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GLYCOZOLINE, A CARBAZOLE DERIVATIVE FROM GLYCOSMIS PENTAPHYLLA (RETZ) DC.*

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Recent reports show that simple carbazole derivative murrayanine (1) $C_{14}H_{11}NO_2$, m.p. 168° and a pyrano-carbazole derivative girinimbine (2) $C_{18}H_{17}ON$, m.p. 176° occur in Murraya koenigii Spreng. (Fam. Rutaceae, sub-fam. Aurantieae). From biogenetic considerations, they may be lined up with the alkaloids of the family Rutaceae derivable from anthranilic acid (3). These alkaloids are a speciality of the family Rutaceae (4,5). G. pentaphylla (6,7), a plant taxonomically related to M. koenigii has been found to elaborate furoquinoline, quinazoline and acridone bases which are formally derivable from anthranilic acid (8). The taxonomic connection of these two plants and the probable common origin of these alkaloids and carbazoles of Rutaceae prompted the present investigation. Previously (9) three furoquinolines, dictamnine, $C_{12}H_9O_2N$, m.p. 130-32°, skimmianine $C_{14}H_{13}O_4N$, m.p. 176° and 7-fagarine $C_{13}H_{11}O_3N$, m.p. 142° were reported from the root bark of the plant. The present report deals with a new carbazole derivative isolated from the same source. It has been named glycozoline.

Glycozoline (I), m.p. 181-82° is an optically inactive, neutral compound having the molecular formula† $C_{14}H_{13}NO$ (molecular weight by

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* Part V in the series Chemical Taxonomy

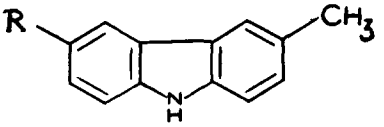
† Satisfactory analyses were obtained for the compounds reported.

mass spectrum, 211). The homogeneity of the compound has been established by paper and thin layer chromatography. It gave a picrate, $C_{20}H_{16}N_4O_8$, m.p. 182°. It has one methoxyl and one C-methyl group.

The infrared spectrum of glycozoline showed bands (KBr) at 3500 (NH), 1600, 1595 (aromatic system), 1380 (C-Me) and 813 cm^{-1} (substituted benzene derivative). Its NMR spectrum (60 mc in $CDCl_3$) showed signals for NH proton at 468 c/s, two aromatic protons around 453 c/s and four aromatic proton multiplets from 444 to 415 c/s besides two singlets for three protons each for aromatic methoxyl and aromatic C-Me at 234 and 150 c/s respectively. The IR, NMR, analytical data and the neutral nature of glycozoline could account for a carbazole nucleus with an aromatic C-methyl and methoxy group on it. The UV absorption spectrum of glycozoline λmax 227 mμ (log ϵ 4.52), 252 mμ (log ϵ 4.16), 264 mμ (logϵ 4.60), and at 304 mμ (logϵ 4.17) is strikingly similar to that of 3-methoxy carbazole (9). Physical data therefore, suggest that glycozoline is a 3- or 6-methoxy carbazole with a methyl substituent on an aromatic ring. The compound on comparison (mixed m.p., IR, UV) was found different from 2-methyl 3-methoxy carbazole m.p. 179-81° (10).

Demethylation of glycozoline with HBr afforded a phenol, $C_{13}H_{11}NO$, (II) m.p. 228-30° ν(KBr) 3400 cm^{-1} (hydroxyl), which could be acetylated to $C_{15}H_{13}NO_2$,(III), m.p. 210°, λmax 230 mμ (logϵ 4.58) 237 mμ (logϵ 4.59), 260 mμ (log ϵ 420) 296 mμ (logϵ 4.22) and 330 mμ (logϵ 3.60). On zinc dust distillation, the compound (I) furnished 3-methyl carbazole $C_{13}H_{11}N$ (IV), m.p. 204-05°. The isolation of 3-methyl carbazole indicates the location of the methyl group at position 3- or 6- of the carbazole

nucleus. The UV spectrum of the phenol acetate (III) is very similar to that of 3-methyl carbazole (1). The phenol (II) on reduction with Raney nickel in alcohol (11) via its tosyl derivative yielded 3-methyl carbazole. These data confirm that the methyl group is at position 3 or 6 of the carbazole nucleus and further show that 3-methyl carbazole obtained by zinc dust distillation is not a rearranged product.



I, R = OCH_3 III, R = O·OC·CH_3

II, R = OH IV, R = H

The data presented lead to the formulation of glycozoline as 3-methyl-6-methoxy carbazole (I). The proposed structure has been confirmed by synthesis which will be reported separately.

The isolation of glycozoline from G. pentaphylla probably provides a circumstantial evidence for the formation of simple carbazoles through anthranilate path-way.

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