Structure of Murrayacine

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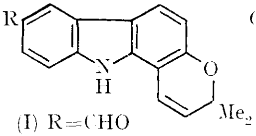
IN continuation of our work on the carbazoles of *Rutaceae*,[1-5] we report the structure of murrayacine, a new addition to the murrayanine[1] group of carbazole alkaloids isolated from *Murraya koenigii* Spreng.

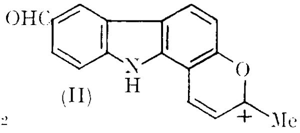
Murrayacine, $C_{18}H_{15}NO_2$ (I), m.p. 244—245°, (M^+ 277) is an optically inactive, homogeneous (t.l.c.) compound, the i.r. spectrum of which (KBr) showed peaks at 3250 (-NH-) 1675 (CO), 1640, 1600 (unsatn. and aromatic system), 895, and 865 cm.$^{-1}$ (substd. Ph). Its n.m.r. spectrum showed signals 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]

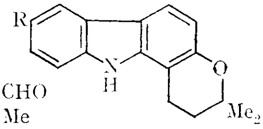
Reduction of murrayacine ($NaBH_4$) gave an alcohol, $C_{18}H_{19}NO_2$ (III), m.p. 200°. The similarity of its u.v. spectrum [λ_{max} 238, 288, 330 mμ (log ϵ 4·51, 4·16, and 3·68)] to that of girinimbine[3b] (IV) shows that their chromophoric systems are identical. On catalytic hydrogenation over Pd–C 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).



(I) R=CHO
(III) R=CH_2OH
(IV) R=Me



(II)



(V) R=CHO
(VI) R=Me

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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