

## SOME CONSTITUENTS OF *DEGENERIA VITIENSIS* BAILEY & SMITH\*

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*Degeneria vitiensis* Bailey & Smith, a small tree confined to the Fiji Islands, is the sole member of the family Degeneraceae, which is thought to be most closely related to the Magnoliaceae, Winteraceae, and Himantandraceae.<sup>1</sup> Since the members (or member) of the latter family have yielded a large number of alkaloids of novel type,<sup>2</sup> it was of interest to examine *D. vitiensis*.

The entire material available, which consisted of a rather small amount of leaves and woody branchlets bearing bark, was extracted in one lot. The basic fractions were negligible but  $\beta$ -sitosterol (0.002%), and a paraffinic wax (0.005%), were separated from neutral fractions and 2-hydroxy-6-methoxybenzoic acid (0.001%) was obtained from acidic fractions. This acid has previously been isolated from plant sources but apparently occurs uncommonly.<sup>3</sup>

### Experimental

Melting points are uncorrected. The n.m.r. spectrum was measured on a Varian A60 spectrometer in deuterochloroform solution with tetramethylsilane as internal standard; the molecular weight was determined by an AEI MS9 mass spectrometer.

#### Extraction of the Plant Material

The dried milled material (1.4 kg) was extracted at room temperature with light petroleum (b.p. 40–60°), ether, and then methanol. The light petroleum and the ether extracts were concentrated and fractionated by extraction with 5% HCl, 5% NaHCO<sub>3</sub>, 2% Na<sub>2</sub>CO<sub>3</sub>, and 2% NaOH. An ether extract obtained by shaking the concentrated methanol extract with water and ether was treated in a similar fashion.

The very small, dark basic fractions yielded no individual substance; materials in the Na<sub>2</sub>CO<sub>3</sub> and NaOH extracts were also small and intractable.

The acidic products in the NaHCO<sub>3</sub> extracts were combined and chromatographed on silica gel. Elution with 3% ether-benzene gave a solid fraction which crystallized from light petroleum in nearly colourless needles (0.016 g), m.p. 137–138°;  $\nu_{\max}$  (Nujol) 3145, 1692 cm<sup>-1</sup>; mol. wt., 168 (calc. for C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>, 168); n.m.r. spectrum: two 1-H singlets at  $\delta$  12.15 and 11.0, both exchangeable with D<sub>2</sub>O (OH and COOH); 3-H multiplet at  $\delta$  7.6–6.4 (3  $\times$  Ar-H); 3-H singlet at  $\delta$  4.07 (OCH<sub>3</sub>). The melting point was undepressed on admixture with synthetic 2-hydroxy-6-methoxybenzoic acid of m.p. 137–138° and the i.r. spectra of the two samples were identical.

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<sup>1</sup> Willis, J. C., "A Dictionary of the Flowering Plants and Ferns." 7th Edn, p. 336. (The University Press: Cambridge 1966.)

<sup>2</sup> Mander, L. N., Prager, R. H., Rasmussen, M., Ritchie, E., and Taylor, W. C., *Aust. J. Chem.*, 1967, **20**, 1705, and preceding papers.

<sup>3</sup> Karrer, W., "Konstitution und Vorkommung der organischen Pflanzenstoffe." p. 361. (Birkhäuser: Basle 1958.)

The light petroleum neutral fraction was chromatographed in benzene on alumina. Material in the benzene eluates after recrystallization from ethyl acetate gave colourless crystals (0.04 g), m.p. 62–64°, which had an i.r. spectrum identical with that of paraffin wax. Elution with ether yielded  $\beta$ -sitosterol (0.03 g), m.p. 134–136°, after recrystallization from methanol; it was identified by mixed m.p., and comparison of i.r. spectra. The ether neutral extract similarly afforded a paraffin wax (0.03 g), but the methanol neutral extract was intractable.

*Preparation of 2-Hydroxy-6-methoxybenzoic Acid*

2-Methylresorcinol was converted into 2,6-dihydroxybenzoic acid by the methylation, oxidation, and demethylation procedures of Cartwright, Jones, and Marmion.<sup>4</sup> Further steps were as follows: The acid (1.6 g) in dry ether (100 ml) was treated gradually with ethereal diazomethane until the yellow colour of the reagent persisted for a few minutes. The ether was evaporated and the residue on recrystallization from methanol gave the ester (1.2 g), m.p. 69–71° (lit.<sup>5</sup> 69–71°).

A mixture of the ester (1.1 g), dimethyl sulphate (0.85 g), dry K<sub>2</sub>CO<sub>3</sub> (1.4 g), and anhydrous acetone (6.5 ml) was stirred and refluxed for 2 hr. The solvent was evaporated and the residue shaken with ether and water. The ethereal solution was extracted three times with 2N NaOH and the product, a brown oil (0.8 g), recovered from the aqueous layers in the usual way.

The oil was saponified with hot aqueous methanolic KOH under nitrogen. Water was added and the mixture was shaken with ether. Addition of conc. HCl to the aqueous layer followed by cooling in ice gave a cream precipitate which on crystallization from ethanol afforded pure 2-hydroxy-6-methoxybenzoic acid (0.2 g), m.p. 137–138° (lit.<sup>5</sup> 136–138°), identical with the natural product.

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<sup>4</sup> Cartwright, N. J., Jones, J. I., and Marmion, D., *J. chem. Soc.*, 1952, 3499.

<sup>5</sup> Doyle, F. P., Hardy, K., Naylor, J. H. C., Soulal, M. J., Stove, E. R., and Waddington, H. R. J., *J. chem. Soc.*, 1962, 1453.