CXVIII.—*The Oxidation of* d-Δ^4-*Carene with Beckmann's Chromic Acid Mixture.*

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For the identification of *d*-Δ^4-carene in essential oils the only satisfactory method at present available consists in the oxidation of the appropriate fraction of the oil with potassium permanganate in acetone solution; *d*-1 : 1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid is then obtained, which can be characterised by the preparation of the semicarbazone, m. p. 182—183° (J., 1922, **121**, 2295). Although this method enabled Semmler and von Schiller (*Ber.*, 1927, **60**, 1591) to establish the presence of the hydrocarbon in various oils and so confirm the conclusion previously reached by Rao and Simonsen (J., 1925, **127**, 2494) that sylvestrene does not occur in nature, it has the inherent defect that, unless great care is taken to remove all traces of α-pinene, the keto-acid is liable to be contaminated with pinonic acid, which would render difficult the purification of the semicarbazone.

d-Δ^4-Carene, on oxidation with Beckmann's chromic acid mixture (compare this vol., p. 305), behaves in a similar manner to the Δ^3-isomeride. As the quantity of the terpene available for oxidation was limited, a complete investigation of the products formed in the reaction was not possible, but *l*-*trans*-caronic acid was isolated in excellent yield and it had the same m. p. and rotatory power as that described previously. The fact that the rotatory power was identical with that of the acid obtained from *d*-Δ^3-carene is of particular interest and enhances the desirability of the resolution of *dl*-*trans*-caronic acid into its optical enantiomorphs being undertaken.

EXPERIMENTAL.

The oxidation of the hydrocarbon, which had been separated from the oil from *Andropogon Jwarancusa* and carefully purified by distillation over sodium, was carried out under the conditions given previously (*loc. cit.*, p. 398) and proceeded much more rapidly and completely than in the case of *d*-Δ^3-carene. The *l*-*trans*-caronic acid obtained (3 g. from 50 c.c. of the terpene), after crystallising from water, had m. p. 202—203° (Found : C, 53·2 ; H, 6·7. Calc. : C, 53·2 ; H, 6·3%). The rotatory power was determined in alcoholic solution at 20° : $c = 2{\cdot}215$, $l = 4$, $\alpha_{5461} = -1{\cdot}05°$, whence $[\alpha]_{5461} = -11{\cdot}85°$. The identity of the acid was confirmed by its conversion into *cis*-caronic acid in the usual manner. From the original aqueous filtrate, by extraction with ether, a further quantity of *l*-*trans*-caronic acid (1·8 g.) was separated, and in addition terebic acid, m. p. 173—174° (alone and in admixture with an authentic specimen) and dimethylmalonic acid, decomp. 185—186° (Found : *M*, 138·8. Calc. : *M*, 138), were isolated.

A neutral oil, yielding a semicarbazone, m. p. 205—207°, was obtained, but the quantity was insufficient for analysis and identification.

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