repeated crystallization, gave colourless needles, mp 282–285°, $[\alpha]_D$ +22°, identified as mortenyl acetate (**3**) by comparison of the spectral data [9]. Further elution of the column with C_6H_6 gave a gummy material, which, on acetylation (Ac_2O–C_5H_5N, room temp, 24 hr) and repeated CC, afforded compounds **1** and **2**

24-Epimeric cycloart-25-ene-3β,24-diol diacetate (**1**). Compound **1** crystallized from $CHCl_3$–MeOH as long needles: mp 122°, $[\alpha]^{30}_D$ +28° ($CHCl_3$; *c* 0.8); ^1H NMR (100 MHz, $CDCl_3$): δ0.3, 0.55 (AB*q*, *J* = 4 Hz, 2 × H-19), 2.0 (2 × OAc), 4.5 (*dd*, *J* = 10, 5 Hz, H-3α), 4.95, 4.9 (*br s*, CH_2), 5.1 (*t*, *J* = 6 Hz, H-24). MS *m/z* (rel. int): 526 $[M]^+$ (7), 511 (3), 480 (7), 466 (100), 451 (50), 423 (35), 406 (25), 397 (3), 391 (1), 357 (17), 354 (25), 344 (30), 337 (20), 297 (55), 287 (32), 269 (32), 255 (25), 251 (17), 203 (37), 187 (25), 178 (42), 175 (42)

Acknowledgement—Our thanks are due to CSIR, New Delhi for the award of a Senior Research Fellowship to G.S.R.

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Phytochemistry, Vol 24, No 7, pp 1612–1614, 1985
Printed in Great Britain

0031-9422/85 $3 00+0 00
Pergamon Press Ltd.

NEOLIGNANS FROM *VIROLA ELONGATA*

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(*Received* 7 *November* 1984)

Key Word Index—*Virola elongata*; Myristicaceae; neolignans, 4-hydroxy-2,3-dimethyl-6,7-dimethoxy-4-piperonyl-1-tetralone, 4-hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone; 1-(3,4-dimethoxyphenyl)-2,3-dimethyl-4-piperonylbutan-1-one.

Abstract—The bark of *Virola elongata* contains the new 8.8′-neolignan, 1-(3,4-dimethoxyphenyl)-2,3-dimethyl-4-piperonylbutan-1-one besides the known 8.8′, 2.7′-neolignans, 4-hydroxy-2,3-dimethyl-6,7-dimethoxy-4-piperonyl-1-tetralone and 4-hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone.

Continuing our studies of Colombian Myristicaceae [1], we have identified two 8.8′,2.7′-neolignans [2]‡ [(**1**) and (**2**)] and a new 8.8′-neolignan (**3**) in the benzene extract of the bark of *Virola elongata* (Benth.) Warburg. This is a plant native to the Colombian Amazonic region and its use by Amazonian Indians as a constituent of hallucinogenic snuff has been reported [3]. Previous studies of the wood of *V. elongata* by Gottlieb and his coworkers [4] demonstrated the presence of virolanol A, virolanol B, virolanol C and (−)-fisetinidol.

The structures of compounds **1** and **2** were deduced from their spectroscopic data (see Experimental). Both compounds have been reported [5] as constituents of the fruits of *V. sebifera*, and comparison with the published data showed agreement, with one exception. Whereas our mp for **1** agrees with that published [5], the value we found for neolignan (**2**) [mp 86–87°] is different from that reported (mp 115–117°) [5]. This is possibly due to different crystalline forms being obtained from different solvents (acetone in our work, methanol in ref. [5]).

The structure of **3**, without regard to stereochemistry, followed from analysis of its NMR spectra and electron impact mass spectrum. The ^1H NMR spectrum showed doublets at δ0.85 (*J* = 7 Hz) and 1.15 (*J* = 7 Hz) assigned to C-methyl groups (H-9′ and H-9, respectively). Methoxy resonances were observed at δ3.90 and 3.95, and the methylenedioxy group gave a singlet at δ5.94. The protons H-8 and H-8′ resonated at δ3.38 (*dq*, *J* = 7 and 7 Hz) and 2.25 (*dddq*, all *J* ≈ 7 Hz). The diastereotopic protons at C-7′ gave signals (*dd*) at δ2.43 (J_{gem} 14.4 Hz, J_{vic} 7.8 Hz) and

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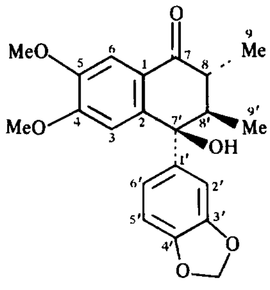
*Authors to whom correspondence should be addressed.

‡The system of nomenclature devised by Gottlieb [2] is used in the discussion of NMR spectral assignments.



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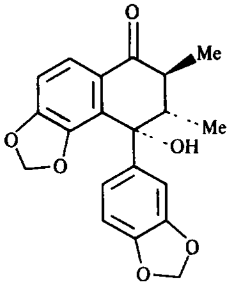

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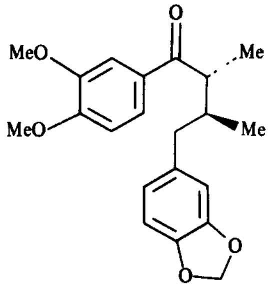


3

2.58 (J_{gem} 14.4 Hz, J_{vic} 7.8 Hz). The H-2 and H-6 protons on the dimethoxybenzene ring were observed in the region δ7.2–7.5. The proton H-5 on this ring and the other aromatic protons resonated in the region δ6.5–7.0. The substitution patterns assigned followed from comparison of the ^{13}C (^{1}H) NMR spectrum for **3** with the data for model compounds [6]. The electron impact mass spectrum of **3** shows a dominant fragment at m/z 194 which arises from a McLafferty rearrangement (cf. Scheme 1). If compounds **1** and **3** have a common biosynthetic precursor, then the absolute stereochemistry of neolignan **3** is as shown.

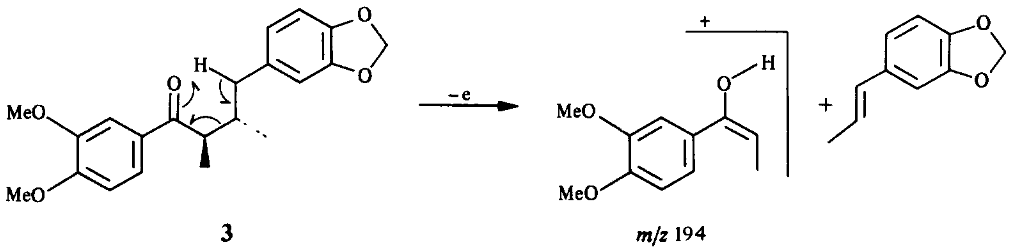
EXPERIMENTAL

The plant samples of *V. elongata* (Benth.) Warburg were collected in the Vaupés region of Colombia on the banks of the Piraparana River, 2 km N. of Sonaná. Identification was made by R. Jaramillo and J. M. Idrobo of the Instituto de Ciencias Naturales, Bogotá. A sample was left at the Colombian National Herbarium (registry number COL 231564). Compounds **1–3** were isolated by C_6H_6 extraction (Soxhlet, 10 days) of the bark (1.01 kg), followed by evaporation to give a residue (11.2 g). Liquid chromatography on silica gel (150 g, 1 m × 2.5 cm diameter column, elution with C_6H_6–EtOAc, 92:8–1:1) gave several fractions which were each further purified by liquid chromatography in a similar manner Homogeneous fractions of **1–3** were eventually obtained

(2R,3R,4S)-4-*Hydroxy*-2,3-*dimethyl*-6,7-*dimethoxy*-4-*piperonyl*-1-*tetralone* (**1**). Crystals (75 mg), mp 177–179° (Me_2CO) (lit. mp 177–180° [5]). R_f 0.2 (silica gel, C_6H_6–EtOAc, 4:1). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (ε): 312 (6650), 278 (12 400), 233 (21 000); $\lambda_{\max}^{\mathrm{MeOH+NaOH}}$ nm (ε): 312 (6650), 278 (12 400), 233 (21 000). MS: similar to that previously reported [5]. ^{1}H NMR (220 MHz, $CDCl_3$) δ7 52 (*s*, H-6), 6.86 (*m*, H-2′, H-5′, H-6′), 6.3 (*s*, H-3), 6.0 (*s*, CH_2O_2-3′, CH_2O_2-4′), 3.93 (*s*, OMe-4), 3.68 (*s*, OMe-5), 2.87 (*dq*, *J* = 12, 6.8 Hz, H-8), 2.32 (*dq*, *J* = 12, 6.8 Hz, H-8′), 2.12 (*s*, OH-7′), 1.29 (*d*, *J* = 6.8 Hz, Me-9), 0.91 (*d*, *J* = 6.8 Hz, Me-9′); ^{13}C NMR (100 MHz, $CDCl_3$) δ125.2 (C-1), 140.0 (C-2), 108.3 (C-3), 152.9 (C-4), 149.2 (C-5), 110.7 (C-6), 198.6 (C-7), 46.9 (C-8), 12.9 (C-9), 56.0 (OMe-5), 55.9 (OMe-4), 141.8 (C-1′), 107.4 (C-2′), 147.4 (C-3′), 146.4 (C-4′), 107.5 (C-5′), 119.9 (C-6′), 76.8 (C-7′), 43.3 (C-8′), 12.4 (C-9′), 101.0 (O_2CH_2-3′, O_2CH_2-4′).

(2S,3S,4R)-4-*Hydroxy*-2,3-*dimethyl*-5,6-*methylenedioxy*-4-*piperonyl*-1-*tetralone* (**2**). Crystals (208 mg), mp 86–87° (Me_2CO) [lit. mp 115–117° (MeOH) [5]]. R_f 0.32 (system as for **1**). UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (ε): 305 (6600), 280 (9375), 232 (22 222), $\lambda_{\max}^{\mathrm{MeOH+NaOH}}$ nm (ε): 305 (6600), 280 (9375), 232 (22 222). MS m/z (rel. int.): 354 $[M]^+$ (36.7), 355 $[M+1]^+$ (7.98), 356 $[M+2]^+$ (1 34), 298 (100), 269 (7.0), 240 (10), 212 (4.0), 149 (28), 120 (8.0), 91 (5.0). ^{1}H NMR (220 MHz, $CDCl_3$) δ7.72 (*d*, *J* = 8.0 Hz, H-6), 6.88 (*d*, *J* = 8.0 Hz, H-5), 6.65–6 75 (*m*, H-2′, H-3′, H-4′), 5.97 (*s*, O_2CH_2-3′, O_2CH_2-4′), 5.85 (*s*, O_2CH_2-3, O_2CH_2-4), 5.72 (*s*, O_2CH_2-3, O_2CH_2-4), 2.83 (*dq*, *J* = 6.8, 12 Hz, H-8), 2.18 (*dq*, *J* = 6.8, 12 Hz, H-8′), 2.43 (*s*, OH-7′), 1.20 (*d*, *J* = 6.8 Hz, Me-9), 0.95 (*d*, *J* = 6.8 Hz, Me-9′); ^{1}H NMR (300 MHz, DMSO-d_6, 32 000 points, Gaussian line narrowing, $k_T = 0\ 35$, LB = – 1.0 Hz): δ7.55 (*d*, *J* = 8.2 Hz, H-6), 7.00 (*d*, *J* = 8.2 Hz, H-5), 6.7–7.0 (*br m*, H-2′, H-3′, H-4′), 5 99 (*d*, *J* = 0 99 Hz, O_2CH_2-3′, O_2CH_2-4′), 5.98 (*d*, *J* = 1.00 Hz, O_2CH_2-3′, O_2CH_2-4′), 5.81 (*d*, *J* = 0.79 Hz, O_2CH_2-3, O_2CH_2-4), 5.73 (*d*, *J* = 0.78 Hz, O_2CH_2-3, O_2CH_2-4), 2.84 (*dq*, *J* = 12.4, 6.5 Hz, H-8), 2.50 (*br s*, OH-7′), 2.14 (*dq*, *J* = 12.3, 6.7 Hz, H-8′), 1.11 (*d*, *J* = 6.7 Hz, Me-9), 0.72 (*d*, *J* = 6.7 Hz, Me-9′). ^{13}C NMR (100 MHz, $CDCl_3$) δ126.6 (C-1), 128.5 (C-2), 144.6 (C-3), 152.4 (C-4), 108.8 (C-5), 118.9 (C-6), 198.4 (C-7), 46.8 (C-8), 12.1 (C-9), 101 9 (O_2CH_2-3, O_2CH_2-4), 140 4 (C-1′), 106.6 (C-2′), 147.2 (C-3′), 146.2 (C-4′), 107.4 (C-5′), 122.8 (C-6′), 74.7 (C-7′), 43.3 (C-8′), 12.0 (C-9′), 100.8 (O_2CH_2-3′, O_2CH_2-4′)

1-(3,4-*Dimethoxyphenyl*)-2,3-*dimethyl*-4-*piperonylbutan*-1-*one*



Scheme 1. McLafferty rearrangement in the electron impact mass spectrum of neolignan 3.

(3). Pale yellow oil (238 mg). R_f 0.54 (silica gel, petrol–EtOAc, 17:3). ($[M]^+$ found: 356.1629. $C_{21}H_{24}O_5$ requires 356.1624.) ν_{max}^{film} cm^{-1}: 1670 (C=O stretch). UV λ_{max}^{MeOH} nm (ε): 274 (12 500), 228 (20 319); $\lambda_{max}^{MeOH+NaOH}$ nm (ε): 274 (12 500), 228 (20 319). MS *m/z* (rel. int.) 356 (7), 194 (100), 165 (27), 135 (16.9), 77 (10), 28 (11). ^{1}H NMR (60 MHz, $CDCl_3$) δ7.32 (*m*, H-2, H-6), 6.85 (*br s*, H-5), 6.65 (*br s*, H-2′, H-5′, H-6′), 5.88 (*s*, O_2CH_2), 3.90 (*s*, OMe-3), 3.85 (*s*, OMe-4), 2.0–3.7 (*m*, H-7, H-7′, H-8, H-8′), 1.15 (*d*, *J* = 6.5 Hz, Me-9), 0.85 (*d*, *J* = 6.5 Hz, Me-9′); ^{1}H NMR (220 MHz, $CDCl_3$) δ7.45 (*br s*, H-2), 7.37 (*dd*, *J* = 9.5, 1.5 Hz, H-6), 6.84 (*d*, *J* = 9.5 Hz, H-5), 6.70 (*m*, H-2′, H-5′, H-6′). 5.94 (*s*, O_2CH_2), 3.95 (*s*, OMe-3), 3.90 (*s*, OMe-4), 3.38 (*dq*, *J* = 7.0, H-8), 2.58 (*dd*, *J* = 14.4, 7.8 Hz, H-7′), 2.43 (*dd*, *J* = 14.4, 7.8, H-7′), 2.25 (*dddq*, *J* = 7.8, 7, 7 and 7, H-8′), 1.15 (*d*, *J* = 7.0, Me-9), 0.85 (*d*, *J* = 7.0, Me-9′). ^{13}C NMR (100 MHz, $CDCl_3$) δ129.7 (C-1), 110.5 (C-2), 148.9 (C-3), 152.9 (C-4), 109.9 (C-5), 122.4 (C-6), 202.4 (C-7), 42.8 (C-8), 14.8 (C-9), 55.7 (3-OMe), 55.8 (4-OMe), 134.5 (C-1′), 108.0 (C-2′), 147.4 (C-3′), 145.6 (C-4′), 109.4 (C-5′), 121.9 (C-6′), 37.4 (C-7′), 41.2 (C-8′), 11.2 (C-9′), 100.5 (3′-O_2CH_2, 4′-O_2CH_2).

Acknowledgements—We thank the following for financial assistance: Multinational Chemistry Project of the Organisation of American States, The Fondo Colombiano de Investigaciones Científicas y Proyectos Especiales 'Franscisco José de Caldas' (grant no. Colciencias, PI-10000-1-135-81), and the Comité de Investigaciones y Desarrollo Científico (grant no. Cindec, P1-1303-118).

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Phytochemistry, Vol. 24, No 7, pp 1614–1616, 1985
Printed in Great Britain
0031–9422/85 $3 00+0.00

FLAVONOIDS FROM *WYETHIA GLABRA*

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(*Revised received* 3 *October* 1984)

Key Word Index—*Wyethia glabra*; Compositae; Heliantheae; prenylated flavanones; isoflavones; flavanones; chalcone.

Abstract—Ten flavonoid compounds, including three new natural products, were isolated from a dichloromethane extract of *Wyethia glabra.* The known compounds are: orobol 7-methyl ether, orobol 3′-methyl ether, naringenin 7-methyl ether, eriodictyol, 8-*C*-prenyleriodictyol, 6-*C*-prenyleriodictyol and 8-*C*-prenylnaringenin. Eriodictyol 7-methyl ether, 2′,4′,6′-trihydroxy-4-methoxychalcone and 6-*C*-prenylnaringenin are new natural products. An additional prenylated flavanone was isolated and partially characterized.

INTRODUCTION

As part of a chemical and morphological study on the related genera *Wyethia* and *Balsamorhiza* (tribe Heliantheae, subtribe Helianthinae), the leaf-surface flavonoids of *Wyethia glabra* Gray were examined. *Wyethia helenioides*, which is in the same section as *W. glabra*, produces 8-*C*-prenyleriodictyol, 6-*C*-prenyleriodictyol, 8-*C*-prenylnaringenin, orobol 7-methyl ether and orobol 3′-methyl ether [1]. From *W. glabra* besides these five compounds, 6-*C*-prenylnaringenin, eriodictyol, eriodictyol 7-methyl ether, naringenin 4′-methyl ether, 2′,4′,6′-trihydroxy-4-methoxychalcone and an additional 8-*C*-prenylflavanone have been found. Similar prenylated flavanones have been isolated from *Flourensia* [2], *Marshallia* [3] and *Helichrysum* [4].

RESULTS AND DISCUSSION

A dichloromethane leaf wash of *W. glabra* afforded orobol 7-methyl ether (10 mg) (**1**) [5], orobol 3′-methyl ether (10 mg) (**2**) [6], eriodictyol (10 mg) (**3**) [7], naringenin 4′-methyl ether (20 mg) (**4**) [8], 8-*C*-prenyleriodictyol (180 mg) (**5**) [1], 6-*C*-prenyleriodictyol (300 mg) (**6**) [1], 8-*C*-prenylnaringenin (50 mg) (**7**) [3], 6-*C*-prenylnaringenin (150 mg) (**8**), eriodictyol 7-methyl ether (5 mg) (**9**), 2′,4′,6′-trihydroxy-4-methoxychalcone (5 mg) (**10**) and a 8-*C*-prenyltrihydroxymonomethoxyflavanone (5 mg) (**11**).

The UV spectrum of **8** exhibited a major *A* of 295 nm which shifted to 325 nm after the addition of sodium methoxide. This is typical of a flavanone with a 5,7-hydroxylation pattern in the A-ring. The mass spectrum of