XLVII.—*Indian Turpentine from* Pinus longifolia, *Roxb. Part V. The Oxidation of* d-Δ^3-*Carene with Beckmann's Chromic Acid Mixture.*

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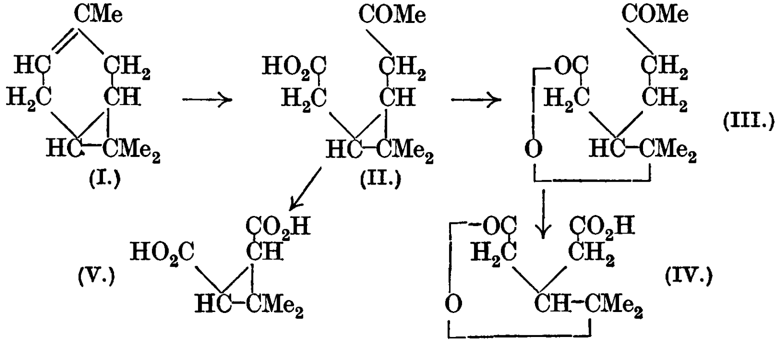
ALTHOUGH the identification of terpenes may in many cases be readily effected by the preparation of crystalline derivatives (nitrosochlorides, nitrosates, etc.), when complex mixtures are under examination these frequently fail to separate. Recently Henry and Paget (J., 1921, **119**, 1714; 1923, **123**, 1878; 1928, 70) have commenced a detailed study of the oxidation of monocyclic terpenes with Beckmann's chromic acid mixture and the results which they have obtained are of more than ordinary interest in that they would appear to afford a new and valuable method for the analysis of terpene mixtures. Before judgment, however, can be passed on the general diagnostic value of the method the investigation of dicyclic terpenes is essential (compare Fittig and Krafft, *Annalen*, 1884, **208**, 71) and with Dr. Henry's consent we have now studied the action of this reagent on *d*-Δ^3-carene.

The oxidation of this hydrocarbon with potassium permanganate (J., 1920, **117**, 576; 1921, **119**, 550) and ozone (Semmler and von Schiller, *Ber.*, 1927, **60**, 1591) has resulted mainly in the formation of acids containing the *cyclo*propane ring, but with the Beckmann reagent, owing doubtless to its strongly acidic properties, the oxidation proceeds in two directions, *l*-*trans*-caronic acid (V) and terpenylic acid (IV) being produced in relatively large yield and *d*-homoterpenyl methyl ketone (III), terebic acid, *cis*-caronic acid, and dimethylmalonic acid in small quantities.



The isolation of *d*-homoterpenyl methyl ketone proves that the oxidation proceeds in accordance with the scheme set forth above, the primary product being the keto-acid (II), the *cis*-modification of which was prepared by Semmler and von Schiller (*loc. cit.*). By hydration and fission of the *cyclo*propane ring this would lead to homoterpenyl methyl ketone and its degradation products terpenylic and terebic acids; on the other hand, direct oxidation without fission would yield caronic acid (V). The separation, however, of *l*-*trans*-caronic acid was unexpected and the possible significance of this is discussed below. The intermediate formation of the keto-acid (II) is not without interest, since it provides corroborative evidence that the mechanism of the oxidation of the hydrocarbon with potassium permanganate suggested previously (*loc. cit.*, p. 551) is correct and eliminates definitely the possibility of the ethylenic group occupying the Δ^2-position.

In the case of α-pinene the direct oxidation products (pinonic acid, etc.) possess the *cis*-configuration and from analogy it might be expected that the same would apply in the case of Δ^3-carene. This would appear to be all the more probable since a consideration of a model of the formula of the hydrocarbon shows the *cis*-configuration to be the one involving the least strain. If this be the case, the keto-acid (II) would be expected to be the *cis*-acid and should lead on further oxidation to *cis*-caronic acid. Our experiments have, however, shown that *cis*-caronic acid is formed only in minimal quantity, whilst *l*-*trans*-caronic acid is obtained in a large yield. This can only be accounted for in one of two ways : (i) that the hydrocarbon and the keto-acid derived therefrom have the *trans*-configuration or (ii) that, although the *cis*-keto-acid is first formed, the configuration of the acid is the less stable one and that either prior to or during the oxidation it passes into the more stable *trans*-form. The rearrangement, if such it be, must take place before oxidation to the caronic acid stage, since the acid obtained is optically active. We incline to the view that the hydrocarbon has the *cis*-configuration and that the *trans*-caronic acid results from either the *cis*-keto-acid or *cis*-homocaronic acid, the *trans*-configuration of either the one or the other of these acids being the more stable form under the conditions of the experiment. We do not consider that we should be justified in arguing that the formation of *l*-*trans*-caronic acid implied a *trans*-configuration for the terpene, an assumption which would only be justified, as Professor Lapworth (private communication) has pointed out, if we could definitely prove that the *cis*-configurations of all the possible intermediate products were under the conditions of the experiment the most stable configurations.

Although *trans*-caronic acid can now be prepared with comparative ease, so far as we are aware it has not been resolved, and therefore we have no criteria as to the optical purity of the acid obtained. It is clearly a mixture of the *l*-acid with the *dl*-acid, since the observed rotatory power is much lower than that of a specimen obtained by Staudinger and Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 206) by the oxidation of chrysanthemum dicarboxylic acid. These authors found that the m. p. (210°) of the *lævo*-acid was almost identical with that of the racemic acid (213°) : our acid has m. p. 202°. An attempt to increase the optical purity by crystallisation of the strychnine salt was unsuccessful. The diastereoisomeric strychnine salts have apparently almost equal solubilities and possibly the strychnine salt of the *dl*-*trans*-caronic acid is a partial racemate. It would be interesting to carry out the resolution of *dl*-*trans*-caronic acid with a view to the construction of the equilibrium diagram of the *d*- and *l*-isomerides.

These experiments show that the method of Henry and Paget may be used as an aid in the analysis of mixtures of dicyclic terpenes. The formation of homoterpenyl methyl ketone and terpenylic acid would be of no diagnostic value, since they can originate equally well from pinene, but the production of caronic acid would definitely prove the presence of Δ^3-carene. At present it is impossible to say whether Δ^4-carene would behave similarly, but it is hoped to examine the oxidation of this rare hydrocarbon under similar conditions.

In view of the somewhat ready fission of the *cyclo*propane ring during the course of these experiments it seemed desirable to study once more the action of sulphuric acid on Δ^3-carene. It was important to investigate this, since, if either limonene or terpineol resulted, the formation of some of the oxidation products would be readily explained. Previous experiments (*loc. cit.*, p. 574) had shown that Δ^3-carene was not attacked by aqueous sulphuric acid (5%) at 100° and we therefore examined the action of this acid in acetic acid solution. Under the conditions given on p. 310 the main product formed was a *diterpene* together with a small amount of a mixture of monocyclic terpenes and a trace of *l*-borneol. The last probably owes its formation to the presence of a little pinene or camphene in the Δ^3-carene used. The diterpene did not yield any crystalline derivatives and therefore its constitution and its relationship to other known diterpenes remain undetermined. The monocyclic terpene also remained unidentified, since it did not yield any crystalline derivatives.*

EXPERIMENTAL.

A mixture of the Beckmann reagent (1500 c.c.) and *d*-Δ^3-carene (75 c.c.) was shaken mechanically for 6 days, the bottles being periodically opened to release the pressure due to the generation of carbon dioxide. The unattacked hydrocarbon (identified as Δ^3-carene) was separated, and the aqueous solution extracted with ether in a constant-extraction apparatus. The ethereal extract was washed with sodium carbonate solution (A) to remove the acidic products of the oxidation, dried over sodium sulphate, and evaporated. The small quantity of a viscid oil that remained was distilled under diminished pressure (18 mm.), the main fraction passing over at 200—210° (yield, 3 g. from 220 c.c. of the terpene). The oil was mixed with an excess of semicarbazide acetate and the *semicarbazone*, which separated immediately, was collected, washed with ether to remove adhering oil, and recrystallised from water con-

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* We desire to take this opportunity of correcting a mis-statement in a paper by Mulany and Watson (*J. Ind. Chem. Soc.*, 1926, **3**, 258) that Indian turpentine contains very little pinene. The total distillate from the oleoresin from *P. longifolia* contains approximately 30% of α- and β-pinenes, an observation amply confirmed by the very careful experiments of Dupont (*Ann. Chim.*, 1924, **1**, 244), who found that the oil contained 2·8% of α-pinene and 9·7% of β-pinene. Mulany and Watson would appear to have worked with an abnormal oil.

taining a little alcohol; it then separated in aggregates of irregular prisms, decomp. 195—196° (Found: C, 54·9; H, 7·9. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9%). The rotatory power was determined in alcoholic solution at 20°: $c = 0{\cdot}1998$, $l = 4$, $\alpha_{5461} = +0{\cdot}40°$, whence $[\alpha]_{5461} = +49{\cdot}9°$.

The semicarbazone, which was insoluble in sodium carbonate solution, was hydrolysed by warming with dilute sulphuric acid (5%), and the *d*-homoterpenyl methyl ketone thus formed extracted with ether. After removal of the solvent the residual oil rapidly solidified and then crystallised from water in radiating needles, m. p. 42—43° (Found: C, 64·9; H, 8·7. Calc.: C, 65·2; H, 8·7%). The rotatory power was observed in aqueous solution at 20°: $c = 0{\cdot}4902$, $l = 4$, $\alpha_{5461} = +1{\cdot}09°$, whence $[\alpha]_{5461} = +55{\cdot}7°$. The identity of this ketone with *d*-homoterpenyl methyl ketone was confirmed by its oxidation to terpenylic acid by Wallach's method (*Annalen*, 1893, **277**, 118). The acid, after crystallisation from water, melted at 57°, and at 88—89° after drying over sulphuric acid.

The sodium carbonate solution (A) was concentrated in a current of carbon dioxide, extracted twice with ether to remove any neutral oil, acidified, and repeatedly extracted with ether. The dried ethereal extract on evaporation yielded an oil which partly crystallised. The solid acid (10 g.) was collected, washed with ether to remove liquid acids (B), and purified by crystallisation from hot water, from which it separated in glistening prisms which melted not quite sharply at 201—202°. This m. p. was not altered by recrystallisation from water or by purification through the ammonium salt. The identity with *l-trans*-caronic acid was proved by analysis (Found: C, 52·9; H, 6·4; *M*, 159·1. Calc.: C, 53·2; H, 6·3%; *M*, 158) and by its conversion into *cis*-caronic acid, m. p. 174°, which was unchanged on admixture with an authentic specimen. The rotatory power was determined in alcoholic solution at 20°: $c = 1{\cdot}9054$, $l = 4$, $\alpha_{5461} = -0{\cdot}94°$, whence $[\alpha]_{5461} = -12{\cdot}3°$. For reasons which have already been given, a portion of the acid was converted into the strychnine salt, which crystallised from water, in which it was somewhat readily soluble, in long needles. The m. p. and the rotatory power of the acid regenerated from the crystalline strychnine salt and from the strychnine salt remaining in the mother-liquor were identical with each other and with the above ($[\alpha]_{5461}$ $-11{\cdot}4°$ and $-12{\cdot}46°$ respectively).

The liquid acids (B) (30 g.), from which the *l-trans*-caronic acid had been separated, were heated with an equal volume of acetyl chloride on the water-bath for some hours. The excess of acid chloride was removed and after the addition of ether the well-cooled solution was washed with dilute sodium carbonate solution (C) and dried and the ether evaporated. The residual oil (7 g.) was esterified with alcohol and sulphuric acid, and the ester distilled under diminished pressure (10 mm.); the main fraction (3 g.) passed over at 140—160°. This was hydrolysed with methyl-alcoholic potassium hydroxide solution and, after removal of the alcohol, the acidified solution was extracted with ether. Removal of the solvent left a thick oil which partly crystallised. After draining on porous porcelain, the solid acid was recrystallised from water and was identified as *cis*-caronic acid, m. p. 174°, both alone and after admixture with an authentic specimen. The higher- and lower-boiling fractions of the ester gave on hydrolysis oils which showed no tendency to crystallise and were not further examined.

The sodium carbonate solution (C), after concentration in a current of carbon dioxide, was acidified and extracted with ether. The liquid acid obtained was esterified, and the ester repeatedly fractionated under diminished pressure (16 mm.); ultimately three fractions were obtained, (i) below 140°, (ii) 140—155°, and (iii) 155—173°. Fraction (i) (3 g.) on hydrolysis with methyl-alcoholic potassium hydroxide solution gave a liquid acid smelling strongly of a lower fatty acid (? *iso*butyric acid) which on long keeping deposited crystals. After draining on porous porcelain and crystallising from a little water, the acid was found to decompose at 185°, and further crystallisation from benzene raised this to 188—190°. This acid was dimethylmalonic acid (Found : M, 131·8; calc., 132).

Fraction (ii) (4 g.) gave on hydrolysis a small amount of a crystalline acid which after purification from water had m. p. 173—174° and was identified as terebic acid by the method of mixed m. p.

Fraction (iii) (15 g.) boiled at 168—173°/16 mm. on redistillation and when cooled in a freezing mixture crystallised in needles, m. p. 37—38°. This was identified as ethyl terpenylate by hydrolysis to the acid, which after crystallisation from water had m. p. 57°, the m. p. rising after dehydration over sulphuric acid to 90°. The composition was confirmed by titration with cold and hot alkali (Found : M, 187, 189·1; calc., 190).

Action of Sulphuric Acid on d-Δ^3-*Carene*.—A mixture of the hydrocarbon (100 g.), acetic acid (250 g.), and sulphuric acid (50%; 10 g.) was heated at 60° (thermostat) for 4 hours. The solution, at first homogeneous, gradually separated into two layers. After cooling, the acid was removed by the addition of sodium carbonate, the oil separated, mixed with an excess of alcoholic potassium hydroxide solution, and heated on the water-bath for 3 hours. After the addition of water, the oil was again separated, dried over potassium carbonate, and repeatedly fractionated under diminished pressure; ultimately the following fractions were obtained, (i) below 120°/100 mm., (ii) 120—140°/100 mm., (iii) 180—185°/15 mm., (iv) above 185°/15 mm.

Fraction (iii), which was the main product of the reaction, distilled at 175°/10 mm. and its analysis corresponded to that of a *diterpene* (Found: C, 87·6; H, 11·7. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%). When freshly distilled over sodium, the diterpene is a colourless, very viscid oil with a somewhat unpleasant smell; it rapidly becomes yellow on exposure to the air. In chloroform solution, bromine is absorbed with evolution of hydrogen bromide. Dissolved in acetic acid, a drop of sulphuric acid produces a deep red coloration which slowly changes to violet and finally to a dirty brown. The following constants were observed: $d_{30^\circ}^{30^\circ}$ 0·9309, n_D^{30} 1·5168, $[\alpha]_{5461}^{20^\circ}$ + 5·69°.

Fraction (iv), which was a viscid oil with no definite boiling point, was not further examined.

Fractions (i) and (ii) were systematically fractionated at the ordinary pressure (755 mm.). The main fraction distilled at 174—176° and after distillation over sodium had $d_{20^\circ}^{20^\circ}$ 0·8500, $n_D^{20^\circ}$ 1·4750, $[\alpha]_{5461}^{20^\circ}$ − 6·5°. Treatment with bromine in either acetic acid or amyl-alcoholic solution gave an oil, and no crystalline nitrosate or nitrosite was obtained. The hydrochloride (b. p. about 115°/15 mm.) did not crystallise when cooled. In acetic anhydride solution the liquid gave no colour with sulphuric acid, showing the absence of sylvestrene. With the material available, further experiments were not possible, but neither *m*- nor *p*-cymene appeared to be present in appreciable quantity.

After removal of the terpene a small fraction, b. p. 195—205°/755 mm., was obtained which partly crystallised on keeping. The solid was collected (3 g. from 300 g. of terpene), drained on porous porcelain, and recrystallised from dilute alcohol; it then separated in glistening plates, m. p. 204—205° (sealed tube). It was identified as *l*-borneol ($c = 1·218$ in alcohol, $l = 4$, $\alpha = - 1·31°$, whence $[\alpha]_{5461}^{20^\circ} = - 26·9°$) by the preparation of the *p*-nitrobenzoyl derivative, m. p. 136—137° (compare Henderson and Heilbron, P., 1913, **29**, 381).

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