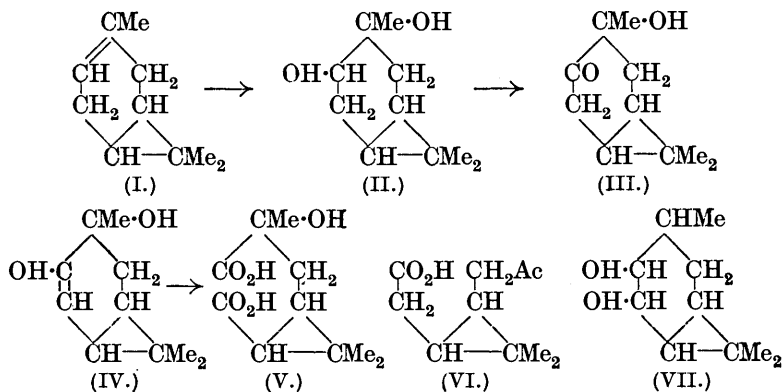


LIII.—*The Constituents of Indian Turpentine from Pinus longifolia, Roxb. Part IV.*

By P. PARAMESWARAN PILLAY and JOHN LIONEL SIMONSEN.

IN Part II of this series (J., 1923, 123, 550) attention was directed to the fact that, although the oxidation of *d*- Δ^4 -carene with potassium permanganate in acetone solution proceeded smoothly with formation of *d*-1:1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acid, the oxidation of *d*- Δ^3 -carene (I) under analogous conditions did not yield the isomeric keto-acid, C₁₀H₁₆O₃ (VI), but proceeded in a more complex manner. The main products of the latter oxidation were two hydroxy-acids (V), the suggested mechanism of their formation being represented by the following scheme :



It appeared to us of interest to attempt (i) the preparation of the keto-acid (VI) and (ii) to determine whether the scheme outlined above actually represents the mechanism of the oxidation of the hydrocarbon.

The simplest method for the preparation of the keto-acid is the oxidation of the terpene with ozone and in preliminary experiments, made over 2 years ago, evidence of its formation was obtained. Unfortunately, owing to a breakdown in our apparatus,

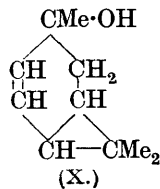
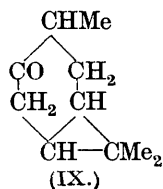
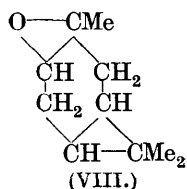
those experiments had to be temporarily abandoned and in the meantime Semmler (*Ber.*, 1927, **60**, 1591) has described the results of his experiments on the oxidation of Δ^3 -carene with this reagent and has rendered unnecessary a resumption of our work.

To solve the second part of our problem it was necessary to devise a convenient method for the preparation of the glycol (II). This substance is formed in small yield when d - Δ^3 -carene is oxidised with potassium permanganate in alkaline solution (J., 1920, **117**, 576), but the process is quite unsuited to its preparation in quantity. A good yield of a glycol was obtained by using hydrogen peroxide; although in the case of pinene fission of the dicyclic structure occurs (Henderson and collaborators, J., 1912, **101**, 2288 *et seq.*), the main product from d - Δ^3 -carene is carene glycol. The glycol, however, is not identical with the one previously described. When anhydrous, it has m. p. 90—91° and is optically inactive both in ethyl-alcoholic and in chloroform solution, whereas the latter has m. p. 69—70° and in chloroform solution $[\alpha]_D + 16.05^\circ$. The glycols may represent *cis*- and *trans*-modifications; optical isomerism, however, is not impossible, since two new asymmetric centres are formed in the oxidation. In the absence of definite evidence, we propose to call the glycol of m. p. 69—70°, d -carene- α -glycol and that of m. p. 90—91°, d -carene- β -glycol.

(The prefix “ d ” is retained, since the β -glycol yields optically active derivatives and the optical inactivity is therefore only “apparent.”)

d -Carene- β -glycol is stable to potassium permanganate in cold acetone and is only very slowly attacked on warming. Attempts to oxidise it to the hydroxy-ketone (III) were unsuccessful. It contains, however, a secondary alcohol group, since, when heated with phthalic anhydride at 110° for some hours, it yields an *acid phthalate*. The formation of this monoacid phthalate furnishes strong evidence against the glycol having formula (VII) (compare *loc. cit.*, p. 551).

When the glycol is treated with dilute sulphuric acid it yields a mixture of *p*-cymene and an oil, b. p. 152°/100 mm., which is strongly laevorotatory. This oil appears to be 1-carene oxide (VIII) and although it was not obtained quite pure (see p. 363) there can be little doubt as to its constitution, since when it is heated with phthalic anhydride to 160° it yields the β -glycol acid phthalate.



The formation of the oxide in this way was somewhat unexpected, since it was anticipated, in view of the instability of *cyclohexene* oxide (Brunel, *Compt. rend.*, 1903, 137, 62), that either the isomeric ketone (IX) or the unsaturated alcohol (X) would be formed. Evidence of the formation of the ketone (IX) was, however, obtained, since the impure oxide in contact with semicarbazide acetate for some months gave a *semicarbazone*, $C_{11}H_{19}ON_3$; the quantity obtained was insufficient for the isolation of the ketone. The oxide is remarkably stable and does not undergo hydration even when shaken with sulphuric acid for some days. This stability is probably connected with the dicyclic structure containing the *gem*-dimethyl group, the marked influence of this group on ring formation having been frequently commented upon, especially by Ingold and Thorpe.

In addition to *d*-carene- β -glycol, an oil having the same composition was separated from the oxidation products of *d*- Δ^3 -carene. This oil was slightly levorotatory in chloroform solution and gave on treatment with dilute sulphuric acid, in addition to *p*-cymene, an oil consisting essentially of *l*-carene oxide. The liquid glycol was therefore probably a mixture of stereoisomerides.

l-Carene oxide is much more readily attacked by potassium permanganate in acetone solution than the glycol. The product of the reaction is a complex mixture of acids showing no tendency to crystallise. From the mixture a small quantity of a keto-acid, $C_9H_{14}O_3$, was separated in the form of its well-crystallised *semicarbazone*, m. p. 165—166°. This semicarbazone was not identical with either of the two semicarbazones of 1:1-dimethyl-2- β -ketopropyl-*cyclopropane*-2-carboxylic acid previously described (*loc. cit.*, p. 559), but since the semicarbazone can exist in twelve isomeric forms, this is not remarkable. The quantity of semicarbazone available was insufficient to allow of a detailed examination of the keto-acid, but the presence of the $CO\cdot CH_3$ group was proved by the formation of bromoform when the keto-acid was oxidised with sodium hypobromite solution.

Some preliminary experiments have been made on the action of hypochlorous acid on *d*- Δ^3 -carene: the reaction does not proceed smoothly and the products tend to decompose on attempted purification.

EXPERIMENTAL.

Oxidation of d- Δ^3 -Carene with Hydrogen Peroxide. *d*-Carene- β -glycol.—A mixture of the hydrocarbon (1 mol.), dissolved in twice its volume of acetic acid, and hydrogen peroxide (30%; 2 mols.) was kept at 40° for some days and finally at 60° until the oxidation was complete (about 148 hours). The yellowish-brown solution

was distilled in steam to remove volatile products (acetic acid and unchanged hydrocarbon), the residue, which deposited a viscid oil on cooling, was repeatedly extracted with ether, the ethereal extracts were washed with sodium carbonate solution until free from acid (A), and the ether was evaporated. The residual oil was digested with an aqueous-alcoholic solution of potassium hydroxide * to hydrolyse any acetyl derivative present and, after addition of water, the solution was extracted with ether. From the dried ethereal extract, a viscid, brown oil was obtained which gradually crystallised in the ice-chest after addition of water. The *d-carene-β-glycol* thus obtained was washed with light petroleum (b. p. 40—60°) drained on porous porcelain to remove adhering oil (the filtrate, B, was reserved) and crystallised from much water, separating in flat prisms, frequently twinned; from light petroleum it crystallised in feathery prisms. It was readily soluble in hot water, methyl alcohol, ethyl alcohol, and benzene, and more sparingly soluble in cold water and light petroleum. The air-dried product had m. p. 75°; after drying in a vacuum over phosphoric acid, it was anhydrous and had m. p. 90—91° and b. p. 147—150°/18 mm. (Found for air-dried material: loss on drying over P₂O₅, 9.0. C₁₀H₁₈O₂.H₂O requires H₂O, 9.5%. Found for anhydrous material: C, 70.4; H, 10.9. C₁₀H₁₈O₂ requires C, 70.6; H, 10.6%). The glycol was optically inactive in ethyl-alcoholic and in chloroform solutions. When treated with chromic acid in acetic acid solution, it underwent complete degradation and did not appear to yield a trace of the hydroxy-ketone; it was not attacked by hydrogen peroxide in the presence of ferrous sulphate (compare Fenton, J., 1896, 69, 224).

The *hydrogen phthalate*, obtained by treating the glycol with phthalic anhydride at 110°, crystallised from dilute methyl alcohol in glistening prisms, m. p. 191—192° (Found: C, 67.7; H, 7.3. C₁₈H₂₂O₅ requires C, 67.9; H, 6.9%).

The filtrate (B) from which *d-carene-β-glycol* had been removed was distilled under diminished pressure; the main fraction passed over at 150—160°/29 mm., leaving a considerable resinous residue. On addition of a little water to the distillate and keeping in the ice-chest, a further quantity of the *β-glycol* crystallised. This was removed, and the filtrate redistilled; it then passed over at 155—157°/28 mm. This oil had the composition of the glycol (Found: C, 70.3; H, 10.8. Calc.: C, 70.6; H, 10.6%) and was optically active in chloroform, $\alpha_D = -0.69^\circ$ ($c = 6.942$). When treated with dilute sulphuric acid under the conditions described below, it yielded *l-carene oxide* and *p-cymene*.

* The alkaline solution contained a small quantity of a phenol which was not examined.

The sodium carbonate solution (A) gave on acidification a mixture of acids which, after conversion into their ethyl esters, distilled irregularly from 90—180°/10 mm, and no homogeneous acid could be isolated.

l-Carene Oxide.—The glycol (60 g.) was mixed with sulphuric acid (5%; 200 c.c.) and heated on the water-bath for 48 hours; steam was passed through the solution, the volatile oil extracted with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure (100 mm.), the following fractions being obtained; (i) 110—120° (10.5 g.), (ii) 120—140° (3 g.), (iii) 140—160° (13 g.), (iv) above 160° (5 g.).

Fraction (i) was distilled over sodium and then had b. p. 170—170.5°/685 mm., D_{30}^{30} 0.8627, and n_D^{30} 1.4869. These figures indicated that the hydrocarbon consisted essentially of *p*-cymene and this was confirmed by analysis (Found: C, 88.9; H, 10.7. Calc.: C, 89.6; H, 10.4%) and by oxidation to *p*- α -hydroxyisopropylbenzoic acid, m. p. 156—157°. Fraction (iii) on redistillation boiled at 150—160°/100 mm. and a portion, b. p. 152°/100 mm., was analysed (Found: C, 79.2; H, 10.5. $C_{10}H_{16}O$ requires C, 79.0; H, 10.5%). This fraction, which had a pleasant smell reminiscent of linalool, was evidently not quite homogeneous, as was shown by the determination of the constants of two fractions: (a) b. p. 150—153°/99 mm., D_{30}^{30} 0.961, n_D^{30} 1.4740, (b) b. p. 155—159°/99 mm., D_{30}^{30} 0.9794, n_D^{30} 1.4768, $[\alpha]_D^{30}$ — 39.16°. There can be no doubt that this substance consisted essentially of *l-carene oxide*; it did not react with the usual ketonic reagents, although, when it was kept for some months with semicarbazide acetate, a small amount of a *semicarbazone* gradually separated. It crystallised from methyl alcohol in lustrous plates, m. p. 193—193.5°, and was probably the semicarbazone of the ketone (IX) (Found: C, 63.1; H, 9.4; N, 20.4. $C_{11}H_{19}ON_3$ requires C, 63.1; H, 9.1; N, 20.1%). When the oxide was heated for 6 hours at 160° with phthalic anhydride, *d-carene*- β -glycol acid phthalate was obtained in excellent yield. It had m. p. 191° and was identical in every way with the phthalate described above. The oxide was stable to bromine in chloroform solution, and to dilute sulphuric acid at the ordinary temperature.

Oxidation of l-carene oxide. The oxide (10 g.) was dissolved in acetone (100 c.c.) and to the solution, well cooled in ice, finely powdered and sieved potassium permanganate (27.7 g.) was added gradually, oxidation being complete in about 7 hours. The manganese dioxide sludge was collected, washed with acetone, and then repeatedly extracted with boiling water. The brown, aqueous extract was concentrated in a current of carbon dioxide, acidified,

and repeatedly extracted with ether, the viscid oil remaining on removal of the solvent was esterified in the usual manner, and the esters were distilled under diminished pressure. The main fraction, b. p. 140—160°/46 mm., was hydrolysed with methyl-alcoholic potassium hydroxide solution; the acid, isolated in the usual manner, was then obtained as a viscid oil. It was dissolved in a slight excess of ammonia and the solution was treated with calcium chloride and boiled; a small quantity of a sparingly soluble resinous salt then separated. This was removed, the solution acidified, and the acid extracted with ether. The pale yellow oil which remained on removal of the solvent yielded on treatment with semicarbazide acetate a *semicarbazone* (0.9 g.) which, after repeated crystallisation from hot water, was obtained in well-formed prisms, decomp. 165—166° (Found: C, 53.1; H, 7.9. $C_{10}H_{17}O_3N_3$ requires C, 52.9; H, 7.5%). On hydrolysis with dilute sulphuric acid, the keto-acid was obtained as a viscid oil which showed no tendency to crystallise; when it was dissolved in sodium hydroxide solution and treated with sodium hypobromite, bromoform was precipitated, but the dibasic acid formed was insufficient in quantity for examination.

Action of Hypochlorous Acid on d- Δ^3 -Carene.—After a large number of experiments, the method briefly described below was found to be the only one to give satisfactory results.

The hydrocarbon (1 mol.) was mixed with freshly prepared sodium hypochlorite solution (2 mols.), and after the addition of an excess of boric acid the mixture was shaken mechanically until free from hypochlorous acid. The reaction product was separated by ether and purified by distillation under diminished pressure (10 mm.); two fractions were separated, (a) b. p. 90—93°, (b) 110—113°.

Fraction (a), which had D_{30}^{20} 1.0123 and n_D^{20} 1.4992, was the pure monochlorohydrin (Found: Cl, 18.5. $C_{10}H_{17}OCl$ requires Cl, 18.8%). *Hydroxychlorocarane* was a colourless oil with a fairly pungent smell. It was an extremely stable substance and was unaltered on treatment with silver oxide at the ordinary temperature. Attempts to prepare crystalline derivatives were unsuccessful.

Fraction (b), D_{30}^{20} 1.0821, n_D^{20} 1.5060, consisted of somewhat impure dichlorodihydroxymethylisopropylcyclohexane (Found: Cl, 25.5. $C_{10}H_{18}O_2Cl_2$ requires Cl, 29.5%). It was a viscid oil which yielded no crystalline derivatives and was probably a mixture of isomerides derived from 1-methyl-4-isopropyl- and 1-methyl-3-isopropyl-cyclohexane.