Structure of Murrayacine

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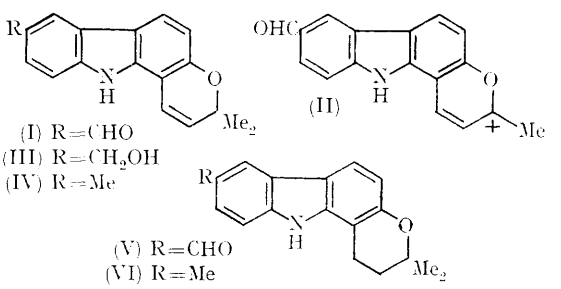
IN continuation of our work on the carbazoles of *Rutaceae*,[1-5] we report the structure of murrayacine, a new addition to the murrayanine[1] group of carbazole alkaloids isolated from *Murraya koenigii* Spreng.

Murrayacine, $C_{18}H_{15}NO_2$ (I), m.p. 244—245°, (M^+ 277) is an optically inactive, homogeneous (t.l.c.) compound, the i.r. spectrum of which (KBr) showed peaks at 3250 (-NH-) 1675 (CO), 1640, 1600 (unsatn. and aromatic system), 895, and 865 cm.$^{-1}$ (substd. Ph). Its n.m.r. spectrum showed signals for an NH proton (δ 12·07), an aldehydic proton (δ 10·68), and five aromatic protons (δ 8·4; 8·1 to 8·2; 7·2 to 7·5). The doublets at δ 5·9 (J 10 c./sec.) and at δ 7·00 (J 10 c./sec.) together with the sharp 6H singlet for a *gem*-dimethyl group at δ 1·52 showed the presence of a 2,2-dimethyl-Δ^3-pyran ring.

The high intensity mass pectral peak[6]† of murrayacine at m/e 262 (M — 15) suggests a carbazolo-pyrylium ion (II) due to loss of a methyl group from the pyranocarbazole skeleton. On further loss of mass 28 from the aldehyde function a peak at m/e 234 is observed. The u.v. spectrum of murrayacine [λ_{max} 226, 284, and 301 mμ (log ϵ 4·60, 4·57, and 4·58)] suggests that murrayacine is a 3-formylcarbazole derivative.[1]

Reduction of murrayacine ($NaBH_4$) gave an alcohol, $C_{18}H_{19}NO_2$ (III), m.p. 200°. The similarity of its u.v. spectrum [λ_{max} 238, 288, 330 mμ (log ϵ 4·51, 4·16, and 3·68)] to that of girinimbine[3b] (IV) shows that their chromophoric systems are identical. On catalytic hydrogenation over Pd–C in alcohol, murrayacine furnished dihydromurrayacine, $C_{18}H_{17}NO_2$ (V), m.p. 176°, (M^+ 279), ν_{max} (KBr) 3325, 1665, 1600, 872, and 755 cm.$^{-1}$. Degradative proof for the carbazole skeleton of murrayacine was provided by the formation of carbazole, $C_{12}H_9N$, m.p. 225°, by zinc dust distillation. These data show that murrayacine is a 2,2-dimethyl-Δ^3-pyranocarbazole with the formyl group in the 3- or 6-position. Dihydromurrayacine (V) on lithium aluminium hydride reduction furnished a compound, $C_{18}H_{19}NO$, m.p. 176°, identical (by mixed m.p., u.v., t.l.c.) with dihydrogirinimbine (VI). This confirms the structure of dihydromurrayacine as (V) and of murrayacine as (I).



It is interesting to note that the formyl or *C*-methyl group in the carbazoles of *Rutaceae*[1-5] occupies the 3- or 6-position, the most active centre for electrophilic attack. It is probable that the formation of the carbazole ring in plants precedes *C*-methylation or formylation of the aromatic ring by electrophilic attack.

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