OXIDATION PRODUCTS

of

β-PINENE.

By

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The oils obtained by distilling the natural exudations of pine and fir trees were known to the ancients as cedar oils. Pliny mentions oil of turpentine (cedar oil) in his Natural History (Bk. XV. chap. 7. ; Pliny's Natural History in Bohn's Classical Library, vol. III. p. 288.). Herodotus, in his account of the Egyptian practice of embalming the dead, gives a description of the use of a crude oil of turpentine (Hist. Bk. 2. chap. LXXXVII. ; Lacher's Notes on Herodotus, London. 1844. vol. I. p. 312.). This oil is said to have been obtained from oleoresin by boiling with water in an open earthern pot, and skimming off the crude oil as it rose to the surface of the water. The very early examples of fine Chinese lacquer work lead to the conclusion that some kind of oil of turpentine was distilled and used by the Chinese in ancient times. It would thus appear that oil of turpentine was the first of all the essential oils to find commercial use and technical application.

Pure oil of turpentine may be defined as the oil obtained by distilling turpentine with water, or with steam which has not been superheated. The definition for oil of turpentine, proposed by M.Vezes, professor at the University of Bordeaux, and adopted by the International Congress for the Suppression of Adulterations, Paris, 1907., contains the following:-

" Turpentine oil is exclusively the product of the
" distillation (with water or non-superheated steam)
" of the resinous exudations of the several species of
" PINUS.
" Turpentine oil should not contain mineral oils or
" other products not resulting from the distillation
" of turpentine with water vapour. It may, however,
" contain small amounts of resin oil and colophony
" which result from the process of distillation (so
" called normal adulterants)"

Oil of turpentine (or pinene)is very widely distributed and can be found optically inactive, as well as in both optically active modifications. This oil is scarcely ever found in flowers, but nearly always occurs in the oils obtained from leaves, barks, and woods. Whilst the principal scource of pinene is the oleoresins of the several species of PINUS it has also been found in the oils of cypress, nutmeg, camphor, coriander, carrot, fennel, rosemary, lemon, rue, parsley, peppermint, and eucalyptus.

Oil of turpentine is a colourless mobile liquid, which undergoes autoxidation on standing in contact with the air, and partly resinifies. The boiling points of nearly all oils of turpentine lie within the range I54°-I75° C.

The earliest observations made on oil of turpentine concerned its behaviour at low temperatures. In I794

Margueron (Journ. de Chim. et de Phys. I794. 2. I78 ; Crell's Annalen, I795. 2. I95, 3I0, and 430.) states that the oil when cooled to -28°C. solidified to a crystalline mass. During an attempt to prepare a "Liquor Antarthriticus Pottii" in which preparation hydrogen chloride is passed into oil of turpentine, the apothecary Kindt, of Eutin, obtained a solid mass of crystals (Trommsdorff's Journ. der Pharm. I803. II. pt. 2. I32.). This substance he and others considered to be "artificial camphor". The same compound was also examined by Gehlen (Gehlen's Allgem. Journ. fur die Chemie, I8I9. 6. 462-469.) and Dumas (Annal. de Chim. et Phys. I833. 2nd. Series, 52. 400.).

Whilst carrying out a study on French oil of turpentine, Biot first observed its rotatory power (Memoires de l'Acad. des Sc. I8I7. p. I3.), and he continued his researches into the other essential oils. French oil of turpentine was shown to be laevorotatory, and a number of years later American oil of turpentine was shown to be dextrorotatory. The rotation of the latter oil was confirmed by Pereira and Gribourt, and Pereira introduced the terms "laevogyrate" and "dextrogyrate" (Pharm. Journ. I854. 5. 70.)

The first elementary analysis of oil of turpentine was made by Houtton-Labilliardiere (Journ. de Pharm. I8I8. 4. 5.) who found the ratio of carbon to hydrogen to be 5 to 8. These results were confirmed by later workers, and Dumas pointed out that essence of lemon had the same composition (Ann. 1833. 6. 245.). It has already been mentioned that French oil of turpentine was found to be laevorotatory, and the American variety to be dextrorotatory. Berthelot (Compt. rend. 1862. 55. 496 and 544.) named the laevorotatory hydrocarbon "terebentene" and the dextrorotatory one "australene". Wallach (Ann. 1885. 227. 300. ; 1907. 356. 227.) suggested the name α-pinene for both modifications, and differentiated the two as l-α-pinene and d-α-pinene.

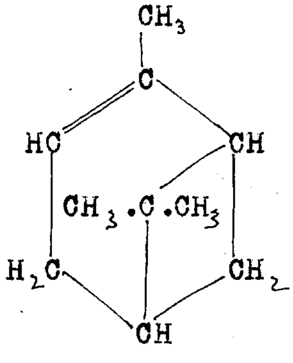
The chemistry of the terpenes and especially of pinene received a new impetus when Tilden and Shenstone prepared the nitroscchlorides (J.C.S. 1877. P. 554.) and from a study of these compounds Tilden classified the then known terpenes into three groups (J.C.S. Trans. 1878. 33. 84.). Pinene nitrosochloride has been largely used as a means of preparing pure α-pinene (Wallach, Ann. 1888. 245. 251. ; 1889. 253. 251. : Baeyer, Ber. 1895. 28,648. : Kremers, Pharm. Rundsh. (New York.) 1895. 13. 135. : Henderson and Gray, J.C.S. 1903. 83. 1299. : Tilden, J.C.S. 1904. 85. 759.).

Pure oil of turpentine from French and American turpentines may be regarded as practically pure α-pinene. It has been found that oil of turpentine from these sources, however, does contain a small amount of another terpene. This fact was first recognised by Baeyer (Ber. 1896. 29. 25.) who carried out the oxidation of French oil of turpentine with concentrated permanganate solution. Among the products he found the sparingly soluble sodium salt of an acid (m.p. I25°C.) isomeric with pinonic acid, $C_{10}H_{16}O_3$. This acid he named nopinic acid, and stated that in all probability it was formed from a terpene, named by him " nopinene ", present in the oil of turpentine. Semmler during his investigations named the same hydrocarbon " pseudopinene " (Ber. I900. 33. I458.). It should be noted that, although this hydrocarbon is present in only small amounts in the oils of turpentine, it is, nevertheless, readily identified as the sodium salt of the acid it gives on oxidation with permanganate, since this salt is only slightly soluble in water, and crystallises out when the reaction mixture is cooled. Ahlstrom and Aschan (Ber. I906. 39. I445.) studied the yields of sodium nopinate obtained by oxidising different fractions of American oil of turpentine. They give results showing that about fifteen times the yield is obtained from the higher boiling fractions as from the lower fractions, and that the greatest yield is from the fraction of b.p. I62°-I63°C. Later Wallach gave this hydrocarbon the name β-pinene to distinguish it from α-pinene (Ann. I907. 357. 50.).

It was not, however, until Wallach had successfully accomplished the synthesis of β-pinene (Ann. I908. 363. I-I9.), and after Gildemeister and Hoehler had isolated it in a fairly pure condition from hyssop oil (Report of Schimmel & Co. I908. April. 58. ; Wallach Festschrift, Göttingen. I909. 4I4 and 4I7.), that it could be conclusively shown that this new hydrocarbon is contained in the fraction of b.p. I62°C.-I65°C. of oil of turpentine.

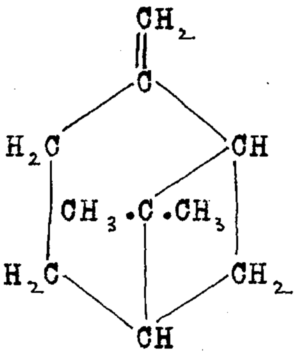
It has since been found that β-pinene is contained in other essential oils, and that it always occurs therein along with α-pinene. Its presence has been proved in oil of lemon (Gildemeister and Müller, Wallach Festschrift, Göttingen, I909. 48.), and in cumin oil (Report of Schimmel & Co. Oct. I909. 49.), and in coriander oil (loc.cit. 48.). It is probable that it will also be found to occur in other essential oils.

The accepted constitutional formula for α-pinene is:-



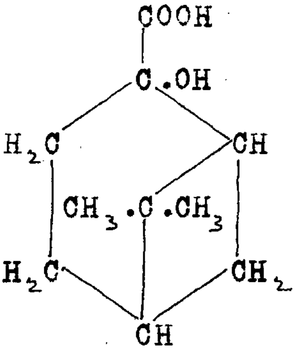
The formula, proposed by Semmler (loc. cit.) for his pseudopinene, and accepted by Wallach for β-pinene, shows the latter to be a methylene derivative.

The formula they assigned to β-pinene is:-

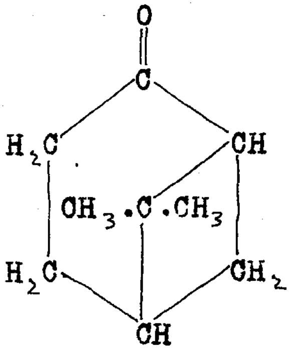


By the oxidation of the fraction b.p. 160°-170°C. of American oil of turpentine, Wallach prepared nopinic acid, which was isolated as the sodium salt (Ann. 1907. 356. 227-228.). Free nopinic acid has a m.p. 126°C.

By further oxidation in acid permanganate solution nopinic acid (1.) can be converted into nopinone (2.). This substance is a ketone, which, in the hands of Wallach, proved the starting point for a number of interesting syntheses.

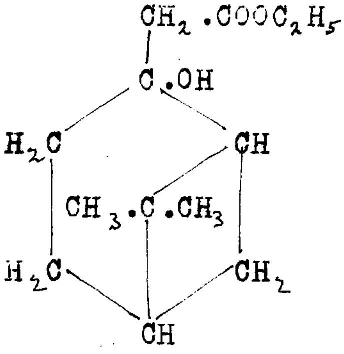


(1.)

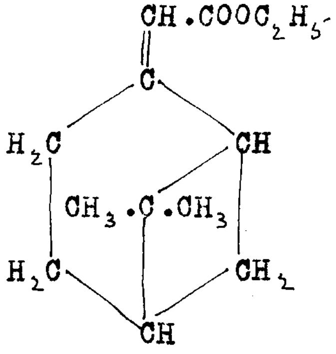


(2.)

The first step was the interaction of nopinone with Zn. and bromacetic ethyl ester (Ann. I907. 357. 50-53.), and on decomposing the intermediary product with water the ethyl ester of nopinol acetic acid (3.) was formed. This was then heated with $KHSO_4$ for two hours at I50°-I60°C. when H_2O was split off giving an unsaturated ethyl ester (4.)



(3.)

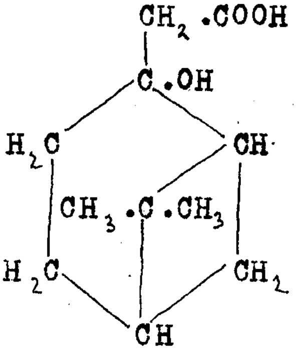


(4.)

On hydrolysis the free acid was obtained, and when this was distilled CO_2 was split off and a hydrocarbon, $C_{10}H_{16}$, resulted.

It was proved later that this hydrocarbon was L-d-fenchene, (Ann. I908. 363. 3.), and not β-pinene, which Wallach sought to obtain, and which he considered the synthesised hydrocarbon at first to be.(Ann. I907. 357. 53.).

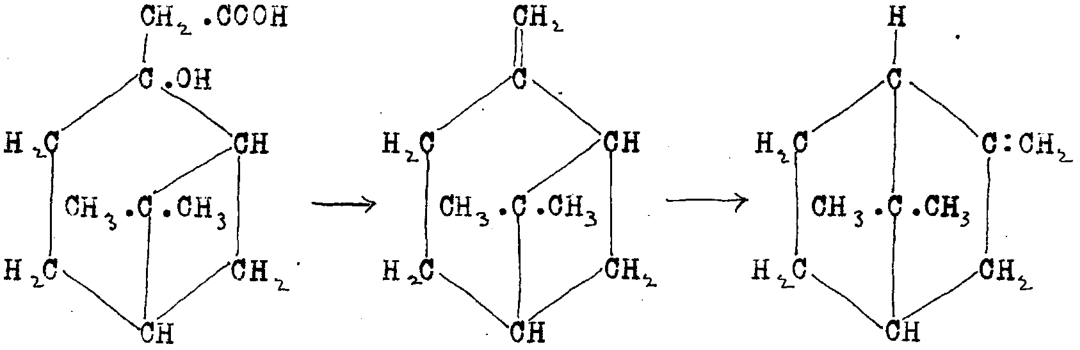
On carefully regulating the foregoing experiments, Wallach (Ann. I908. 363. 7.) obtained free nopinolacetic acid (5.).



(5.)

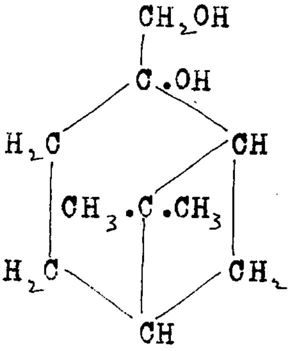
On heating this acid with acetic anhydride, two other acids were obtained. One of these was so unstable that it immediately broke up, giving off CO_2, and forming a hydrocarbon which was proved to be β-pinene. The second acid on distillation split off CO_2 and gave fenchene.

Wallach gives the following scheme, and states that he considers β-pinene to be an intermediary stage in the formation of fenchene from nopinone. (loc. cit. p.18.).



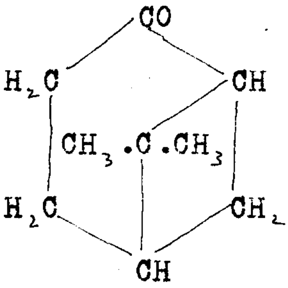
nopinolacetic acid. β-pinene. fenchene.

By the careful oxidation, in alkaline permanganate solution, of his synthetical β-pinene Wallach obtained β-pinene glycol (loc. cit. p.II.).

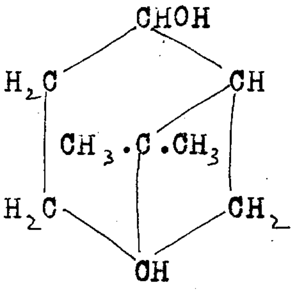


This substance he found to be a crystalline compound of m.p. 75°-77° C.

On reducing nopinone, Wallach obtained the corresponding alcohol, nopinol (Ann. I907. 356. 236.).

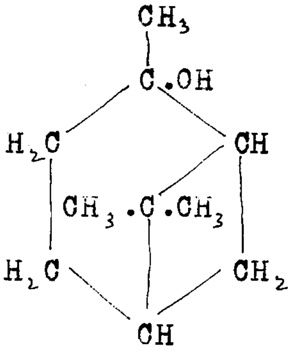


nopinone.

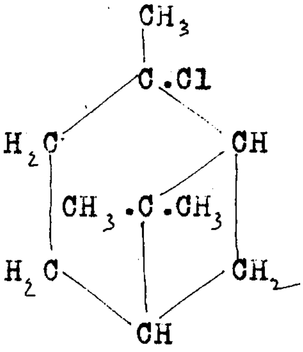


nopinol.

With the aid of the Grignard reaction he converted nopinol into pinene hydrate (Ann. I907. 356. 239.), and from the latter he prepared the true pinene hydrochloride (Ann. I908. 360. 88.).

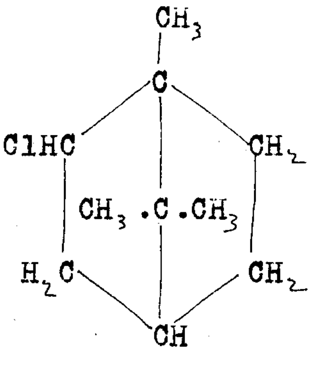


Pinene hydrate.

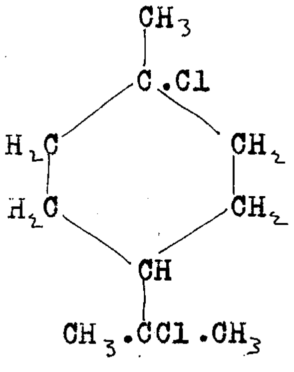


Pinene hydrochloride.

Wallach dissolved β-pinene in dry ether, and saturated the solution with dry hydrogen chloride, when he obtained a mixture of bornylchloride and dipentene dihydrochloride.



Bornylchloride.

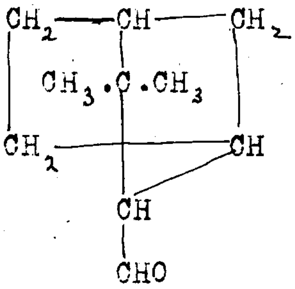


Dipentene hydrochloride.

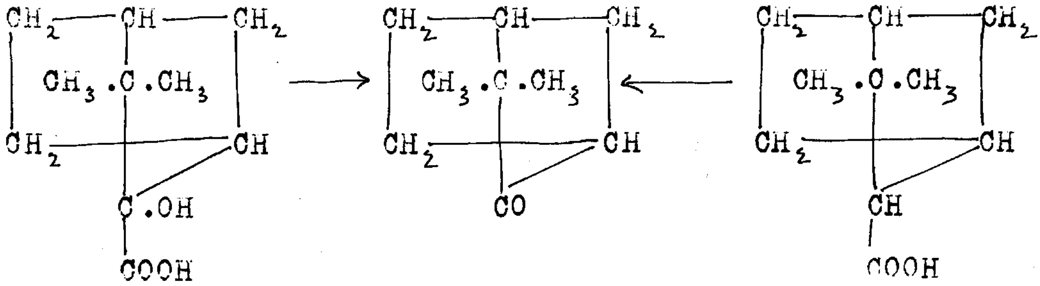
A solution of β-pinene in glacial acetic acid gave similar results (Ann. I908. 363. I5.).

It will thus be seen that β-pinene gives the same products with hydrogen chloride as α-pinene does. Pariselle (Compt. rend. I921. I72. I496.) shows that hydrogen bromide also gives the same products with β-pinene as with α-pinene. It has long been known that when chromyl chloride is added to any of the terpene hydrocarbons, dissolved in an anhydrous solvent, a solid addition product is formed. When this compound is decomposed by water a number of oxidation products result. Henderson and Gray (J.C.S. I903. 83. I299.) and Henderson and Heilbron (ibid. I908. 93. 288.) obtained by this method a solid addition product from α-pinene, and by the decomposition of this compound with water several oxidation products were secured. If we assume that it be possible to obtain the same addition product from β-pinene, as from α-pinene, by the action of chromyl chloride, it would be expected that the same series of oxidation products would result. One portion of the present work shows how far this assumption is justified.

Etard first noted the action of chromyl chloride on the terpene hydrocarbons, and by the decomposition of the camphene compound with water he obtained an aldehyde and an acid (Compt. rend. I893. II6. 434.). Bredt and Jagelki (Ann. I899. 3I0. II2.) repeated Etard's experiments with camphene, and they gave the name camphenilanic aldehyde to the aldehyde and camphenilanic acid to the acid product. Bouveault (Bull. soc. chim. I900. 23. III. 535.), in the light of Wagner's new formula for camphene (Journ. russ. Phys. chem. Ges. I899 3I. 630.) assigned the following formula to camphenilanic aldehyde:-



From camphenilanic acid Bredt and Jagelki obtained an hydroxycamphenilanic acid which was identical with the camphenylic acid of Wagner (ibid. I896. 28. 64. ; I897. 29. I24.). Both acids on oxidation give camphenilone (Wagner, loc. cit. ; Bredt and Jagelki, loc. cit.).



Camphenylic acid. Camphenilone. Camphenilanic acid.

Henderson and Gray (loc. cit.) dissolved α-pinene in 10 volumes of pure dry carbon disulphide and slowly added a 10% solution of CrO_2Cl_2 in the same solvent. The solid addition product was precipitated, and after being allowed to settle, the carbon disulphide was decanted off. The solid compound was then shaken up with ice cold water. The oil thus obtained was separated and steam distilled. From the purified oil the following products were isolated:-

a/. A saturated aldehyde - $C_9H_{15}.CHO$.

m.p. 33°C.

b.p. 205-207°C/755 mm.

Semicarbazone m.p. 191°C.

On exposure to the air the aldehyde passed over into the corresponding acid - $C_9H_{15}.COOH$.

m.p. 117°C.

b/. An unsaturated ketone - $C_9H_{14}O$.

Liquid.

b.p. 209-210°C/757 mm.

Semicarbazone m.p. 226°-228°C., with decomposition.

c/. A chloro-compound - $C_{10}H_{15}OCl$.

m.p. 168°C.

This substance was a colourless crystalline solid which gave no oxime, no semicarbazone, and was inert towards most reagents.

In a later investigation Henderson and Heilbron (loc. cit.) prepared from the acid (m.p. 117° C.) the following:-

a/. The acid chloride - $C_9H_{15}.COCl$.

b.p. 130° C./30 mm.

b/. A crystalline bromo-acid - $C_9H_{14}Br.COOH$.

c/. The hydroxyacid - $C_9H_{14}.OH.COOH$.

m.p. 227° C.

The Na-salt of this acid is sparingly soluble in water.

As bye-products they obtained:-

A bromo-compound - $C_{10}H_{13}OBr$.

m.p. 173° C.

This compound was found to be neutral.

A small quantity of another acid - $C_9H_{13}.COOH$.

m.p. 144° C.

By reduction of the ketone - $C_9H_{14}O$ - they obtained an unsaturated alcohol - $C_9H_{15}OH$.

b.p. 147°-148° C./90 mm.

Phenylurethane m.p. 96° C.

Acid phthalate m.p. 107° C.

By treatment of the chloro-compound - $C_{10}H_{15}OCl$ - with sodium ethoxide in boiling alcohol solution, a colourless crystalline substance was ultimately secured. This compound was free from chlorine, had an odour similar to that of camphor, and gave a m.p. 165° C.

When β-pinene was treated with chromyl chloride in the same manner as α-pinene, a similar oil was obtained by decomposing the solid addition product with water. On examination this oil was found to contain:-

a/. A very small quantity of an aldehyde or mixture of aldehydes. The sodium bisulphite compound was decomposed, and the resulting oil treated with semicarbazide acetate. On purification of the semicarbazone, small white nodules were obtained, which began to soften at 30° C. and completely liquified at 50° C. It would appear highly probable that the oil consisted of a mixture of two aldehydes. An attempt to separate the semicarbazones by fractional crystallisation from hot methyl alcohol failed owing to the small quantity available.

b/. The main product was a ketone, isolated as the semicarbazone. The latter, after purification, gave

m.p. 225° C.

and when mixed with the semicarbazone of the ketone obtained from α-pinene, showed no lowering of the melting point. The ketone obtained from β-pinene was thus shown to be identical with that from α-pinene, i.e. it is the ketone:-

$C_9H_{14}O$.

A large number of recrystallisations from hot methyl alcohol ultimately gave the semicarbazone in the form of delicate, colourless, needle-shaped crystals, which were found to have a:-

m.p. 232° C.

and decomposing at the same temperature. From the semicarbazone the free ketone was prepared. Its properties were the same as the properties of the ketone obtained by Henderson and Gray (loc. cit.).

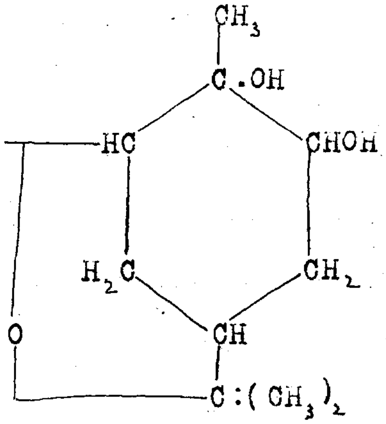
c/. A small amount of a volatile neutral product

m.p. 125° C.

Analysis gave the formula:-

$C_{10}H_{18}O_3$.

It is shown that this compound is identical with the trans-inactive form of pinol-glycol described by Wagner and Slawinski (Ber. 1899. 32. 2067.).



Pinol-glycol.

No trace whatever of any chloro-compound, corresponding to the substance - $C_{10}H_{15}OCl$ - obtained from α-pinene, was observed.

It will be seen, therefore, that, while β-pinene, so far as the main product of the reaction with chromyl chloride is concerned, does give rise to the same ketone as α-pinene, all the subsidiary products show marked differences. With β-pinene, also, it was found that the yield of ketone in comparison to the total yield of oxidation products was greater than in the case of α-pinene.

It is remarkable that this ketone - $C_9H_{14}O$ - first prepared in 1903 from α-pinene , still remains unidentified. When one considers the ease with which the pinenes, on treatment with various reagents, give rise to derivatives of borneol, camphene, or even fenchene, it will be seen that speculation as to the constitution of this ketone is neither advisable nor profitable. The characteristics of this ketone certainly do not agree with those of nopinone, any of the known isopropylcyclohexenones, camphenilone, fenchocamphorone camphorone, pinophorone, nor isocamphorone. Similar uncertainty exists with regard to the alcohol - $C_9H_{15}OH$ - obtained from this ketone by reduction.

It has been shown that when α-pinene is oxidised with hydrogen peroxide in glacial acetic acid solution, several products are obtained (Henderson and Sutherland, J.C.S. I9I2. IOI. 2288-2293.). The most important of these are three in number:-

a/. Borneol.
b/. α-Terpineol.
c/. I:4:8-Trihydroxymenthane.

β-pinene, under exactly similar conditions, was oxidised with hydrogen peroxide to find out whether the same, or analogous compounds are produced. In this case three products were also obtained, and these are shown to be:-

a/. Borneol.
b/. Fenchyl alcohol.
c/. A polyhydroxy-compound which is probably 2:8:9-Trihydroxymenthane.

The borneol was isolated and identified as the p-nitrobenzoate:-

m.p. I37°C.

It was observed that fenchyl alcohol did not react so readily with p-nitrobenzoyl chloride as borneol did, and this property was utilised to separate the two alcohols. It is interesting to note that Wallach (Nachr. k. Ges. Wiss. Gottingen, I905 6-I2.) separated fenchone from camphor by acting on a mixture of the two with semicarbazide, when the camphor formed a semicarbazone, and the fenchone did not react.

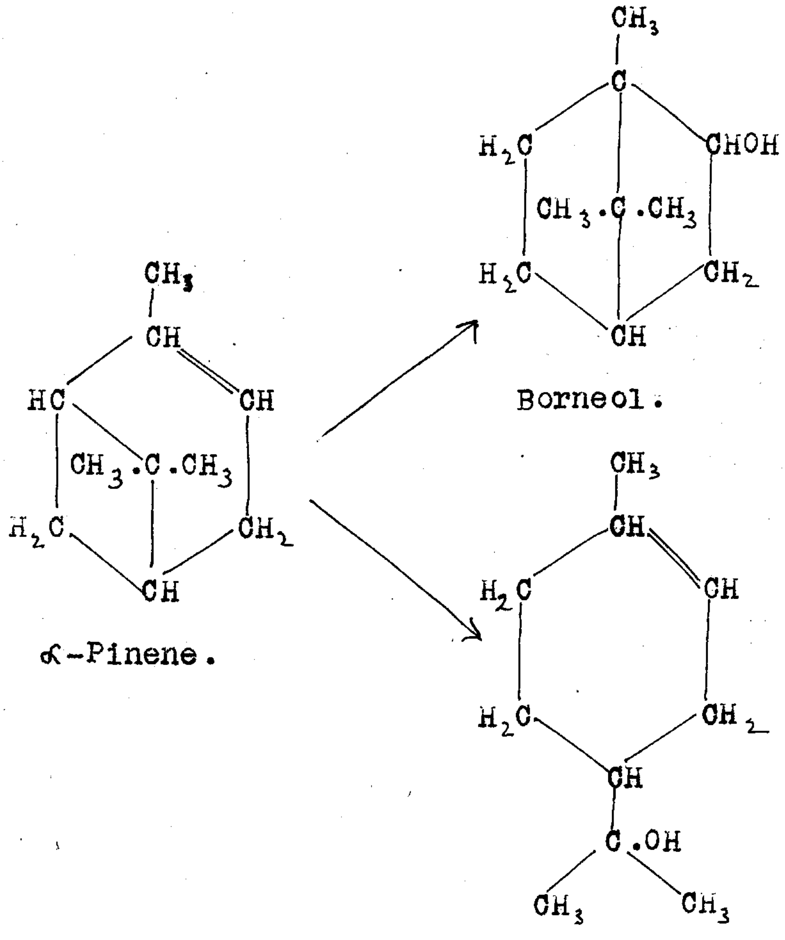
The fenchyl alcohol, after removal of the borneol p-nitrobenzoate, was distilled in a current of steam, and was obtained as a waxy solid:-

m.p. 40°C.

Some fenchyl alcohol was prepared by reducing fenchone. The fenchyl alcohol so obtained was found to have:-

m.p. 41°C.

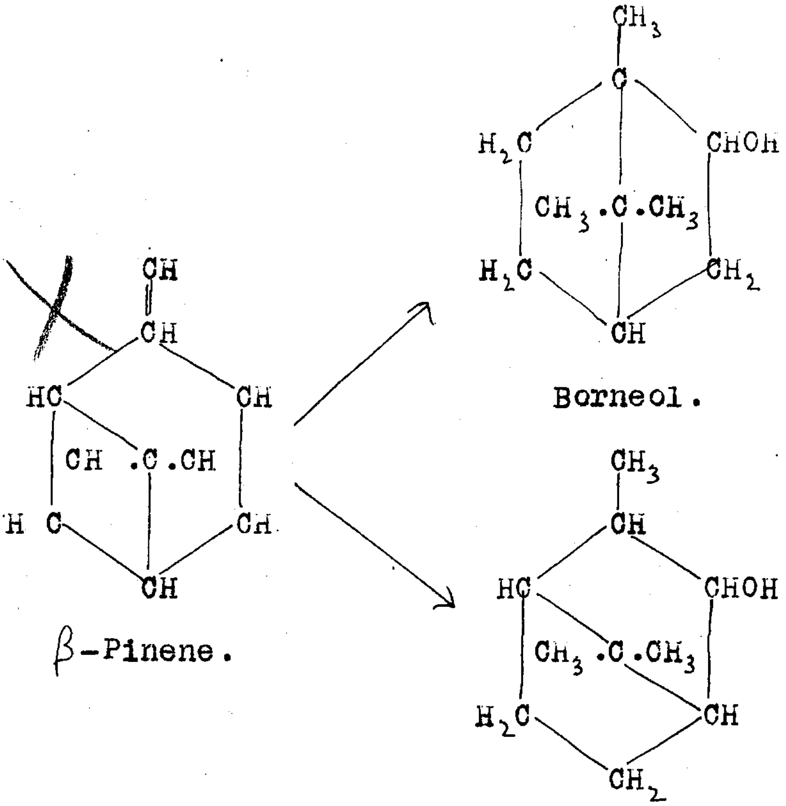
On mixing the two no lowering of the melting point was observed. It is, therefore, evident that fenchyl alcohol was one of the products.



Borneol.

α-Pinene.

α-Terpineol.



β-Pinene.

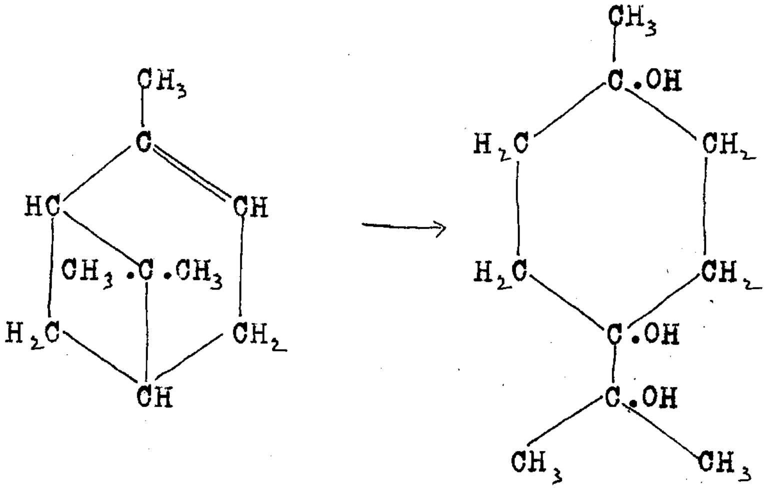
Borneol.

Fenchyl Alcohol.

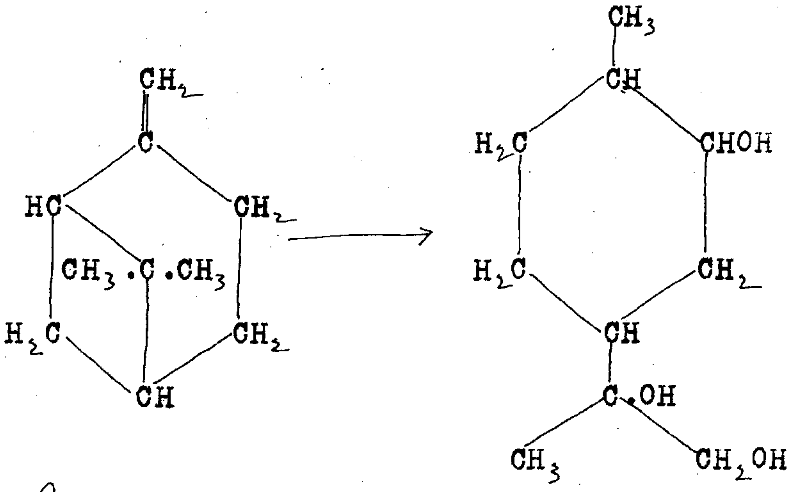
In connection with the formation of fenchyl alcohol from β-pinene, it has already been pointed out that Wallach synthesised β-pinene and fenchene simultaneously from nopinol acetic acid. Bouchardat and Lafont (Compt. rend. I898. I26. 756.) obtained fenchyl alcohol by the action of mineral acids on laevo oil of turpentine. Barbier and Grignard (Bull. soc. chim. I909. 4. (5). 5I2. 5I9.) state that fenchyl alcohol results together with other alcohols when French oil of turpentine is hydrated. These investigators assume that it is formed from the β-pinene present in the oil of turpentine.

The borneol and fenchyl alcohol were obtained from that part of the oxidation product which distilled in a current of steam. The non-volatile portion, which appeared to consist mostly of resin, was further examined. A small quantity of a very viscid, colourless liquid was ultimately secured. This substance could not be obtained in a crystalline condition. It decomposed when it was heated. and also when it was distilled in vacuo. If it be a tri-hydroxy compound, analogous to the one prepared from α-pinene, its properties seem to suggest that it is the 2:8:9-trihydroxymenthane described by Wallach (Ann. 1893. 275. 155. ; 277. 151. : 1894. 279. 386.) and Tiemann and Semmler (Ber. 1895. 28. 2142.).

An attempt was made to secure a p-nitrobenzoate from this non-volatile oxidation product. The ester obtained did not give a definite melting point, and this suggested that a mixture of p-nitrobenzoates had been formed. A consideration of the formula assigned to 2:8:9-trihydroxymenthane showed that such a mixture could quite easily occur with this compound. It will be seen that this tri-hydric alcohol contains a primary alcohol group, a secondary alcohol group, and a tertiary alcohol group. Experience has shown that it is a matter of extreme difficulty to obtain a p-nitro benzoate from a tertiary alcohol, so that the formation of a possible tertiary p-nitrobenzoate need not be considered. It is probable, then, that an ester could be formed at either of the other alcohol groupings, and somewhat less likely that a di-p-nitrobenzoate could be formed from both.



α-Pinene. I:4:8-Trihydroxymenthane.



β-Pinene. 2:8:9-Trihydroxymenthane.

Although a large excess of p-nitrobenzoyl chloride was used, nevertheless, a pure product was not obtained. This seemed to bear out the assumption that a mixture of mono-p-nitrobenzoates had been formed. With the small quantity of esters available, it was found to be impossible to effect a separation by repeated recrystallisations from hot methyl alcohol. The entire yield of this polyhydric compound was used up in the foregoing investigation, and consequently any further work on its constitution has had to be suspended for the present.

Preparation of β-Pinene.

During the course of the present work, β-pinene was prepared from three different sources. These different oils of turpentine were:-

French oil of turpentine.

American oil of turpentine.

Indian oil of turpentine (from Pinus Excelsa).

French oil of turpentine is produced from the pine (Pinus Maritima) growing on the dunes ("Landes") of south-western France. The physical constants of a sample examined by Flavitzky (Ber. I879. I2. 2357.) were:-

b.p. = I55°C.

$d_{20^\circ} = 0.8587$.

$\alpha]_D = -43.4^\circ$

American oil of turpentine is produced in the turpentine forests of the Southern States of U.S.A. The turpentine is principally obtained from three species of Pinus:-

Pinus Palustra. Mill.

Pinus Heterophylla. Ell.

Pinus Echinata. Mill.

Of these the first named is by far the most important. As a rule American oil of turpentine is dextrogyrate, but it can sometimes be found laevogyrate. The Bureau of Chemistry, U.S. Dept. of Agriculture, Bulletin I44. I9II. p. 22, gives the following range of physical constants:-

$d_{20°}$ from 0.8617 to 0.8889.

$[\alpha]_{D20°}$ from $-34.8°$ to $+29.6°$

$n_{D20°}$ from 1.4684 to 1.4818.

The Indian oil of turpentine was obtained through the courtesy of the British Xylonite Co. This oil was distilled at Jallo, Punjab, from the oleoresin of Pinus Excelsa. The following details regarding Indian oil of turpentine from Pinus Excelsa are given in the Bulletin of the Imperial Institute, vol. XV. No. 4. Oct./Dec. 1917. p. 563.:-

$d^{15°C}_{15°C} = 0.862.$

$[\alpha]_D = +42°.30'.$

It is also stated that 90% of this oil distils over between 157°-160° C., and that this fraction was found to be practically pure d-α-pinene.

In view of the results published by Pariselle (Compt. rend. 1921. 172. 1496. ; Ann. chim. 1923. (IX.) 19. 119.) it seemed probable that French oil of turpentine would prove to be the best source of β-pinene. Accordingly two gallons of French oil of turpentine were procured, and after purification, one litre was submitted to a test fractionation using a " Ramsay " fractionating column. After a large number of distillations, carried out at a rate of 70 drops per minute, a very small quantity of oil, with a constant

b.p. 163°-165°C.

was obtained. The total yield of fairly pure β-pinene , distilling at this temperature, was found to be:-

9.5 c.c's per I.000 c.c's of oil of turpentine.

This yield, compared with the large percentages quoted by Pariselle, was disappointing. It is true that he separated the β-pinene by fractional distillation under reduced pressure, using an " Otto " still-head with 5 bulbs, whereas the present fractionation was carried out at ordinary atmospheric pressures, and using a fractionating column which could only deal with a small quantity of liquid at a time. It became evident, however, that it would be necessary to distil a very large volume of oil of turpentine, and it was desirable, therefore, to find out the most efficient form of fractionating column to use. Half litre samples of French oil of turpentine were distilled with each of the following fractionating columns:-

Rod and Disc.
Ramsay.
Hempel (glass beads).
Hempel (Lessing's rings).
Dutton's.
"Pear" bulb column - with I2 "Pears".
Modified Evaporator.

The "Rod and Disc" type did not give particularly good results in the separation of β-pinene from α-pinene. The boiling points of the two hydrocarbons were probably too close together, on the one hand, and on the other, the temperature of the vapours was too high to enable them to be efficiently separated by this column. The " Ramsay " gave somewhat better results, but the column was too narrow, and only a limited volume of oil of turpentine could be distilled at a time. The " Hempel " fractionating column, filled with glass beads, or with Lessing's rings, caused too much condensation of liquid in the column, with the result that the latter gradually filled with liquid, and distillation could not be continued. Wrapping the outside of the column with asbestos wool did not improve matters to any great extent. With " Dutton's " column, it was found that separation could not be effected unless the rate of distillation were slowed down to 20 drops per minute, or thereby. This entailed packing the outside of the column in asbestos wool, and even then the rate of distillation could not be maintained at this low value for any length of time without the total cessation of distillation. It was found in all these experiments with fractionating columns that a constant rate of distillation less than 70-80 drops per minute could not be maintained at the temperatures - I55°C. to I70°C. - at which the fractionation of oil of turpentine was attempted.

The " Pear " fractionating column with I2 " Pears " was then tried, and quite good results were obtained, especially after it had been jacketted with a wide glass tube to prevent the access of draughts to the column. A constant rate of 75 drops per minute could be maintained. The " Modified Evaporator " column was found to give results as good as, or even better than, the " Pear " . The " Modified Evaporator " column used had three compartments, and since it could not deal with the larger quantities of oil of turpentine, it was used throughout to give a cleaner separation of that fraction of the oil which was collected at a temperature of I60° C. and upwards from the " Pear " fractionating column.

The joint use of these two columns, however, did not give a yield of β-pinene exceeding I% of the volume of French oil of turpentine distilled. To make quite certain regarding the history of the oil of turpentine used in the fractionation, a quantity - I0 kilograms - of French turpentine was procured from France, and this was submitted to steam distillation in the laboratory. A yield of I623 c.c's of pure dry French oil of turpentine was secured, and over 8 kilograms of a very clean, water-white colophony obtained as a bye-product. The supply of French oil of turpentine so prepared was repeatedly fractionated, and I5.I c.c's of β-pinene, in a pure dry condition, were obtained. The fraction which passed over unchanged at I62° C.-I64° C. after several distillations was taken to be β-pinene and was found to give the following constants:-

b.p. I62°C. to I64°C.

$d^{15} = 0.8722$.

$n_D^{15} = 1.477$.

$[\alpha]_D^{15} = -19.9°$

Pariselle (Compt. rend. I92I. I72. I496.) gives:-

b.p. I63°C. to I64°C./ 760 mm.

$d^{15} = 0.8728$. $d^{0} = 0,8848$.

$n_D^{13} = 1.479$.

$[\alpha]_D^{15} = -19.8°$.

Wallach (Ann. I908. 363. 9.) gives for β-pinene from Amer-oil of turpentine:-

b.p. I62°C.-I63°C.

$d = 0.866$.

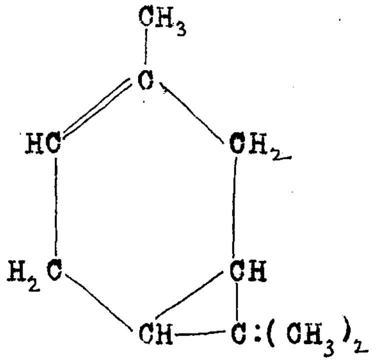
$n_D^{22} = 1.4724$.

$[\alpha]_D = -22° 20'$

An additional 2 gallons of French oil of turpentine, belonging to the I920 crop, were obtained through the courtesy of the British Xylonite Co. This oil, likewise, gave no better yield of β-pinene.

The 2 gallons of Indian oil of turpentine from Pinus Excelsa, procured through the same firm, were next examined for their content of β-pinene. This particular variety of oil of turpentine was found to be rich in α-pinene. In addition, it was shown to contain a small proportion of β-pinene, and also of a third hydrocarbon, boiling about

I73°C. At first the latter hydrocarbon was considered to be sylvestrene. It did not, however, give the colour reaction for sylvestrene, and it is probably identical with the d-Δ^3-Carene isolated by Simonsen from Indian oil of turpentine, distilled from the oleoresin of " Pinus Longifolia " (J.C.S. I920. II7. 570. ; I922. I2I. 2292.).



d-Δ^3-Carene.

b.p. I68°C.-I69°C./ 705 mm.

Owing to the presence of this third hydrocarbon, with a boiling point only a little higher than that of β-pinene, the isolation of β-pinene from Indian oil of turpentine, from " Pinus Excelsa ", proved to be a long and tedious process. For this reason the attempted preparation of β-pinene from this source was dropped.

Since the composition of oils of turpentine from the Indian " Pinus Longifolia ", and from Swedish and Russian pines, are sufficiently well known, no attempt was made to prepare β-pinene from these oils. Attention was turned to obtaining β-pinene from American oil of turpentine. It was found that the yield of β-pinene from this source was slightly better than from the French oil. The yield was a shade more than I% of the total American oil distilled. The fact that American oil of turpentine was found to be richer in β-pinene than the French variety is in accordance with Wallach's statement (Ann. I908. 363. 9.), but he does not give any details regarding the comparative yields. Altogether 4 gallons of American oil of turpentine were distilled. Since the same laevogyrate β-pinene is obtained from both American and French oils of turpentine, the total supply of turpentine oils - a little more than 8 gallons - was mixed, and distilled indiscriminately.

To purify the oil of turpentine, it was allowed to stand in contact with solid caustic potash for several days. The oil was then separated from the solid potash, precipitated resin, and the concentrated aqueous solution of potash formed from the water present in the turpentine oil. The oil of turpentine was next steam distilled. Each batch of oil of turpentine - about I$\frac{1}{2}$ litres - was distilled in three, approximately equal, stages. That is to say, that, when about one third of the oil had distilled over with the steam, the receiver was changed, and was changed again when the second third had passed over. The three portions of the distillate obtained in this manner were then examined separately for their content of β-pinene. It was found that the last third of the distillate was somewhat richer in β-pinene than the other two. The first portion of the distillate, however, did contain a small proportion of β-pinene, and since it was desirable to secure as much β-pinene as possible, no useful purpose would be served by neglecting the yield from this source. The three portions of each distillate, however, were accumulated separately, since by this means a rough-and-ready primary fractionation of the oil was secured.

The fresh steam distilled oil was separated from the layer of distilled water, and dried over freshly ignited anhydrous sodium sulphate. The dried oil was then submitted to fractional distillation in the " Pear " apparatus.

The greater portion passed over at 155°C.-156°C.
Fractions were taken:- 156°C.-157°C.
157°C.-158°C.
158°C.-159°C.
159°C.-160°C.
Over 160°C.

The fraction passing over under 156°C. was found to be practically pure α-pinene. It was, nevertheless, run through the distillation apparatus twice more, before being finally laid on one side, and an additional small quantity of higher boiling oil was thus secured from it. The remaining fractions were redistilled separately, the higher boiling portion of each fraction being added to the next higher fraction, and so on, until a quantity of oil boiling above I60°C. was isolated. This portion was dealt with separately in the " Modified Evaporator " column and fractions were taken:-

Under I60°C.
I60°C.-I62°C.
I62°C.-I64°C.
I64°C.-I66°C.
Over I66°C.

The fraction separating under I60°C. was returned to the " Pear ". The fractionation was continued until a portion of the oil, passing over constantly at I62°C.-I64°C., was isolated. It gave constants:-

$$d^{13} = 0.87I0.$$

$$n_D^{14} = I.4760.$$

It was assumed that this fraction of the oil of turpentine consisted of β-pinene sufficiently pure to carry out the oxidations. A total yield of 3I2 c.c's of this β-pinene was obtained.

The Oxidation of β-Pinene with Chromyl Chloride.

A 10% solution of β-pinene was prepared by dissolving 40 grams of the hydrocarbon in 400 grams of carbon disulphide. A 10% solution of chromyl chloride was prepared by dissolving 100 grams of the reagent in a kilogram of carbon disulphide. The carbon disulphide had previously been carefully purified by distillation with a small quantity of chromyl chloride. Any unchanged chromyl chloride was decomposed by shaking up the distillate with a little distilled water. The carbon disulphide was separated from the aqueous solution, and dried over anhydrous sodium sulphate.

The quantities of chromyl chloride and β-pinene used were sufficient to give slightly more than 2 molecular proportions of the former to 1 of the latter. Both solutions were kept well cooled in ice, and small quantities of the chromyl chloride were added, at short intervals, to the β-pinene solution. The latter solution was kept in a state of constant agitation. A heavy brownish-black precipitate, of chromyl chloride β-pinene addition product, was gradually deposited. This compound is characteristic of the action of chromyl chloride on the terpene hydrocarbons, and has the composition:-

$$C_{10}H_{16}.2CrO_2Cl_2.$$

During the addition of the chromyl chloride, any local overheating, due to failure in maintaining the β-pinene solution in constant agitation, or neglect in keeping the reacting substances well cooled, results in serious losses due to resinification. After the calculated amount of chromyl chloride had all been added the precipitate was allowed several days in which to settle. If the supernatant layer were clear, small quantities of chromyl chloride were added until it possessed a permanent reddish tinge. After the formation of the addition product was thus completed, the liquid layer of carbon disulphide was decanted off. A brownish-black paste remained. A little of this paste was dried and washed with carbon disulphide at the pump. The addition product was obtained as a dirty white powder. It was found that it readily absorbed moisture from the air, and was quickly converted into a viscid green liquid possessing a peculiar sweetish odour. The powder is completely decomposed with water.

The brownish-black paste was slowly run into ice-cold water, with which it was well stirred. On standing, the carbon disulphide separated, and was run off. It was of a dark brown colour, and was found to contain most of the oxidation products in solution. The green aqueous solution was extracted several times with ether, and finally with light petroleum. After the aqueous solution had been extracted it was laid aside, but when several weeks had elapsed, it was noted that portions of resinous matter had been deposited on the sides and bottom of the Winchester flask containing the liquid. It would thus appear that, under the above conditions, the decomposition of the brown addition product, and the extraction of the aqueous solution, were not so complete as they were previously thought to be. Consequently, when a second portion of β-pinene was oxidised the previous procedure was somewhat altered. After the carbon disulphide layer had been separated, the aqueous solution was placed in a Winchester and gently warmed in a thermostat. Experiment showed that the best temperature, to ensure complete decomposition, was in the neighbourhood of 25°C. The Winchester was kept in the thermostat at this temperature for a day, and the solution, after cooling, was extracted as before. In this case the decomposition and extraction were complete, and no resin was deposited from the green aqueous solution even after the lapse of six months.

The carbon disulphide solution of the oxidation products, and the several extracts were washed with water, and dried over anhydrous sodium sulphate. The solvents were distilled off, and the residues mixed. The oxidation product was thus obtained as a dark brown viscid oil, which apparently contained a large proportion of resin. The oil was submitted to steam distillation, when a quantity of a clear yellowish oil passed over, and collected with the distilled water in the receiver. The resin remained behind in the distillation flask.

Separation of the Aldehydes.

The distillate from the steam distillation was saturated with sodium chloride and repeatedly extracted with ether. The ethereal solution was separated, and dried over anhydrous sodium sulphate. The ether was separated by distillation from a water-bath. The remaining oil was mixed with slightly more than its volume of freshly prepared, saturated aqueous solution of sodium bisulphite. The mixed liquids were placed in a conical flask, loosely stoppered with cotton wool, and kept in a cool place for several weeks. The flask was shaken at frequent intervals. A small crop of crystals, of an aldehyde bisulphite compound and of sodium bisulphite, was slowly formed. These crystals were carefully filtered off at the pump, washed with alcohol and ether, and dried. The unchanged oil was extracted from the filtrate and again mixed with saturated sodium bisulphite solution. A further very small crop of crystals was secured. The combined yield of crystals was boiled with sodium carbonate solution, in a distilling-flask, to decompose the bisulphite compound. The aldehydes volatilised, and distilled over with the steam, accumulating in the receiver as a few drops of semi-solid oil. These were extracted with ether, the solution dried over anhydrous sodium sulphate, and the ether separated by distillation. A very small quantity of a thick greenish-yellow oil - with an odour similar to that of camphor - was thus obtained. This oil was immediately weighed and dissolved in pure ethyl alcohol. To prepare the semicarbazone, the calculated quantity of semicarbazide hydrochloride - one molecular proportion - was weighed, and dissolved in the minimum volume of distilled water. Similarly one molecular proportion of potassium acetate was dissolved in ethyl alcohol. The three solutions were mixed and sufficient ethyl alcohol added to give a homogeneous solution. After standing for several days the semicarbazone was precipitated by the addition of distilled water, and allowed to settle. The precipitate was separated by filtration, washed, and dissolved in methyl alcohol, in a hot solution of which it was readily soluble. The bulk of the methyl alcohol was distilled off, and on cooling the remaining solution, the semicarbazone crystallised out in the form of whitish nodules. These were collected, dried, and a melting point taken. It was found that the substance began to soften about 30°C. and was completely liquid at 50°C. A further recrystallisation from a small volume of hot methyl alcohol gave no better results. It appeared evident that the indefinite melting point was not due to any chance impurity. It was much more probable that the result was occasioned by a mixture of aldehyde semicarbazones, in all likelihood, two in number. Attempts were made to separate the semicarbazones by fractional crystallisation from methyl alcohol, but with the very small amount available no satisfactory results were obtained.

Separation of the Ketone.

The oily oxidation product, from which the aldehydes had been removed by sodium bisulphite, was washed successively with aqueous sodium carbonate and water, and then dried over anhydrous sodium sulphate. The dried oil was dissolved in ethyl alcohol, and the calculated amounts of semicarbazide hydrochloride and potassium acetate were added. On standing for several days, crystals were slowly deposited, and by the daily addition of a few drops of distilled water, the yield was greatly increased. After standing for a fortnight, the ethyl alcohol was distilled off, using a short fractionating column in case there should be any volatile neutral products in the oil. The alcohol which accumulated in the receiver was found to possess a peculiar penetrating odour. Some distilled water was added to a small sample of the alcohol, and a white turbidity resulted. So it appeared that the oil contained a volatile substance, which distilled with alcohol vapour, even although a fractionating column was used. All the distilled alcohol was accordingly set on one side for further examination. The liquid remaining in the distilling flask was decanted from the solid semicarbazone, the latter powdered up and washed with water, and the decanted liquor and washings were submitted to steam distillation. The distilled water in the receiver also showed turbidity, and was likewise set on one side. Nothing else was obtained except a drop or two of a mobile oil, which further examination showed to consist of unchanged β-pinene, containing in solution a little of the same volatile substance as the ethyl alcohol.

The washed semicarbazone, of which a fair yield was obtained, was dissolved in hot methyl alcohol. A small quantity of a yellowish, sandy substance remained undissolved and on further examination it was found to be a condensation product of semicarbazide. The hot methyl alcohol solution was filtered free from the insoluble residue. The solution was concentrated by distilling over about half the bulk of methyl alcohol, and allowed to cool. The semicarbazone of the ketone was deposited in minute colourless needles, and after purification, by recrystallisation several times from hot methyl alcohol, gave a melting point of 225°C., decomposing at the same time. The ketone semicarbazone obtained by Henderson and Gray (loc. cit.) from α-pinene melted at 226°C. A small quantity of this semicarbazone was procured and mixed with the semicarbazone from β-pinene. The melting point of the mixture was 224°C. There is therefore no doubt that the ketone prepared from β-pinene is identical with that from α-pinene.

The ketone has the composition:-

$$C_9H_{14}O.$$

A portion of the semicarbazone was repeatedly recrystallised from hot methyl alcohol, and a melting point taken after each crystalliaation. It was found that the melting point rose steadily, but slowly, with each additional crystallisation. Ultimately a series of crystallisations gave a product melting constantly at 232°C. (uncorrected.).

The ketone itself was obtained by decomposing the semicarbazone with a slight excess of oxalic acid, and steam distilling the mixture. The distillate was saturated with sodium chloride, repeatedly extracted with ether, and the extracts dried over anhydrous sodium sulphate. The ether was separated by distillation from the water-bath, and the ketone was obtained as a colourless, oily liquid with a pleasant aromatic odour. The ketone is soluble in methyl and ethyl alcohols, in ether, chloroform, benzene, acetone, petroleum ether, and glacial acetic acid. It is insoluble in water. It boils at 207°C.-208°C. It discharges the colour of permanganate solution, and combines with two molecular proportions of bromine. There was no necessity to prepare the corresponding alcohol, and the amine therefrom, since these compounds have already been described by Henderson and Heilbron (J.C.S. 1908. 93. 292 - 293.).

Separation of the Neutral Compound.

The ethyl alcohol distilled from the ketone semicarbazone, and the distillate from the steam distillation were mixed, and a further large bulk of distilled water added. The mixture was repeatedly extracted with petroleum ether, and the combined extracts dried over anhydrous sodium sulphate. The petroleum ether extracted most, but not all, of the product which caused the turbidity. On account of the volatility of this substance the petroleum ether was evaporated at the pump, thus getting free of the solvent at a low temperature. The substance appeared to be readily soluble in petroleum ether, and it was only obtained in the crystalline state by pouring the last of the solution on to a watch glass and allowing the solvent to spontaneously evaporate. Small colourless crystals, possessing an odour reminiscent of that of camphene, but sharper, were obtained. These crystals were found to melt, not very sharply, about II0°C. A further purification, by crystallisation from a little chloroform, gave a sample which had a melting point of I23°C.-I25°C. It seemed possible that another one or two recrystallisations might still further raise the melting point, but with the small quantity available it was not considered advisable to run the risk of further loss. During the melting point determinations it was found that the substance sublimed on to the sides of the test-tube containing the thermometer. The substance did not immediately discharge the colour of permanganate solution. It was also found to be saturated towards bromine.

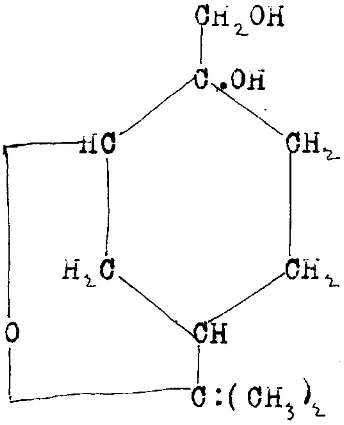
Analyses showed:-

0.1334gms. gave 0.1190gms. H_2O. : H = 9.89%
" " 0.3150gms. CO_2. : C = 64.4%
0.1236gms. gave 0.1068gms. H_2O. : H = 9.67%
" " 0.2896gms. CO_2. : C = 64.2%

$C_{10}H_{18}O_3$ requires C = 64.54% : H = 9.68%.

Details regarding the following compounds of formula $C_{10}H_{18}O_3$ were found in the literature:-

The compound described by Wagner and Slawinski (Ber. 1899. 32. 2082.) and named nopinolglycol.



It had a m.p. 126°C.-127°C.

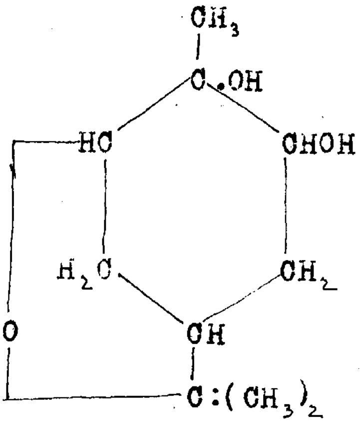
Gave a red colour with conc. sulphuric acid in the cold.

Was sparingly soluble in light petroleum.

Three different modifications of pinolglycol are described.

a/. The cis-modification of pinolglycol by Slawinski (J. russ. Chem. phys. Ges. 1898. 30. 195. : Centralblatt.

1898. (2.). 543.).



Has a m.p. 123°C.-124°C.

Gives a golden-yellow colour with conc. H_2SO_4.

b/. Trans-active modification, by Wagner and Slawinski (Ber. 1899. 32. 2072.).

m.p. 73°C.-74°C.

Sublimes.

c/. Trans-inactive modification, by Wagner and Slawinski (Ber. 1899. 32. 2067.).

m.p. 126°C.-127°C.

Sublimes.

Gives a golden-yellow colour with conc. H_2SO_4 in the cold.

The compound $C_{10}H_{18}O_3$ obtained from β-pinene also gives a golden-yellow colour with conc. H_2SO_4 in the cold. It sublimes, and has a m.p. 123°C.-125°C., this figure being regarded as low for the reasons already given. There is therefore, a great deal of justification in identifying the compound secured from β-pinene as the trans-inactive modification of pinolglycol described above. Since this compound was prepared from β-pinene, it was at first thought that it might prove to be nopinolglycol. This conclusion was, however, untenable in view of the properties of the compound from β-pinene which have already been set forth, and also because this compound was found to be readily soluble in light petroleum.

The sodium bisulphite solution, from which the aldehyde-bisulphite crystals had been deposited, and from which all the oxidation oil had been extracted, was diluted with an equal volume of water. Dilute sulphuric acid was slowly added to the solution until all effervescence had ceased. The solution was then heated until all the sulphur dioxide had been expelled. When cool, a sufficient volume of dilute sulphuric acid was added to make the solution faintly acidic. This acidic solution was repeatedly extracted with small volumes of ether. The combined extracts were dried over anhydrous sodium sulphate, and the ether distilled from the water-bath. There was practically no residue left in the distilling flask. The few drops of liquid which did remain were washed out with a small quantity of distilled water. The solution showed an acidic reaction, but no trace of any acid other than sulphuric acid could be detected.

The sodium carbonate solution, with which the oxidation oil had been washed after the extraction of the aldehydes, was examined in a similar fashion. A trace of an organic acid was found after the ether had been distilled off. This acid occurred as a drop of thick oil, possessing a sour smell. The quantity was far too small to permit of further examination, but in all probability the acid was formed from the aldehydes by air oxidation.

At no point in the examination of the volatile portion of the original oxidation product was a substance isolated analogous to the chloro-compound obtained by Henderson and Gray from α-pinene (loc. cit.).

The resin, which remained in the distillation flask after the steam distillation of the original oxidation oil was dissolved in ether. The dark brown solution was repeatedly washed with water until a sample failed to show any trace of chromium salts, or soluble chlorides. A small quantity of the ethereal solution was evaporated to dryness, and the residue examined for combined chlorine. No trace of chlorine was found. The ethereal solution was then shaken up with a solution of sodium carbonate. No effervescence was observed, but the sodium carbonate solution became tinted with the dark brown colour of the resin. It was not found possible, however, to isolate the sodium salt of any definite acid. The ethereal solution was washed free from sodium salts and dried. The ether was distilled off, and the resin submitted to distillation under reduced pressure. Nothing distilled over except water, and a carbonaceous mass remained behind in the flask.

The Oxidation of β-Pinene with Hydrogen Peroxide.

In order to carry out the oxidation 2 molecular proportions of hydrogen peroxide were added to 50gms. of β-pinene dissolved in 130gms. of glacial acetic acid. The hydrogen peroxide used was " Perhydrol ", - a 30% aqueous solution - and 2 molecular proportions of this strenght were calculated to be 78 c.c's. The mixture was heated on the water-bath at 50 C.-55 C. until the β-pinene, which separated, on the addition of the hydrogen peroxide, had again passed into solution. Under these conditions the oxidation proceeded somewhat slowly, but attempts to hasten the process by carrying it out at higher temperatures resulted in the formation of much resinous matter. After constant heating for about a week all the upper layer had disappeared, and the oxidation was taken to be complete. The solution was now of a light yellowish brown tint. It was diluted with distilled water, and the acetic acid completely neutralised by the addition of sodium carbonate. An oily liquid which separated was extracted by means of ether. The ether extractions had to be very exhaustive, as even the tenth extract, when tested, was found to contain a small quantity of product. The extractions were continued until the solution had been extracted fourteen times. The ethereal extracts were combined, washed with successive small quantities of water, to extract any sodium acetate, and dried over anhydrous sodium sulphate.

The original aqueous solution would still contain the sodium salt of any acid which might have been formed during the oxidation. A small quantity of dilute acetic acid was, therefore, added until the solution was just acid to litmus. The solution was then extracted with ether. The residue from the extract, after the ether had been distilled, contained no other acid than acetic. In case the acid, if any were formed, should be a stronger acid than acetic, a few drops of dilute sulphuric acid were added to the solution, and it was again extracted with ether. The residue, on examination, contained no other organic acid except acetic acid. It was, therefore, concluded that no free acid was formed during the oxidation.

The ether was distilled off from the dried ethereal extract of the oxidation products, and a brown viscid oil was obtained. This was mixed with an equal volume of freshly prepared, saturated aqueous sodium bisulphite. After standing in a cool place for several days, with occasional shaking, a few crystals were deposited. On examination, however, these were found to consist of nothing else than sodium bisulphite. The solution was allowed to stand in contact with the sodium bisulphite for several weeks longer, but no aldehyde-bisulphite compound was secured. It seemed fairly well established that no aldehydes were formed during the oxidation. Similarly, on treatment with semicarbazide acetate, no sign of any ketone was observed.

The oxidation oil was recovered from these several processes, washed free from the reagents, and submitted to steam distillation. About three-quarters of the total oil passes over with the steam, and the non-volatile portion remained behind in the distilling flask as a dark brown resinous mass. The volatile portion was extracted from the distillate with ether, the ethereal solution dried, and the ether distilled off. A practically colourless, fairly mobile oil, with a not unpleasant odour, was obtained. This oil was dissolved in methyl alcohol and the calculated amount of potassium hydroxide, dissolved in methyl alcohol, was added. The mixture was heated on the water-bath, under a reflux condenser, for half-an-hour. The methyl alcohol was distilled off, using a short fractionating column, and the residue was submitted to steam distillation. The aqueous residue remaining behind in the distilling flask was acidified with dilute sulphuric acid. Acetic acid was liberated, but no trace of any other organic acid could be detected. It was thus shown that the esters in the volatile portion of the oxidation oil consisted solely of acetates, and that esters of any acid formed during the oxidation did not occur.

The steam distillate was extracted with ether, the extract dried, and the ether distilled off. The residual oil was then submitted to distillation under reduced pressure, when it was found that practically the whole of it passed over at 116°C.-120°C./18mm. The oil showed no signs of separating into different fractions. Henderson and Sutherland observed (loc. cit.) that α-pinene, when oxidised with hydrogen peroxide, gave rise to a mixture of α-terpineol and borneol. Although no distinctive odour was noticeable, it was considered that a similar mixture might have been formed in the case of β-pinene. A sample of the oil was seeded with a crystal or two of α-terpineol (m.p. 35°C.) and cooled in a freezing mixture. No crystals were formed, and in fact the α-terpineol passed into solution in the oil. It became evident that the constituents of the oil were somewhat different from those obtained from α-pinene. It was also evident that the oil consisted either of a single liquid alcohol or glycol or a mixture of at least two such compounds, possessing boiling points close to each other. It was determined, therefore, to attempt the preparation of p-nitrobenzoates, in order, if possible, to throw more light on this problem.

A portion of the oil was dissolved in 10-12 times its volume of pure dry pyridine. The calculated quantity of powdered p-nitrobenzoyl chloride was weighed out, and gradually added to the solution, care being taken to prevent undue heating. After all the p-nitrobenzoyl chloride had been added, the mixture was gently warmed on the water-bath for a few days. After the reaction was considered to be complete the dark brown solution which resulted was allowed to cool. The liquid set to a pasty crystalline mass, and this was drained at the pump. The filtrate was dissolved in 5% sulphuric acid, in order to dissolve the pyridine, and to precipitate any free p-nitrobenzoic acid. This solution was filtered at the pump through the same filter paper as before, and the residue on the filter washed with 5% sulphuric acid until no more pyridine remained. The filtrate, after it had stood for a little time, was observed to be covered with an oily film, and it was set on one side for further examination. The residue on the filter was shaken up with dilute sodium bicarbonate in order to dissolve any free sulphuric acid, or any p-nitrobenzoic acid formed during the reaction. When all evolution of carbon dioxide was at an end the mixture was filtered at the pump. The residue was washed with water, and dissolved in hot methyl alcohol. The alcohol solution was heated under a reflux, and a little activated animal charcoal added to the solution. The solution was filtered free from charcoal, and allowed to cool. Small glistening plates, with a pale yellow colour, separated out. After several recrystallisations from methyl alcohol, when they became almost white in colour, the crystals were found to melt sharply at I37° C. A specimen of pure borneol p-nitrobenzoate was prepared in a similar manner, and it was also found to melt at I37°C. The two p-nitrobenzoates were mixed, but no lowering of the melting point was observed. It was, therefore, established that borneol was one of the products obtained by oxidising β-pinene with hydrogen peroxide.

Since the volatile portion of the oxidation oil was liquid at ordinary temperatures, it was evident that it was a mixture. No great difficulty had been encountered in purifying the borneol p-nitrobenzoate, and on that account it appeared likely that the other constituent, or constituents, of the mixture did not react so readily with the p-nitrobenzoyl chloride as borneol did. This observation suggested a possible means of separating the constituents of the mixture. The remaining portion of the volatile oil was, therefore, treated with rather less than the calculated quantity of p-nitrobenzoyl chloride.

The filtrates and pyridine sulphate solutions were all collected, and the oily surface film extracted with ether. The ether was distilled off and the residue steam-distilled. A small quantity of a greasy looking solid accumulated in the receiving flask, and floated on the surface of the condensed water. A small sample was collected and dried, and the melting point of this sample was found to be about 40° C. This substance had rather an unpleasant smell, resembling that of fenchyl alcohol.

A small volume of D-fenchone was obtained and dissolved in methyl alcohol. The solution was boiled under a reflux, and slightly more than the theoretical amount of metallic sodium gradually added. When all reaction had ceased the mixture was dissolved in water, and the methyl alcohol distilled off, using a fractionating column. The residue was steam-distilled, and the fenchyl alcohol extracted from the distillate by means of ether. On drying the solution, and separating the ether by distillation, the fenchyl alcohol was obtained in the solid condition. This fenchyl alcohol was observed to melt at 41°C. A portion was mixed with the solid of m.p. 40°C. secured from the volatile oxidation oil. No appreciable lowering of the melting point was observed. There is, therefore, no doubt that fenchyl alcohol occurs amongst the oxidation products of β-pinene. Experiment also showed that borneol and fenchyl alcohol readily form a liquid mixture Also, since the normal boiling points of the two compounds lie within 10°C. of each other, it can be understood why distillation under reduced pressure failed to separate them.

The dark brown resinous portion of the oxidation product which did not distil in steam was dissolved in methyl alcohol. A solution of potassium hydroxide in the same solvent was added, and the whole heated, under a reflux, on the water-bath for half-an-hour. The caustic potash was then neutralised by passing in carbon dioxide as the solution cooled. When neutralisation was complete, the hydrolysed product was extracted with ether. The ethereal solution was dried, and the ether distilled off. A few c.c's of a dark brown, very viscid liquid remained. It was found to dissolve by being stirred up with boiling water. The aqueous solution was boiled with animal charcoal and filtered. The filtrate was saturated with ammonium sulphate and repeatedly extracted with ether. The extracts were dried and the ether distilled off. The residue was a clear, water-white, very viscid liquid. Fractional distillation of this liquid was attempted, but it was found that it readily decomposed. This pointed, if anything, to a high hydroxyl content. A little of the substance was dissolved in a small volume of benzene, cooled in a freezing mixture, and stirred with a glass rod. No crystals were obtained. A negative result, under similar conditions, was also obtained with ether, light petroleum, chloroform, carbon tetrachloride, carbon disulphide, ethyl acetate, acetone, and pyridine. On attempting to prepare a p-nitrobenzoate, a very small quantity of crystals was obtained, and these, after purification, showed a melting point ranging from 50° C. to 70° C. The ester was, therefore, evidently a mixture, either of p-nitrobenzoates of different substances, or else different p-nitrobenzoates of the same substance. The crystals were not amenable to fractional recrystallisation from hot methyl alcohol. The total yield of this compound was entirely used up in the foregoing experiments, and no further work on its constitution could be carried out. From a review of the general properties of this compound it seems probable that it is identical with the 2:8:9-trihydroxymenthane described by Wallach, and Tiemann and Semmler. The arguments in favour of this view have already been set out (p. 22.).

In the oxidation with chromyl chloride, 120gms of β-pinene were used. In the oxidation with hydrogen peroxide, 150gms. of β-pinene were used. The total weight of β-pinene used in these experiments was, therefore, 270gms.

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