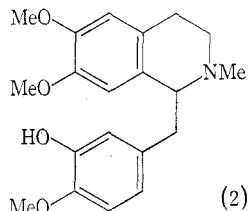
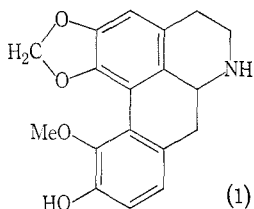


# ALKALOIDS FROM *HERNANDIA PAPUANA* (HERNANDIACEAE)

By F. N. LAHEY\* and K. F. MAK\*

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Two species of *Hernandia* belonging to the family Hernandiaceae, *H. bivalvis*<sup>1</sup> and *H. ovigera*,<sup>2-5</sup> have been studied recently and shown to be rich in aporphine alkaloids, several of which had not been reported previously in the literature. We now wish to report the results of our chemical investigation of a further species in the same genus, *Hernandia papuana*. From an alcoholic extract of the bark, we have isolated and identified hernangerine (1) which also occurs in *H. ovigera* and the benzyloquinoline alkaloid L-(+)-laudanidine (2).



We also isolated a yellow alkaloid which at the time was not recorded. It is only sparingly soluble in the common organic solvents and crystallized from ethyl alcohol as fine bright yellow needles, m.p. 298–300° (dec.). It is optically inactive, while its solution in chloroform gives a bright green fluorescence under ultraviolet light. On treatment with mineral acids, it develops a deep red colour. Elementary analysis indicated a composition  $C_{18}H_{19}O_5N$  suggestive of a highly unsaturated ring system. The molecular formula was confirmed by mass spectrometry† which showed the molecular ion peak ( $M^+$  319) as the base peak and no ready skeletal fragmentation consistent with a fully aromatic structure.

\* Department of Chemistry, University of Queensland, St. Lucia, Qld. 4067.

† We are grateful to Dr J. MacLeod of the Australian National University, Canberra, for measurement of the mass spectrum.

<sup>1</sup> Soh, K. S., Lahey, F. N., and Greenhalgh, R., *Tetrahedron Lett.*, 1966, 5279.

<sup>2</sup> Cava, M. P., Besso, K., Douglas, B., Markey, S., Raffan, R. F., and Weisbach, J. A., *Tetrahedron Lett.*, 1966, 1577.

<sup>3</sup> Cava, M. P., Besso, K., Douglas, B., Markey, S., and Weisbach, J. A., *Tetrahedron Lett.*, 1966, 4279.

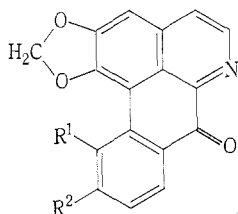
<sup>4</sup> Tomita, M., Lu, S. T., and Chen, Y. Y., *Yakugaku Zasshi*, 1966, **86**, 763–5 (*Chem. Abstr.*, 1967, **65**, 18635).

<sup>5</sup> Furukawa, H., and Lu, S. T., *Yakugaku Zasshi*, 1966, **86**, 1143 (*Chem. Abstr.*, 1967, **66**, 85909).

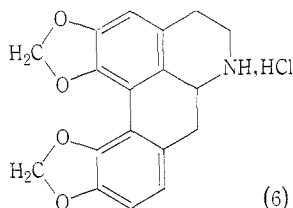
The ultraviolet spectrum showed  $\lambda_{\max}$  (ethanol) 226 ( $\log \epsilon$  4.58), 256sh (4.45), 264 (4.46), 365 (4.12), and 430 (4.07) nm.

The infrared spectrum exhibited no OH or NH absorption, but a strong band at  $1650\text{ cm}^{-1}$  indicative of a highly conjugated carbonyl group and bands at 1450, 1410, 1360, 1060, and  $960\text{ cm}^{-1}$  considered diagnostic for the methylenedioxy group.<sup>6</sup> The presence of a carbonyl group was further supported by the formation of an oxime which crystallized from ethanol as orange needles, m.p.  $264\text{--}265^\circ$  (dec.).

The complex ultraviolet and infrared spectra suggested an oxoaporphine type of chromophore as found in liriodenine (3).<sup>7,8</sup>



	$R^1$	$R^2$
(3)	H	H
(4)	MeO	MeO
(5)	$\text{OCH}_2\text{O}$	



The n.m.r. spectrum\* showed signals due to two unsplit methylenedioxy groups at  $\delta$  6.35 and 6.59 and five aromatic protons consisting of a one-proton singlet at  $\delta$  7.58 and two AB quartets centred at  $\delta$  7.24, 8.39 ( $J$  9 Hz) and at  $\delta$  8.42, 8.72 ( $J$  6 Hz), suggesting a 1,2,10,11-substitution pattern, confirmed by comparison with the spectra of 10,11-dimethoxy-1,2-methylenedioxy-7-oxodibenzo[de,g]quinoline (4) which we prepared from *o*-methylbulbocapnine by the method of Tomita *et al.*<sup>9</sup>

Zinc and sulphuric acid reduced the yellow alkaloid to a colourless aporphine characterized as its hydrochloride salt  $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}\cdot\text{HCl}$  identified as ovigerine hydrochloride by comparison (u.v., i.r., t.l.c.) with an authentic sample (6) kindly supplied by Professor M. P. Cava.

In a recent publication,<sup>10</sup> Ito and Furakawa reported a new oxoaporphine, hernandonine, with structure (5) from *Hernandia ovigera*. It is clear that our alkaloid is identical with hernandonine although a direct comparison has not been carried out.

\* The n.m.r. spectrum was measured on a Varian A60 spectrometer in  $\text{CF}_3\text{COOH}$  solution with tetramethylsilane as internal standard.

<sup>6</sup> Briggs, L. H., Colebrook, L. D., Fales, H. M., and Wildman, W. C., *Analyt. Chem.*, 1957, **29**, 604.

<sup>7</sup> Buchanan, M. A., and Dickey, E. E., *J. org. Chem.*, 1960, **25**, 1389.

<sup>8</sup> Taylor, W. I., *Tetrahedron Lett.*, 1961, 42.

<sup>9</sup> Tomita, M., Yang, T. H., Furakawa, H., and Yang, H. M., *Yakugaku Zasshi*, 1962, **82**, 1514.

<sup>10</sup> Ito, K., and Furakawa, H., *Tetrahedron Lett.*, 1970, 3023.