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EUSIDERINS AND OTHER NEOLIGNANS FROM AN *ANIBA* SPECIES*

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Key Word Index - *Aniba* sp.; Lauraceae; benzodioxane neolignans; bicyclo[3.2.1]octanoid neolignans; hydrobenzofuranoid neolignan.

Abstract– A previous report disclosed the presence of benzodioxan and bicyclo[3.2.1]octanoid neolignans in the benzene extract of the trunk wood of an Amazonian *Aniba* (Lauraceae) species. The chloroform extract of the same material contains additionally two new benzodioxan neolignans [*rel*-(7*S*,8*R*)-$\Delta^{8'}$-7-hydroxy-3,4,5,5'-tetramethoxy-7.*O*.3',8.*O*.4'-neolignan; *rel*-(7*R*,8*R*)-$\Delta^{7'}$-3,4,5,5'-tetramethoxy-9'-oxo-7.*O*.3',8.*O*.4'-neolignan], two new bicyclo[3.2.1]-octanoid neolignans [(7*R*,8*S*,1'*S*,2'*S*,3'*S*,4'*R*)-$\Delta^{8'}$-2',4'-dihydroxy-3,3'-dimethoxy-4,5-methylenedioxy-1',2',3',4',5',6'-hexahydro-5'-oxo-7.3',8.1'-neolignan; (7*R*,8*S*,1'*R*,2'*S*,3'*S*)-$\Delta^{8'}$-2'-hydroxy-3,3',5'-trimethoxy-4,5-methylenedioxy-1',2',3',4'-tetrahydro-4'-oxo-7.3',8.1'-neolignan] and a hydrobenzofuranoid neolignan [(7*S*,8*R*,1'*S*,5'*S*)-$\Delta^{8'}$-3,3',5'-trimethoxy-4,5-methylenedioxy-1',4',5',6'-tetrahydro-4'-oxo-7.*O*.2',8.1-neolignan].

INTRODUCTION

The benzene extract of trunk wood pertaining to an unclassified *Aniba* species, voucher INPA, Manaus, No. 42183, yielded the simple allylbenzene dillapiol (**1**), the benzodioxane-type neolignan eusiderin-A (**2a**) and four bicyclo[3.2.1]octanoid-type neolignans: methoxycanellin-A (**3**), **4a**, **4b** and **5**, all described in a previous paper [2]. The chloroform extract of the same plant material yielded in addition to these compounds two new benzodioxane-type neolignans, eusiderin-F (**6a**) and eusiderin-G (**7**), two new bicyclo[3.2.1]octanoid-type neolignans, **8** and **9a** and the hydrobenzofuranoid-type neolignan **10a** previously isolated from *A. ferrea* [3]. Nomenclature and numbering of the neolignans follow the rules detailed in a review [4].

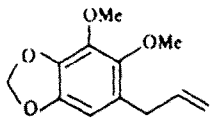
RESULTS AND DISCUSSION

The molecular formulae of **6a** ($C_{22}H_{26}O_7$) and of **7** ($C_{22}H_{24}O_7$) determined by HR mass spectrometry could be expanded to $C_6H_2 \cdot C_6H_2 \cdot COHCHMe \cdot CH_2CH{=}CH_2(OMe)_4O_2$ and $C_6H_2 \cdot C_6H_2 \cdot CHCHMe \cdot CH{=}CHCHO(OMe)_4O_2$, respectively, after analysis of their ^{1}H NMR spectra. The compounds thus were immediately suspected to represent two new members of the small group of benzodioxan neolignans. By analogy with the eusiderins A (**2a**), B (**2b**) [5, 6], C (**6b**), D (**6c**) [7] and E (**11**) [8] they were named eusiderins F (**6a**) and G (**7**) and given the constitutions shown. These were consistent with the mass spectrum. The spectrum of **6a** included a prominent peak at *m/z* 224 (42%), attributed to the ion radical **12a**, and only a minor one at *m/z* 208 (11%), while the spectrum of **7** did not contain the former peak and the latter, attributed to **12b**, showed an enhanced relative intensity (33%). All possible ^{1}H NMR decoupling experiments confirmed the aliphatic proton sequences. Chemical shifts and multiplicities of the aromatic proton signals left no doubts concerning the localization of the aromatic hydrogens at positions 2 and 6 of the symmetric aryl and at the *meta*-positions of the asymmetric aromatic ring. The localization of the substituents on this ring, a delicate problem in the structure elucidation of the eusiderins [5], was achieved for **6a** by analysis of ^{1}H NMR solvent effects. With respect to CCl_4, C_6D_6 shields the methoxyls with unsubstituted vicinal positions (OMe-3,5 $\Delta = -0.25$ ppm, OMe-5' $\Delta = -0.30$ ppm). In contrast, the signal due to the hindered OMe-4 is shifted downfield ($\Delta = +0.21$ ppm). Downfield shifts were also noted for the aromatic proton signals, the H-2,6 singlet ($\Delta = +0.29$ ppm) and the *meta*-split doublets ($\Delta = +0.14$ and $+0.48$ ppm). The magnitude of one of the latter shifts places the corresponding proton into the action sphere of the solvated trimethoxyphenyl group, i.e. at C-2'.

The relative stereochemistry of benzodioxan neolignans is easily verified by analysis of the chemical shift of the methyl protons and the H-7, H-8 coupling constant (*cis* δ_{Me} 1.12 ± 0.03, $J_{H\text{-}7,H\text{-}8} = 2$ Hz; *trans*: δ_{Me} 1.30 ± 0.03, $J_{H\text{-}7,H\text{-}8} = 7.5 \pm 0.5$ Hz [5–8]). According to this criterion eusiderin-F (**6a**) is a *cis*-derivative (δ_{Me} 1.10), while eusiderin-G (**7**) is *trans* (δ_{Me} 1.32, $J_{H\text{-}7,H\text{-}8} = 8$ Hz). In the former compound H-7 is replaced by a hydroxyl; $J_{H\text{-}7,H\text{-}8}$ is of course not observed.

The ORD curves of **6a** and of the two other known 7,8-*cis*-eusiderins **6b** and **6c** [7] are all closely comparable ($\lambda^{u}_{254\pm4}$, $\lambda^{pk}_{269\pm1}$, $\lambda^{u}_{280\pm5}$, $\lambda^{pk}_{291\pm4}$) and thus their absolute stereochemistry must also be identical. In opposition the

* Part 77 in the series "The Chemistry of Brazilian Lauraceae". For Part 76 see ref. [1]. Taken from the Doctorate thesis presented by SMCD to Universidade de São Paulo (1985).



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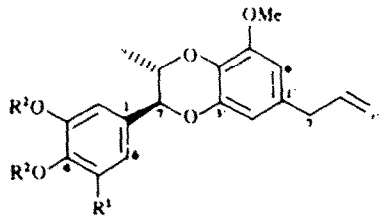
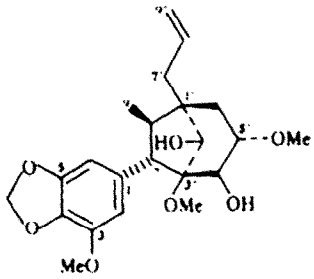


2a R^1 = OMe, R^2 = Me
2b R^1 = H, R^1 - R^2 = CH_2



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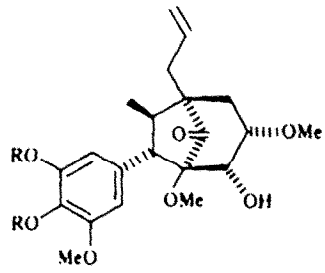
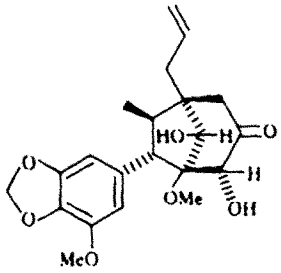


4a R R = CH_2
4b R = Me



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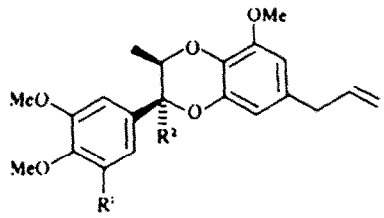
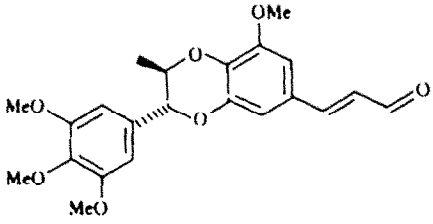


6a R^1 = OMe, R^2 = OH
6b R^1 = OMe, R^2 = H
6c R^1 = R^2 = H



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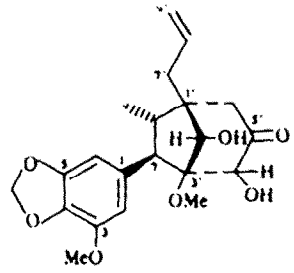
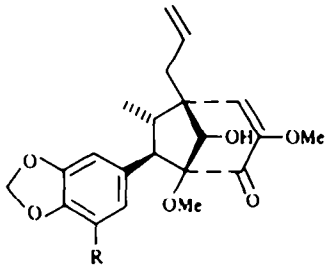


8

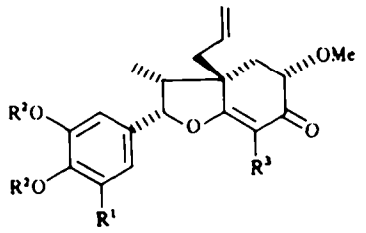
ORD curves of **7** and of another 7,8-*trans*-eusiderin **2a** [7] are very nearly antipodal. All the configurations given in the formulae of the seven eusiderins are only relative.

Compound **8**, $C_{21}H_{26}O_7$, $=C_6H_2 \cdot C_3H_4CO(OH)_2 \cdot CHCHMe \cdot CH_2CH{=}CH_2(OMe)_2O_2CH_2$, is an isomer of the previously described compound **5** [2]. As in **5**, the Ar-7/Me-8 substituents must be *trans*-oriented (**8** and **5**: Me-8 $\delta 0.85 \pm 0.08$), since for the *cis*-arrangement strong shielding of the methyl protons by the aromatic ring would be expected. As in **5**, the aryl must be *exo*-oriented, since for the *endo*-orientation in compounds of type **13** [9] non-equivalence of methylene protons at C-6' (**13**: H_{eq}

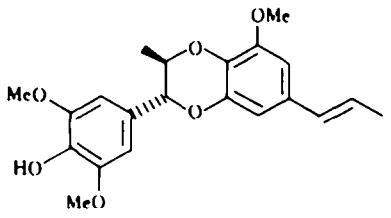
δ2.54, *dd*, J = 16, 1 Hz; H_{ax} 2.38, *d*, J = 16 Hz; 8: 2H δ2.24, *s*) occurs. Hence with respect to relative stereochemistry the sole difference between **5** and **8** concerns the configurations of the carbinolic carbons. This fact is confirmed by the relatively small differences in their spectra. Thus in **5** the axial hydroxyl at C-4' interacts only with the axial hydrogen at C-6' determining a considerable non-equivalence of the methylene protons (δ1.75–2.65, *m*). Neither the C-5' carbonyl (ν_{max} 1715 cm^{-1}) nor the methoxyl at C-3' (δ2.83) are apparently affected. In contradistinction in **8** the hydroxyl at C-4' must lie in the plane of the ring. It does not interact



9a R = OMe
9b R = H



10a $R^1 = R^3 = OMe$, $R^2 - R^2 = CH_2$
10b $R^1 = R^3 = H$, $R^2 = Me$
10c $R^1 = R^3 = H$, R^2 $R^2 = CH_2$



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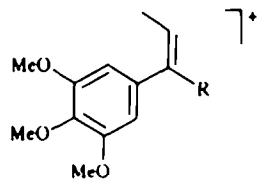
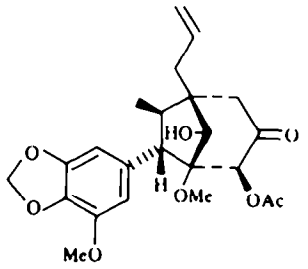


12a R = OH
12b R = H



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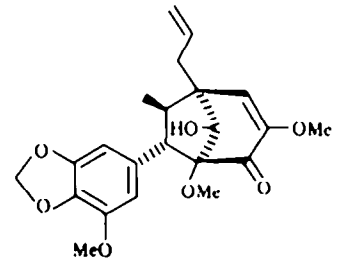

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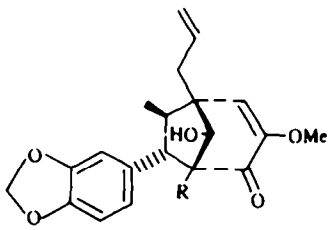
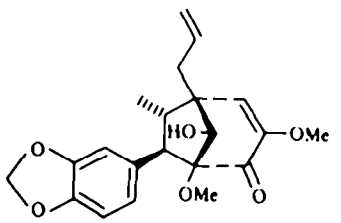


15a R = H
15b R = OMe



16

with the equivalent methylene hydrogens (δ2.24), but forms hydrogen bridges with the vicinal carbonyl (ν_{max} 1705 cm^{-1}) and methoxyl, deshielding the latter rather strongly (δ3.52, *s*). Furthermore in **5** the hydroxyl at C-2' interacts with the aromatic ring deshielding its two protons (δ6.55, 6.73, two *d*, J = 1.2 Hz). In contradistinction in **8** the hydroxyl at C-2' must be directed towards the carbonyl since the aromatic protons are now not only equivalent but also relatively shielded (δ6.20, *s*).

The ORD curves of compounds **5** and **8** show negative and positive Cotton effects, respectively, at *ca* 250 nm. Their chiralities at the benzylic carbons must hence be antipodal and, since the absolute stereochemistry of **5** is known [2], structure **8** can be proposed for the new compound.

Compound **9a**, $C_{22}H_{26}O_7 \equiv C_6H_2 \cdot C_5H_2CO(OH)$-$CHCHMe \cdot CH_2CH{=}CH_2(OMe)_3O_2CH_2$, is an isomer of the previously described compound **14** [3, 10, 11]. As in **14**, the Ar-7/Me-8 substituents must be *trans*-oriented (**9a** and **14**: Me-8 $\delta 0.98 \pm 0.08$). As in **14**, H-7 and Me-8 must be *endo*-oriented (**9a** and **14**: H-7 $\delta 2.60 \pm 0.06$, Me-8 $\delta 0.98 \pm 0.08$), since for the *exo*-orientation in guianin-type compounds [10, 12, 13] shielding by the α,β-unsaturated ketone moiety does not occur (**15a**: H-7 δ3.55, Me-8 δ1.23). Hence, considering relative stereochemistry only the sole difference between **9a** and **14** must concern the configuration of the carbinolic carbon. Oriented towards the pentacycle in **14**, the hydroxyl at C-2' should be directed towards the hexacycle in **9a** as in the known semisynthetic compound **9b** [14]. The chemical shifts of H-2, H-6, H-2' and H-6' are sensitive to this difference. As seen above the spatial vicinity of aryl and hydroxyl deshields the aromatic protons (**14**: δ6.49, 6.68 *vs.* **9a** δ6.27, 6.30). Furthermore this situation not only locates H-2' over the α,β-unsaturated carbonyl moiety where it is also relatively shielded (**14**: 4.00 *vs.* **9a** and **9b**: 4.29 ± 0.03), but also causes deshielding of H-6' (**14**: δ5.70 *vs.* **9a** and **9b**: $\delta 5.18 \pm 0.10$). Besides, only when the hydroxyl is directed towards the hexacycle H-2' and H-6' are part of a planar W-system. The consequent small H-2',H-6' long range coupling was confirmed for **9a** by double resonance experiments.

The ORD curves of **14** of known absolute configuration [10] and of the new compound are antipodal and **9a** must thus possess the structure shown in the formula. It is interesting to note that the ORD curve of guianin (**15a**), also of known absolute configuration [10], and of **9a** show identical Cotton effects (due to enone absorption) above 260 nm and antipodal effects (due to aryl absorption) below this wavelength. Guianin's stereochemistry has been previously proposed for a series of compounds including **15b** [12]. Indeed all of them give identical ORD curves above 260 nm (troughs at 293 nm, peaks at 277 nm) and, with the exception of **15b**, below 260 nm (two troughs at 254 and 242 nm). Compound **15b** gives only one ORD trough below 260 nm (at 242 nm), precisely as does **9a**, and its structure should hence be revised to **16**. Indeed ^{13}C NMR evidence has already been adduced to show that its aryl group must be *exo*- rather than *endo*-oriented [1].

The UV and ORD data which are missing from the original description of compound **10a** [3] are given in the Experimental. They are very similar to the analogous data of **10b** and **10c** and include the positive Cotton effects at *ca* 310 nm, main evidence for the proposed absolute configuration of these porosins [15, 16]. Hence **10a** must possess the structure shown in the formula.

The botanical identity of the analysed species remains undetermined. The chemical composition, however, leaves little doubt concerning its affinity with a species designated *A. ferrea* Kubitzki in a previous paper [3]. As *A. ferrea* the present *Aniba* species possesses a rather peculiar series of neolignans. Indeed among 10 neolignans isolated, seven (**4a**, **4b**, **5**, **6a**, **7**, **8** and **9a**, the latter a stereoisomer of a constituent of *A. ferrea*) are new compounds, two (**3**, **10a**) occur also in *A. ferrea* and only one (**2a**) is of common occurrence in the Lauraceae and Myristicaceae.

EXPERIMENTAL

Isolation of constituents. Trunk wood of the *Aniba* species previously described [2] was reduced to powder (1 kg) and percolated with $CHCl_3$. Evapn of solvent yielded an oily residue (5 g). This was chromatographed on a dry column (200 g silica gel deactivated by 10% H_2O, Et_2O). Eluates of 10 equal portions of the extruded material were treated as follows. Eluate 1 (1 g) was separated by TLC (silica gel, C_6H_6) into fatty material (0.8 g) and **1** (0.1 g). Eluate 2 was separated by prep. TLC (silica gel, $CHCl_3$) into **2a** (0.5 g), **6a** (50 mg) and **7** (60 mg). Eluate 3 (0.2 g) gave by prep. TLC (silica gel, $CHCl_3$-Et_2O, 49:1) **4a** (50 mg). Eluate 4 (1 g) was purified by recrystallizations from MeOH into sitosterol (0.7 g). Eluate 5 (0.3 g) was separated by prep. TLC (silica gel, C_6H_6-Me_2CO, 4:1) into **3** (100 mg) and **8** (5 mg). Eluate 6 (0.4 g) was separated by prep. TLC (silica gel, Et_2O) into **4b** (15 mg), **10a** (20 mg) and **9a** (20 mg). Eluate 7 (0.2 g) was separated by prep. TLC (silica gel, $CHCl_3$-EtOH, 9:1) into **5** (15 mg) and polar material.

rel-(7S,8R)-Δ^8-*7-Hydroxy-3,4,5,5'-tetramethoxy-7.O.3',8.O.4'-neolignan* (**6a**). Viscous oil ([M]$^+$ found 402.1651, $C_{22}H_{26}O_7$ requires 402.1678). UV λ_{max}^{MeOH} nm: 235 inf., 255 (ε1500). IR ν_{max}^{film} cm^{-1}: 3380, 1585, 1500, 1450, 1415, 1340, 1330, 1230, 1125, 1095, 995, 910, 815, 745. ^1H NMR (60 MHz, CCl_4): δ6.42 (*s*, H-2, H-6), 6.32 (*d*, J = 2 Hz, H-2'), 6.15 (*d*, J = 2 Hz, H-6'), 5.4–6.1 (*m*, H-8'), 4.75–5.3 (*m*, 2H-9'), 4.69 (*d*, $J \sim 3$ Hz, OH-7), 4.1–4.6 (*m*, H-8), 3.80 (*s*, OMe-5'), 3.75 (*s*, OMe-3, OMe-5), 3.70 (*s*, OMe-4), 3.25 (*dd*, J = 6, 1.5 Hz, 2H-7'), 1.10 (*d*, J = 6 Hz, 3H-9). ^1H NMR (60 MHz, C_6D_6): δ6.71 (*s*, H-2, H-6), 6.80 (*d*, J = 2 Hz, H-2'), 6.29 (*d*, J = 2 Hz, H-6'), 3.91 (*s*, OMe-4), 3.50 (*s*, OMe-3, OMe-5, OMe-5'), 3.30 (*dd*, J = 6, 1.5 Hz, 2H-7'), 1.38 (*d*, J = 6 Hz, 3H-9). MS *m/z* (rel. int.): 402 (3), 225 (10), 224 (42), 208 (11), 197 (11), 196 (10), 195 (49), 193 (10), 180 (45), 169 (14), 165 (11), 151 (10), 87 (19), 85 (89), 83 (100). ORD (*c* 2.66 mg/100 ml, MeOH, 400–240 nm): $[\phi]_{400}$ – 2700, $[\phi]_{285}^{tr}$ – 10 200, $[\phi]_{270}^{pk}$ – 5900, $[\phi]_{250}^{tr}$ – 10 650, $[\phi]_{240}$ 0.

rel-(7R,8R)-Δ^7-*3,4,5,5'-Tetramethoxy-9'-oxo-7.O.3',8.O.4'-neolignan* (**7**). Viscous oil ([M]$^+$ found 400.1513, $C_{22}H_{24}O_7$ requires 400.1522). UV λ_{max}^{MeOH} nm: 230, 280, 328 (ε8850, 1700, 3400). IR ν_{max}^{film} cm^{-1}: 1672, 1665, 1620, 1585, 1494, 1455, 1424, 1380, 1325, 1295, 1274, 1230, 1184, 1124, 1070, 1040, 1000, 970, 930, 885, 830, 750. ^1H NMR (270 MHz, $CDCl_3$): δ9.62 (*d*, J = 8 Hz, CHO-8'), 7.36 (*d*, J = 16 Hz, H-7'), 6.89 (*d*, J = 2 Hz, H-2'), 6.77 (*d*, J = 2 Hz, H-6'), 6.60 (*dd*, J = 8, 16 Hz, H-8'), 6.59 (*s*, H-2, H-6), 4.58 (*d*, J = 8 Hz, H-7), 4.18 (*dq*, J = 8, 6.5 Hz, H-8), 3.94 (*s*, OMe-5'), 3.86 (*s*, OMe-3, OMe-5), 3.85 (*s*, OMe-4), 1.32 (*d*, J = 6.5 Hz, 3H-9). MS *m/z* (rel. int.): 401 (2), 400 (5), 209 (16), 208 (33), 205 (17), 195 (34), 193 (31), 165 (10), 109 (10), 105 (10), 97 (10), 95 (10), 85 (39), 83 (100). ORD (*c* 2.0 mg/100 ml, MeOH, 400–250 nm): $[\phi]_{400}$ + 8800, $[\phi]_{360}^{tr}$ + 7500, $[\phi]_{295}^{inf}$ + 12 900, $[\phi]_{275}^{pk}$ + 13 850, $[\phi]_{270}^{tr}$ + 13 000, $[\phi]_{255}^{pk}$ + 14 800, $[\phi]_{250}^{tr}$ + 13 800.

(7R,8S,1'S,2'S,3'S,4'R)-Δ^8-*2',4'-Dihydroxy-3,3'-dimethoxy-4,5-*

methylenedioxy-1',2',3',4',5',6'-hexahydro-5'-oxo-7.3',8.1'-neolignan (**8**). Viscous oil ([M]$^+$ found 390.1653, $C_{21}H_{26}O_7$ requires 390.1679). UV λ_{max}^{MeOH} nm: 238 inf., 270 (ε2800, 1150). IR ν_{max}^{film} cm^{-1}: 3390, 1704, 1629, 1502, 1451, 1429 sh., 1210, 1134, 1095, 1069, 1044, 933, 835. ^{1}H NMR (60 MHz, CCl_4): δ6.2 (*ca s*, H-2, H-6), 5.94 (*s*, O_2CH_2), 5.4–6 (*m*, H-8'), 4.7–5.2 (*m*, 2H-9'), 4.30 (*s*, H-4'), 4.07 (*s*, H-2'), 3.90 (*s*, OMe-3), 3.52 (*s*, OMe-3'), 1.6–3.1 (*m*, H-7, H-8, 2H-7'), 2.24 (*s*, 2H-6'), 0.93 (*d*, J = 7 Hz, 3H-9). MS *m/z* (rel. int.): 390 (66), 349 (14), 317 (98), 318 (23), 300 (32), 285 (6), 259 (13), 192 (22), 181 (19), 167 (22), 165 (31), 149 (61), 137 (13), 123 (11), 91 (16). ORD (*c* 1.04 mg/100 ml, MeOH, 400–240 nm): $[\phi]_{400}$ – 4420, $[\phi]_{333}^{tr}$ – 4770, $[\phi]_{310}^{pk}$ – 4270, $[\phi]_{285}^{tr}$ – 8100, $[\phi]_{258}^{pk}$ – 6180, $[\phi]_{240}^{tr}$ – 8400.

(7R,8S,1'R,2'S,3'S)-$\Delta^{8'}$-*2'-Hydroxy-3,3',5'-trimethoxy-4,5-methylenedioxy-1',2',3',4'-tetrahydro-4'-oxo-7.3',8.1'-neolignan* (**9a**). Viscous oil ([M]$^+$ found 402.1732, $C_{22}H_{26}O_7$ requires 402.1679). UV λ_{max}^{MeOH} nm: 231 inf., 268 (ε8750, 4350). IR ν_{max}^{film} cm^{-1}: 3472, 1695, 1631, 1499, 1453, 1429, 1348, 1319, 1238, 1205, 1154, 1124, 1081, 1042, 1000, 971, 935, 823, 787, 758. ^{1}H NMR (270 MHz, $CDCl_3$): δ6.30 (*d*, J = 1.5 Hz, H-6), 6.27 (*d*, J = 1.5 Hz, H-2), 5.95, 5.94 (AB syst., O_2CH_2), 5.8–6 (*m*, H-8'), 5.2 5.4 (*m*, 2H-9'), 5.07 (*br s*, H-6'), 4.25 (*br s*, H-2'), 3.87 (*s*, OMe-3), 3.69 (*s*, OMe-5'), 5.68 (*s*, OMe-3'), 2.66 (*d*, J = 8.2 Hz, H-7), 2.39 (*dd*, J = 14, 6 Hz, H-7'), 2.23 (*dd*, J = 14, 8 Hz, H-7'), 2.16 (*dq*, J = 7, 8.2 Hz, H-8), 1.57 (OH-2'), 1.06 (*d*, J = 7 Hz, 3H-9). MS *m/z* (rel. int.): 402 (6), 317 (10), 267 (15), 263 (10), 236 (11), 217 (14), 213 (15), 212 (18), 210 (5), 201 (10), 192 (8), 186 (16), 182 (12), 169 (21), 163 (21), 151 (28), 135 (5), 133 (15), 132 (11), 124 (15), 113 (37), 112 (14), 104 (100), 101 (13), 96 (55), 85 (19), 70 (17). ORD (*c* 3.29 mg/100 ml, MeOH, 400–240 nm): $[\phi]_{400}$ + 7650, $[\phi]_{350}^{pk}$ + 10750, $[\phi]_{292}$ 0, $[\phi]_{287.5}^{tr}$ – 1450, $[\phi]_{282}$ 0, $[\phi]_{267.5}^{pk}$ + 3100, $[\phi]_{247.5}^{tr}$ 0, $[\phi]_{240}$ + 3850.

(7S,8R,1'S,5'S)-$\Delta^{8'}$-*3,3',5'-Trimethoxy-4,5-methylenedioxy-1',4',5',6'-tetrahydro-4'-oxo-7.O.2',8.1'-neolignan* (**10a**). Viscous oil ([M]$^+$ found 402.1595, $C_{22}H_{26}O_7$ requires 402.1679). UV λ_{max}^{MeOH} nm: 213, 258 (ε8800, 6150). IR, ^{1}H NMR and MS data in ref. [3]. ORD (*c* 1.06 mg/100 ml, MeOH, 400–250 nm): $[\phi]_{400}$ – 5350, $[\phi]_{355}$ 0, $[\phi]_{338}^{pk}$ + 3850, $[\phi]_{330}$ 0, $[\phi]_{292}^{tr}$ – 62450, $[\phi]_{265}$ 0, $[\phi]_{255}^{pk}$ + 8900, $[\phi]_{250}$ + 6550.

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