The Synthesis of Murrayanine

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FROM the petroleum extract of the mature stem-bark of *Murraya koenigii* Spreng. (Fam. Rutaceae), the Indian medicinal plant called the "curry-leaf tree," Chakraborty and co-workers[1] isolated a crystalline alkaloid, $C_{14}H_{11}NO_2$, which they designated murrayanine and formulated as 3-formyl-1-methoxycarbazole. A recent communication by Chakraborty[2] reports that from *Glycosmis pentaphylla* Retz, also a member of the Rutaceae family, an alkaloid glycozoline, $C_{14}H_{13}NO$, has been isolated and assigned the structure of 3-methyl-6-methoxycarbazole. This alkaloid has been synthesized.[3]

We report herein the synthesis of murrayanine, the first carbazole alkaloid, and thus confirm the preliminary formulation of murrayanine as 3-formyl-1-methoxycarbazole.

4-Bromo-2-methoxyaniline (I)[4] was diazotized

and then reduced with stannous chloride yielding 4-bromo-2-methoxyphenylhydrazine (II) m.p. 63°, 87% yield. The hydrazine (II) and cyclohexanone were refluxed in 25% acetic acid giving 3-bromo-1-methoxy-5,6,7,8-tetrahydrocarbazole (III) m.p. 69—70°, 50% yield. Dehydrogenation of the tetrahydro-compound (III) with chloranil gave 3-bromo-1-methoxycarbazole (IV) m.p. 110—112°, 31% yield. The bromo-compound (IV) was treated with 3 equivalents of n-butyl-lithium in ether and then with *N*-methylformanilide to yield 3-formyl-1-methoxycarbazole (V) m.p. 166·5°, 44% yield (lit. 168°), which gave an oxime, m.p. 153·5—155° (murrayanine oxime,[1] 155—156°) and an *N*-methyl derivative, m.p. 150·5—151·5° (*N*-methylmurrayanine,[1] m.p. 148—149°). The u.v. spectrum (MeOH) showed λ_{max} (log ϵ) at 237 (4·59), 248 (4·42), 272 (4·65), 285 (4·46), and 335 (4·24) mμ and the i.r. spectrum of (V) ($CHCl_3$) showed peaks at 3470 (NH), 1680 (C=O), and 1630, 1612, and 1586 (aromatic ring) cm.$^{-1}$ The n.m.r. spectrum of (V) ($CDCl_3$) showed an aldehydic proton at 600 c./sec., three methoxyl protons at 241 c./sec., six aromatic protons with two protons being at 487 c./sec. and the other four aromatic protons at 447 c./sec., and one NH proton at 523 c./sec. These spectral data are in general agreement with those reported for murrayanine by Chakraborty.[1]

The structure of murrayanine has therefore been established by synthesis as 3-formyl-1-methoxycarbazole.

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[1] D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Tetrahedron*, 1965, **21**, 681.
[2] D. P. Chakraborty, *Tetrahedron Letters*, 1966, 661.
[3] W. Carruthers, *Chem. Comm.*, 1966, 272.
[4] M. Kohn, *J. Org. Chem.*, 1953, **18**, 532.