from algae to the lower vascular plants in sterol biosynthetic capability. This is particularly interesting since the liverworts are considered by virtue of their anatomy and reproductive strategy to represent an early evolutionary branch of the land plants.

EXPERIMENTAL

Organism. Palavicinnia lyellii was collected in large mats of nearly pure culture from the pine barrens of New Jersey, U.S.A. The thallus was cleaned of all soil and detritus.

Extraction and separation. Lipids of *P. lyellii* (61.6 g) were extracted with Me_2CO for 48 hr in a Soxhlet. The solvent was evaporated and the extracts were saponified at reflux for 4 hr with 5% KOH in 50% MeOH. Extraction with Et_2O (× 3) yielded a neutral lipid (278 mg). This was chromatographed on a 3% deactivated Al_2O_3 column with a solvent system of dry Et_2O graded into hexane, and finally with MeOH. The sterol fraction was then chromatographed on Si gel TLC with C_6H_6–EtOAc (9:1). The 4-desmethylsterols (9.7 mg) had $R_f = 0.17$, were detected by dichlorofluorescein under UV and were eluted with dry Et_2O. GC was performed on a 6 m × 2 mm 1% XE-60 column at 240° with He at 45 ml/min. All RR_t's are relative to cholesterol. Prep. HPLC was performed on a Whatman M-20 column (25 × 2.5 cm) packed with Whatman ODS-3 chromatographed at 28° with MeOH–MeCN (1:9) 7.5 ml/min. Analytical HPLC was performed on a C_{18} μBondpak column (30 cm × 3 mm) chromatographed at 55° with MeCN–*iso*-PrOH (8:2) at 1 ml/min. The α_c's (K′ sample/K′ cholesterol) [9] are reported only from the analytical column. Detection for both HPLC techniques was by UV at 205 nm. EIMS (probe) was performed at 70 eV. ^{1}H NMR was performed at 360 MHz at ambient temp. in $CDCl_3$ with TMS as an int. standard.

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REFERENCES

1. Marsili, A. and Morelli, I. (1968) *Phytochemistry* **7**, 1705.
2. Marsili, A. and Morelli, I. (1970) *Phytochemistry* **9**, 651.
3. Matsuo, A., Nakayma, N., Maeda, M., Hayashi, S. and Yasuda, S. (1973) *Phytochemistry* **12**, 2413.
4. Nes, W. R. and McKean, M. L. (1978) *Biochemistry of Steroids and Other Isopentenoids*. p. 411. University Park Press, Baltimore.
5. Knights, B. A. (1967) *J. Gas Chromatogr.* **5**, 273.
6. Chiu, P. L. and Patterson, G. W. (1981) *Lipids* **15**, 203.
7. Patterson, G. W. (1971) *Lipids* **6**, 120.
8. Barton, D. H. R. and Robinson, C. H. (1954) *J. Chem. Soc.* 3045.
9. DiBussolo, J. M. and Nes, W. R. (1982) *J. Chromatogr. Sci.* **20**, 193.

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7-DEHYDROSITOSTEROL FROM *RAUWOLFIA SERPENTINA*

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Key Word Index—*Rauwolfia serpentina*; Apocynaceae; 7-dehydrositosterol.

Abstract—7-Dehydrositosterol has been isolated from the roots of *Rauwolfia serpentina*.

From previous reports [1–3], it appears that the sterols of *Rauwolfia serpentina* are a mixture of stigmasterol and sitosterol. In this paper we report the isolation of 7-dehydrositosterol from the roots of *Rauwolfia serpentina*.

A homogeneous sterol, $C_{29}H_{48}O$, $[\alpha]_D^{30} - 2.2°$ ($CHCl_3$), $[M]^+$ at *m/z* 412, mp 138° was isolated from the neutral fraction of *R. serpentina* roots. The sterol showed a UV spectrum [λ_{max} nm: 292, 281, 270.5, 261 (with log ε: 3.76, 3.94, 3.92 and 3.83)] characteristic of a homoannular diene system. The IR spectrum of the sterol showed bands at 3400 (hydroxyl), 1635 (substituted double bond), 1365 and 1375 cm^{-1} (C-methyl and gem-dimethyl). The ^{1}H NMR spectrum (90 MHz in $CDCl_3$) showed the presence of two vinylic protons (δ 5.32–5.5, 1H, doublet and δ 5.07–5.3, 1H, complex multiplet) of the homodiene system. The base peak in the mass spectrum of the sterol at *m/z* 353 also showed the presence of the $\Delta^{5,7}$-diene system [4]. The peak at *m/z* 271 (35.9%) could be accounted for by cleavage of the C-17, C-20 bond of a sterol [5].

A shift of the ^{1}H NMR signal from (δ 3.4–3.75, 1H, *br m*) to (δ 4.45–4.9, 1H, *br m*) was readily discernible in the spectrum of its monoacetate, mp 126°, IR ν_{max}^{KBr} 1720 cm^{-1},

(δ 2.0, 3H, *s*) which showed that the sterol had a 3β-hydroxy group.

All these data suggested that the sterol could be 7-dehydrositosterol (pro-vitamin D_5 or stigmasta-5,7-dien-3β-ol). This has been confirmed by the identity of the tetrahydro derivative with dihydrositosterol (stigmastanol) obtained by the hydrogenation of sitosterol (mmp and IR data).

7-Dehydrositosterol (pro-vitamin D_5) has previously been reported from *Cronartium fusiforme* [5], *Brassica napus* [6] and *Cyanidium caladarium* [7] in a mixture of sterols which have been characterized by GC analysis, mass spectral examination and other physical data of the mixtures.

EXPERIMENTAL

All mps are uncorr. Petrol used had bp 60–80°. All solvent extracts were dried over Na_2SO_4. Samples were analysed after drying *in vacuo* at 80° over P_2O_5 for 24 hr. The UV spectra were taken in 95% EtOH; IR spectra were recorded in KBr. ^{1}H NMR spectra were taken in $CDCl_3$ (90 MHz) with TMS as int. standard.

Isolation of 7-*dehydrositosterol*. The petrol extract of the air-dried finely powdered roots of *Rauwolfia serpentina* Benth. (1 kg) was fractionated into (i) basic, (ii) acidic and (iii) neutral parts. The residue from the neutral fraction was taken up in petrol and after two crystallizations from petrol furnished a colourless compound mp 138°. TLC (Si gel; C_6H_6–$CHCl_3$–EtOAc, 30:30:8; R_f 0.48). (Found: C, 84.43; H, 11.66; $C_{29}H_{48}O$ calcd C, 84.46; H, 11.65%.)

The sterol (15 mg) was dissolved in 2 ml Ac_2O and two drops of dry pyridine added and the mixture heated on a water bath for *ca* 2.5 hr and then allowed to stand overnight. On working-up the reaction product, a solid residue was obtained which on recrystallization from petrol furnished colourless crystals of the acetate, mp 126°. TLC (Si gel, C_6H_6–$CHCl_3$, 1:1, R_f 0.62).

The sterol (35 mg), was dissolved in EtOH and then hydrogenated using a 10% Pd–C catalyst. This yielded a colourless compound, mp 136°, which was found homogeneous by TLC (Si gel; C_6H_6–MeOH, 94:6; R_f 0.59). (Found C, 83.67; H, 12.4, $C_{29}H_{52}O$ calcd C, 83.65; H, 12.5%.) An authentic sample of sitosterol was dissolved in EtOH and then hydrogenated as above to furnish a colourless compound mp 137° identified as stigmastan-3β-ol.

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REFERENCES

1. Siddiqui, S. and Siddiqui, R. H. (1931) *J. Indian Chem. Soc.* **8**, 668.
2. Ghosh, B. P. and Basu, R. K. (1955) *Naturwissenschaften* **42**, 130.
3. Hampel, B. and Rosenberg, W. (1962) *Naturwissenschaften* **49**, 395.
4. Smith, F. R. and Korn, E. D. (1968) *J. Lipid Res.* **9**, 405.
5. Weete, J. D. and Kelley, W. D. (1977) *Lipids* **12**, 398.
6. Homberg, E. E. and Schiller, H. P. K. (1973) *Phytochemistry* **12**, 1767.
7. Ikan, R. and Seekbach, J. (1972) *Phytochemistry* **11**, 1077.

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DEHYDRODIEUGENOLS FROM *NECTANDRA POLITA**

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Key Word Index—*Nectandra polita*; Lauraceae; allylbenzenes; dehydrodieugenols.

Abstract—The wood of *Nectandra polita* contains sitosterol, *O*-methyleugenol, eugenol, dehydrodieugenol, *O*-methyldehydrodieugenol and di-*O*-methyldehydrodieugenol, whose isolation from a natural source is reported here for the first time.

Nectandra polita Nees, an arboreous Lauraceae species from the Andes region, contains in its trunk sitosterol, *O*-methyleugenol, eugenol, dehydrodieugenol, *O*-methyldehydrodieugenol and the new natural compound di-*O*-methyldehydrodieugenol (**1**). Dehydrodieugenol has been separated previously from *Litsea turfosa* [1], and the dehydrodieugenol and its monomethyl ether from *Ocotea cymbarum* [2] and *Virola carinata* [3].

Identification of known products was based on spectra and direct comparison with authentic samples. The reiso-

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*Part I in the proposed series "Studies of Colombian Lauraceae". Based on part of the Masters thesis presented by M.S., to Universidad Nacional de Colombia, Bogotá (1981).