10.98%. $C_{21}H_{20}O_7$ requires C, 65.62; H, 5.28; acetyl 11.19%.) ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.5 (1H, *s*, C-2), 6.3 (1H, *s*, C-6), 6.7–6.9 (3H, *m*, C-2′, C-5′, C-6′), 3.8–4.0 (9H, *m*, OMe, C-7, C-3′, C-4′), 2.4 (3H, *s*, Me-8).

REFERENCES

1. Asahina, V. and Inubuse, M. (1928) *Ber.* **61**, 1646.
2. Asahina, V. and Inubuse, M. (1931) *Ber.* **64**, 1256.
3. Shinoda, J. (1928) *J. Chem. Pharm. Soc. Jpn.* **48**, 214.
4. Geissman, T. A. (1962) *The Chemistry of Flavonoid Compounds* p. 72. Pergamon Press, New York.
5. Heilbron, I., Bunbury, H. M., Jones, W. E. (1946) in *Dictionary of Organic Compounds* Vol. III, p. 842. Eyre & Spottiswoode, London.
6. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids* p. 267. Springer, Berlin.
7. Kutney, J. P., Warnock, W. D. C. and Gilbert, B. (1970) *Phytochemistry* **9**, 1877.
8. Sherwood, R. T. and Sharma, M. (1973) *Phytochemistry* **12**, 2275.

Phytochemistry, Vol. 22, No. 4, pp. 1064–1065, 1983.
Printed in Great Britain.

0031-9422/83/041064-02$03.00/0
Pergamon Press Ltd.

GLYCOZOLININE, A CARBAZOLE DERIVATIVE FROM *GLYCOSMIS PENTAPHYLLA*

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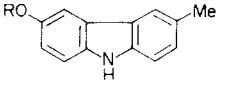
(*Received* 9 *August* 1982)

Key Word Index—*Glycosmis pentaphylla*; Rutaceae; seeds; alkaloids; glycozolinine; carbazole.

Abstract—A new carbazole derivative, glycozolinine, was isolated from the seeds of *Glycosmis pentaphylla*. From physical and chemical evidence its structure is 6-hydroxy-3-methylcarbazole.

In continuation of our investigations on the chemistry of carbazole alkaloids [1–4], we wish to report the isolation and structure elucidation of a new carbazole derivative from the seeds of *Glycosmis pentaphylla*.

Glycozolinine (**1**), $C_{13}H_{11}NO$ (M^+ 197, determined by MS), mp 231–232° was isolated from the benzene extract of the defatted seeds of the plant. The homogeneity of glycozolinine was confirmed by TLC using various solvent systems. Glycozolinine gave a red colour with ferric chloride indicating the presence of a phenolic hydroxyl in the molecule. The UV spectrum showed absorption at λ_{max} nm (log ε): 224 (3.92), 254 (4.02), 269 (3.96) and 298 (4.04). The IR spectrum showed absorption peaks at ν_{max}^{KBr} cm^{-1}: 3440 (–NH– function), 3390 (phenolic hydroxyl), 1630, 1570, 1480 (aromatic residue), 1390 (aromatic C–Me) and 790 (substituted benzene derivative). The ^{1}H NMR spectrum showed signals for one indolic proton (broad singlet at δ 7.65, confirmed by D_2O exchange), two aromatic protons (doublet around δ 7.8), four aromatic protons (multiplet at δ 7.20 6.85), three protons of an aromatic C–Me group (singlet at δ 2.38) and a phenolic hydroxyl (broad singlet at δ 11.04, confirmed by D_2O exchange).



1 R=H
2 R=COMe
3 R=Me

Glycozolinine on treatment with acetic anhydride and pyridine at room temperature for 16 hr gave acetate **2**, which crystallized from benzene, mp 210°. The UV spectrum of the acetate showed absorption maxima at λ_{max} nm (log ε): 230 (4.62), 239 (4.14), 266 (4.26), 299 (4.20) and 332 (3.48). The IR spectrum showed absorption at ν_{max}^{KBr} cm^{-1}: 3438 (–NH– function), 1746 (acetyl function), 1628, 1590, 1445 (aromatic residue), 1390 (C–Me group) and 778, 730 (substituted aromatic system). The UV spectrum was very similar to that of 3-methylcarbazole suggesting that the methyl group in glycozolinine is in either the 3- or 6-position in the carbazole skeleton. That the methyl group of glycozolinine is in the 3-position was confirmed by the fact that on zinc dust distillation of glycozolinine 3-methylcarbazole was obtained. On treatment with diazomethane, glycozolinine furnished a carbazole derivative **3**, $C_{14}H_{13}NO$, mp 182° which was identical with glycozoline [5]. The above data, therefore, lead to the formulation of glycozolinine as 3-methyl-6-hydroxycarbazole (**1**).

EXPERIMENTAL

All mps were uncorr. UV and IR spectra were recorded in EtOH and as KBr pellets, respectively. ^{1}H NMR was measured at

90 MHz with TMS as an int. reference. $CDCl_3$ was used as solvent.

Extraction. Air dried finely powdered seeds (1 kg) of *G. pentaphylla* were defatted with petrol (60–80°) for 48 hr. The defatted seeds were further extracted with C_6H_6 for 48 hr. The C_6H_6 extract was evaporated to dryness and the residue left was digested with 10% HCl (v/v) for 2 hr at 100°. The residue was filtered, washed with H_2O until free from acid and dried. The dried residue was extracted × 5 with $CHCl_3$ (150 ml) and the $CHCl_3$ extract concd (30 ml) and chromatographed over Si gel (150 g). The column was eluted with petrol, C_6H_6 and $CHCl_3$ in succession. A white crystalline solid was obtained from C_6H_6 fractions, which was recrystallized from C_6H_6, mp 231–232°. TLC on Si gel G in petrol–C_6H_6 (1:1), R_f 0.22 and in C_6H_6–$CHCl_3$ (3:1), R_f 0.48. Analytical data: found: C, 79.31; H, 5.51; N, 7.03; calcd for $C_{13}H_{11}NO$: C, 79.19; H, 5.58; N, 7.11%.

Glycozolinine acetate. Recrystallized from C_6H_6, mp 210°. TLC: C_6H_6–$CHCl_3$ (3:1), R_f 0.59. Analytical data: found: C, 75.22; H, 5.54; N, 5.78; calculated for: $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85%.

Zn dust distillation product of glycozolinine. Obtained on distillation with Zn dust and subsequently crystallized from C_6H_6–petrol (1:1), mp 206–207°. Analytical data: found: C, 86.06; H, 6.21; N, 7.68; calculated for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73%.

Methylation product of glycozolinine. Mp 178–179°. TLC: petrol–C_6H_6 (1:4), R_f 0.61.

Acknowledgements—The NMR and mass spectra were obtained through the courtesy of Mr. E. Vonbank of Organisch-Chemisches Institut, Zurich, Switzerland and Professor Beckman of Wyane State University, Detroit, U.S.A. The financial assistance to one of us (S.M.) from C.S.I.R., India is gratefully acknowledged.

REFERENCES

1. Chakraborty, D. P., Chatterjee, D. and Ganguly, S. N. (1969) *Chem. Ind. (London)* 1662.
2. Bordner, J., Chakraborty, D. P., Chowdhury, B. K., Ganguly, S. N., Das, K. C. and Weinstein, B. (1972) *Experientia* **28**, 1406.
3. Chakraborty, D. P., Ganguly, S. N., Maji, P. N., Mitra, A. R., Das, K. C. and Weinstein, B. (1973) *Chem. Ind. (London)* 322.
4. Ganguly, S. N. and Sarkar, A. (1978) *Phytochemistry* **17**, 1816.
5. Chakraborty, D. P. (1969) *Phytochemistry* **8**, 769.