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NEOLIGNANS FROM *ANIBA LANCIFOLIA**

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Key Word Index—*Aniba lancifolia*; Lauraceae; neolignans; 2-hydroxy-4,5-dimethoxyallylbenzene; lancilin; lancifolins A to F.

Abstract—The branches of the shrub *Aniba lancifolia* Kubitzki et Rodrigues (Lauraceae) contain besides 2-hydroxy-4,5-dimethoxyallylbenzene and its dimer cyclohexan-2-allyl-5-en-4,5-dimethoxy-4-*O*-(2′-allyl-4′,5′-dimethoxyphenyl)-1-one (lancilin, **2**) 6 further novel neolignans: (4*S*,2′*R*)- and (4*R*,2′*E*)-cyclohexan-2-allyl-2,5-dien-4,5-dimethoxy-4-[2′-(1′-guaiacyl)-propyl]-1-one (lancifolins A and B, **3a** and **3b**), (4*S*,2′*R*)- and (4*R*,2′*R*)-cyclohexan-2-allyl-2,5-dien-4,5-dimethoxy-4-[2′-(1′-veratryl)-propyl]-1-one (lancifolins C and D, **3c** and **3d**), (4*S*,2′*R*)- and (4R,2′*R*)-cyclohexan-2-allyl-2,5-dien-4,5-dimethoxy-4-[2′-(1′-piperonyl)-propyl]-1-one (lancifolins E and F, **3e** and **3f**).

INTRODUCTION

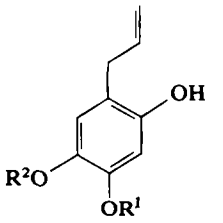
Aniba lancifolia Kubitzki et Rodrigues, to date known only from the type locality 130 km north of Manaus, is the sole species of its genus with shrubby habit and broadly cordate leaf bases. The rocky campina in which it was discovered would merit to be preserved as a relic, due not only to the very peculiar characteristics of its vegetation, but also to the wealth of endemic and rare species. Unfortunately, this area is at present being irreversibly destroyed, as many others in Amazonia [2].

Branches of the shrub were found to contain a simple allylbenzene (**1a**) together with 7 related compounds belonging to two novel neolignan types in which two allylbenzene units are linked either head to head by a 2.O.3′ bridge (lancilin type, **2**) or tail to head by a 8.3′ bridge (lancifolin type, **3**).

Systematic nomenclature, which we have used so far for neolignans (cf. [3] and previous papers), detracts from the fact that, in spite of diversity of skeletons and functions, they form a singularly homogeneous biogenetic group of natural compounds. This homogeneity is honoured in a system of nomenclature and numbering outlined in a recent review [4] which is adopted in the present paper.

RESULTS AND DISCUSSION

Compound **1a**, $C_{11}H_{14}O_3$, was characterized as a hydroxy-dimethoxyallylbenzene by ^{1}H NMR. In this spectrum the aromatic protons are represented by singlets and hence are *para*-related. Among the three possible alternatives, the *meta*-dimethoxy structure can be excluded by MS evidence. Intense M^+-15 and M^+-15-28 peaks are typical of *ortho*- and *para*-dimethoxybenzenes [5]. From the remaining alternatives **1a** was selected by analysis of the ^{1}H NMR shifts upon acetylation which are closely comparable to analogous shifts for **1b** [6] ($\Delta\delta$ **1a/1b**: CH_2



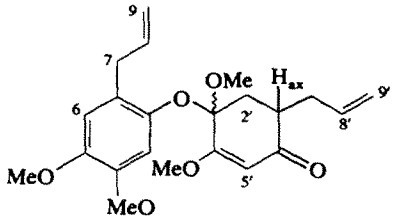
1a $R^1 = R^2 = Me$
1b R^1–$R^2 = CH_2$

$-0.1/-0.1$, H-3 $+0.33/+0.27$, H-6 $-0.08/-0.07$).

The recognition of 2-hydroxy-4,5-dimethoxyallylbenzene as a constituent of the species proved biosynthetically significant. Indeed, the additional constituent lancilin (**2**), $C_{22}H_{28}O_6$, is simply a dimer of **1a**, as shown by the MS which, besides the M^+ peak (1% rel. int.), shows only peaks for the monomer ($[C_{11}H_{14}O_3]^{+\cdot}$, formed by a 1,4-hydrogen rearrangement, 100%), and by acid hydrolysis which leads only to **1a**. This evidence is compatible with the formulation of lancilin as the biogenetically reasonable ketal **2**. ^{1}H NMR data fully confirm this proposal and indicate the axial conformation of H-1′ [δ H-2′ *ax* 1.68 (*t*, J = 12 and 12 Hz), H-2′ *eq* 2.2 (*dd*, J = 12 and 4 Hz)].

All further isolates can be considered oxidative coupling products of **1a** with ethers of 3,4-dihydroxypropenylbenzene. The MS of all lancifolins

*Part 54 in the series 'The Chemistry of Brazilian Lauraceae'. For Part 53 see ref. [1]. Based on part of the Doctorate thesis presented by P. P. D. D., on leave from Universidad Nacional de Colombia, Bogotá, to Universidade de São Paulo (1978).



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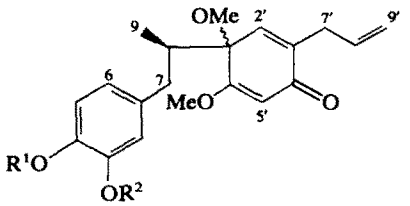
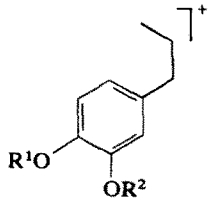
(**3a–3f**) show prominent peaks with the *m/e* for **1a** (**3a** 100%, **3b** 100%, **3c** 19%, **3d** 18%, **3f** 42%) and for **4** (**3a** 88%, **3b** 85%, **3c** 100%, **3d** 100%, **3f** 100%).



3a $R^1=H$, $R^2=Me$, C-3′*S*
3b $R^1=H$, $R^2=Me$, C-3′*R*
3c $R^1=R^2=Me$, C-3′*S*
3d $R^1=R^2=Me$, C-3′*R*
3e $R^1-R^2=CH_2$, C-3′*S*
3f $R^1-R^2=CH_2$, C-3′*R*

Futoquinol (**5**) [7] includes such an oxidized **1a**-moiety and, indeed, all pertinent ^1H NMR signals of **3a–f** and **5** are closely comparable (H-2′ 6.17–6.27/6.13, singlets with sec. splitting; H-5′ 5.49–5.64/5.81, singlets).



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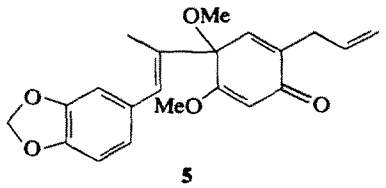

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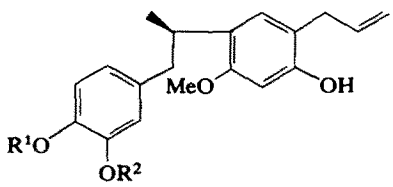
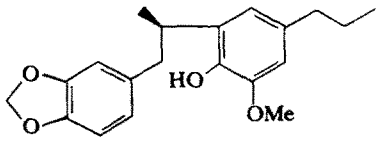
The presence of a β-substituted **4**-moiety is also evident in all lancifolins. Indeed, the ^1H NMR data show the 3,4-oxygenation of all aryls (H-2,5,6 δ 6.4–6.8, *m*), represented in **3a**, **b** by guaiacyl, in **3c**, **d** by veratryl and in **3e**, **f** by piperonyl groups. At 60 MHz the 2H-7 and the H-8 protons give rise to unresolved bands (δ 6.4–6.8). At 100 MHz, however, for **3a** the signals of the two C-7 protons appear as *dd* (δ 2.17, $J=13$ and 5 Hz) and *d* (δ 1.9, $J=13$ Hz) and only the H-8 signal remains a *m* (δ 2.1–2.4).

In the UV the lancifolins cause two benzenoid (*ca* 247 and 285 nm) and an enone (*ca* 290 nm) absorptions. Their ORD curves all show positive Cotton effects at 253±5 nm and hence all compounds are of identical stereochemistry at C-8. This is formulated



6a $R^1=R^2=Me$
6b $R^1-R^2=CH_2$

8*R* in **3a–3f**, since **6a** and **6b**, obtained by treatment of lancifolins D (**3d**) and F (**3f**) with Zn and HOAc, and the model compound **7**, obtained by hyd-



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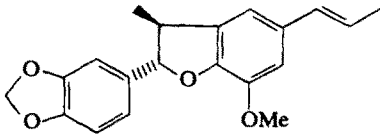
rogenolysis of licarin-B (**8**) [8] show comparable CD curves. Although the 8-position of all lancifolins possess an identical absolute configuration, their environment is clearly different in **3a**, **3c**, **3e** (3H-9, δ 0.56±0.03,



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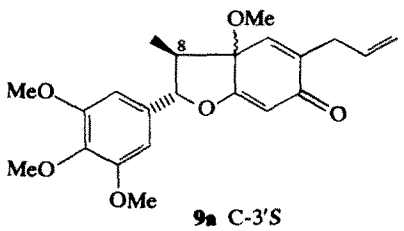
d, $J=7$ Hz) and in **3b**, **3d**, **3f** (3H-9, δ 0.94±0.03, *d*, $J=7$ Hz). This fact can be rationalized by differential stereochemistry at C-3′. Indeed, lancifolins C (**3c**) and D (**3d**) are comparable respectively to mirandins B (**9b**) and A (**9a**) concerning Cotton effects due to the



9a C-3′*S*
9b C-3′*R*

enone chromophore (Table 1). The 8*R*,3′*S* and 8*R*,3′*R* neolignan configurations can thus be assigned respectively to lancifolins A (**3a**), C (**3c**), E (**3e**) and lancifolins B (**3b**), D (**3d**), F (**3f**).

For additional data on the mirandins consult ref. [9], where the configuration at C-8, shown correctly in the structural formulae, is named *S* instead of *R* for the mirandins A and B, as well as for *epi*-mirandin-A.

Chemically *A. lancifolia* thus does not belong to the pyrone containing group 1 of the genus, but rather to the neolignan containing group 2 [10]. All 4 species which have so far been assigned to this group, however, contain hydrobenzofuranoid and bicyclo [3.2.1]-octanoid neolignans, a fact for which their interconversion by acid-catalysed rearrangement [11] provides

Table 1. Cotton effects of lancifolins (**3c**, **3d**) and mirandins (**9b**, **9a**)

	$\pi \rightarrow \pi^*$				$n \rightarrow \pi^*$			
	nm	ORD	nm	CD	nm	ORD	nm	CD
3c	278	−	290	−	*ca* 335	−[y]		
9b	280	−			370	−		
3d	*ca* 290	+[x]			330	+	335	+
9a	*ca* 290	+	295	+	370	+	360	+

x expressed by a shoulder.
y observation based on $[\alpha]_{400} - 1500°$.

a rationale. The biosynthesis of both these types requires fundamentally only oxidation [3], while the biosynthesis of the lancifolins requires additionally hydride addition. The peculiar morphology of *A. lancifolia* thus corresponds to a characteristic chemistry.

EXPERIMENTAL

Isolation of constituents. Branches of a specimen (voucher herbarium INPA, Manaus, 43479), collected near km 130 of the Manaus-Caracaraí highway, were dried and their powder (3 kg) was percolated with EtOH. The extract (165 g) was washed exhaustively with $CHCl_3$. $CHCl_3$ was evaporated and residue (30 g) chromatographed on a Si gel column (400 g). Elution with the following solvents gave the indicated fractions: petrol–C_6H_6 1:1 (A), 3:7 (B, C), C_6H_6 (D to G). Fraction A (1.9 g) was composed of aliphatic esters. Fraction B (70 mg) was crystallized from MeOH to yield sitosterol. Fraction C (4.3 g) was separated by TLC (Al_2O_3, petrol –C_6H_6, 1:9) into **3f** (120 mg) and a mixture of **3e** and **3f**. Fraction D gave by TLC (Si gel, $CHCl_3$–Me_2CO, 99:1) **1a** (175 mg). Fraction E gave by TLC (Si gel, C_6H_6–EtOAc, 3:1) **2** (130 mg). Fraction F (850 mg) was separated by TLC (Al_2O_3, C_6H_6–EtOAc, 49:1) into **3c** (93 mg) and **3d** (72) mg). Fraction G (75 mg) was separated by TLC (Al_2O_3, C_6H_6–EtOAc, 24:1) into **3a** (9 mg) and **3b** (12 mg).

2-*Hydroxy*-4,5-*dimethoxyallylbenzene* (**1a**). Oil (Found: C, 68.49; H, 6.98. $C_{11}H_{14}O_3$ requires: C, 68.02; H, 7.27%). λ_{max}^{MeOH} nm: 230, 290 (ε 4300, 2770). ν_{max}^{film} cm^{-1}: 3356, 1639, 1620, 1520, 1471, 1214, 1125, 1015. ^1H NMR (60 MHz, CCl_4): δ 3.28 (*d*, *J* = 7 Hz, CH_2-1), 3.62, 3.75 (2*s*, 2 OMe), 4.9–5.2 (*m*, $=CH_2$), 5.48 (*s*, OH-2), 5.6–6 (*m*, CH=), 6.27 (*s*, H-3), 6.57 (*s*, H-6). MS (*m/e*): 194 (100%) M^+, 179 (77), 167 (19), 163 (15), 151 (23), 123 (38). *Acetate*, oil, ν_{max}^{film} cm^{-1}: 1761, 1639, 1616, 1517. ^1H NMR (60 MHz, CCl_4): δ 2.19 (*s*, OAc), 3.15 (*d*, *J* = 7 Hz, CH_2-1), 3.82 (*s*, 2 OMe), 4.8–5.2 (*m*, $=CH_2$), 5.6–6.2 (*m*, CH=), 6.49 (*s*, H-6), 6.6 (*s*, H-3).

$\Delta^{8,8'}$-4,5,3′,4′-*Tetramethoxy*-1′,2′,3′,6′-*tetrahydro*-6′-*oxo*-2.O.3′-*neolignan* (lancilin, **2**). Oil (Found: C, 67.75; H, 7.00. $C_{22}H_{28}O_6$ requires: C, 68.02; H, 7.27%). λ_{max}^{MeOH} nm: 242, 286 (ε 30700, 9050). ν_{max}^{film} cm^{-1}: 1667, 1613, 1515. ^1H NMR (100 MHz, $CDCl_3$): δ 1.68 (*t*, *J* = 12, 12 Hz, H-2′ ax), 2.2 (*dd*, *J* = 12, 4 Hz, H-2′ *eq*), 1.9–2.5 (*m*, 2H-7′), 2.5–2.8 (*m*, H-1′), 3.24 (*d*, *J* = 6 Hz, 2H-7), 3.48 (*s*, OMe-3′), 3.76 (*s*, OMe-5, OMe-4′), 4.8–5.1 (*m*, 2H-9, 2H-9′), 5.32 (*s*, H-5′), 5.4–6 (*m*, H-8, H-8′), 6.65 (*s*, H-6), 6.58 (*s*, H-3). MS (*m/e*): 388 (1%) M^+, 194 (100), 179 (23), 167 (8), 163 (10), 153 (36), 151 (2), 125 (5), 123 (3). *Hydrolysis.* A soln of **2** (40 mg) and TsOH (30 mg) in Me_2CO–H_2O, 1:1 (12 ml) was stirred at room temp. (24 hr), concd and extracted with Et_2O. The Et_2O soln was dried and evaporated. The residue was purified by TLC (Si gel, hexane–EtOAc, 4:1) to **1a** (16 mg).

(8R,3′S)-$\Delta^{8'}$-4-*Hydroxy*-3,3′,4′-*trimethoxy*-3′,6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-A, **3a**). Oil (Found: C, 69.98; H, 7.50. $C_{21}H_{26}O_5$ requires: C, 70.37; H, 7.31%). λ_{max}^{MeOH} nm: 235, 285 (ε 12500, 4950). $\lambda_{max}^{MeOH+NaOH}$ nm: 243, 294 (ε 12 400, 4450). ν_{max}^{film} cm^{-1}: 3350, 1665, 1640, 1616, 1515, 1466, 1282, 1235. MS (*m/e*): 358 (60%) M^+, 326 (12), 221 (8), 194 (100), 193 (17), 191 (23), 165 (88), 164 (11), 149 (20), 137 (36). ORD (4 mg/100 ml MeOH, 230–400 nm): $[\phi]_{240}^{tr}$-12500, $[\phi]_{257}$ 0, $[\phi]_{270}^{pk}$+6250, $[\phi]_{330}$ 0.

(8R,3′R)-$\Delta^{8'}$-4-*Hydroxy*-3,3′,4′-*trimethoxy*-3′, 6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-B, **3b**). Oil (Found: C, 70.21; H, 7.12. $C_{21}H_{26}O_5$ requires: C, 70.37; H, 7.31%). λ_{max}^{MeOH} nm: 231, 283 (ε 12500, 4900). $\lambda_{max}^{MeOH+NaOH}$ nm: 241, 293 (ε 12500, 4900). ν_{max}^{film} cm^{-1}: 3344, 1669, 1631, 1613, 1517, 1466, 1285, 1238. MS (*m/e*): 358 (59%)M^+, 326 (12), 221 (6), 194 (100), 191 (24), 165 (85), 164 (12), 149 (26), 137 (38). ORD (4 mg/100 ml MeOH, 230–400 nm): $[\phi]_{242}^{tr}$-19250, $[\phi]_{255}$ 0, $[\phi]_{270}^{pk}$+12550, $[\phi]_{297}$ 0, $[\phi]_{320}^{tr}$-3700, $[\phi]_{350}$ 0, $[\phi]_{400}$+950. *Acetate.* Oil, ν_{max}^{film} cm^{-1}: 1761, 1667, 1639, 1603, 1550. ^1H NMR (60 MHz, CCl_4): δ 0.9(*d*, *J* = 7 Hz, 3H-9), 2.17 (*s*, OAc), 1.9–2.7 (*m*, 2H-7, H-8), 3 (*s*, OMe-3′), 3.03 (*d*, *J* = 7 Hz, 2H-7′), 3.43 (*s*, OMe-4′), 3.73 (*s*, OMe-3), 4.8–5.3 (*m*, 2H-9′), 5.36 (*s*, H-5′), 5.5–6 (*m*, H-8′), 6.17 (sec. split *brs*, H-2′), 6.4–6.8 (*m*, H-2,5,6).

(8R,3′S)-$\Delta^{8'}$-3,4,3′,4′-*Tetramethoxy*-3′,6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-C, **3c**). Oil (Found: C, 70.74; H, 7.90. $C_{22}H_{28}O_5$ requires: C, 70.94; H, 7.58%). λ_{max}^{MeOH} nm: 280, 285 inf. (ε 6800, 6550). ν_{max}^{film} cm^{-1}: 1667, 1639, 1613, 1515, 1462, 1266, 1227, 1157, 1143. MS (*m/e*): 372 (42%) M^+, 340 (11), 194 (19), 179 (100), 178 (10), 164 (11), 151 (31). ORD (5 mg/100 ml MeOH, 230–400 nm): $[\phi]_{238}^{tr}$-47300, $[\phi]_{260}$ 0, $[\phi]_{270}^{pk}$+5950, $[\phi]_{287}$ 0, $[\phi]_{317}^{tr}$-6700, $[\phi]_{400}$-4450. CD (5.0 mg/100 ml MeOH, 240–400 nm): $[\Theta]_{253}^{max}$+15650, $[\Theta]_{278}$ 0, $[\Theta]_{290}^{max}$-8550, $[\Theta]_{302}^{max}$-9650.

(8R,3′R)-$\Delta^{8'}$-3,4,3′4′-*Tetramethoxy*-3′,6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-D, **3d**). Oil (Found: C, 71.34; H, 7.77. $C_{22}H_{28}O_5$ requires: C, 70.94; H, 7.58%). λ_{max}^{MeOH} nm: 281, 286 (ε 6900, 6650). ν_{max}^{film} cm^{-1}: 1658, 1634, 1605, 1508, 1453, 1258, 1225, 1157, 1075, 1031. MS (*m/e*): 372 (35%) M^+, 194 (18), 193 (11), 179 (100), 178 (12), 164 (10), 151 (38). ORD (4.8 mg/100 ml MeOH, 230–400 nm): $[\phi]_{242}^{tr}$- 9300, $[\phi]_{250}$ 0, $[\phi]_{265}^{pk}$+28700, $[\phi]_{305}^{pk}$+2700, $[\phi]_{310}$ 0, $[\phi]_{320}^{tr}$-1150, $[\phi]_{330}$ 0, $[\phi]_{400}$+3450. CD (4.0 mg/100 ml MeOH, 240–400 nm: $[\Theta]_{252}^{max}$+13800, $[\Theta]_{267}$ 0, $[\Theta]_{285}^{max}$-7600, $[\Theta]_{314}$ 0, $[\Theta]_{335}^{max}$+1700.

(8R,3′S)-$\Delta^{8'}$-3,4-*Methylenedioxy*-3′,4′-*dimethoxy*-3′,6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-E, **3e**). This was not obtained in a pure state. For ^1H NMR data determined by difference from a spectrum of a mixture (**3e** and **3f**) see below.

(8E,3′R)-$\Delta^{8'}$-3,4-*Methylenedioxy*-3′,4′-*dimethoxy*-3′,6′-*dihydro*-6′-*oxo*-8,3′-*neolignan* (lancifolin-F, **3f**). Oil (Found: C, 70.56; H, 6.99. $C_{22}H_{24}O_5$ requires: C, 70.77; H, 6.79%). λ_{max}^{MeOH} nm: 236, 286 (ε 11550, 5850). ν_{max}^{film} cm^{-1}: 1667, 639, 1610, 1513, 1495, 1260, 1242, 1087, 1053. MS (*m/e*): 356 (42) M^+, 324 (12), 194 (42), 179 (17), 163 (100), 162 (13), 135 (45), 105 (27) ORD (4 mg/100 ml MeOH 230–400 nm): $[\phi]_{240}^{tr}$-16000, $[\phi]_{253}$ 0, $[\phi]_{265}^{pk}$+13350, $[\phi]_{301}$ 0, $[\phi]_{325}^{tr}$-2300, $[\phi]_{345}$ 0, $[\phi]_{400}$ 900. ^1H NMR of **3a**, **3b**, **3e**, **3f** (60 MHz, CCl_4, δ): 0.53/0.95/0.55/0.91 (*d*, *J* = 7 Hz, 3H-9), 1.8–2.5 (*m*, 2H-7, H-8), 3–3.2 (*m*, 2H-7′), 3.1 (*s*, OMe-3′), 3.73/3.65/—/— (*s*, OMe-3), 3.88/3.88/3.78/3.8 (*s*, OMe-4′), 4.9–5.3 (*m*, 2H-9′), 5.24/5.23/—/— (*brs*, OH-4),

5.5–6 (*m*, H-8'), 5.56/5.49/5.58/5.61 (*s*, H-5'), —/—/5.84/5.91 (*s*, O_2CH_2), 6.17/6.2/6.17/6.21 (sec. split *brs*, H-2'), 6.4–6.8 (*m*, H-2,5,6). ^{1}H NMR of **3c**, **3d** (100 MHz, $CDCl_3$, δ): 0.59/0.97 (*d*, *J* = 7 Hz, 3H-9), 1.91 (*d*, *J* = 13 Hz, H-7), 2.17 (*dd*, *J* = 13, 5 Hz, H-7), 2.1–2.4 (*m*, H-8), 3–3.2 (*m*, 2H-7'), 3.12 (*s*, OMe-3'), 3.71/3.68 (*s*, OMe-4'), 3.78, 3.8/3.8, 3.8 (*s*, OMe-3,4), 5.06 (*dd*, *J* = 16, 2 Hz, H-9'), 5.07 (*dd*, *J* = 10, 2 Hz, H-9'), 5.5–6.1 (*m*, H-8'), 5.64 (*s*, H-5'), 6.24 (*s*, H-2'), 6.4–6.8 (*m*, H-2,5,6).

Aromatization. A soln of the lancifolin (35 mg) in HOAc (12 ml) was stirred with 200 mg Zn powder at 40° (6 hr), filtered, neutralized with aq Na_2CO_3 and extracted with Et_2O. The Et_2O soln was dried and evaporated. The residue was fractionated by TLC (Si gel, C_6H_6–EtOAc, 17:3). **3d** (34% recovered) gave **6a** (43% yield), **3f** (27% recovered) gave **6b** (53% yield).

(8R)-$\Delta^{8'}$-6'-*Hydroxy*-3,4,4'-*trimethoxy*-8.3'-*neolignan* (**6a**). Oil (Found: C, 73.30; H, 7.75. $C_{21}H_{26}O_4$ requires: C, 73.66; H, 7.65%). λ_{max}^{MeOH} nm: 225 inf., 282 (ε 16800, 6350). ν_{max}^{film} cm^{-1}: 3448, 1603, 1508, 1458, 1414, 1030. ^{1}H NMR (60 MHz, CCl_4): δ 1.15 (*d*, *J* = 6 Hz, 3H-9), 2.59 (*dd*, *J* = 13, 8 Hz, H-7), 2.8 (*dd*, *J* = 13, 5 Hz, H-7), 3.1–3.45 (*m*, H-8), 3.3 (*d*, *J* = 7 Hz, 2H-7'), 3.6, 3.65, 3.7 (3*s*, 3 OMe), 4.75 (*brs*, OH-6'), 4.9–5.3 (*m*, 2H-9'), 5.5–6.1 (*m*, H-8'), 6.25 (*s*, H-5'), 6.4–6.7 (*m*, H-2,5,6), MS (*m/e*): 342 (50%) M$^+$. CD (7.6 mg/100 ml MeOH, 240–400 nm): $[\Theta]_{280}^{max}$-2050, $[\Theta]_{286}$-550, $[\Theta]_{288}^{max}$-1150, $[\Theta]_{292}$ 0, $[\Theta]_{295}^{max}$ + 360, $[\Theta]_{303}$ 0.

(8R)-$\Delta^{8'}$-6'-*Hydroxy*-4'-*methoxy*-3,4-*methylenedioxy*-8,3'-*neolignan* (**6b**). Oil (Found: C, 73.12; H, 6.90; $C_{20}H_{22}O_4$ requires: C, 73.60; H, 6.79%). λ_{max}^{MeOH} nm: 230 inf., 287 (ε 19850, 11950). ν_{max}^{film} cm^{-1}: 3390. 1600, 1500, 1438, 1054, 1010. ^{1}H NMR (60 MHz, CCl_4): δ 1.1 (*d*, *J* = 7 Hz, 3H-9), 2.45 (*dd*, *J* = 13, 9 Hz, H-7), 2.8 (*dd*, *J* = 13, 5 Hz, H-7), 3.1–3.5 (*m*, H-8), 3.3 (*d*, *J* = 7 Hz, H-7'), 3.7 (*s*, OMe-4'), 4.5 (*brs*, OH-6'), 4.9–5.3 (*m*, 2H-9'), 5.55–6.15 (*m*,H-8'), 5.9 (*s*, O_2CH_2), 6.3 (*s*, H-5'), 6.4–6.65 (*m*, H-2,5,6), 6.75 (*s*, H-2'). MS (*m/e*): 326 (45%) M$^+$. CD (8 mg/100 ml MeOH, 240–400 nm): $[\Theta]_{282}^{max}$-1900, $[\Theta]_{287}$ 0, $[\Theta]_{289}^{max}$ + 2100, $[\Theta]_{292}$ 0, $[\Theta]_{293}^{max}$-350, $[\Theta]_{295}$ 0, $[\Theta]_{300}^{max}$ + 1800, $[\Theta]_{310}$ 0.

(8R)-4'-*Hydroxy*-5'-*methoxy*-3,4-*methylenedioxy*-8.3'-*neolignan* (**7**). A soln of **8** in MeOH–HOAc 19:1 was hydrogenated over Pd/C at room temp., filtered and evaporated. Residue was purified by TLC to **7**, oil (Found: C, 73.45; H, 7.52. $C_{20}H_{24}O_4$ requires: C, 73.15; H, 7.37%). ν_{max}^{film} cm^{-1}: 3490, 1600, 1480, 1450, 1360, 1150. ^{1}H NMR (CCl_4, 60 MHz): δ 0.9 (*t*, *J* = 7 Hz, Me-9'), 1.16 (*d*, *J* = 7 Hz, Me-9), 1.3–1.9 (*m*, 2H-8'), 2.5 (*t*, *J* = 8 Hz, 2H-7'), 2.52 (*dd*, *J* = 16, 9 Hz, H-7), 2.97 (*dd*, *J* = 16, 6 Hz, H-7), 3–3.6 (*m*, H-8), 3.87 (*s*, OMe), 5.5 (*s*, OH), 5.75 (*s*, O_2CH_2), 6.4-6.7 (*m*, H-2,5,6,2',6'). CD (16 mg/100 ml MeOH, 240–400 nm): $[\Theta]_{279}^{max}$-600, $[\Theta]_{282}$ 0, $[\Theta]_{284}^{max}$ + 650, $[\Theta]_{289}^{max}$-100, $[\Theta]_{292}$ 0, $[\Theta]_{294}$ + 1050, $[\Theta]_{304}$ 0.

(7S,8R,3'S)-$\Delta^{8'}$-3,4,5,3'-*Tetramethoxy*-3,6-*dihydro*-6'-*oxo*-7.O.4',8.3'-*neolignan* (*mirandin* A, **9**). CD (8.4 mg/100 ml MeOH, 240–420 nm): $[\Theta]_{255}^{min}$-37700, $[\Theta]_{285}$ 0, $[\Theta]_{295}^{max}$ + 3700, $[\Theta]_{317}$ + 1850, $[\Theta]_{360}^{max}$ + 13350, $[\Theta]_{420}$ 0.

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