Phytochemistry, 1978, Vol 17, pp. 837–838. Pergamon Press Printed in England.

OXOAPORPHINE ALKALOIDS FROM *DUGUETIA EXIMIA**

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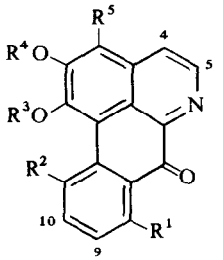
(*Received* 5 *July* 1977)

Key Word Index—*Duguetia eximia*; Annonaceae; alkaloids; 2,4,5-trimethoxystyrene; oxoaporphines.

Duguetia eximia Diels (Annonaceae) was collected near Manaus, AM, and identifed by Dr. W. A. Rodrigues. Voucher INPA, Manaus, 42236. There is no previous work recorded for this species although two aporphines and a (6*aS*, 7*S*)-7-hydroxyaporphine (duguetin) were isolated from an unclassified Brazilian *Duguetia* sp. [2].

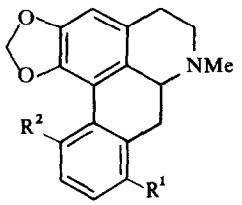
In the present work the C_6H_6 extract (6 g, 0.15%) of a trunk wood sample was separated by Si gel column and TLC into the following compounds, listed in order of increasing polarity: 2,4,5-trimethoxystyrene (11 mg), sitosterol (40 mg), *O*-methylmoschatoline (35 mg) (**1a**), 11-methoxy-1,2-methylenedioxyoxoaprophine (110 mg) (**1b**) and 11-hydroxy-1,2-methylenedioxyoxoaporphine (10 mg) (**1c**).

The styrene, previously isolated from *Pachypodanthium staudtii* Eng. *et* Diels (Annonaceae) [3] and **1a**, previously isolated from *Triclisia patens* Oliv. [4], *T. gilletti* Oliv. [5] (Menispermaceae) and *Guatteria subsellis* (Annonaceae) [6], were identifed by comparison of mp, UV, IR, PMR and MS with reported data. The new compounds **1b** and **1c** were also charaterized as oxoaporphines by their colour and bathochromic UV shifts in acid solution, as well as by their carbonyl absorptions at 1660 cm^{-1} [7]. The molecular formulae $C_{18}H_{11}O_4N$ (**1b**) and $C_{17}H_9O_4N$ (**1c**), determined by elementary analyses and MS, could be expanded, respectively, to $C_{15}H_6N.CO.O_2CH_2.OMe$ and $C_{15}H_6N.CO.O_2CH_2.OH$ after inspection of the PMR spectra. Indeed, as was consequently expected, methylation of **1c** gave an *O*-methyl derivative which proved to be



1a $R^1 = R^2 = H$, $R^3 = R^4 = Me$, $R^5 = OMe$
1b $R^1 = R^5 = H$, $R^2 = OMe$, $R^3—R^4 = CH_2$
1c $R^1 = R^5 = H$, $R^2 = OH$, $R^3—R^4 = CH_2$
1d $R^1 = OMe$, $R^2 = R^5 = H$, $R^3—R^4 = CH_2$

identical, in all respects, with natural **1b**. The 6 undefined hydrogens in these compounds cause 3 groups of PMR bands: (i) two doublets (J = 5 Hz) at low field, typical



2a R^1 = OMe, R^2 = H
2b R^1 = H, R^2 = OMe

of H-5 and H-4 of the isoquinoline system [7], (ii) a singlet and (iii) two double doublets (J = 8.5, 2 Hz) and one triplet (J = 8.5 Hz). Double irradiation experiments, performed on the *O*-methyl derivative, confirmed the vicinality of two and three protons, indicated respectively by signal groups (i) and (ii). Among the structural alternatives consistent with the coupling constants, **1b** seemed most consistent with the chemical shift data. Indeed, **1d** represents oxostephanine [ex. *Stephania japonica* Miers (Menispermaceae)], which has a considerably higher mp (270–272°), and had its proposed structure supported by reduction and N-methylation to (±)-stephanine (**2a**). Analogously, successive MeI-methylation and Clemmensen reduction of **1b** gave (±)-*O*-methypukateine (**2b**) identified by direct comparison (IR and PMR) with an authentic sample, and was thus designated oxo-*O*-methylpukateine.

EXPERIMENTAL

Oxo-O-methylpukateine (**1 b**). Yellow crystals, mp 241–242° ($CHCl_3$), $[\alpha]_D^{25°}$ ±0° (*c* 1, $CHCl_3$) [Found: C, 71.02; H, 3.65; N, 4.49. $C_{18}H_{11}O_4N$ requires: C, 70.82; H, 3.63; N, 4.59%]. $\lambda_{max}^{CHCl_3}$ (nm): 249, 276, 290 *sh*, 312 (log ε 4.64, 4.21, 4.00, 3.60); $\lambda_{max}^{CHCl_3+NHCl}$ (nm): 229, 259, 294, 328 (log ε 4.28, 4.28, 4.22, 3.61). ν_{max}^{KBr} (cm^{-1}): 1660, 1595, 925. PMR ($CDCl_3$, 60 MHz, δ): 3.96 (*s*, OMe), 6.22 (O_2CH_2), 7.08 (*s*, H-3), 7.25 (*dd*, J = 8.5, 2 Hz, H-10), 7.54 (*t*, J = 8.5 Hz, H-9), 7.7 (*d*, J = Hz, H-4), 8.17 (*dd*, J = 8.5, 2 Hz, H-8), 8.64 (*d*, J = 5 Hz, H-5). MS (*m/e*): 305 (100%) M, 291 (32), 262 (19), 248 (25), 234 (15). *N*-methylation with MeI in THF, followed by Zn/HCl reduction [9] gave (±)-*O*-methylpukateine, identical with respect to HPLC, IR and PMR with a sample [9] kindly supplied by Dr. Karl Bernauer, Hoffmann-La Roche, Basel, Switzerland.

11-Hydroxy-1,2-methylenedioxyoxoaporphine (**1c**). Yellow crystals, mp 255–257° (C_6H_6) Found: C, 69.98; H, 3.01; N, 4.95. $C_{17}H_9O_4N$ requires: C, 70.10; H, 3.11; N, 4.81. λ_{max}^{EtOH} (nm) 248, 260 *sh*, 274, 311 (log ε 4.14, 3.92, 4.04, 3.39). $\lambda_{max}^{EtOH+NaOH}$ (nm) 226, 248 *sh*, 254 *sh*, 260 *sh*, 272 *sh*, 301 (log ε 4.36, 4.30, 4.26, 4.19, 3.92, 4.08); $\lambda_{max}^{EtOH+NaOH+HCl}$ (nm): 249 *sh*, 254, 257, 273 *sh*, 293, 328 *sh* (log ε 4.06, 4.11, 4.11, 3.67, 3.98, 3.29). ν_{max}^{KBr} (cm^{-1}): 3250, 1660, 1600, 1580, 1460, 1309, 1066, 1050, 976. PMR ($CDCl_3$, 60 MHz, δ): 6.33 (*s*, O_2CH_2), 7.17 (*s*, H-3), 7.47 (*m*,

* Part 3 in the series 'The Chemistry of Brazilian Annonaceae'. For Part 2 see ref. [1].

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**).

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

LEAF ALKALOIDS OF *FAGARA MAYU*

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(*Revised received* 25 *August* 1977)

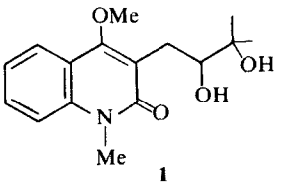
Key Word Index—*Fagara mayu*; Rutaceae; alkaloids, skimmianine, (—)-edulinine; ribalinine.

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



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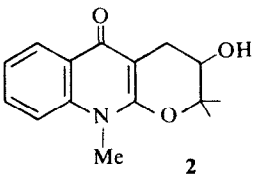

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of OH^- on *N*-methylplatydesminium and/or the hypothetical *N*-methylribalininium cation, neither of which has yet been found in this plant. The apparent lack of optical activity of ribalinine at the sodium D line [10], should not be taken as an indication that this substance is a racemic mixture.

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).