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NEOLIGNANS FROM *MEZILAURUS ITAUBA**

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Key Word Index—*Mezilaurus itauba*; Lauraceae; wood bark; dimeric lignoids; neolignans; benzofuranoid neolignans; bicyclo[3.2.1]octanoid neolignans.

Abstract—The wood bark of *Mezilaurus itauba* afforded in addition to seven known neolignans, three new compounds rel- (7*R*,8*R*,1′*S*,3′*S*)-$\Delta^{5',8'}$-5′-methoxy-3,4-methylenedioxy-1′,2′,3′,4′-tetrahydro-2′,4′-dioxo-7.3′,8.1′-neolignan, rel-(7*S*,8*S*,1′*S*,2′*S*,3′*R*,4′*S*)-$\Delta^{8'}$-2′,4′-dihydroxy-3,4-methylenedioxy-1′,2′,3′,4′,5′,6′-hexahydro-5′-oxo-7.3′,8.1′-neolignan and rel-(7*S*,8*S*)-$\Delta^{8'}$-6′-hydroxy-5′-methoxy-3,4-methylenedioxy-7·*O*·2′,8.3′-neolignan. The latter compound has been detected previously in *Aniba terminalis*. The structures were elucidated by spectroscopic methods and comparison with related compounds.

INTRODUCTION

Mezilaurus is a genus of the Lauraceae; comprising nine mostly arboreal species distributed mainly in the Amazon basin [1]. Only *M. synandra* has been investigated chemically and its trunk wood contains benzylisoquinoline alkaloids and γ-lactones [2].

The present paper describes the results obtained in a study of *M. itauba* (Meissn.) Taubert ex Mez., which grows in the Comisarías del Amazonas and Guaviare, Colombia; the plant is commonly known as itauba-stone wood, 'Japi-u-dlr' and 'Macmemorae' (dialects: Puinave and Witoto, respectively) [3]. The chloroform extract of the wood bark of *M. itauba* yielded seven benzofuranoid neolignans and three bicyclo[3.2.1]octanoid neolignans. The nomenclature and numbering of these neolignans follow the rules which were outlined in a recent review [4].

RESULTS AND DISCUSSION

Ten neolignans were isolated from *M. itauba*. Among these compounds **1b**, **2a**, **4a** and **5a** were reported earlier from *Aniba terminalis* [5, 6], neolignans of structural types **1b**, **3a** and **6a** co-occur in *A. burchellii* [7, 8] and **7a** was previously isolated from an *Aniba* species [9].

Compound **1a** showed IR absorption at 3500 cm^{-1} indicative of a hydroxyl group; confirmation of the presence of this functionality was provided by the UV spectrum (λ_{max}^{MeOH} 325 nm; $\lambda_{max}^{MeOH+NaOMe}$ 344 nm). The complex UV spectrum of **1a**, is indicative of a highly aromatic structure. Particularly informative was the ^{1}H NMR spectrum measured in carbon tetrachloride which showed a hydroxyl signal as a broad peak at δ5.51, three aromatic protons as a multiplet at δ6.68–6.90 and one aromatic proton singlet at δ6.42. The AMX_3 system was analysed by ^{1}H NMR; (A): δ4.93 (*d*, *J* = 8.0 Hz); (M): δ3.10–3.50 (*m*); (X_3): δ1.35 (*d*, *J* = 7.0 Hz). A *trans*-7,8-dihydrobenzofuran structure of **1a**, was suggested by correlation with representatives of established structure [7]. An allyl group is also evident from the ^{1}H NMR spectrum which also exhibited signals due to methylene (δ3.38, *d*, *J* = 6.0 Hz) and vinyl (δ5.60–6.20, *m*, =CH and δ4.80–5.20, *m*, $=CH_2$) groups as well as signals due to methoxy (δ3.83, *s*) and methylenedioxy (δ5.90, *s*) groups. Additional structural evidence was gained by preparation of **1c**. Convincing evidence for the structure of **1a** was provided by the mass spectrum ($[M]^+$ at *m/z* 340 and fragment at *m/z* 162). This compound has been previously detected in a mixture [5].

For compound **7b**, $C_{20}H_{20}O_5$ ($[M]^+$ *m/z* 340), $[\alpha]_D$ −7.31°, the formula, established by mass spectrometry and expanded by inspection of UV, IR and ^{1}H NMR spectra, showed that the two C_6–C_3 units in this neolignan are linked only by C–C bonds and suggest that the compound is a bicyclo-octanoid [4]. Mass spectra were very helpful in defining one of the C_6–C_3 units by the fragment at *m/z* 162 (47%) which corresponded to an $[ArCH{=}CHMe]^+$ fragment. The constitution of the second C_6–C_3 unit was defined by spectroscopic methods. Compound **7b** showed IR absorptions at 1770 and 1718 cm^{-1} (>CO) corresponding to part of the five-membered and six-membered rings, respectively. The stereochemical assignments of **7b** are corroborated by ^{1}H NMR spectral comparisons with a model compound [10].

Compound **8a** is a crystalline compound, mp 158–160°, $[\alpha]_D$ −0.69°, $[M]^+$ *m/z* 330 showing aromatic ring absorption at λ_{max} 289 nm (log ε3.51) in the UV spectrum and carbonyl absorption at 1698 cm^{-1} in the IR spectrum. Absorption at 3504–3378 cm^{-1} is attributed to hydroxyl groups and bands at 1640, 985 and 921 cm^{-1} indicate the presence of an allyl group. The aliphatic nature of the hydroxyl group was deduced by inspection of the ^{13}C and ^{1}H NMR spectra, which in addition gave further structural information (Table 1). C-2′ and C-4′ are represented by doublets at δ79.0 and δ75.7 and the two carbinol protons resonate at δ4.60–4.76 (*m*, H-2′) and

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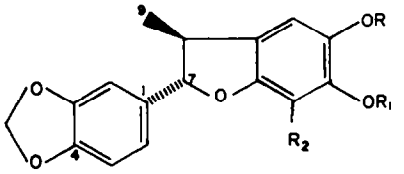
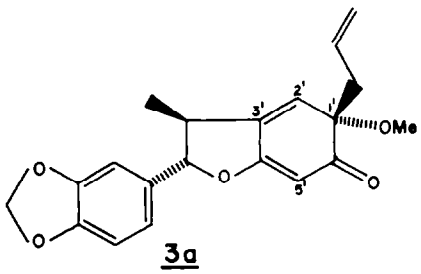
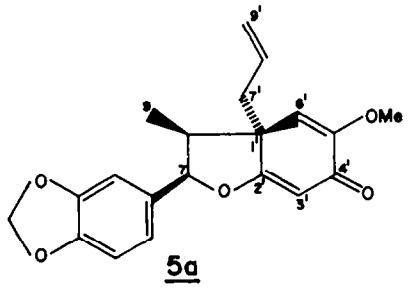


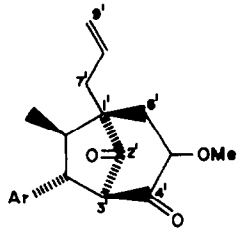
1a R = Me, R_1 = H, R_2 = $CH_2CH{=}CH_2$
1b R = Me, R_1 = $CH_2CH{=}CH_2$, R_2 = H
1c R = Me, R_1 = Ac, R_2 = $CH_2CH{=}CH_2$



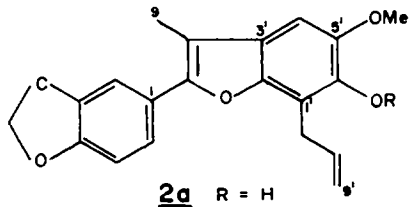
3a



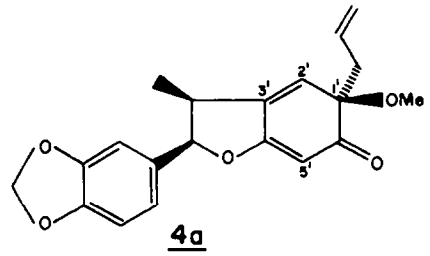
5a



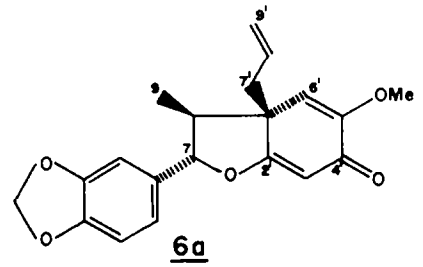
7a Ar = GUAIACYL
7b Ar = PIPERONYL



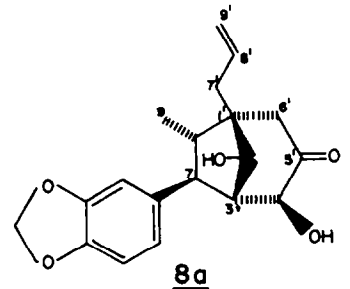
2a R = H
2b R = Ac



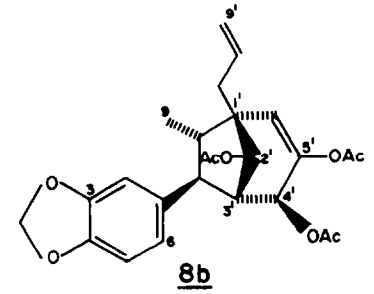
4a



6a



8a



8b

3.76–3.96 (*m*, H-4'). The aromatic ring is evident from two ^{13}C oxygen bearing singlets at δ148.7 and 147.6, three doublets at δ108.1, 109.5 and 122.3 and a singlet at δ140.4. This is confirmed by signals for three aromatic protons at δ7.3 (*d*, J = 2.0 Hz, H-2), 6.78 (*d*, J = 6.0 Hz, H-5) and 6.78 (*dd*, J = 6.0 and 2.0 Hz) in the ^1H NMR spectrum which shows a signal for one methylenedioxy group at δ5.96 (*s*). The remaining sp^2 ^{13}C signals are ascribed to a carbonyl group at δ210.5 and a monosubstituted double bond responsible for a doublet at δ136.3 (C-8') and a triplet at 117.8 (C-9'). The substituent of the double bond is a methylene group responsible for a multiplet (δ1.7–2.2), coupled to a vinyl proton that appears as a multiplet (δ5.6–6.2, H-8') further coupled to two vinyl protons (δ4.88–5.36, *m*, 2H-9'). In the ^{13}C NMR spectrum C-7' appeared as a triplet at δ38.6. The doublet at δ0.87 (J = 7.0 Hz, 3H-9) indicate an Ar-7/Me-8-*trans*-relationship where the methyl is *endo* with

Table 1. ^{13}C and ^{1}H chemical shifts for **8a**

Assignment	^{13}C δMe_2CO-d_6*	^{13}C APT†	^{1}H δMe_2CO-d_6‡
1	140.4	C	—
2	108.1	CH	7.30
3	148.7	C	—
4	147.6	C	—
5	109.5	CH	6.78
6	122.3	CH	6.78
7	55.2	CH	2.70
8	49.2	CH	2.20–2.60
9	12.3	Me	0.87
1′	51.7	C	—
2′	79.0	CH	4.60–4.76
3′	55.9	CH	2.20–2.60
4′	75.7	CH	3.76–3.96
5′	210.5	C	—
6′	43.4	CH_2	2.20–2.60
7′	38.6	CH_2	1.70–2.20
8′	136.3	CH	5.60–6.20
9′	117.8	CH_2	4.88–5.36
O_2CH_2	101.6	CH_2	5.96

*Measured at 20.0 MHz with TMS as internal reference.
†Information obtained from the APT.
‡Measured at 60 MHz with TMS as internal reference.

respect to bicyclo [11]. The clearest evidence for the *endo* orientation of C-9 and C-6′ was given by ^{13}C NMR signals at δ12.3 (C-9) and δ43.4 (C-6′) corresponding to height values by the reciprocal γ-effect [12].

Acetylation transformed **8a** into the triacetate **8b**. A low resolution mass spectrum obtained at 30 eV, with significant peaks at *m/z* 456 (100%) $[M]^+$, 414 (5%), 355 (5%), 296 (3%) and 162 (59%), confirmed this reaction. This information, the strong IR band at 1748 cm^{-1}, the disappearance of the absorption at 1698 cm^{-1} present in **8a** and the number and chemical shifts of ^{13}C and ^{1}H NMR signals suggested the formation of acetate **8b** with enolization of **8a**. The acetate **8b** contains three acetoxy groups localized in 2′ (δ2.08, *s*, 3H; δ20.86, *q*, 1C and δ169.38, *s*, 1C), 4′ (δ2.13, *s*, 3H; δ21.04, *q*, 1C and δ169.79, *s*, 1C) and 5′ (δ2.16, *s*, 3H; δ21.29, *q*, 1C and δ170.39, *s*, 1C). Further inspection of the ^{1}H and ^{13}C NMR spectra of **8a** and **8b** is of particular relevance. In **8b** there are four olefinic protons (**8a** contains three olefinic protons) and the multiplet at δ2.2–2.6 present in **8a** is absent. In the ^{13}C NMR spectrum there is disappearance of the signals at δ43.4 (8α: *t*, 1C) and δ210.50 (**8a**: *s*, 1C) and the appearance of a doublet at δ121.44 (C-6′) and a singlet at δ147.93 (C-5′). Preliminary information about the number of directly attached protons to each carbon atom was obtained from APT (attached proton test) experiments (Table 1). Spectral comparison of **8a** and of its triacetate **8b** with canellin-C [11, 13] and other related compounds [9] indicates that **8a** and canellin-C to possess identical configurations.

EXPERIMENTAL

The plant material from the Bajo Guaviare, Comisaría del Guainía (Colombia), voucher Xiloteca de la Facultad de Ingeniería Forestal, Universidad Distrital, Bogotá, Colombia, 424, was collected and identified by Drs. A. Roa and E. Acero.

Isolation of constituents. Wood bark (2 kg) was extracted with EtOH. The $CHCl_3$ soluble part (20 g) of the extract (76 g) was chromatographed on a silica S column (200 g). Fractions eluted with C_6H_6 were rechromatographed and further purified by prep. TLC (petrol–C_6H_6 and petrol–$CHCl_3$ with gradually increasing polarity) gave in order of elution, **2a** (16 mg), **1a** (35 mg), **1b** (143 mg) and sitosterol (31 mg). Fractions eluted with $CHCl_3$ were separated and purified by successive prep. TLC on silica gel HF_{254}. The developing solvents were different mixtures of petrol, hexane, EtOAc and Me_2CO and gave in order of elution, **5a** and **6a**-component mixture (79 mg), **7a** (23 mg), **3a** (66 mg), **4a** (17 mg), **7b** (18 mg) and **8a** (43 mg).

Identification of known compounds. The known compounds were identified by direct comparison of mp, $[\alpha]_D$ and spectral data with published data (**1b**, **2a**, **3a**, **4a**, **5a**, **6a** and **7a**). For these compounds only new data are included.

Rel-(7S,8S)-$\Delta^{8'}$-*6′-hydroxy-5′-methoxy*-3,4-*methylenedioxy*-7-O-2′,8.3′-*neolignan* (**1a**). Oil. UV λ_{max}^{MeOH} nm (log ε): 224 sh (4.41), 293 (4.05), 308 sh (3.86), 325 (3.69), 345 sh (3.45); $\lambda_{max}^{MeOH+MeONa}$ nm: 223, 294, 309 sh, 344. IR ν_{max}^{film} cm^{-1}: 3500, 3075, 3003, 2956, 2922, 1636, 1610, 1504, 1490, 1466, 1443, 1388, 1337, 1245, 1216, 1118, 1096, 987, 930, 911, 871, 833, 799, 752. ^{1}H NMR (60 MHz, CCl_4): δ6.68–6.90 (3H, *m*, H-2, H-5 and H-6), 4.93 (1H, *d*, *J* = 8.0 Hz, H-7), 3.10–3.50 (1H, *m*, H-8), 1.35 (3H, *d*, *J* = 7.0 Hz, H-9), 6.42 (1H, *s*, H-4′), 3.38 (2H, *d*, *J* = 6.0 Hz, H-7′), 5.60–6.20 (1H, *m*, H-8′), 4.80–5.20 (2H, *m*, H-9′), 5.90 (2H, *s*, OCH_2O), 5.51 (1H, *s*, OH-6′), 3.83 (3H, *s*, OMe-5′). MS 70 eV, *m/z* (rel. int.): 340 $[M]^+$ (100), 339 (12), 338 (44), 325 (16), 324 (10), 310 (4), 297 (13), 285 (10), 279 (8), 205 (20), 179 (4), 177 (5), 175 (5), 173 (7), 165 (7), 162 (4), 150 (3), 149 (20), 147 (9), 135 (17).

Rel-(7S,8S)-$\Delta^{8'}$-*6′-acetoxy-5′-methoxy*-3,4-*methylenedioxy*-7-O-2′,8.3′-*neolignan* (**1c**). (Ac_2O–pyridine, 24 hr room temp.). Oil. IR ν_{max}^{film} cm^{-1}: 3082, 2963, 2920, 2860, 1763, 1638, 1612, 1502, 1440, 1368, 1346, 1250, 1190, 1115, 1030, 990, 930, 889, 854, 755. ^{1}H NMR (60 MHz, CCl_4): δ6.60–6.88 (3H, *m*, H-2, H-5 and H-6), 4.93 (1H, *d*, *J* = 8.0 Hz, H-7), 3.07–3.90 (1H, *m*, H-8), 1.36 (3H, *d*, *J* = 7.0 Hz, H-9), 6.46 (1H, *s*, H-4′), 3.20 (2H, *d*, *J* = 6.0 Hz, H-7′), 5.66–6.20 (1H, *m*, H-8′), 4.66–5.30 (2H, *m*, H-9′), 5.88 (2H, *s*, OCH_2O), 3.73 (3H, *s*, OMe-5′), 2.20 (3H, *s*, OAc-6′). MS 70 eV, *m/z* (rel. int.): 382 $[M]^+$ (36), 341 (14), 340 (100), 325 (18), 311 (2), 297 (9), 249 (3), 179 (4), 162 (2), 135 (15).

Rel-(7*S*,8*S*)-$\Delta^{8'}$-*6′-methoxy*-3,4-*methylenedioxy*-7-O-3′,8.4′,1′-O-7′-*neolignan* (**1b**). $[\alpha]_D^{20°C}$ = +6.90° ($CHCl_3$; *c* 4.2). ^{13}C NMR (20 MHz, $CDCl_3$): δ144.28 (*s*, C-1), 106.37 (*d*, C-2), 147.82 (*s*, C-3), 147.33 (*s*, C-4), 107.84 (*d*, C-5), 119.44 (*d*, C-6), 92.59 (*d*, C-7), 45.64 (*d*, C-8), 18.12 (*q*, C-9), 134.76 (*s*, C-1), 97.28 (*d*, C-2′), 148.88 (*s*, C-3′), 122.25 (*s*, C-4′), 109.35 (*d*, C-5′), 153.31 (*s*, C-6′), 69.94 (*t*, C-7′), 133.41 (*d*, C-8′), 117.29 (*t*, C-9′), 100.76 (*t*, OCH_2O), 57.19 (*q*, OMe-6′).

Rel-(7R,8R,1′S,3′S)-$\Delta^{5',8}$-4-*hydroxy*-3,5′-*dimethoxy*-1′,2′,3′,4′-*tetrahydro*-2′,4′-*dioxo*-7.3′,8.1′-*neolignan* (**7a**). Oil. $[\alpha]_D^{25°C}$ = −0.60° ($CHCl_3$; *c* 0.83). Acetate of **7a** (Ac_2O–pyridine, 24 hr, room temp.). Oil. IR ν_{max}^{film} cm^{-1}: 3060, 2920, 2860, 1760, 1713, 1620, 1530, 1515, 1455, 1436, 1375, 1275, 1200, 1160, 1120, 1040, 1003, 920, 860. ^{1}H NMR (60 MHz, CCl_4): δ6.50–6.90 (3H, *m*, H-2, H-5 and H-6), 3.81 (3H, *s*, OMe-3), 2.23 (3H, *s*, OAc-4), 2.68 (1H, *d*, *J* = 8.0 Hz, H-7), 1.83–2.45 (1H, *m*, H-8), 0.98 (3H, *d*, *J* = 7.0 Hz, H-9), 3.42 (1H, *s*, H-3′), 3.62 (3H, *s*, OMe-5′), 5.66 (1H, *s*, H-6′), 2.45–2.87 (2H, *m*, H-7′), 5.65–6.05 (1H, *m*, H-8′), 4.93–5.55 (2H, *m*, H-9′). MS 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (6), 343 (24), 342 (100), 327 (5), 301 (19), 206 (1), 178 (7), 137 (12).

Rel-(7R,8R,1′S,3′S)-$\Delta^{5',8'}$-5′-*methoxy*-3,4-*methylenedioxy*-1′,2′,3′,4′-*tetrahydro*-2′,4′-*dioxo*-7.3′,8.1′-*neolignan* (**7b**). Oil. $[\alpha]_D^{25°C}$ = −7.31° ($CHCl_3$; *c* 0.20). UV λ_{max}^{MeOH} nm (log ε): 236

(3.60), 289 (3.46). IR ν_{max}^{film} cm^{-1}: 3085, 2985, 2940, 2860, 1770, 1718, 1650, 1618, 1515, 1498, 1452, 1390, 1335, 1265, 1245, 1225, 1187, 1114, 1088, 1045, 1005, 938, 895, 872, 760. ^{1}H NMR (60 MHz, CCl_4): δ6.42–6.79 (3H, *m*, H-2, H-5 and H-6), 2.47 (1H, *d*, J = 7.3 Hz, H-7), 1.77–2.20 (1H, *m*, H-8), 1.04 (3H, *d*, J = 6.6 Hz, H-9), 3.56 (1H, *s*, H-3'), 5.64 (1H, *s*, H-6'), 2.25–3.05 (2H, *m*, H-7'), 5.60–6.12 (1H, *m*, H-8'), 4.95–5.36 (2H, *m*, H-9'), 3.67 (3H, *s*, OMe-5'), 5.92 (2H, *s*, OCH_2O). MS 70 eV, *m/z* (rel. int.): 340 [M]$^+$ (100), 325 (6), 312 (2), 299 (27), 284 (10), 271 (27), 243 (5), 178 (5), 162 (47), 150 (4), 137 (6), 135 (25).

Rel-(7S,8S,1'S,2'S,3'R,4'S)-$\Delta^{8'}$-*2',4'-dihydroxy-3,4-methylenedioxy-1',2',3',4',5',6'-hexahydro-5'-oxo-7.3',8.1'-neolignan* (**8a**). Crystals, mp 158–160° (CCl_4). $[\alpha]_D^{25°C} = -0.69°$ (Me_2CO; *c* 2.15). UV λ_{max}^{EtOH} nm (log ε): 237 (3.58), 289 (3.51). IR ν_{max}^{KBr} cm^{-1}: 3504, 3450, 3378, 3078, 3014, 2956, 2915, 1698, 1640, 1610, 1501, 1485, 1451, 1390, 1321, 1250, 1210, 1185, 1152, 1118, 1100, 1070, 1040, 1015, 985, 963, 938, 921, 892, 880, 795, 730. ^{1}H NMR (60 MHz, Me_2CO-d_6): see Table 1; ^{13}C NMR (20 MHz, Me_2CO-d_6) and APT experiment, see Table 1. MS 30 eV, *m/z* (rel. int.): 330 [M]$^+$ (100), 271 (6), 240 (15), 199 (3), 177 (7), 149 (3), 162 (13), 135 (4).

Rel-(7S,8S,1'S,2'S,3'R,4'S)-$\Delta^{5',8'}$-*2',4',5'-triacetoxy-3,4-methylenedioxy-1',2',3',4'-tetrahydro-7.3',8.1'-neolignan* (**8b**). (Ac_2O–pyridine, 120 hr room temp.). Oil. IR ν_{max}^{film} cm^{-1}: 3074, 3019, 2960, 2920, 2872, 1748 vs, 1668, 1641, 1610, 1502, 1486, 1442, 1368, 1220 s, 1035, 978, 923, 858, 810, 790, 748. ^{1}H NMR (60 MHz, $CDCl_3$): δ6.70–6.95 (3H, *m*, H-2, H-5 and H-6), 2.10–2.80 (2H, *m*, H-7 and H-8), 0.99 (3H, *d*, J = 7.0 Hz, H-9), 5.60 (1H, *br s*, H-2'), 2.10–2.80 (1H, *m*, H-3'), 4.88–5.08 (1H, *m*, H-4'), 5.30 (1H, *br s*, H-6'), 1.70–2.10 (2H, *m*, H-7'), 5.55–6.10 (1H, *m*, H-8'), 4.88–5.55 (2H, *m*, H-9), 5.94 (2H, *s*, OCH_2O), 2.08 (3H, *s*, OAc-2'), 2.13 (3H, *s*, OAc-4'), 2.16 (3H, *s*, OAc-5'). ^{13}C NMR (20 MHz, $CDCl_3$): δ134.20 (*s*, C-1), 108.10 (*d*, C-2), 146.10 (*s*, C-3), 143.84 (*s*, C-4), 108.20 (*d*, C-5), 125.97 (*d*, C-6), 53.02 (*d*, C-7), 50.83 (*d*, C-8), 12.75 (*q*, C-9), 50.65 (*s*, C-1'), 73.77 (*d*, C-2'), 53.02 (*d*, C-3'), 77.60 (*s*, C-4'), 147.93 (*s*, C-5'), 121.44 (*d*, C-6'), 36.10 (*t*, C-7'), 137.08 (*d*, C-8'), 117.76 (*t*, C-9'), 100.91 (*t*, OCH_2O), 20.86 (*q*, MeCO-2'), 21.04 (*q*, MeCO-4'), 21.29 (*q*, MeCO-5'), 169.38 (*s*, MeCO-2'), 169.79 (*s*, MeCO-4'), 170.39 (*s*, MeCO-5'). MS 30 eV, *m/z* (rel. int.): 456 [M]$^+$ (100), 414 (5), 355 (5), 354 (9), 336 (9), 296 (3), 295 (11), 294 (31), 276 (8), 253 (9), 162 (59), 135 (7).

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