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SOME MINOR CONSTITUENTS FROM *GLYCOSMIS PENTAPHYLLA**

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Key Word Index—*Glycosmis pentaphylla*; Rutaceae; glycophymine; amide; glycomide.

Abstract—A quinazolone alkaloid, glycophymine and an amide, glycomide have been isolated from *Glycosmis pentaphylla*.

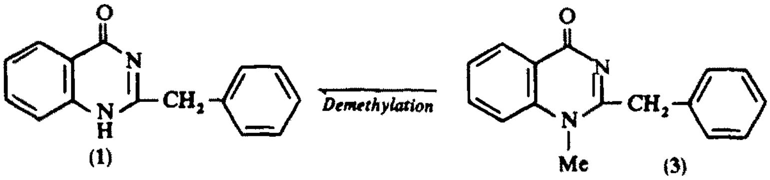
INTRODUCTION

Acridones, furoquinolines, quinazolones and carbazole alkaloids are some of the alkaloids reported from the different species of the Genus *Glycosmis* [1–3]. We were interested to examine the flower heads of *Glycosmis pentaphylla* (Retz) DC† which being a growing tissue might provide some information regarding the biogenetic intermediate of the alkaloids of the genus. We now report here the isolation and structure of a new alkaloid glycophymine (1) and an amide, glycomide (2) from the flowers of the plant.

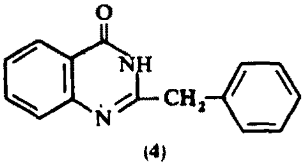
RESULTS AND DISCUSSION

Glycophymine, an optically inactive homogeneous alkaloid, $C_{15}H_{12}N_2O$, mp 254° was soluble in $CHCl_3$, EtOAc and MeOH. The IR spectrum showed the presence of an —NH function (3350 cm^{-1}), $>C{=}O$ function (1700 cm^{-1}), a quinazolone system (1535 cm^{-1}, 1620 cm^{-1}), aromatic system (1600 cm^{-1}) and an isolated phenyl nucleus (711 cm^{-1}). The UV spectrum of the compound was very similar to that of the quinazolone alkaloids (λ_{max}^{EtOH} 225, 265, 273 (*sh*), 302, 312 nm with log ε 4.4, 3.82, 3.75, 3.65, 3.48). The IR and UV data of glycophymine suggest the presence of the quinazolone system like those of arborine (3) [5] or glycosminine (4) [3].

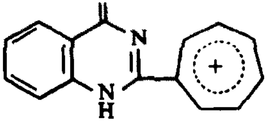
The MS of glycophymine, like a quinazolone system, gave an intense peak at *m/e* 235 (M$^+$-1), 119 and 91 which could be represented by the following species (5–7). The analytical data and the MS fragmentations were suggestive that glycophymine was either identical with glycosminine (4) or (1). Since by direct comparison it was found to be different from glycosminine [TLC and mmp (230–238°)], structure (1) was preferred, as (1) was obtained by demethylation of arborine (3). Structure (1) has been confirmed by an unambiguou synthesis following the method of Ray and De [6]. Phenylacetanilide (2) mp 120° was refluxed with urethane (8) in boiling xylene in presence of P_2O_5 when (1) was obtained.



(1) (3)



(4)



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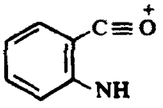

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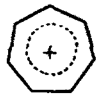

(7)

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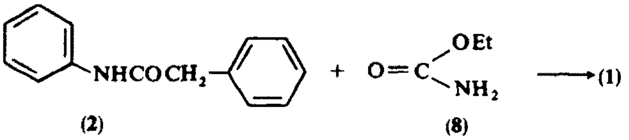
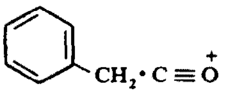
* Part 40: in the Series Chemical Taxonomy (Molecular Taxonomy). Part 39: P. Bhattacharyya *et al. J. Indian Chem. Soc.* in press.

† *G. pentaphylla* has been retained instead of *G. arborea* (see *Index Kewensis* (1895), p. 1039. Clarendon Press, Oxford; Narayanaswami V. (1941). Record Botanical Survey of India 14, 2; Brizcky, G. and Arnold, J. (1962) *Arber.* 43, 30; Chopra, R. N. (1956) *Glossary of Indian Medicinal Plants* p. 126. C.S.I.R., New Delhi.

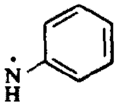


(2) (8)

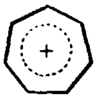
Glycomide, the second colourless crystalline compound $C_{14}H_{13}NO$, (M^+ 211), mp 120° was soluble in C_6H_6, $CHCl_3$, and MeOH. The IR spectrum of this compound showed the bands at 3320 cm^{-1} (for —NH function), 1670 cm^{-1} (for $>C=O$), 1605, 1590 cm^{-1} (for aromatic system). The UV spectrum showed λ_{max}^{EtOH} 240 nm with log ε 4.40. MS showed the peaks at m/e 119 and 92, 91 which could be represented as follows (**9**–**10**, **7**).



(**9**)



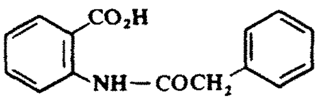
(**10**)



(**7**)

The PMR spectrum (60 MHz, $CDCl_3$) showed signals for two benzylic protons at δ 3.80, one NH proton at δ 7.0–7.6 and complex multiplets of aromatic protons. This compound (**2**) on hydrolysis gave phenylacetic acid and aniline. From the above physical and analytical data the structure (**2**) was conceivable for the compound, and this structure was confirmed by direct comparison with the synthetic compound prepared above (TLC, mmp and MS).

The glycomide has not so far been reported from a plant source. The occurrence of glycomide and the quinazolones like arborine, glycosminine and glycophymine in the same genus provides a circumstantial evidence for the biosynthesis [7] of quinazolones from the phenylacetanilide carboxylic acid (**11**) and NH_3 when glycomide could be obtained by decarboxylation of (**11**).



(**11**)

EXPERIMENTAL

All mps are uncorr. Analytical samples were analysed after drying over P_2O_5 *in vacuo* usually at 80° for 10 hr. The Al_2O_3 used was of Brockmann grade as prepared by Sarabhai Merck Co. of India.

Isolation of glycophymine (**1**). The residue obtained from the air dried finely powdered flowers of *G. pentaphylla* (1 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 a mixture of C_6H_6 and petrol (1:3) glycophymine was obtained, which was recrystallised from C_6H_6 (mp 254°). Yield 0.0015%. (Found: C, 76.23; H, 5.10; N, 11.84%; Calculated for $C_{15}H_{12}N_{12}O$ requires: C, 76.25; H, 5.12; N, 11.86%).

Demethylation of arborine (**3**) *to glycophymine* (**1**). Arborine (50 mg) isolated from the leaves of *arborea* was boiled with HOAc (0.7 ml) and HI (0.25 ml) with frequent shaking during 1 hr on a water bath and then a further quantity of HOAc (0.2 ml) and HI (0.2 ml) was added and heated (5 hr) on a water bath. The reaction mixture was cooled and poured in ice H_2O and extracted with Et_2O. On working up the reaction products and purification, the compound mp 253–54°, identical with (**1**) was obtained.

Synthesis of Glycophymine (**1**). (i) Phenyl acetic acid (2 g) was refluxed with 2 ml of aniline in presence of few drops of Py for 3 hr. On working up and purification by crystallisation from hot H_2O, the anilide of phenylacetic acid (**2**) was obtained, mp 120° (lit. mp 120°). (ii) The compound (**2**) (1.5 g) and urethane (0.8 g) in xylene (100 ml) were refluxed at 140–145° (4 hr) with P_2O_5 (0.75 g). After working up the reaction mixture by the method of ref. [6], the crude product was obtained, which on recrystallisation from EtOH melted at 254° and was identidal with glycophymine (mmp, TLC, m^+ 236).

Isolation of Glycomide. The residue from the neutral fraction of the alcoholic extract 2 of *G. pentaphylla* was dissolved in C_6H_6 and chromatographed over Al_2O_3. On elution with C_6H_6 glycomide, mp 116° was obtained. On recrystallisation from C_6H_6-petrol (1:1) the pure compound, mp 120° was obtained. Yield 0.02%. (Found: C, 79.59; H, 6.20; N, 6.63%. Calc for $C_{14}H_{13}NO$ requires C, 79.62; H, 6.45; N, 6.64%.

Hydrolysis of glycomide (**2**): *formation of phenyl acetic acid and aniline*. Glycomide (100 mg) was refluxed with 70% H_2SO_4 (10 ml) for 30 min and poured into ice H_2O. The phenylacetic acid was filtered, washed and recrystallised from hot H_2O, mp 77° (lit. mp 77°). The filtrate was made alkaline and aniline was isolated. This was identified as its HCl, mp 198° (lit. mp 198°).

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