Thunbergene[1)], *a Macrocyclic Diterpene**

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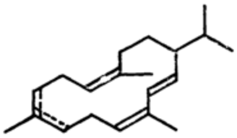
Thunbergene, $C_{20}H_{32}$, m. p. 61°C, $[\alpha]_D$ (benzene) +260°, is a monocyclic diterpene hydrocarbon obtained from several kinds of pine roots. Isolation and some properties of this compound were reported previously by one of the authors (S. A.)[2)] and by some other investigators[3-5)].

This communication comprises the results of the dehydrogenation and of the ozonolysis of thunbergene, the most probable structure of this interesting compound being proposed.

The dehydrogenation of thunbergene with selenium gave 7-isopropyl-2, 9-dimethylphenanthrene, m. p. 78°C, the picrate melting at 133°C[6)] (Found: C, 91.90; H, 8.19. Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12%). The structure of the dehydrogenation product was assigned on the basis of the spectroscopic data[7,8)] UV λ_{max}^{hexane} 224, 249, 257, 274, 281, 288, 299, 319, 328 and 335 mμ, log ε 4.44, 4.84, 5.00, 4.41, 4.37, 4.19, 4.08, 2.46, 2.40 and 2.45. NMR (in carbon tetrachloride solution with water as an external reference) δ −3.5, −2.5, 3.0 and 4.0 p. p. m., relative intensities 2, 5, 6 and 6 respectively), and was confirmed by infrared spectra and mixed melting point test with an authentic sample synthesized by the standard method from eudalene.

The ozonization at low temperature followed by the oxidative decomposition gave levulinic acid (semicarbazone, m. p. 184°C) and 2-isopropyl-5-oxohexanoic acid, $[\alpha]_D$ ($CHCl_3$) −30° (semicarbazone, m. p. 138∼140°C[9)]. Found: C, 52.30; H, 8.55; N, 18.14. Calcd. for $C_{10}H_{19}\cdot O_3N_3$: C, 52.38; H, 8.35; N, 18.33%). The latter was identified by infrared spectral comparison with a racemic authentic sample. Other fragments on ozonolysis have not been determined yet. As known already, thunbergene has a conjugated diene system which does not undergo the Diels-Alder's addition (UV λ_{max}^{hexane} 240 and 246 mμ, log ε 4.15 both) and octahydrothunbergene is optically inactive. Therefore, the carbon skeleton of thunbergene together with the positions of four double bonds can be reconstructed as shown below with an assistance of the isoprene rule.



According to this formula, thunbergene is hydrogenated to a mixture of eight stereoisomers of octahydrothunbergene; four symmetric isomers and two pairs of enantiomers. The product should be optically inactive as a whole even if the asymmetric center** of thunbergene would be retained.

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1) The old name "*d*-Thumbelen" proposed by one of the authors (S. A.) is revised according to the kind suggestion of Professor H. Erdtman, The Royal Institute of Technology, Stockholm, Sweden.

2) S. Akiyoshi, *Rep. Osaka Ind. Res. Inst.*, **17**, No. 10 (1937).

3) Y. Sebe, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **56**, 1118 (1935).

4) H. Wienhaus, *Nord. Kemistmötet*, (1926) 211; *Chem. Abstr.*, **24**, 1635 (1930).

5) a) A. J. Haagen-Smit, T. H. Wang and N. T. Mirov, *J. Am. Pharm. Assoc.*, **40**, 557 (1951); b) N. T. Mirov and P. M. Iloff, Jr., ibid., **44**, 424 (1955); c) P. M. Iloff, Jr. and N. T. Mirov, ibid., **45**, 77 (1956).

6) This phenanthrene seems to be identical with C_{20}-phenanthrene reported by Sebe, Ref. 3.

7) a) E. Heilbronner, H. U. Däniker and Pl. A. Plattner, *Helv. Chim. Acta*, **32**, 1723 (1949); b) T. Sugasawa, *Chem. Pharm. Bull.* (*Tokyo*), **9**, 889 (1961).

8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance" McGraw-Hill, Inc., New York (1959), p. 247.

9) O. Wallach, *Ann.*, **379**, 182 (1911).

** *Added in proof.*

The absolute configuration at the asymmetric center: (−)-2-isopropyl-5-oxohexanoic acid was oxidized with hypobromite to 2-isopropylglutaric acid, m. p. 94°C, $[\alpha]_D$ −20°, the absolute configuration of which had been confirmed by Fredga (*Acta Chem. Scand.*, **1**, 371 (1947)).

Since the asymmetric center is not affected in the course of degradation, the isopropyl group of thunbergene seems to project up ward from the plane of paper when the ring framework being placed as shown above.

Thunbergene is a hydrocarbon with the fourteen membered macroring. This type of diterpene seems to be very rare. No example could be found in literature. Details will be presented elsewhere in the near future.

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