

GLYCOZOLIDAL, A NEW CARBAZOLE ALKALOID FROM *GLYCOSMIS PENTAPHYLLA*

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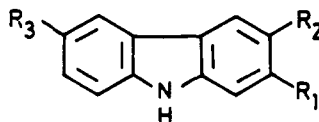
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In continuation of our work on carbazole alkaloids of the Rutaceae (1), we now report the structure of another new carbazole alkaloid, glycozolidal (**1**), from the root of *Glycosmis pentaphylla* (Retz) DC., a reputed Indian medicinal plant known to furnish carbazole alkaloids (2,3).

Glycozolidal (**1**) was found to be homogeneous by tlc and ms. It gave a picrate, formed a 2,4 dinitrophenyl hydrazone, and reduced ammonical AgNO₃ solution, indicating the presence of an aldehyde function. Analytical data indicated the presence of two methoxy groups. The uv spectrum of the compound was characteristic of 3-formyl carbazole (4). The ir spectrum showed it to be an aromatic compound with -NH, aldehyde and aromatic ether functions. In the ¹H-nmr spectrum, the C-4 and C-5 protons of the carbazole nucleus, which appeared at a lower field than the other aromatic protons, are readily recognized (5). Thus, the signals at δ 8.4 and δ 7.6 were assigned to C-4 and C-5 hydrogens, respectively. The proton at C-4 was deshielded due to the close proximity of the aldehyde function at C-3. Moreover, the C-4 proton was not *ortho*- or *meta*-coupled, suggesting substitutions at positions 3 and 2. The C-5 proton was also not *ortho*-coupled which suggested substitution at position 6.

From these observations, the structure of glycozolidal was formulated as **1**. This has been confirmed by oxidation of glycozolidine (**2**) with 2,3-dichloro-5,6-dicyanobenzoquinone when a compound identical in all respects with natural glycozolidal was obtained.



- 1 R₁=R₃=OCH₃; R₂=CHO
- 2 R₁=R₃=OCH₃; R₂=CH₃

Evidently glycozolidal could be considered as the biological oxidation product of glycozolidine where the Ar-Me group has been oxidized to Ar-CHO group. This type of oxidation has its precedence in the genus *Murraya* (6), which is taxonomically close to *G. pentaphylla*.

EXPERIMENTAL

PLANT MATERIAL.—*G. pentaphylla* was collected locally and identified by Dr. S.R. Das, Survey Officer, Regional Research Institute (AY), Calcutta, and a voucher specimen has been deposited at Bose Institute.

ISOLATION OF GLYCOZOLIDAL (**1**).—Air-dried, finely powdered roots (2 kg) of *G. pentaphylla* were extracted with petroleum ether (40-60°) in a Soxhlet for 48 h. After solvent evaporation, the residue was taken in a little C₆H₆ and chromatographed over silica gel (450 g). The column was eluted with petroleum ether, petroleum ether-C₆H₆ (1:1), C₆H₆, CHCl₃, and MeOH, in succession. The petroleum ether-C₆H₆ (1:1) eluate furnished a solid, which, on crystallization from C₆H₆, furnished glycozolidal (150 mg).

GLYCOZOLIDAL (**1**).—mp 185°, C₁₅H₁₃NO₃ (M⁺, 255); uv λ max (EtOH) 235, 248, 303, 340 nm (log ε 4.4, 4.2, 4.2, 4.06); ir ν max (KBr) 3500 (-NH), 1675 (aromatic aldehyde) 1600, 1595 (aromatic residue) 1220, 1200 cm⁻¹ (aromatic ether); ¹H nmr (60 MHz, CDCl₃) δ 9.9 (s, 1H, CHO) 8.8 (brs, 1H, NH, confirmed by D₂O exchange), 8.4 (s, 1H, H-4), 7.6 (d, 1H, J=2 Hz, H-5) 6.85 (dd, 1H, J=7.0 Hz and 2.0 Hz, H-7) 7.3 (d, 1H, J=7.0 Hz, H-8) in addition to two singlets at δ 3.9 (3H) and 3.7 (3H) for two methoxy groups.

OXIDATION OF GLYCOZOLIDINE (2).— Glycozolidine (100 mg) was dissolved in dry C_6H_6 and stirred with 2,3-dichloro-5,6-dicyanobenzoquinone at room temperature for 30 min. The reaction mixture was washed successively with 5% HCl and H_2O and then dried. The residue was taken in a little C_6H_6 and chromatographed on silica gel (10 g). Elution with C_6H_6 furnished a compound (25 mg) found to be identical with glycozolidal by direct comparison in all respects (mp, mmp, tlc, uv, ir).

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