

## THE ALKALOIDS OF *MELODORUM PUNCTULATUM* (ANNONACEAE)

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*Melodorum punctulatum* Baill. (Annonaceae) is a small rain-forest tree endemic in New Caledonia. Although the family Annonaceae is well known as a source of aporphine and protoberberine alkaloids,<sup>1</sup> it appears that alkaloids have not previously been isolated from the genus *Melodorum*. The plant material was collected from Monts des Koghis in southern New Caledonia. Voucher specimens (P49 and P50) are preserved in the herbarium of the Office de la Recherche Scientifique et Technique Outre-Mer, Noumea, New Caledonia.

The known aporphine alkaloids, asimilobine<sup>2</sup> (0.005%) and michelalbine<sup>2,3</sup> (0.003%), and the known oxoaporphine alkaloid, liriodenine<sup>4-6</sup> (0.004%), have been isolated from a mixed sample of leaves and bark; the small quantity of plant material available and the relatively low abundance of alkaloids precluded the separate work-up of bark and leaves.

### Experimental

Milled, dried leaves and bark (4280 g) were extracted by percolation with Prollius solution<sup>7</sup> until the residue from the evaporation of a 50-ml extract gave only a faintly positive Mayer's test. The extraction was then completed by percolation with 20% acetic acid (10 l.).

The Prollius extract, concentrated below 40° under reduced pressure to 1.5 l., was mixed with glacial acetic acid (100 ml) and combined with the aqueous acid extract. Precipitated material was filtered, washed with 20% acetic acid and discarded, the washings being combined with the acid extract. This was made alkaline with ammonia and extracted with chloroform (1 × 2.4 l., 1 × 1.8 l.). Further purification of the basic material was achieved by a second acid extraction with 5% sulphuric acid (4 × 500 ml), from which 4 g crude alkaloids was recovered and applied to a chromatography column of silica gel. Liriodenine was eluted with chloroform, and a mixture of two alkaloids was eluted with chloroform containing 5–10% methanol. The n.m.r. spectrum of the mixture suggested that it consisted of asimilobine and michelalbine.

(i) *Liriodenine*.—Yellow needles from methanol, m.p. 276–277° (dec.). This compound had i.r. and u.v. spectra identical with those of an authentic sample obtained from *Atherosperma moschatum* Labill.,<sup>5,6</sup> and the melting point was undepressed on admixture with this sample.

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<sup>3</sup> Yang, T.-H., *Yakugaku Zasshi*, 1962, **82**, 811.

<sup>4</sup> Buchanan, M. A., and Dickey, E. E., *J. org. Chem.*, 1960, **25**, 1389.

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<sup>6</sup> Bick, I. R. C., and Douglas, G. K., *Tetrahedron Lett.*, 1964, 1629.

<sup>7</sup> Henry, T. A., in "Allan's Commercial Organic Analysis." 5th Edn, Vol. 7, p. 6. (Churchill: London 1929.)

(ii) *Asimilobine*.—This phenolic alkaloid was separated from michelalbine by extraction with 2% sodium hydroxide, but even after purification by preparative thin-layer chromatography (silica gel, 40% methanol in benzene), it did not crystallize until seeded with an authentic sample of asimilobine. It then crystallized as prisms, m.p. 178–179° (from acetone). N.m.r. and u.v. spectra were identical with those of an authentic sample from *Asimina triloba* Dunal,<sup>2</sup> and the melting point was undepressed on admixture with this sample.

(iii) *Michelalbine*.—Separated from asimilobine as indicated above, michelalbine was purified by preparative thin-layer chromatography (silica gel, 40% methanol in benzene) and crystallized as prisms, m.p. 198–200° (dec.) (from methanol). N.m.r. and u.v. spectra were identical with those of an authentic sample from *Asimina triloba* Dunal,<sup>2</sup> and the melting point was undepressed on admixture with this sample. The mass spectrum showed the molecular ion,  $m/e$  281, as base peak, with an intense peak at  $m/e$  280 caused by loss of hydrogen. Metastable peaks were present for the fragmentations  $m/e$  280  $\rightarrow$   $m/e$  262 and  $m/e$  281  $\rightarrow$   $m/e$  263 (loss of H<sub>2</sub>O in both cases) and for  $m/e$  281  $\rightarrow$   $m/e$  252 (loss of CH<sub>2</sub>=NH), the last process being characteristic of aporphine alkaloids containing the NH group.<sup>8</sup>

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<sup>8</sup> Ohashi, M., Wilson, J. M., Budzikiewicz, H., Shamma, M., Slusarchyk, W. A., and Djerassi, C., *J. Am. chem. Soc.*, 1963, **85**, 2807.