# Some Experiments on the Volatile Oil of the Myrcia Acris

by

Chas. C. R. Fish

# Some experiments on the volatile oil of the Leaves of the Myrcia Acris

The following experiments are necessarily incomplete in as much as they were undertaken in connection with some that Prof G.F.H Markoe had already tried and also with some that he is now trying

Prof Markoe's first paper on the subject is published in the Proceedings of the American Pharmaceutical Association for the year 1877 from which is made the following brief abstract

Prof Markoe distilled the leaves of the Myrcia Acris with water in a jacketed copper still heated by steam.

During the first part of the distillation an oil came over that was lighter than water, it was collected in separate portions & after separation from the water the Specific Gravity was taken. The Specific Gravities ran from .870 @ .990°

The latter part of the distillate was a heavy oil of a specific gravity from 1.023 & 1.037° O

After redistilling the heavy oil to separate the resin the Specific Gravity was:

@ 77° F. 1.052
@ 60° F. 1.055

The Oil as received from Prof. Markoe of a light yellowish brown color and had the characteristic odor of Bay rum

The specific gravity = .9715 @ 12° C., the Saccharometer showed a deviation of the ray of light 20° to the left, the index of refraction =

The Oil was distilled several times under a partial vacuum (250 – 300 mm Hg) to free it from the resin to which the slight color was due and which caused the oil to bump violently.

When the oil was freed from the resin it was very carefully distilled to separate it into heaps (as Prof Warren calls them) but having so little of the oil to work upon (less than 500 cc) it was found impossible to fractionate the heaps (from 10 to 30 cc) separately.

The 1st heap taken was at 130° C (300 mm Hg) about 30 cc the 2d heap 160° C. (300 mm Hg) about 40 cc – the 1st two heaps were colorless – the 3d heap at 170° C – the 4th 5th & 6th heaps @ 210° – 220° C they apparently did not vary much in temperature altho the distillate became more colored.

After the 6th heap the pressure was diminished to 630 mm Hg, for fear of decomposing the oil, the highest temperature being 190°

At the suggestion of Prof. Wing I fractionated the fractions in the following manner:

Nos. 1 & 2 were mixed and distilled under a diminished pressure of 460 mm Hg. (having Mr Holman's modified form of Prof. Wing's pressure regulator I was to get some very fine results the mercury staying steadily @ 460 mm, with a continuous stream of hydrogen gas passing through, during the whole distillation, about 4 hours). The temperature went up to 150°-155°C, and was kept there until about 30 cc had been collected which was marked I - the residue in the flask was set aside for a subsequent operation and was marked residue from 1 & 2.

Fractions nos. 3 & 4 were treated in a similar way the temperature being allowed to go up to 150°-155°C. and the distillate obtained was mixed with no. I. The residue from 3 & 4 was mixed with residue from 1 & 2 no. 5 being also added, the mixture thus obtained distilled @ 183°-185°C. leaving a very small residue - the distillate was marked II - the residue was mixed with No. 6 - and heated to 205°C the liquid remaining at that temperature until about 40 cc had been collected which was marked III - it was then heated to 210° C where there seemed to be another heap, the distillate collected at that point was marked IV. the residue from the above was mixed with no. 7 and distilled the distillation being carried to dryness all distilling over at 220° 222° C the distillate was marked V a very small amount of resin was left in the retort.

I will say here that all the distillations were conducted in a current of hydrogen gas and pieces of coke were put into the flasks to prevent bumping.

Distillates IV & V were mixed, put into a small flask and distilled to obtain a product pure enough for analysis; altho. coke was used and a current of hydrogen passed through, it bumped so that it was impossible to keep a constant pressure it being necessary at times to open the safety valve so as to prevent the oil from boiling over

Four portions were obtained:

1st boiling @ 194° C marked A.
2d " @ 210° C " B
3d " @ 215° C " C.
4th " @ 220° C " D

The portion marked B boiling @ 210° C was taken for analysis. Portion C was mixed with solution KOH 1.27 sp. gr. and the excess of KOH being neutralized with $CO_2$ the liquid became solid with crystals of Eugenate of Potash – the crystals were dried between blotting paper and then analyzed (they should have been recrystallized from Alcohol to free them from water but the authorities, Storer's Solubilities &c, consulted stated that alcohol decomposed them).

The Specific gravity and also the Index of Refraction was taken of each of the 4 portions but they did not differ materially.

Specific Gravity of B = 1.0489 @ 23° C
Index of Refraction B = 1.56816

As will be seen by the figures given below the results of the analyses of B were not very satisfactory altho. perhaps tending to prove that the body is Eugenol which the Physical character seem to prove

| Eugenol | Theory | Found |
|---|---|---|
| C | 73.17 | 71.5 |
| H | 7.317 | 7.34 |

$C_{10}H_{12}O_2$

Eugenate Potassium

| Found | Theory | |
|---|---|---|
| 61.00 | 59.68 | C |
| 6.989 | 6.71 | H |

($C_{10}H_{11}O_2K\ C_{10}H_{12}O_2 + 2H_2O$)

I hope before leaving this subject to learn more about the bodies which were obtained and if so should be pleased to make an addition to this paper

In closing this paper I want to thank Prof C.R. Wing for his kindness and attention during my work on this subject

Chas C.R. Fish

A short account of some of
theories of the Terpene series
together with
Abstracts of and references to
some of the more recent work
on the series.

The terpene series as it is sometimes called is one of the most important in Organic chemistry, it includes the Essential oils, turpentines, resins, gums &c, and although a vast amt. of work has been done on the series but very little is really known about it.

Not only is it impossible in most cases to purify the substances by fractional distillation, and other methods, but in a great many cases the substances themselves are changed by the action of heat while attempting to separate them.

A great many of the substances are very stable, not easily acted upon by reagents

The essential oils are very numerous and many of them have been examined in great detail.

For the purposes of chemical description, they may conveniently be arranged into 4 class, namely: 1 Essential oils composed of carbon + hydrogen only
2 – Essential oils composed of carbon hydrogen and oxygen
3 – Camphors, or concrete essential oils
4 – Essential oils containing nitrogen and sulphur

J. H. Gladstone has done the latest work on the essential oils and he has treated the subject very exhaustively, his papers (pages 39, 42, & 44) are of great value, for he has carefully tabulated his result so that it is possible to see the relation that the different oils bear to each other in their physical properties

The hydrocarbons

Almost every essential oil contains a hydrocarbon, which probably acts as a solvent for the true oil, camphor or resin

The hydrocarbons are nearly all lighter than water, they may be divided into 3 polymeric groups.

$C_{10}H_{16}$ = the terebenes

$C_{15}H_{24}$ of which oil of cubebs is an example

and $C_{20}H_{32}$ or Colophene group

The terebene group is the largest and the most important and although one would expect a certain number of isomeric bodies, it is not probable that there are as many as some writers suppose

For as in the case of Cymene by the long and thorough labors of Gladstone, Wright and others (page ) the so called isomers of Cymene were proved to be nothing but Cymene itself, so when the terebenes are as thoroughly worked up, there is reason to expect that the number will be reduced from the several dozen which are now tabulated to a very few, probably to two (one having the right handed rotary power the other having the left handed power, as in the case of tartaric acid) which when changed by heat and mixed in diff proportions with the addition of various impurities would answer the description of the various so called isomers.

That it is reasonable to expect this, one need only examine a tabulated statement of the physical properties of the different hydrocarbons and consider the impossibility of there competts separation, and that a very small per cent of a foreign body will perhaps change all the physical properties while an unweighable quantity of an odoriferous principal, perfume the entire mass, for what would be more likely than for the hydrocarbon to smell of the odorous substance that it held in solution, which it would be impossible to entirely distill off

Besides the isomers of the same degree of saturation, 4 isomers ought to be found corresponding to each of the following formular

$$\overset{VI}{C_nH_{2n-4}} \qquad \overset{IV}{C_nH_{2n-4}} \qquad \overset{II}{C_n\overline{H_{2n-4}}}$$

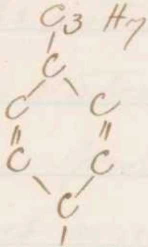
$$C_nH^{0}_{2n-4}$$

One of these being saturated, a second biatomic, a third triatomic and a fourth hexatomic

The essence of turpentine and some of its isomers act like tetratomic radicals and perhaps when better studied some may be found which act as biatomic; Valylene recently discovered by M. Reboul (page 37) is hexatomic

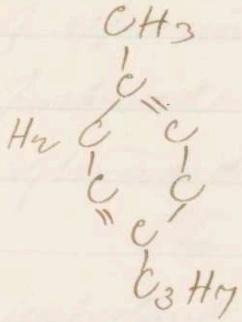
Some of the physical conditions" (if they can be so called) of these bodies are peculiar to themselves:
There is a liquid hydrocarbon $C_{10}H_{16}$ (turpentine) and a crystalline solid one (β Camphene)
A liquid Camphor (oil of camphor) $C_{10}H_{16}O$ a semi-crystaline solid camphor, a liquid camphor $C_{10}H_{18}O$ and a solid one and the same might be said of several of the compounds of these bodies

Chemists do not agree as to the method of writing the graphical formulae of these bodies, for camphor a great many have been proposed some of them are given (page 97-101) while for turpentine Schorlemmer proposes the following



that is if it has the same formula as terebene, which he considers this to represent for as terebene has been formed from di'amylene (page 15) the~~ugh~~ double bonding must be in the centre

Kekulé (Wurtz vol III 307) thinks that the formula below is to be prefered



It seems unfortunate that Chemists have not the means of easily determining the amount of heat given out in the combustion of substances and also the amts. of heat given out or absorbed in reactions, for as stated by Wright (page 58) such determinations would probably throw a great deal of light on this subject as well as on a great many others.

The study of the action of different degrees of heat for different lengths of time would probably prove an interesting study; when the following notes were collected it was proposed to try a series of experiments on the subject, but they had to be postponed at first for want of facilities and afterwards for lack of time,

The experiments might have been without important results but it seemed from the results of various experiments that have been tried on this and other subjects that some insight might be gained into the physical and perhaps molecular character of these bodies

The following are some of the experiments that have been tried on the subject

Hoffman by heating methyl aniline for

a long time at a high temperature converted it into toluidine (See page 132)

$$(C_6H_5)'-N\begin{matrix}\diagup CH_3\\ \diagdown H\end{matrix}$$

$$CH_3-(C_6H_4)''-N\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$$

Wright (page 52 ) speaks of a hydrocarbon having one odor before distillation, another after, and a third after standing some time, when turpentine hydrochlorate is heated with lime and the hydrocarbon formed is treated with HCl gas and the compound thus formed distilled with lime. The odor of the last compound formed is not like that of the first or second; when turpentine is heated in sealed tubes for two hours @ 300°, isoterebenthene a liquid boiling @ 173° @ 177° with an orange odor

Several chemists claim to have formed Camphor from oil of turpentine (pages 88, 90, + 91) and from Cymene (page 88) but it is not definitely proved.

It has not yet been decided what kind of a body Camphor is Berthelot has the honor of having called it about every possible compound and yet he still seems as far from establishing its identity as anyone else.

Nearly all chemists agree that Camphor has a closed chain and is double bonded in one place but no one knows where, they also seem to agree that in Camphoric Acid the Chain is broken but they do not agree as to the parts that are oxidized

The formation of Phorone cannot be explained from any of the proposed formulae for camphoric acid, but if the aldehyde corresponding to the acid could be formed it might throw a little light on the subject

Riban (page 24) thinks that the × elle (B-camphene) is the hydrocarbon corresponding to Camphor, and that Camphor might be formed from it, but there are no records of the experiments being tried

Chas F Kingzett in some experiments on turpentine (not published, or if published reference not known) passed air or oxygen through for some time. He said he formed hydrogen peroxide and camphoric acid. If such is the case he probably first formed Camphor, a result that might be expected as Berthelot says he formed it by oxidizing oil of turpentine with dilute permanganate of potassium (page 88)

Bouchardat (page ) by heating isoprene $C_5H_8$ formed as one of the products a hydrocarbon of the formula $C_{10}H_{16}$ with an odor resembling isoterebenthene, this he thinks tends to show that turpentine and other camphenic compounds are polymerides of hydrocarbons having the formula $C_5H_8$

A theory has been advaced that need to be mentioned, it is, that Camphor is a body similar to oxide of mesityle and that it can be formed in a like manner starting with a higer Ketone it seems likely that either camphor or an isomer of it would be formed, and probably the experiment will be tried

An examination of the work done on this subject shows that while a great deal of work has been done there still remains a great deal to do before the subject is made clear. The results when obtained will be of great value practically as well as theoretically and it seems as though it would not be long before it is answered and I hope that the answer may come from the Institute of Technology

In concluding I want to thank Prof. Charles H. Wing for the very kind assistance and encouragement that he has given me in this and previous work

I remain

Your obedient Servant

Charles C. R. Fish

Verhalten zu Brom

Deville ann Pharm u Chem XXXVII 191

Bromide of Turpentine

Bromide decomposes oil of turpentine eliminating HCl and forming brominated oil of turpentine (Deville)

On mixing of oil of turpentine with a few drops of Br HBr 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 1/6 of its bulk of water becomes heated when bromine is gradually added to it, destroys the color of bromine till (4 at) 228 pts of Br to 100 pts oil of turpentine are added and is converted into a colorless aromatic oil (G. Williams)

Gmelin Eng. Ed. Vol XIV

# Terpene Dibromide, $C_{10}H_{16}Br_2$

By Biedermann & Oppenheim

(Deut Chem Ges Ber V 627-628)

As hydrobromic acid is readily eliminated from terpene dibromide, it was resolved to study the action of oxidizing agents on it. Altho readily attacked by $HNO_3$ it only yields a resinous body, from which no definite nitro compound could be isolated.

A better result, however, is obtained by digesting it with acid potassium chromate & $H_2SO_4$ The solid product after purification by repeated solution in soda and reprecipitation, was found to concist of terephthalic acid $C_8H_6O_4$ a small quantity of a colorless body found in the upright condenser, the author believes to have been the monobromhydrate of turpentine oil $C_{10}H_{17}Br$ It had an odor resembling that of Camphor and melting at 60°

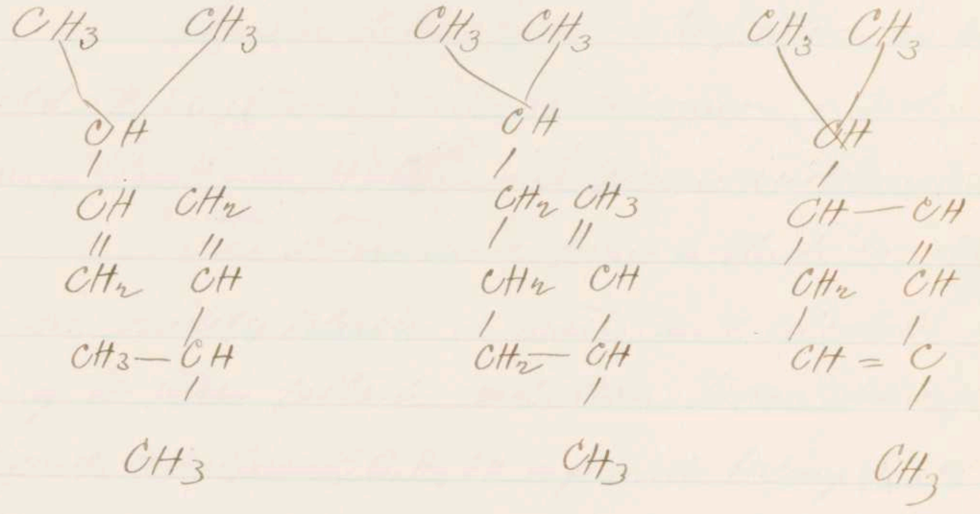
The reaction would therefore seem to concist of the splitting up of the dibromide into hydrobromic acid and cymene and the oxidating of the latter to terephthalic acid the action of heat alone into a body having double the number of Carbon atoms and this seems to show that turpentine and other camphenic compounds are polymerides of hydrocarbons having the formula $C_5H_8$

(Bull. Soc. Chim XXIV III)

On the Condensation of Amylene

By V von Richter (Deut Chem Ges Ber V 334)

2 mol Amylene    Diamylene    Terebene



Sur la transformation directe de l'amylene en polymères

par M. Berthelot (Bull Soc Chim t IV 266

Relations existing between Amylene & Oil of turpentine

Drs Bauer + Vesson (Am Chem + Pharm 1869

Aromatic Addition Compounds

By C. Graebe (D. Ch. G. B. V - 677-681)

(naphthalene tetrahydride $C_{10}H_{12}$)

Cymene $C_{10}H_{16}$

Volckker obtained this hydrocarbon by the action of phosphorus pentoxide on oil of worm seed, but it is more conveniently prepared by distilling this oil with $P_2S_5$ It boils at 174-175° and yields on oxidation with ($CrO_3$) solution terephthalic acid and not phthalic acid, as Kraut has stated.

Cymene differs from oil turpentine in dissolving in cold $H_2SO_4$ (conc) without coloration, or evolution of $SO_2$ ($C_{10}H_{15}-SO_4H$) Cymene sulphonic acid being formed

The free acid forms a thick syrup, its salts are readily soluble in water and alcohol. By fusing it with potash oxidation takes place, and a liquid cymophenol $C_{10}H_{13}OH$ is formed boiling @ 232° 235° and probably identical with that obtained by Wheeler and Pott from cymene sulphonic acid. From these reactions it would appear that Cymene is the dihydride of Cymene he heuffen Cymene from Cymene By heat Cymene with HI + P to 280°-290° for 16 hours a mixture of unaltered cymene & a hydrocompound is obtained the chief portion of which boils at 170-176 (Cymene boiling at 175-176) This prod. as well as the small portion boiling @ 160° is unacted upon by $H_2SO_4$ like Cymene

Sur la modification moleculaire de l'essence de terebenthine qui la rend propre a dissoudre plus facilement le caoutchouc

par MS Bouchardat

Compt rend V 20 (1836 p)

Remarque de M. Biot On the above

(Compt rend V. 21 p1)

Etudes sur l'essence de terebenthine

M Deville (Compt rend t 12 - 394

(1841 1st series)

Untersuchungen über das Terpenthinöl

von M. Deville (Ann Ch. u. Ph. (37) 176-196)

Tetra terebenthene, a solid Polomeride of Essence of Turpentine

By J Riban (Compt rend lxxix 393)

The new compound is produced by the action of antimonious chloride $SbCl_3$ on terebenthene It is an amorphous, brittle solid, of slightly yellow color, almost insoluble in alcohol, soluble in ether, carbonic sulphide benzene, petroleum and essence of turpentine, which on evaporation leave it as a colorless varnish Tetra terebenthene rotates the plane of polarization to the right $(\alpha)_j = 20°$ whilst the hydro. from which it is produced has a left handed rotation. Its density is .977 @ 0° It melts below 100° but passes into a viscous condition, which renders it impossible to determine the point precisely. Heated to 350° it is not volatilized but above that temperature it undergoes a transformation into hydrocarbon of the same composition but of less condensation. From compounds formed he infers its composition to be $C_{40} H_{64}$

## Synthesis of Terpilene

By G. Bouchardat (Comp. rend. lxxx 1446-1448)

The author submitted isoprene $C_5H_8$, one of the products of the distillation of Caoutchouc, to a temp. of between 280°-290°, in a sealed tube from which air had been expelled by carbonic gas. After 10 hours the liquid was found completely changed; it had become viscous, its density had increased, and it no longer boiled at a constant temp.

On distilling the liquid, a certain quantity of the primitive hydrocarbon came over unchanged, but at 176°-181° a liquid distilled over which possessed a pleasant odor resembling that of isoterebenthene

Its composition is exactly indicated by the formula $C_{10}H_{16}$; it has no rotatory power, and, like Terebenthene, rapidly absorbs oxygen from the air. It combines directly with HCl gas and from the product a liquid and a solid hydrochloride may be separated. The former appears to have the composition $C_{10}H_{16}\,HCl$ the latter $C_{10}H_{16}\,2HCl$, and this has all the properties of the dihydrochloride of essence of turpentine or hydrochloride of terpilene. Thus isoprene is condensed by

Sur l'isoterebenthene — (p 245)
par M. J. Riban

De l'isoterebenthene au point de vue physique
par J. Riban (p 250)

Sur un polymère solide de l'essence de
tetra terebenthene par J Riban (p 253)
Bull Soc Chim t VI

---

Isoterebenthene By J. Riban (Compt Rend / XXIX 223-227

The Physical properties of Isoterebenthene
By J Riban (Compt Rend / XXIX 314 317

Sur les éthers de la terpine
par M Oppenheim
(Compt Rend t LVII p 399)
Bull Soc Chim t I 365

Recherches sur les terpènes
par MM. A. Oppenheim et S. Pfaff
(Deut Chem Ges Ber t VII 625 474)
They call them (terebene, borneene, geraniene and eucalyptene) paramethyl propyl benzene
Bull Soc Chim XXII 398

Contributions to our knowledge of the Terpenes
By A Oppenheim and Pfaff
Deut Chem Ges Ber VII 625 628

# Camphenes by J. Riban

Compt rend (lxxx 1307-1311)

Contrary to Berthelot the author finds that the hydrochlorides of turpentine $C_{10}H_{16}HCl$ is changed into a Camphene by the action of alcoholic potash in a sealed tube, which fuses at 45°-47° boils @ 156°-157°, density @ 80° is 0.824 and it has in solution a levogyratory power = to 53.3°.

By heating the mono hydrochloride of terebenthene with twice its weight of potassium acetate for 24 hours @ 170°, and then distilling, another Camphene chemically identical with the former, but without action on polarized light, was obtained from the distillate.

From hydrochloride of terebene the author also procured a third Camphene which he regards as probably isomeric with the last.

M. Riban (Bull. Soc Chim XIX 242)
Recherches on the terebique series heating turpen with $H_2SO_4$ (Devilles process for obtaining terebene) he obtained in the products boiling 190 @ 220 liquids which deposited on cooling a matter ~~ml~~ with persistent odor and characteristics external of Campre of Laurel fusing @ 169 and identical or isomerique with it

Riban
Recherches on the isomerism of the $C_{10}H_{16}HCl$ compounds
"The chlorhydrique ether of borneol pertaining to that class of bodies treated with alcoholic K @ 180° is transformed into the carbone $C_{10}H_{16}$ xelle the
Water at the temperature of 100° the same transformation with elim of H Cl
He thinks that these xelle camphenes are the generators of camphor
Bull Soc Chim XXIII 98

Sur le camphene
par M. H. Schwanert
(Ann der chem u Pharm t CXXIII p 298 1862)
Rept de chem v Wurtz

Sur les Camphènes
par J Riban
He gives a method for obtaining large quantities to work with and their properties
Bull Soc Chem XXIV 8

Isomérie des chlorhydrates $C_{10}H_{16}HCl$
par J Riban
Same as above p 13

Sur les terpenes par MM. Beilstein et Hirzel
(Zeit fur chem. N.S. t 11 p 204)

In considering that essence as a homologue of a hydrocarbon $C_6H_8$ the same as xylene is a homologue of Benzine one has for the isomerics of the essence of terebinthine the following

I $C_6H_7(C_4H_9)$

II $C_6H_5\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$

III $C_6H_5\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$

$C_6H_6\left\{\begin{matrix}C.H_3\\C_3H_7\end{matrix}\right.$

The terpenes of the form I ought to give by oxidation the acide benzoique; those of the form III ought to give the acide xylique or one of its deriv The essence turpine belongs to class II as giving the acide toluique or the acid terephtalique

They conclude that the terpenes have a less number of isomeric forms than one thinks

Bull Soc Chim t VI 389

Sur les terpenes par Beilstein & Hirzel
(Zeit fur chem. N.S. t II 204) (Bull Soc Chim t VI 388)

## Oxidation products of Terpin

By Carl Hempel

(Liebigs Annalen CLXXX 71-87)

These expts. were performed in order to decide whether the toluic and terephthalic acids obtainable by the oxidation of oil of turpentine are formed from that body or from cymene using pure terpin hydrate they obtained the acids.

Terpin hydrate was prepaired according to the processes of Deville & Wiggers

8 parts of oil
2 " " $HNO_3$ of Sp Gr 1.25 _ 1.3
2 " " Alcohol

were found to give the best yields
Shallow basins being employed the xlle commenced in 3 days or less and was completed in two days more

Oppenheim has shown that terpin is a diacid alcohol $\Big\}\ C_6H_8\begin{cases}OH\\OH\\C_3H_7\\CH_3\end{cases}$

## On the alleged Synthesis of Terebene

By V. Longuinine (Deut Chem Ges Ber V 930)

The author finds that perfectly pure Cymene (boiling at 172°-175° (cor)) undergoes no alteration when its alcoholic solution is treated with Na or with an amalgam containing 3 per cent of sodium and hence infers that the cymene from which terebene has been said to be formed by reactions similar to those above mentioned must have been prepaired from cumin oil adulterated with oil of turpentine

## Physical properties of Terebene & Terebenthene

By J. Riban (Compt rend lxxxiii 288-291)

Terebene By J Riban (Compt rend lxxvi-1547-1550)

Transformation du Cymene en Terebene
par M.M. Longuinine et Pogarescki
Deut Chem Ges V 439 (1872)

Cymene from Cummin oil boiling @ 175–180° dissolved in 6 times its wt. of alcohol aqueous with addition of Ether and after several weeks action of Na amal. The product fractionated furnishes a notable quantity of a liquid boiling @ 159–161. This portion has the odor of turpentine and gives terpine by the action of alcohol and $HNO_3$ also the chlorhydrate by HCl. M H Schiff also found for it the density 868 @ 16. It comported with I as ordinary turpentine. It is lævogyle and the cymene which formed it was inactive.

Bul Soc Chim 18 . 407

Distinctions between the Isomeric Hydrochlorides having the formula $C_{10}H_{16}HCl$

By J Riban

(Compt Rend LXXX 1330-1332)

A summary of the information already abstracted in this Journal is given and curves are drawn to show the influence of boiling water on several members of the group. A scheme for detecting an unknown hydrochloride of the series is also described

On Terebene hydrochloride and on a method of distinguishing from one another the isomeric bodies having the formula $C_{10}H_{16}HCl$

By J Riban

Bull Soc Chim ② XIX 244

Constitution of Terebic and Pyroterebic Acids
By Bertram Mielck
(Liebigs Annalen ClXXX 45-70)

Terebic and Pyroterebic Acid
By W. Carleton Williams
(Deut Chem Ges Ber VI 1094)

Constitution of Terebic Acid
By R. Fittig and B Mielck
(Deut Chem Ges Ber VII 649-651)

## Oxidation Products of Colophony

By J Shreder (Deut Chem Ges Ber VI 413)

Fused caustic potash does not act on the terpine resins, but nitric acid oxidizes them. Colophony yields a resinous acid, and principally isophthalic acid besides a large quantity of trimellitic acid

## Sur l'acide pimarique et sur ses Modifications

par M. J. Duvernoy

Ann Chem und Pharm t CXLVIII p 143 (1868)
Bull Soc Chim t XI 1869 493

Sur les produits de decomposition de quelques resines sous l'influence de la potasse caustique

par MM H Hlasiwetz et L Barth

Bull Soc Chim t V p 62 – t VI p 336 et t VII-431

Sur la Synthese des resines

par MM. H. Hlasiwetz et L Barth et Grabowski

ann der Chem und Pharm t LXIII N.S. 83

Bull Soc Chim t VII p 432

## Action of Chlorine on Aromatic Substances by G. Ruoff

(Deut Chem Ges Ber IX 1048)

Most bodies of the aromatic series when heated with $ICl_3$ to 360° (if necessary) are converted into perchlorobenzene

Phenol — Cresol — Thymol
and Chloranil

Recorcin — Camphor and oil of Turpentine (also he speaks of the reaction on other substances

# On the ultimate Action of Chlorine on some Hydrocarbons

by. F. Krafft and V. Merz

(Deut. Chem Ges Ber VIII 1296–1304)

Propane = { perchlor ethane $C_2Cl_6$
chloro methane $CCl_4$

Isobutane { perchlor methane
per chlor propane & a little
per chlor ethane

Cumene { per chloro methane
per chloro benzene

Cymene { per chloro benzene
per chloro methane
per chloro ethane the last

product & half of the second being evidently formed by the breaking up of the Isopropyl group in Cymene

On Ozone as a Concomitant of the
Oxidation of the Essential Oils Part I
By Chas. T. Kingzett
Jour Chem Soc.

On the Oxidation of the Essential Oils
by Chas T. Kingzett
— Slow oxidation —
Part I in Jour Chem Soc 1874
" II " " " " 1875 – 210

Sur un Nouveau carbure de la series $C_nH_{2n-2}$ – par M. A Bauer

Ann Chem u Pharm CXXXV (1865) p 344

$C_{10}H_{18}$ rutylene

Isomeric with Menthene, Campholene

Stilbene —

Sur un Nouvel homologue de l'acetylene le Valerylene par M Reboul
(Compt rend. t lviii 214)

| | |
|---|---|
| Acetylene | $C_2H_2$ |
| Allylene | $C_3H_4$ |
| Crotonylene | $C_4H_6$ |
| Valérylene | $C_5H_8$ |

Bull Soc Chim I 463

Sur quelques corps non saturés appartenant au groupe des éthers mixtes
par M. Reboul (compt rend t lviii 1058 (1864))
Bull Soc Chim II 202

Bromhydrates et bromures de Valérylène
par M. E Reboul (Compt rend lviii 974)
Bull Soc Chim II 203

Sur un Nouveau carbure d'hydrogene le Valerylene par M. E. Reboul
(Compt Rendus t lx 803
Bull Soc. Chim IV 203

# Transformation de l'oxide de mesityle en Mésitylene et en un hydrocarbure $C_{10}H_{14}$ par M— A Holtmeyer

Zeit für Chem N. S t III 685

$2\,C_3H_6O - H_2O = C_6H_{10}O$

acetone — Oxide mesityle

$3\,C_6H_{10}O - 3H_2O = 2\,C_9H_{12}$

Oxide mesityle — (Mesitylene

The latter (mesitylene) boiled a long time with $H_2SO_4$ & distilled over sodium gives $C_{10}H_{14}$

Bull Soc. Chim X 39

# On Cymene from different sources. Optically considered

by J. H. Gladstone

He determined the Optical properties of the Cymenes made by Wright & tabulated them as follows

| Source of Cymene | Temp. | Specific Gravity | Refractive Index A | D | H |
|---|---|---|---|---|---|
| Cumin oil | 16° | 0.8569 | 1.4819 | 1.4901 | 1.5173 |
| Preexisting in Turpentine | 16 | 0.8555 | 1.4775 | 1.4851 | 1.5111 |
| " " " Myristicol | 16 | 0.8630 | 1.4799 | 1.4876 | 1.5145 |
| From hesperidene dibromide I | 13 | 0.8605 | 1.4835 | 1.4916 | 1.5196 |
| " " " II | 15.5 | 0.8638 | 1.4834 | 1.4909 | 1.5187 |
| From Camphor by $PCl_5$ | 16° | 0.8621 | 1.4852 | 1.4935 | 1.5218 |
| " Myristicol " $ZnCl_2$ | 14.5° | 0.8424 | 1.4706 | 1.4776 | 1.5021 |
| " " " $PCl_5$ | 13 | 0.8620 | 1.4815 | 1.4888 | 1.5172 |

From these numbers may be deduced the following optical data the Specific refractive energy and refractive equivalent being calculated for the line A and the Specific dispersion being the difference between the Specific refractive energies for A & H

| Source of Cymene | Specific refractive energy for A | Specific Dispersion | Refractive Equivalent for A |
|---|---|---|---|
| Cumin oil | 0.5623 | 0.0414 | 75.3 |
| Preexisting in turpentine | 0.5581 | 0.0393 | 74.7 |
| " " Myristicol | 0.5561 | 0.0401 | 74.5 |
| From hesperiden dibromide I | 0.5619 | 0.0419 | 75.3 |
| " " II | 0.5596 | 0.0409 | 75.0 |
| From Camphor by $PCl_5$ | 0.5628 | 0.0424 | 75.4 |
| " Myristicol " $ZnCl_2$ | 0.5586 | 0.0374 | 74.8 |
| " " " $PCl_5$ | 0.5596 | 0.0404 | 75.0 |

These numbers are practically identical they agree in fact as closely as values derived from different specimens of the same substance usually do.

The optical data for Cymene may be expressed by the mean values

| | |
|---|---|
| Specific refractive energy . . . | 0.5599 |
| " dispersion | 0.0405 |
| Refractive equivalent | 75.0 |

Jour. Chem. Soc.
1873 — 970.

# Heat of Combustion of Compounds in Oxygen

| Substance | Formula | molecular | By 1 grm of Sub | By 1 molecule of Sub | Observer |
|---|---|---|---|---|---|
| Amylene | $C_5 H_{10}$ | 70 | 11491 | 804370 | F. & S. |
| Paramylene | $C_{10} H_{20}$ | 140 | 11303 | 1582420 | " " |
| Hydrocarbon (form amylic alcohol boil pt 180°) | $C_{11} H_{22}$ | 154 | 11262 | 1734348 | " " |
| Cetylene | $C_{16} H_{22}$ | 224 | 11055 | 2476328 | " " |
| Metamylene | $C_{20} H_{40}$ | 280 | 10928 | 3059840 | " " |
| Oil of Lemons | $C_{10} H_{16}$ | 136 | 10959 | 1490424 | " " |
| Oil of turpentine | $C_{10} H_{16}$ | 136 | 10852 | 1475872 | " " |
| Terebene | $C_{10} H_{16}$ | 136 | 10662 | 1450032 | " " |

F & S assign to oil of lemons half the molecular weight of oil of turpentine but without giving any reason for so doing

Wats. dict. vol III

# On the Essential Oils Part I -

J. H. Gladstone

Crude oils.

He gives a full and valuable table of the optical properties of the crude oils which he examined.

The hydrocarbons -

The crude oils were fractionally distilled, to separate the hydrocarbon, which was several times distilled over sodium to separate it completely from oxidized products.

He then determined the physical properties of these hydrocarbons into 2 quite well defined classes. The first (1st) class contains the larger number of hydrocarbons, the specific gravities running from .8460 @ .8900 the boiling points from 160° @ 176°; The members are more limpid and dissolve freely in Aqueous Alcohol than those of the 2nd group; and probably all have the formula $C_{10}H_{16}$.

the first group may be subdivided into smaller groups some of which are composed of hydrocarbons from different sources which if perfectly purified would prove to be one & the same hydrocarbon.

The second class with specific gravities between .9041 & .9300 and boiling point 249° @ 315°; probably have the formula $C_{30}H_{24}$ which is assigned to Oil of Cubebs (one of the class) from its compounds with HCl.

The pure hydrocarbons have rarely powerful odors, and it is often difficult to remove every trace of the oxidized compound to which the characteristic fragrance is due.

Yet the odor of these liquids afford some support to the classification founded on other properties. Those which have the specific gravity 0.846 emit a more or less lemony odor when freshly distilled & some of those which resemble closely oil of turpentine in their general characters, resemble it also in this respect.

Jour. Chem. Soc.
(1864 2 1-21)

# Gladstone on Essential Oils

Part II Jour Chem Soc 1872 X (1)

He gives the physical properties of the following oils: Citron — Lign Aloes — Pimento — Vitivert —

The hydrocarbons —

Polymeric Group.

That colophene also has its isomerides is rendered probable by the descriptions given of para-cajputene and of the substance from other oils which have been named colophene, but which are probably not identical with it.

There seems to be little doubt in his mind that there are 3 groups $C_{10}H_{16}$ — $C_{15}H_{24}$ — $C_{20}H_{32}$

The general result of his experiments together with previous ones make it evident that the middle group is intermediate in all its properties and that these 3 groups do not pass by insensible gradations into one another, but are separated by strongly marked divisions.

| | 10 Carbon Group | 15 Carbon group | Colophene |
|---|---|---|---|
| Formula | $C_{10}H_{16}$ | $C_{15}H_{24}$ | $C_{20}H_{32}$ |
| Vapor density | 4.7 | 7.1 | |
| Character of liquid | limpid | viscid | very viscid |
| Sp. Gr. @ 20° C | .846 - .880 | .904 - .927 | .939 |
| Refrac Index for A @ 20° | 1.457 - 1.467 | 1.488 - 1.497 | 1.5084 |
| Dispersion | about .027 | about .029 | .031 |
| Sensitiveness | about 48 | " 43 | 41 |
| Boiling point | 160° - 176° | 249 - 260 | 315° |
| Action of $H_2SO_4$ | Polymerizes | Doubtful | none |
| Sol. in Aqueous Alcohol | Freely sol | Sparingly soluble | Insoluble |
| Combinations with HCl | $\{C_{10}H_{16}\,2HCl$<br>$\{C_{10}H_{16}\,HCl$ | $C_{15}H_{24}\,2HCl$ & in smaller proportions | very small quantity |

There is no difference in specific refractive energy, and the various members of the 10 & 15 carbon groups at least have powerful odors and rotate the plane of polarization strongly sometimes in one sometimes in the other direction

## Oils containing Oxygen:

"Many of the essential oils consist of a body containing oxygen, mixed usually with a hydrocarbon of the 1st or 2nd group

This is sometimes a product of the

direct oxidation of the hydrocarbon, and then is generally a feeble acid resin; but in most cases the relation between the 2 is not apparent.

Few of the oils have hitherto been carefully studied.

My attention has been confined almost exclusively to those neutral oils which contain only one atom of Oxygen".

# Isomeric Terpenes & their Derivatives

Part III On the essential oils of wormwood & Citronella
by C.R.A. Wright

Oil of Wormwood. proximate constituents:-
About 1% of $C_{10}H_{16}$; the larger part boiled @ 200-201 & = $C_{10}H_{16}O$ hence this substance is isomeric with camphor & with myristicol but unlike the latter continued distillation does not seem materially to change its composition either in raising its boiling point or causing decomposition into water & other bodies

Oil of Citronella    Proximate constituents:-
$C_{10}H_{16}O$ & $C_{10}H_{18}O$

Action of $ZnCl_2$ on Absinthol & Citronellol
Absinthol gave 20% of $C_{10}H_{14}$
Citronellol probably gave a mixture of hydro's
Action of Phosphorus pentasulphide on the above
with absinthol gave Cymene
" Citronellol more mixed
Action of $PCl_5$ on Citronellol
" " Br " "

Oxidation products of Cymene from above gave terephthalic Acid    Jour Chem Soc 1874 317

## Isomeric Terpenes & their Derivatives

## Part IV On Cajeput Oil

By C. R. A. Wright

Citronellol & the main oxidized constituent of oil of cajeput are isomeric.

The cymene that he obtained appeared to be identical with the others

Jour Chem Soc 1874
6 --- 619

## On the Action of Pentasulphide on Terpenes & their Derivatives

By C. R. A. Wright

Jour Chem Soc 1874
619

Preliminary Notice on the Oils of Wormwood and Citronella by C. R. A. Wright

absinthol + $PS_x$ gave cymene

citronellol + dehydrating agents gave rise not to Cymene but to a terpene

$C_{11}H_{18}O - H_2O = C_{10}H_{16}$

(Jour Chem Soc 1874 - 1 -)

# Isomeric Terpenes and their Derivatives

Part V G. H. Beckett & C. R. A. Wright

## Peppermint Camphor from Japan

Oppenheim has already shown (this Jour (1) XV 24) that this substance is an Alcohol (Menthylic alcohol) of the form $C_{10}H_{19}OH$, and that by the action of dehydrating agents it splits up into water and a hydrocarbon, menthene $C_{10}H_{18}$, bearing the same relation to terpenes that these do to Cymene (i.e.: containing $H_2$ more). The following figures were obtained for the camphor

| | Oppenheim | Wright |
|---|---|---|
| Melting point | 36° | 39° |
| Solidifying " | — | 37.5° |
| after exposure to the air & recrystallizing | melted | @ 42.° |
| boiled | 210° | 212° cor<br>corrected |

Analysis gave $C_{10}H_{20}O$

After treatment with $ZnCl_2$ the hydrocarbon gave $C_{10}H_{18}$ – distilled 164.5–165.5 (Oppenheim 163°). Treated with Br gave Cymene:

$$C_{10}H_{18}Br = 4HBr + C_{10}H_{14}$$

Its production from Menthene is of interest, as showing not merely a connection between the benzene hydrocarbons & the homologues of Allylic Alcohol (Menthylic Alcohol belonging to the series $C_nH_{2n}O$) but also as being an instance of the passage from a paraffin derivative (tetrabromodecane) to a benzene derivative, Cymene, by a single action of decomposition

Oppenheim raises the question whether di-ethyl-benzene is formed as well as propyl-methyl benzene (Deut Chem Ges Ber VII 625).

Taking into consideration the results obtained in this & the preceding 4 portions of these researches, together with those of Barbier, Oppenheim, Kekulé, Fittica, Beilstein & Kupffer, Riban, G. Williams, & others, it may be concluded that by the action of a large number of agents on terpenes & bodies related to them, absolutely the same Cymene results, this Cymene being identical with the para-methyl-propyl-benzene recently obtained synthetically by Fittica by acting with sodium on a mixture of normal propyl bromide & solid para-bromo-toluene melting at 28° —

Since at least 4 distinct isomerides of formula $C_{10}H_{16}$ can by losing $H_2$ produce the same Cymene, & as only 3 such isomerides can readily be predicted from Kekulé's benzene formula, cymene being viewed as a 1..4 derivative, it results that in the production of Cymene from at least 1 of these terpenes (and therefore possibly in the production of Cymene from all its sources) the reaction is not so simple as would at first sight appear, but that it belongs to that class of reactions where "change of position" is said to occur i.e. in the symbolic representation of which, groups of symbols not otherwise affected must be made to alter their relative positions

On clove oil hydrocarbons $C_{15}H_{24}$

On the liquid oil from Camphor sublimation

it seemed to be a mixture $C_{10}H_{16}$ + $C_{10}H_{15}O$

## Isomeric Terpenes & their Derivatives

by C.R.A. Wright  Part I (Jour Chem Soc. 1873 549)

He used oils of nutmeg & orange peel, he found Cymene mixed with most of his fractions and thinks it is a common impurity of the various terpenes.

After boiling hesperidene (orange oil terpene) with $H_2SO_4$ & $K_2Cr_2O_7$ several days, he says the unattacked oil had a powerful odor of mint which became more like that of Anise on standing for some months, it was separated by a funnel, washed and distilled; the greater part came over below 180° & smelt like orange oil with a minty odor, a portion however was left, & did not wholly distill at the limits of mercurial thermometer.

This portion of higher boiling point resembled the similar mixtures obtained from Nutmeg oil and pure orange in as much as it appeared to consist chiefly of a portion boiling near 215° of formula $C_{10}H_{16}O$ aquiring a higher boiling point with out appreciable change of composition.

On continual heating it had a powerfull smell of Mint when fresh.

"From the foregoing results, it is evident that turpentine oil (b.p 160°) the terpene of Nutmeg oil (b.p 163°) & hesperidene (b.p. 178°) are 3 different isomerides, since the former gives Camphrenic Acid by its oxidation". ...

"(Schwanert): the number of formulae conceivable for bodies $C_{10}H_{16}$ is great, but it appears not improbable that many bodies now believed to be different and peculiar terpenes may like Myristicene turn out, on closer inspection, to be mixtures perhaps of previously know bodies."

# Isomeric Terpenes and their Derivatives

## Part II Cymene from various sources

By C. R. A. Wright (Jour. Chem. Soc 1873. 686)

In part I it has been shown that the oil of Nutmeg contains an isomeride of Camphor $C_{10}H_{16}O$ (Gladstone called Myristicol) this substance is difficult to obtain pure in as much as it occurs mixed with hydrocarbons of lower boiling point from which it cannot be completely freed by fractional distillation, in as much as the Myristicol itself alters by repeated distillation, becoming changed into polymeric modifications of higher boiling point & finally into a volatile resin.

The action of phosphorus penta chloride on the Camphor-isomeride forming the chief constituent of Myristicol is expressed by the equation

$C_{10}H_{16}O + PCl_5 = HCl + POCl_3 + C_{10}H_{15}Cl$

which is perfectly parallel with the reaction of phosphorus penta chloride on Alcohols generally $MOH + PCl_5 = HCl + POCl_3 + MCl$

The action of this reagent on Camphor is however different (Gerhardt) being indicated by the equation

$C_{10}H_{16}O + PCl_5 = POCl_3 + C_{10}H_{16}Cl_2$

whence it appears that Camphor is a substance not belonging to the same series of compounds as Myristicol, the former being apparently an Aldehyde $C_9H_{15}CHO$.

Gerhardt & also Pfaundler have further shown (Ann Chem Pharm. CXV. 29) that this dichlorinated Camphor derivative splits up by heating into HCl & a body $C_{10}H_{15}Cl$ (also obtained by treating camphor with less $PCl_5$ than that required to form the dichloride) this derivative is only isomeric with the body of the same composition derived from Myristicol, being, when pure, a crystalline body melting at 60°

Longuinine & Lippmann have shown (Bull Soc Chim (II) VII 374) that when this crystalline body is heated for some time or repeatedly distilled at a very slow rate, it splits up (like the chlorides of secondary alcohols) into HCl and a hydrocarbon containing the elements of water less than the original Camphor; thus —

$C_{10}H_{15}Cl = HCl + C_{10}H_{14}$

The hydrocarbon thus produced appears to be ordinary Cymene.

The action of $ZnCl_2$ on Myristicol is expressed by the following reaction

$2C_{10}H_{16}O = H_2O + C_{20}H_{30}O = 2H_2O + 2C_{10}H_{14}$

The body $C_{20}H_{30}O$ is perhaps, the ether of the alcohol $C_{10}H_{15}OH$ (Myristicol) viz $\left.\begin{matrix}C_{10}H_{15}\\C_{10}H_{15}\end{matrix}\right\}O$ not impossibly, however, it may be a polymeride.

Myristicol was gently heated in a retort with about 1/2 its weight of solid $ZnCl_2$; before the boiling point was reached, an action was perceptible and water distilled over, at 170° & upwards a hydrocarbon passed over and @ 250° a yellow-brown non-volatile resin was left in the retort; this could readily be separated from $ZnCl_2$ by decantation and filtration while hot & semifluid;

It gave on analysis $C_{20}H_{30}O$, the hydrocarbon produced at the same time was Cymene

Cymene from Camphor by the action of $PCl_5$
Cymene " Nutmeg hydrocarbon (Precontained)
Cymene " Oil of turpentine ( " )
Cymene " Hesperidene dibromide

Cymene from the dibromide of the terpene of Nutmeg oil: the hydrocarbon boiling @ 163°–164° contained in oil of nutmeg, is a mixture of a terpene (dissimilar from the terpenes of turpentine, lemon oil & orange oil) with 10 @ 12 % of cymene. When heated with 2 equivalents of bromine, dibromide is formed: the union of a given weight of bromine with the Nutmeg hydrocarbon evolves much more heat than is produced by the combination of the same quantity of bromine with hesperidene; it was not however found practicable to obtain any very accurate calorimetric determinations of the actual quantity of heat produced in each case. Without doubt this circumstance together with the similar result noticed in the case of the action of $H_2SO_4$ on these 2 terpenes (p 55, this vol) is intimately connected with the difference in boiling point of the 2 terpenes (163°-166° for the Nutmeg terpene, 178° for hesperidene) and with the different chemical reactions undergone by them; i.e.: is intimately associated with the question of the nature of their isomerism. It would be of great interest to examine carefully the different amounts of heat generated by the combustion of equal weights of isomeric terpenes but independently of the difficulties in the way of obtaining sufficiently accurate results to be of any use in investigating the character of the differences between such isomerides, the previous experiments indicate that it is not improbable that many bodies supposed to be pure terpenes may really be mixtures and that in particular small percentages of Cymene may be contained in them; the presence of this hydrocarbon would of course vitiate the results. It may be predicted with considerable probability that the heat of combustion of hesperidene will be found to be less than that of the Nutmeg terpene, a result quite in harmony with Julius Thomsen's results (Deut Chem G.B, v 769) Thomsen finds that in the case of analogous compounds the higher the "molecular weight" the less is the heat of combustion, thus

$H_2O$ = + 68357 $HCl$ — + 22001
$H_2S$ = + 4512 $HBr$ — + 8440
$\overline{HI}$ — − 6336

As a rule the higher the "molecular weight" the higher the boiling point in comparative cases (e.g. the well known increase of boiling point by about 20° for each additional $CH_2$ in truly homologous series) so that it appears not improbable that it may be a general rule that, caeteris paribus, the higher the boiling point the less is the heat rendered sensible in the formation of a given compound and therefore the greater is the "energy" of that compound.

It is well known that the greater

the heat evolved in the formation of a compound, the more stable it is; thus metallic Zinc decomposes water (as in the "couple" of Gladstone & Tribe) because more heat is evolved in the formation of $ZnO$ than in that of $H_2O$ & for the same reason Mercury displaces silver from its salts, Copper precipitates mercury & Zinc — copper &c. Hence it might be inferred that the compounds of Hesperidene would probably be less stable than those of its isomerides of lower boiling point, which seems to be the case at any rate with the dibromide, Oppenheim having found that the dibromide of turpentine (the hydrocarbon boiling at 160°-161° is but little affected by heat whilst as stated above the dibromide of Hesperidene (b.p. 176°) is readily split up into Cymene & $HBr$ by simply heating it, the dibromide of nutmeg hydrocarbon (b.p. about 164°) having an intermediate stability. The cymene obtained from the nutmeg dibromide boiled @ 176°-178°

# Cymene from Cumin Oil - - -

- - - - - - - - - - -

Boiling points of the foregoing varieties of Cymene corrected:

| | |
|---|---|
| From Myristicol by action of $PCl_5$ | 176 – 178 |
| " " by " $ZnCl_2$ | 173 – 177 |
| " Camphor " " " $PCl_5$ | 175 – 178 |
| Precontained in Nutmeg hydrocarbon distilling @ 163 – 164 } | 173 – 177 |
| Precontained in oil of turpentine | 174 – 177 |
| From Hesperiden dibromide | 176 – 178 |
| Contained in Cumin oil | 175.5 – 177.5 |

---

| | |
|---|---|
| Noad found | 171.5° |
| Gerhardt & Cahours | 175. |
| Church before treatment with $H_2SO_4$ | 171° |
| " after " | 175 – 176° |
| Warren (for Cymene from Cumin oil | 179.5° |
| Fittig &c (for Cymene from Camphor by $ZnCl_2$ | 173° – 176° |
| Kekulé Lehrbuch | 177 – 179° |
| De la Lande (from Camphor + $P_2O_5$) | 175° |
| Oppenheim (from dibromide of citrene & turpentine) | 176. – 179 |
| Longuinine & Lippmann (from the product of Camphor & $PCl_5$) | 175° – 178 |

Action of Chromic liquor on the foregoing varieties of Cymene the following percents of Cymene were obtained

1 = 40% (Myristicol by $PCl_5$)
2 = 35% about (Camphor by $PCl_5$)
3 = 30% " (Terpentine " $H_2SO_4$)
4 = 45% nearly (Hesperidene dibromide)
5 = 25% " (dibromide Nutmeg hydro )
6 = 60% " (Cumin oil )

---

Hoffmann found (Ann Chem Pharm XCVII 197) that Cymene from Cumin oil yielded by oxidation with Chromic acid an acid which had the characters of terephthalic acid but to which he attributes the formula $C_9H_8O_4$

De la Rue & Müller (Ann Chem Pharm 121-88) & Schwanert (Ann. Chem Pharm 132-254) found that this so called isolinic acid was only impure terephthalic acid.

Fittig & Ferber found that the Cymene formed from Camphor by $ZnCl_2$ did not yield terephthalic acid by oxidation (Kekule Lehrbuch II 542)

De la Rue & Muller on the other hand, found (loc cit) that terephthalic acid was produced by oxidizing this variety of Cymene

These contradictory results, together with those obtained by Riche & Berard (Jahres 1864 531), which led Kekulé (Lehrbuch loc cit) to regard the Cymene from Cumin oil as different from that obtained from Camphor, may no doubt be explained by the observations of Fittig, Köbrich & Jilke that Camphor yeilds a very complex mixture of products by the action of $ZnCl_2$ & consequently that the Cymene thus obtained is exceedingly impure

In odor the varieties of Cymene described above were indistinguishable one from another . . . .

## Conclusions —

The foregoing results (tabulated above) indicate that there is but one variety of Cymene produced from & existing in the bodies experimented with; this boils at 176–177° & yields by oxidation terephthalic acid (in quantities much less than those those theoretically obtainable) free from isophthalic acid; Acetic acid free from higher homologues is also produced.

The production of terephthalic acid from Cymene by oxidation shows that (2) "lateral chains" are present; and as toluic acid is also obtainable from Cymene one of these chains must be Methyl (since toluic acid gives rise to methyl benzene or toluene) Cymene therefore is either a Methyl-propyl-benzene or a Methyl-isopropyl-benzene

If terephthalic acid be regarded as a 1-4 benzene derivative, there are but 3 formulae attributable to bodies which can form Cymene by loss of $H_2$ viz:—

$C_6\ (Pr\,H)\ H_2 \cdot H \cdot Me \qquad H \cdot H$

$C_6\ (Pr)\ H_2\, H_2\, Me \qquad H \cdot H \cdot$

$C_6\ Pr \quad H\ H_2 (Me H) \qquad H \cdot H \cdot$

(where it is not stated whether Pr is ordinary propyl or iso propyl)

Four bodies are however, now known which are apparently homogeneous & different substances, and yielding the same Cymene by removal of $H_2$ viz:—

The terpene of turpentine oil } Williams
" " " lemon oil = citrene } Barbier Oppenheim
" " " Orange oil } Wright
" " " Nutmeg "

Hence it must be supposed either that terephthalic acid is not a 1-4 di-carboxyl-benzene or else that one at least of these hydrocarbons is really the dihydride not of a 1-4 but of a 1-3 or a 1-2 methyl-propyl-benzene, the radicals Methyl & propyl altering their mutual relations to one another during the elimination of the $H_2$ and finally arriving at the 1-4 position.

Whatever may be the actual character of the process thus symbolically indicated, there can be little doubt that it corresponds to the performance of "internal work" of some kind, and therefore that a change of this kind is probably coincident with the evolution of a quantity of heat less than that which would be produced by the removal of $H_2$ from the hydride of a 1-4 compound; if therefore it were possible to estimate the quantity of heat involved in the reactions

$C_{10}H_{16} + Br_2 = C_{10}H_{16}Br_2$

$C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr$

some light might be thrown on the subject of the "structural" formula of the terpenes unfortunately such determinations appear to be impracticable.

If the phthalic acid be viewed as a 1-3 benzene derivative 6 formulae exist indicating the dihydrides of cymene & if as a 1-2 derivative, there will be 6 other formulae

Viz:

1-3

$C_6(PrH)\ H_2\ Me\quad H.H.H.$
$C_6\,Pr\quad H_2(MeH)\quad H.H.H.$
$C_6\,Pr.\quad H\,(MeH)\quad H_2.H.H.$
$C_6\,Pr.\quad H\quad Me\quad H_2H_2H$
$C_6\,Pr\quad H\quad Me\quad H\,H_2H_2$
$C_6\,(PrH)\ H\quad Me\quad H\ H\ H_2$

1-2

$C_6(PrH)\ (MeH)\ H\ H\ H\ H$
$C_6\,Pr\quad (MeH)\ H_2H\ H\ H$
$C_6\,Pr\quad Me\quad H_2H_2HH$
$C_6\,Pr\quad Me\quad H\ H_2H_2H$
$C_6\,Pr\quad Me\quad H\ H\ H_2H_2$
$C_6(PrH)\ Me\quad H\ H\ H\ H_2$

so that if it be supposed that the Methyl & propyl groups can alter their mutual connections during the removal of $H_2$ there are altogether 15 different possible formulae for dehydride of Cymene

Jour. Chem Soc
1873 686-701

Sur les essences de Fenouil de bachine
et d'anis par M Auguste Cahours
(ann de Chim de Phys (3) 2 - 274)

Recherches sur la coumarin ou Stearoptène
des fèves de Tonka par M. Z. Delalande
(ann de chim et Phys (3) 6 - 343 (1842))

Recherches Chimique sur les resines
par M. H. Deville
(ann de Chim Phys (3) 2 - 151)

Sur les huiles Essentielles
par M. M. Gerhardt et Cahours
ann Chim et Phys. (3) 1 - 60 (1841)

Note sur l'essence de Cèdre crystallisée
et l'essence de Cèdre liquide
par M Phillippe Walter
ann de chim et Phys (3) (3) 1 - 498

Researches on Calamus Oil
By A Kurbatow (Deut Chem Ges Ber VI 1210)

The oxidation products of Colophony and Oil of turpentine By J Schreder
Ann Chem Pharm CLXXII 93-101

Dill Oil By R. Nietzki (Ann Pharm (3) IV 317-324)

The reactions of acids with oil of Peppermint and their bearing on the formation of Chlorophyll
By A. Frebault (Pharm J Trans (3) IV 977

Essential Oils By A. Kurbatow (Ann Chem Pharm CLXXIII 1-5)
Oil of Olibanum Calamus oil

Oil of Eucalyptus By Faust & Homeyer (Deut C.G.B. VII 1429-1430)

Oil of Wormseed (wormseed) & Cymene
By Faust & Homeyer (Deut G G B VII 1427-1429)

Sur l'essence de cresson de fontaine

par M. A.W. Hofmann (Deut Chem Ges Ber 6 VII 520 1874)

It gave a nitrile + hydrocarbon

Bull Soc Chim t XXII 378

Recherches sur le Menthol

par M. Oppenheim

(Compt Rend t LVII p 360 (1863) Rept Chim pur t IV p 14-1862)

Bull Soc Chim t I p 364 1864

Recherches sur l'essence de Myrtus pimenta

par M. C. Oeser

Ann. der Chemie und Pharm t CXXXI p 277 (1864)

Bull Soc Chim t III 434

Sur l'essence de Sassafras

Note de MM E. Grimaux et Ruotte

(composed of 2 liquids $C_{10}H_{16}$ + $C_{10}H_{10}O_2$)

Bull Soc Chim 1869 p 462 V. XI

On the products of reduction and the composition of Anethol
By F Landolph (Compt rend LXXXII 849-852)

$C_{10}H_{12}O$ or as he thinks $C_{20}H_{24}O_2$

Sur la composition de l'essence de Laurier
par M. C. Blas
Ann Chem u Pharm t CXXXIV p. I

$C_{10}H_{16}$ he gives the various properties
Bull. Soc Chim t IV p 371

Ane reaction of Oil of Mint
By O Roucher
(J Pharm Chim (4) XX 354)

With acetic acid

Action of Baryta on Oil of Cloves
By A. H. Church

nothing definite
Jour Chem Soc 1875 113

# Researches on some Derivations of Natural and Synthethically prepaired Thymol

By E Paterno' (Gaz chim ital 1875-13-24)

It was shown some years ago by R. Pott (Deut Chem Ges Ber 11 121) + H Miller (ibid 130), that by fusing the potassium salt of cymene sulphonic acid with potash, a phenol is obtained, having the composition of thymol from oil of thyme viz. $C_{10}H_{14}O$ but differing from it in being liquid at ordinary temps. whereas natural thymol is crystalline. Subsequently, the isomerism of these two thymols was traced through several of their derivations viz. in the thiophenols $C_{10}H_{14}S$. obtained by treating them with phosphorous pentasulphide (Fleischer, chem Soc J. (2) XI 1029 Fittica ibid 1027) in the oxyacids $C_{11}H_{14}O_3$ prepaired by treating them with sodium and carbon dioxide (Kekulé + Fleischer, ibid XII 64) and in the cresols produced by treating them with phosphoric anhydride (Kekulé ibid XIII 64) Other experiments showed that the synthetically prepaired thymol was identical with the product which Claus obtained by the action of iodine or camphor and with Schweizer's Carvacrol (Kekule + Fleischer ibid XI 1228, XII 66)

The present paper contains a comparison of some
other derivatives of their two thymols.
The Acetyl, Methyl and Ethylene derivatives
Methy Thymol sulphuric acids
Thymol sulphonic Acid
Jour Chem Soc 1875 637

Sur les dérivés alcooliques du thymol
par M. Emile Jungfleisch
Bull Soc Chim t IX 17

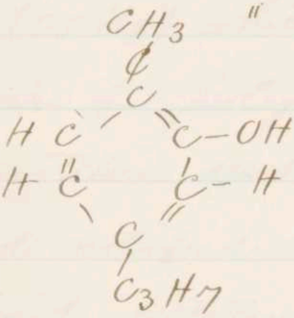
On some derivatives of Thymol

By E. Carstanjen (J pr Chem [2] III 50-68)

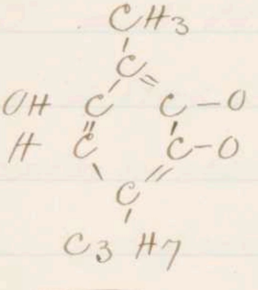
The author describes some of the compounds of thymol

| | | |
|---|---|---|
| | Thymoquinone | $C_{10}H_{12}O_2$ |
| dibromo | " | $C_{10}H_{10}Br_2(O_2)''$ |
| monobromo | " | $C_{10}H_{11}Br(O_2)''$ |
| Oxy | " — | $C_{10}H_{11}(HO)(O_2)''$ |
| Dioxy | " — | $C_{10}H_{11}(HO)_2(O_2)''$ |

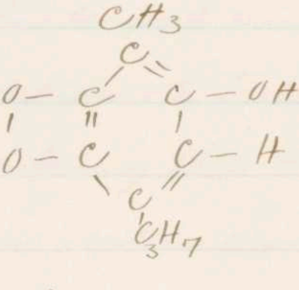
He obtained the hydrocarbon $C_{10}H_{14}$ he thinks from the products of oxidation the formula should be written thus



it follows that the position of the alcohol radicals methyl and propyl (or isopropyl) in thymol may consequently be represented by the formula



Oxythymoquinone from monobromo thymoquinone



oxythymoquinone from Diamidothymol (Jour Chem Soc 1871 p 350)

## Dry distillation of Caoutchouc

By G. Bouchardat (Bull. Soc. Chim (2) XXIV 108)

5 kilos of new Caoutchouc yielded 250 grms of Isoprene $C_5H_8$. 2000 grms of Caoutchine $C_{10}H_{16}$, volatile at 176°–180°; and 600 grms of heveene $C_{15}H_{24}$, volatile at 255°–265°. There remained other less volatile products, less and less fluid, some distilling below 360° among which is probably the carbide $C_{40}H_{32}$ and others which decompose by heat and produce the preceding carbides. It may then be said that caoutchouc is a certain carbide $n(C_5H_8)$ which is decomposable by heat into a series of polymerides of the carbide $C_5H_8$. Caoutchin washed with slightly acidulated water and rectified repeatedly from sodium, is a volatile liquid distilling @ 177–179°. Its density is 855 @ 0° and 842 @ 20°. In odor and many other properties it bears a strong resemblance to turpentine especially in absorbing and combining with HCl. $H_2SO_4$ conc. modifies it and produces a certain quan. of cymene $C_{10}H_{14}$, but the larger part is converted into polymeric carbons $C_{15}H_{24}$ + $C_{20}H_{32}$ + the latter by dry distillation reprod. a carbide $C_{10}H_{16}$.

[does not boil below 173°

No terebene seems to be found by the action of $H_2SO_4$ as the most volatile of the products

## Abietine, a new Hydro carbon

By Wm Wenzel (Pharm Jour Trans [3] 11 789)

This hydro is the product of the distillation of the exudation of a coniferous tree (Pinus Sabiniana or nut pine) indigenous in California; the resin exudes from incisions which are made in the tree during winter. The hydro was found to distil almost constantly about 101°, its specific gravity is 694 @ 16.5° it is nearly insoluble in water and sol in 5 pts of alcohol containing 95%. $HCl$ gas and $H_2SO_4$ do not act on it; $HNO_3$ on boiling attacks it moderately; chlorine gives rise to substitution products. It burns with a brilliant flame, white and smokeless, and dissolves fixed and volatile oils, except castor oil which is insoluble in it. Its vapor has powerful anesthetic properties; it has a penetrating odor resembling oil of oranges. No analysis of this hydro. or of its compounds is given, but the distinguishing properties between it and benzine are noticed at some length

## Essential Oil of Poplar

By J. Piccard (Deut. Chem. Ges Ber VII 1485; Chem Cent 1875-4)

The author found the composition of this oil to be C=87.57 H=12.21 its boiling point to be 260° and Sp. Gr. 0.9002 (Centr 1873 584) and from these data he regards it as a higher polymeride of turpentine oil with the formula $n(C_{10} H_{16})$ The vapor density as det. by Dumas' method is 8.94 while that of ordinary oil of turpentine is 4.69, so that it is clearly a diterpene $C_{20} H_{32}$ It exhibits a right handed rotatory power of 19° at ordinary temp with Wilds' polariscope

On Blue Chamomile Oil

By J Kachler (Deut Chem Ges Ber IV 36)

(See Mörsner ann de Pharm CXIX 257)

That it is a mixture was at once evident on on rectifying the crude oil, previously distilled in a current of steam; it began to boil at 105° and between this and 188 a small quantity — 206 grms crude gave 9 grms — of a faintly blue oil, smelling strongly of chamomile passed over and between 188° and 225° a second fraction of 17 grms of a somewhat darker color was obtained. The magnificent blue vapor which characterized this oil was formed above 225°; the temp. rose to above 295° was still blue but more syrupy. The temperature finally became too high for thermometer, the vapor became violet and 43 grms of a thickish, but still blue oil were obtained. Finally there remained in the retort 41 grms of a brownish. A portion of the 1st two fractions gave $C_{16}H_{10}O$. The portion 165°–185° gave $C_{10}H_{16}$ Bizio (Wien. akad. Ber. XLIII [2] 292.

The intense blue portion 270°-300° from results]
(K) Bazio + Bornträger (Ann Ch Pharm xlix 243)
it evidently an isomeride or polymeride of
camphor certainly double and probable
treble that of camphor.

Azulene, principe colorant des huiles
volatiles
par M. Piesse
(See his book Traité des odeurs des et des
cosmetiques)

Azulene = $C_{10} H_{12} HO$

Bull Soc chim 1865 t III 291.

On Indian Oil of Geranium

By Oscar Jacobsen (Ann de Pharm ClVII 232)

The commercial oil had greenish yellow liquid smell of rose – acid reaction –

Below 210° obtained valeric

Between 210° + 240° a liquid was obtained, boiling at 232° – 233° "Geraniol" $C_{10}H_{18}O$

Geraniol is a colorless, strongly refracting liquid which does not solidify at –15° and does not act on polarized light. Its density is 0.8851 @ 15°, with alcohol and ether it mixes in all proportions. With calcium chloride, it forms the compound $CaCl_2 \; 2C_{10}H_{18}O$ Fused potash produces valeric acid – oxidised by a cold neutral solution of potassium permanganate yields valeric – with a hot solution of $K_2Cr_2O_4 + H_2SO_4$ principally a valeric and succinic in smaller amount Nitric Acid produces nitro benzene hydrocyanic, oxalic acid and a resin but no analogue of Camphoric acid. An unstable chloride $C_{10}H_{17}Cl$ by HCl (other compounds describe shortly that is mentioned) Geraniol like its isomeride, borneol, appear to function as a monatomic alcohol; the fact that geraniol and its derivatives are liquids and inactive towards polarized light, constitutes a physical diff. between them and Borneol. The hydro Geraniene $C_{10}H_{16}$ was obtained by distilling Geraniol with $ZnCl_2$ ~~to~~ $P_2O_5$

(Jour Chem Soc 1871 p 261)

Oil of Geranium

$C_{20}H_{18}O_2$ or $C_{10}H_{18}O$ new
Soluble in alcohol, Ether
Fused with $CaCl_2$ (sic) a yellow mass
with KOH gives valeritanic acid
$K_2Cr_2O_7 + H_2SO_4$ gives succinic
Acetin
Valerian

On the Essential oil of Orange
(Read at the meeting of the British Pharm conference) (Portugal)

It contains a large amt of $C_{10}H_{16}$ (b pt 180)
a small quantity $C_{10}H_{16}O$ (b pt 220°) and a soft
resin $C_{20}H_{30}O_3$ ('240°-250°) gave a portion $C_{40}H_{64}O_5$

Pharm Jour + Trans Oct 18 1873

Am Jour Pharm. XLV 545

On the Oxidation products of Essential Oil of Orange peel (Portugal)
By C. R. A. Wright and Chas H Piesse
(British An Rpt 1871 — Chem News XXIV 147)

Soubeiran + Capitaine also Dr Gladstone have shown that
the essential oil of orange peel consists principally of
a hydrocarbon Hesperidene $C_{10}H_{16}$.
They have simply fractionated and commenced
to work up the formula of this + similar
hydros

Jour Chem Soc 1871 p 1187

Oleum Cajuputi (Pharmacog)
Page 247 Chemical Composition

The researches of Schmidt (1860) & J. Gladstone (1872) have shown that Cajuput oil consists chiefly of "Bihydrate of Cajuputene or Cajuputol" $C_{10}H_{16}, H_2O$ which may be obtained from the crude oil by fractional distillation from anhydrous phosphoric acid cajuputene $C_{10}H_{16}$ passes over @ 160-165° C it has an agreeable odour of hyacinths. After the Cajuputene, Isocajuputene distills @ 177° and Paracajuputene @ 310°-316° both agreeing in composition with cajuputene

Like most essential oils having the formula $C_{10}H_{16}$ Crude cajuput oil is capable of forming the xlle compound $C_{10}H_{16}\,3H_2O$. This we have obtained by adding to the oil double its weight of dilute $H_2SO_4$ about Sp gr 1.09 and shaking the two liquids together occasionally during a few weeks

Various xlle compounds of Cajuputene with chlorine, bromine and iodine have also been obtained

(Histed in Pharm Jour Apr. 6, 1872 804)

Researches on Compounds belonging to the Campher group By J. Kachler (Ann Ch Ph CLIX 281)

Products resulting from Oxidation of Campher by $HNO_3$

---

Compounds belonging to the Campher by J. Kachler (Deut Chem Ges Ber V 165)

Campholic Acid $C_{10}H_{18}O_2$

Camphic Acid

$$2C_{10}H_{16}O + KOH = C_{10}H_{18}O + C_{10}H_{15}KO_2$$

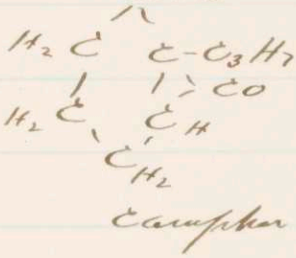
Campher Borneol Potassium Camphate

---

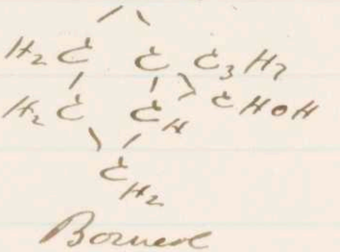
Compounds of the Campher Group By J. Kachler (Ann Chem Pharm CLXIV 75.)

Borneol - Camphrene or Phorone

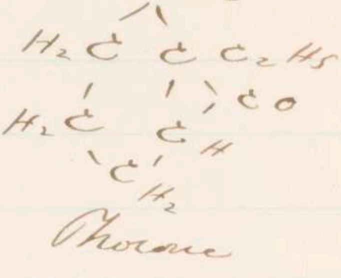
He gives the following formulae



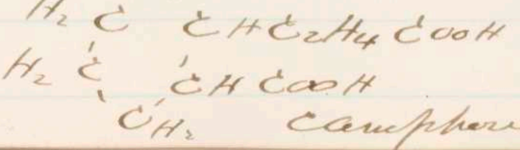
Campher



Borneol



Phorone



Camphoric Acid

On certain derivatives of Camphor
par Baubigny (Compt. rend LXIII 221 – 1866)
(Bull Soc Chim VI 480)

Camphre sodé
Ethylate of Camphor
Acetylure de "

---

On some derivatives of Camphor
par Baubigny (Bull Soc Chim X 210)

He speaks of the various ethers that he has formed &c

He speaks of heating Acetyl Chloride with Camphor 4 hours to 140° then 2 hours to 230° which gave .. nothing .. Its action on ethyl camphor was also negative

He then formed the $CO_2$ compounds.

---

Decomposition de l'acide Camphorique par la potasse en fusion

par MM. H. Hlasiwetz et Grabowski

(Ann fur Chem u Pharm CXLV 205 1868)

(Bull Soc Chim X 268)

---

Camphor & Camphoric Acid

par Weyl (Deut C G B. 1868 - 94) (Bull Soc Chim X 473)

He treated Camphoric Acid with HI and obtained $C_9H_{18}$.

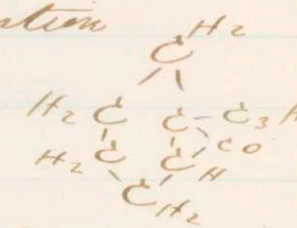
---

# Compound from Camphor

By J. Kachler

(ann Ch u Pharm CLXIX 168-205)

The author regards Camphor as a ketonic body having the composition and this view is supported by a general comparison of Acetone derivatives with those of Camphor



Moreover there is good grounds for believing that the group $C_3H_7$ exists as normal propyl but there is at present, no evidence to show what position this ($C_3H_7$) and the group CO occupy on the closed ring

## Artificial formation of Camphor.

By Oppenheim (Deut. Chem G. B. V 631)

By oxidizing Cymene obtained from oil of turpentine he obtained a white crystalline substance having the appearance, odor and composition of Camphor

## Synthesis of Camphors by Oxidation

By M Berthelot (Compt. rend LXXX 1625-1628)

In this paper the author claims priority for his part in researches on the subjects which M. Riban has more recently worked out in detail & refers to his memoires published in 1858-1870-71-74.

## Action of Benzyl Chloride on Laurel Camphor Part I Preliminary

By Donato Tommasi

(Jour. Chem Soc 1874 312)

He did not find out what he formed.

# Transformation of Laurel Camphor into Camphene and the inverse transformation

By J. Riban (Compt. rend lxxx 1381–1384)

Laurel camphor ($C_{10}H_{16}O$) was first changed into Borneo Camphor ($C_{10}H_{18}O$) by Baubigny's process and the latter substance was converted by heating with HCl into $C_{10}H_{16}HCl$ which possessed no rotatory power. By treatment with alcoholic potash this substance yeilded a solid crystallized Camphene melting @ 47° boiling @ 157°, and forming with HCl a monohydrochloride having the characteristics of the hydrochloride of Camphene

For the inverse transformation, levogyrating Camphene derived from French essence of turpentine, was oxidized by $K_2Cr_2O_7$ & dilute $H_2SO_4$ in quantity insufficient to saturate the oxides produced in the reaction. The mixture was heated for 11 hours with reflux of the hydrocarbon, when crystals of Camphor were found in the cooler parts of the apparatus, and purified by distillation in a stream of steam and by fractional distillation.

The rotatory power is in the opposite direction to that of ordinary Camphor, being $[a]_D = -13.7°$

This shows that to obtain a Camphor which deflects polarized light in the same direction as Laurel Camphor, we must begin with a deflecto gyrating Camphene derived from English essence of turpentine

From the Camphor thus synthetically produced the Author obtained Camphoric acid having rotatory power $[a]_D = -6.5°$ and melting @ 197°-198° the acid derived from Common Camphor melting according to the Authors Experiments @ 187°.

(Bull Soc Chim XXIV 17)

## Camphor a product of the action of $HNO_3$ on Amber by O. Doepping

(Ann Ch u. Pharm xlix)

On distilling Amber $HNO_3$ & evaporating the solution and redistilling and re evaporating several times small crystals of Succinic are obtained. Neutralizing the acid solution with KOH it becomes hot and when the acid odor has disappeared a powerful odor of Camphor is evolved.

If the filtrate when cooled be shaken with ether and poured into a flask and evaporating a crystalline residue is obtained resembling Camphor.

## Researches on the Camphor from Amber par Berthelot et Buignet (Compt rend l 606-1860)

The Camphor is obtained by distilling the powdered Amber with ¼ its weight of KOH & a great quantity of water. It is volatilized with the water. 1 kilo gave 3 grms Camphor $C_{10}H_{18}O$ isomer of Borneo

## Helenin & Inula Camphor

by Kallen (Deut Chem G.B. IX 156-167)

Inulol = $C_{10}H_{16}O$

Inulic anhydride = $C_{15}H_{20}O_2$

" acid $C_{15}H_{22}O_3$

---

## Sur un homologue du Camphre de Bornéo par M. H. Gal (Bull Soc Chim XI 305)

The camphor of Patchouli = $C_{30}H_{26}O_2$

---

## Camphor of Patchouli

Montgolfier (Compt. Rend Jan 8 '77)

This compound has the composition indicated by the formula $C_{30}H_{26}O_2$ and is therefore an isomer of the Camphor of Cubebs and belongs to the type of the hydrates derived from the Carbides ($C_{10}H_8$) or

## The isomeric Camphors & Borneols

by J de Montgolfier (Bull Soc Ch (2) XXV 17-19)

The borneol which the author obtained together with Camphic acid by the action of alcoholic potash on Camphor, has the rotatory power 9.6° for the line D, while Berthelot found 44° and Kachler 42° for the product prepared by Baubigny's process: but Riban found it only to be 2.6° and the author in one case 1.5° and in another in which a high temperature was used 29.5°.

Similar results are obtained by using Rosemary Camphor, from which it appears that the different Borneols are mixtures of an active and an inactive modification which readily change into each other.

# Le Camphre est il une Aldehyde

par M.M Tollens et Fittig

(Ann der Chem Ph (N.S) t III p 371 1864) (Bull Soc Chim II 457 1864)

Berthelot is of the opinion and the authors think without reason, that camphor is the aldehyde of Borneol.

They heated a mixture of Camphor, $H_2SO_4$ and $K_2Cr_2O_7$, for a long time without obtaining anything. The acid $HNO_3$ (conc) formed $C_{10}H_{16}O_4$ & $C_{10}H_{14}O_7$ but it did not form the acid $C_{10}H_{16}O_2$ by the direct oxidation of Camphor

The action of nascent H does not transform it to Borneol.

Camphor does not combine with Alkaline bisulphites.

The acid sulphurous forms with it a liquid combination

One does not succeed in reducing $C_{10}H_{16}O_4$ by the action of Iodine, phosphorus and water.

acid from Carbonic Oxide.

4. The Carbonyls can be converted into bibasic acids by fixation of 3 atoms of Oxygen E.g:- $\underset{\text{camphor}}{C_{10}H_{16}O} + O_3 = \underset{\text{camphoric acid}}{C_{10}H_{16}O_4}$

These bodies are thus clearly distinguished both from primary aldehydes, the oxidation of which results in the production of a single monobasic acid and from secondary aldehydes or Ketones which, when oxidized generally yield two distinct acids.

On a new class of Organic compounds the Carbonyls and on the true function of ordinary Camphor by M Berthelot

(Bull Soc Chim XXIII 146) (Compt rend LXXIX 1093)

The author proposes the recognition of a new class of Aldehydes, the Carbonyls comprising at present 3 members, namely: ordinary Camphor, oxide of Allylene or dimethylene-carbonyl and diphenylene-carbonyl, called by Fittig & Ostermayer, who discovered it diphenylene ketone

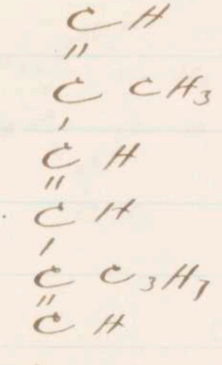
Suberone $C_7H_{12}O$ probably possesses a similar constitution

These bodies are characterized by the following general properties:-

1. They unite directly with hydrogen producing alcohols, from which the carbonyls may be regenerated by oxidation.
2. They are formed by substituting O for $H_2$ in certain unsaturated hydrocarbons.
3. By union with the elements of water they furnish Monobasic acids, the typical reaction being the production of Formic

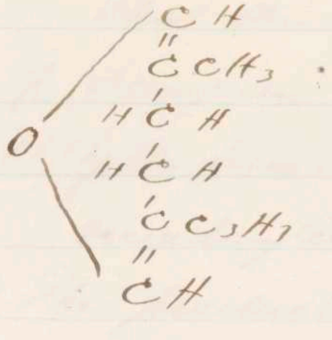
Watts deduces the following formulae

2^d Suppl. p 234.

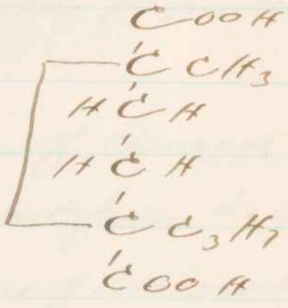


$$\begin{array}{l} CH \\ \| \\ C\ CH_3 \\ | \\ CH \\ \| \\ CH \\ | \\ C\ C_3H_7 \\ \| \\ CH \end{array}$$

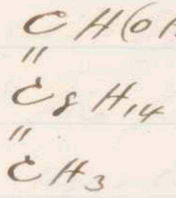
Cymene



Camphor

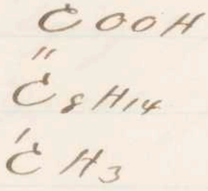


Camphoric acid



$$\begin{array}{l} CH(OH) \\ \| \\ C_8H_{14} \\ \| \\ CH_3 \end{array}$$

Borneol



$$\begin{array}{l} COOH \\ \| \\ C_8H_{14} \\ | \\ CH_3 \end{array}$$

Campholic acid

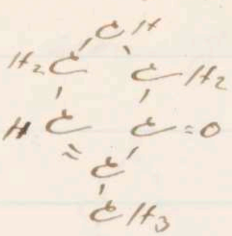
Theorie de la Serie Camphenique

par M. Berthelot (Bull Soc Chim XI 187

nothing very definite.

See also Bull Soc Chim VII (315)(317)(318)

# Camphor (New Hand Bk)



Kekulé

That this is the proper structure of camphor

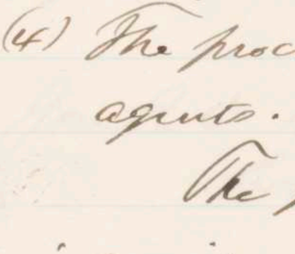
(1) By the formation of Borneol as a secondary Alcohol from Ketone

(2) The productions of monobasic campholic acid by the action of alkalies

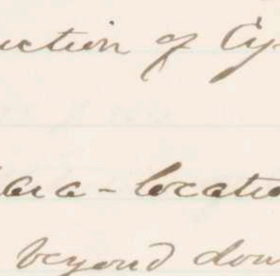
(3) The change of this into dibasic Camphoric acid by the use of oxidizing agents

(4) The production of Cymol by dehydrating agents.

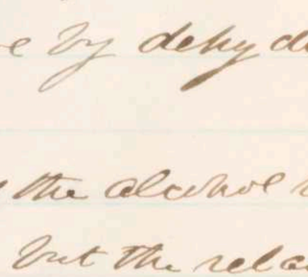
The para-location of the alcohol radicals is considered beyond doubt, but the relative position of O and the double bonding, both as regards one another & as regards the Alcoholic side chains is not yet established



Borneol



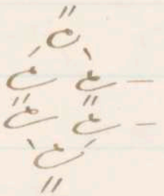
Campholic acid



Camphoric acid

Jour Reim Chem 1873 308

Kekule assumes that the 6 atoms of carbon in terpenes are bound together

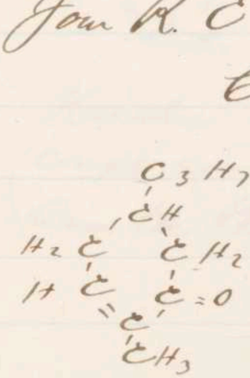


assigned by Schorlemmer

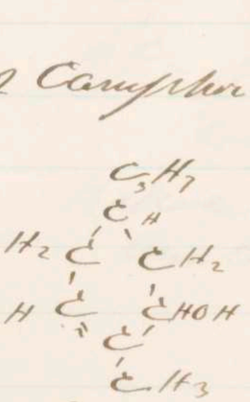
Formation of cymol by action of Iodine forming first di-iodine-addition products which by separation of 2 HI forms cymole

Jour R. C 1873 p 364

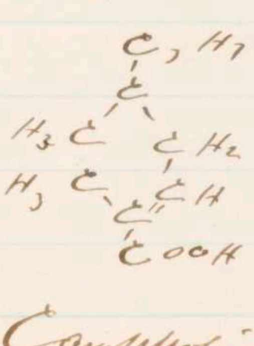
Constitution of Camphor



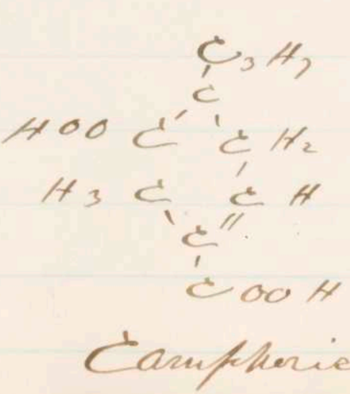
Camphor



Borneol



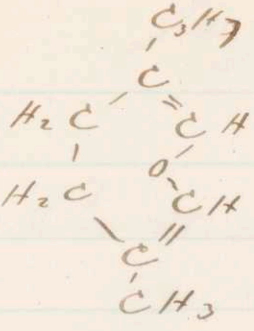
Campholic Acid



Camphoric Acid

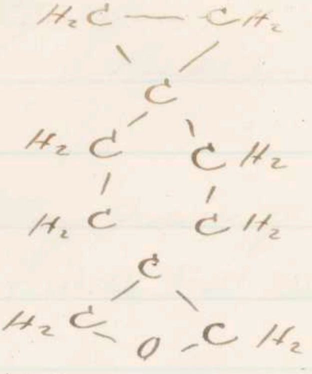
# Constitution of Camphor

(Neue Hand der Chem p 372)



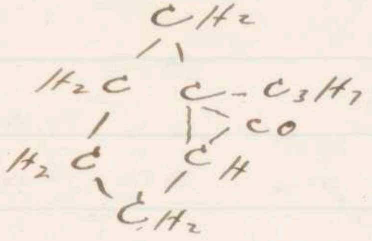
V Meyer

Ann Ch. Phys. (2) 65 p 329



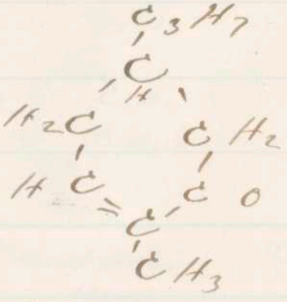
Hlasiwetz

Compt rend 43 p 394



Kachler

(Compt rend 43 p 394
Ann Ch Pharm 100 S 352)



Kekule

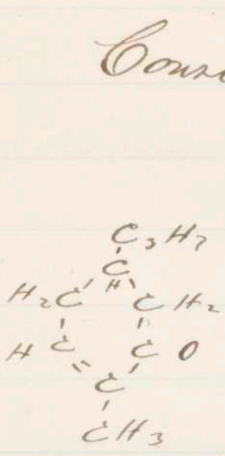
Ann Ch Pharm 110 S 33

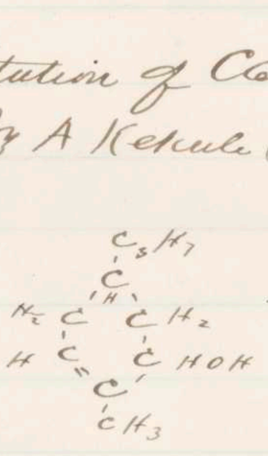
## Observations sur pouvoirs rotatoires du Camphre et de quelques autres Corps*
## par J. de Montgolfier

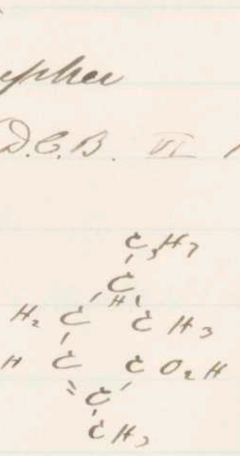
(Bull Soc Chim XXII 487)

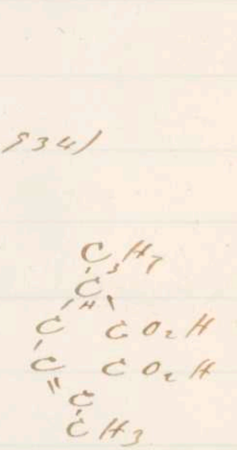
## On the Specific rotary power of Camphor
## by H Landolt (D. Ch G B. IX 914-917).

## Constitution of Camphor
## by A Kekule (D.C.B. VI 929-934)


Camphor


Borneol


Campholic acid


Camphoric acid

In assuming these formulae it must be stated that the positions of the radicals $CH_3$ & $C_3H_7$ are known, but those of the Oxygen & of the double linked carbon atoms must at present be left undecided.

Camphor is therefore a kind of Ketone and Borneol the corresponding secondary Alcohol.

Action of bromine on Camphor
By Perkin
(See Swarts Institute 1862 p 63)
Bull Soc Chim t VI p 135

Bromo-Camphocarbonic Acid
By J de Santos e Silva (Deut Ch G. B. VI 1092)

Mono bromo Camphor
By J M. Maisch
(Chem Centr. 1873. 437) (Jour Chem Soc 1874 582)

Ngai Camphor
By Sidney Plowman (Pharm J. Trans. 3) IV 712)
He regards it as isomeric with Bromo Camphor
Jour Chem Soc 1874 583

Action of some Monatomic Sodium Alcohols on Camphor
By R D Silva
(Bull Soc. Chim (2) XXIII 225)

Mono Bromo and Dibromo Camphor
By J de Montgolfier
(Bull Soc Chim (2) XXIII 553-556)

Monobrom Camphor $C_{10}H_{15}BrO$

Lloyd Arch Pharm (3) 7-452 Also American
Jour Pharm (4) 47-165 (1875)

Gault Arch Pharm (3)-47-165

Am Jour Pharm Chem (4) 20-435

Pharm Jour Trans (3) Oct 1876-321

Sur les dérivés bromés du Camphre
par M Swarts
(See Perkin Bul Soc Chim t VI p 135)
Zeit für Chem t 11 p 728 et
Institut no 1705 p 287
Bull Soc Chim t VII 498

Bromide of Camphor — Laurent (J. Pr. Chem. 20-498)
(Rev Scient 11-233) (J Pr Chem 28-333) (Compt rend — 10-532)
Claus (J. Pr. Chem. 25-260)

Preparation — Camphor is dissolved in cold bromine and the xtls 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) (Gmelin Eng. Ed. Vol XIV

Camphor Bromide

by A Laurent (Revue scient. et industrielle tov. 1842 S 263)

Ann Chem & Pharm 48-251

Camphorschwefelsaüre und ihre Salze

Ph Walter (Annal de chim. et de Phys t IX p177)

Ann Chem & Pharm 48-248

Campher bromür

Darstellung, Eigenschaften und Zusammensetzung

Laurent Ann Chem & Pharm XLVIII 251

On monobromated Camphor

By John M. Maisch

Am Jour chem 1872-337

Camphic Acid

By J de Montgolfier (Bull Soc Chim (2) XXV 13-17)

Sur le Camphre monobromé et dibromé par

M. J. de Montgolfier

Bull Soc Chim XXIII 153

$C_{10}H_{16}OBr_2$

The Swarts (Instit 1862-63) prepared this compound by mixing a saturated solution of camphor in chloroform with an equivalent quantity of bromine; the compound then partly separates after a few hours as a red powder and the remainder is deposited from the mother liquid in beautiful orange colored prisms. The bromide $C_{10}H_{16}OBr_2$ is resolved by heating to 100° in sealed tubes (Swarts) or by distillation (Perkin Chem Soc Jour (2) III 22) into $HBr + C_{10}H_{15}OBr$.

This compound may also be produced directly by heating bromine and camphor in sealed tubes for 3 hours in the water bath (Swarts)

It ×llizes in transparent prisms very much like those of ordinary sodium sulphate, having a faint odor of camphor and a turpentine like taste, dissolves easily in alcohol and ether; melts at about 76° & solidifies at 74° or when left at rest, sometimes not till cooled to 54° (Perkin) to 36° (Swarts) boils at 274° (Perkin; Swarts)

It is not decomposed by alcoholic potash (Swarts). Heated with alcoholic ammonia to 180°, it decomposes to a slight extent, with formation of ammonium bromide and a peculiar base (Perkin) - It unites with HBr forming an oily compound 6($C_{10}H_{15}BrO\ HBr$)

This latter compound smells like turpentine has a bitter taste, is insoluble in water and less soluble in alcohol than camphor or the monobrominated compound.

It melts at 114.5° becomes liquid even under boiling water and distills with partial decomposition.

(Swarts Zeit f Chem. (2) II 628)

Bromide of Camphor $C_{20}H_{16}O_2Br$ is a xelle body produced by the action of Br in contact with camphor

On contact with the air it is promptly liquified disengaging Br and depositing camphor

On distillation it breaks up into Br. Camphor and at the same time a little H Br. and there is formed a little quantity of a brominated oil

(Gerhardt V. III p 696 § 1945)

Bromo Camphoric Anhydride $C_{10}H_{13}BrO_3$

When 1 mol. Br. is heated with 1 mol. Camphoric Acid in presence of water to 170° and the mixture is left to cool, long prismatic x elle are formed, probably having the composition $C_{10}H_{16}O_4Br_2$ are obtained, when exposed to the air are slowly resolved into Br. and Camphoric acid.

In the absence of water $C_{10}H_{13}BrO_3$ is formed

$C_{10}H_{16}O_4 + Br_2 = C_{10}H_{13}BrO_3 + HBr + H_2O$

1 grm Camphoric Anhydride and 18 grms dry Br. in a sealed tube, heated to 130°-140° for 3 hours

(Watts' Dictionary 2d. Supl. p 236)

Recherches sur l'action que la potasse exerce sur le Camphre

Par M. L. Delalande

(Ann de Chim & Phys. (3) 1-120)

Note sur un Nouvel Acide dérivé du Camphogène

Par M. L. Delalande

(Ann. de. Chim et Phys. (3) 1-368)

Researches on the Turpentine Oils and Camphors

By V. Meyer and F. V. Spitzer

No. 1 (Deut Chem. Ges. Ber. IX 877-880)

Pfaundler by acting on Camphor with $PCl_5$ obtained $C_{10}H_{15}Cl$ which they think there is reason to think is a chlorine substitution product of terpene

$$C_{10}H_{16}O + PCl_5 = POCl_5 + HCl + C_{10}H_{15}Cl$$

its relation is represented thus

| $C_{10}H_{14}$ | $C_{10}H_{14}\left\|\begin{matrix}H\\H\end{matrix}\right.$ | $C_{10}H_{14}\left\|\begin{matrix}H\\Cl\end{matrix}\right.$ |
|---|---|---|
| cymene | Terpene | monochloroterpene<br>Pfaundler's chloride |

The replacement of chlorine by Ethyl is very easy

They found Ethyl terpene $C_{16}H_{15}C_2H_5$ "altho substitution products of T cannot be found in the direct way by the replacement of H by a halogen element &c"

Sur la formation de l'acide Campholique
par M. H. Baubigny
(See Malin Ann der Chem & Pharm t CXIV p 201)

$$C_{10}H_{16}O + \left.\begin{matrix}C_{10}H_{15}\\K\end{matrix}\right/O = \left.\begin{matrix}C_{10}H_{17}O\\K\end{matrix}\right/O = C_{10}H_{14}$$

Bull Soc Chem X 110

Etude sur le camphre par M. Malin
(ann fur chem & Pharm + CXIV 201)

Malin thinks Campholique de Na or K is formed by the direct action of sodium &c while Baubigny thinks there are 2 steps

$$3C_{10}H_{16}O + 2Na = 2C_{10}H_{16}NaO + C_{10}H_{18}O$$

Bull Soc Chem X 150

Camphic Acid
By Berthelot (Bull. Soc Chim (2) XVII 390)

Constitution of Camphoric Acid

By Felix Wreden (Deut Chem Ges Ber V 764)

He regards it as one of the dimethyl Benzenes

On Camphoric Acid

By F Wreden (Deut Chem Ges Ber V 1106)

On Optically Inactive Camphoric Acid

By F Wreden (Deut Chem Ges Ber VI 565)

On the action of Sodium amalgam on Dinitroheptylic Acid

By H. A. Kullhem (Ann Chem Pharm CLXVII 45-48)

The author has described under the name dinitro heptylic Acid, a body which is obtained by boiling Camphor for a long time with $HNO_3$

By the action of sodium amalgam on the alcoholic solution of the body, a corresponding mononitro heptylic acid $C_6H_{11}(NO_2)O_2$ is formed which furnished a sodium salt $[C_6H_{10}(NO_2)NaO_2$ $3H_2O$ a barium salt $[C_6H_{10}(NO_2)O_2]_2Ba\,3H_2O$ and a silver salt $C_{11}H_{10}(NO_2)AgO_2$ all of which are crystallizable

Camphor Acids

By J de Montgolfier (Bull Soc Chim (2) XVIII 114)

He confirms Berthelot statements and gives rotatory power of the diff acids

Basicity of Camphoric acid & mesocamphoric acid

By F Wreden (Zeit f. Chem (2) VII 419-421)

Camphoric Acid $C_8H_{14}(CO_2H)_2$

Mesocamphoric acid $C_{10}H_{16}O_4$

On Amido Camphoric Acid

By F Wreden (Zeit f Chem (2) Vii 418-419)

Amido Camphoric anhydride $C_{10}H_{13}(NH_2)O_3$

" " Acid = $C_{10}H_{15}(NH_2)O_4 + H_2O$

Oxy Camphoric Anhydride $C_8H_{13}(OH)C_2O_3$

Jour Chem Soc 1872 146-147

On Optically Inactive Camphoric Acid

By F Wreden (Deut Chem Ges Ber VI 565

On some Derivatives of Camphoric Acid

By F Wreden (Zeit. f. Chem (2) VII 97)

Bromo Camphoric acid $C_{10}H_{16}O_4 + Br_2 = C_{10}H_{13}BrO_3 + HBr + H_2O$

Oxycamphoric Acid

Camphoric acid and hydriodic Acid

Jour Chem. Soc. 1871 p 549

On Camphoric Acid

F. Wreden (Deut Chem Ges Ber IV 570-571

This acid is best prepaired by dissolving 150 grms of Camphor in 2 liters of $HNO_3$ (Sp gr 1.27) and heating the solution in a warm bath, till the gases which escape are only slightly colored From 1.5 Kilo of camphor 725-805 grms of pure acid were obtained

Camphoric Acid

By F Wreden

(Ann Chem Pharm CLXIII 323-342

Action d'acide Azotique sur le Camphre les huiles essentielles et les resines par M H Schwanert (Ann de Chem und Pharm lii 77(1863))
(Bull Soc Chim t 2 p56

He finds in addition to Camphoric Acid a tribasic acid already described by Laurent (Ann de Chim et de Phys (2) (iii p20) & by Blumenan (Ann. der Chem und Pharm t lxvii p119) which he called Camphoresinique and which can not only be formed from Camphor but also from the essential oils and the resins ($C_{10}H_{14}O_7$)

He also found as some of the products Acetic Acid, Acetone & a new acid plffocamporesinique ($C_{10}H_4O_4$) the acid metacamphoresinique.

Camphol $C_{10}H_{16}O$ according to Macfarlane gives equally the acid Camphoresinique (Ann der Chem und Pharm t XXXI p72)

On cautiously oxidizing one finds a small amt. of insolinique acid (memoire de Hoffman Ann der chem und Pharm t XCVII p197)

The acide camphoresinique derived from terebenthene gives by dry distillation the same products as that from Camphor.

(Bull Soc Chim t II p56)

Remarks sur le memoire de M. Hugo Schwanert relatif á l'action de l ácide azotique sur le camphre les huiles essentielles et les resines par M. Ferdinand Monoyer
(see Bull Soc chim t X p 529 (p 578 (Nov. 1863)) (Bull Soc Chim t 1 p 5 (1864 p 52)) (B.S.Ch. t II p 56) (Bull S.Ch. 1864 t II)

---

Sur les Acides terephtalique et camphoresinique par M. Hugo Schwanert (ann Chem u Pharm t CXXXII p 257 1864)

Bull Soc Chim t IV 143

Sur les produits d'oxydation du Camphre par J Kachler (Deut Chem Ges t VII p 1728)
He says that the camphoresinique or Camphoresinique is only a mixture of acide Camphorique et other acid camphoronique

Bull Soc Chim XXIV 315

Sur les produits de l'action du perchlorure de phosphore sur le camphre
par W L Pfaundler
(ann der chim u Pharm t CXV p 29 1860)

Rept de Chim III Wurtz

On the action of hydrated hypochlorous acid on oil of turpentine and camphor

By C Gilbert Wheeler (Silliman's jour. XLV 1868 (481))
(Compt. rend. LXV-1046 (1867)) (Bull Soc chim X 288)

| | | |
|---|---|---|
| $C_{10}H_{20}$ | $C_{10}H_{16}$ | $C_{10}H_{14}$ |
| Diamylene | Oil of Turpentine | Cymene |
| $C_{10}H_{10}$ | this is to that | $C_{10}H_{20}O_2$ |
| turpentine | so is | Capric acid |
| $C_2H_2$ | this is to that | $C_2H_4O_2$ |
| Acetylene | | Acetic acid |

If oil of turpentine (boiling point 159°) is added to a dilute aqueous solution of (ClOH) and shaken it at once becomes yellow, thick and heavy, and settles to the bottom of the vessel. Were conc. (ClOH) used the mixture would rapidly become heated and other products form than that sought, or under the most favorable circumstances, but very little of the new body would be obtained. The oil should be very slowly added, not allowing an increase of temperature and ceasing when on adding a fresh portion but slight change in color is produced or before the characteristic odor of the hypochlorous acid can no longer be readily recognized. The heavy oil is separated from the aqueous solution by filtration. The latter contains chloride of mercury, originating from the oxyd of that metal employed in the preparation of the (ClOH) also an organic substance, which on evaporating the solution, separated as an oil with more or less decomposition. This is the most interesting of the products of the reaction, and in order to obtain it pure from the solution it is necessary to avoid the application of a high temperature. To effect this a quantity of common salt is added till the solution is saturated, which is then shaken with small portions of ether. The ethereal extracts are united and shaken with a concentrated solution of $NH_4Cl$ which takes up the $HgCl_2$ the ether is then removed with a pipette and $CaCl_2$ is added to dry it. The filtrate distilled

Analysis gave $C_{10}H_{18}Cl_2O_3$

$$C_{10}H_{16} + 2(ClOH) = C_{10}\begin{matrix}H_{16}\\H_2\end{matrix}\Big\}\begin{matrix}Cl_2\\O_2\end{matrix}$$

The heavy oil he supposes to be a mixture.

On treating Oil of Turpentine with Chloric Acid a finely xelle body having the formular $C_{10}H_{18}Cl_2O_4$. I allow camphor to remain in a weak solution of ClOH for 8 days and thereupon 1 day in a concentrated solution. The products of the reaction a white indistinctly xelle solid was washed with water till no acid remained dissolved in alcohol and again prec. by $H_2O$ and pressed between filter papers

Anal. = $C_{20}H_{27}Cl_5O_3$

$$2(C_{10}H_{60}O) + 5\,ClOH = C_{20}H_{27}Cl_5O_2 + 5H_2O$$

The result is a diff and a much simpler one when camphor is immediately brought in contact with conc. hypochlorous acid it is at once transformed into a thick fluid, becomes warm and after some time again hardens to a xelle solid. This body is the chief product of the reaction, though a very small quantity of another organic substance is found in the solution. The xelle substance is dissolved in alcohol pure with $H_2O$ and thoroughly washed with cold water.

Anal. = $C_{10}H_{15}ClO$

$$C_{10}H_{16}O + ClHO = C_{10}H_{15}ClO + H_2O$$

Mono chlorinated camphor has not heretofore been obtained, though Claus has obtained products containing 4 & 6 atoms of Cl by the action of clorine on camphor dissolved in $PCl_3$ (Ann Chem Phar CXXXVI 323)(X/IX 301)

Mono chlorinated camphor is a white xtlle solid soluble in ether and $C_2H_6O$ insoluble in water Its solution in concentrated alcohol on evaporation remains for a long time of a syrupy consistency, from dilute alcohol it crystalized more readily and in very small imperfectly formed needles. It melts at 95° C. is decomposed with liberation of HCl @ 200° C. and another substance having an agreeable odor is sublimed over. The taste and smell of this body are similar to ordinary camphor. It is acted on with difficulty by $HNO_3$ even when boiling; by $H_2SO_4$ it is dissolved at ordinary temperature and again prec. on diluting with $H_2O$. With $AgNO_3$ its alcoholic solution yields AgCl. Heated to 120° with conc. solution of $NH_3$. $NH_4Cl$ is formed and a derivative soluble in water is treated with $PCl_5$ there remained, after the removal of the Oxychloride of Phosphorus formed, a substance which blackened on attempting to distill a portion. Its distillation was not proceeded with but it was washed with water, dissolved in $C_2H_6O$ and again prec by $H_2O$ he merely guesses what it is or may be. A considerable quantity of $C_{10}H_{15}ClO$ was treated with a solution of potash in alcohol for 6 to 8 hours. The whole thereby became brownish red and a large quantity of $KCl$ was formed On dilution with twice its volume of water a voluminous ppt (A) was obtained. The filtrate gave no ppt on farther addition of water, and contained the potash salt of a new organic acid. The latter was isolated on addition of $H_2SO_4$ then dissolved in ether filtered and dried

Anal. = $C_{10}H_{14}O_3$ or $(C_9H_{13}O)COOH$

The ppt A dissolved in alcohol yielded on evaporation beautiful xtals needles

Anal = $C_{10}H_{16}O_2$

$$C_{10}H_{15}ClO + KOH = C_{10}H_{16}O_2 + KCl$$

Oxy camphor xalls in small white needles is very easily soluble in Alcohol, insoluble in water, melts at 137° may be sublimed without change, volatilizes somewhat even in boiling and resembles ordinary camphor in taste and and odor. It is isomeric with Camphinic Acid

$2(C_{10}H_{16}O) + KOH = C_{10}H_{18}O + C_{10}H_{15}KO_2$

Oil of Turpentine = camphene $C_{10}H_{16}$

Camphor = Oxy camphene $C_{10}H_{16}O$

Oxy Camphor = Dioxy Camphene $C_{10}H_{16}O_2 = C_{10}\left(\begin{smallmatrix}H_{15}\\ OH\end{smallmatrix}O\right.$

Camphinic Acid $C_{10}H_{16}O_2 = (C_9H_{15})COOH$

Oxy Camphinic Acid $C_{10}H_{16}O_3 = (C_9H_{15}O)COOH$
(hydro phornylic acid)

Phornylic Acid $C_{10}H_{14}O_3 = (C_9H_{13}O)COOH$

Monochlorinated Camphor $C_{10}H_{15}ClO$

Terpen di Chlohydrine $C_{10}H_{18}Cl_2O_2$

## On an Aromatic Glycollic Acid
### by W. Dittmar & Aug. Kekulé

Deut. Chem Ges. Ber iii 894

They formed their toluic Acid from Cymene "this hydrocarbon when slowly oxidized yeilds only one of the 3 known toluic Acids and by a more powerful oxidation terephthalic acid."

"They Cymene employed is prepared from Camphor by means of phosphorus sulphide and oxidized by long boiling with $HNO_3$, whereby toluic & nitrotoluic acids are formed and generally a little terephthalic acid. As a considerable quantity of Acetic acid is produced at the same time it may be inferred that this Cymene contains normal propyl and not isopropyl..."

## The oxidation of Camphor Cymene in the Animal organism by Nencki & Ziegler

(Deut C. G. B. V - 745 - 751)

It was oxidized to terephthalic acid & a small amount of toluic acid

# On certain Cymene Derivatives

by F. Landolph (Deut Chem Ges Ber V 267)

Cymene prepared by the action of Phosphorus pentasulphide on Camphor was treated with bromine drop by drop, a little iodine being added, and the whole well cooled. After distillation with water and fractionating monobrom cymene $C_6H_3Br\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$ was obtained as a liquid of weak Cymene-like odor boiling at 233°-235° & of Sp. Gr. 1.269 @ 17.5° The bromine in the body is retained with great force, as sodium and methyl iodide, as well as sodium & Carbonic oxide failed to cause its elimination. This appears to be connected with the position of the bromine atom in the molecule, haloid atoms occupying the para place being readily replaceable, but only with difficulty or not at all, when occupying either of the other positions .... The higher boiling products from Camphor and Phosphorus penta-sulphide are of a phenolic character; while $ZnCl_2$ forms Laurene $C_{11}H_{16}$ (Fittig Köbrich, & Jilke)

Nouveau mode de preparation du Cymene du camphre

par MM Longuinine et Lippmann

They use $PCl_5$

Bull Soc Chim 1867 t VII - 374

Sur la decomposition du champhre par le $ZnCl_2$ en fusion

by Fittig Kobrich et Jilke

Formation of Cymene and other hydrocarbons

(Ann chem et Pharm CXLV 129 1868 and Bull Soc Chim XI 78 1869)

( Lippmann et Longuinine (Bull Soc Chim VII 374 1867) Baubigny (Bul Soc Chim VI(6) 480 1866)

Sulphur derivatives of Cymene
By A P Flesch (Deut. Chem. G. B. VI 478-480)

Oxy Cymene + Thio Cymene
By F. Rodeburg (Deut Chem Ges Ber VI 669-670)
Oxy cymene (cymic phenol)

Derivatives of Cymene
By F Landolph (Deut chem Ges Ber VI 936 938

Identity of the Cymenes from Camphor Ptychotis oil & Thymol
By F Fittica (Deut Chem Ges Ber VI 938-943

Oxy Cymene from Camphor
By A Fleischer & A Kekule (Deut Chem Ges Ber VI 934-936)

Cymene
By F Beilstein & A Kupffer (Deut Ch Ges Ber VI 1181-1183)

Oil of Wormwood
By F Beilstein & A Kupffer (Deut Chem Ges Ber VI 1183/184)

## On the production of Cymene from Hydrate of Turpentine

By P. Barbier (Compt rend lxxiv$^{194}$)

The Author remarking that camphor with phosphoric chloride yields chlorinated compounds which furnish Cymene by distillation, applies a similar process to turpentine.

Crystallized terpin $C_{10}H_{20}O_2 + H_2O$ treated with two atoms of bromine, gives a yellowish semi fluid body apparently a brominated derivate from terpilene bromhydrate, decomposed on distillation into bromhydrate acid and cymene The latter, purified by caustic potash, is a mobile colorless liquid having a penetrating odor of lemons, a boiling point of 176°-179° and a Spgr at 15° of .864

Fuming $HNO_3$ dissolves it with formation of an insoluble nitrated body; warm $H_2SO_4$ gives with it a conjugated sulpho acid; bromine gives brominated compounds, analysis = 89.54 C ; 10.51 H

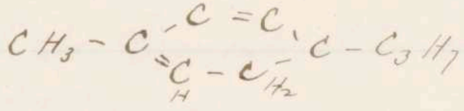
Cymene from Oil of Turpentine

By A Oppenheim (Deut. Chem Ges Ber V 94-100)

When finely powdered terpin $C_{10}H_{18}(OH_2)$ is mixed with bromine and the mixture heated to 50° or allowed to stand at a common temp. the dibromide $C_{10}H_{16}Br_2$ is formed, a colorless heavy oil which decomposes when heated, with loss of hydrobromic acid. The same dibromide is obtained by adding bromine to oil of turpentine or oil of lemons at a low temp. When this compound is heated with Aniline it loses two molecules of HBr and the hydrocarbon $C_{10}H_{14}$ is formed which boil at 175.5°-178.5° and appears to be identical with a cymene or methyl propyl benzene from cumin oil. This is the more probable as both cymene and oil of turpentine occur as essential oils and yield on oxidation terephthalic acid. Oil of turpentine is therefore cymene hydride and belongs to the additive compounds of the aromatic group.

Baeyer has pointed out that in these

additive compounds the partial separation of the carbon atoms of the benzene ring most readily takes place where Alcohol radicals have entered. The constitution of oil of turpentine is therefore probable the following



$$CH_3-C\begin{matrix}\diagup C=C\diagdown \\ \diagdown \underset{H}{C}-C_{H_2}\diagup\end{matrix}C-C_3H_7$$

## Cymene from Turpentine and from Lemon Oil

By A Oppenheim (Deut. Chem Ges Ber V 628-631)

He comes to the conclusion that the Cymenes are identical and that terpene and citrene consist of the same Cymene combined with two atoms of hydrogen differing from each other only in the relative position of the latter.

## New conversion of Turpentine into Cymene

By A Kekule (Deut Chem G B VI 437)

He treats turpentine with sodium in flask with inverted condenser and obtains considerable amt of a colophene like polymeride of turpentine, with a certain amt of Cymene 50 grms turpentine and 23 of iodine gave 10 grms Cymene

## Determination of the Specific Gravity of Cymene from various sorces; also Cymene and Benzene

By G. Pisati and E. Paternò

(Gaz. Chim. Ital. iii 551-578 Jour. Chem. Soc. 1874 686)

## Identity of the Cymenes obtained from Camphor and from Oil of Turpentine

By E. Paternò

(Gaz. Chim. Ital. iv 113-119 Jour. Chem. Soc. 1874 687)

He prepared Cymene from Camphor by mixing 100 grms. red phosphorus 265 g flowers of sulphur and 780 g Camphor and heating over a gas flame. Under these circumstances the two reactions go on together without violence and by the time the whole is fused the reaction is so far complete that it only remains to boil the mixture for a few hours as long as $H_2S$ escapes. The Cymene is then distilled, heated with KOH, washed with water, dried over calcium chloride and finally distilled over sodium and rectified. By this method 3 Kilos of Camphor yield in two days 1 Kilo of Cymene boiling (@ 175°-178° uncor.)

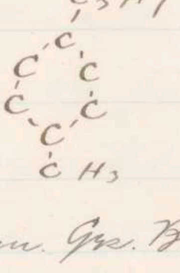
Cymene from Turpentine be obtained by the action of $H_2SO_4$ on turpentine

On the Cymenes produced synthetically from Normal Propyl Bromide and crystallizable

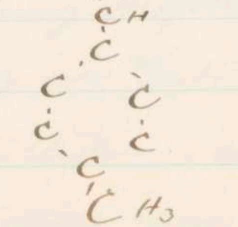
By F Fittica

(Deut. Chem. Ges. Ber. VII 323 - 325)

The identity of the products thus obtained from the artificial Cymene with those from Camphor, ptychotis, and thymol cymenes show therefore that the three latter are normal propyl methyl benzenes, in which as already shown the methyl and propyl occupy the para position



Fittig (Deut. Chem. Ges. Ber. (7) 651) concludes that Cymol from turpentine oil contains iso propyl.



## Observations on Cymene

By J. Guareschi (Jour. Chem. Soc. 1874-685)
(Gazzetta chimica Italiana iii 545_550)

This paper contains a discription of Experiments relating to the conversion of cymene into oil of turpentine. They are not very conclusive

## Cymene

By F. Fittica (Ann Chem. clxx ii 303)

The Cymene was prepaired by heating together four (4) parts of thymol and one (1) part of phosphorus pentasulphide in fine powder in a flask with an inverted condenser; much $H_2S$ was evolved and Thiocymene (b. p. 230°) was simultaneously formed; the hydrocarbon isolated from this by fractioning treated with soda ley and repeated distillation over sodium boiled at 175° (Hg column wholly in the vapor) and dissolved in strong $H_2SO_4$, without evolving sulphurous acid; this serves as a good test for purity.

Oil from Ptychotis agowan gave cymene

Camphor cymene was prepaired by acting

on Camphor with phosphoric anhydride in quantity sufficient to form (theoretically) Cymene and Meta phosphoric acid; the yield is thus 60 - 80 %, whereas Potts' method with pentasulphide of phosphorus gives only 25 to 30 %; after purification as before, this specimen boiled at 175° (mercury column wholly in the vapor) Beilstein and Kupffer formed the same

These three hydrocarbons were oxidized by dropping into gently boiling red nitric acid (Sp G 1,5) in each case nitro toluic acid melting @ 189° was produced: hence all these are methyl propyl benzenes. Normal propyl methyl benzene was prepaired by acting with sodium on recrystalized bromotoluene melting at 29°, together with pure normal propyl bromide dissolved in ether free from water and alcohol. It boiled at 175° to 176°; gave paratoluic acid melting at 177° and terephthalic acid, on oxidation by nitric (acid) and chromic acids respectively; with HNO it also yielded a fluid & a solid nitro cymene

# Synthesis of Aromatic Monamines by the moving about of atoms in a molecule

By A. W. Hoffmann

(Deut Chem Ges Ber V 704)