Imenine, a Ring-B Substituted Aporphine Alkaloid

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Summary Imenine, the first B-ring-substituted aporphine alkaloid, has the structure 1,2,3,4-tetramethoxydibenzo-[*de, g*]quinazolin-7-one.

THE aporphines consist of a group of over ninety alkaloids having the condensed tetracyclic nucleus shown below. The known aporphines vary widely in their degree of unsaturation and particularly in their oxygenation pattern, oxygenated functions having been found at virtually all positions of rings A, C, or D but never in ring B.[1,2] We now report the isolation and structure determination of imenine (I), the first ring B-oxygenated aporphine.

The woody, climbing stems of the Amazonian vine *Abuta imene* (Menispermaceae) have been found to contain a complex mixture of highly coloured, weakly basic alkaloids. The most abundant of these is a new yellow, non-phenolic base, imenine, m.p. 206—207°, $C_{20}H_{17}NO_5$.‡ Mass spectrometry confirmed the molecular weight as 351. Imenine

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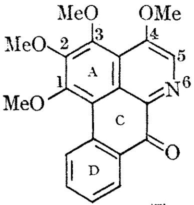
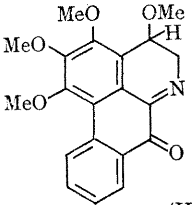
showed a conjugated carbonyl group in the i.r. spectrum at 1650 cm.$^{-1}$; its u.v. spectrum in ethanol showed the following absorption: λ_{max} (log ϵ) 240 (4·15), 275 (4·38), 345 (3·58), and 438 nm. (3·42). Its n.m.r. spectrum revealed only a complex multiplet of five aromatic protons and four clearly resolved aromatic methoxy-groups at δ 4·05, 4·10, 4·15, and 4·25. The aforementioned data strongly suggested that imenine was a tetramethoxy-keto-aporphine, although the complex n.m.r. pattern for its aromatic protons ruled out all conventional structure patterns.

Catalytic reduction of imenine (PtO_2) in methanol gave an initially colourless solution which became orange on contact with air and afforded the reddish-orange dihydroimenine, m.p. 205°, $C_{20}H_{19}NO_5$. The n.m.r. spectrum of dihydroimenine revealed in additon to three aromatic methoxy-groups at δ 4·09, 4·13, and 4·22, an aliphatic methoxy-group at δ 2·04, a feature in accord with the structure (II) for dihydroimenine.



(I)



(II)

The structure (I) for imenine was determined by *X*-ray analysis; this study represents the first crystallographic determination of a keto-aporphine structure. Imenine crystallizes in space group $P\bar{1}$ with lattice parameters $a = 9{\cdot}087$, $b = 8{\cdot}539$, $c = 11{\cdot}660$ Å, $\alpha = 111{\cdot}68°$, $\beta = 91{\cdot}41°$, $\gamma = 101{\cdot}17°$. Iterative application of the Sayre[3] equation by least-squares refinement yielded a conventional discrepancy factor of 0·068.

The protoberberine alkaloids berberastine[4] and thalidastine[5] are the only benzylisoquinoline-derived alkaloids of any kind other than imenine in which oxygenation has been observed in the B-ring of the original isoquinoline system.

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‡ Satisfactory analyses for (I) and (II) were obtained.

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