Pergamon

PII: S0031-9422(96)00541-9

Phytochemistry, Vol. 44, No. 2, pp. 345–346, 1997

0031-9422/97 $17.00 + 0.00

NEOLIGNANS FROM *ANAXAGOREA CLAVATA*

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(*Received in revised form* 8 *July* 1996)

Key Word Index—*Anaxagorea clavata*; Annonaceae; neolignans.

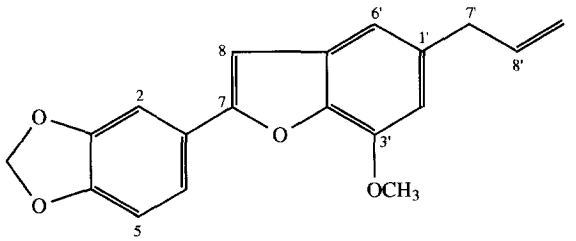
Abstract—From the ethanolic extract of the wood of *Anaxagorea clavata* were isolated 3′-methoxy-3,4-methylenedioxy-4′7-epoxy-9-nor-8,5′-neolignan-7,8′-diene, 3′-methoxy-3,4-methylenedioxy-4′,7-epoxy-9-nor-8,5′-neolignan-7-en-9′-oic acid and β-sitosterol. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Anaxagorea is a genus in the Annonaceae family with approximately 30 species [1]. Plants of this genus have previously yielded aporphine alkaloids, fatty acids, polyprenols and cyanogenic glucosides [1]. Voucher specimens of Colombian species of *Anaxagorea* on deposit in the Herbario Nacional Colombiano (COL) are: *A.* aff. *crassipetala* Hemsl, *A. brachicarpa*, R. E. Fries, *A. brevipes* Benth, *A. dolichocarpa* Sprange & Sandiwith, *A. mutica* R. E. Fries, *A. panamensis* Standley, *A. petiolata* R. E. Fries, *A. phaeocarpa* Mart, *A. rufa* A. Timmerman and *A. clavata* R. E. Fries. This paper describes the results obtained from a study of wood of *A. clavata* R. E. Fries which is widely used in carpentry. The major constituents are 3′-methoxy-3,4-methylenedioxy-4′,7-epoxy-9-nor-8,5′-neolignan-7,8′-diene (**1**), 3′-methoxy-3,4-methylenedioxy-4′,7-epoxy-9-nor-8,5′-neolignan-7-en-9′-oic acid (**2**) and β-sitosterol. There are no prior reports concerning the occurrence of neolignans in the genus *Anaxagorea* and only four lignoids have been recorded to date from the Annonaceae family [1–4]. This is in sharp contrast to the large number of lignans present in the dicotyledons, subclass Magnoliidae [2].

RESULTS AND DISCUSSION

The molecular formula of $C_{19}H_{16}O_4$ was suggested for **1** by the results obtained from EI-mass spectroscopy EIMS and proton and carbon counts obtained from the ^1H and ^{13}C NMR spectra. The ^1H (^{13}C) NMR spectra showed a methylenedioxy group at δ 5.95 (^{13}C NMR: δ 101.2), a methoxyl group at δ 4.00 (δ 56.0) and a



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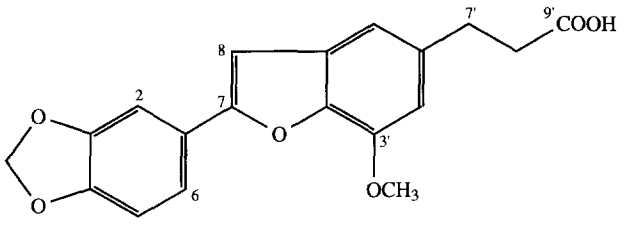

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singlet aromatic proton at δ 6.73 (δ 100.3), which was assigned to H-8 by analogy with established data for closely related neolignans [5, 6]. An allyl group was also evident displaying signals due to methylenic (δ 3.40, *d*, $J = 7$ Hz, 2H) and vinylic (δ 5.7–6.2, *m*, =CH and δ 4.9–5.2, *m*, $=CH_2$) groups, and this portion of the molecule was confirmed by a ^1H–^1H COSY spectral analysis. This side-chain was also evidenced by the resonances of C-7′ (^{13}C NMR: δ 40.5), C-8′ (δ 137.8) and C-9′ (δ 115.6). The remaining aromatic ^1H signals were ascribed to H-2′ (δ 6.58, *d*, $J = 2$ Hz) and H-6′ (δ 7.40, *d*, $J = 2$ Hz, H-6′) in one ring, and H-2, H-5 and H-6 (δ 6.77–7.33, 3H, *m*) in the other. The complete ^{13}C NMR spectral assignment was achieved through analysis of ^1H–^{13}C COSY spectra. Additional structural information was provided by the mass spectrum, $[M]^+$ *m/z* 308 (100%) and fragment ions at *m/z* 121 and 146, characteristic of a piperonyl residue in neolignans [7].

Compound **2** has the molecular composition $C_{19}H_{16}O_6$, as suggested by low resolution mass spectrometry (EI-MS $[M^+$ *m/z* 340), which can be rewritten as $C_{16}H_{10}O \cdot O_2CH_2 \cdot OMe \cdot COOH$ after inspection of the ^1H NMR, IR and mass spectra. The ^1H NMR spectrum showed a methylenedioxy group at δ 5.89 and singlets at δ 3.92, indicating the presence of one methoxyl group, and at δ 6.71 assigned to H-8. Two sets of aromatic protons were observed: one had two *meta* coupled signals at δ 6.62 (*d*, $J = 2$ Hz) and δ 6.95 (*d*, $J = 2$ Hz) corresponding to H-2′ and H-6′; and the other had three signals at δ 6.75 (*d*, $J = 8$ Hz), δ 7.24 (*d*, $J = 2$ Hz) and δ 7.33 (*dd*, $J = 8$ and 2 Hz) corresponding to H-5, H-2 and H-6, respectively. Compound **2** showed IR absorptions at 3100–2730 and 1709 cm^{-1}, which are indicative of a carboxyl group.

The mass spectral fragmentation pattern is in accordance with the proposed structure, as there are important fragment peaks indicating the sequential loss of carboxyl at *m/z* 295 ($M^+ - COOH$), *m/z* 281 ($M^+ - CH_2COOH$) and *m/z* 267 ($M^+ - CH_2CH_2COOH$). The α and β protons to the carboxylic group are represented in the ^1H NMR spectra by resonances at δ 2.66 (*t*, $J = 8.5$ Hz, 2H-8′) and δ 3.00 (*t*, $J = 8.5$ Hz, 2H-7′), respectively.

EXPERIMENTAL

Plant material. Anaxagorea clavata R. E. Fries, plant material was collected in Apartadó, Antioquia, Colombia, by Dr J. Brand (Col. No. 1261) and identified by Drs J. Brand and P. J. Mass. A voucher specimen is deposited in the Herbarium Jardín Botánico Joaquín Antonio Uribe, Medellín, Colombia (JAUM 7078).

Isolation of constituents. A wood sample (1.86 kg) was extd with EtOH. The toluene soluble part (24 g) of the extn (83 g) was CC on Si gel (300 g). Toluene elution gave successively fatty material (2.3 g (0.12%)), (0.230 g (0.012%)) **1** and β-sitosterol (1 g (0.05%)); elution with toluene–ethyl acetate (2:8) gave **2** (0.025 g (0.0013%)).

3′-Methoxy-3,4-methylenedioxy-4′,7-epoxy-9-nor-8,5′-neolignan-7,8′-diene (**1**). Mp 69–70° (toluene). IR (ν_{max}^{KBr} cm^{-1}): 3064, 3003, 2974, 2943, 2901, 1621, 1599, 1475, 1451, 1363, 1332, 1287, 1271, 1237, 1040, 930, 924, 821. UV (λ_{max}^{EtOH} nm) (log ε): 218 (4.78), 248 sh (4.33), 300 sh (4.67), 315 (4.70), 330 sh (4.60). MS *m/z* (rel. int.): 308 ($[M]^+$, 100), 293 (4), 281 (16), 278 (3), 277 (5), 176 (3), 146 (6), 121 (3). ^1H NMR (90 MHz, $CDCl_3$): δ 3.40 (*d*, $J = 7.0$ Hz, 2H-7′), 4.90–5.20 (*m*, 2H-9′), 5.70–6.20 (*m*, H-8′), 4.00 (*s*, OMe-3′), 5.95 (*s*, $OC\underline{H}_2O$), 6.73 (*s*, H-8), 6.58 (*d*, $J = 2.0$ Hz, H-2′), 7.40 (*d*, $J = 2.0$ Hz, H-6′), 6.77–7.33 (*m*, 3H); ^{13}C NMR (22.4 MHz, $CDCl_3$): δ 40.5 (C-7′), 56.0 (OMe), 100.4 (C-8), 101.2 ($OC\underline{H}_2O$), 105.5 (C-2), 107.5 (C-2′), 108.6 (C-5), 112.6 (C-6), 115.6 (C-9′), 119.1 (C-6′), 124.7 (C-1), 131.0 (C-5′), 135.6 (C-1′), 137.8 (C-8′), 142.6 (C-7), 144.8 (C-4′), 147.9 (C-4), 148.0 (C-3), 156.0 (C-3′).

3′-Methoxy-3,4-methylenedioxy-4′,7-epoxy-9-nor-8,5′-neolignan-7-en-9′-oic acid (**2**). Mp 113′–114° (EtOH). IR (ν_{max}^{KBr} cm^{-1}): 3100, 3002, 2917, 2850, 2705, 1709, 1622, 1598, 1561, 1504, 1478, 1269, 1254, 1144, 1039, 931, 825. UV (λ_{max}^{EtOH} nm) (log ε): 216 (4.15), 247 sh (3.58), 300 sh (3.97), 316 (4.05), 332 sh (3.91). MS *m/z* (rel. int.): 340 ($[M]^+$, 100), 295 (10), 281 (44), 267 (5), 146 (2). ^1H NMR (200 MHz, $CDCl_3$ + pyridine-d_5): δ 2.66 (*t*, $J = 8.5$ Hz, 2H-8′), 3.00 (*t*, $J = 8.5$ Hz, 2H-7′), 3.92 (*s*, OMe-3′), 5.89 (*s*, $OC\underline{H}_2O$), 6.71 (*s*, H-8), 6.62 (*d*, $J = 2.0$ Hz, H-2′), 6.95 (*d*, $J = 2.0$ Hz, H-6′), 6.75 (*d*, $J = 8.0$ Hz, H-5), 7.24 (*d*, $J = 2.0$ Hz, H-2), 7.33 (*dd*, $J = 8.0$, 2.0 Hz, H-6).

Acknowledgements—The author is indebted to Dr B. Rodríguez, Instituto de Química Orgánica, CSIC, Juán de la Cierva, Madrid, Spain, for ^1H NMR (200 MHz) spectra. Thanks are also due to COLCIENCIAS (Colombia) for financial support.

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