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STRUCTURE OF HERNANDONINE, A NEW OXOAPORPHINE ALKALOID FROM HERNANDIA OVIGERA L.

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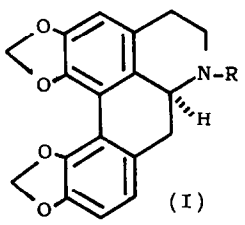
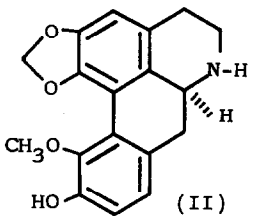
From the methanolic extract of the trunk-bark of Hernandia ovigera L. (Hernandiaceae) collected in Ogasawara island, we isolated a non-phenolic oxoaporphine alkaloid, hernandonine, in addition to the known aporphine alkaloids hernovine[1] (ovigerine[2])(I, R=H), hernangerine[3] (nandigerine[2])(II), and their N-methyl derivatives.

Hernandonine, sparingly soluble in common organic solvents, crystallized from chloroform solution in orange-yellow needles, m. p. $> 280^{\circ}$. The high resolution mass spectrometry confirmed the molecular formula as $C_{18}H_9O_5N$. Hernandonine showed a conjugated carbonyl group in the i. r. spectrum in nujol at 1650 cm^{-1}, and its u. v. spectrum in ethanol showed the following absorptions: λ max mμ (log ε): 222(4.55), 265(4.37), 3.64(4.03), and 426(3.99). Its n. m. r. spectrum in deuteriochloroform, in which all the nine protons were accounted for, revealed two methylenedioxy groups at δ 6.10 and 6.20. In the aromatic proton region of the spectrum of hernandonine, indicated a one-proton singlet at δ 7.07, and two AB-type quartets centered at δ 6.98, 8.21(J=8.5 Hz), and at δ 7.05, 8.80 (J=5.0 Hz). The mass spectrum of hernandonine exhibited the molecular ion peak at m/e 319 as the base peak.

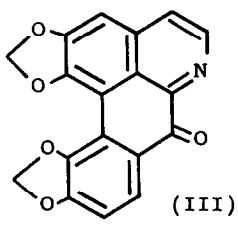
These data mentioned above, we suggested the structure III for hernandonine.



(I)



(II)



(III)

Chemical proof for the structure of this alkaloid was obtained by the synthesis of III from N-methylhernovine (I, R=CH_3) according to the method previously reported by Tomita et al.[4] Oxidation of N-methylhernovine(I, R=CH_3) with chromium trioxide in pyridine solution afforded, in 8 % yield, an aromatic oxoaporphine, 1,2,10,11-bismethylenedioxydibenzo [de, g] quinolin-7-one(III), m.p. $>280^{\circ}$, u. v. spectrum: λ max mμ (log ε): 222(4.53), 265(4.36), 364(4.00), and 426(4.06). The i. r. spectrum in nujol of this compound was identical with that of hernandonine.

Consequently, the structure of hernandonine is unambiguously assigned to the formula III.

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