(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.

Acknowledgements—We thank Dr. S. C. Bhattacharyya, Director, and Dr. A. K. Barua, Head of the Department of Chemistry, Bose Institute. The financial support to T.K. by C.S.I.R. is gratefully acknowledged.

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.

Phytochemistry, Vol. 22, No. 2, pp. 609–610, 1983.
Printed in Great Britain.

0031-9422/83/020609-02$03.00/0

DEHYDRODIEUGENOLS FROM *NECTANDRA POLITA**

MARGOTH SUAREZ, JORGE BONILLA, AURA M. P. DE DIAZ and HANS ACHENBACH†

Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia; † Institut für Pharmazie und Lebensmittelchemie, Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany

(*Received* 13 *July* 1982)

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

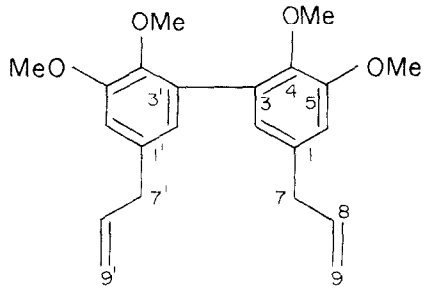
Abstract—The wood of *Nectandra polita* contains sitosterol, *O*-methyleugenol, eugenol, dehydrodieugenol, *O*-methyldehydrodieugenol and di-*O*-methyldehydrodieugenol, whose isolation from a natural source is reported here for the first time.

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-

*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).

lation of the dehydrodieugenol, was, therefore, an opportunity to test the proposed formula by ^{13}C NMR. The assignment of the signals was aided by the ^{13}C NMR spectrum of eugenol and other related compounds [4]. The structure of di-*O*-methyldehydrodieugenol resulted from a comparison of the spectral data with those of dehydrodieugenol and its monomethyl ether [1–3]. The three compounds showed ^1H NMR spectra which were identical, with the exception of the signals due to the methoxyl groups at the aromatic ring. This fact, the absence of hydroxyl group vibration in the IR and the molecular ion at *m/z* 354 in the mass spectrum, together with an analogous mass spectral fragmentation confirmed the structure proposed for **1**.



1*

EXPERIMENTAL

Isolation of the constituents of Nectandra polita. Wood was collected in the vicinity of Salto de Tequendama, Cundinamarca, Colombia and identified by Dr. J. Idrobo from the Instituto de Ciencias Naturales, Universidad Nacional de Colombia, Bogotá (voucher specimen No. JMI-9409 deposited at the Herbario Nacional, Universidad Nacional, Bogotá, Colombia). Dried ground wood (2.5 kg) of *N. polita* was percolated with EtOH. The extract (54 g) was extracted successively with petrol and $CHCl_3$. The petrol-soluble part (12g) was chromatographed on a Si gel column (200 g) and yielded: aliphatic esters (0.6 g) from the C_6H_6 eluent; sitosterol (2.6 g), *O*-methyleugenol (0.04 g) and eugenol (0.06 g) from C_6H_6–$CHCl_3$ (8:2 → 7:3), and a fraction (0.18 g) from the C_6H_6–$CHCl_3$ (6:4 → 1:1) and $CHCl_3$ eluents. This latter fraction after prep. Si gel TLC using C_6H_6–$CHCl_3$ (7:3) gave dehydrodieugenol (0.06 g), *O*-methyldehydrodieugenol (0.04 g) and di-*O*-methyldehydrodieugenol (0.01 g).

The $CHCl_3$-soluble part (3 g) was also chromatographed on a Si gel column (55 g) to give sitosterol (0.6 g), a mixture (0.9 g) and dehydrodieugenol (0.06 g) using C_6H_6–$CHCl_3$ (9:1 → 8:2) as the eluent. The mixture was separated by prep. Si gel TLC (petrol–C_6H_6, 7:3) giving aliphatic esters (0.03 g), eugenol (0.04 g) and *O*-methyleugenol (0.007 g).

Eugenol (*4-hydroxy-3-methoxyallylbenzene*). ^{13}C NMR (20.15 MHz, $CDCl_3$): δ 39.89 (*t*, C-1'), 55.86 (*q*, OMe), 111.36 (*d*, C-2), 114.50 (*d*, C-5), 115.44 (*t*, C-3'), 121.27 (*d*, C-6), 131.93 (*s*, C-1), 137.93 (*d*, C-2'), 144.07 (*s*, C-4), 146.62 (*s*, C-3).

Dehydrodieugenol ($\Delta^{8,8'}$-*4,4'-dihydroxy-5,5'-dimethoxy-3,3'-neolignan*). Mp 103–104° (from C_6H_6–petrol), lit. 106–107° [2]. Identified by direct comparison with an authentic sample. ^{13}C NMR (20.15 MHz, $CDCl_3$): δ 40.02 (*t*, C-7, C-7'), 56.14 (*q*, 2 × OMe), 110.84 (*d*, C-6, C-6'), 115.72 (*t*, C-9, C-9'), 123.26 (*d*, C-2, C-2'), 124.52 (*s*, C-3, C-3'), 131.93 (*s*, C-1, C-1'), 137.70 (*d*, C-8, C-8'), 141.10 (*s*, C-4, C-4'), 147.32 (*s*, C-5, C-5'). *Acetate*, oil, ^{13}C NMR (62.83 MHz, $CDCl_3$): δ 20.50 (*q*, 2 × $COCH_3$), 40.13 (*t*, C-7, C-7'), 56.02 (*q*, 2 × OMe), 112.14 (*d*, C-6, C-6'), 116.34 (*t*, C-9, C-9'), 122.65 (*d*, C-2, C-2'), 131.34 (*s*, C-3, C-3'), 135.89 (*s*, C-1, C-1'), 137.04 (*d*, C-8, C-8'), 138.22 (*s*, C-4, C-4'), 151.26 (*s*, C-5, C-5'), 168.97 (*s*, 2 × $\underline{O}\underline{C}$OMe).

O-Methyldehydrodieugenol ($\Delta^{8,8'}$-*4-hydroxy-4',5,5'-trimethoxy-3,3'-neolignan*). IR, UV, ^1H NMR and MS identical with those of an authentic sample [2].

Di-O-methyldehydrodieugenol ($\Delta^{8,8'}$-*4,4',5,5'-tetramethoxy-3,3'-neolignan*). Oil: UV λ_{max}^{EtOH} nm (log ε): 281 (3.51); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2940, 2830, 1640, 1580, 1485 (infl.), 1464, 1410, 1360, 1312, 1265, 1140, 1045, 1000, 910; ^1H NMR (250 MHz, $CDCl_3$): δ 3.36 (4H, *d*, *J* = 6.5 Hz, $C\underline{H}_2$-7, $C\underline{H}_2$-7'), 3.63 (6H, *s*, 2 × $OC\underline{H}_3$), 3.89 (6H, *s*, 2 × $OC\underline{H}_3$), 5.04–5.14 (4H, *m*, $C\underline{H}_2$-9, $C\underline{H}_2$-9'), 5.99 (2H, *ddt*, J_1 = 17 Hz, J_2 = 10 Hz, J_3 = 6.5 Hz, $C\underline{H}$-8, $C\underline{H}$-8'), 6.69 (2H, *d*, *J* = 2 Hz) and 6.75 (2H, *d*, *J* = 2 Hz, $C\underline{H}$-2, $C\underline{H}$-2' and $C\underline{H}$-6, $C\underline{H}$-6'); MS (MAT 312/SS200, 70 eV, data for $m/z \geq m/z$ 40, % $\geq$ 10%): *m/z* (%) 354.1823 $[M]^+$ (100): $C_{22}H_{26}O_4$, 353 (8), 298.1202 (37); $C_{18}H_{18}O_4$, 283 (24), 282 (21), 115 (10), 41 (28); metascan studies proved the metastable process: *m/z* 354 $\xrightarrow{*}$ *m/z* 298 + 56.

Acknowledgements—We gratefully acknowledge the financial support received from the Fondo Colombiano de Investigaciones Científicas (Colciencias grant No. 010-1-51-74) and the Programa Multinacional de Química OEA-UN de Colombia, Bogotá.

REFERENCES

1. Holloway, D. M. and Scheinmann, F. (1973) *Phytochemistry* **12**, 1503.
2. Díaz, A. M. P. de, Gottlieb, H. E. and Gottlieb, O. R. (1980) *Phytochemistry* **19**, 681.
3. Kawanishi, K. and Hashimoto, Y. (1981) *Phytochemistry* **20**, 1166.
4. Wenkert, E., Gottlieb, H. E., Gottlieb, O. R., Pereira, M. D. da S. and Formiga, M. D. (1976) *Phytochemistry* **15**, 1547.
5. Gottlieb, O. R. (1978) *Prog. Chem. Org. Nat. Prod.* **35**, 1.

*The nomenclature and numbering of neolignans follow the rules which were outlined in a recent review [5].