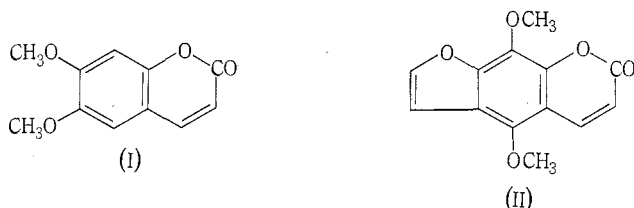


IDENTIFICATION OF COUMARINS ISOLATED FROM *LEPINIOPSIS TERNATENSIS* (APOCYNACEAE), *PTEROCAULON SPHACELATUM* (COMPOSITAE), AND *MELICOPE MELANOPHLOIA* (RUTACEAE)*

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In the course of investigations aimed primarily at the isolation of alkaloid constituents, simple coumarins of known structure have been obtained from three unrelated species. These isolations are recorded as they may be of some chemotaxonomic interest, although precise yields cannot be quoted because of the extraction procedures followed.

A major constituent from *Pterocaulon sphacelatum* B. & H., a Queensland species of the family Compositae, has been identified as 6,7-dimethoxycoumarin (I). The genus *Pterocaulon* of the family Compositae has received little chemical attention.



Melicope melanophloia C. T. White has been found to contain negligible amounts of alkaloids, but a neutral constituent has been identified as isopimpinellin (II). Isopimpinellin has been isolated previously from other rutaceous species such as *Luvunga scandens* Ham.,¹ *Citrus aurantifolia* Swingle,² and *Flindersia bennettiana* F. Muell.³

Leaves and bark of *Lepiniopsis ternatensis* Val. (Apocynaceae), a New Guinea species, afforded a high yield of unsubstituted coumarin. The occurrence of coumarin in this family is not unprecedented, as it has been reported to occur in the leaves of *Macrosiphonia velame* M.-Arg.⁴ and in the leaves and bark of *Alyxia stellata* Roem. & Schult.⁵

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¹ Späth, E., Bose, P. K., Schmid, H., Dobrovolny, E., and Mookerjee, A., *Ber. dt. chem. Ges.*, 1940, **73**, 1361.

² Caldwell, A. G., and Jones, E. R. H., *J. chem. Soc.*, 1945, 540.

³ Galbraith, M. N., Ritchie, E., and Taylor, W. C., *Aust. J. Chem.*, 1960, **13**, 427.

⁴ Peckolt, T., *Ber. deut. pharm. Ges.*, 1909, **19**, 537.

⁵ Greshoff, M., "Onderzoek naar de plantenstoffen van Nederlandsch-Indie." Meded. Buitenzorg's Lands Plantent., No. 25, Batavia 1898; cited by Hegnauer, R., "Chemotaxonomie der Pflanzen." Vol. 1, p. 30. (Birkhäuser: Basel 1964.)

Experimental

(i) Milled dried whole plants (1.5 kg) of *P. sphacelatum* collected at Inkerman in northern Queensland were extracted with methanol. From the portion of the concentrate not soluble in aqueous acid, a crystalline fraction (c. 2.0 g) was isolated by chromatography on alumina. Crystallization from benzene gave 6,7-dimethoxycoumarin as colourless needles, m.p. 145°. It was characterized by the identity of the mass spectrum with that published for 6,7-dimethoxycoumarin,⁶ by the presence of bands typical of a coumarin in the i.r. spectrum, and by the n.m.r. spectrum which showed two three-proton singlets at δ 3.90 and 3.93 (methoxyl groups), a pair of AB doublets (J 9.7 c/s) at δ 6.25 (H 3) and δ 7.63 (H 4), and two one-proton singlets at δ 6.79 and δ 6.86 (H 5, H 8).

(ii) *Melicope melanophloia*.—Milled bark (123 g) was extracted with boiling methanol and the extract concentrated to a small volume. This concentrate was extracted repeatedly with dilute hydrochloric acid to remove alkaloidal material, and the dark brown acid-insoluble residue (5.0 g) was dissolved in benzene and chromatographed on alumina. The fractions (2.8 g) eluted by benzene were combined, dissolved in benzene–light petroleum (1 : 1) and again chromatographed on alumina. The earlier fractions were not examined but a series of fractions eluted by benzene were combined and on crystallization from methanol gave isopimpinellin (150 mg) as faintly yellow needles, m.p. 149–150° (Found: C, 63.6; H, 4.2; OCH₃, 24.8. Calc. for C₁₃H₁₀O₅: C, 63.5; H, 4.1; 2 × OCH₃, 25.2%). The identity of the isopimpinellin was confirmed by comparison of its i.r., n.m.r., and mass spectra with those of authentic isopimpinellin, and by a mixed melting point determination.

(iii) Extraction of dried leaves of *Lepiniopsis ternatensis* Val. (20 kg) by the normal procedure⁷ for the extraction of alkaloids gave a crude "alkaloidal" fraction (80 g) which in fact contained little alkaloid, but became partly crystalline on standing. Chromatography of an 8-g portion of this fraction gave 3.0 g of crystalline coumarin, m.p. 70°. The i.r. spectrum was identical with that of authentic coumarin, and there was no depression of m.p. in a mixed m.p. determination. Extraction of the bark of *L. ternatensis* in the same manner gave a similar yield of coumarin, m.p. 70°.

⁶ Barnes, C. S., and Occolowitz, J. L., *Aust. J. Chem.*, 1964, **17**, 975.

⁷ Johns, S. R., Lamberton, J. A., and Sioumis, A. A., *Aust. J. Chem.*, 1966, **19**, 2331.