Pergamon

0031-9422(95)00498-X

Phytochemistry, Vol. 40, No. 5, pp. 1511–1513, 1995

0031-9422/95 $9.50 + 0.00

LIGNANS FROM *APOLLONIAS BARBUJANA*

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(*Received in revised form* 5 *June* 1995)

Key Word Index—*Apollonias barbujana*; Lauraceae; leaves; dibenzylbutane and tetrahydrofurofuran lignans.

Abstract—Two new lignans, 2,3-*bis*[(4-hydroxy-3,5-dimethoxyphenyl)-methyl]-1,4-butanediol and demethylpiperitol, together with three already-known ones, have been isolated from the leaves of *Apollonias barbujana* (Lauraceae). The structures were fully characterized by spectroscopical methods. The known lignans were identified as sesamin, syringaresinol and the neolignan, dihydro-dehydrodiconiferyl alcohol.

INTRODUCTION

Apollonias barbujana [1] (common name barbusano) is a species endemic to the Canary and Madeira Islands [2]. It is an evergreen tree, growing to a height of 10–25 m and is localized in the low regions of the islands up to an altitude of 300–600 m.

The present work describes the isolation and identification of five lignans from leaves of this species.

RESULTS AND DISCUSSION

Lignan (**1**) was obtained as an optically active syrupy oil. The molecular formula $C_{22}H_{30}O_8$ was established by high resolution mass spectroscopy data. The ^1H and ^{13}CNMR spectra of **1** showed only half the expected number of proton and carbon signals, which suggests that it has a symmetrical structure. The ^1H NMR showed a singlet at δ6.30 which was assigned to aromatic protons of the tetrasubstituted aromatic rings of the syringyl type, and another singlet at δ3.72 indicating the presence of methoxyl groups. It also show signals attributable to two hydroxymethylenes, two benzylic methylenes and two aliphatic methines.

Acetylation of **1** gave a tetraacetate (**1a**). The ^1H NMR spectrum showed two signals as singlets at δ2.32 and 2.08, indicating the presence of aromatic and aliphatic acetates, respectively.

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^1H and ^{13}C NMR spectral data showed that compound **1** is a symmetrical 1,4-*bis*-(phenyl)-2,3-dimethylbutane-type lignan. Recently, a lignan glycoside has been isolated [3], the spectral data of its aglycone being identical with those of product (**1**).

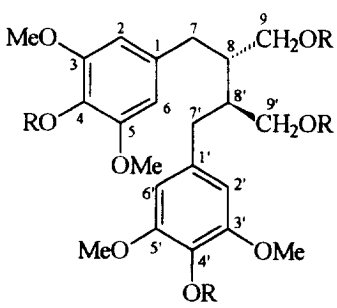
Lignan (**2**) was obtained as an optically active amorphous powder. The molecular formula, $C_{19}H_{18}O_6$, was determined by high-resolution mass spectroscopy data. The ^1H NMR spectrum of **2** showed the typical pattern of two 1,3,4-trisubstituted benzene rings, one methylenedioxy group at δ5.95 and five signals at δ4.71, 4.69, 4.23, 3.86 and 3.05, assigned to a *cis*-diequatorial substituted 2,6-diaryl-3,7-dioxabicyclo[3,3,0]octane [4]. The ^1H and ^{13}C NMR spectral data observed for product **2** are very similar to those of (+)-piperitol [5, 6]. Methylation of **2** afforded the dimethoxy derivative **2a** as an oil and its spectroscopic properties were similar to those of methyl piperitol [7, 8].

The compounds sesamin, syringaresinol and the neolignan, dihydro-dehydrodiconiferyl alcohol, were isolated, and identified by direct comparison with authentic samples as well as by mass, ^1H and ^{13}C NMR spectra.

EXPERIMENTAL

General. ^1H and ^{13}C NMR were measured at 200 and 50 MHz, respectively. MS were recorded at 70 eV.

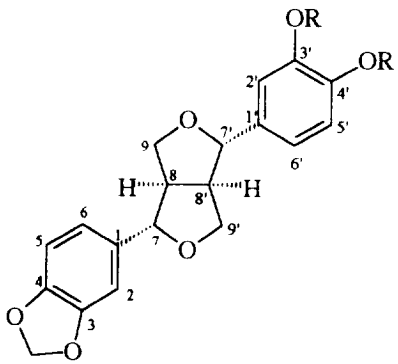
Plant material. Leaves of *A. barbujana* (Cav.) were collected in San Andrés y Sauces, La Palma, Canary Islands in september 1989 and verified by Prof. Marcelino del Arco. A voucher specimen (TFC 25324) is



R

1 H

1a Ac



R

2 H

2a Me

deposited at the Herbarium of the Department of Botany, Faculty of Biology, University of La Laguna (TFC 25324).

Extraction and separation. Air-dried and powdered leaves were extracted in a Soxhlet with MeOH. The extracts were concd and the resulting suspension was extracted with EtOAc. After filtration and evapn of the solvent, the residue, a viscous oil (45 g, 226% dry wt), was chromatographed on silica gel using *n*-hexane with gradually increasing proportions of EtOAc as eluent. The frs eluted with *n*-hexane–EtOAc (3:2) were combined and rechromatographed to obtain 165 mg. The lignans **1** and **2** were obtained by multiple CC and TLC chromatography.

2,3-bis[(4-*Hydroxy*-3,5-*dimethoxyphenyl*)-*methyl*]-1,4-*butanediol* (**1**). Syrupy oil (20 mg) $[\alpha]_D^{25}$ + 12.8 (MeOH; *c* 0.32). $C_{22}H_{30}O_8$. ^{1}H NMR ($CDCl_3$): δ1.91 (2H, *s*, H-8 and H-8'), 2.50 (2H, *dd*, *J* = 13.8 and 8.5 Hz, H-7a and H-7'a), 2.69 (2H, *dd*, *J* = 13.8 and 6.4 Hz, H7b and H'b), 3.54 (2H, *dd*, *J* = 10.9 and 5.6 Hz, H-9a and H-9'a), 3.72 (12H, *s*, OMe), 3.64 (2H, *dd*, *J* = 10.9 and 4.5 Hz, H-9b and H-9'b), 6.30 (4H, *s*, H-2, H-2', H-6 and H-6'). ^{13}C NMR ($CDCl_3$): δ149.24 (C-3, C-3', C-5 and C-5'), 135.00 (C-1 and C-1'), 133.38 (C-4 and C-4'), 107.66 (C-1 and C-1'), 62.53 (C-9 and C-9'), 56.90 (O-CH3), 44.31 (C-8 and C-8'), 36.93 (C-7 and C-7'). EIMS 70 eV *m/z* (rel. int.): 422 $[M]^+$ (34), 404 $[M - H_2O]^+$ (3), 274 (12), 259 (10), 168 (100), 167 (23), 157 (27), 115 (31).

Acetylation of (**1**). By standard procedures. The crude product was purified by CC on silica gel with hexane–EtOAc 3:2) to afford **1a** (9 mg) ^{1}H NMR ($CDCl_3$): δ2.00 (2H, *m*, H-8 and H-8'), 2.08 (6H, *s*, O-$COCH_3$), 2.32 (6H, *s*, O-$COCH_3$), 2.67 (2H, *m*, H-7 and H-7'), 3.37 (12H, *s*, O-CH_3), 4.00 (2H, *dd*, *J* = 11.5 and 6.3 Hz, H-9b and H-9b'), 4.32 (2H, *dd*, *J* = 11.5 and d 2 Hz, H-9a and H-9'a), 6.28 (4H, *s*, H-2, H-2', H-6 and H-6'). ^{13}C NMR ($CDCl_3$): δ170.78 and 168.5 (O-$COCH_3$) 152.13 (C-3, C-3', C-5 and C-5'), 139.40 (C-4 and C-4'), 138.10 (C-1 and C-1'), 105.55 (C-2, C-2', C-6 and C-6'), 64.21 (C-9 and C-9'), 56.13 (O-CH_3), 39.49 (C-8 and C-8'), 36.15 (C-7 and C-7'), 20.80 and 20.34 (O-$COCH_3$). EIMS 70 eV *m/z* (rel. int.): 506 (19), 333 (8), 291 (5), 168 (65), 167 (70).

Demethylpiperitol (**2**). Amorphous powder (9 mg). $[\alpha]_D^{25}$ + 46.3 ($CHCl_3$; *c* 0.27). $C_{19}H_{18}O_6$. ^{1}H NMR ($CDCl_3$): δ3.05 (2H, *m*, H-8 and H-8'), 3.86 (2H, *ddd*, *J* = 9.0, 3.7 and 1.9 Hz, H-9_{endo} and H-$9'_{endo}$), 4.23 (2H, *dd*, *J* = 9.0 and 6.8 Hz, H-9_{exo} and H-$9'_{exo}$), 4.69 (1H, *d*, *J* = 5.2 Hz, H-7'), 4.71 (1H, *d*, *J* = 4.9 Hz, H-7), 5.95 (2H, *s*, O-CH_2-O), 6.75 (2H, *dd*, *J* = 7.8 and 1.7 Hz, H-6 and H-6') 6.77 (1H, *d*, *J* = 1.7 Hz, H-2), 6.82 (2H, *d*, *J* = 7.8 Hz, H-5 and H-5'), 6.84 (1H, *s*, H-2'). ^{13}C NMR ($CDCl_3$): δ148.00 (C-3). 147.12 (C-4), 143.84 (C-3'), 143.42 (C-4'), 135.11 (C-1), 131.5 (C-1'), 119.38 (C-5), 118.82 (C-6'), 115.11 (C-5'), 113.32 (C-2'), 108.19 (C-6), 106.49 (C-2), 101.07 (O-CH_2-O), 85.66 (C-7), 85.64 (C-7'), 71.72 (C-9), 71.62 (C-9'), 56.17 (O-CH_3), 54.22 (C-8), 54.00 (C-8'). EIMS 70 eV *m/z* (rel. int.): 342 $[M]^+$ (93), 311 (12), 243 (2), 207 (11), 202 (18), 194 (22), 178 (14), 161 (28), 150 (45), 149 (100), 131 (28), 123 (32), 115 (13), 110 (14), 103 (15), 77 (13).

Methylation of (**2**). Compound **2** (5.3 mg) was suspended in Me_2CO (25 ml) and MeI (0.5 ml) and Na_2CO_3 (100 mg) added. The mixt. was refluxed for 8 hr and extracted in the usual manner. The product **2a** was purified by CC and isolated as an oil (4 mg). $[\alpha]_D^{25}$ + 28 ($CHCl_3$; *c* 0.25). ^{1}H NMR ($CDCl_3$): δ3.06 (2H, *m*, H-8 and H-8'), 3.85 (2H, *m*, H-9_{endo} and H-$9'_{endo}$), 3.85 (3H, O-CH_3), 3.88 (3H, O-CH_3), 4.25 (2H, *ddd*, *J* = 9.0, 6.0 and 2.5 Hz, H-9_{exo} and H-$9'_{exo}$), 4.73 (1H, *d*, *J* = 4.3 Hz, H-7'), 4.75 (1H, *d*, *J* = 4.5 Hz, H-7), 5.96 (2H, *s*, O-CH_2-O), 6.77 (1H, *dd*, *J* = 7.8 and 1.7 Hz, H-6), 6.79 (1H, *d*, *J* = 1.7 Hz, H-1), 6.85 (1H, *s*, C-2'), 6.88 (1H, *dd*, *J* = 7.8 and 1.8 Hz, H-6'), 6.88 (2H, *d*, *J* = 7.8 Hz, H-5 and H-5'). EIMS 70 eV *m/z* (rel. int.): 370 $[M]^+$ (68), 340 (2), 339 (8), 252 (6), 219 (8), 203 (15), 192 (19), 189 (12), 178 (12), 177 (36), 165 (62), 161 (27), 151 (33), 149 (100), 135 (36), 131 (19), 121 (15), 95 (16).

Acknowledgements—This work was supported by the Gobierno de Canarias, Consejería de Educación, grant number 24/310789.

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