245. *The Constitution of Copæne.*

By Lindsay H. Briggs and William I. Taylor.

The constitution of copæne has been elucidated on the basis of the following sequence of reactions. Perbenzoic acid yields the oxide, converted by methylmagnesium iodide into the corresponding methylcarbinol which after dehydration and dehydrogenation furnishes the known compound, 1 : 6 : 7-trimethyl-4-*iso*propylnaphthalene.

The tricyclic sesquiterpene copæne is a comparatively rare constituent of essential oils, and so far it has only been detected in the oils of *Oxystigma mannii* (Schimmel's Report, 1914, April, p. 48), *Sindora wallichii* (Henderson, McNab, and Robertson, *J.*, 1926, 3077), *S. inermis* (Huzita, *J. Chem. Soc. Japan*, 1941, **62**, 431), *Dysoxylum fraseranum* (Penfold, *J. Proc. Roy. Soc. New South Wales*, 1928, **61**, 337) and *Cedrela toona* (Pillai and Rao, *J. Soc. Chem. Ind.*, 1931, **50**, 220T). More recently it has been identified by Briggs and Sutherland (forthcoming publication) in the oil of the New Zealand tree, *Phyllocladus trichomanoides*, the source for the present investigation.

From the molecular refraction, the formation of a dihydro-derivative, and the oxidation by ozone or potassium permanganate to a monobasic ketonic acid, copæne ketonic acid, $C_{15}H_{24}O_3$, copæne was shown by Semmler and Stenzel (*Ber.*, 1914, **47**, 2555) to be tricyclic with one ethylene linkage. Since it also gave *l*-cadinene dihydrochloride with hydrogen chloride it must contain the cadinene skeleton and a *cyclo*propane ring, later confirmed by Henderson *et al.* (*loc. cit.*) by dehydrogenation with sulphur to cadalene. By further oxidation of copæne ketonic acid with sodium hypobromite, Semmler and Stenzel obtained a dibasic acid, copæne-dicarboxylic acid, $C_{12}H_{18}O_4$ (*vide infra*), apparently by the elimination of an *iso*propyl group. The provisional formula (I) suggested by Semmler and Stenzel was changed to (II) by Henderson *et al.* in view of the structure (III) proposed by Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, **7**, 84) for cadinene.

(I.)   (II.)   (III.)   or   (IV.)
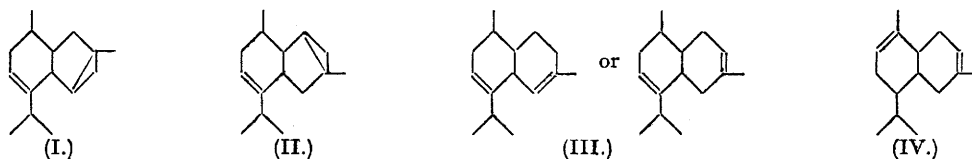
In view of the revised structure for cadinene (IV) put forward on a firm experimental basis by Campbell and Soffer (*J. Amer. Chem. Soc.*, 1942, **64**, 417) that of copæne also required revision.

The position of the double bond at C_6–C_7 in copæne has now been established by the method used by Ruzicka and Sternbach (*Helv. Chim. Acta*, 1940, **23**, 124) for determining the position of the double bond in *d*-pimaric acid and applied by Campbell and Soffer (*loc. cit.*) and Soffer, Steinhardt, Turner, and Stebbins (*J. Amer. Chem. Soc.*, 1944, **66**, 1520) for the constitution of cadinene and *iso*zingiberene respectively.

Copæne was converted quantitatively into the oxide by the action of perbenzoic acid. On distillation in high vacuum, however, three fractions were obtained, indicating that some isomerisation to the ketone or fission of the *cyclo*propane ring had occurred. Since the isomeric ketone should give the same product ultimately as the oxide, the combined distillate was treated with excess of methylmagnesium iodide and the resultant methylcarbinol dehydrated with formic acid. Dehydrogenation with palladised charcoal failed to yield an aromatic hydrocarbon, but this was formed with selenium. The dehydrogenation products, after being washed with alkali, were distilled, small fractions being taken off empirically and converted into picrates. From two fractions the picrate of 1 : 6 : 7-trimethyl-4-*iso*propylnaphthalene was obtained after repeated crystallisation, the purest specimen having m. p. 121—122°. Campbell and Soffer (*loc. cit.*) record m. p. 122—123° for their synthetic material. The double bond in copæne must therefore be in the 6—7 position.

From the alkaline washings of the dehydrogenation product a crystalline *naphthol*, $C_{15}H_{18}O$, was obtained (picrate, trinitrobenzoate) which is probably the previously unknown 7-hydroxy-1 : 6-dimethyl-4-*iso*propylnaphthalene arising from the dehydrogenation of unmethylated copæne oxide or the isomeric ketone. We hope to report later on this compound.

Since copæne forms *l*-cadinene dihydrochloride with hydrogen chloride, the three-membered ring must have one point of attachment at C_1 and the other at C_3 (V) or C_{10} (VI). If the latter, then dehydrogenation should yield an azulene as well as cadalene as in the case of ledene

(Komppa and Nyman, *Compt. rend. Trav. Lab. Carlsberg*, 1938, **22**, 272) or azulene alone as in aromadendrene (Radcliffe and Short, *J.*, 1938, 1200). Since no trace of azulene is obtained from copæne the three membered ring must be at C_1–C_3 and copæne must be formulated as (V).

(V.)   (VI.)   (VII.)   (VIII.)   (IX.)
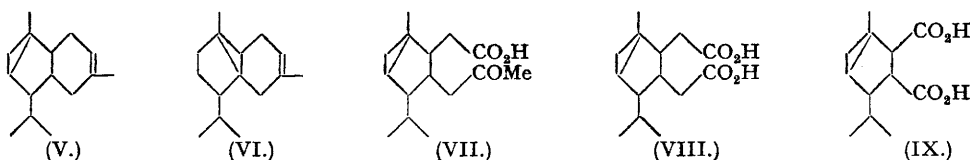
The copæne ketonic acid, $C_{15}H_{24}O_3$, of Semmler and Stenzel must now be revised to (VII), and the dibasic acid, copænedicarboxylic acid, obtained on sodium hypobromite oxidation, is more probably the normal product (VIII), $C_{14}H_{22}O_4$, rather than (IX) $C_{12}H_{18}O_4$, with which, however, the analytical figures agree.

EXPERIMENTAL.

The copæne used in these experiments was repeatedly fractionated, finally through a 20 plate column, and then had the following constants : b. p. 114—114·5°/10 mm. ; $d_4^{25°}$ 0·9055 (constant) ; $n_D^{25°}$ 1·4880—1·4895 ; $[a]_D^{13·5°}$ − 0·44° to + 1·20° ; it had been identified by Briggs and Sutherland (*loc. cit.*) by the formation of *l*-cadinene dihydrochloride with hydrogen chloride, dehydrogenation to cadalene with palladised charcoal, and oxidation to copæne ketonic acid, characterised as the semicarbazone, m. p. 222°, and the semicarbazone of its methyl ester, m. p. 194—196°.

Copæne Oxide.—A solution of copæne (11·1 g.) in chloroform (200 c.c.) was added to a twofold excess of perbenzoic acid in chloroform (300 c.c.) at 6° and left overnight. Titration of an aliquot portion against standard thiosulphate solution after addition of potassium iodide then showed that reaction was complete. The chloroform solution, after being washed with sodium carbonate and sodium thiosulphate solutions, yielded a viscous colourless oil (11·9 g.), separated by distillation into the following fractions : (1) b. p. 112—120°/0·5 mm., 4·09 g. ; (2) b. p. 95—105°/0·03 mm., 2·24 g. ; (3) b. p. 127—130°/0·05 mm., 1·37 g.

Methylation and Dehydration.—The combined fractions (7·3 g.) in dry ether (30 c.c.) were slowly added to an ethereal solution of methylmagnesium iodide (3 molal excess), and after the first action had ceased the mixture was refluxed for 30 hours. After decomposition with saturated ammonium chloride solution the reaction mixture was extracted with ether, and the extract, after being washed with brine containing sodium carbonate, then with water, and dried (Na_2SO_4), yielded on distillation of the ether a syrupy product (6·43 g.) in 82% yield. This was boiled under reflux with formic acid (15 c.c.) for 15 minutes and, after addition of water, the product was isolated through light petroleum ; yield 5·97 g.

Dehydrogenation.—The dehydrated oil (1·43 g.) and selenium (2·08 g.) were heated slowly to 200° until water ceased to be evolved, the temperature was then maintained at 220° for 16 hours and at 300° for a further 9 hours. The product was extracted with light petroleum, and the solution washed with sodium hydroxide solution and water, and dried ; after removal of the solvent 0·864 g. of a slightly fluorescent oil was obtained. On distillation at 10 mm. (bath temperature 120°) five fractions were obtained weighing successively 0·2286 g., 0·0987 g., 0·0736 g., 0·1466 g., and 0·0411 g., leaving 0·2090 g. of a residual black tar. The first three fractions failed to yield a pure picrate. From the fourth fraction a crude red picrate (200 mg.) was obtained, m. p. 95°, which after six crystallisations from methyl alcohol furnished 8 mg. of long needles of constant m. p. 121—122° (Found : C, 60·10 ; H, 5·47 ; N, 9·35. Calc. for $C_{16}H_{20},C_6H_3O_7N_3$: C, 59·85 ; H, 5·25 ; N, 9·52%). From the mother liquors of the fourth fraction a small amount of impure cadalene picrate, m. p. 110—111°, was isolated which on being mixed with an authentic specimen softened at 100° and melted at 109—112°. The fifth fraction yielded the impure picrate of 1 : 6 : 7-trimethyl-4-*iso*propylnaphthalene, m. p. 117—118°, undepressed by a pure specimen obtained from the fourth fraction.

From the alkaline washings of the dehydrogenation product a crude *naphthol* was obtained on acidification and purified by sublimation at 100°/0·01 mm. ; yield 30 mg. The product recrystallised from methyl alcohol as woolly needles, m. p. 116° (Found : C, 83·54, 83·58 ; H, 8·50, 8·66. $C_{13}H_{18}O$ requires C, 84·05 ; H, 8·46%). The dark red picrate separated from methyl alcohol in short needles, m. p. 139°, and the bright red trinitrobenzoate similarly in long needles, m. p. 139—140°.

The analyses are by Drs. Weiler and Strauss, Oxford.

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