Otomasu, H. (1978) *Phytochemistry* **17**, 1817.
4. Murakoshi, I., Toriizuka, K., Haginiwa, J., Ohmiya, S. and Otomasu, H. (1979). *Chem. Pharm. Bull. (Tokyo)* **27**, 151.
5. Murakoshi, I., Ogawa, M., Toriizuka, K. Haginiwa, J., Ohmiya, S. and Otomasu, H. (1977) *Chem. Pharm. Bull. (Tokyo)* **25**, 527.
6. Podkowinska, H. and Wiewiorowski, M. (1965) *Bull. Acad. Polon. Sci. Ser. Sci. Biol.* **13**, 623.
7. Kabasakalian, P., Kalliney, S. and Westcott, A. (1974) *Clin. Chem.* **20**, 606.
8. Podkowinska, H. and Wiewiorowski, M. (1967) *Bulll Acad. Polon Sci. Ser. Sci. Chim.* **15**, 467.

Phytochemistry, 1979, Vol. 18, pp. 700–701. ©Pergamon Press Ltd. Printed in England. 0031-9422/79/0401-0700 $02.00/0

RUDRAKINE, A NEW ALKALOID FROM *ELAEOCARPUS GANITRUS**

A. B. RAY, LAL CHAND and V. B. PANDEY

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

(*Received* 20 *April* 1978)

Key Word Index—*Elaeocarpus ganitrus*; Elaeocarpaceae; alkaloid; rudrakine.

INTRODUCTION

In continuation of our search for chemical constituents from different *Elaeocarpus* species [1–3], we have isolated a minor alkaloid, rudrakine, from the leaves of *Elaeocarpus ganitrus* Roxb. (Sanskrit: Rudraksh). *E. granitrus*, which grows in the Himalayan region, is valued in India for its attractive fruit stones and also for its medicinal properties [4, 5]. The present communication describes the structural elucidation of rudrakine.

RESULTS AND DISCUSSION

Rudrakine, $C_{16}H_{23}NO_3$, M^+ 277, mp 159–60°, was characterized as an indolizidine alkaloid like other C_{16}-alkaloids of *Elaeocarpus* species [6] from its MS which showed the base peak at *m/e* 122 (ion **a**) and an important peak at *m/e* 97 (ion **b**). The similarity of the UV and IR spectra of rudrakine (λ_{max} 272 nm, ε 7300; ν_{max} 1660 cm^{-1}) with those reported for pseudoepi-isoelaeocarpiline (**1**) (λ_{max} 275 nm, ε 7600; ν_{max} 1665 cm^{-1}) suggested the presence of a dihydro-γ-pyrone chromophore in the molecule. Recognition of the third oxygen function as OH from the IR band at 3450 cm^{-1}, and the absence of any olefinic or aromatic proton and presence of a secondary C-Me group (3H, $d\,\delta$ 1.2; $J = 7$ Hz) from the PMR spectrum of the alkaloid, led to a tetracyclic structure for rudrakine similar to that of **1** but differing from the latter by the presence of a OH group and the absence of 14,15 double bond. The position of the OH group in the tetracyclic skeleton was considered to be at C-14 on biogenetic grounds and MS evidence. The genesis of the ion species **a** and **b** on electron impact and their abundance as discerned from the spectrum of rudrakine clearly indicates that the OH is not attached to any of the carbon atoms of the indolizidine part of the molecule. Again, the presence of the secondary C-Me group excludes the possibility of its linkage to C-16. Of the remaining 3 sites in ring A, C-14 is the most appropriate site for this group, as C_{16}-alkaloids of *Elaeocarpus* species are known to be derived from 6 acetate and one ornithine units [6]. The placement of the OH group at C-14 also rationalizes the appearance of a small but significant MS peak at *m/e* 207 (ion **c**). The structure of rudrakine was thus established as **2**.

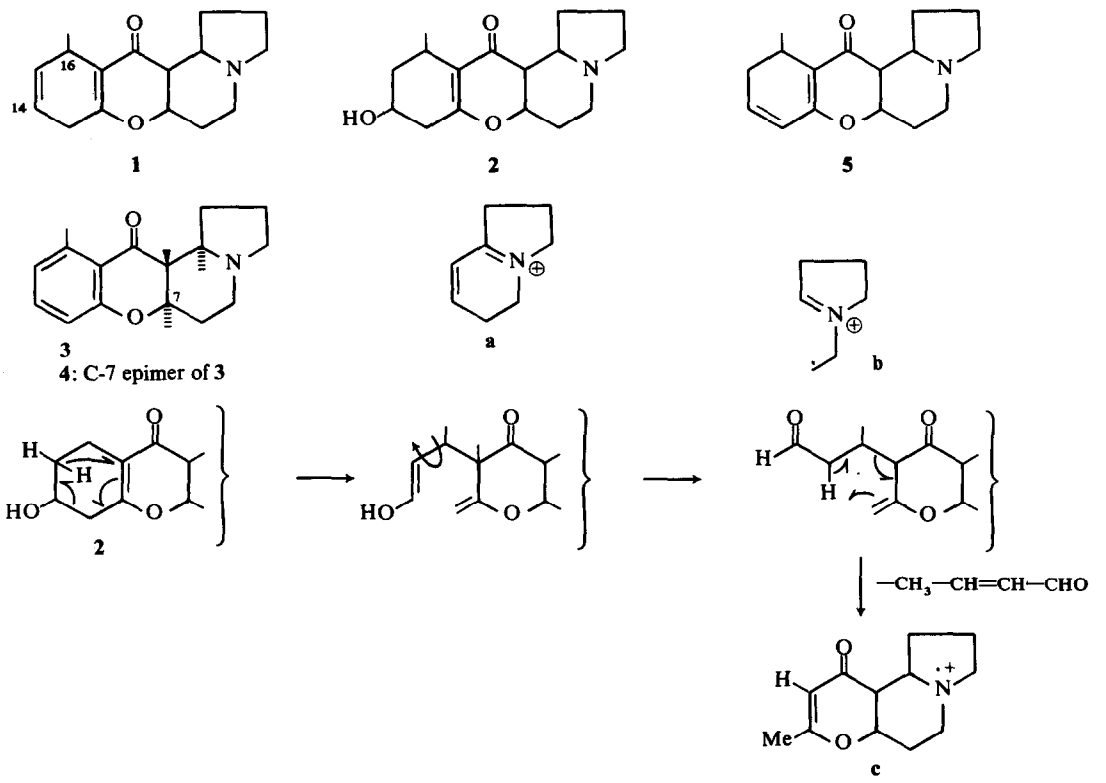
A number of C_{16}-dienone alkaloids including (±)-elaeocarpine (**3**) and (±)-isoelaeocarpine (**4**) as minor constituents have been isolated from the leaves of *E. sphaericus* (Gaertn.) K. Schum. of New Guinea [7], a plant reported to be synonymous with *E. ganitrus* Roxb. of India [8]. An ecological variation is manifested in the Indian species which reveals the presence of aromatic alkaloids **3** and **4** as major constituents [1, 9], absence of dienone alkaloids and the presence of a new alkaloid rudrakine. Isolation of rudrakine is indeed of biogenetic significance because it appears to be an intermediate which by loss of H_2O can give rise to both conjugated and non-conjugated dienone alkaloids like elaeocarpiline (**5**) and pseudoepi-isoelaeocarpiline (**1**).

EXPERIMENTAL

Mps were determined in open capillary and are uncorr. UV spectra were measured in MeOH; IR in Nujol and PMR at 60 MHz.

Isolation of alkaloids. Dried and powdered leaves (10 kg) of *E. ganitrus* Roxb. were defatted with petrol (60–80°) and then extracted with EtOH (95%) by cold percolation. The extract was concd under red. pres. to a dark brown syrup, stirred with citric acid (5%) and filtered. The filtrate was made alkaline with NH_4OH (pH 9) and exhaustively extracted with $CHCl_3$.

* Paper presented at the 37th International Congress of Pharmaceutical Sciences, Hague, Holland, 5 September, 1977.



The $CHCl_3$ layer was dried, concd and chromatographed over Brockmann neutral Al_2O_3 monitoring at every stage for homogeneity of the eluates by Si gel TLC. Fractions eluted with petrol (60–80°) furnished (±)-elaeocarpine (0.7 g), mp 81–82° (Me_2CO), $[\alpha]_D \pm 0°$ ($CHCl_3$), hydrobromide, mp 290–92°. Petrol–C_6H_6 (1:1) eluates afforded (±)-isoelaeocarpine (0.1 g), mp 51–52°, $[\alpha]_D \pm 0°$, hydrobromide, mp 258°. Identity of these two alkaloids was proved by direct comparison (mmp co-TLC, IR) with authentic samples.

Rudrakine (2). Fractions eluted with C_6H_6–EtOAc (19:1) were combined and rechromatographed over Si gel. Elution with EtOAc–MeOH (19:1) afforded rudrakine (2) (0.03 g) which crystallized from MeOH as colourless needles, mp 159–60°, λ_{max} 272 nm, ε 7300; ν_{max} 3450, 1660 cm^{-1}; PMR: δ 1.2 (3H, *d*, *J* = 7 Hz; CH–CH_3); 4.15 (2H, *m*, two CH–O–); MS 70 eV, *m/e* (rel. int.): 277 M^+ (48), 259 (4) $M^+ - 18$, 276 (15), 262 (48), 260 (17), 207 (7), 122 (100), 109 (22), 97 (37), 82 (35). (Found: C, 68.97; H, 8.22; N, 5.17. $C_{16}H_{23}NO_3$ requires: C, 69.28; H, 8.36; N, 5.05%).

Acknowledgements—The authors express their sincere thanks to Prof. J. A. Lamberton, Division of Applied Chemistry, C.S.I.R.O., Melbourne, Australia for kind supply of (±)-elaeocarpine and isoelaeocarpine hydrobromides. Thanks are also due to Dr. B. C. Das, I.C.S.N., Gif-sur-Yvette, France for MS.

REFERENCES

1. Lal Chand (1975) *Phytochemistry* **14**, 2727.
2. Ray, A. B., Dutta, S. C. and Dasgupta, S. (1976) *Phytochemistry* **15**, 1797.
3. Lal Chand, Dasgupta, S., Chattopadhyay, S. K. and Ray, A. B. (1977) *Planta Med.* **32**, 197.
4. Chopra, R. N., Nayer, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 105. C.S.I.R., New Delhi.
5. Bhattacharya, S. K., Debnath, P. K., Pandey, V. B. and Sanyal, A. K. (1975) *Plant Med.* **28**, 174.
6. Johns, S. R. and Lamberton, J. A. (1973) in *The Alkaloids* (Manske, R. H. F., ed) Vol. 14, pp. 324–346. Academic Press, New York.
7. Johns, S. R., Lamberton, J. A., Sioumis, A. A., Saures, H. and Willing, R. I. (1971) *Aust. J. Chem.* **24**, 1679.
8. (1952) *Wealth of India, Raw Materials*, Vol. 3, p. 140. C.S.I.R., New Delhi.
9. Barua, A. K., Dasgupta, C., Chakravarti, S., Choudhury, M. K. and Ghosh, A. (1976) *J. Indian Chem. Soc.* **53**, 531.