

3 β ,22-DIHYDROXYHOPANE AND OTHER CONSTITUENTS FROM THE LEAVES OF *CASTANOPSIS EYREI* TUTCH. OF HONG KONG*

By H. R. ARTHUR† and PHYLLIS D. S. KO†

Castanopsis eyrei Tutch. (family Fagaceae) is a glabrous tree whose stalked leaves, 2–3 in. or rarely 4 in. long, are ovate-lanceolate, shining, green, and glabrous on both sides, and with always a few coarse serratures. It is indigenous to Hong Kong. Friedelin, friedelan-3 β -ol, β -sitosterol, 22-hydroxyhopan-3-one (hydroxyhopanone), and 3 β ,22-dihydroxyhopane have been isolated from the leaves of the plant. This dihydroxyhopane has not been reported to occur naturally before but has been prepared^{1,2} from hydroxyhopanone. However, 3 β -acetoxy-22-hydroxyhopane has been isolated² from Dammar resin. Other dihydroxyhopanes are known but of these only 15 α ,22-dihydroxyhopane occurs naturally.^{3,4}

Experimental

Microanalyses were by the Microanalytical Laboratory, University of Singapore, and agreed with calculated values. Optical rotations are for chloroform solutions. Light petroleum had b.p. 60–80°. Alumina was B.D.H. preparative grade. The technique of gradient-elution was used for chromatography with solvents in the order of light petroleum, benzene, chloroform. The mixtures of these reported below are average values.

All compounds were identified by m.p. and mixed m.p. with authentic samples. The i.r. spectra of all compounds were found to be identical with those of authentic specimens.

Extraction and Isolation of Products

Milled air-dried leaves (7 kg) were extracted at room temperature twice with light petroleum (2 \times 22 l.). The combined extracts were distilled and the residue (100 g) was dissolved in light petroleum (3 l.) and applied to a column of alumina. Elution with petroleum–benzene (7 : 3) gave friedelin (1.65 g), m.p. 262–264°, $[\alpha]_D -21.5^\circ$ (c, 0.40); with petroleum–benzene (1 : 1) gave friedelan-3 β -ol (0.9 g), m.p. 289–290°, $[\alpha]_D +25.1^\circ$ (c, 0.64); with benzene–chloroform (9 : 1) gave β -sitosterol (0.25 g), m.p. 139°, $[\alpha]_D -36.9^\circ$ (c, 0.68); with benzene–chloroform (7 : 3) gave 22-hydroxyhopan-3-one (0.04 g), m.p. 250–254°, $[\alpha]_D +62.9^\circ$ (c, 0.82); with benzene–chloroform (3 : 7) gave 3 β ,22-dihydroxyhopane (0.02 g), m.p. 285–286°, $[\alpha]_D +36.7^\circ$ (c, 0.52).

Identification of 3 β ,22-Dihydroxyhopane

Hydroxyhopanone (0.1 g) was boiled under reflux for 2 hr in a mixture of methanol (40 ml) and dioxan (4 ml) containing sodium borohydride (0.13 g). The solvent was distilled, the residue

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† Department of Chemistry, University of Hong Kong, Hong Kong.

¹ Dunston, W. J., Fazakerly, H., Halsall, T. G., and Jones, E. R. H., *Croat. chem. Acta*, 1957, **29**, 173.

² Cerny, J., Vystreil, A., and Huneck, S., *Chem. Ber.*, 1963, **96**, 3021.

³ Tsuda, Y., and Isobe, K., *Tetrahedron Lett.*, 1965, 3337.

⁴ Corbett, R. E., and Young, H., *J. chem. Soc. (C)*, 1966, 1564.

was acidified with dilute sulphuric acid, and the product so obtained was collected and dried. After recrystallization from chloroform-ethanol, 3 β ,22-dihydroxyhopane (0.08 g), m.p. 285-287°, $[\alpha]_D +40^\circ$ (c, 0.50), was obtained.

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