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THE STRUCTURE OF HIBAENE

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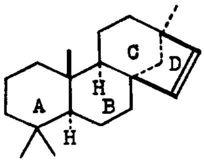
HIBAENE,[1] $C_{20}H_{32}$, m.p. 29.5-30°, molecular weight 272 from mass spectrum, $[\alpha]_D^{23}$ -49.9° (in $CHCl_3$), is a diterpene isolated from the essential oil of the leaves of Thujopsis dolabrata Sieb. et Zucc. It is shown to have structure (I) from the following evidence.

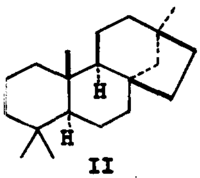


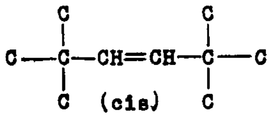
I

Hibaene absorbed one mole of hydrogen on catalytic reduction to give a saturated hydrocarbon, dihydrohibaene (II), m.p. 41.5-42.5°, and on peracid oxidation it afforded a monoepoxide, m.p. 70-71°; it is therefore a tetracarbocyclic.

The I.R. spectrum of hibaene shows absorption due to a gem-dimethyl (1385, 1363 cm^{-1}) and a cis-CH:CH- (750 cm^{-1}), and its NMR spectrum indicates the presence of four methyls (9.03, 9.15, 9.19, 9.27 τ; singlets),[2] and the group (III) (4.39, 4.64 τ; quartet; J=6.0 cps; typical AB type).

Selenium dehydrogenation of hibaene afforded pimanthrene (IV). Potassium permanganate oxidation of hibaene gave the dicarboxylic acid (V), ν_{max}^{KBr} 1710 cm^{-1}, which on being heated above 210°, or by treatment with acetic anhydride, easily formed an anhydride (VI), m.p. 253-254°, ν_{max}^{KBr} 1790, 1758 cm^{-1}. Selenium dehydrogenation of (V) gave (IV), therefore the double bond is contained in the D-ring. The dimethyl ester (VII), m.p. 144-145°, of the acid (V) resisted alkaline hydrolysis, and the anhydride (VI) remained unchanged when heated to 300°.

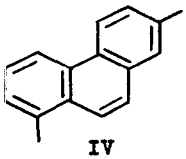

II

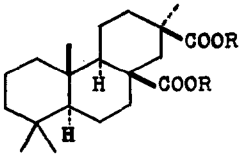


$$\mathrm{C-\underset{C}{\overset{C}{C}}-CH=CH-\underset{C}{\overset{C}{C}}-C}$$

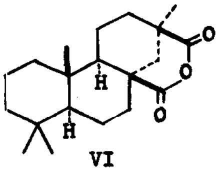
(cis)

III


IV

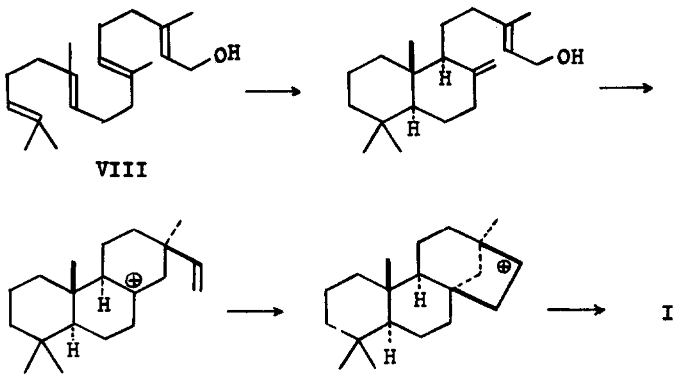


V ; R = H
VII ; R = Me



VI

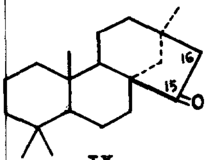
From a consideration of the biosynthetic mechanism[3] for the cyclization of geranylgeraniol (VIII), or an equivalent precursor, structure (I), or its enantiomer is thought to be the most probable structure for hibaene (Scheme 1).



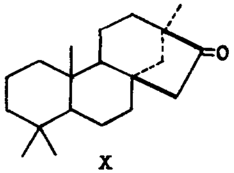
Scheme 1

Hydroboration of hibaene, followed by oxidation with dichromate, and separation of the products by alumina chromatography, afforded two ketones of different type; a polar ketone, m.p. 102-103°, $\nu_{max}^{CCl_4}$ 1736 cm^{-1}, which formed a 2,4-dinitrophenylhydrazone m.p. 231-231.5°, and on peracid oxidation yielded a lactone, m.p. 111-112°, ν_{max}^{KBr} 1713 cm^{-1}; and a less polar ketone, m.p. 88-89°, $\nu_{max}^{CCl_4}$ 1727 cm^{-1}, which was recovered unchanged in the above reactions. The unreactivity of this less polar ketone is attributed to its carbonyl group being subject to strong steric hindrance. It is considered that this steric hindrance would be most apparent when the C_{10}-angular methyl and the D-ring, which contains the carbonyl group, are on the same side of the molecule, and when the carbonyl group is at C_{15}. The less polar ketone and the polar ketone are therefore as depicted in (IX) and (X), or their enantiomers, respectively. The RD of the polar ketone ($[\alpha]_{318}$ +1528° $[\alpha]_{278}$ -1720°; in methanol),[4] is antipodal to that of isosteviol[5] (XI), so the absolute configuration of the C/D ring in the polar ketone can be shown as in (X).

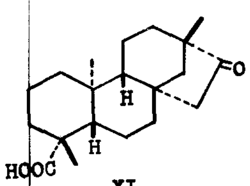
If (I) represents the absolute configuration of hibaene, then dihydrohibaene (II) should be an enantiomer of isostevane (XII)[6]. The I.R. and RD (300 to 700 mμ, specific rotation: 0°) of both these compound coincide, but a mixed melting point showed an apparent depression. The absolute configuration of hibaene is thus confirmed as (I).



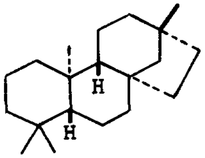
IX



X



XI



XII

We are grateful to Dr. Yoshio Sato of the National Institute of Health for the donation of a sample of isostevane.

REFERENCES

1. Satisfactory elemental analyses were obtained for all new compounds.

2. Assignment of the methyl signals will be reported in Bull. Chem. Soc. Japan, No. 5 (1964).

3. Cf. L. Ruzicka, Experientia 9, 357 (1953); Proc. Chem Soc., 1959, 341.

4. The RD of the less polar ketone (IX): $[\alpha]_{323}$ -2040°, $[\alpha]_{285}$ +2010° (in methanol).

5. C. Djerassi, R. Riniker, and B. Riniker, J. Am. Chem. Soc., 78, 6362 (1956); cf. C. Djerassi, P. Quitt, E. Mosettig, R.C. Cambie, P.S. Rutledge, and L.H. Briggs, ibid, 83, 3720 (1961).

6. E. Mossettig and W.R. Nes, J. Org. Chem., 20, 884, (1955).