, silver, or copper salts.

Camphoramate of Ammonia. Prepared as above, or by dissolving camphoramic acid in alcoholic ammonia, and purified by recrystallisation, washing with absolute alcohol, and drying at a moderate heat. — Slightly acid, bitter crystals, from the solution of which, chloride of platinum precipitates half the nitrogen as chloroplatinate of ammonium. — The salt melts at 100°, and, between 150° and 160°, gives off ammonia and 21·6 p. c. water, and is converted into camphorimide which solidifies in a vitreous mass; likewise by distillation.

			Malaguti.	Laurent.
20 C	120	51·2	50·1	51·1
2 N	28	11·9	12·1	11·7
22 H	22	9·4	9·1	9·3
8 O	64	27·5	28·7	27·9
$C^{20}AdH^{14}O^5,NH^4O + 2Aq$	234	100·0	100·0	100·0

Malaguti regarded the salt which he examined, as a peculiar camphorate of ammonia (comp. p. 468).

Camphoramate of Lead. — The concentrated boiling solution of camphoramate of ammonia in alcohol, mixed with less than the equivalent quantity of alcoholic neutral acetate of lead, deposits on cooling small needles, which, when washed with a little alcohol and dried at a gentle heat, contain 33 p. c. of lead, and are therefore $C^{20}AdPbH^{14}O^6$ (calculation = 34·5 p. c. Pb). Dissolves with moderate facility in alcohol.

Camphoramate of Silver. — The concentrated alcoholic solution of camphoramate of ammonia, mixed while hot with alcoholic nitrate of silver, solidifies on cooling to a jelly containing crystals. These are washed with absolute alcohol and pressed between paper. — Very slender, long, microscopic needles, containing 34·7 p. c. silver ($C^{20}AdH^{14}AgO^6$ = 35·1 p. c. Ag.).

Camphoramic acid dissolves in *alcohol* more readily than in water (Laurent.)

Oxyamidogen-nucleus $C^{20}Ad^2H^{14}O^2$

Camphoramide.

$$C^{20}N^2H^{18}O^4 = C^{20}Ad^2H^{14}O^2,O^2.$$

Laurent. *Rev. scient.* 10, 123; *J. pr. Chem.* 27, 314; *Repert.* 80, 114.

Oxyde d'amed camphèse (Laurent, *Rev. scient.* 14, 506).

When ammonia-gas is passed through the solution of camphoric anhydride in absolute alcohol, and the saturated solution is evaporated, there remains a thick syrup, which is not decomposed by cold hydrochloric acid,—gives off ammonia when treated with hydrate of potash, and forms camphorate of potash,—is insoluble in water, but soluble in alcohol. This is probably camphoramide.

Conjugated Amides of Camphoric Acid.

Camphoranilic Acid.

$$C^{32}NH^{21}O^6 = C^{20}(C^{12}NH^6)H^{15}O^2,O^4.$$

Laurent & Gerhardt. (1848.) *N. Ann. Chim. Phys.* 24, 191; *Ann. Pharm.* 68, 36; abstr. *Pharm. Centr.* 1849, 74.

Phenyl-camphoramic acid.

Formation. By heating camphoric anhydride with aniline, camphoranil being formed at the same time.

Preparation. Camphoric anhydride is heated with aniline, and after the vitreously solidified mass has cooled, the camphoranilic acid is dissolved out of it by hot aqueous ammonia, camphoranil then remaining undissolved. The solution is precipitated by nitric acid, and the precipitated flocks are washed.

Properties. Flocks which melt in boiling water to a resin, becoming crystalline by continued boiling with water. From dilute, lukewarm, weakly alcoholic solutions, it may be obtained in needles, but from concentrated strongly alcoholic solutions it separates as a resin :

			Laurent & Gerhardt.	
32 C	192	69·82	68·6	69·5
N	14	5·09		
21 H	21	7·64	7·7	7·6
6 O	48	17·45		
$C^{32}NH^{21}O^6$	275	100·00		

Decompositions.. 1. By *distillation*, it is completely resolved into aniline and camphoric anhydride. — 2. When slightly heated with *oil of vitriol*, it gives off carbonic oxide. — 3. Fused with *hydrate of potash*, it gives off aniline.

It dissolves sparingly in boiling *water*, and solidifies in the crystalline form on cooling.

With *bases*, it forms the *camphoranilates*. The ammonia-salt does not precipitate the salts of *lime* or *baryta*.

Camphoranilate of Ammonia. — The solution of camphoranilic acid in alcoholic ammonia leaves when evaporated, a syrup from which water separates a portion of the camphoranilic acid. It may be obtained, like the acid, as a resin or in crystals, corresponding to the different states of camphoranilic acid.

Camphoranilate of Silver. — Obtained by mixing the ammonia-salt with nitrate of silver, as a white precipitate, which contains 28·25 p. c. silver, and is therefore $C^{32}NA^{20}AgO^6$ (calculation = 82·27 p. c. Ag), slightly soluble in water.

Camphoranilic acid dissolves very easily in *alcohol* and in *ether*. (Laurent & Gerhardt.)

Camphoranil.

$$C^{32}H^{19}NO^4 = C^{20}(C^{12}NH^6)H^{13}O^4 ?$$

LAURENT & GERHARDT. (1848.) *N. Ann. Chim. Phys.* 24, 191; *Ann. Pharm.* 68, 35; abstr. *Pharm. Centralbl.* 1849, 73.

Phenylcamphorimide.

Comp. p. 468. Camphoric anhydride is heated with aniline; the vitreous mass which forms on cooling is treated with hot dilute aqueous ammonia to extract camphoranilic acid; the residue is dissolved in alcohol or in ether; and the solution is left to evaporate:

$$C^{20}H^{14}O^6 + C^{12}H^7N = C^{32}H^{19}O^4 + 2HO$$

Properties. Shining needles, which sublime without decomposition, melt at 116°, and solidify to a somewhat crystalline mass on cooling:

			Laurent & Gerhardt.
32 C	192	74·70	74·3
N	14	5·44	
19 H	19	7·39	7·4
4 O	32	12·47	
$C^{32}H^{19}NO^4$	257	100·00	

Decompositions. 1. Camphoranil is not decomposed by *aqueous potash*, but with *hydrate of potash* in the state of fusion, it gives off aniline. — 2. It dissolves slowly concentrated aqueous *ammonia* containing a little alcohol, whereupon camphoranilate of ammonia crystallises on cooling.

Combinations. Insoluble in *cold*, but somewhat soluble in *boiling water*. — Part melts in boiling water, while the rest dissolves and crystallises as the liquid cools. — The solution of camphoranil in very weak aqueous ammonia containing alcohol, forms with nitrate of silver a white crystalline precipitate, probably $C^{32}H^{18}AgNO^4$.

Camphoranil dissolves readily in *alcohol* and *ether*, and crystallises on cooling from very weak alcohol, in long shining needles. (Laurent & Gerhardt.)

Oxyazo-nucleus $C^{20}NH^{15}O^2$.

Camphorimide.

$$C^{20}NH^{15}O^4 = C^{20}NH^{15}O^2,O^2.$$

LAURENT. (1845.) *Compt. chim.* 1845, 147; abstr. *J. pr. Chem.* 35, 503; *Ann. Pharm.* 60, 326; *Repert.* 100, 89.

Bicamphorimide. (Löwig.)

Formation and Preparation. Camphoramic acid or its ammonia-salt is heated to 150°—160° (whereupon water and ammonia are given off) or distilled, and the colourless mass, which solidifies in the vitreous form on cooling, is crystallised from alcohol.

Properties. Colourless six-sided tables. Melts when heated; solidifies in the vitreous form on cooling; volatilises without decomposition at a stronger heat; and sublimes partially in white fern-like laminæ, apparently terminated with faces of a rhombic dodecahedron:

			Laurent.
20 C	120	66·3	65·90
N	14	7·7	
15 H	15	8·3	8·14
4 O	32	17·7	
$C^{20}NH^{15}O^{4}$	181	100·0	

Camphorate of ammonia — 2 At. HO and 1 At. NH^{3}, or bicamphoramate of ammonia. — 2 At. HO, or camphoramic acid — 2 At. HO. (Laurent.)

Decompositions. Hydrate of potash boiled with alcoholic camphorimide eliminates ammonia.

Combinations. Camphorimide dissolves in gently heated *oil of vitriol.* Water added to the solution throws down white microscopic crystals, consisting of acute six-sided pyramids.

It dissolves readily in boiling *alcohol.* — The solution in weak alcohol solidifies after evaporation to a transparent gum, which solidifies in 24 hours to opaque nodules. (Laurent.)

Primary Nucleus $C^{20}H^{20}$.

Capric Acid.

$$C^{20}H^{20}O^{4} = C^{20}H^{20},O^{4}.$$

Chevreul. (1818.) *Ann. Chim. Phys.* 23, 22; *Schw.* 32, 179; *Recherches sur les corps gras.* 143.
Lerch. *Ann. Pharm.* 49, 223.
Iljenko & Laskowsky. *Ann. Pharm.* 55, 78.
Gottlieb. *Ann. Pharm.* 57, 64.
Cahours. *Thèse presenté à la faculté des sciences à Paris, le* 15 *Janvier,* 1845, 132; *Compt. rend.* 26, 263.
Gerhardt. *N. Ann. Chim. Phys.* 24, 96; *J. pr. Chem.* 45, 327.
Görgey. *Ann. Pharm.* 66, 290; *Pharm. Centralbl.* 1849, 8; *N. Ann. Chim. Phys.* 25, 102.
Rowney. *Ann. Pharm.* 79, 236; *J. pr. Chem.* 54, 211; *Quart. J. Chem. Soc.* 4, 332; *Chem. Gaz.* 1852, 32.
Redtenbacher. *Ann. Pharm.* 57, 150; 59, 54.
Fehling. *Dingler. pol. Journ.* 130, 77; *N. J. Pharm.* 25, 94.

Acide caprique. (Chevreul.) *Acide rutique.* (Cahours.) Discovered by Chevreul in 1828, but according to Lerch, not obtained by him in the pure state.

Sources. In the butter of cow's milk (Chevreul); in Limburg cheese (Iljenko & Laskowsky); in cocoa-nut oil (Görgey); in train-oil (Wagner, *J. pr. Chem.* 46, 115); in Scotch fusel-oil (Rowney); in the perspiration of the human foot (Brendecke, *N. Br. Arch.* 70, 26 and 34); in fusel-oil from maize and rye (Wetherill, *Chem. Gaz.* 1853, 218; *J. pr. Chem.* 60, 202); in the so-called oil of grapes from Leipzig (Fehling); in the molasses of mangold-wurzel (Fehling); in potato fusel-oil (S. W. Johnson, *J. pr. Chem.* 62, 262). According to Wagner, it may be recognised, since it is always accompanied by capric aldehyde, by heating the body under examination with oil of vitriol, and adding hydrate of potash in excess, whereupon the odour of oil of rue becomes perceptible. (*J. pr. Chem.* 45, 155.)

Formation. In the dry distillation of oleic acid or of fats containing olein. (Gottlieb.) In the oxidation of the following substances by nitric acid: oil of rue (Cahours, Gerhardt); oleic acid and choloïdic acid (Demarçays, Redtenbacher). — In the putrefaction of casein and fibrin. (Brendecke.) — Generally, it is formed simultaneously with the other volatile fatty acids.

Preparation. A. *From Butter of Cow's milk.* (Comp. x, 80.) — 1. When the mixture of caprylate and caprate of baryta obtained in the preparation of butyrate of baryta, is completely dissolved in boiling water, the filtrate, on cooling becomes filled with thin scales of caprate of baryta having a fatty lustre, and the mother-liquor filtered therefrom and evaporated down to $\frac{3}{4}$, yields an additional quantity (Lerch).

From the baryta-salt thus obtained and purified by recrystallisation, the acid may be obtained in two ways. — 1. To 10 pts. of the baryta-salt is added a solution of 8 pts. glacial phosphoric acid in 32 pts. of water, and the oily layer (still containing a little of the watery solution) which rises to the surface is decanted. — 2. One hundred pts. of the baryta-salt are decomposed by a mixture of 47·5 pts. oil of vitriol and 47·5 pts. water, and the anhydrous acid which rises to the surface of the liquid is decanted. (The liquid below the oily layer yields, when neutralised with baryta-water, an additional quantity of caprate of baryta.) (Chevreul.) — B. *From Limburg Cheese.* (See xiii, 191.) — C. *From Scotch fusel-oil.* — The liquid is subjected to fractional distillation, whereupon water, alcohol, and fusel-oil pass over, and there remains a dark-coloured fœtid oil, insoluble in water and in boiling aqueous carbonate of potash. When this oil is digested for several days with concentrated potash-ley, amyl-alcohol is separated, and there is formed a solution of caprate of potash, which, if mixed after cooling with hydrochloric or sulphuric acid, yields a dark-coloured oil, to be filtered and washed with cold water. For purification, the acid thus obtained is dissolved in very dilute aqueous ammonia, the solution precipitated by chloride of barium, and the precipitate separated by filtration, washed with cold water, and recrystallised from boiling water. Sometimes the precipitate dissolves but slowly in hot water, because it cakes to a hard mass during the boiling. The nearly colourless baryta-salt obtained by repeated crystallisation is decomposed by boiling with carbonate of soda; the liquid is filtered from the carbonate of baryta; and the filtrate is decomposed by dilute sulphuric acid, whereby nearly colourless solid capric acid is separated: it is to be dissolved in alcohol, precipitated by mixing the solution with a large quantity of water, and purified by repeated solution in alcohol and precipitation by water. The mother-liquor, treated in like manner, yields an additional quantity of capric acid, containing, however, traces of another oily acid. (Rowney.) — D. *From Oleic Acid and Fats containing Olein* (see xiii, 191.)

Properties. White mass, composed of small needles. (Chevreul, Rowney.) Melts at 18° (Chevreul); at 30° (Görgey); when pure, partially at 27·2°, completely at 46·6° (Rowney): hence even at the heat of the hand (Görgey, Rowney); forming a yellow oil (Görgey); becoming somewhat coloured and emitting a faint odour (Rowney); solidifies in contact with the air at 15° (Chevreul); at 27·2°, crystalline (Rowney). — When cooled in closed vessels, it remains liquid at 11·5°, not solidifying till the vessel is opened and shaken. (Chevreul.) — Sp. gr. 0·9103 at 18°. (Chevreul.) — Boils above 100° and volatilises undecomposed. Its odour slightly resembles that of capric acid, and at the same time that of the goat. (Chevreul, Görgey.) Tastes sour, burning, somewhat like goat. (Chevreul.)

With *pentachloride of phosphorus*, it forms volatile chloride of caprinyl, $C^{20}ClH^{19}O^2$, which is resolved by potash-ley into chloride of potassium and caprate of potash. (Cahours.)

Combinations. Capric acid dissolves in about 1000 pts. of water at 21°. (Chevreul.) It dissolves (very little according to Rowney) in boiling water, and on cooling separates almost completely (in scales, according to Rowney), so that the water scarcely retains any acid reaction. (Görgey.)

It dissolves in strong *nitric acid*, and is precipitated therefrom by water in its original state. (Rowney.)

With Bases. — Caprates. — All caprates, excepting those of the alkalis, dissolve but sparingly in water. (Lerch.) The caprates of the earths, and likewise the silver-salt, are insoluble in water; when dry they float on the surface without being wetted, and become soluble only after being treated with alcohol. (Rowney.) They are unctuous to the touch and become electrical by friction. (Fehling, *Handwörterb. Supplem.* 715.)

Caprate of Ammonia. — Difficult to obtain pure. (Rowney.)

Caprate of Soda. — Remains, after the evaporation of the aqueous or alcoholic solution, as a horny somewhat crystalline mass. Dissolves in warm absolute alcohol, and forms a translucent mass on cooling. (Rowney.)

Caprate of Baryta (p. 486). — 1. Baryta-water is neutralised with capric acid, and the solution quickly cooled after evaporation. (Chevreul.) — 2. Caprate of ammonia is precipitated by chloride of barium, and the baryta-salt which separates is collected and washed with cold water. (Rowney.)

Prepared by the first process, it forms thin, very light scales (needles, according to (Lerch) of a fatty lustre (silky, according to Redtenbacher); by spontaneous evaporation of the solution, it separates in dull grains of the size of hemp-seed (Chevreul); likewise in thin cohering scales, different from the granules of caprylate of baryta (xiii, 192). (Lerch.) From aqueous alcohol, it crystallises in needles and prisms. (Rowney.) — Permanent in the air at mean temperature and at 100°. Does not contain water of crystallisation. (Lerch.) In vacuo over oil of vitriol, it gives off 2·4 p. c. water, without further change. (Chevreul.) Calculation 1 At. Aq. = 3·6 p. c. Smells of capric acid, with somewhat of a goat-like odour, especially when rubbed in the moist state between the fingers. Tastes bitter, alkaline, and of capric acid. Has an alkaline reaction. (Chevreul.) When heated, it softens, emits an empyreumatic and goat-like odour, melts and turns brown, giving off an odour like that of the *Labiatæ*, and leaving carbonate of baryta mixed with charcoal. (Chevreul.) By distillation, it yields a reddish, yellow, neutral, partly solidifying oil, gives off olefiant gas, with a small quantity of carbonic acid, and leaves carbonate of baryta mixed with charcoal. (Chevreul.)

Dissolves in 200 pts. of water at 20°. (Chevreul.) According to Chevreul, the solution decomposes when exposed to air; according to Lerch, it is permanent in the air. It is but slightly precipitated by carbonic acid. (Chevreul.) It dissolves in boiling alcohol. (Rowney.)

			Lerch.	Iljenko & Laskowsky.	Gottlieb.	Rowney. *Dried at* 100°.
20 C	120·0	50·08	50·26	50·05	50·41	49·73
19 H	19·0	7·93	7·87	7·83	8·01	8·15
3 O	24·0	10·02	10·17	10·44	9·86	10·35
BaO	76·6	31·97	31·70	31·68	31·72	31·77
$C^{20}H^{19}BaO^4$	239·6	100·00	100·00	100·00	100·00	100·00

Contains 36·08 p. c. BaO (Chevreul); 32·07 p. c. BaO. (Redtenbacher.)

Caprate of Strontia. — Obtained by saturating strontia-water with capric acid, and leaving the solution to evaporate. — When heated, it melts, blackens, and gives off an aromatic and empyreumatic odour. Dissolves in 200 pts. of water at 18°. Contains 27·62 p. c. SrO. (Chevreul.) ($C^{20}H^{19}SrO^4$ = 24·11 p. c. SrO.) According to Chevreul, it is $C^{18}H^{17}SrO^4$; calculation, 26·19 p. c. SrO.

Caprate of Lime. — Crystallises from the hot aqueous solution in very fine shining laminæ; very bulky. (Gottlieb.) Resembles the baryta-salt, but is more easily soluble in hot water and in alcohol. (Rowney.) Contains 14·79 p. c. CaO (Gottlieb), and is therefore $C^{20}H^{19}CaO^4$ (calculation = 14·66 p. c. CaO).

Caprate of Magnesia. — Crystallises like the baryta-salt and resembles it in other respects; but dissolves more readily in hot water and in alcohol. Contains 11·37 p. c. MgO ($C^{20}H^{19}MgO^4$ = 10·92 p. c. MgO.)

Caprate of Lead. — The combination of capric acid with oxide of lead is attended with evolution of heat. (Chevreul.) The salt is insoluble in water, and very slightly soluble in hot alcohol, whence it crystallises in rounded grains on cooling. (Rowney.)

Caprate of Copper. — Insoluble in water and in alcohol; soluble in ammonia. (Rowney.)

Caprate of Silver. — The solution of capric acid in a slight excess of ammonia is precipitated by nitrate of silver. — The salt is insoluble in cold, sparingly soluble in boiling water, and crystallises in needles from the solution on cooling. It is very soluble in ammonia, and crystallises from the solution when left to stand in a warm atmosphere. (Rowney.) It dissolves more readily in boiling alcohol than in water, and the solution yields darker-coloured crystals. (Rowney.) — It blackens when exposed to the air in the moist state, but not when dry. (Rowney.)

Dried in vacuo over oil of vitriol.			Rowney.
20 C	120	43·01	42·43
19 H	19	6·81	6·77
AgO	116	41·57	41·64
3 O	24	8·61	9·16
$C^{20}H^{19}AgO^4$	279	100·00	100·00

Capric acid mixes in all proportions with *absolute alcohol.* (Chevreul.) It dissolves in *ether.* (Rowney.)

Caprate of Ethyl.

$C^{24}H^{24}O^4 = C^4H^5O,C^{20}H^{19}O^3.$

Rowney. *Ann. Pharm.* 79, 236.

Capric ether, Caprinsaures Aethyloxyd, Caprinvinester.

When a solution of capric acid in absolute alcohol is saturated with hydrochloric acid gas and precipitated by water, capric ether separates on the surface of the liquid, as an oil, which must be removed, washed with cold water, dehydrated by chloride of calcium, and rectified.

Oil of sp. gr. 0·862.

Insoluble in cold *water;* easily soluble in *alcohol* and in *ether*.

Appendix to Capric Acid.

Oil of Rue.

Will. (1840.) *Ann. Pharm.* 35, 235.
Cahours. *Thèse presenté à la faculté des sciences, le* 15 *Janvier*, 1845, 132; *Compt. rend.* 26, 262.—Further, *Chem. Soc. Qu. J.* 3, 240.
Gerhardt. *N. Ann. Chim. Phys.* 24, 96; *J. pr. Chem.* 45, 327; *Compt. rend.* 26, 226.
R. Wagner. 46, 155; further, 52, 48.
Chiozza. *Compt. rend.* 35, 797; *J. pr. Chem.* 58, 216.
Bertagnini. *Ann. Pharm.* 85, 283.
C. Greville Williams. *Phil. Trans.* 1858, 199; *Chem. Centr.* 1858, 734.
Hallwachs. *Ann. Pharm.* 113, 107.

Capric aldehyde, Caprol, Hydride of Rutyl.—First examined by Will.

The volatile oil of rue, obtained by distilling garden rue, *Ruta graveolens,* with water, was long regarded, according to the results of Cahours & Gerhardt, as capric aldehyde, $C^{20}H^{20}O^2$; but according to the more recent investigations of G. Williams, which have been confirmed by Hallwachs, it is chiefly $= C^{22}H^{22}O^2$, and is regarded by Williams as enodic aldehyde mixed with a small quantity of lauric aldehyde; by Hallwachs, as a compound not belonging to the class of aldehydes.

Fresh rue yields 3·4 grains of oil per pound; dry rue, 18; the dry flowers, 15; the seeds, 17 grains. (Zeller, *N. Jahrb. Pharm.* 1, 30.)—Crude oil of rue is greenish yellow, has a strong unpleasant smell of rue, and a sharp bitterly aromatic taste. Sp. gr. = 0·837 at 18°. It contains 77·5 p. c. C, 12·87 H, and 9·56 O (Will.); 77·65 p. c. C, 12·80 H, and 9·55 O. (Gerhardt.) — Oil of rue is supposed by Wagner to exist: in train-oil, in butter, in rich cheese, and in herring, inasmuch as train-oil heated with oil of vitriol, and then mixed with excess of hydrate of potash, gives off an odour of oil of rue, and the alkaline mixture yields by distillation drops of oil smelling of rue.

Preparation. 1. Gerhardt obtained his caprol or capric aldehyde by subjecting oil of rue to fractional distillation, setting aside the small quantity of non-oxygenated oil which first passed over, and collecting the principal portion which distilled at 233°. — Cahours likewise isolates his capric aldehyde, — which, according to him, passes over from 228° to 230°, — by fractional distillation of oil of rue. — 2. Williams agitates oil of rue with aqueous bisulphite of ammonia, and obtains thereby a crystalline mass, regarded by him as a mixture of the compounds of enodic and lauric aldehydes with bisulphite of ammonia,—which mass, after being separated from the other constituents of the oil of rue (a substance isomeric with oil of turpentine and another homologous with borneol), yields by its decomposition, enodic and lauric aldehydes. These two bodies may be separated, though not completely, by fractional distillation, enodic aldehyde which boils at 213° passing over first, and afterwards the small quantity of lauric aldehyde present, which boils at 232°. (Williams.) — 3. Commercial oil of rue, subjected to fractional distillation, yields (probably from admixture of turpentine) a considerable quantity of products, which pass over between 160° and 205°, and do not form solid compounds with bisulphite of ammonia. The portions which distil between 205° and 240° (amounting to nearly the entire residue), solidify when shaken up with bisulphite of ammonia, and then left to cool quickly, into a crystalline mass, which, after being washed with alcohol and pressed, yields an oil by decomposition with potash-ley. When this oil is once more shaken up with bisulphite of ammonia, and the resulting compound is again decomposed, the oil thus obtained passes over between 213° and 216°. (Hallwachs.)

Properties. Colourless, oil having a faint agreeable odour of rue (Will, Hallwachs), solidifying completely, in shining laminæ between — 1° and — 2°. (Cahours.) Boiling point (vid sup.). Sp. gr. of the portion distilling between 218° and 245° = 0·838. (Will.) — Vapour-density 5·83 (Gerhardt), 7·822 (Will), 5·87 (Williams).

Calculation according to Cahours & Gerhardt.

20 C	120	76·92
20 H	20	12·82
2 O	16	10·26
$C^{20}H^{20}O^2$	156	100·00

Calculation according to Williams.

a.			*b.*		
22 C	132	77·64	24 C	144	78·26
22 H	22	12·94	24 H	24	13·04
2 O	16	9·42	2 O	16	8·70
$C^{22}H^{22}O^2$	170	100·00	$C^{24}H^{24}O^2$	184	100·00

	Will.	Gerhardt.	Cahours.	Williams.		Hallwachs.
				a.	*b.*	
C	76·67	76·82	76·74	77·71	78·1	77·65
H	12·62	12·86	12·83	13·07	12·9	12·96
O	10·71	10·32	10·43	9·22	9·0	9·39
	100·00	100·00	100·00	100·00	100·0	100·00

	Vol.	Density.		Vol.	Density.
C-vapour	20	8·3200		22	9·1520
H-gas	20	1·3860		2	1·5246
O-gas	1	1·1093		2	1·1093
Capric Aldehyde	2	10·8153	Enodic Aldehyde	2	11·7859
	1	5·4076		1	5·8929

	Vol.	Density.
C-vapour	24	9·9840
H-gas	24	1·6632
O-gas	1	1·1093
Lauric aldehyde	2	12·7565
	1	6·3782

All the analytical results are mean numbers. Will originally gave the formula $C^{28}H^{28}O^{3}$. The oil *a* analysed by Williams is his enodic aldehyde; *b* his lauric aldehyde. Hallwachs found the portion which passed over between 205° and 240° to be of uniform composition throughout.

Decompositions. 1. Slightly heated oil of rue (prepared by 3), is easily inflammable and burns with a bright, slightly coloured flame. (Hallwachs.) — In contact with *iodine*, oil of rue becomes viscid and brown-red (Flaschhoff, *Br. Arch.* 33, 225), but does not form any product analogous to anisoin. (Will, *Ann. Pharm.* 65, 230.) — 3. It absorbs dry *chlorine gas* abundantly, becoming hot, giving off hydrochloric acid gas, and thickening. (Will.) — 4. Alcoholic oil of rue (prepared by 1), through which hydrochloric acid gas is passed, is converted, without change of composition, into metacaprol. (Gerhardt.) — 5. Oil of rue is attacked by *fuming nitric acid*, with evolution of nitrous gas (Will); strong nitric acid converts it into capric acid, or, according to the duration of the action, likewise into pelargonic (xiii, 369), caprylic (xiii, 189), and œnanthylic acid (xii, 451), with which also may be mixed acids containing a smaller proportion of carbon. (Cahours.) Nitric acid diluted with an equal quantity of water forms pelargonic acid; more dilute nitric acid forms capric acid (Gerhardt); the more dilute acid likewise forms pelargonic, and after prolonged boiling, ultimately also suberic and sebacic acids. (Wagner, *J. pr. Chem.* 57, 435.) Under circumstances not yet thoroughly understood, nitroso-pelargonic acid (xiii, 371), may also be produced. (Chiozza.) — 6. With alcoholic *hydrosulphate of ammonia,* oil of rue forms, after a few days, white shining crystals which are decomposed by recrystallisation. They are probably $C^{60}NH^{16}S^{4}$, and related to capric aldehyde in the same manner as thialdine to acetic aldehyde, inasmuch as, when boiled with potash-ley, they yield ammonia, capric aldehyde, and hydrosulphate of potash. (Wagner.) — 7. When oil of rue is heated to the boiling point with *potash-lime,* it resinises, without giving off gas, and leaves a yellowish residue, from which hydrochloric acid separates resin and a large quantity of unaltered oil. (Gerhardt.) — 8. Oil of rue distilled with 8 pts. of *chloride of lime* and 24 pts. of water, yields chloroform. (Chautard, *Compt. rend.* 34, 485; *J. pr. Chem.* 56, 238.) — 9. By the passage of its vapour over melting *chloride of zinc,* it is converted into a hydrocarbon. (Gerhardt.) — 10. *Ammoniacal silver-solution* is quickly reduced by boiling with oil of rue. (Gerhardt.) If the boiling with excess of ammoniacal silver-solution be continued as long as any reduction of silver takes place, the filtrate yields with aqueous potash, a precipitate of oxide of silver, which, when dissolved in dilute sulphuric acid, leaves a small quantity of metallic silver, while the alkaline liquid filtered from the oxide of silver contains a little capric acid. (Wagner.) — From these experiments, Wagner infers the existence of an acid corresponding to aldehydic acid (viii, 181), viz., *caprinylous acid*$=C^{20}H^{20}O^3$, or in the hyp. anhydrous state$=C^{20}H^{19}O^2$. — 11. In contact with dry *nitro-prusside of copper*, oil of rue becomes brownish yellow and forms an ash-grey deposit. (Heppe, *N. Br. Arch.* 89, 57.)

Combinations. Oil of rue dissolves in *oil of vitriol*, with a fine brown-red colour, and is separated again colourless by water. (Will.) — It is scarcely altered by *hydrochloric acid gas*, merely acquiring a brown colour, which it loses by agitation with water. (Will.)

With Ammonia, — $NH^3,C^{20}H^{20}O^2$? When oil of rue dissolved in alcohol is saturated at a low temperature with ammonia, a white crystalline mass is formed, which melts at about 0°, and is resolved into ammonia and oil of rue. (Wagner.) Wagner regards these crystals as a compound of ammonia with capric aldehyde. — For the decomposition of capric aldehyde-ammonia, by sulphuretted hydrogen see page 491.

With Bisulphite of Ammonia. 1. When sulphurous acid gas is passed through an alcoholic solution of ammoniacal oil of rue, and the solution left for several days in a very cold place, crystalline laminæ are deposited. (Wagner.) — 2. Oil of rue is shaken up with aqueous bisulphite of ammonia of 29° B., till the mixture, which is buttery at the commencement, becomes solid, and the product is recrystallised from warm alcohol. — The compound is likewise obtained in crystalline laminæ, by passing ammonia and sulphurous acid gases into an alcoholic solution of oil of rue. (Bertagnini.) — White shining laminæ. (Wagner.) Aggregated, transparent scales, unctuous to the touch, and having somewhat of the odour of oil of rue. (Bertagnini.) It is decomposed by heat, without previous fusion. (Wagner.) By heating its aqueous solution, it is readily decomposed, with separation of oil of rue, but not in presence of sulphites. With bromine in aqueous solution, it forms sulphuric acid, and a heavy brominated oil of peculiar odour. (Bertagnini.) — It is insoluble in water, but dissolves readily in boiling alcohol. (Wagner.) It is soluble in water and in alcohol. (Bertagnini.)

Calculation according to Bertagnini.			Bertagnini.	Wagner.
20 C	120	43·96	44·12	
N	14	5·13		5·00
27 H	27	9·89	9·71	
2 S	32	11·72	11·41	13·83
10 O	80	29·30		
$C^{20}H^{20}O^2,NH^3,2SO^2 + 4Aq$	273	100·00		

Calculation according to Wagner.

20 C	120	50·63
N	14	5·91
23 H	23	9·71
2 S	32	13·50
6 O	48	20·25
$C^{20}H^{20}O^2,NH^3,2SO^2$	237	100·00

With Bisulphite of Potash. — Prepared by agitating oil of rue with aqueous bisulphite of potash of 28°—30° Bm, a crystalline mass then forming after the action has been continued for several hours. — The compound dissolves with tolerable facility in boiling alcohol, and the solution deposits scales on cooling. (Bertagnini.)

With Bisulphite of Soda. — Oil of rue in contact with aqueous bisulphite of soda, of 27° Bm. forms a buttery mass, which after a while becomes crystalline. — Shining crystalline scales, unctuous to the touch, having the smell of oil of rue and a fruity taste. — The concentrated, but not the dilute solution of the compound in boiling alcohol, solidifies on cooling to a gelatinous mass, changing in the course of 24 hours into delicate laminæ, arranged concentrically in spherical crystalline masses. (Bertagnini.)

Metacaprol.

Gerhardt. *N. Ann. Chim. Phys.* 24, 105.

When oil of rue (prepared as described at p. 490, 1) is dissolved in 3 or 4 vol. alcohol and excess of hydrochloric acid gas is passed into the solution, the brown and fuming mixture, if mixed with water after the most volatile portion has been distilled off, deposits metacaprol.

Oil having a highly agreeable fruity odour. Solidifies, after a while, at a temperature at which oil of rue remains liquid, and melts again at 13°. Boils between 230° and 235°.

			Gerhardt.
20 C	120	76·92	77·10
20 H	20	12·82	12·95
2 O	16	10·26	9·95
$C^{20}H^{20}O^2$	156	100·00	100·00

Isomeric with capric aldehyde. (Gerhardt.)

Dissolves in *oil of vitriol* almost without colour. On heating the mixture, a conjugated acid is formed, the baryta-salt of which is soluble in water. It is not altered by *caustic potash* or by *nitrate of silver.*

Oxygen-nucleus $C^{20}H^{18}O^2$.

Sebacic Acid.

$$C^{20}H^{18}O^8 = C^{20}H^{18}O^2,O^6.$$

Thénard. (1802.) *Ann. Chim. Phys.* 39, 193; *Schw. J.* 8, 127.
V. Rose. *A. Gehl.* 275, 3, 170.
Berzelius. *N. Gehl.* 2, 275; *Lehrbuch.* 3, Aufl. 8, 667.
Dumas & Peligot. *Ann. Chim. Phys.* 57, 332; *Ann. Pharm.* 14, 73.
Redtenbacher. *Ann. Pharm.* 35, 188.
St. Evre. *N. Ann. Chim. Phys.* 20, 93; *J. pr. Chem.* 41, 144.
Schlieper. *Ann. Pharm.* 70, 121; *Pharm. Centr.* 1849, 459.
Bouis. *Compt. rend.* 33, 141. — *N. Ann. Chim. Phys.* 44, 100; 48, 99; *Ann. Pharm.* 80, 303; 97, 34.

W. MAYER. *Ann. Pharm.* 83, 143; 95, 160.
ROWNEY. *Chem. Soc. Qu. J.* 4, 334; *Ann. Pharm.* 82, 123; *J. pr. Chem.* 55, 325.
CARLET. *Compt. rend.* 37, 129; *J. pr. Chem.* 60, 181; *N. J. Pharm.* 24, 176.

Brenzoleic acid, Pyroleic acid, Sebacylsäure, Fettsäure. Discovered in 1802 by Thénard, who at the same time showed that the product of the distillation of animal fat, to which the name of *Fettsäure* or *Acide gras* had been applied by Crell (*Crell. chem. J.* 1, 60; 2, 112; 4, 47), and Guyton Morveau, consisted partly of acetic, partly of hydrochloric acid. Thénard's experiments were confirmed by V. Rose. Berzelius regarded Thénard's sebacic acid as identical with benzoic acid, an opinion which was shown to be incorrect by the experiments of Dumas & Peligot.

Mayer's *ipomæic acid* (not Sandrock's, *N. Br. Arch.* 64, 164), agrees with sebacic acid in most of its relations, but melts at a different temperature and exhibits a different behaviour to bases: for this reason, the statements respecting it are given separately.

Formation. 1. By the dry distillation of hog's lard (Thénard), fat oil (Berzelius), and other fats, in so far as they contain oleic acid: hence also by the dry distillation of oleic acid. (Redtenbacher.) — 2. When ricinolate of potash or castor-oil is distilled with excess of potash-hydrate, hydrogen is given off, caprylic alcohol (p. 183) passes over, and sebate of potash remains behind. (Bouis.) — The largest amount of sebacic acid is obtained when a large excess of alkali is used and the mixture is rapidly heated to the melting point, whereas by slow heating to at most 225°—230°, neither sebacic acid nor caprylic acid is obtained, but the acid $C^{20}H^{18}O^4$ and caprylic aldehyde. (Bouis.) — Limpricht (*Private communication*) by using an excess of alkali, always obtained sebacic acid, whether caprylic alcohol or caprylic aldehyde was produced; similarly Malaguti (Cimento, 4, 401; *Liebig u. Kopp's Jahresber.* 1856, 579). According to Dachauer (*Ann. Pharm.* 106, 270), the products obtained with excess of alkali, are caprylic alcohol, methyl-œnanthyl (isomeric with caprylic aldehyde), and sebate of potash; (according to Städeler, *J. pr. Chem.* 72, 241), oenanthylic alcohol, and sebate of potash (see xiii, 587). — 3. By continued boiling of oil of rue with dilute nitric acid. (Wagner, *J. pr. Chem.* 57, 435.) — 4. Convolvulic acid, convolvulinolic acid, jalapin, jalapic acid, and jalapinolic acid, treated with moderately strong nitric acid, or with the fuming acid, yield ipomæic and oxalic acids. (Mayer.)

Preparation. Method II. is the most advantageous. — 1. *From Olive oil, Hog's lard, or other fats containing Oleic acid.* Crude oleic acid from the stearin manufactories is best adapted for the purpose. (Redtenbacher.) — 1. The fat is distilled *per se*, and the distillate is repeatedly treated with hot water, then filtered, and evaporated to the crystallising point. — Or the solution obtained by treating the fat with hot water is precipitated with neutral acetate of lead; and the precipitate is collected and decomposed by heating with dilute sulphuric acid, whereupon the sebacic acid rises to the surface as a melted mass, which is taken off, washed with cold water, and recrystallised from boiling water. (Thénard.) Redtenbacher likewise obtains sebacic acid from the products of the distillation of fats by repeated boiling with water, and purifies it by recrystallisation, till it becomes white and scentless. — Berzelius washes the distillate of fat oil with cold water to separate acetic acid, and then boils it with coarsely powdered carbonate of lime, whereby only the sebacic acid is converted into a lime-salt, not the other acids. After long-continued boiling, the solution is filtered, deodorised with charcoal, and mixed with nitric acid, whereby sebacic acid is precipitated: it may be purified by washing with cold water, recrystallisation from boiling water, and finally by sublimation, in the apparatus used for the subliming benzoic acid.

2. The distillate of crude commercial oleic acid is repeatedly boiled with water; the extracts are saturated with carbonate of soda, and evaporated to dryness; and the residue is freed from caprylate and caprate of soda by means of hot absolute alcohol. The undissolved sebate of soda is dissolved in water and precipitated by hydrochloric acid, and the sebacic acid thereby separated, is purified by recrystallisation from boiling water. The still yellow sebacic acid obtained by this and other methods, is obtained pure by once boiling it with 5 to 6 pts. of nitric acid, and pouring the solution into a large quantity of boiling water, whereupon it crystallises on cooling. (Schlieper.)

II. *From Castor-oil.* The residue left in the retort in the preparation of caprylic alcohol (xiii, 183) is decomposed by hydrochloric acid, and the sebacic acid is extracted by boiling water from the mixture of insoluble acid which separates. (Bouis.) — Petersen boils the residue with water; strains; precipitates the other fatty acids by adding a small quantity of hydrochloric acid; then, after separating these by filtration, precipitates the sebacic acid by excess of hydrochloric acid, and purifies it by recrystallisation from hot water with the aid of animal charcoal. (*Ann. Ch. Pharm.* 103, 184.)

Properties. White, pearly needles, very much like those of benzoic acid. (Redtenbacher.) Under certain circumstances, it may be obtained in long, large, strongly shining laminæ. (Thénard.) Bulky and of a feathery lightness. (Berzelius.) — Ipomæic acid is dazzling white, of feathery lightness, and presents under the microscope the appearance of thin colourless needles, some of which are united in tufts, while others lie separate, sometimes in very thin flexible laminæ. (Mayer.) Sebacic acid melts at 125° (St. Evre), at 127° (Redtenbacher, Mayer, Bouis), to a colourless oil which solidifies in the crystalline form on cooling, and sublimes at a higher temperature, partly pulverulent, partly in minute laminæ, generally with some decomposition and separation of charcoal. (Berzelius, Redtenbacher). Ipomæic acid melts at 104° to a colourless oil, lighter than water, and solidifying in the crystalline state. It sometimes sublimes between two watch-glasses in very small, proportionally short needles radially grouped round a point, leaving a small quantity of charcoal, whereas sebacic acid sublimed in like manner, forms larger and more definite crystals. (Mayer.) — Sp. gr. of melted sebacic acid = 1·1317. (Carlet.) Scentless (Thénard); has a faint empyreumatic odour (Berzelius). The vapours, both of sebacic and of ipomæic acid, produce a scratching sensation when inhaled. (Redtenbacher, Mayer.) Has a faint, rather acid taste (Thénard), pungent, but not exactly sour (Berzelius). Reddens litmus strongly (Thénard), slightly (Redtenbacher). Ipomæic acid is scentless, has a pungent, sour taste, with irritating after-taste, a slight acid reaction, and becomes strongly electrical by friction. (Mayer.)

			Dumas & Peligot.	Redtenbacher.	St Evre.
			mean.		
20 C	120	59·40	59·52	59·52	59·30
18 H	18	8·91	9·08	8·90	9·04
8 O	64	31·69	31·40	30·90	31·66
$C^{20}H^{18}O^8$	202	100·00	100·00	99·32	100·00

	Mayer.		Bouis.	Carlet.
	mean.			
	a.	*b.*		
C	59·44	59·20	60·52	59·25
H	9·01	8·97	8·97	9·07
O	31·55	31·83	30·51	31·68
	100·00	100·00	100·00	100·00

Bouis and Carlet analysed sebacic acid prepared from castor-oil; Mayer analysed ipomæic acid: *a* obtained from convolvulic and convolvulinolic acid; *b* from jalapin, jalapic acid and jalapinolic acid. The formula $C^{10}H^9O^4$, given by Mayer, is here doubled in accordance with the principles of the Handbook.

Decompositions. 1. Ipomæic acid heated on platinum foil, volatilises in white fumes, which burn slowly and with a feebly luminous flame. (Mayer; see also *infra.*)

2. *Nitric acid* of sp. gr. 1·4 dissolves sebacic acid with the aid of heat, giving off red vapours and acquiring an orange-red colour, and if the boiling be continued, and the exhausted nitric acid removed, slowly converts it into pyrotartaric acid (Schliesser, xi, 83); into succinic acid (Carlet); into a mixture of succinic and oxypyrolic acid $C^7H^6O^5$ (Arppe, *Ann. Pharm.* 95, 242); of succinic, pimelic (xii, 463), and perhaps also adipic acid. (Wirz, *Ann. Pharm.* 104, 280). After two or three hours boiling with nitric acid, the greater part of the sebacic acid remains unaltered, the decomposition not being completed in less than a week. (Schliesser.) — Ipomæic acid is not altered by being heated with nitric acid on the water-bath for many days, and separates out unaltered when the nitric acid is evaporated. (Mayer.) — 3. Sebacic acid is attacked by *pentachloride of phosphorus,* with formation of hydrochloric acid gas, chlorophosphoric acid and sebacic anhydride. (Gerhardt & Chiozza, *Compt. rend.* 30, 1050; *Ann. Pharm.* 87, 294.) — 4. *Chlorine* acts on sebacic acid only in sunshine, forming two yellow substitution-products, $C^{20}ClH^{17}O^8$ and $C^{20}Cl^2H^{16}O^8$, which are pasty at mean temperature. (Carlet.) — 5. The *lime-salt* of sebacic acid, subjected to *dry distillation,* gives off hydrogen gas, and yields an oil boiling between 80° and 200°. — On rectifying this oil, a liquid passes over between 85° and 90°, which has a pleasant ethereal odour and appears to be propionic aldehyde,—then, between 156° and 200°, œnanthol (xii, 446) distils over. (Calvi.) When sebate of lime is distilled with *excess of lime,* sebacin (p. 447) is obtained, together with an oil boiling between 80° and 280°. The latter, when rectified, first yields a product which, when treated with nitric acid, forms nitrobenzene, and is therefore probably benzene,—then, between 90° and 100°, propionic aldehyde,—and at 160°, œnanthol, inasmuch as the portion which distils at these temperatures forms, with nitric acid, propionic and œnanthylic acids. (Petersen, *Ann. Pharm.* 103, 184.) By distillation with excess of *baryta,* sebacic acid yields carbonate of baryta and a hydrocarbon, $C^{16}H^{18}$, boiling between 125° and 130°, chiefly at 127°. (A. Riche, *Par. Soc.*

Bull. 1, 88; *Rep. Chim. pure,* 2, 127.) — 6. When *alcoholic* sebacic acid is treated with *hydrochloric acid gas,* an oil is produced which with ammonia forms sebamide and sebamic acid, and is therefore probably a mixture of sebacic ether and ethylsebacic acid. (Rowney, see page 502.)

Combinations. Sebacic acid dissolves sparingly in cold *water.* It dissolves abundantly in boiling water (Thénard); in all proportions (Berzelius), so that the solution solidifies on cooling. Ipomæic acid is slightly soluble in cold, very easily soluble in hot water. (Mayer.)

Sebacic acid is *bibasic.* Its *semi-acid* or *bibasic* (*neutral*) salts are $C^{20}M^2H^{16}O^8$. The *mono-acid* or *monobasic* (*acid*) salts are, excepting the ammonia-salt, easily decomposible. (Carlet.) It decomposes alkaline carbonates, forming with them, easily soluble salts, whose solutions precipitate the salts of the alkaline earths and heavy metallic oxides (not ferrous salts, according to Berzelius). Acids separate sebacic acid from them and cause concentrated solutions to solidify. Aqueous sebacic acid does not precipitate baryta-, strontia-, or lime-water. It precipitates lead-, silver-, and mercuric-salts. (Thénard.) Sebacic acid obtained from marrow does not precipitate lead- or silver-salts, or only if prepared from marrow having membranes or blood-vessels adhering to it. (Berzelius.) Berzelius likewise found that sebate of potash is divided by absolute alcohol into two parts, and that only the acid of the insoluble, not that of the soluble salt, precipitates lead and silver-salts. Redtenbacher, however, did not succeed in separating from his sebate of potash by absolute alcohol, a salt whose acid did not precipitate mercurous and silver salts.

The *ipomæates,* excepting those of the alkalis, are sparingly soluble or insoluble in water. Ipomæate of ammonia forms a white precipitate with lead-salts, flesh-coloured with ferric chloride, bluish-green with cupric salts, and white with silver-salts. With bichloride of platinum, it forms a yellow precipitate which dissolves in boiling water, separates again on cooling, and then becomes crystalline after long standing. — The ipomæates become electrical by friction. (Mayer.)

Sebate of Ammonia. — *a. Bibasic.* — Indistinct crystals, which are easily soluble in water, and in drying, give off ammonia and turn acid. (Redtenbacher.) Yields sebamic acid by dry distillation. (Kraut.)

b. Monobasic. — The easily prepared solution of sebacic acid in excess of ammonia gives off ammonia when evaporated, and leaves the monobasic salt, sparingly soluble in water. Crystallises from boiling water by slow cooling, in pointed feathery crystals; by rapid cooling, in small grains. Dissolves with difficulty in alcohol. (Berzelius.) — Ipomæic acid, saturated with aqueous ammonia, continually gives off ammonia by spontaneous evaporation or on the water-bath, and yields a white cauliflower-like salt, probably $C^{20}H^{17}O^7,NH^4O$, therefore ipomæate of ammonia.

Sebate of Potash. — *Bibasic.* — Obtained by neutralising the acid with carbonate of potash. Small granular nodules. (Redtenbacher.) Does not deliquesce on exposure to the air. (Thénard, Redtenbacher.) Easily soluble in water, sparingly in absolute alcohol. (Redtenbacher.)

			Redtenbacher.
20 C	120·0	43·11	43·00
2 KO	94·4	33·91	
16 H	16·0	5·74	5·94
6 O	48·0	17·24	
$C^{20}K^2H^{16}O^8$	278·4	100·00	

Redtenbacher did not obtain an acid sebate of potash by treating the neutral salt with sebacic acid.

Sebate of Soda resembles the potash-salt, but is somewhat more soluble in water. (Redtenbacher.) Insoluble in absolute alcohol. (Schlieper.)

Sebate of Lime. — Bibasic. — Chloride of calcium solution precipitates sebate of ammonia. The precipitate, which dissolves with some difficulty in water, is obtained, by spontaneous evaporation of its dilute solution, in white, shining crystalline scales. (Redtenbacher.) The precipitate obtained with sebate of ammonia and chloride of calcium is crystalline when formed; but that which is produced by ipomæate of ammonia becomes crystalline only after standing for some time. (Mayer.) — For the decomposition of the lime-salt by dry distillation, see page 497.

			Redtenbacher.
20 C	120	50·00	49·49
2 CaO	56	23·33	22·91
16 H	16	6·67	6·76
6 O	48	20·00	20·84
$C^2Ca^2H^{16}O^8$	240	100·00	100·00

Sebate of Lead. — The white precipitate insoluble in water, which sebate of potash forms with solution of neutral acetate of lead, is converted by ammonia into a basic salt. (Berzelius.) — The precipitate obtained by treating acetate of lead with ipomæate of ammonia, is a white powder, insoluble in water, which, after drying over oil of vitriol, contains 54·70 p. c. oxide of lead, and is therefore $C^{20}Pb^2H^{16}O^8$ (calculation = 54·00 PbO). (Mayer.)

Ferric Sebate, obtained by double decomposition, is a flesh-coloured precipitate, which, when treated with aqueous carbonate of ammonia or caustic potash, dissolves partially, with red colour, leaving a highly basic salt. When heated, it melts, swells up, and decomposes. (Berzelius.)

Sebate of Copper. — The precipitate which soluble sebates produce in aqueous sulphate of copper is bluish, and redissolves at first, but becomes permanent on addition of a larger quantity of sebate, and exhibits a fine green colour when dry. The filtered liquid, when left to evaporate, becomes covered with a green crystalline crust and deposits green granules. (Berzelius.) — Cupric acetate is precipitated by ipomæate of ammonia, and the precipitate is dried in vacuo over oil of vitriol. (Contains 29·92 p. c. cupric oxide, corresponding to the formula $C^{20}Cu^2H^{16}O^8$ (calculation 30·30 CuO). (Mayer.)

Sebate of Silver. — Bibasic. — Nitrate of silver is precipitated by sebate of ammonia (ipomæate: Mayer), and the precipitate is washed, and dried in vacuo at 120° (Dumas & Peligot); over oil of vitriol. (Mayer.)

White curdy precipitate (Redtenbacher). White, rather light powder. (Mayer.) Heated in a glass tube, it yields metallic silver and a sublimate of sebacic acid (Redtenbacher), of ipomæic acid (Mayer.) Dissolves with difficulty in water (Redtenbacher), not at all (Mayer). Dissolves with difficulty in alcohol and ether. (Mayer.)

			Redtenbacher.	Mayer.
20 C	120	28·84	29·19	29·14
2 AgO	232	55·76	55·45	54·89
16 H	16	3·84	3·97	4·02
6 O	48	11·56	11·39	11·95
$C^{20}Ag^2H^{16}O^8$	416	100·00	100·00	100·00

Contains 54·9 p. c. oxide of silver. (Dumas & Peligot.)

Sebasic acid dissolves readily in *alcohol*, in ether, and in oils, both fixed and volatile. (Berzelius.) — Ipomæic acid dissolves readily in alcohol and in ether. (Mayer.)

Sebate of Methyl.

$$C^{24}H^{22}O^8 = 2C^2H^3O,C^{20}H^{16}O^6.$$

Henry Carlet. (1853.) *Compt. rend.* 37, 129; *N. J. Pharm.* 24, 176; *J. pr. Chem.* 60, 181; *Pharm. Centr.* 1853, 669; *Chem. Gaz.* 1853, 324.

Methylsebacic ether. Sebacylformester.

Formation and Preparation. Sebacic acid is dissolved in oil of vitriol, wood-spirit carefully added, the liquid being agitated and cooled to prevent too great heating; and the resulting ether is precipitated by water, washed first with alkaline, then with pure water, and crystallised from alcohol.

Beautiful needles, which melt at 25·5°, and boil without decomposition at 285°. In the solid state, it dissolves in water with comparative difficulty, in the fused state more readily. Has a very faint odour.

By *ammonia* it is converted into sebamide and wood-spirit, by *hydrate of potash*, into sebate of potash and wood-spirit.

Sebate of Ethyl.

$$C^{28}H^{26}O^8 = 2C^4H^5O,C^{20}H^{16}O^6.$$

Redtenbacher. (1840.) *Ann. Pharm.* 35, 193.

Sebacic ether, fettsaures Aethyloxyd, Fettnaphta, Sebacylvinester.

Formation and Preparation. Sebacic acid is dissolved in a small quantity of alcohol; hydrochloric acid is passed into the solution to saturation; and the chloride of ethyl thereby produced is volatilised by gentle heating. The residue is washed with water, then with aqueous carbonate of soda, dehydrated by chloride of calcium, and rectified. (Redtenbacher.) — Alcoholic sebacic acid, treated with hydrochloric acid gas, yields a mixture of sebacic ether and ethylsebacic acid. (Rowney, *Ann. Pharm.* 82, 124.)

Properties. Colourless oil, lighter than water. Solidifies in the crystalline form at — 9°. Boils above 100° (Redtenbacher), at 308° (Carlet, *Compt. rend.* 37, 130). Has an agreeable odour of melons.

						Redtenbacher.
28 C	168	....	65·12	....	64·45
26 H	26	....	10·08	....	10·24
8 O	64	....	24·80	....	25·31
$2C^4H^5O,C^{20}H^{16}O^6$	258	....	100·00	....	100·00

By *hydrate of potash,* it is resolved into alcohol and sebate of potash (Redtenbacher); *ammonia,* after long continued action, converts it into sebamide. (Rowney.)

It is insoluble in cold *water,* but dissolves very easily in *alcohol.* (Rowney.)

Sebin.

$$C^{32}H^{30}O^{16} = 2C^6H^7O^5,C^{20}H^{16}O^6.$$

M. BERTHELOT. *N. Ann. Chim. Phys.* 41, 293.

Formation. 1. Sebacic acid, heated with glycerin to 200° for some time, forms a small quantity of neutral crystallisable sebin:

$$C^{20}H^{18}O^8 + 2C^6H^8O^6 = C^{32}H^{30}O^{16} + 4HO.$$

2. By the action of hydrochloric acid gas on a mixture of sebacic acid and glycerin heated to 100°, a considerable quantity of liquid sebin is obtained, mixed with chlorhydrin, $C^6H^7ClO^4$, which, after strong drying at 120°, solidifies partially after a few days, and completely at — 40°.

					Berthelot.
32 C	192	....	54·85	....	52·7
30 H	30	....	8·57	....	9·6
16 O	128	....	36·58	....	37·7
$2C^6H^7O^5,C^{20}H^{16}O^6$	350	....	100·00	....	100·0

Forms acrolein when *heated.* — *Oxide of lead* converts it into sebacic acid and glycerin; with *alcoholic hydrochloric acid,* it yields sebacic ether and glycerin. (Berthelot.)

Nitro-nucleus $C^{20}XH^{19}$.

Nitrocapric Acid.

$$C^{20}NH^{19}O^8 = C^{20}XH^{19},O^4.$$

WIRZ. (1857.) *Ann. Pharm.* 104, 289.

Obtained by the process described at page 217, vol. xiii, but mixed with nitrocaprylic acid, from which it cannot be completely separated.

When the solution of this mixture in ammonia is fractionally precipitated in three portions by nitrate of silver, the precipitate first produced contains 28·89 to 29·3 p. c. silver, the second portion 32·8 to 33·3 p. c., and the last 37·4 p. c., corresponding to nitrocaprylate of silver.

Nitrocaprate of Silver.			Wirz.
20 C	120	37·0	33·57 to 35·97
N	14	4·3	
18 H	18	5·6	5·14 ,, 6·30
Ag	108	33·3	34·04 ,, 31·90
8 O	64	19·8	
$C^{20}AgXH^{18}O^4$	324	100·0	

Amidogen-nucleus $C^{20}AdH^{19}$.

Capramide.

$C^{20}NH^{21}O^2 = C^{20}AdH^{19},O^2$.

Rowney. *Ann. Pharm.* 79, 236.

Rutamide.

Caprate of ethyl dissolved in alcohol is precipitated by strong aqueous ammonia, till the ether disappears and is completely converted into crystals; and the crystals are collected,—an additional quantity being obtained from the mother liquor by evaporation to dryness, solution of the residue in alcohol, and precipitation by water,—and recrystallised from warm dilute alcohol.

Colourless shining scales, acquiring a silvery lustre when dry. Melts below 100°.

			Rowney.
20 C	120	70·17	70·62
N	14	8·18	
21 H	21	12·28	12·17
2 O	16	9·37	
$C^{20}AdH^{19}O^2$	171	100·00	

Insoluble in *water* and in *ammonia*.

Dissolves readily in cold *alcohol*, and is precipitated therefrom in needles by water. Easily soluble in *ether*, but does not crystallise therefrom.

Oxyamidogen-nucleus $C^{20}AdH^{17}O^2$.

Sebamic Acid.

$C^{20}NH^{19}O^6 = C^{20}AdH^{17}O^2,O^4$.

Rowney. (1851.) *Chem. Soc. Qu. J.* 4, 334; *Ann. Pharm.* 82, 123; *J. pr. Chem.* 55, 325.

Fettaminsäure, Sebaminsäure, Sebacylaminsäure.

Formation. 1. By the action of ammonia on ethylsebamic acid. (Rowney.) — 2. By the dry distillation of neutral sebamate of ammonia. (Kraut.)

Preparation. 1. The oily mixture of sebacic ether and ethyl-sebacic acid obtained by the action of hydrochloric acid gas on an alcoholic solution of sebacic acid, is digested with strong aqueous ammonia for several weeks in a closed vessel, or till the oil is converted into a granular mass, the sebamide which separates from the liquid containing sebamic acid, being removed by filtration, and washed to free it from mother-liquor. The several portions of liquid are then united and concentrated over the water-bath; the sebamic acid is precipitated by hydrochloric acid, washed with cold water, and dissolved in dilute aqueous ammonia, which still leaves a small quantity of sebamide undissolved; the solution filtered therefrom is again precipitated by hydrochloric acid; and the resulting precipitate, after being washed, is purified by recrystallisation from water. (Rowney.) — 2. Neutral sebate of ammonia yields by simple distillation, first a colourless, then a yellowish empyreumatic distillate, which is to be dissolved in ammonia, filtered from a small quantity of oil which separates, and precipitated with hydrochloric acid. The precipitate is washed with cold water, and recrystallised from boiling water. (Kraut.)

Properties. Rounded granules. (Rowney.) White, crystalline, pulverulent mass. (Kraut.) Has an acid reaction. (Rowney.)

			Rowney. *mean.*	Kraut. *Dried over oil of vitriol.*
20 C	120	59·70	59·65	59·98
N	14	6·97	6·70	7·09
19 H	19	9·45	9·53	9·81
6 O	48	23·88	24·12	23·12
$C^{20}AdH^{17}O^6$	201	100·00	100·00	100·00

Decompositions. 1. Gives off ammonia when boiled with *potash.* (Rowney.) — 2. The soda-salt brought in contact with *chloride of benzoyl,* yields chloride of sodium and an oil, which may be dissolved out by ether, is left behind when the ether evaporates, gives off ammonia when fused with hydrate of potash, is insoluble in water and ammonia, and, when washed with ammonia, gives up to it only a small quantity of free acid. (Kraut.)

Combinations. Sparingly soluble in cold, easily in warm *water.*

Easily soluble in *ammonia.* (Rowney.) Boiled with *carbonate of lime,* it gives off carbonic acid, and forms a lime-salt slightly soluble in water. (Kraut.) The solution of sebamic acid in ammonia does not precipitate the alkaline earths; it precipitates *acetate of lead,* and forms with *nitrate of silver,* a precipitate soluble in ammonia and in nitric acid. (Rowney.)

Sebamic acid is easily soluble in *alcohol.* (Rowney.)

Oxyamidogen-nucleus $C^{20}Ad^2H^{16}O^2$.

Sebamide.

$$C^{20}H^{20}N^2O^4 = C^{20}Ad^2H^{16}O^2,O^2.$$

ROWNEY. (1851.) *Chem. Soc. Qu. J.* 4, 334; *Ann. Pharm.* 82, 123; *J. pr. Chem.* 55, 325.
H. CARLET. *Compt. rend.* 37, 128; *N. J. Pharm.* 24, 176; *J. pr. Chem.* 60, 181; *Pharm. Centr.* 1853, 669; *Chem. Gaz.* 1853, 324.

Fettsäureamid.

Formation and Preparation. 1. Sebamide obtained in the manner just described (p. 502). is purified by two recrystallisations from alcohol, (Rowney.) — 2. It is produced by the action of ammonia on sebate of methyl. (Carlet.)

Properties. Hard rounded granules composed of microscopic needles. Neutral.

			Rowney. *mean.*
20 C	120	60·	59·94
2 N	28	14·	13·85
20 H	20	10·	10·01
4 O	32	16·	16·20
$C^{20}Ad^2H^{16}O^4$	200	100·	100·00

Decompositions. Water gradually converts it into sebate of ammonia. (Carlet.) It is not attacked by potash-ley in the cold, but gives off ammonia when boiled therewith. (Rowney.)

It is insoluble in cold, moderately soluble in boiling *water*. Insoluble in *ammonia*. Dissolves very sparingly in cold *alcohol*, very easily in boiling alcohol. (Rowney.)

Primary Nucleus $C^{20}H^{26}$: *Oxygen-nucleus* $C^{20}H^{18}O^8$.

Anisoic Acid.

$$C^{20}H^{18}O^{12} = C^{20}H^{18}O^8,O^4.$$

LIMPRICHT & RITTER. (1856.) *Ann. Pharm.* 97, 364; abstr. *J. pr. Chem.* 68, 160; *Chem. Centr.* 1856, 446.

Formation and Preparation. When oil of star-anise is heated with nitric acid of sp. gr. 1·2, as long as it floats on the surface of the acid, and the product is shaken up with a warm aqueous solution of bisulphite of soda, anisoate of soda crystallises on cooling. This salt is recrystallised from a small quantity of hot water, mixed with a quantity of dilute sulphuric acid exactly sufficient to decompose it, the solution evaporated to dryness on the water-bath, and the residue exhausted with absolute alcohol, whereupon anisoic acid passes into solution and may be converted into a baryta or silver-salt, by digestion with carbonate of baryta or carbonate of silver. By decomposing the baryta-salt with dilute sulphuric acid, or the silver-salt with hydrochloric acid, a solution of anisoic acid is obtained, which may be brought to the crystallising point by evaporation.

Properties. Separates from warm solutions by concentration in small laminæ, by spontaneous evaporation in small thick tablets, which melt at about 120° and have a strong acid reaction.

Decompositions. Heated on platinum-foil, it turns brown, gives off an empyreumatic odour, also that of anisylous acid, and burns with a bright flame. It cannot be distilled without decomposition, and by dry distillation appears to yield a sublimate of anisic acid (vid. *Ann. Pharm.* 97, 366).

Combinations. Anisoic acid dissolves very easily in *water*.

With bases it forms the *anisoates*.

Anisoate of Soda. — Preparation (p. 503.) By recrystallisation from hot water, it is obtained in white crystalline nodules. Dissolves readily in water. Dried at 100°, it contains 8·9 p. c. sodium, and is therefore $C^{20}NaH^{17}O^{2}$ (calculation = 8·9 p. c. Na).

Anisoate of Baryta. — Preparation (sup.). Easily soluble nodules resembling those of the soda-salt.

			Limpricht & Ritter. *mean.*
20 C	120·0	39·78	39·44
Ba	68·6	22·74	22·39
17 H	17·0	5·65	5·44
12 O	96·0	31·83	32·73
$C^{20}BaH^{17}O^{12}$	301·6	100·00	100·00

Anisoate of Silver. Obtained as above described, or by decomposing the baryta-salt with sulphate of silver.

Crystalline nodules, which in the moist state blacken on exposure to light.

Dried over oil of vitriol.			Limpricht & Ritter.
20 C	120	35·19	34·1
Ag	108	31·67	32·2
17 H	17	4·98	4·0
12 O	96	28·16	29·7
$C^{20}AgH^{17}O^{12}$	341	100·00	100·0

Anisoic acid dissolves very readily in *alcohol* and *ether*.

Addenda to compounds containing 20 At. Carbon.

Product of the decomposition of Amalic Acid.

$C^{20}N^{4}H^{14}O^{11}$.

Rochleder & Schwartz. *Wien. Akad. Ber.* 12, 190.

Amalic acid (xi, 433) dissolves with pale yellow colour in warm concentrated bisulphite of ammonia, the solution when heated becoming darker and depositing needles, which, after boiling for some time, cause the liquid to solidify. The whole is left to cool, and the needles are collected, washed, and pressed.

White, silky needles, free from sulphur.

	In vacuo.		Rochleder & Schwartz. *mean.*
20 C	120	43·17	43·24
4 N	56	20·14	20·27
14 H	14	5·04	5·38
11 O	88	31·65	31·11
$C^{20}N^{4}H^{14}O^{11}$	278	100·00	100·00

The compound acquires a rose-colour by exposure to moist *air* (containing ammonia). — It decomposes when *heated,* giving off colourless and purple smoke, consisting of crystalline spangles. — Left for some time in contact with *bichloride of platinum,* it decomposes, yielding light yellow crystals which contain 58·77 p. c. platinum, and are probably therefore Reiset's ammonio-platinous chloride (vi, 300; calculation 58·79 p. c. Pt.). Perhaps formed in this manner:

$$C^{20}N^{4}H^{14}O^{11} + HO + PtCl^{2} = N^{2}H^{6}PtCl + C^{20}H^{8}N^{2}O^{12} + HCl.$$

(Rochleder & Schwartz.)

The compound dissolves very readily in *acids,* but not in other liquids. The hydrochloric acid solution does not precipitate bichloride of platinum, even after addition of ether-alcohol.

¶ Derivatives of Sulphonaphthalic Acid.

Kimberly. *Ann. Pharm.* 114, 129; abstr. *Rep. Chim. pure,* 2, 258.

Sulphite of Chloronaphthalin. $C^{20}H^{7}Cl,2SO^{2}$. — *Naphthylsulphurous Chloride, Chlorür der naphtylschwefligen Saure.* — Produced by the action of pentachloride of phosphorus on sulphonaphthalate of soda (p. 17):

$$C^{20}H^{8},2SO^{3} + PCl^{5} = C^{20}H^{7}Cl,2SO^{2} + PCl^{3}O^{2} + NaCl.$$

1 At. of the soda-salt dried at 100° is intimately mixed in a slightly heated capsule with 1 At. pentachloride of phosphorus; and the solidified mass is triturated and washed with water, till the oxychloride of phosphorous is completely decomposed and the chloride of sodium dissolved: the residue consists of sulphite of chloronaphthalin. It is purified by drying on filtering paper, dissolving in ether free from alcohol, filtering, evaporating, and drying at 100°.

White, inodorous solid body, which melts at 65° and solidifies at a lower temperature in rounded lamellar masses. Partially volatile without decomposition, but begins to decompose, even at 120°.

20 C	120·0	52·95	
7 H	7·0	3·14	
Cl	35·5	15·67	15·62
2 S	32·0	14·12	14·03
6 O	32·0	14·12	
$C^{20}H^7Cl,2SO^2$	226·5	100·00	

May be regarded as $\left.\begin{matrix}(S^2O^2)''\\(C^{20}H^7)'\end{matrix}\right\}\begin{matrix}O^2\\Cl\end{matrix}$, deriving from the mixed type $\left\{\begin{matrix}H^2O^2\\HCl\end{matrix}\right.$.

The compound is decomposed by *water* and by the aqueous and alcoholic solutions of *potash*, especially with the aid of heat, yielding hydrochloric acid and sulphonaphthalic acid:

$$C^{20}H^7Cl,2SO^2 + 2HO = HCl + C^{20}H^8,2SO^3:$$

With absolute *alcohol*, it forms hydrochloric acid and sulphonaphthalate of ethyl:

$$C^{20}H^7Cl,2SO^2 + C^4H^6O^2 = HCl + C^{20}H^7(C^4H^5),2SO^3.$$

Sulphite of chloronaphthalin is insoluble in water, but dissolves in *sulphide of carbon, oxychloride of phosphorus, ether* and *benzene;* likewise in *alcohol,* but not without alteration.

SULPHONAPHTHALATE OF ETHYL. $C^{24}H^{12}S^2O^6 = C^{20}H^7(C^4H^5), 2SO^3$. — *Sulphonaphthalic ether, Ether naphtylsulfureux, Naphtylschwefligsaures Aethyl.* (Kimberly.) — Produced by the action of absolute alcohol on sulphate of chloronaphthalin (*vid sup.*) — In preparing the ether, it is best to use 2 At. alcohol to 1 At. of the sulphite. — The excess of alcohol is expelled by distillation, and the residue is washed with water. The hydrochloric acid produced at the same time, acts upon the alcohol, forming chloride of ethyl and water, which then decomposes a portion of the sulphite of chloronaphthalin.

Sulphonaphthalic ether, recently prepared, is, at ordinary temperatures, a viscid liquid, which does not solidify, even at —8° or —10°. If care has been taken not to heat it as high as 50° during the preparation and purification, it crystallises, after a few days, in aggregated laminæ; but if it has been more strongly heated, it does not crystallise for a much longer time.

			Kimberle.
24 C	144	61·01	60·77
12 H	12	5·09	5·19
2 S	32	13·56	13·77
6 O	48	20·34	20·27
$C^{20}H^7(C^4H^5),2SO^3$	236	100·00	100·00

It is decomposed by distillation, with formation of sulphurous acid, naphthalin, and carbonaceous matter. — Heated with *water* to about 150° in a sealed tube, it yields alcohol, naphthalin, and sulphuric acid, without any secondary products, according to the equation:

$$C^{20}H^7(C^4H^5),2SO^3 + 4HO = C^4H^6O^2 + C^{20}H^8 + 2(HO,SO^3).$$

Potash transforms it into alcohol and sulphonaphthalate of potash. —

With *pentachloride of phosphorus*, it yields sulphite of chloronaphthalin, chloride of ethyl, and oxychloride of phosphorus.

It is insoluble in *water*, but mixes in all proportions with *alcohol* and *ether*.

NAPHTHYLTHIONAMIDE. $C^{20}H^{9}NS^{2}O^{4}=C^{20}H^{7}Ad,2SO^{2}$. — Produced by the action of ammonia on sulphite of chloronaphthalin. The sulphite triturated in a basin with aqueous ammonia, becomes heated and melts to a yellow oil, solidifying in a light yellow amorphous mass, which may be purified by washing with water, solution in alcohol, and crystallisation. — It forms microscopic crystals apparently belonging to the right prismatic system, greyish yellow when dry, light yellow when moist, and becoming reddish by exposure to the air. In boiling water, it melts to a viscid mass, without decomposing. It is soluble in hydrochloric acid, ammonia, glacial acetic acid, alcohol and ether. Potash decomposes it into ammonia and sulphonaphthalic acid:

			Kimberly.	
20 C	120	57·96	57·58	
9 H	9	4·36	4·55	
N	14	6·77	6·64	6·36
2 S	32	15·45	15·57	
4 O	32	15·46	15·66	
$C^{20}H^{7}Ad,2SO^{2}$	207	100·00	100·00	

May be regarded as $\left.\begin{matrix}(S^{2}O^{2})''\\(C^{20}H^{7})'\\H^{2}\end{matrix}\right\}\begin{matrix}N\\O^{2}\end{matrix}$, deriving from the mixed type $\left.\begin{matrix}H^{3}N\\H^{2}O^{2}\end{matrix}\right\}$

Argento-naphthylthionamide. $C^{20}H^{8}AgNS^{2}O^{4}=C^{20}AdH^{6}Ag,2SO^{2}$. — A slightly ammoniacal alcoholic solution of naphthylthionamide is not precipitated by nitrate of silver, but as the ammonia evaporates in the air, argento-naphthylthionamide is deposited in small radiating needles, which alter by exposure to light. They are soluble in ammonia, alcohol, and ether, and likewise, without apparent alteration, in glacial acetic acid. — Contains 34·10 p. c. silver, the formula requiring 34·39 p. c.

Benzoyl-naphthylthionamide, $C^{34}H^{13}NS^{2}O^{6} = C^{20}AdH^{6}(C^{14}H^{5}O^{2}),2SO^{2}$. — Obtained by melting naphthylthionamide with chloride of benzoyl. It is soluble in alcohol and in glacial acetic acid, and crystallises from its solutions in prisms apparently belonging to the oblique prismatic system. Potash decomposes it, yielding ammonia, benzoate of potash and sulphonaphthylate of potash. — Contains 4·36 p. c. nitrogen and 10·41 sulphur (calculation = 4·50 p. c. N and 10·28 S).

Argento-benzoyl-naphthylthionamide. $C^{20}AdH^{5}Ag(C^{14}H^{5}O^{2}),2SO^{2}$. — The solution of the preceding compound in absolute alcohol forms, with ammonia and nitrate of silver, as the ammonia evaporates, an amorphous flocculent precipitate, sparingly soluble in alcohol and decomposed by boiling. By precipitating its ammoniacal alcoholic solution with a slight excess of acetic acid, and raising the temperature for a few seconds to 30° or 40°, the compound may be obtained in shining microscopic crystals. — Contains 24·94 p. c. silver and 7·75 sulphur (calculation = 25·83 p. c. Ag and 7·65 S). (Kimberly.)

Cumylamines.

A. Rossi. *Compt. rend.* 51, 570; *Rep. Chim. pure*, 2, 465.

Cuminamines. — These bodies which are analogous to the ethylamines, methylamines, &c., are produced by the action of ammonia on chloride of cumyl (p. 165). When a mixture of chloride of cumyl and strong alcoholic ammonia is heated for some hours in a sealed tube placed in the water-bath, and then left to cool, sal-ammoniac separates, together with a few drops of oily tricumylamine. The liquid filtered and evaporated, leaves a crystalline residue consisting of the hydrochlorates of cumylamine and bicumylamine, mixed with oily tricumylamine, which may be dissolved out by ether, and remains after evaporation of the ether as an oil, which may be made to crystallise by agitation. — The hydrochlorates of the other two bases are separated by fractional crystalline from water, the hydrochlorate of bicumylamine being much less soluble in water than the cumylamine-salt. The bases are separate from the hydrochlorates by distillation with potash.

Cumylamine, $C^{20}H^{15}N = C^{20}H^{11}Ad,H^2 = N,H^2,C^{20}H^{13}$. — *Cuminamine primaire.* — Isomeric with biethylaniline (xi, 307). — Colourless oily liquid, which does not solidify in a mixture of ice and salt. — Volatile at ordinary temperatures, and produces white fumes in the approach of a rod moistened with hydrochloric acid. Begins to boil at about 280°, with partial decomposition sparingly soluble in water, soluble in alcohol and ether. Absorbs carbonic acid, forming a solid compound. — The *hydrochlorate* crystallises in nacreous, rhomboïdal laminæ. — The *chloroplatinate* is slightly soluble in cold water, whence it crystallises in small yellow plates.

Bicumylamine, $C^{40}H^{27}N = C^{20}H^{10}(C^{20}H^{13})Ad,H^2 = N.H(C^{20}H^{13})^2$. — *Cuminamine secondaire.* Dense, colourless oily liquid, beginning to boil, with decomposition, above 300°. Insoluble in water, soluble in alcohol and ether. The *hydrochlorate* crystallises in needles slightly soluble in cold water. — The *chloroplatinate* is sparingly soluble in cold water, and crystallises from alcoholic solution in small roseate needles.

Tricumylamine, $C^{60}H^{39}N = C^{20}H^9(C^{20}H^{13})^2Ad,H^2 = N.(C^{20}H^{13})^3$. — *Cuminamine tertiaire.* Crystallises in small rhomboïdal laminæ, which melt at 81° — 82°. Insoluble in water, very soluble in ether and in boiling alcohol, slightly in cold alcohol. It does not affect the colour of litmus. The *hydrochlorate*, which crystallises in needles grouped in crosses, is nearly insoluble in water, very soluble in alcohol. — The *chloroplatinate* crystallises with difficulty ; the alcoholic solution deposits it in a viscous mass which solidifies in drying.

Oxidising properties of Oil of Turpentine (comp. p. 256). — Berthelot has examined the oxidation of various substances in contact with oil of turpentine which has been exposed to the air. 5 cubic centimetres of oil of turpentine, rectified a few weeks previously, were introduced into a 10-litre bottle, together with 50 grammes of water and 100 cub. cent. of a standard solution of indigo (requiring for decoloration 50 cub. cent. of chlorine = 25 cub. cent. oxygen). The whole was left to itself at 20° to 30° for eight months, the indigo-solution being added by portions of 50 vols. at a time. The quantities of oxygen absorbed by 1 vol. of the oil of turpentine were as follows:

In	7 days	20 vols. oxygen.
,,	16 ,,	40 ,,
,,	25 ,,	60 ,,
,,	37 ,,	80 ,,
,,	63 ,,	102 ,,
,,	77 ,,	108 ,,
,,	160 ,,	135 ,,
,,	182 ,,	146 ,,
,,	220 ,,	168 ,,

At the end of the time, the oil of turpentine was found to be completely resinised, and had lost all its characteristic properties. The quantity of oxygen absorbed by the indigo amounted to 12 times as much as would be sufficient for the complete combustion of the oil of turpentine, that is to say: 1 At. oil of turpentine, $C^{20}H^{16}$, determines the absorption of 4·7 At. oxygen by the indigo. — The rate of absorption varied considerably during the experiment.

The oxidation of *pyrogallate of potash* by active oil of turpentine takes place immediately, attaining its extreme limit in a few seconds. — *Mercury* shaken up with active oil of turpentine is quickly *killed;* at the same time a black powder is formed, which appears to be the suboxide. — A solution of *cane-sugar* left for seven months in a large bottle, together with a small quantity of slaked lime, the whole being covered with a layer of oil of turpentine, yielded a considerable quantity of oxalic acid.

Oil of turpentine acquires the oxidising power when merely left to itself in a vessel containing air; sunshine accelerates the action, but is not necessary to it. The time required for the development of the oxidising power is not very long: for oil of turpentine cannot be absolutely deprived of it, unless very carefully excluded from the air. — Active oil of turpentine retains its power for several years, probably till it is completely resinised. The oxidating power may be destroyed by boiling or by agitation in a close vessel with deoxidising substances, such as indigo or pyrogallate of potash. — The oxygen absorbed by oil of turpentine may be partly displaced by a stream of carbonic acid; but the quantity thus displaced does not exceed the $\frac{1}{100}$ pt. of that which is absorbable by indigo. The amount of this active oxygen is also much greater than that which is merely soluble in the oil of turpentine, amounting in fact to half the volume of the oil of turpentine, whereas the portion simply dissolved does not exceed one-fifth of the volume of the liquid. — From these phenomena, Berthelot concludes that the active oxygen of oil of turpentine is in a state of combination, similar to that of the transferable oxygen of peroxide of nitrogen. (*N. Ann. Chim. Phys.* 58, 426; *Rep. Chim. pure.* 2, 269.)

Volatile Oil of Citrus Lumia.

S. de Luca. *Compt. rend.* 51, 258; *Rep. Chim. pure.* 2, 462.

Obtained by expressing the rind of the fruit of *Citrus Lumia*, a plant which grows abundantly in Calabria and Sicily, and yields a fruit very much like the lemon. The greater part of the oil distils between 180° and 190°, yielding a limpid colourless liquid.

The portion boiling at 180° is isomeric with oil of turpentine, and has a density of 0·853 at 18°. It possesses a dextro-rotatory power = 34° for the sensitive tint. It is slightly soluble in alcohol, very easily soluble in ether and in sulphide of carbon. It is resinised by *nitric acid.* — Mixed with *alcohol* and *nitric acid*, it produces after a while, a crystallised hydrate. With *hydrochloric* acid, it yields both a liquid and a crystalline compound. The crystallised compound, which has a peculiar odour and melts at a low temperature, is a *bihydrochlorate* $C^{20}H^{16},2HCl$.

Amber-camphor. $C^{20}H^{18}O^{2}$.

Berthelot & Buignet. *Compt. rend.* 50, 606; *Rep. Chim. pure,* 189.

Obtained by distilling powdered amber with a fourth of its weight of potash and a large quantity of water; it then passes over with the vapour of water, a kilogramme of amber yielding 3 grammes of the camphor. — It resembles common camphor in its physical properties, excepting in having a more penetrating and persistent odour. It is isomeric with borneol (p. 332), but is distinguished therefrom by its smaller dextro-rotatory power which is only 4·5°, whereas that of natural borneol is 33·4°, and that of artificial borneol, prepared from common camphor by the action of alcoholic potash is 44·9°.

It unites with *hydrochloric acid* (with elimination of water), forming the compound, $C^{20}H^{17}Cl$; similarly with *stearic acid*. The latter compound distilled with an alkaline hydrate, reproduces the amber-camphor with its original rotatory power and other physical properties. The camphor probably exists in the amber in the form of a compound ether.

Oil of Cajeput.

Max. Schmidl. *Transactions of the Royal Society of Edinburgh,* 22, 369; abstr. *Proceedings of the same,* 4, 326 (Session 1859–60).

This oil consists mainly of the bihydrate of a hydrocarbon (cajputene), isomeric with oil of turpentine. It has a green colour, even when purified by distillation from the copper-salts, which it generally contains (see page 335). Its specific gravity is 0·926 at 10°. On submitting it to fractional distillation, bihydrate of cajputene, which constitutes about two-thirds of the crude oil, passes over between 175° and 178°; smaller fractions, perhaps products of decomposition, are obtained from 178° to 240° and from 240° to 250°, and at 250° only a small residue is left, consisting of carbonaceous and resinous matter mixed with metallic copper. On treating this residue with ether, a green solution is obtained, which, when evaporated, leaves a green resin, soluble in the portion which boils between 175° and 178°, and capable of restoring its original colour.

Cajputene. $C^{20}H^{16}$. — Obtained, together with two isomeric hydrocarbons, (*isocajputene* and *paracajputene*) by cohobating bihydrate of cajputene with anhydrous phosphoric acid for half an hour, and then distilling off the liquid, whereupon cajputene passes over at 160°—165°, isocajputene at 176°—178°, and paracajputene at 310°—316°.

Cajputene is perfectly colourless, and has a very pleasant odour resembling that of hyacinths. Sp. gr. = 0·850 at 15°. Vapour-density 4·717.

			Schmidl.	
20 C	120	88·24	88·29	88·34
16 H	16	11·76	11·91	11·78
$C^{20}H^{16}$	136	100·00	100·20	100·12

	Vol.	Density.
C-vapour	20	8·3200
H-gas	16	1·1088
Vapour of cajputene	2	9·4288
	1	4·7144

Cajputene is permanent in the *air*. — It is not affected by *iodine* at ordinary temperatures, but at a higher temperature, hydrogen is evolved and a black liquid is formed. — *Bromine* acts quickly on it, producing a dark viscid oil. — With *gaseous hydrochloric* acid, it forms a beautiful violet liquid, but no crystalline compound, even at —10°. — A mixture of ordinary *nitric* and *sulphuric acids* act upon it with violence, forming a yellow brittle resin.

Cajputene is insoluble in *alcohol*, but dissolves in *ether* and in *oil of turpentine.*

Isocajputene $C^{20}H^{16}$. — Obtained: (1.) as above. — (2.) By distilling the bihydrate of cajputene with oil of vitriol.

Oil boiling between 176° and 178°. Has an odour less agreeable than that of cajputene, and becoming more pungent and aromatic by exposure to the air, the oil at the same time acquiring a yellow colour. Sp. gr. = 0·857 at 16°. Vapour-density of (1) = 4·82; of (2) = 4·52.

			Schmidl.			
			Prepared by (1)		*Prepared by* (2)	
20 C	120	88·24	88·16	88·18	88·05	88·23
16 H	16	11·76	11·64	11·68	11·90	11·83
$C^{20}H^{16}$	136	100·00	99·80	99·86	99·95	100·06

Iodine, bromine, gaseous hydrochloric acid, and a mixture of *nitric* and *sulphuric acids*, act upon isocajpetene in the same manner as on cajputene. With *oil of vitriol*, and with *dilute sulphuric hydrochloric* or *nitric acids* (neither of which acts upon cajputene), it forms dark viscid liquids.

Isocajputene is insoluble in *water* and in *alcohol,* but mixes in all proportions with *ether* and with *oil of turpentine.*

Paracajputene $C^{40}H^{32}$. — Obtained as above mentioned by distilling bihydrate of cajputene with anhydrous phosphoric acid; passes over between 310° and 316°. It is very viscous, has a lemon-yellow colour, and in certain directions exhibits deep-blue fluorescence. Vapour-density 7·96.

			Schmidl.
40 C	240	88·24	88·30
32 H	32	11·76	12·06
$C^{40}H^{32}$	272	100·00	100·36

	Vol.	Density.
C-Vapour	40	16·6400
H-gas	32	2·2176
Vapour	2	18·8576
		9·4288

The difference between the experimental and calculated vapour-densities is probably due to decomposition, taking place at the high temperature required for the determination.

Paracajputene oxidises rapidly in contact with the *air*, acquiring a red colour and resinous consistence. — A mixture of *nitric* and *sulphuric* *acids* does not act so violently on it as on cajputene and isocajputene. — With *hydrochloric acid gas*, it forms a dark viscid liquid which does not yield crystals, even at —10°.

Insoluble in *water, alcohol* and *oil of turpentine;* soluble in *ether*.

HYDRATES OF CAJPUTENE.—*a. Mono-hydrate*, $C^{20}H^{16},HO$. — Obtained by the action of oil of vitriol on oil of cajeput. When the crude oil is raised to the boiling point in a deep open vessel, and oil of vitriol continuously dropped into it, violent ebullition takes place, accompanied, after a while, by a peculiar crackling sound. As soon as this is observed, the flame must be lowered and the acid very cautiously added till the liquid suddenly assumes a dark colour, extending in an instant from the surface throughout the whole depth. — The vessel must then be immediately removed from the fire, otherwise further decomposition will take place, attended with evolution of sulphurous acid. The upper oily liquid is separated from the acid on which it floats, well washed, and distilled, and the portion which passes over from the 170° to 175° is collected and rectified.

Oily liquid, having a vapour-density of 5·19 to 5·27.

			Schmidl. *mean.*		Vol.	Density.
20 C	120	82·75	82.71	C-vapour	20	8·3200
17 H	17	11·72	11·77	H-gas	17	1·1781
O	8	5·53	5·52	O-gas	½	0·5548
$C^{20}H^{17}O$	145	100·00	100·00	Vapour	2	10·0529
					1	5·0264

The vapour-density is anomalous, inasmuch as the molecule $C^{20}H^{17}O$, which occupies two volumes of vapour, contains but 1 At. oxygen. Probably the true formula of the body is $C^{40}H^{34}O^{2} = C^{40}H^{32} + H^{2}O^{2}$, this molecule splitting up at high temperatures into $C^{40}H^{32}$ and $H^{2}O^{2}$, each of which occupies two volumes of vapour, and consequently the two together occupy 4 volumes (compare xiii, 487.)

b. Bihydrate. $C^{20}H^{18}O^{2} = C^{20}H^{16},2HO$. This is the chief constituent of oil of cajeput (p. 510), and passes over in the fractional distillation between 175° and 178°. After rectification, it is a colourless oil which boils constantly at 175°, has a specific gravity of 0·903 at 17°, and vapour-density = 5·43.

			Schmidl.		Vol.	Density.
20 C	120	77·92	77·84	C-vapour	20	8·3200
18 H	18	11·68	11·91	H-gas	18	1·2465
2 O	16	10·40	10·25	O-gas	1	1·1093
$C^{20}H^{18}O^{2}$	154	100·00	100·00	Vapour	2	10·6758
					1	5·3379

Decompositions. 1. Exposed to the *air* for a considerable time in the moist state, it changes to a reddish liquid which ultimately exhibits a rather strong acid reaction with litmus. — 2. *Iodine* dissolves in the oil, and under certain circumstances forms crystalline compounds (p. 515). — 3. *Bromine* acts quickly upon it, and forms crystalline compounds under similar circumstances (p. 514). — 4. *Chlorine gas* passed into the oil raises the temperature, but does not appear to act upon it further; but *nascent* chlorine (evolved by passing hydrochloric acid gas into the oil mixed with dilute nitric acid) converts it into bichloride of cajputene $C^{20}H^{16}Cl^{2}$. — 5. *Anhydrous phosphoric acid* heated with the bihydrate, takes away the whole of its water, converting it into cajputene, isocajputene and paracajputene (p. 511). — 6. *Chloride of zinc* likewise dehydrates it, but less completely. — 7. *Oil of vitriol* acts but very slowly on the oil at low temperatures; but if the temperature be allowed to rise, sulphurous acid is given off, and the oil blackens and ultimately suffers complete decomposition. If the action be checked at a certain point, a sulpho-acid is formed, which yields a soluble baryta-salt. Oil of vitriol dropped into the oil at the boiling heat, in the manner described at page 512, takes away half the water, forming monohydrate of cajputene. — *Dilute sulphuric acid* on the contrary causes the bihydrate to take up 4 At. more water, converting it into $C^{20}H^{16}+6HO$. — *Fuming oil of vitriol* converts the bihydrate into a thick brown liquid, which boils above 360°. — 8. *Fuming nitric acid* rapidly oxidises the oil, even at ordinary temperatures, forming a large quantity of oxalic acid. Ordinary nitric acid produces the same effect at the boiling heat, but at ordinary temperatures, it acts very slowly, converting the oil into a red liquid. — 9. Distilled over *permanganate* or *bichromate of potash* in presence of sulphuric acid, it forms a thick resinous liquid. — 10. It does not appear to be altered by digestion with *peroxide of lead*. —11. In contact with aqueous *potash*, or when dropped into melting potash, it forms a soluble salt, the acid of which is precipitated as a resin by hydrochloric or sulphuric acid. — 12. Heated with *sodium*, it forms a crystalline mass, soluble in water and alcohol, and consisting of soda and an organic substance, which is separated by strong acids in the form of a fragrant resin. — 13. When the vapour of the bihydrate is passed over red-hot *soda-lime*, a yellow oil distils over, having a peculiar odour quite different from that of the bihydrate, and at the same time the soda-lime becomes blackened by deposited charcoal, and when treated with acids, gives off a large quantity of carbonic acid. The yellow oil thus formed yielded by distillation a fraction boiling between 180° and 185°, which gave in two analyses, 79·76 and 80·03 p. c. C, 12·20 and 12·07 H, agreeing nearly with the formula $C^{26}H^{24}O^{26}$ which requires 79·59 p. c. C, 12·44 H, and 7·97 O.

Combinations. Bihydrate of cajputene dissolves in all proportions in *alcohol*, *ether*, and oil of turpentine.

c. *Hexhydrate*, $C^{20}H^{22}O^{6} = C^{20}H^{16},6HO$. — Produced by the action of dilute sulphuric acid on the bihydrate, or on crude oil of cajeput. — Two pts. of dilute sulphuric acid are added to 1 pt. of the crude oil; and the mixture is well shaken for several days till the watery layer acquires a yellowish colour, and then left to itself for about ten days, whereupon it deposits crystalline tufts of the hexhydrate, adhering to the sides of the vessel.

The crystals melt at 120°, and solidify again at 85°. On submitting them to dry distillation, an oily liquid passes over and condenses again in the colder parts of the apparatus, apparently as the unaltered hexhydrate. The crystals dissolve sparingly in cold, easily in boiling alcohol:

			Schmidl. *mean.*
20 C	120	63·15	63·20
22 H	22	11·57	11·96
6 O	48	25·28	24·84
$C^{20}H^{22}O^{6}$	190	100·00	100·00

Crystals having the same composition were deposited from a secondary fraction of crude cajeput-oil, which distilled at 210° — 230°, and was left for a very long time moist and exposed to the air. The crude oil mixed with nitric acid and alcohol changes, in the course of seven or eight months, into a black heavy liquid in which crystals are suspended, perhaps consisting of the hexhydrate. The same compound appears likewise to be formed in beautiful long prisms, when the crystalline mass produced by passing hydrochloric acid gas into rectified oil of cajeput is thrown into water or alcohol.

CHLORIDE OF CAJPUTENE. $C^{20}H^{16}Cl^2$. — Produced by the action of nascent chlorine on the bihydrate. When the portion of cajeput-oil, distilling between 175° and 178°, is mixed with very dilute nitric acid, and hydrochloric acid gas is passed into the liquid, a violent action takes place in a few minutes, yellow and red fumes of chlorine and nitrous gas being evolved, and if the passage of the gas be continued, chloride of cajputene ultimately sinks to the bottom, as a limpid brown oil, which may be freed from adhering nitric and nitrous acid by distillation over strong potash-ley. It has a fragrant odour, and may be kept for any length of time without alteration, but is decomposed by distillation. Boiled with nitrate of silver, it detonates in a peculiar manner and forms chloride of silver.

			Schmidl. *mean.*
20 C	120	57·97	57·45
16 H	16	7·73	8·09
2 Cl	71	34·30	34·39
$C^{20}H^{16}Cl^2$	207	100·00	99·93

Crystals were once obtained by keeping the oil at a low temperature, but not in sufficient quantity for analysis.

MONOHYDROCHLORATE OF CAJPUTENE. $C^{20}H^{16},HCl$. — Obtained by distilling the bihydrochlorate, and collecting apart the fraction which boils at 160°:

			Schmidl. *mean.*
20 C	120·0	69·76	69·70
17 H	17·0	9·88	10·00
Cl	35·5	20·36	20·53
$C^{20}H^{17}Cl$	172·5	100·00	100·23

A product having the same composition is obtained by treating the bihydrochlorate for several days with aqueous or alcoholic potash; but its odour is different from that of the product obtained by simple distillation of the hydrochlorate, and resembles that of pelargonic ether.

BIHYDROCHLORATE OF CAJPUTENE. $C^{20}H^{16},2HCl$. — Obtained by passing hydrochloric acid gas through rectified cajeput-oil, mixed with a third of its volume of alcohol or strong aqueous hydrochloric acid. Crystallises from alcohol in beautiful radiating tufts. Melts at 55°, and solidifies again at 30°. It has no taste or smell. — By dry distillation, it gives off hydrochloric gas at 60°, and splits into several fractions, one of which is the monohydrochlorate. — It is also deprived of half its chlorine by heating with aqueous or alcoholic potash. It dissolves sparingly in cold, easily in boiling alcohol or ether.

			Schmidl. *mean.*
20 C	120	57·41	57·57
18 H	18	8·61	8·94
2 Cl	71	33·98	34·49
$C^{20}H^{18}Cl^2$	201	100·00	101·00

When hydrochloric acid gas is passed through rectified oil of cajeput, kept at a low temperature, a violet liquid is formed which in 10 or 15 minutes solidifies in a crystalline mass. This crystalline compound is extremely deliquescent, liquefying rapidly even when pressed between blotting paper cooled to —25°: the resulting liquid rapidly gives off fumes of hydrochloric acid, and is completely decomposed by distillation. If the crystalline mass, immediately after its formation, be thrown into water or alcohol, beautiful long prisms are formed, after a few days, apparently consisting of hexhydrate of cajputene (p. 513).

BROMIDE OF CAJPUTENE. $C^{20}H^{16}Br^4$. — Obtained by the action of bromine on oil of cajeput. When dry bromine is dropped into the rectified oil, a very brisk action takes place, and the sides of the vessel become covered with yellow needles, which however soon disappear; but if the addition of the bromide be continued till the reaction almost ceases, a dark, thick, viscous oil is formed, which, after several weeks, deposits a granular substance. By boiling the mixture with alcohol, the granular substance is extracted; a heavy oil is left behind; and the alcoholic solution, on cooling, deposits bromide of cajputene as a soft crystalline substance, having a fatty lustre and much resembling cholesterin.

Bromide of cajputene melts at 60°, and solidifies again at 32°. By dry distillation, it yields a liquid which crystallises again in the cooler parts of the retort. It is not altered by boiling with aqueous potash. It dissolves in ether and in boiling alcohol.

			Schmidl.	
20 C	120	26·31	26·32	25·97
16 H	16	3·52	4·24	4·15
4 Br	320	70·17	70·03	
$C^{20}H^{16}Br^4$	456	100·00		

Rectified oil of cajeput shaken up with bromine-water forms a red resin, from which a solid substance separates in small white prisms extremely deliquescent and rapidly decomposing.

Another crystallised bromine-compound (probably a hydrobromate analogous to the hydriodate), is formed in the same manner as that compound (*vid. inf.*), dissolved in bisulphide of carbon.

HYDRIODATE OF CAJPUTENE. — *a. Anhydrous*, $C^{20}H^{16},HI$. — Obtained by adding a solution of phosphorus in bisulphide of carbon to a solution of iodine and oil of cajeput in the same liquid. Brisk action then takes place, the vessel becoming very hot; red oxide of phosphorus is precipitated; and the oily liquid becomes reddish, giving off vapours probably containing phosphuretted hydrogen, and if left to itself for 10 or 12 days, deposits crystals of the hydriodate. The reaction probably takes place as represented by the equation:

$$3C^{20}H^{16} + 3PI + 6HO = 3C^{20}H^{17}I + PH^3 + PO + PO^5$$

The crystals of the hydriodate are deposited in cells like those of beehives, and possess a black metallic lustre. They are soluble in alcohol and in ether, and are very stable, not being altered, even by boiling with potash:

			Schmidl.	
20 C	120	45·45	45·29	45·36
17 H	17	6·43	6·31	6·35
I	127	48·12	48·85	
$C^{20}H^{17}I$	264	100·00		

b. *Hydrated,* $C^{20}H^{18}IO = C^{20}H^{16},HI + HO$. — When iodine is added in small quantities to cajeput-oil, crude or rectified, at ordinary temperatures no visible action takes place (if external heat be applied, the action goes too far and nothing but a viscous mass is produced which does not crystallise); but on stirring rather constantly, the action is assisted, partly by the heat resulting from the friction of the glass rod, partly by the mechanical distribution of the iodine, and the temperature of the liquid soon rises from 10° to 40°. The addition of iodine must then be discontinued, and the vessel immersed in cold water. A black crystalline compound then separates after a short time; and on separating this substance from the oily liquid by filtration, pressing it between blotting paper, and when it is nearly dry, dissolving it in alcohol or ether, a solution is obtained, from which the hydrated hydriodate crystallises in prisms having a fine yellow-green colour and metallic lustre. They are very deliquescent, and melt at 80° into a liquid which does not recrystallise in the cold. Potash-ley liquefies the compound, abstracting part of the iodine, and with the aid of heat abstracts the whole.

			mean.
20 C	120	43·95	43·11
18 H	18	6·50	6·90
I	127	46·52	46·51
O	8	2·04	3·48
$C^{20}H^{18}IO$	273	59·01	100·00

Regarded by Schmidl as *hydriodate of monohydrate of cajputene* = $C^{20}H^{17}O,HI$.

It is insoluble in *water,* and is not decomposed thereby; very soluble in *alcohol* and *ether.*

COMPOUNDS CONTAINING 22 AT. CARBON.

Primary Nucleus $C^{22}H^{10}$: *Oxygen-nucleus* $C^{22}H^{4}O^{6}$.

Graphitic Acid.

$$C^{22}H^{4}O^{10} = C^{22}H^{4}O^{6},O^{4}.$$

B. C. Brodie. *Ann. Pharm.* 114, 6.

Formation. By the repeated action of chlorate of potash and nitric acid on graphite.

Preparation. Graphite carefully purified by boiling with acids and fusion with hydrate of potash in a silver crucible, is intimately mixed with 3 At. chlorate of potash; the strongest nitric acid is added in sufficient quantity to render the mixture fluid; and the whole is either exposed to sunshine or heated on the water-bath to 60° for three or four days. If at the end of this time, no more yellow vapours are evolved, the mixture is to be shaken out into a large quantity of water, the undissolved portion completely washed by decantation, then dried on the water-bath, and again brought in contact with the same quantities of nitric acid and chlorate of potash, and the same treatment is to be repeated four times or as often as any further alteration of the substance appears to be produced. — Graphite cannot be completely converted into graphitic acid by one warming with chlorate of potash and nitric acid, even for a long time. — Graphitic acid obtained as above contains about ½ p. c. ash, probably derived from the glass vessels.

Properties. Perfectly transparent, thin crystals, belonging either to right or the oblique prismatic system.

			Brodie.	
	At 100° *or in vacuo.*		*a.*	*b.*
22 C	132	61·11	60·74	61·04
4 H	4	1·85	1·85	1·85
10 O	80	37·04	37·41	37·11
$C^{22}H^{4}O^{10}$	216	100·00	100·00	100·00

a, mean of eight analyses; *b,* mean of the same analyses after deducting ½ p. c. ash. The formula should perhaps be doubled, inasmuch as Brodie, from the analysis of the baryta-salt, is inclined to regard the acid as bibasic.

Decompositions. 1. The acid decomposes when *heated,* with explosion, incandescence, and evolution of gas, and leaves a black finely divided residue. — When graphitic acid is suspended in Rangoon naphtha (rectified over sodium and boiling at 270°) and heated, a large quantity of water distils over between 100° and 200°, whilst at first a small and afterwards a larger quantity of carbonic acid escapes, the naphtha acquires a deep red colour, and a black residue is left having the appearance of charcoal. This residue, collected after 3 — 4 hours heating of the graphitic acid with the naphtha to 250°, weighed 66·77 to 66·98 p. c., but still contained traces of transparent crystals; after 14 hours heating, it weighed 65·77 p. c., and had then the composition $C^{44}H^{2}O^{8}$. — Brodie gives the following decomposition-formula as probable:

$$7\,C^{22}H^{4}O^{10} = 3\,C^{44}H^{2}O^{8} + 12\,HO + 12\,CO^{2} + 10\,CO.$$

(But this equation gives no account of the disappearance of 10 At. H; *Kr.*) The formation of 3 At. $C^{44}H^{2}O^{8}$ from 7 At. $C^{22}H^{4}O^{10}$, should give a residue of 65·48 per cent.

The black residue obtained by heating graphitic acid with Rangoon naphtha, after being washed with ether and alcohol, contains on the average 80·13 p. c. C, 0·58 H, and 19·29 O (after heating for a short time, it is comparatively poor in carbon, but becomes richer after longer heating). Calculation 80·00 p. c. C, 0·60 H, and 19·40 O. The residue obtained by heating graphitic acid *per se*, contained 80·36 p. c. C, 0·71 H, and 18·93 O. Heated for some time to 250° in nitrogen gas; it gives off 2·26 to 2·30 p. c. water and traces of carbonic oxide, leaving a residue amounting to 97·16 — 97·38 p. c. The latter residue contains, on the average, 81·82 p. c. C, 0·44 H, and 17·74 p. c. O: it is therefore $C^{132}H^{4}O^{22}$ (calculation 81·48 p. c. C, 0·41 H, and 18·41 O), and is formed as shown by the equation $3\,C^{14}H^{2}O^{8} = C^{132}H^{4}O^{22} + 2\,HO$. — If it be again strongly heated, carbonic acid and carbonic oxide are evolved; but even after several hours exposure to a red heat, it still retains hydrogen and oxygen.

2. When *hydrosulphate of ammonia* or *sulphide of potassium* is poured upon graphitic acid, it decomposes with decrepitation, forming a graphitoidal substance having the metallic lustre.

3. It is decomposed in like manner by boiling with acid solutions of *cuprous* or *stannous chloride*.

Combinations. Graphitic acid is somewhat soluble in pure water, not in water containing acids or salts.

It unites with *alkalis*. Shaken up with *aqueous ammonia*, it is transformed into a transparent jelly, without dissolving, and on addition of acids, is precipitated as a jelly, like silicic acid, which after drying in vacuo, has the same weight as the graphitic acid originally employed.

Graphitate of Baryta. — Moist graphitic acid, shaken up with baryta-water, washed and dried at 100°, yielded a compound which contained 21·19 p. c. Ba, and after being suspended in water and decomposed by a stream of carbonic acid, still contained at 100°, 13·30 p. c. Ba. Hence Brodie regards the former salt as essentially containing $C^{22}H^{3}BaO^{10}$ (calculation 24·13 p. c. Ba), and the latter as $C^{44}H^{7}BaO^{20}$ (calculation 13·73 p. c. Ba), and graphitic acid probably as bibasic. — The baryta-salts are hygroscopic and detonate with violence when heated. (Brodie.)

Azo-nucleus $C^{22}NH^{9}$.

Cryptidine.

$C^{22}NH^{11} = C^{22}NH^{9},H^{2}$.

Gr. Williams. *Trans. Roy. Soc. Edinb.* 21, Pt. iii. 377; *Chem. Gaz.* 1856, 261 and 283; abstr. 69, 355; *Lieb. Kopp. Jahresber.* 1856, 537.

Known only as a platinum-salt.

Found, together with many other products, in coal-tar, and obtained in the preparation of chinoline (xiii, 243) among the products boiling at about 274°. As however these products still contain chinoline and lepidine (xiv, 103), from which the cryptidine, on account of its small quantity, cannot be completely separated by fractional distillation, the hydrochloric acid solution of the portion which distils at 274° is mixed with bichloride of platinum; and the platinum-salt, which precipitates as a yellow pasty mass, soon becoming crystalline, is recrystallised from boiling water, and washed with ether alcohol; — or the portion distilled between 270° and 274° is treated with nitric acid, whereby an insoluble powder is separated, and this is converted into a platinum-salt.

Platinum-salt.			Williams. *mean.*
22 C	132·0	36·31	35·89
N	14·0	3·85	
12 H	12·0	3·30	3·37
Pt	99·0	27·24	27·17
3 Cl	106·5	29·30	
$C^{22}NH^{11},HCl,PtCl^{2}$	363·5	100·00	

Cryptidine is isomeric with ethyl-chinoline and methyl-lepidine.

Primary Nucleus $C^{22}H^{14}$: *Oxygen-nucleus* $C^{22}H^{8}O^{6}$.

Limettic Acid.

$C^{22}H^{8}O^{12} = C^{22}H^{8}O^{6},O^{6}$.

H. Vohl. *N. Br. Arch.* 74, 16; abstr. *Pharm. Centr.* 1853, 318.

Formation. Produced, together with formic and acetic acids, by the action of bichromate of potash and sulphuric acid on oil of lime (p. 304), and oil of rosemary (p. 396).

Preparation. Oil of lime is added by small portions to a mixture of bichromate of potash and sulphuric acid; and the portion of the oil which is volatilised in consequence of the great heat developed, is collected and poured back. As soon as the action is finished, the liquid is diluted with water, and the limettic acid which separates as a resin is washed, and purified by repeated solution in aqueous carbonate of potash, precipitation with nitric acid, and recrystallisation from alcohol.

Properties. White, crystalline. Volatilises when heated, and forms a crystalline deposit on cold bodies. It has neither taste nor smell.

At 100°.			Vohl. *mean.* *a.*	*b.*
22 C	132	55·93	55·79	55·97
8 H	8	3·39	3·46	3·43
12 O	96	40·86	40·75	40·60
$C^{22}H^8O^{12}$	236	100·00	100·00	100·00

a, from oil of lime; *b*, from oil of rosemary. According to Vohl, it is monobasic and $= C^{11}H^4O^6$.

Limettic acid is sparingly soluble in *water*.

Limettate of Silver. — Obtained by adding nitrate of silver to the acid neutralised with ammonia. Powder sparingly soluble in water, and blackening on exposure to light. Contains 51·44 p. c. oxide of silver ($C^{22}H^6Ag^2O^{12} = 51{\cdot}56$ p. c. AgO.)

Limettic acid dissolves readily in *alcohol.*

Oxygen-nucleus $C^{22}H^{10}O^4$.

Rottlerin.

$$C^{22}H^{10}O^6 = C^{22}H^{10}O^4,O^2.$$

ANDERSON. *Edinb. New Phil. J.* (new series) 1, 300; abstr. *Pharm. Centr.* 1855, 372; *Lieb. Kopp.* 1855, 669.

The stellate hairs and glands which cover the fruit of *Rottleria tinctoria,* and are used in the East Indies as a dye, contain rottlerin, together with a flocculent substance, $C^{40}H^{34}O^8$, and a resinous colouring matter, $C^{40}H^{30}O^{14}$.

Preparation. The colouring matter is exhausted with ether, and the greater part of the ether distilled off, the rottlerin then crystallising from the residue.

Properties. Yellow, silky crystals.

			Anderson.
22 C	132	69·47	69·11
10 H	10	5·26	5·55
6 O	48	25·27	25·34
$C^{22}H^{10}O^6$	190	100·00	100·00

Melts when *heated*, giving off pungent vapours and leaving charcoal. — By bromine, it is quickly decolorised, with formation of a non-crystallisable substitution-product. — With cold *oil of vitriol*, it forms a yellow solution, but hot oil of vitriol chars it, giving off sulphurous acid. — *Nitric acid* first converts it into a yellow resin, and then decolorises it.

It is soluble in *water*, and with red colour in *alkalis*. Its alcoholic solution is not precipitated by *neutral acetate of lead*.

It is slightly soluble in cold *alcohol*, more soluble in boiling alcohol, easily soluble in *ether*.

Primary Nucleus $C^{22}H^{16}$: *Oxygen-nucleus* $C^{22}H^{12}O^4$.

Sinapic Acid.

$$C^{22}H^{12}O^{10} = C^{22}H^{12}O^4,O^6.$$

v. Babo & Hirschbrunn. (1852.) *Ann. Pharm.* 84, 19; abstr. *Pharm. Centr.* 1852, 916; *J. pr. Chem.* 58, 283; *N. Ann. Chim. Phys.* 38, 108; *N. J. Pharm.* 33, 293; *Chem. Gaz.* 1853, 81.

Formation. Hydrosulphocyanate of sinapine is resolved by boiling with potash or baryta-water into sulphocyanide of barium, sincaline, and sinapate of baryta:

$$C^{32}NH^{23}O^{10},C^2NHS^2 + 3\,BaO = C^2NBaS^2 + C^{22}H^{10}O^8,2BaO + C^{10}H^{13}NO^2,HO.$$

By exhausting aqueous mustard-paste with ether, distilling off the ether, and treating the residual acrid extract with cold water, Simon (*Pogg.* 44, 601) obtained his *Senfsäure*, which is perhaps identical with Babo's sinapic acid. It remains behind when the aqueous solution is cautiously evaporated (if too much heat is applied, sulphurous acid escapes), and may be freed from soft resin by washing with ether and crystallised from alcohol. It does not colour *alkalis* yellow, but reddens *ferric salts*, like hydrosulphocyanic acid; it dissolves easily in *alcohol*, slowly in *ether*, and is not easily converted into hydrosulphocyanate of sinapine. (Simon.)

Preparation. Hydrosulphocyanate of sinapine is boiled with potash-ley; the liquid is supersaturated with hydrochloric acid; and the resulting precipitate is purified by recrystallisation from boiling alcohol of 60 p. c. If the solution be left for some time exposed to the air, it becomes red-brown and suffers partial decomposition, but the unaltered portion may be recovered by treatment with animal charcoal. — The acid is obtained as an insoluble baryta-salt, in the preparation of sincaline by boiling hydrosulphocyanate of sinapine with baryta-water.

Properties. Small prisms which melt between 150° and 200°, and solidify in the crystalline form.

	At 110°.		v. Babo & Hirschbrunn.	
22 C	132	58·93	58·67	58·92
12 H	12	5·35	4·87	5·67
10 O	80	35·72	36·46	35·41
$C^{22}H^{12}O^{10}$	224	100·00	100·00	100·00

Decompositions. 1. When *heated* above its melting point, it gives off a colourless oil, and leaves a brown residue, which turns red after some hours, and chars at a low red heat. Ammonia-gas produces from the oil and the residue, crystalline yellow substances, which dissolve with difficulty in water, and scarcely turn red. — 2. The acid neutralised with *potash* or *soda* turns red on exposure to the air, then brown. The other sinapates likewise alter quickly (see below). — 3. By *chlorine-water*, especially when warm, it is coloured rose-red and then purple-red, but not dissolved. — 4. It dissolves in *nitric acid* with red colour changing to orange-yellow, apparently with formation of oxalic acid and a nitro-compound. — In the form of potash-salt, it immediately reduces *gold* from the *terchloride.*

Combinations. Sinapic acid dissolves very slowly in cold, somewhat more readily in hot *water.* — It unites with *bases,* forming *salts,* among which those of the alkalis are easily soluble and crystallisable, while the rest are difficultly soluble.

Sinapate of potash forms white precipitates with *chloride of calcium* and with solution of *alum;* the latter precipitate treated with chlorine-water, assumes first a rose-red and then a dirty red colour. With *sesquichloride of iron,* it forms a rose-red or sometimes a purple-red precipitate, with formation of ferrous oxide. — From solution of *copper* and *lead-salts,* it throws down precipitates which soon turn blue-green; with *mercuric* and *silver salts,* white precipitates which decompose, with separation of metal, especially on addition of more alkali.

Sinapate of Potash. — Precipitated from the aqueous solution by absolute alcohol, in iridescent laminæ, which soon change after the alcohol has been poured off.

Sinapate of Baryta. — (Vid. p. 520.) Sinapic acid is boiled with excess of baryta-water out of contact with the air, and the precipitate is washed with water free from carbonic acid.

			v. Babo & Hirschbrunn. *mean.*
22 C	132	36·80	36·45
10 H	10	2·78	2·90
8 O	64	17·82	18·12
2 BaO	153	42·60	42·53
$C^{22}H^{10}O^8,2BaO$	359	100·00	100·00

Sinapic acid is sparingly soluble in cold, easily in *hot alcohol,* insoluble in *ether.*

Interpolation : Sincaline.

$$C^{10}NH^{13}O^2 = C^{10}NH^{11}O^2,H^2.$$

v. Babo & Hirschbrunn. *Ann. Pharm.* 84, 22.

Formation. By boiling hydrosulphocyanate of sinapine with baryta-water or potash-ley (p. 520).

Preparation. Hydrosulphocyanate of sinapine is heated with baryta-water till the sinapate of baryta is completely separated ; the filtrate mixed with a slight excess of dilute sulphuric acid, is freed from hydrosulphocyanic acid by precipitation with aqueous sulphate of iron or copper ; the liquid is filtered from the precipitated sulphocyanide of copper ; the filtrate precipitated with baryta-water ; carbonic acid passed through it ; and the solution filtered from the carbonate of baryta is evaporated on the water-bath : carbonate of sincaline then remains behind. By neutralising the carbonate with aqueous hydrochloric acid, digesting the hydrochlorate with oxide of silver, and evaporating the solution filtered from the chloride of silver and excess of oxide, in vacuo or on the water-bath, sincaline is obtained as a colourless crystalline mass.

Sincaline, according to v. Babo, is $C^{10}NH^{14}O^2$; the formula here adopted, which is that proposed by Gerhardt, contains 1 At. hydrogen less.

Sincaline chars when *heated,* giving off an odour of methylamine and a combustible vapour.

Combinations. Sincaline exposed to moist air, deliquesces and becomes heated. — It dissolves *sulphur,* with formation of (penta?) sulphide and sulphate of sincaline, and on adding an acid to the solutions, sulphuretted hydrogen is evolved and milk of sulphur is precipitated.

Sincaline is a strong *base.* Its aqueous solution acts upon metallic salts like potash, precipitating the oxides, even from the salts of *baryta, lime* and *mercuric oxide.* The precipitates formed in solutions of *alumina* and *chromic salts* dissolve in excess of sincaline, the chromic precipitate being reprecipitated on boiling. — The *sulphate, hydrochlorate* and *nitrate of sincaline* are deliquescent.

Carbonate of Sincaline. — Aqueous sincaline absorbs carbonic acid from the air, and forms a deliquescent salt.

Chloro-aurate of Sincaline is precipitated as a yellow crystalline powder, on adding terchloride of gold to aqueous hydrochlorate of sincaline, and may be obtained in plumose crystalline needles and laminæ by washing with cold and recrystallising from boiling water.

	At 110°.		v. Babo & Hirschbrunn.
10 C	60·0	13·55	13·63
14 H	14·0	3·16	3·38
N	14·0	3·16	
2 O	16·0	3·61	
Au	196·6	44·42	44·54
4 Cl	142·0	32·10	
$C^{10}H^{13}NO^2,HCl,AuCl^3$	442·6	100·00	

So according to Gerhardt (*Traité*, 2, 431); according to v. Babo & Hirschbrunn, it is $C^{10}H^{14}NO^2,HCl,AuCl^3$.

Chloroplatinate of Sincaline. — Crystallises on mixing hydrochlorate of sincaline with bichloride of platinum and evaporating, in splendid orange-coloured prisms; by slow evaporation, it is obtained in six-sided plates half an inch in diameter. — At 110°, it gives off 5·32 p. c. water (by calculation, 2 At. = 5·50 p. c. Aq).

			v. Babo & Hirschbrunn.
10 C	60·0	19·40	19·65
14 H	14·0	4·53	5·13
N	14·0	4·53	
2 O	16·0	5·18	
Pt	98·7	31·92	31·30
3 Cl	106·5	34·44	
$C^{10}H^{13}NO^2,HCl,PtCl^2$	309·2	100·00	

Conjugated Compounds of Sinapic Acid.

Sinapine.

$C^{32}H^{23}NO^{10}$.

O. Henry & Garot. *J. Pharm.* 17, 1. — further, 20, 63.
Pelouze. *Ann. Chim. Phys.* 44, 214; *Pogg.* 20, 358; *N. Tr.* 23, 2, 253; *Schw.* 60, 468; *J. Chim. méd.* 6, 577; further, *J. Pharm.* 17, 271; *Schw.* 63, 93.
Boutron & Robiquet. *J. Pharm.* 17, 279.
Fauré. *J. Pharm.* 17, 279.
O. Henry & H. Plisson. *Ann. Chim. Phys.* 46, 198.
Winckler. *Repert.* 41, 169; further, 67, 257.
Simon. *Pogg.* 43, 651; further, 44, 593.
Boutron & Fremy. *J. Pharm.* 26, 50.
v. Babo & Hirschbrunn. *Ann. Pharm.* 84, 10; abstr. *Pharm. Centr.* 1852, 916; *J. pr. Chem.* 58, 283; *N. Ann. Chim. Phys.* 38, 108; *N. J. Pharm.* 23, 294; *Chem. Gaz.* 1853, 81.

O. Henry & Garot described, in 1825, a peculiar sulphuretted acid of white mustard, *Acide sulphosinapique,* which they extracted from the fixed oil. These experiments however partly relate to hydrosulphocyanic acid, which was obtained from white mustard at the same time by Hornemann (*Berl. Jahrb.* 29, 1, 29), and afterwards by Pelouze, according to the process given by Henry & Garot. Pelouze likewise pointed out certain discrepancies in the statements of Henry & Garot, who thereupon discovered hydrosulphocyanate of sinapine. Von Babo & Hirschbrunn, starting apparently from some observations of Will (*Ann. Pharm.* 65, 213), first recognised the true nature of this body, and studied its products of decomposition. — Hydrosulphocyanate of sinapine is synonymous with the *sulphosinapisine*, or *sinapine* of Henry & Garot, the *sulphosinapic acid* of Henry & Plisson, the *sinapisine* of Boutron & Fremy, the *sulphosinapine* of Boutron & Robiquet and of Winckler, the *sulphocyanide of sinapine* (*Schwefelcyansinapin*) of v. Babo, and exhibits certain reactions in common with the (not isolated) acid of mustard (*Senfsäure*) of older authors. — Different from this is the *sinapisine* of Simon (*Pogg.* 43, 652), a solid fatty acid from black mustard (*Pogg.* 50, 379).

Source. In white mustard, the seed of *Sinapis alba,* as hydrosulphocyanate of sinapine (v. Babo & Hirschbrunn). Also in the seed of *Turritis glabra* and *Sinapis nigra.* (Henry & Garot, Fauré.)

Known only in aqueous solution and in combination with acids.

Preparation of Hydrosulphocyanate of Sinapine. 1. Dry mustard powder, exhausted with ether and thereby freed from fixed oil, is treated with cold absolute alcohol as long as the alcohol acquires a reddish-yellow colour, whereby a small quantity of sinapine is taken up, to be recovered as described further on; the residue is boiled with alcohol of 90 p. c., then pressed, and the boiling and pressing are repeated twice more. The hot-filtered tinctures yield, after half the alcohol has been distilled off, colourless crystals of hydrosulphocyanate of sinapine, an additional quantity of which may be obtained from the mother-liquors by further evaporation and addition of sulphocyanide of potassium. Sulphocyanide of potassium likewise precipitates hydrosulphocyanate of sinapine from the above-mentioned extracts prepared with cold alcohol.

2. Mustard-flour, freed from fixed oil by pressure in the oil-mill, is exhausted with cold and then with hot alcohol of 80 p. c.; about $\frac{3}{4}$ of the alcohol is distilled from the united tinctures in the salt-bath, or so much, that a sample of the residue separates on cooling into two equal layers consisting of oil and aqueous hydrosulphocyanate of sinapine. If the concentration is carried too far, the hydrosulphocyanate of sinapine no longer crystallises; and, on the other hand, if a sufficient quantity of the alcohol be not distilled off, part of the sinapine remains dissolved in the alcoholic oily layer, and is somewhat difficult to obtain in the form of crystallised hydrosulphocyanate: the best way of effecting this is to add a small quantity of alcoholic sulphocyanide of potassium. — The upper layer is removed, and the lower watery liquid is either left to itself for a week or as long as hydrosulphocyanate of sinapine continues to crystallise from it; and the crystals are collected on linen, separated from the viscid mother-liquor by means of a centrifugal machine; moistened with alcohol; strongly pressed between filtering paper, and recrystallised from alcohol of 90 p. c., then from a small quantity of boiling water, with addition of animal charcoal; — or better, the lower watery layer is mixed with alcoholic sulphocyanide of potassium, and the crystals which separate are purified as above. The mother-liquors also yield an additional quantity of hydrosulphocyanate of sinapine on addition of sulphocyanide of potassium. (v. Babo & Hirschbrunn.)

3. Bruised white mustard-seed, freed from the greater part of the fixed oil by pressure at 50°, is exhausted with ether; the residue is digested with 7 pts. of alcohol of 80 p. c., then with 2 pts. more; the alcohol is distilled off from the tinctures till the residue is reduced to one-fourth of the weight of mustard-powder used; this residue is set aside for 14 days to crystallise; and the crystals, after being freed by ether from a red-brown matter, are purified by repeated crystallisation from water and alcohol, with addition of animal charcoal. (Winckler.)

Winckler also digests white mustard with 3 pts. of alcohol of 80 p. c., evaporates the tincture to $\frac{1}{8}$ of the weight of mustard used; treats the residue, which is covered with oil drops, with ether, as long as the ether is thereby coloured; and purifies the residual hydrosulphocyanate of sinapine by solution in water and recrystallisation as above. — A similar process is adopted by Simon, who, however, at each extraction of the mustard-flour, uses only enough alcohol to moisten the mustard-flour, and subjects the whole to strong pressure: by this treatment, the exhaustion is effected more quickly than when a larger quantity of alcohol is used.

Older Methods. O. Henry & Garot boil mustard-flour for a few seconds with water; strain the liquid through cloth; press the residue;

evaporate the decoction to the consistence of honey; and shake it up with 6 to 8 vol. alcohol of 40°. The alcoholic tincture freed from alcohol by distillation is set aside to crystallise; and the crystals are purified by pressure, recrystallisation from alcohol, washing with ether (to remove a volatile red substance), and another crystallisation from alcohol. The mother-liquors become acid, in consequence of the continual liberation of hydrosulphocyanic acid. — This process does not easily yield hydrosulphocyanate of sinapine in the crystalline state. (v. Babo & Hirschbrunn.) — Fauré evaporates the decoction of black mustard, boils the extract with alcohol, evaporates to the consistence of honey, and dilutes with water, whereupon hydrosulphocyanate of sinapin is precipitated. This product is purified as above. Or he first exhausts black mustard with hot ether, then boils it with alcohol, and suspends the alcoholic extract in water, whereupon the greater part of the hydrosulphocyanate of sinapine is precipitated, part however remaining dissolved in the water.

Sinapine cannot be obtained in the free state, because it quickly decomposes when separated from its salts. If baryta-water be added from a burette to aqueous bisulphate of sinapine, till the colourless solution turns yellow in consequence of the conversion of the acid sulphate into a neutral salt, a second quantity of baryta-water then added equal to the former, and the liquid filtered from the sulphate of baryta, an aqueous solution of sinapine is obtained, having a deep yellow colour and distinct alkaline reaction. This solution added to the solutions of many metallic salts precipitates the oxides (forming a green precipitate with copper-salts, yellow with mercuric salts and grey-brown with silver-salts), and, on standing or heating, reduces the metal. (v. Babo & Hirschbrunn.)—Sinapine is not separated from its solution by alcohol or ether. Neither can it be obtained by treating the sulphate or hydrosulphocyanate with oxide of lead, the product thence resulting being a gelatinous compound containing lead, and somewhat soluble in boiling water. (v. Babo & Hirschbrunn.)

Sinapine is, according to v. Babo & Hirschbrunn, $C^{32}H^{24}NO^{10}$, according to Gerhardt, it is $C^{32}H^{23}NO^{10}$, which formula is here adopted.

Decompositions. 1. The aqueous solution of sinapine acquires by evaporation first a green, then a brown, and then a red colour, and does not leave a crystalline residue. — 2. Aqueous sinapine reduces *gold* from the *terchloride*. — 3. When its salts are mixed with aqueous *alkalis* or *baryta-water*, it instantly turns yellow, and is resolved on boiling into sincaline and a salt of sinapic acid. (v. Babo & Hirschbrunn.)

Decompositions of Hydrosulphocyanate of Sinapine. — 1. When *heated*, it melts to a yellow liquid, which then decomposes, giving off stinking products—among which are a brown oil, carbonate of ammonia and hydrosulphate of ammonia,—and leaving charcoal. (Henry & Garot.) Combustible gases are evolved in this decomposition. (Winckler.) The vapours do not smell of sulphuretted hydrogen, sulphide of carbon, or hydrocyanic acid. In the course of the decomposition, volatile bases are evolved, together with gases and empyreumatic oils, which burn with luminous flame and formation of sulphurous acid. (v. Babo & Hirschbrunn.) — 2. It dissolves readily in *oil of vitriol*, with greenish yellow colour and slight rise of temperature, turns brown when the solution is heated, and then chars. (Winckler.) Hydrosulphocyanic acid is likewise evolved. (v. Babo & Hirschbrunn.) — 3. With *iodic acid*, it acquires a light reddish brown colour and separates iodine (Winckler); probably because it contains free hydrosulphocyanic acid. (Kr.) — 4. In contact with *iodine*, it immediately assumes a light yellow-brown colour, and when heated, melts, gives off iodine, and leaves a brown-red brittle resin. (Winckler.) — 5. Its aqueous solution is coloured by *chlorine*, first brown-red, then red, and finally yellow, with formation of sulphuric and evolution of hydrocyanic acid. (Henry & Garot.) According to v. Babo & Hirschbrunn, no formation of hydrocyanic acid takes place in this and similar cases. — 6. With nitric acid of sp. gr. 1·4, or weaker, it immediately assumes a deep red colour, giving off red vapours, and when heated, turns yellow with formation of sulphuric acid. (Henry & Garot, and others.) — 7. When hydrosulphocyanate of sinapine is boiled with *peroxide of manganese* and dilute sulphuric acid, the distillate contains hydrocyanic acid (*vid. sup.*), and the residue contains a substance which dissolves in water with dark brown-red colour. (Winckler.) — 8. With *alkalis* (*vid. sup.*). It is likewise coloured yellow by the *alkaline earths* (Henry & Garot); and by *ammonia*, *strychnine*, *morphine*, and *quinine* (but not by *narcotine* or *salicine*). (Winckler.) A trace of tobacco-smoke is sufficient to produce this colouring. (v. Babo & Hirschbrunn.) — The behaviour of hydrosulphocyanate of sinapine to *dilute acids* and *saline solutions* is the same as that of other hydrosulphocyanates (comp. Henry & Garot, *J. Pharm.* 17, 10 and 11; Winckler, *Repert.* 41, 88.) — For its behaviour with *sesquichloride of iron*, see *Hydrosulphocyanate of Sinapine.* According to Henry & Garot, oil of mustard is given off in many of the decompositions of hydrosulphocyanate of sinapine; but according to Boutron & Robiquet, v. Babo & Hirschbrunn, and others, this statement is erroneous.

Compounds of Sinapine. With water. — *Aqueous Sinapine* (vid. sup.)

With Acids. — Salts of Sinapine. — Sinapine unites with acids, forming colourless salts, which are less decomposable than free sinapine (v. Babo & Hirschbrunn).

Sulphate of Sinapine. — a. *Neutral* — Half the acid of bisulphate of sinapine is precipitated by baryta-water, and the colourless filtrate is evaporated. — Colourless crystalline mass easily soluble in water (v. Babo & Hirschbrunn).

b. *Acid.* — When a small quantity of oil of vitriol is added to a hot concentrated solution of hydrosulphocyanate of sinapine in alcohol of 90 p. c., the liquid on cooling deposits rectangular laminæ, which may be purified by washing with absolute alcohol, and repeated crystallisation from water and alcohol. — Contains 4 At. water, which are given off at 110° (Will; Babo & Hirschbrunn).

At 100°.			v. Babo & Hirschbrunn.
32 C	192	47·19	46·99
25 H	25	6·14	6·37
N	14	3·44	
12 O	96	23·57	
2 SO^3	80	19·66	19·82
$C^{32}H^{23}NO^{20},2SO^3,2HO$	407	100·00	

Hydrochlorate of Sinapine. — Slender very soluble needles, obtained by decomposing sulphate of sinapine with chloride of barium (v. Babo & Hirschbrunn).

Nitrate of Sinapine. — Obtained by decomposing the sulphate with nitrate of baryta, or the hydrocyanate with nitrate of silver. — Colourless, very soluble needles. (v. Babo & Hirschbrunn.)

Chloroplatinate of Sinapine. — When hydrochlorate of sinapine is mixed with bichloride of platinum, a resinous precipitate is formed, which turns brown when heated, and yields flocks. (v. Babo & Hirschbrunn.)

Hydrosulphocyanate of Sinapine. — *Formation, Preparation, and Synonymes* (pp. 523, 524). — White needles having a pearly lustre and loosely aggregated in tufts. (Henry & Garot.) Colourless, nearly transparent, glassy prisms, mostly rectangular, truncated, grouped in stars or thin nodules. (Winckler.) Melts when heated (at 130° according to v. Babo), forming a yellow liquid, which solidifies in a gummy mass on cooling. (Winckler.) Scentless, tastes bitter, then like mustard. Neutral. (Henry & Garot.) — Hydrosoulphocyanate of sinapine for the most part reddens ferric salts immediately, like other hydrosulphocyanates; sometimes, however, it is obtained in such a condition that it does not redden ferric salts till heat is applied. (Will; v. Babo & Hirschbrunn.) Boutron & Robiquet obtained hydrosulphocyanate of sinapine not possessing the power of reddening ferric salts, by treating mustard-flour with alcohol after it had been exhausted with ether. This variety of the compound contains, according to them, less nitrogen than that which reddens ferric salts, and is less soluble in alcohol. But Winckler, following their directions, obtained hydrosulphocyanate of sinapine which did possess the power of reddening ferric salts.—Hydrosulphocyanate of sinapine dissolves with yellow colour in water and in alcohol,—in greatly increased quantity when the liquid is hot, and crystallises on cooling. — A drop of acid renders the solution colourless (v. Babo & Hirschbrunn). — It likewise crystallises without alteration from acidulated water (Henry & Garot). — It dissolves in ether, sulphide of carbon and oil of turpentine. (Simon.) According to Boutron & Fremy, hydrosulphocyanate of sinapine is decomposed by emulsion, with formation of the acrid principle of white mustard. According to Simon, and v. Babo & Hirschbrunn, on the other hand, emulsin has no effect on it.

			Henry & Garot.	Boutron & Robiquet.	v. Babo & Hirschbrunn. *mean.*
34 C	204	55·43	57·92	54·06	55·42
24 H	24	6·53	7·80	10·65	6·84
2 N	28	7·61	4·94	2·84	7·21
2 S	32	8·69	9·66	9·37	8·97
10 O	80	21·74	19·68	23·08	21·56
$C^{32}H^{23}NO^{2},C^{2}NHS^{2}$	368	100·00	100·00	100·00	100·00

So, according to Gerhardt (*Traité*, 2, 426); v. Babo's formula contains 1 At. H more. Boutron & Robiquet's hydrosulphocyanate of sinapine did not redden ferric salts. — Comp. Henry & Garot (*J. Pharm.* 17, 1 and 20, 63); Pelouze (*J. Pharm.* 17, 271); Henry (*J. Pharm.* 17, 273); Henry fils (*J. Chim. méd.* 6, 582).

Appendix to Sinapine.

1. *Acrid principle of White Mustard.* — White mustard owes its sharpness, as appears from the preceding, not to hydrosulphocyanate of sinapine (neither can volatile oil of mustard be obtained from it by any treatment whatever), but to a non-volatile, easily decomposable substance,

perhaps containing sulphur. — This acrid principle is produced, according to Boutron & Fremy, by the action of emulsin on hydrosulphocyanate of sinapine; but Simon and Babo & Hirschbrunn could not perceive that any decomposition of hydrocyanate of sinapine was produced by emulsin. — Winckler, on the other hand, thinks it more probable that hydrosulphocyanate of sinapine is a product of the decomposition of the acrid principle. (*Repert.* 67, 257.)

White mustard stirred up with *water*, yields a milk which has a mild odour, but sharp taste, and yields by distillation with water, not a trace of mustard-oil, but only insipid water, the residue also losing its acridity. (Boutron & Robiquet.)

Alcohol of 94 p. c. or absolute alcohol does not extract any acrid principle from white mustard; the residue no longer becomes acrid when moistened with water. (Simon.) The alcoholic tincture has a sharp taste at first, but loses its sharpness by evaporation, and then yields crystals of hydrosulphocyanate of sinapine. (Winckler.)

Ether does not extract any acrid principle from the seeds, after they have been freed from oil.

The acridity of aqueous mustard-paste is destroyed by heating, even below the boiling point, and without evolution of acrid vapours; also by addition of alcohol or of dilute carbonate of potash, and is not restored by acids. It is destroyed by drying the paste, even by quick and careful drying in vacuo, and remains in the residue when an aqueous emulsion of mustard is filtered, the filtrate being insipid. (Simon.)

When white mustard is moistened with water, the acrid principle thereby developed may be completely extracted by ether, so that the ethereal liquid, if allowed to run over the hand, produces a roseate inflammation, attended with pain which lasts for several days. (Alcohol extracts from the residue very pure hydrosulphocyanate of sinapine, which therefore is not the cause of the acridity.) The ether, when distilled, leaves a very acrid and acid extract, the alcoholic solution of which separates on standing, into two layers, with evolution of sulphuretted hydrogen and separation of resin. The lower resinous layer is with difficulty deprived of all its acid (Simon's *Senfsäure* p. 523) by cold water, more easily by warm water (but with evolution of sulphuretted hydrogen) or by alkalis. At the same time it loses all its acridity. The acrid and acid resin contains sulphur; that which has been deprived of its acridity is free from sulphur. (Simon, *Pogg.* 43, 651, and 44, 593.)

When a pressed cake of white mustard is exhausted with ether in the displacement apparatus, a mild fixed oil first runs away, then an acrid ethereal tincture. The latter leaves on evaporation an acrid oil, which, when repeatedly agitated with cold alcohol, gives up to that liquid its acrid principle, together with a small quantity of oil, which may for the most part be separated by repeatedly evaporating the alcohol and redissolving the residue in alcohol. In this manner, the acrid principle is obtained as a thick reddish oil, scentless, with a biting taste of horse-radish, soluble in alcohol and in ether. This oil burns when heated, without leaving any fixed residue, and does not yield any volatile acrid principle by distillation with potash or ammonia. (Boutron & Robiquet, *J. Pharm.* 17, 279.)

2. *Erucine.* — When white mustard-flour is moistened with water and then exhausted with ether, the ether distilled off from the acrid extract, and the acrid residue left to itself for some time in an open dish,

small hard points are produced in it, consisting of erucine. This substance may be freed from soft resin by sprinkling with aqueous alkalis, then dissolved in ether containing alcohol; the solution left to evaporate in the air; the alcoholic mother-liquor poured off; the erucine on the filter freed from the last traces of sinapine by sprinkling with ammoniacal water, then dissolved in ether; and the ether left to evaporate. — Fine, non-crystalline, yellowish white powder, free from sulphur. It does not dissolve in *water*, in aqueous *ammonia*, or in aqueous *fixed alkalis*, which do not even colour it yellow. It does not redden ferric salts. It dissolves easily in *sulphide of carbon*, *ether*, and *oil of turpentine*, slightly only in boiling *alcohol*. (Simon, *Pogg.* 44, 600.)

Unknown Primary Nucleus $C^{22}H^{22}$.

Enodic aldehyde.

$$C^{22}H^{22}O^2 = C^{22}H^{22},O^2.$$

This body is, according to Williams, the chief constituent of volatile oil of rue (p. 489.)

Digitaloic Acid.

$$C^{22}H^{22}O^4 = C^{22}H^{22},O^4.$$

WALZ. (1858.) *N. Jahrb. Pharm.* 9, 310; further, 10, 324.

Respecting Kosmann's fatty acid from *Digitalis* and Morin's digitalic acid, see *Digitalin.*

From commercial digitaline (*vid. inf.*) ether extracts Walz's digitalacrin or digitalicrin, which, by the treatment presently to be described, yields digitalin-fat, the acrid principles of digitalis, A and B, and digitaloic acid. — Walz's digitalin (*vid. inf.*) is digested with absolute ether; and the residue left after the distillation of the ether is washed with water as long as the water which runs away from it has a bitter taste, and then dried. (The product thus obtained was formerly described by Walz, *Jahrbr. pr. Pharm.* 21, 40, as digitalicrin.) On digesting the brownish, crumbling mass thus obtained with alcoholic solution of subacetate of lead, that substance takes up the colouring matter, and the wine-yellow filtrate leaves on evaporation (after removal of the lead? Kr.) a gold-yellow resin. The resin is freed by agitation with water from admixed digitalin and its products of decomposition; the undissolved portion (Walz's digitalacrin, *N. Jahrb. Pharm.* 9, 311) is digested with water containing a few per cent. of ammonia; and the white flocks which separate are filtered from the brown solution and completely washed with ammoniacal water. (The ammoniacal solution contains the acrid principle *A*; *vid. inf.*) The undissolved white flocks, containing digitaloic acid and the acrid principle B, are washed with cold alcohol, and the residual shining white mass is dissolved in boiling alcohol. The solution thus formed yields, on cooling, white pearly laminæ of digitaloic acid, an additional quantity of which is obtained by concentrating the mother-liquor, and likewise by precipitating with water the cold alcohol which has been used for washing. Part of the digitaloic acid still remains in solution, together with the acrid principle B: to separate these substances, the liquid is evaporated, and the residue, which solidifies to a white jelly, is digested with potash-ley and thoroughly washed. Digitaloic acid then remains behind, while the acrid principle B dissolves. The latter is precipitated with dilute sulphuric acid, dissolved in alcohol, and treated with animal charcoal (which however exerts a decolorising action), and obtained in the solid state by spontaneous evaporation of the solution.

Properties. Oblique truncated prisms, scentless at first, afterwards smelling of fat.

			Walz. *mean.*
22 C	132	70·96	70·86
22 H	22	11·82	11·90
4 O	32	17·22	17·24
$C^{22}H^{22}O^4$	186	100·00	100·00

It is not easy to see why Walz designates this body as an acid, inasmuch as it is insoluble in alkalis.

Insoluble in *ammonia*, or in *potash*, but soluble in *alcohol*.

Appendix to Digitaloic Acid.

1. Digitalin-fat.

WALZ. *N. Jahrb. Pharm.* 9, 312; further, 10, 324.

Extracted by ether from crude digitalin, together with the substances above mentioned, and remains — in the preparation of digitaloic acid as above described — dissolved in the aqueous ammonia, together with the acrid principle A. — When this ammoniacal solution is neutralised with dilute sulphuric acid, a copious white precipitate is formed, which soon unites with the resin. The resin is dissolved in alcohol; the solution precipitated with alcoholic subacetate of lead (the acrid principle A then remaining dissolved); and the precipitate is completely washed with alcohol and decomposed under alcohol, with sulphuretted hydrogen. The solution filtered from the sulphide of lead leaves, by spontaneous evaporation, digitalin-fat in white scales, which melt to an oil at a gentle heat:

Calculation according to Walz.			Walz. *dried.* *mean.*
25 C	150	73·17	73·41
23 H	23	11·21	11·33
4 O	32	15·62	15·26
$C^{25}H^{23}O^4$	205	100·00	100·00

Walz calculates his analyses incorrectly. He regards the fat as consisting of an acid $C^{22}H^{22}O^4$ and Berzelius's oxide of lipyl (ix, 487) C^3H^2O; or perhaps also as

$C^{74}H^{71}O^{12}$, produced from 3 At. $C^{22}H^{22}O^{22}$ and 1 At. $C^{8}H^{5}O^{6}$. According to the first of these formulæ, the acrid principles A and B of digitalis consist of digitalin with 2 and 3 At. oxygen added to it.

2. Acrid Principle of Digitalis, A.

WALZ. *N. Jahrb. Pharm.* 9, 314; 10, 324.

Extracted by ether, together with other substances, from crude digitalin, and remains, in the preparation of digitalin-fat, as above, in solution, on the evaporation of which it is left in the form of a resin. Separates by spontaneous evaporation from alcohol, at the bottom of the vessel, in yellowish red oil-drops, on the edge in warty resinous spherules, and appears, after complete evaporation of the alcohol, as a yellowish mass having the consistence of honey.

Calculation according to Walz.						Walz. *mean.*
25 C	68·33	32 C	67·60	40 C	67·80	68·18
23 H	10·40	28 H	9·85	34 H	9·60	9·61
6 O	21·27	8 O	22·55	10 O	22·60	22·21
$C^{25}H^{23}O^{6}$	100·00	$C^{32}H^{28}O^{8}$	100·00	$C^{40}H^{34}O^{10}$	100·00	100·00

Walz is undecided between these formulæ: the relations of this body to the other constituents of digitalis may be seen under *Digitaliretin* and *Digitalin-fat* (p. 530).

Decompositions. 1. When *heated*, it gives off a smoke having a peculiar odour, and at a higher temperature burns away without residue. — 2. Blackens with *oil of vitriol;* dissolves with brown colour in *fuming nitric acid*, whence it is precipitated by water; and with green colour in warm *hydrochloric acid*.

It is insoluble in *water*, but imparts to the liquid its acid reaction and very sharp taste. Soluble in *alcohol* and in *ether*.

3. Acrid Principle of Digitalis B.

WALZ. (1858.) *N. Jahrb. Pharm.* 9, 314; further, 10, 324.

Preparation. (See Digitaloic Acid, p. 529.)

Uniform, yellowish mass, friable at ordinary temperature, melting at 100°, and solidifying again but slowly. Its aqueous solution has a burning taste and slight acid reaction.

Calculations according to Walz.						Walz. *mean.*
25 C	65·5	32 C	65·54	40 C	66·14	65·89
23 H	10·0	29 H	9·89	35 H	9·64	9·73
7 O	24·5	9 O	24·57	11 O	24·22	24·38
$C^{25}H^{23}O^{7}$	100·0	$C^{32}H^{29}O^{9}$	100·00	$C^{40}H^{35}O^{11}$	100·00	100·00

Walz is undecided between these formulæ: the relations of the compound to the other constituents of digitalis may be seen under *Digitaliretin* and *Digitalin-fat* (p. 530).

Turns brown in contact with *oil of vitriol,* and olive-green with *hydrochloric acid,* which partially dissolves it. Dissolves with yellow colour in nitric acid.

Scarcely soluble in *water,* easily in *ether.* (Walz.)

4. Digitalosmin.

Walz. (1852.) *N. Jahrb. Pharm.* 24, 86.

The odorous principle of fox-glove (*Digitalis purpurea*).

On subjecting 80 pounds of dry fox-glove a year old to slow distillation by steam, 15 to 18 lbs. of slightly acid distillate were obtained, with fatty scales floating on the surface. By agitating the distillate with ether, removing the ethereal layer, and leaving the ether to evaporate, the substance composing these scales is obtained as a yellowish white, pearly residue, having a strong odour of infusion of digitalis, and a nauseating, scratching, very persistent taste.

Heated on platinum, it melts and volatilises in vapours, which burn with a non-smoking flame. — Softens when triturated with *oil of vitriol,* and is decomposed by heating. — It is slightly altered by cold fuming *nitric acid,* and coloured yellow by hot nitric acid, with evolution of nitrous gas.

It is insoluble in cold *water,* but imparts to it the odour of digitalis; in warm water, it melts and separates in scales on cooling. It dissolves in alcoholic *potash,* and is precipitated apparently unaltered by water. In aqueous *ammonia,* it softens without dissolving.

It dissolves readily in *alcohol,* with slight coloration, and is precipitated therefrom by water. — Dissolves with great facility in *ether.*

Oxygen-nucleus $C^{22}H^{16}O^{6}$.

Volatile Oil of *Aristolochia Clematitis.*

? $C^{22}H^{16}O^{6}$.

G. F. Walz. *Jahrb. pr. Pharm.* 24, 65.

The volatile oil of *Aristolochia* was previously observed by F. L. Winckler (*Jahrb. pr. Pharm.* 19, 71) and by Frickhinger (*N. Repert.* 7, 1). — Winckler obtained about 0·4 p. c. by distillation from the dried roots; Walz obtained the oil from the dried plant by vapour-distillation.

Viscid, gold-yellow oil, having a sp. gr. of 0·903 at 15° and a strong acid reaction (arising probably from adhering acid: Kr.).

			Walz. *mean.*
22 C	132	67·34	66·51
16 H	16	8·16	8·65
6 O	48	24·50	24·84
	196	100·00	100·00

Walz heated the oil that he analysed to 100° for some time previously, which temperature was probably not sufficient for dehydration. The calculations of his analyses, which vary from 65·18 to 67·13 p. c. in the carbon, and from 7·98 to 9·26 p. c. in the hydrogen, are partly incorrect. (Kr.)

By exposure to the *air*, the oil becomes more viscid, but does not resinise. — According to Winckler, it resinises when exposed to the air. — It colours oil of vitriol liver-brown when cold, black when heated, and finally becomes carbonised. — It dissolves *iodine* with rise of temperature, forming a yellowish brown, tough mass, which resinises when heated. — By *nitric acid* of sp. gr. 1·5, it is violently attacked, with evolution of nitrous gas, becomes brown-red and resinises. — With alcoholic *potash*, it forms a deep red liquid, becoming red-brown when boiled, and remains in red drops when the alcohol evaporates. — With *caustic ammonia* it forms an orange-yellow emulsion. With aqueous *bichromate of potash* and sulphuric acid it acquires a yellow-green colour.

Dissolves in 15—28 pts. *alcohol* of sp. gr. 0·85.

END OF VOL. XIV.

ERRATA.

VOL. XIII.

Page 576, lines 9—20 belong to page 577 where they should follow line 9.

VOL. XIV.

Page.	Line.				
139	9 from bottom	for	$2BaO,HO$	read	$2(BaO,HO)$.
140	5 from top	,,	$3BaO,HO$	,,	$3(BaO,HO)$.
,,	11 from bottom	,,	$3CaO,HO$	,,	$3(CaO,HO)$.
158	21 from top	,,	C^{16}	,,	C^{14}.
176	11 ,,	,,	$C^{20}NH^{17}O^{4}$	,,	$C^{24}NH^{17}O^{4}$.
268	17 ,,	,,	HQ	,,	HCl.

Gmelin, L. 40867
Hand-book of chemistry.
[4th ed.] Organic chemistry.


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