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STRUCTURES OF MAHANIMBIN AND KOENIMBIN

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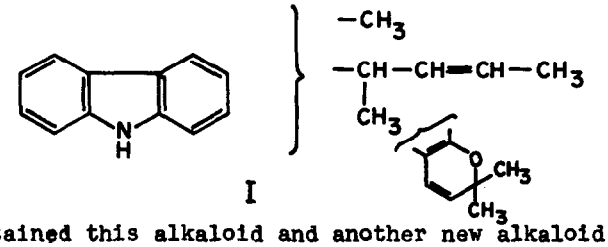
The alkaloid mahanimbin has been isolated from the stem bark of Murraya koenigii and has been alloted the part structure I.[1]



I

We have obtained this alkaloid and another new alkaloid, which we have named as koenimbin, from the petroleum-ether extract of the fruits of the plant and have determined the complete structure of both. Our structure for mahanimbin differs in considerable detail even from the part structure proposed for the molecule.

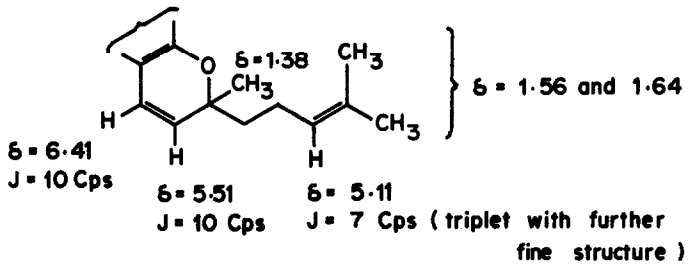
Mahanimbin*

Mahanimbin, $C_{23}H_{25}NO$, m.p. 94-95°, $[\alpha]_D$ + 52°, Mol.wt. (mass spectrum) 331, U.V: λ_{max} - 357, 343, 328, 315, 300, 288, 277 (log ϵ - 3.81, 3.87, 3.86, 3.78, 3.97, 4.68, 4.44), had a carbazole skeleton. It had two double bonds which could be stepwise reduced to the dihydro $C_{23}H_{27}NO$, m.p. 101°, and the tetrahydro $C_{23}H_{29}NO$, m.p. 108° derivatives. The UV of tetrahydromahanimbin, λ_{max} - 335, 305, 268, 260, 240 (log ϵ - 3.45, 4.12, 4.02, 4.27, 4.59), was markedly similar to that of 2-methoxy carbazole[2], which then placed the oxygen function at 2-position in a carbazole ring.

* All compounds reported here have satisfactory analytical and spectral data.

The PMR of mahanimbin revealed five aromatic protons. Two of these appeared at considerably lower fields, δ = 7.62 and 7.87 and were identified with the mutually deshielded 4 and 5-protons of the carbazole ring[3]. The 4-proton was essentially a singlet and indicated the absence of protons at 2 and 3-positions. The 5-proton, on the other hand, was a broad complex multiplet and clearly showed the presence of protons at 6,7 and 8-positions. The last three protons themselves appeared as a multiplet in the region δ = 7.05 to 7.35.

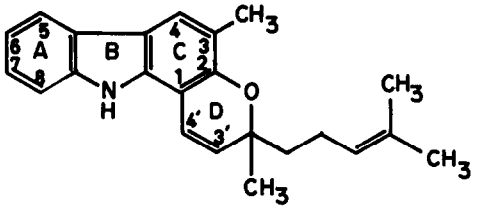
The PMR of mahanimbin further revealed the presence of an aromatic methyl group, δ = 2.3 and the structural feature II.



II

The feature II was further supported by the mass spectrum of the molecule, where fragments corresponding to loss of $-CH_3$ (15), $-CH_2-CH=CMe_2$ (69), $-CH_2-CH_2-CH=CMe_2$ (83) and $CH_3CO\ CH_2CH_2CH = CMe_2$ (126) units were observed.

Regarding the fusion of the C and D rings, it was observed that the 4'-proton in the pyran ring appeared at δ = 6.41, about 0.1 ppm downfield with respect to the analogous 4-proton (δ = 6.31) in chromene itself. Such shifts are indeed observed[4] when the chromene carried an oxygen function at 5-position, and in our case was explained by placing the carbazole nitrogen in a similar position. This then suggested structure III for the molecule, which was finally established by ozonolysis of mahanimbin, when a phenolic aldehyde, $C_{14}H_{11}NO_2$, m.p. 193-194°, was obtained whose UV spectrum λ_{max}-392, 352, 294, 287, 233 (log ϵ - 3.84, 3.72, 4.27, 4.26, 4.60), was in agreement with that of 1-formyl carbazole[5].

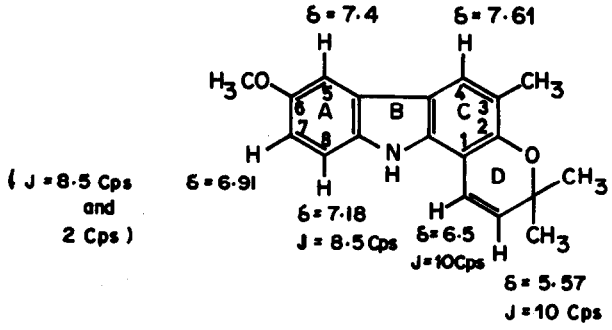


III

Koenimbin

Koenimbin, $C_{19}H_{19}NO_2$, m.p. 194-195°, mol.wt. (mass spectrum) 293, UV : λ_{max}- 360, 340, 300, 240, 230 (log ε - 4.2, 4.24, 4.62, 4.69, 4.68), had one double bond which was reduced to give the dihydroderivative, $C_{19}H_{21}NO_2$, m.p. 250°, UV : λ_{max}- 345, 332, 312, 300, 258, 242 (log ε - 3.42, 3.82, 4.29, 4.12, 4.35, 4.50).

Its structural elucidation was similar to that of mahanimbin and led to structure IV for the molecule.



IV

The methoxyl was placed at 6-position on the basis of the fact that, in comparison with mahanimbin, both the 5 and 7-protons appeared at higher fields. The mode of fusion of the C,D rings was inferred, as earlier, from the position of the signal of the 4'-proton, which occurred at δ = 6.5. The last feature was finally confirmed by ozonolysis, when a phenolic aldehyde,

$C_{15}H_{13}NO_3$, m.p. 203-204° was obtained, whose UV : λ_{max}- 395, 307, 302, 276 (log ε - 3.95, 4.18, 4.17, 4.21), indicated it to be a 1-formyl carbazole.

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