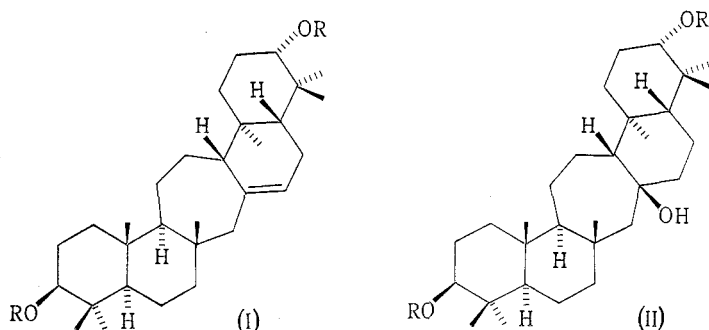


TRITERPENE CONSTITUENTS OF *LYCOPodium COMPLANATUM* L. FROM NEW GUINEA*

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Investigation of the triterpene constituents of certain *Lycopodium* species growing in Japan has resulted in the isolation of serratenediol (I; R = H), tohogenol (II; R = H) and several related triterpenes,¹⁻³ all of which have a new type of triterpene skeleton. *Lycopodium complanatum* L. from New Guinea has now been examined and the triterpene fraction shown to contain serratenediol and tohogenol, isolated as their diacetates^{4,5} after column chromatography and thin-layer chromatography of the crude acetate mixture.



Experimental

Melting points, which are uncorrected, were determined in open capillaries in a sulphuric acid/potassium sulphate (6 : 4) bath.

Extraction of the Crude Triterpenes

The plant was collected by T. G. Hartley at Edie Creek and a specimen is lodged at the Herbarium, Lae, under the number TGH12,608. Air-dried, comminuted whole plant (850 g) was extracted three times with hot methanol and the combined extracts evaporated under reduced pressure. The residue was dissolved in 5% methanolic KOH (300 ml) and heated on the water-bath for 5 hr. The cooled methanolic solution was poured into water and the precipitated solid collected by filtration with the aid of Celite. The precipitate was extracted (Soxhlet) successively with

* Manuscript received September 28, 1966.

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² Inubushi, Y., Tsuda, Y., Ishii, H., Hosokawa, M., Sano, T., and Harayama, T., *Yakugaku Zasshi*, 1964, **84**, 1108.

³ Inubushi, Y., Tsuda, Y., Sano, T., and Nakagawa, R., *Chem. pharm. Bull., Tokyo*, 1965, **13**, 104.

⁴ Inubushi, Y., Sano, T., and Tsuda, Y., *Tetrahedron Lett.*, 1964, 1303; Tsuda, Y., Sano, T., Kawaguchi, K., and Inubushi, Y., *Tetrahedron Lett.*, 1964, 1279.

⁵ Inubushi, Y., Tsuda, Y., and Sano, T., *Chem. pharm. Bull., Tokyo*, 1965, **13**, 750.

(1) n-hexane, (2) chloroform, and (3) chloroform/methanol (1 : 1), each for 16 hr. After evaporation of solvents the residues from the three extracts were (1) 3.0 g, (2) 1.262 g, and (3) 0.245 g respectively.

Isolation of Triterpene Diacetates

The chloroform-soluble fraction (2) (1.262 g) was extracted with hot benzene, giving 1.015 g of benzene-soluble material which was acetylated by standing overnight with acetic anhydride (6 ml) and pyridine (10 ml). After working up in the usual manner the oily product (1.12 g) was dissolved in benzene and chromatographed on deactivated alumina (8 g) prepared by washing Merck basic alumina with 5% acetic acid followed by water, and drying at 100° for 64 hr. Evaporation of the benzene eluate gave 0.62 g solid, from which after several recrystallizations from methanol/chloroform was obtained 98 mg colourless crystals melting above 300°. Thin-layer chromatography on SiO_2 (Merck) showed two spots. The procedure was employed on a preparative scale using eight plates (SiO_2 ; 20 cm by 20 cm by 0.5 mm) with chloroform as solvent. The upper zone, extracted with chloroform, gave 61 mg crystalline material which on recrystallization from chloroform/methanol yielded serratenediol diacetate (prisms, 36 mg), m.p. and mixed m.p. with an authentic specimen 336–338°. The identity was confirmed by infrared spectra and thin-layer chromatograms. The lower zone, extracted with chloroform, yielded tohogenol diacetate (15 mg) after recrystallization from chloroform/methanol, m.p. and mixed m.p. with an authentic specimen 305–306°. The substance gave a negative tetranitromethane test and was identical with tohogenol diacetate in respect of infrared spectrum and thin-layer chromatographic behaviour.

Examination of other fractions did not yield any further crystalline material.