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GLYCARPINE, A NEW ALKALOID FROM *GLYCOSMIS CYANOCARPA**

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Key Word Index—*Glycosmis cyanocarpa*; Rutaceae; alkaloids; glycarpine; evolitrine; structural determination.

Abstract—Glycarpine, a new furoquinolone alkaloid and evolitrine have been isolated from *Glycosmis cyanocarpa*.

The genus *Glycosmis* has provided various alkaloids belonging to furoquinoline, acridone, quinazolone and carbazole groups which are of taxonomic significance [1]. We have already demonstrated several carbazoles [2], quinazolone [3] and furoquinoline [4] in this genus. Our interest in the chemistry of this genus from chemotaxonomic considerations prompted us to undertake investigations on *Glycosmis cyanocarpa*. A previous report on this species resulted in the isolation of three coumarins (**1–3**) [5]. We now report the structure of a new very minor alkaloid named glycarpine (**4**) and the isolation of evolitrine (**5**) [6] from the leaves of the *Glycosmis cyanocarpa*. Glycarpine $C_{14}H_{13}NO_4$, mp 171° (M^+ 259), $[\alpha]_D^{CHCl_3} \pm 0°$ was homogeneous by TLC and MS. It was soluble in C_6H_6, $CHCl_3$ and MeOH. The UV spectrum of the compound showed (λ_{max}^{EtOH} 244, 249, 306, 334 nm with log ε 4.96, 4.95, 4.29, 4.19) very similar to those of isoskimmianine, isoacronycidine and isomaculosidine types of alkaloids suggesting the presence of the skeleton (**6**). The IR spectrum of glycarpine ν_{max}^{KBr} 3260, 1720, 1620, 1580, 1540 cm^{-1} indicated the presence of an aromatic system, a ketonic function and furanoid ring system.

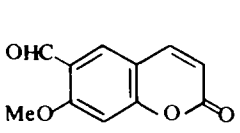
The PMR spectrum (60 MHz, $CDCl_3$) showed the presence of one N-Me group (δ 3.8, 3 proton singlet), two methoxyl groups (δ 4.4, 6 proton singlet), singlets for two aromatic protons, one at δ 7 and other at δ 7.28. The α and β furan protons were readily discernible for the PMR (δ 7.5 and 6.98). The absence of a signal for the aromatic proton at C-5, deshielded by the —CO— group at C-4, showed that C-5 is substituted. Hence one of the methoxy groups must be at C-5. Two aromatic protons appear as a singlet hence the two aromatic protons are not *ortho* to each other. This rules out the substitution of the other methoxyl at C-6 or C-8. From these data, glycarpine could be represented by structure (**4**).

The second alkaloid obtained in larger quantity analysed for $C_{13}H_{11}NO_3$, mp 115° (M^+ 229) $[\alpha]_D^{CHCl_3} \pm 0°$ showed a UV spectrum λ_{max}^{EtOH} 248, 308 nm with log ε 4.75, 3.92 characteristic of furoquinolines. The IR spectrum showed ν_{max}^{KBr} 1620, 1580, 1450, 1150 cm^{-1}. The PMR spectrum of this compound showed the presence of two OMe groups (δ 3.92 and 4.4), and two furan protons (δ 6.96 and 7.56). The proton doublets at δ 8.1 could be assigned to the proton at the C-5 position like that in skimmianine. The other two aromatic protons at (δ 7.14 and 7.28), one as a doublet (δ 7.28) the other (δ 7.14) as a singlet suggested C-7 as the position of the methoxyl group. All these data were in agreement with the identity of the compound as evolitrine.

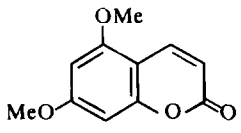
EXPERIMENTAL

The plant was identified from the herbarium sheet kept at the Botany Department, Science College, Calcutta. All mps are uncorr., analytical samples were analysed after being dried over P_2O_5 *in vacuo*, usually at 80° for 16 hr. The Al_2O_3 used was of Brockmann grade.

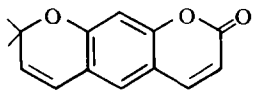
*Part 42 in the series "Chemical Taxonomy". For Part 41 see Chakraborty, D. P., Bhattacharyya, P., Roy, S., Bhattacharyya, S. P. and Biswas, A. K. (1978) *Phytochemistry* **17**, 834.



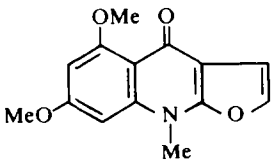
(1)



(2)



(3)



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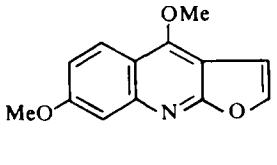

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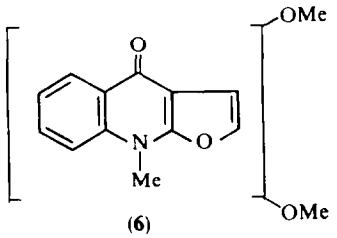

(6)

Isolation of glycarpine and evolitrine. The residue obtained from a petrol (40–60°) extract of the powdered leaves of *Glycosmis cyanocarpa* (2 kg) for 72 hr 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 on a column of Al_2O_3. On elution with C_6H_6–petrol (1:1) glycarpine was obtained which was recrystallized from a mixture of C_6H_6–petrol (3:1); mp 170–171°). R_f: 0.25 in MeOH–C_6H_6 (99:1) and 0.1 in C_6H_6–$CHCl_3$ (1:1). Yield: 0.0018%. (Found: C, 64.86; H, 5.05; N, 5.40. Calculated for $C_{14}H_{13}NO_4$: C, 64.84; H, 5.00; N, 5.35%).

Elution of the Al_2O_3 column with C_6H_6–$CHCl_3$ (2:1) gave a residue which on crystallization from C_6H_6–petrol furnished colourless needles, mp 115°. (Found: C, 68.11; H, 4.84; N, 6.11. Calc for $C_{13}H_{11}NO_3$: C, 68.10. H, 4.80; N, 6.09%). Direct comparison of evolitrine with a pure specimen was not possible.

Acknowledgements– Thanks are due to Dr. S. C. Bhattacharyya, Director and Prof. A. Sen, Head of the Dept. of Chemistry for their interest in the work.

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ALCALOIDES DE *GEISSOSPERMUM ARGENTEUM* (APOCYNACEAE)

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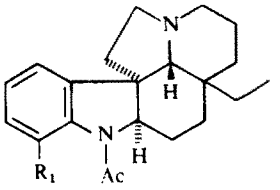
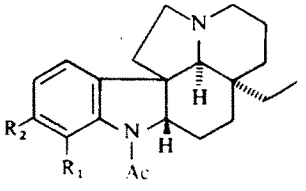
Key Word Index—*Geissospermum argenteum*; Apocynaceae; (−)-desmethoxy-aspidospermine; ( )-aspidospermine; (+)-aspidocarpine; (+)-desmethylaspido-spermine; chemotaxonomy.

Le genre *Geissospermum* est riche en alcaloïdes indoliques [1–10]. Cependant, à l'encontre des deux espèces étudiées: *G. vellosii* [1–5] et *G. laeve* [6–10]†, *G. argenteum* Wood. n'a fait l'objet d'aucun travail. Cet arbre dressé (20–30 m), originaire de la Guyane Française, présente des feuilles alternes pubescentes à pétioles courts. Les feuilles et les écores de tige ont été étudiées simultanément†. L'extraction à l'aide de chloroforme de la plante séchée, broyée et alcalinisée par de l'ammoniaque fournit 0,8% d'alcaloïdes totaux pour les écorces et les feuilles.

Des chromatographies sur colonne de silice, éventuellement suivies de purifications par chromatographies sur couche épaisse de silice permettent d'isoler quatre alcaloïdes purs identifiés grâce à leurs constantes physiques et à leurs propriétés spectrales (SM, RMN, IR, UV): (−)-desméthoxyaspidospermine **1** (11) F 114° (hexane); $[\alpha]_D^{20}$ − 15° (*c* 1%, $CHCl_3$). Cet alcaloïde n'avait encore jamais été signalé cristallisé à l'état de base; (−) aspidospermine **2** (12): F 202° (Et_2O–hexane); $[\alpha]_D^{20}$ − 98° (*c* 1%), EtOH); (+) aspidocarpine **3** (13):



1 (−) Desméthoxyaspidospermine R_1 = H
2 (−) Aspidospermine R_1 = OMe



3 (+) Aspidocarpine R_1 = OH, R_2 = OMe
4 (+) Desméthylaspidospermine R_1 = OH, R_2 = H

F 166° (Et_2O–hexane) $[\alpha]_D^{20}$ + 140° (*c* 1%, $CHCl_3$); (+) desméthylaspidospermine **4** (11): 170° (perchlorate, MeOH); $[\alpha]_D^{20}$ + 94° (*c* 1%, MeOH). Ces quatre alcaloïdes majoritaires ont été retrouvés à la fois dans les feuilles et les écorces de tige.

G. argenteum se différencie nettement du point de vue composition chimique par le fait qu'il ne renferme que des alcaloïdes du type aspidospermane (type III) alors que les deux espèces précédemment étudiées [1–10] ne contiennent que des alcaloïdes du type corynane (type I).

* Nous remercions M. C. Sastre pour la récolte du premier échantillon botanique (Ref. Sastre 1386, récolte effectuée à la rivière Inini, station de l'Institut Pasteur, Guyane Française) et MM. J. J. de Granville et Ch. Moretti pour les réapprovisionnements. Nous remercions également Mme L. Allorge et M. P. Boiteau pour l'identification des différentes espèces.

† *G. sericeum* précédemment examiné [6] était en réalité *G. laeve*. Nous remercions M. le Professeur R. Paris (Faculté de Pharmacie de Paris) pour la communication d'échantillons botaniques.