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ALKALOIDS OF *MAGNOLIA CAMPBELLII* AND *MAGNOLIA MUTABILIS*

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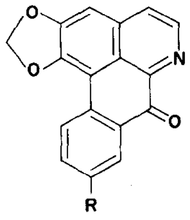
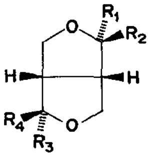
Key Word Index—*Magnolia campbellii*, *M. mutabilis*; Magnoliaceae; lanuginosine; liriodenine, sitosterol and (−)-sesamin.

The genus *Magnolia* comprises nearly 70 species [1], many of which have been chemically examined because of the occurrence of compounds covering a diversified series of skeletal patterns in the Magnoliaceae. Two uninvestigated species of this genus, *M. campbellii* H.f. and T. and *M. mutabilis* Regel. which are mainly distributed in the forests of Sikkim and Bhotan in Eastern Himalayas, were collected at an altitude of 2000–3000 m.



(**1**) R = OMe
(**2**) R = H



(**3**) R_1, R_3 = H; R_2, R_4 = 3, 4-methylenedioxyphenyl
(**4**) R_1, R_4 = H; R_2, R_3 = 3, 4-methylenedioxyphenyl

Magnolia campbellii was found to contain the oxoaporphine alkaloids, lanuginosine [2] (**1**) and liriodenine [3] (**2**) from the basic part of the $CHCl_3$ extract and sitosterol [4] from the light petrol extract and the neutral part of the $CHCl_3$ extract. This is the first report of the occurrence of an oxygenated liriodenine in the genus *Magnolia*, although liriodenine itself occurs in a number of *Magnolia* species [3]. The leaves of *M. mutabilis* afforded liriodenine [3] (**2**) from the basic fraction of $CHCl_3$ and (−)-sesamin [5] (**3**) from light petrol extract.

The spectral data (UV, IR, PMR) of (−)-sesamin were as already reported [6]. The MS peaks of sesamin, not reported earlier, are similar to its epimer, episesamin [7] (≡asarinin) (**4**), but the relative abundances of the peaks differ.

EXPERIMENTAL

Dried and milled stem-bark of *M. campbellii* and leaves of *M. mutabilis* were exhaustively extracted successively with light petrol (60–80°) and $CHCl_3$ (Soxhlet). From the extract concentrates the neutral and basic components were separated in the usual way.

M. campbellii. The basic fraction of the $CHCl_3$ extract chromatographed several times on alumina with $CHCl_3$ gave (from $CHCl_3$ solution) pure lanuginosine [2] (**1**) in glistening orange needles (12 mg/kg), m.p. 312–314° *d*; single iodine-stained and UV fluorescent (orange) spot, R_f 0·61, silica gel G, $CHCl_3$–MeOH (93:7); MS: *m/e* 305 (100%, M^+) and 275 (5%, $M^+ - CH_2O$); identified by direct comparison (UV, IR, m.m.p., Co–TLC). The residue, m.p. 295–298° *d*, from the mother liquors was found to be mainly lanuginosine contaminated with a minor amount of liriodenine (R_f 0·58, TLC as before). The MS showed two strong peaks at *m/e* 305 and 275 due to molecular ions of (**1**) and (**2**) respectively.

Sitosterol was isolated from the light petrol extract of *M. campbellii*, in the usual way, m.p. 137°, $[\alpha]_D$ −34° ($CHCl_3$); acetate, m.p. 134°, $[\alpha]_D$ −37° ($CHCl_3$).

M. mutabilis. The $CHCl_3$ extract treated as above gave liriodenine (33 mg/kg) (m.m.p., Co–TLC, IR). The light petrol extract chromatographed over silica gel G. with light petrol–C_6H_6 (1:1) gave needles (2·9 g/kg), m.p. 125–126°, $[\alpha]_D$ −44·3° ($CHCl_3$), R_f 0·65, silica gel G, C_6H_6–$CHCl_3$ (1:1); MS: *m/e* 354 (54%, M^+), 203 (21·6), 178 (14·9), 161 (55·4), 150 (33·8), 149 (100), 135 (50), 131 (33·8), 122 (25·7), 121 (13·5). Its dibromo derivative, prepared in the usual way, had m.p. 172–173° and was identical with an authentic sample of dibromosesamin (m.m.p., Co–TLC, IR).

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REFERENCES

1. Hooker, J. D. (1875) *The Flora of British India*, Vol. I, p. 39, L. Reeve, London.
2. Talapatra, S. K., Patra, A. and Talapatra, B. (1969) *Chem. Ind. (London)* 1056.
3. Shamma, M. (1972) *The Isoquinoline Alkaloids in Organic Chemistry*, Vol. 25, pp. 244–258, Academic Press, New York.
4. Heilbron, I., Cook, A. H., Bunbury, H. M. and Hey, D. H. (1965) *Dictionary of Organic Compounds*, Vol. 5, p. 2902, Eyre & Spottiswoode, London.
5. Atal, C. K., Dhar, K. L. and Pelter, A. (1967) *J. Chem. Soc. C.*, 2228.
6. Jones, W. A., Beroza, M. and Beaker, E. D. (1962) *J. Org. Chem.* **27**, 3232.
7. Pelter, A. (1967) *J. Chem. Soc. C.*, 1376.

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JURUENOLIDE: A γ-LACTONE FROM *IRYANTHERA JURUENSIS*[*]

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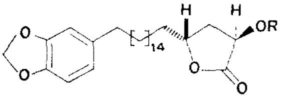
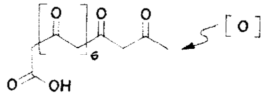
Key Word Index—*Iryanthera juruensis*; Myristicaceae; 2*R*,4*R*-dihydroxy-20-piperonyleicosanoic acid γ-lactone; juruenolide.

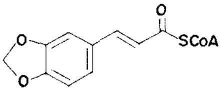
The chemical investigation of the trunk wood of a specimen of *Iryanthera juruensis* Warb. (Myristicaceae), revealed the presence of sitosterol, sitostenone, (±)-2′-hydroxy-7-methoxy-4′,5′-methylenedioxyflavan [1] and a lactone, $C_{27}H_{42}O_5$, designated juruenolide. The PMR spectra of the compound and of its acetate allowed expansion of the formula to **1a**. This contains a piperonylethyl unit (τ 3·3–3·5, 3ArH; 4·16, O_2CH_2; 7·53, *t*, *J* 7·5 Hz, $ArC\underline{H}_2CH_2$), a methylene chain (τ 8·2–8·8, 15 CH_2), whose signal covers an additional one H signal, and a hydroxy-γ-lactone unit (**1a** ν_{max} 1745 cm^{-1}; **1b** ν_{max} 1770, 1730 cm^{-1}). The allocation of the hydroxyl to C-2 and of the methylene chain to C-4 of this lactone was based on the analysis of the signals associated with its 2 oxymethine and 2 methylene protons. The latter can only be situated on C-3. Double irradiation experiments revealed one of them (τ 8·7) to be coupled to H-4 (τ 5·52) and the other one (τ 7·44) to H-2 (τ 5·88). Further correlation of the τ 5·88 doublet with the carbinolic proton was based on the paramagnetic shift (Δ − 0·86 ppm) of this signal upon acetylation.



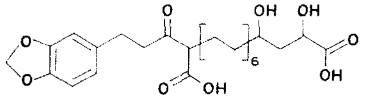
(**1a**) R = H
(**1b**) R = Ac



(**2**)



(**3**)



(**4**)

The relatively high τ value (8·7) of one of the methylene proton signals indicated that the corresponding H-3 is situated well over the plane of the carbonyl. Coupling and absence of coupling was seen as evidence, respectively, for its *cis*-relation to H-4 and *trans*-relation to H-2. An identical conclusion about the relative stereochemistry of juruenolide was reached upon observing the coupling of the relatively deprotected (τ 7·44), and hence *quasi*-equatorial, H-3 to H-2 and the absence of coupling to H-4. According to the modified Hudson rule [2], formula **1a** represents also the absolute configuration of the lactone, since this is more dextrorotatory, $[\alpha]_D^{20}$ + 12·5 (MeOH), than its potassium salt $[\alpha]_D^{20}$ + 10·0 (MeOH).

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