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YELLOW ALKALOIDS OF ATHEROSPERMA MOSCHATUM LABILL.

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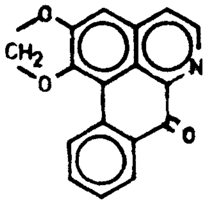
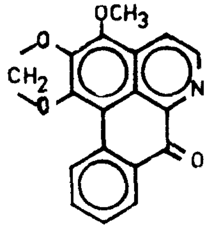
In the course of studies on the alkaloids of the Australian Monimiaceae, Bick, Clezy and Crow reported (1) the isolation of two yellow alkaloids from *Atherosperma moschatum* Labill, which they called atherospermidine and spermatheridine. These alkaloids were present in only very small amounts, along with small quantities of colourless alkaloids and large amounts of berbamine and isotetrandrine.

Spermatheridine has now been shown to be identical with liriodenine, a weak base isolated subsequently from *Liriodendron tulipifera L*. (2), and whose structure was shown to be I (5). Spectral measurements have allowed the structure II to be assigned to atherospermidine.

Spermatheridine crystallised from chloroform as yellow needles which melted with decomposition at 275-276°C., analyzed for $C_{17}H_9O_3N$, and gave a positive methylenedioxy group test (3). The infra-red spectrum indicated, in addition to the latter group (4), the presence of a highly conjugated carbonyl group. Spermatheridine and an authentic sample of liriodenine showed no melting point depression upon admixture. The infra-red spectra of the two compounds were identical, as were their ultra-violet spectra.



I



II

Atherospermidine also crystallised from chloroform as orange-yellow needles which melted at 275-276°C (decomp). It analyzed for $C_{17}H_{8}O_{3}N(OCH_{3})$ and contained a methylenedioxy group. Its ultra-violet spectrum was closely related to that of spermatheridine (Table I).

The free base showed infra-red absorptions attributable to a methylenedioxy group (4) and a highly conjugated ketone function (1657 cm^{-1}) ; it formed an oxime whose infra-red spectrum showed neither hydroxyl nor carbonyl absorptions (5). From these properties, atherospermidine was clearly a methoxyspermatheridine, and the position of the methoxy group was indicated by a comparison of their I.R. and P.M.R. spectra; the latter are summarised in Table II.

TABLE I.

Ultraviolet Absorption Spectra of Atherospermidine and Spermatheridine.

	In Ethanol		In 0.1 N HCl	
	λ_{max}		λ_{max}	
	mμ	logϵ	mμ	logϵ
Spermatheridine	247.5	4.23	256.5	4.33
	269	4.16	280	4.25
	302	3.70	334	3.70
Atherospermidine	247	4.38	262.2	4.24
	281	4.52	283	4.16
	312 (shoulder)	3.95		

TABLE II.

P.M.R. Spectra[*] of Atherospermidine and Spermathridine

		δ values	
Group	No. of protons	Spermatheridine	Atherospermidine
$-OCH_3$	3, singlet	----	4.55
$O-CH_2-O$	2, singlet	6.72	6.72
$C_7H(6)$	1, singlet	7.63	----
Remaining aromatic protons	6, (multiplet)	7.7 - 8.9	7.7 - 8.9

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[*] Measured in F_3CCO_2H at 60 Mc using $SiMe_4$ as internal reference.

Spermatheridine showed an absorption in the aromatic proton region (δ 7.63) of intensity one proton which was not present in the spectrum of atherospermidine. This fact can only be accounted for if the methoxyl group of the latter is at C_3.

Both spermatheridine and atherospermidine showed a strong band at 750 cm^{-1} in their infra-red spectra (due to C-H out-of-plane deformation of four adjacent aromatic protons (7)). However a medium band at 861 cm^{-1} in the spectrum of spermatheridine (C-H out-of-plane deformation of a single aromatic proton) was missing from that of atherospermidine.

Thus atherospermidine must be 1,2-methylene-dioxy-3-methoxyl-7-oxo-dibenzo (de,g) quinoline (II). Degradative and synthetic work is in hand to confirm this conclusion.

Addendum:

The alkaloid psilopine, recently isolated from an anonaceous plant, has been shown by Dr. T. A. Geissman (8) to have the same structure as that proposed for atherospermidine. A direct comparison of the two compounds has not yet been made.

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