H-9, H-10), 7.67 (*d*, $J = 5$ Hz, H-4), 8.23 (*dd*, $J = 8$ and 2 Hz, H-8), 8.9 (*d*, $J = 5$ Hz, H-5). MS (*m/e*): 291 (39 %) M, 275 (50), 247 (13), 246 (10), 177 (9), 85 (45), 83 (70), 78 (100). Methylation with CH_2N_2 in Et_2O gave oxo-*O*-methylpukateine (**1b**).

REFERENCES

1. Braz Fo., R., Gabriel, S. J., Gomes, C. M. R., Gottlieb, O. R., Bichara, M. das G. A. and Maia, J. G. S. (1976) *Phytochemistry* **15**, 1187.
2. Casagrande, C. and Ferrari, G. (1970) *Farmaco (Pavia) Ed. Sci.* **25**, 442.
3. Waterman, P. G. (1976) *Phytochemistry* **15**, 347.
4. Dwuma-Bade, D., Ayim, J. S. K., Tackie, A. N., Knapp, J. E., Slatkin, D. J. and Schiff Jr., P. L. (1975) *Phytochemistry* **14**, 2524.
5. Huls, R. (1972) *Bull. Soc. Roy. Sci. Liege* **41**, 686.
6. Hasegawa, M., Sojo, M, Lira, A. and Marquez, C. (1972) *Acta Cient. Venezolana* **23**, 165.
7. Shamma, M. (1972) *The Isoquinoline Alkaloids* p. 245 Academic Press, New York.
8. Watanabe, Y., Matsui, M., Iibuchi, M. and Hiroe, S. (1975) *Phytochemistry* **14**, 2522.
9. Bernauer, K. (1967) *Helv. Chim. Acta* **50**, 1583

Phytochemistry, 1978, Vol 17, pp 838–839 Pergamon Press Printed in England

LEAF ALKALOIDS OF *FAGARA MAYU*

RENE TORRES and BRUCE K. CASSELS

Universidad Técnica del Estado, Facultad de Ciencia, Departamento de Química, Santiago 2, Chile

(*Revised received* 25 *August* 1977)

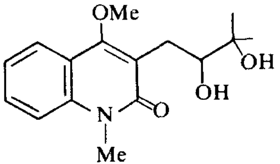
Key Word Index—*Fagara mayu*; Rutaceae; alkaloids, skimmianine, (—)-edulinine; ribalinine.

Fagara mayu (Bert. ex Hook. et Arn.) Engler (= *Zanthoxylum mayu* Bert.) is the most abundant tree in the rain forest of Robinson Crusoe Island (Juan Fernández Group) [1]. Morphologically, this species seems to be somewhat removed from the rest of its genus, and Engler created the monotypic section *Mayu* to differentiate it from the large sections *Macqueria* and *Blackburnia* [2].

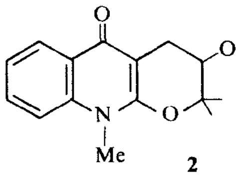
An earlier publication showed that the trunk bark contains the tetrahydrobenzylisoquinoline-derived chelerythrine and magnoflorine, the anthranilic acid-derived canthin-6-one and the furanoquinolines skimmianine, dictamnine and γ-fagarine, and an unidentified slightly laevorotatory alkaloid melting at 139–140°, apparent MW 273 (MS) [3]. The presence of furanoquinolines, which are lacking in all American species of the *Zanthoxylum*/*Fagara* complex studied so far with the exception of *F. coco* [4], *Z. belizense* [5] and *Z. americanum* [6], indicates a relatively advanced position in the phylogeny of this group [7]. The isolation of the furanocoumarins psoralen, bergapten, xanthotoxin and isopimpinellin from the leaves [8], on the other hand, is not considered significant for the sake of comparison with South American *Fagara* species, as several of these which have been shown to contain alkaloids have not been examined for neutral components [9].

The leaves of *Fagara mayu* also contain a small amount of alkaloids (0.1 %). This paper reports the separation and identification of these compounds as skimmianine, (−)-edulinine (**1**), and ribalinine (**2**). As mentioned above, skimmianine has been found in the bark [3], where it is accompanied by another two common furanoquinolines which are not present in the leaves. The unidentified bark alkaloid is probably (—)-edulinine, whose MS taken in the usual way shows an extremely faint molecular ion peak and a weak signal at *m/e* 273; the discrepancies in the mp of this compound are probably due to polymorphism.

It seems unlikely, given the weakly basic conditions under which the alkaloids were extracted, that (−)-edulinine is an artefact. The possibility cannot be ruled out, however, that this substance is formed by the attack of OH^- on *N*-methylplatydesminium and/or the hypothetical *N*-methylribalininium cation, neither of which has yet been found in this plant. The apparent lack of optical activity of ribalinine at the sodium D line [10], should not be taken as an indication that this substance is a racemic mixture.



1



2

To the best of our knowledge, no other member of the *Zanthoxylum*/*Fagara* complex has been shown to contain edulinine or ribalinine (or its quarternary precursors, if it should be proved to be an artefact), and the accumulation of these uncommon offshoots of the main biogenetic route to furanoquinoline alkaloids may be of some taxonomic significance. In this connection, it should be pointed out that the African species *Fagara chalybea* [11] and the Puerto Rican *Zanthoxylum monophyllum* [12] contain angular pyranoquinolones, while *F. mayu* is the only member of this group which is known to synthesize a linear pyranoquinolone.

EXPERIMENTAL

All mps are uncorr. UV, IR and PMR (60 MHz, TMS as int. stand.) spectra were determined in EtOH, KBr and $CDCl_3$, respectively. MS were recorded using electron impact ionization at 70 eV and 200°. TLC was carried out on Si gel HF_{254} using $CHCl_3$–MeOH (9:1).

Isolation of bases. 1.3 kg air-dried leaves, collected in February (summer), 1973 (voucher specimen deposited in the herbarium of the Museo Nacional de Historia Natural, Santiago de Chile), finely ground, were extracted successively with petrol and MeOH. Removal of MeOH gave a residue which was suspended in 2N HCl, filtered and extracted with $CHCl_3$. The aq. soln was basified to pH 9 with NH_4OH and re-extracted with $CHCl_3$. The solid, yellowish-white residue (1.56 g) from the $CHCl_3$ extract of the basified solution showed three Dragendorff-positive spots on TLC (R_f 0.8, 0.3 and 0.2), the foremost of which was very much larger than the others. The product with R_f 0.8 was separated by crystallisation from Me_2CO and Me_2CO–MeOH (1:1). Column chromatography of the residual solutions on Al_2O_3 yielded further amounts of this first base, and allowed separation of the two minor components.

Skimmianine. R_f 0.8, mp 176–177°, UV, IR and PMR spectra as in ref. [13]. Picrate, mp 197° (MeOH).

Edulinine. 95 mg, R_f 0.3, mp 103–105° (EtOAc) (lit. 140–142° [14], 111–114° [15], 114–117° [15]), $[\alpha]_D^{20}$ −17° ($CHCl_3$; c = 1), UV, IR, PMR and MS as described in refs [14, 16].

Ribalinine. 15 mg, R_f 0.2, mp 235–236° (EtOH), UV spectrum as described in ref. [10]. MS ions at m/e 259.1215 (M^+, calc. for $C_{15}H_{17}NO_3$, 259.1208, base peak), 188.0711 (M^+-C_4H_7O, calc. for $C_{11}H_{10}NO_2$, 188.0711, 85%). The IR spectra of this substance and of an authentic sample of ribalinine were found to be identical.

Acknowledgements—We thank Dr. Gert Eckhardt for MS, Prof. O. O. Orazi for the IR comparison of ribalinine, and an anonymous referee for pointing out recent literature. This work was supported by DICYT.

REFERENCES

1. Skottsberg, C. (1921) *The Phanerograms of the Juan Fernández Islands.* Almquist and Wiksells, Uppsala.
2. Engler, A. (1931) *Die Natürlichen Pflanzenfamilien* 2nd ed., Vol. 19a. Engelmann, Leipzig.
3. Benages, I. A., de Juárez, M. E. A., Albónico, S. M., Urzúa, A. and Cassels, B. K. (1974) *Phytochemistry* **13**, 2891.
4. Deulofeu, V., Labriola, R. and de Langhe, J. (1942) *J. Am. Chem. Soc.* **64**, 2326.
5. Najjar, S., Cordell, G. A. and Farnsworth, N. R. (1975) *Phytochemistry* **14**, 2309.
6. Sun, G. C. (1975) *Dissertation Abstr.* **35B**, 5826.
7. Fish, F. and Waterman, P. G. (1973) *Taxon* **22**, 177.
8. Torres, R. and Cassels, B. K. (1975) *Anales Asoc. Quím. Arg.* **63**, 187.
9. Kuck, A. M., Albónico, S. M., Deulofeu, V. and Escalante, M. G. (1967) *Phytochemistry* **6**, 1541.
10. Corral, R. A., Orazi, O. O. and Benages, I. A. (1973) *Tetrahedron* **29**, 205.
11. Hostettmann, K., Pettei, M. J., Kubo, I. and Nakanishi, K. (1977) *Helv. Chim. Acta* **60**, 670.
12. Sharifi, I. A. and Stermitz, F. R. (1977) personal communication.
13. Mitscher, L. A., Bathala, M. S., Clark, G. W. and Beal, J. L. (1975) *Lloydia* **38**, 117.
14. Iriarte, J., Kincl, F. A., Rosenkranz, G. and Sondheimer, F. (1956) *J. Chem. Soc.* 4170.
15. Boyd, D. R. and Grundon, M. F. (1970) *J. Chem. Soc. (C)* 556.
16. Toube, T. P., Murphy, J. W. and Cross, A. D. (1967) *Tetrahedron* **23**, 2061.

Phytochemistry, 1978, Vol 17, pp 839–840 Pergamon Press. Printed in England.

ALKALOIDS AND A STEROL FROM *CHELIDONIUM JAPONICUM*

H. Itokawa, A. Ikuta, N. Tsutsui and I. Ishiguro
Tokyo College of Pharmacy, Hachioji, Tokyo, Japan

(*Received* 11 *July* 1977)

Key Word Index—*Chelidonium japonicum*; Papaveraceae; alkaloids; 6-hydroxymethyldihydrosanguinarine; bocconoline; norchelerythrine; norsanguinarine; α-spinasterol

The presence of several alkaloids in root and aerial parts of *Chelidonium japonicum* Thunb have been reported by Slavik [1] on the basis of TLC and PC evidence. We now report isolation and identification on the alkaloids and sterols of this plant.

The basic $CHCl_3$ soluble fraction gave two compounds **1** and **2** after chromatographic separation. **1** and **2** showed identical UV spectra of characteristic benzo(*c*)-phenanthridine alkaloids. **1** contained two methylenedioxy groups at 6.25 and 6.50 (each *s*, 2H) by NMR and also a base peak at m/e 317 (M^+) in MS. **2** had one methylenedioxy group at 6.24 (*s*, 2H), two methoxyls at 4.23 and 4.4 (each *s*, 3H) by NMR, and a base peak at m/e 333 (M^+) by MS. From the available data **1** and **2** were identified as norsanguinarine and norchelerythrine respectively. The identities were confirmed by direct comparison with the authentic samples.

Elution with $CHCl_3$–EtOAc afforded **3** and crude **4** and **4** was rechromatographed on Al_2O_3 (grade IV) with benzene. **3** and **4** showed identical UV spectra and IR respectively. **3** had the following spectral properties: UV bands at 212, 228, 283, 320 and 350 (*sh*) and IR at 3440 (OH). NMR indicated the presence of two methoxyls at 3.92 and 3.96 (each *s*, 3H), one methylenedioxy group at 6.07 (*s*, 2H), N–Me at 2.76 (*s*, 3H), C_6–H at 4.72 (*q*, 1H), $C\underline{H}_2OH$ at 3.10 (*t*, 1H) and 3.53 (*q*, 1H).

The hydroxymethyl group was also suggested by m/e 348 (M^+-31) eliminated from the substituent at C_6. Slavik *et al.* [3] suggested that the loss of a substituent at C_6 in the MS was characteristic of 6-substituted dihydrobenzo-(*c*)-phenanthridine alkaloids. The above data suggested that this compound was identical with bocconoline isolated from *Bocconoria cordata* [2]. The identities were confirmed by direct comparison with the data of an