GLYCOPHYMOLINE, A NEW MINOR QUINAZOLINE ALKALOID FROM GLYCOSMIS PENTAPHYLLA*

M. SARKAR and D. P. CHAKRABORTY Bose Institute, Calcutta 7000009, India

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Key Word Index-Glycosmis pentaphylla; Rutaceae; flower head; alkaloid; glycophymoline.

In continuation of our investigation of the alkaloids of *Glycosmis pentaphylla*[†], we now report a new quinazoline alkaloid from the flower heads which we consider to be the enol ether of the alkaloid glycophymine reported previously [1].

RESULTS AND DISCUSSION

Glycophymoline, an optically inactive alkaloid, $C_{16}H_{14}N_2O$, mp 165° was isolated from the flower heads of the *G. pentaphylla*. It was soluble in C_6H_6 , CHCl₃ and MeOH. The IR spectrum showed the presence of a quinazoline system (1545 cm⁻¹), an aromatic system (1618, 1610 cm⁻¹) and a OMe group (1208 cm⁻¹). The UV spectrum of the compound (λ_{max}^{EVH} 312, 302, 276, 268, 230 nm with log ε 3.45, 3.50, 3.78, 3.85 and 4.35) was very similar to that of a quinazoline alkaloid. The MS of glycophymoline, like a quinazoline system, gave an intense peak at m/e 249 (M⁺ - 1), 235, 119 and 91.

The ¹H NMR spectrum (60 MHz, CDCl₃) showed the presence of 3 protons for one aromatic OMe group at δ 3.7, two protons for a benzylic methylene group at δ 4.23 and 5 protons for an isolated phenyl nucleus at δ 7.25. The aromatic proton signal at δ 8.1 could be attributed to the deshielded aromatic proton in the peri-position either to a C=O group of a quinazolone system [2] or to a OMe group in a furanoquinoline system (i.e. evolitrin [3]). The signals at δ 7.5–7.8 could be attributed to the other aromatic protons. These data lead to the assignment of the structure 2 for glycophymoline. The structure has been confirmed by partial synthesis of glycophymoline 2 from glycophymine 1.

* Part 45 in the series "Chemical Taxonomy". For Part 44 see Chakraborty, D. P. et al. (1979) J. Indian Chem. Soc. (in press). † For the retention of the name of species see ref. [1]. The glycophymine [1], synthesized previously, on treatment with Me_2SO_4 and alkali gave a compound which was identical to glycophymoline.

The isolation of glycophymoline, glycophymine and glycomide [1] 4 in the flower heads of the plant and arborine 3 [4] in the leaves provides circumstantial evidence for the formation of arborine and glycophymoline from the precursor of glycomide 4a via glycophymine. Arborine could be considered to be the N-methylated product of glycophymine while glycophymoline could be considered to be the enol ether of glycophymine.

EXPERIMENTAL

All mps are uncorr. Analytical samples were analysed after drying over P_2O_5 in vacuo usually at 80° for 15 hr. The Al_2O_3 used was of Brockmann grade as prepared by Sarabhai Merck Co. of India.

Isolation of glycophymoline 2. The residue obtained from the air-dried finely powdered flowers of G. pentaphylla (Retz.) DC (2 kg) after extraction with petrol was extracted with EtOH for 4 days. The residue left after removal of the solvent was fractionated into basic, neutral and phenolic fractions in the usual way. The residue from the basic fraction was dissolved in C_6H_6 and chromatographed over Al_2O_3 . On elution of the column with C_6H_6 -MeOH (8:1), glycophymoline was obtained, which was recrystallized from the above mixture of the solvents, mp 165°, yield 0.0005%. (Found: C, 76.70; H, 5.60; N, 11.2. Calculated for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19%).

Partial synthesis of glycophymoline from glycophymine. Glycophymine (30 mg) was mixed with 10% NaOH soln and cooled, Me_2SO_4 added dropwise with continuous stirring for 1 hr and the reaction mixture refluxed for 2 hr. The reaction mixture was then poured into ice-H₂O and extracted with alkaline CHCl₃. Theresidue obtained from the CHCl₃ layer was chromatographed, when a crystalline compound was obtained. This on





recrystallization had mp 165° and was identical to glycophymoline (mmp, TLC and IR).

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MINOR ALKALOIDS OF FUMARIA INDICA SEEDS

V. B. PANDEY, A. B. RAY and B. DASGUPTA

Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi-221005, India

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In continuation of our search for alkaloidal constituents of the different parts of *Fumaria indica* (Haussk) Pugsley [1-3], we now report the isolation of three alkaloids, A, B and C which were eventually proved to be fumariline (1), 8-methoxydihydrosanguinarine (2) and oxysanguinarine (3) respectively.





Alkaloid A, $C_{20}H_{17}NO_5$, mp 144°, shows UV absorption characteristic of a ketonic spirobenzylisoquinoline. The IR shows a carbonyl absorption band at 1720 cm⁻¹ characteristic of a conjugated 5-membered cyclic ketone. The 60 MHz PMR in CDCl₃ gave signals for a N-Me (δ 2.33, s), two methylenedioxy (δ 5.83, 6.16, s each), two