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NEOLIGNANS FROM THE FRUITS OF *LICARIA ARMENIACA**

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Key Word Index *Licaria armeniaca*; Lauraceae; fruits; benzofuranoid neolignans; bicyclo[3.2.1]octanoid neolignans.

Abstract—Fruits of *Licaria armeniaca* contain, besides eight known lignoids, three novel neolignans: (1*S*,5*R*,6*S*,7*R*,8*R*)-8-acetoxy-1-allyl-3,5-dimethoxy-7-methyl-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-4-oxobicyclo[3.2.1]oct-2-ene; (1*S*,5*R*,6*S*,7*R*)-1-allyl-3-methoxy-7-methyl-6-(3′-methoxy-4′,5′-methylenedioxyphenyl)-4,8-dioxobicyclo[3.2.1]oct-2-ene and (1*S*,5*R*,6*S*,7*R*)-1-allyl-3-methoxy-7-methyl-6-(3′,4′,5′-trimethoxyphenyl)-4,8-dioxobicyclo[3.2.1]oct-2-ene.

INTRODUCTION

Previous work on the trunk wood of *Licaria armeniaca* (Ness) Kosterm. led to the isolation of 6,7-dimethoxycoumarin [2, 3], the oxoaporphine alkaloid tri-*O*-methylmoscatoline [3], the furofuran lignan magnolin **1a** [3], the hexahydrobenzofuran neolignans armenin-A and -B [2] as well as the bicyclo[3.2.1]octanoid neolignan **2a** [3]. Work on the fruits and fruit calyces of the same species reported in the present paper yielded, besides **1a** and **2a**, and additional furofuran lignan **1b**, the additional bicyclooctanoid neolignans **2b**, **3a** and **3b**, and the tetrahydrobenzofuranoid neolignans **4a**, **4b**, **5a**, **5b** and **6**. The biogenetic nomenclature and numbering of neolignans follow the rules outlined in a review [4].

RESULTS AND DISCUSSION

Compounds **1a** and **1b** are known constituents of a *Magnolia* [5] and a *Piper* [6] species, respectively. Compound **2a** [3, 7] served as a model in the structural elucidation of the novel compound **2b**. The spectral differences can all be attributed to the presence of a 3,4-methylenedioxyphenyl group in **2a** versus a 3-methoxy-4,5-methylenedioxyphenyl group in **2b**. The chiroptical data of compounds **2a** and **2b** are also closely comparable. Compound **3a** had been obtained previously by partial synthesis [8]. It served as a model for the structural elucidation of the new compound **3b**. Again the spectral differences could all be attributed to diverse substitution of the aromatic parts of the molecules, a 3-methoxy-4,5-methylenedioxyphenyl group in **3a** and a 3,4,5-trimethoxyphenyl group in **3b**. And again both isolates **3a** [8] and **3b** gave nearly superimposable ORD and CD curves. All other compounds have been isolated previously from other sources: **4a** from *Licaria camara* [9], *Aniba terminalis* [10] and another *Aniba* species [11]; **4b** from *A. williamsii* [8, 12, 13]; **5a** from *A. terminalis* [10] and another *Aniba* species [11]; **5b** from *A. williamsii* [8, 12, 13] and **6** from *A. williamsii* [12]. Stereochemical assignments of the neolignans were based on published data [14–16].

Most of these neolignans have been isolated previously from *A. williamsii*. This species was designated *A. simulans* in all the original papers. The revision of the name has been reported [17].

* Part 82 in the series "The Chemistry of Brazilian Lauraceae". For Part 81 see ref. [1]. Taken from part of the doctorate thesis presented by J.M.B.-F. to the Universidade de São Paulo (1986).

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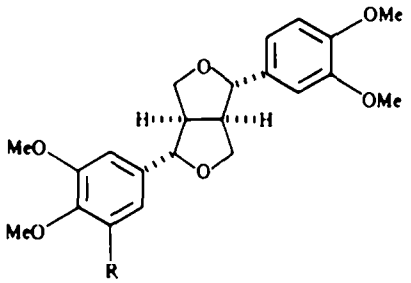

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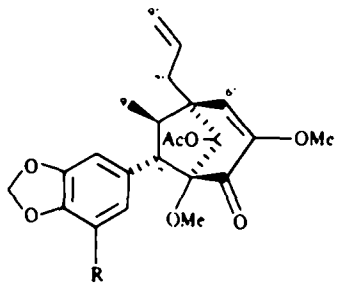
1b R = H



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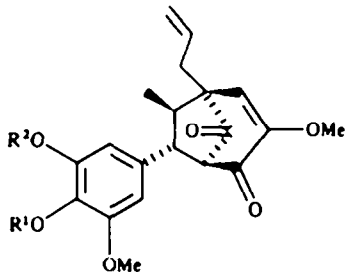
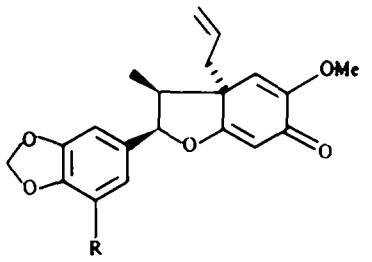


3a $R^1 = R^2 = CH_3$
3b $R^1 = R^2 = Me$



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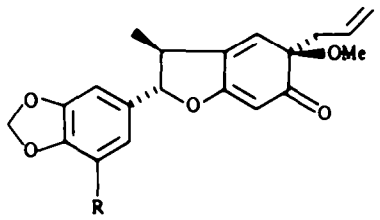

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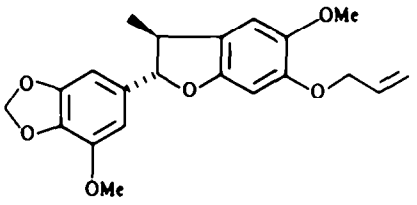
5b R = OMe



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EXPERIMENTAL

Isolation of constituents. Fruits of *L. armeniaca* were collected by Dr. H. F. Paulino Fo. near Humaitá, Amazonas State. Dried fruits (100 g) were extracted with EtOH–H_2O (9 : 1). The solvent was evaporated. The residue (12.4 g) was washed in succession with hexane to remove fatty material, and with $CHCl_3$. The $CHCl_3$ soln was evaporated and the residue was submitted to CC (silica gel). All fractions were purified by prep. TLC (silica gel), yielding in order of increasing polarity **3a** (3 mg), **2a** (4 mg), **2b** (15 mg), **3b** (3 mg), **5a** (15 mg), **5b** (9 mg), **4a** (25 mg), **4b** (12 mg) and **6** (10 mg). Dried fruit calyces (250 g), treated in the same way, gave **1b** (180 mg) and **1a** (55 mg).

(7S,8R,1'R,2'R,3'S)-$\Delta^{8'}$-*2'-Acetoxy-3',5'-dimethoxy-3,4-methylenedioxy-1',2',3',4'-tetrahydro-4'-oxo-7.3',8.1'-neolignan* (**2a**). CD (0.01 g/100 ml MeOH): $[\theta]_{310}$ −3300, $[\theta]_{253}$ +1850. For other data, see ref. [3].

(7S,8R,1'R,2'R,3'S)-$\Delta^{8'}$-*2'-Acetoxy-3,3',5'-trimethoxy-4,5-methylenedioxy-1',2',3',4'-tetrahydro-4'-oxo-7.3',8.1'-neolignan* (**2b**). Mp 137–139°. UV λ_{max}^{MeOH} nm: 242, 260 (ε 9750, 8000). IR ν_{max}^{KBr} cm^{-1}: 1750 (2'-CO), 1708 (4'-CO), 1620, 1515 (Ar), 1095. ^{1}H NMR (60 MHz, CCl_4): δ0.90 (*d*, *J* = 6 Hz, 3H-9), 2.24 (*s*, AcO-2'), 2.3 2.6 (*m*, 2H-7'), 2.15–2.6 (*m*, H-8), 3–3.2 (*m*, H-7), 3.19 (*s*, MeO-3'), 3.60 (*s*, MeO-5'), 3.88 (*s*, MeO-3), 5.25 (*s*, H-2'), 4.9–5.4 (*m*, 2H-9'), 5.88 (*s*, CH_2O_2-4,5), 5.50 (*s*, H-6'), 5.5–6 (*m*, H-8'), 6.32, 6.55 (2*d*, *J* = 2 Hz, H-2, H-6). ^{13}C NMR (20 MHz, $CDCl_3$): δ133.6 (C-1), 104.2 (C-2), 148.5 (C-3), 131.5 (C-4), 142.6 (C-5), 110.8 (C-6), 57.6 (C-7), 49.3 (C-8), 13.7 (C-9), 50.7 (C-1'), 77.3 (C-2'), 90.0 (C-3'), 193.4 (C-4'), 151.8 (C-5'), 119.3 (C-6'), 36.9 (C-7'), 133.6 (C-8'), 118.5 (C-9'), 54.6 (MeO-3'), 55.4 (MeO-5'), 56.6 (MeO-3), 101.1 (CH_2O_2-4',5'), 21.0 and 168.9 (AcO-2'). MS *m/z* (rel. int.): 444 [M]$^+$ (24), 402 (7), 210 (100), 181 (55). CD (0.01 g/100 ml MeOH): $[\theta]_{305}$ −4200, $[\theta]_{258}$ +900.

(7S,8R,1'R,3'S)-$\Delta^{8'}$-*3,5'-Dimethoxy-4,5-methylenedioxy-1',2',3',4'-tetrahydro-2',4'-dioxo-7.3',8.1'-neolignan* (**3a**). CD (0.01 g/100 ml MeOH): $[\theta]_{310}$ −1850. For other data, see ref. [8].

(7S,8R,1'R,3'S)-$\Delta^{8'}$-*3,4,5,5'-Tetramethoxy-1',2',3',4'-tetrahydro-2',4'-dioxo-7.3',8.1'-neolignan* (**3b**). Oil. UV λ_{max}^{MeOH} nm: 268 (ε 3975). IR ν_{max}^{film} cm^{-1}: 1755 (2'-CO), 1690 (4'-CO), 1595, 1515 (Ar), 1130. ^{1}H NMR (60 MHz, CCl_4): δ1.08 (*d*, *J* = 6 Hz, 3H-9), 2.3–2.6 (*m*, 2H-7'), 1.9–2.3 (*m*, H-8), 2.57 (*m*, H-7), 3.48 (*br s*, H-3'), 3.68 (*s*, MeO-5'), 3.84 (*s*, 3MeO-Ar), 5–5.3 (*m*, 2H-9'), 5.68 (*s*, H-6'),

5.6–6 (*m*, H-8'), 6.25 (*s*, H-2, H-6). ^{13}C NMR (20 MHz, $CDCl_3$): δ137.1 (C-1), 104.1 (C-2), 153.4 (C-3), 137.1 (C-4), 153.4 (C-5), 104.1 (C-6), 55.4 (C-7), 47.0 (C-8), 14.1 (C-9), 50.4 (C-1'), 202.5 (C-2'), 70.0 (C-3'), 189.4 (C-4'), 152.3 (C-5'), 119.0 (C-6'), 35.2 (C-7'), 132.8 (C-8'), 117.9 (C-9'), 55.6 (MeO-5'), 56.2 (MeO-3), 60.6 (MeO-4), 56.2 (MeO-5). MS *m/z* (rel. int.): 386 $[M]^+$ (100), 371 (24), 358 (15), 346 (21), 221 (75), 208 (73), 193 (48), 177 (37), 166 (34). CD (0.01 g/100 ml MeOH): $[\theta]_{308}$ −3650, $[\theta]_{295}$ +400.

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