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NEOLIGNANS FROM *ANIBA FERREA*[*]

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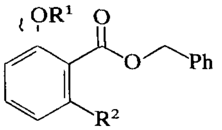
Key Word Index—*Aniba ferrea*; Lauraceae; hydrobenzofuranoid neolignans; bicyclo [3.2.1] octanoid neolignans.

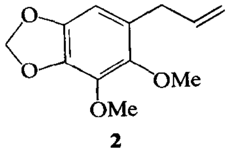
Abstract—The trunk wood of the Amazonian *Aniba ferra* Kubitzki contains, besides three benzyl benzoates (**1a, b, c**) and dillapiol (**2**), four hydrobenzofuranoid and two bicyclo [3.2.1] octanoid neolignans. The former comprise two representatives (**3a, b**) of the novel ferrearin- (3a-allyl-2-aryl-7a-hydroxy-3-methyl-3a,4,7,7a-tetrahydro-7-oxobenzofuran) type, and two further representatives (**4a, b**) of the known porosin- (3a-allyl-2-aryl-5-methoxy-3a,4,5,6-tetrahydro-6-oxobenzofuran) type. The latter comprises a new representative (**5a**) of the known canellin- (1-allyl-6-aryl-7-methylbicyclo [3.2.1] octane) type, and the methyl ether (**6a**) of a known guianin- (1-allyl-6-aryl-7-methyl-4-oxobicyclo [3.2.1] oct-2-en) type neolignan.

INTRODUCTION

Aniba ferrea Kubitzki, a Lauraceous tree popularly known as 'louro ferro', occurs in the vicinity of Manaus, Amazonas. Its heartwood gave besides three benzyl benzoates (**1a, b, c**), the simple allylbenzene dillapiol (**2**) and six new neolignans belonging to the novel ferrearin type (**3a, b**), the porosin [2] type (**4a, b**), the canellin [3] type (**5a**) and the guianin [4] type (**6a**). For reasons stated in a previous paper of this series [5], nomenclature and numbering of neolignans follow the rules outlined in a recent review [6].



1a $R^1 = R^2 = H$
1b $R^1 = Me, R^2 = H$
1c $R^1 = Me, R^2 = OMe$



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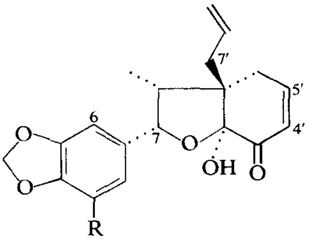
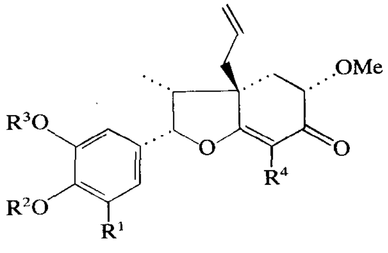
RESULTS AND DISCUSSION

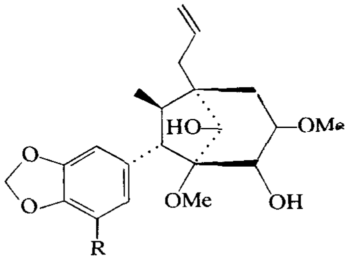
Dillapiol (**2**) [3] and benzyl salicylate (**1a**) [7] were identified by direct comparison with authentic samples. Benzyl 2-methoxybenzoate (**1b**) and benzyl 2,6-dimethoxybenzoate (**1c**) were characterized spectroscopically as components of a mixture. The identification was confirmed by hydrolysis, which, as expected,



3a $R = OMe$
3b $R = H$



4a $R^1 = R^4 = OMe, R^2-R^3 = CH_2$
4b $R^1 = H, R^2-R^3 = CH_2, R^4 = OMe$
4c $R^1 = R^4 = H, R^2 = R^3 = Me$



5a $R = OMe$
5b $R = H$

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[*] Part 57 in the series "The Chemistry of Brazilian Lauraceae". For Part 56 see ref. [1]. Based on part of the doctorate thesis submitted by C.H.S.A. to Universidade de São Paulo (1978).

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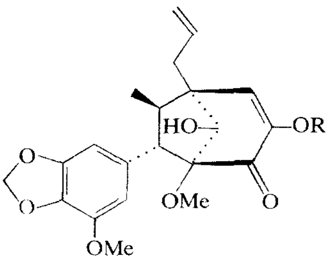
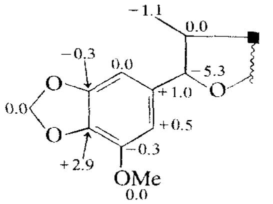


6a R = Me
6b R = H

proceeded at a faster rate for **1b** than for **1c**, and separation of the corresponding acids and alcohol.

Analysis of the NMR spectrum of ferrearin-A (**3a**), $C_{20}H_{22}O_6$, suggested its classification as a neolignan of partial constitution **7**. This was confirmed by the complete series of ^{1}H NMR double irradiation experiments which established the sequence CHCHMe; by MS which shows peaks at *m/e* 192 (33%) (**8**) and 181 (45%); and ^{13}C NMR data which are close (cf. Δδ-values shown in **7**) to the data reported for the naturally occurring neolignan **9** [8]. The sole significant differential value refers to C-7, more highly deshielded in **9** due to electronic delocalization towards the carbonyl.



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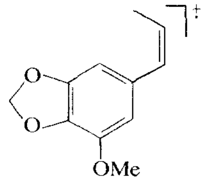

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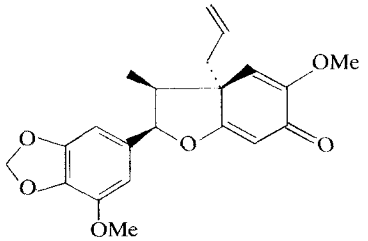

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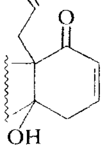
The yet undefined $C_9H_{10}O_2$ moiety contains the sequences $CH_2CH{=}CH_2$ and $CH_2CH{=}CHCO$ (ν_{max} 1680 cm^{-1}) again established by a complete series of ^{1}H NMR double irradiation experiments. Both sequences are linked to unprotonated positions. ^{13}C NMR not only confirms these assignments, but gives additional evidence of two fully substituted carbons; one linked only to C (δ 52.5) and the other linked also to O (δ 99.7), i.e. to the non-acylatable hydroxyl causing a ^{1}H NMR singlet at δ 4.7 which disappears upon addition of D_2O.

Among the alternative partial constitutions **10** and **11** compatible with these data, **11** was selected. Indeed, the C-1′ resonance (δ 52.5) in **3a** occurs only 2 ppm downfield from the resonance of the analogous carbon in porosin (**4c**) [8]. Introductions of an α-oxo group as in **10** would be expected to result in a much stronger effect (cf. data for **12** and **13** [9]). In another independent comparison with a model, virtual coincidence of the chemical shifts of the allylic ring carbons in **11** and carvone (**14**) [10] is incompatible with the existence of a vicinal oxygenated C as in **10**.



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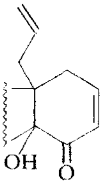

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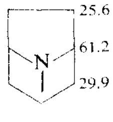

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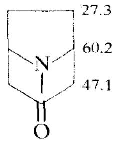

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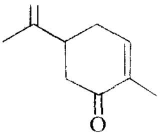
Joining of the partial constitutions **7** and **11** must take into consideration the existence of only two carbons with oxy-substituents (δ 81.8, 99.7) and thus leads to the constitution **3a**. One of the mentioned carbons must thus be part of a hemiketal, as corroborated by ^{13}C NMR evidence (cf. chemical shifts for hemiketal carbons of **3a** vs the model compound **15** [11], δ 99.7 vs 102.2). Hemiketals are easily cleaved by acid, and, indeed, treatment of the compound with TsOH in dry MeOH at room temperature leads to the ketals **16** and **17**, as well as to the Cope rearrangement product **18**.



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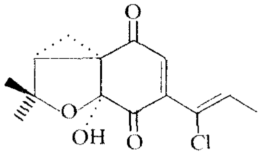

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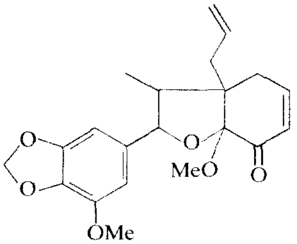

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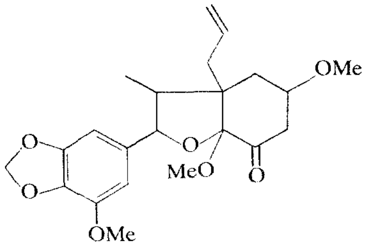

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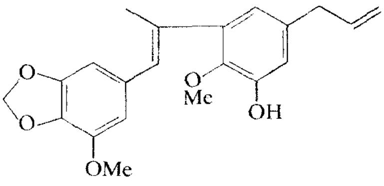

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With respect to stereochemistry, a *cis* Ar/Me relation is indicated by the high field $C\underline{H}_3$-resonance (δ 0.76). This fact, together with the *trans* Me/allyl relation is also evidenced by the near identity of selected chemical shifts (see above) of **7** (incorporated in **3a**) and **9** (chiefly for C-9, δ respectively 10.8 and 11.9). A better model for the comparison of the chemical shift value for C-7′ of **3a** is, of course, **4c** (δ respectively 40.4 and 39.0). The closeness of these values also reflects the absence of a γ-effect on C-7′ which would be contributed by a *cis*-hydroxyl at C-2′. The *trans–cis* Ar/Me/allyl arrangement, which is more common among neolignans of the burchellin type **9** requires the C-9 and C-7′ resonances at δ 8.5 and 36.7 [8].

Comparison of IR, ^{1}H NMR (Table 1) and MS of ferrarin-A (**3a**) and ferrearin-B (**3b**) shows all significant differences to be due solely to the absence of the methoxyl in the latter. Its constitution and stereochemistry may thus be formulated as shown.

The structural proposals for the neolignans of the porosin-type **4a** and **4b**, and of the canellin-type **5a** relied on UV, NMR (Table 1) and MS comparisons with the compounds **4c** [2] and **5b** [3]. All proton sequences in the new compounds were confirmed by ^{1}H NMR double resonance experiments. Compound **6a** had already been obtained previously by Me_2SO_4-methylation of the naturally occurring **6b** [12] and was identified by direct comparison with an authentic sample. This comparison did not include ORD curves, and thus the configurations indicated in the formula **6a** and, for that matter, in all other formulae of the present report, are only relative.

The ferrearins (**3a, b**) lack oxygenation at C-4′. Not considering neolignan types whose genesis seems to involve allyl rearrangement [6], only the recently reported cytotoxic megaphones [13] share this biosynthetically interesting feature.

EXPERIMENTAL

Isolation of constituents. A sample of trunk wood of *Aniba ferrea* Kubitzki (voucher herbarium INPA, Manaus, 21226) from the vicinity of Manaus, Amazonas, was reduced to powder (5 kg) and percolated with C_6H_6. The extract (80 g) was adsorbed on Si gel and the powder washed with C_6H_6. Evaporation of the solvent gave an oily residue (19 g) which was chromatographed on Si gel (360 g). Elution with petrol–C_6H_6(1:1), C_6H_6–$CHCl_3$(1:1), $CHCl_3$ and $CHCl_3$–MeOH (99:1) gave 4 fractions which were separated by Si gel TLC with the indicated developers into **3a**, **3b**, **1b** + **1c**, **2** and **1a** (1st fraction, C_6H_6–$CHCl_3$, 3:1), **4a** (2nd fraction, $CHCl_3$–Et_2O, 4:1), **5a** (3rd fraction, C_6H_6-$CHCl_3$, 3:2), **6a** and **4b** (4th fraction, C_6H_6–EtOAc, 3:2).

$\Delta^{8'}$-2′-Hydroxy-3-methoxy-4,5-methylenedioxy-1′,2′,3′,6′-tetrahydro-3′-oxo-7.O.2′,8.1′-neolignan (*ferrearin-A*, **3a**). Oil, $C_{20}H_{22}O_6$ by NMR C and H counts and MS. ν_{max} Film cm^{-1}: 3425, 1680, 1480, 1450, 1100, 1040. ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 133.9 (*s*, C-1), 100.2 (d, C-1), 100.2 (*d*, C-2), 148.6 (*s*, C-3), 133.9 (*s*, C-4), 143.1 (*s*, C-5), 105.5 (*d*, C-6), 81.8 (*d*, C-7), 44.5 (*d*, C-8), 10.8 (*q*, C-9), 52.5 (*s*, C-1′), 99.7 (*s*, C-2′), 192.6 (*s*, C-3′), 125.7 (*d*, C-4′), 150.9 (*d*, C-5′), 31.0 (*t*, C-6′), 40.4 (*t*, C-7′), 133.9 (*d*, C-8′) 117.6 (*t*, C-9′), 56.4 (*q*, OMe), 101.2 (*t*, O_2CH_2). MS (*m/e*): 358 (8%) M$^+$, 203 (38), 192 (33), 181 (45), 180 (45), 179 (38), 165 (33), 137 (100), 109 (45). *Dihydro*-**3a**. A soln of **3a** (50 mg) in $CHCl_3$ (50 ml) was hydrogenated over 10% Pd/C (50 mg), filtered and evaporated. The residue was purified by TLC (Si gel, C_6H_6–$CHCl_3$, 1:1) to an oil, ν_{max}^{Film} cm^{-1}: 3420, 1680, 1630, 1500. ^{1}H NMR (100 MHz, $CDCl_3$): δ identical to spectrum for **1a** with the exception of signals of $CH_2CH{=}CH_2$ replaced by 8.2–8.7 (*m*, 2 CH_2), 9.1 (*t*, $J = 7$ Hz, Me). MS (*m/e*): 360 (8%) M$^+$, 204 (46), 192 (54), 181 (56), 180 (100), 165 (54), 137 (72), 110 (81).

Acid-catalysed reactions of **3a**. A soln of **3a** and TsOH in dry MeOH was kept at room temp. (24 hr), neutralized and evaporated. The residue was fractionated by TLC into **15**, **16**

Table 1. ^{1}H NMR comparison of ferrearin- (**3a**, **3b**), porosin- (**4a**, **4b**, **4c**) and canellin- (**5a**, **5b**) type neolignans in $CDCl_3$

						4c			**5b**	
	3a	**3b**		**4a**	**4b**	[2, 14]		**5a**	[3]	
MHz	270	100		100	60	220		60	220	
	δ	δ	J(Hz)	δ	δ	δ	J(Hz)	δ	δ	J(Hz)
H-2	6.40	6.72	*br.s*	6.15	6.5–6.8	6.76		6.35	6.95	
H-5	—	6.72	*br.s*	—	6.5–6.8	6.93		—	6.64	
H-6	6.40	6.72	*br.s*	6.15	6.5–6.8	6.83		6.48	6.75	
H-7	5.34	5.38	*d*, 10	5.82	5.75	5.89	*d*, 5.5	1.9–2.8	3.25	*d*, 9
H-8	2.84	2.85	*dd*, 10, 8	2.6	2.6	2.6	*m*	1.9–2.8	2.4–2.5	*m*
3H-9	0.76	0.76	*d*, 8	0.56	0.55	0.52	*d*, 7.5	0.9	0.86	*d*, 7
H-2′	—	—	—	—	—	—		3.52	—	
H-3′	—	—	—	—	—	5.59	*s*	—	—	
H-4′	6.24	6.22	*dd*, 10, 3	—	—	—		4.00	4.03	*d*, 6.5
H-5′	6.95	6.93	*ddd*, 10, 5, 3	3.94	3.80	4.02	*dd*, 12, 5	3.70	3.62	*t*, 6.5
H-6′ax	2.06	2.01	*dd*, 13, 5	1.84	1.7–2.7	1.92	*t*, 12	1.5–1.9	1.54	*dd*, 15, 8, 6.5
H-6′eq	2.49	2.45	*dt*, 13, 3, 3	2.20	1.7–2.7	2.22	*dd*, 12, 5	1.5–1.9	1.86	*d*, 15.8
H-7′	2.1–2.4	2.1–2.4	*m*	2.4–2.7	1.7–2.7	2.56	dd, 14.7, 7	1.9–2.8	2.4–2.5	*m*
H-7′	2.1–2.4	2.1–2.4	*m*	2.4–2.7	1.7–2.7	2.69	*dd*, 14.7, 7	1.9–2.8	2.05	*dd*, 13.5, 9.2
H-8′	5.4–5.8	5.4–5.8	*m*	5.7–6.1	5.5–5.9	5.9–6.1	*m*	3.4–4.2	3.8–4.0	*m*
2H-9′	4.8–5.2	4.8–5.2	*m*	5.2–5.4	4.9–5.3	5.3–5.4	*m*	4.8–5.2	5.0–5.2	*m*
CH-2′	4.7	4.7	*br.s*	—	—	—	—	—	—	—
OMe-3	3.85	—	*s*	3.90	—	3.90	*s*	3.85	—	*s*
OMe-4	—	—	—	—	—	3.90	*s*		—	—
O_2CH_2'	5.93	5.96	*s*	6.00	5.92	—	*s*	5.90	5.88, 5.89	2*d*
OMe-3′	—	—	—	3.80	3.80	—	*s*	3.20	3.22	*s*
OMe-5′	—	—	—	3.62	3.62	3.62	*s*	3.40	3.40	*s*

and **17**. **15**, ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.43, 6.5 (2*d*, $J = 2$Hz, 2 H-2,6). 5.18 (*d*, $J = 9$ Hz, H-7), 2–3 (*m*, H-8, 2 H-6′, 2 H-7′), 0.6 (*d*, $J = 8$ Hz, 3 H-9), 6.03 (*dd*, $J = 10$, 3 Hz, H-4′), 6.7–6.9 (*m*, H-5′), 5.5–5.8 (*m*, H-8′), 4.9–5.2 (*m*, 2 H-9′), 3.7 (*s*, OMe-2′), 3.86 (*s*, OMe-3), 5.96 (*s*, O_2CH_2). MS (*m/e*): 372 (27%) M$^+$, 344 (35), 330 (13), 192 (93), 179 (30), 165 (70). **16**, ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.4–6.5 (*m*, 2 H-2,6), *ca* 5.2 (*d*, H-7), 2–3 (*m*, H-8, 2 H-4′, 2H-6′), 0.68 (*d*, $J = 8$ Hz, 3 H-9), 5.5–5.9 (*m*, H-8′), 5.0–5.2 (*m*, 2 H-9′), 3.34, 3.48 (2*s*, 2 OMe-2′,5′), 3.92 (*s*, OMe-3), 5.98 (*s*, O_2CH_2). MS (*m/e*): 354 (20%) M$^+$, 179 (21), 165 (100), 149 (30), 135 (15). **17**, ^{1}H NMR (100 MHz, $CDCl_3$): δ 6.5–6.75 (*m*, 4 ArH), 6.62 (*s*, H-7), 2.2 (*s*, 3H-9), 3.36 (*d*, $J = 7$ Hz, 2 H-7′), 5.5–5.9 (*m*, H-8′), 5.0–5.3 (*m*, 2 H-9′), 3.9 (*s*, 2 OMe), 5.98 (*s*, O_2CH_2). MS (*m/e*): 404 (13%) M$^+$, 372 (6), 376 (25), 344 (12), 192 (100), 162 (40).

$\Delta^{8'}$-*2′-Hydroxy-3,4-methylenedioxy-1′,2′,3′,6′-tetrahydro-3′-oxo*-7.O.2′,8.1-*neolignan* (*ferrearin-B*, **3b**). Oil, $C_{19}H_{20}O_5$ by NMR C and H counts and MS. $\nu_{\max}^{\text{Film}}$ cm^{-1}: 3440, 1680, 1505, 1490, 1100, 1040. MS (*m/e*): 328 (8) M$^+$, 300 (14), 178 (44), 173 (57), 162 (64), 151 (67), 149 (77), 137 (100), 135 (67), 109 (90), 107 (77).

$\Delta^{8'}$-*3,3′,5′-Trimethoxy-4,5-methylenedioxy-1′,4′,5′,6′-tetrahydro-4′-oxo*-7.O.2′,8.1′-*neolignan* (**4a**). Oil, $C_{22}H_{26}O_7$ by NMR C and H counts and MS. $\nu_{\max}^{\text{Film}}$ cm^{-1}: 1645, 1530, 1455, 1210, 1100. MS (*m/e*): 402 (52%) M$^+$, 371 (40), 361 (100), 333 (100), 331 (62), 303 (54), 301 (34), 271 (22), 241 (30), 209 (22), 192 (58), 181 (28), 179 (28), 165 (50), 149 (20), 135 (33). *Dihydro*-**4a**. Hydrogenation of **4a** in $CHCl_3$ over Pd/C and purification of the product by TLC gave an oil, $\nu_{\max}^{\text{Film}}$ cm^{-1}: 1640, 1515, 1460, 1430. MS (*m/e*): 404 (10%) M$^+$, 333 (30), 328 (27), 303 (18), 195 (28), 192 (100), 184 (25), 165 (53), 153 (32), 135 (25).

$\Delta^{8'}$-*3′,5′-Dimethoxy-3,4-methylenedioxy-1′,4′,5′,6′-tetrahydro-4′-oxo*-7.O.2′,8.1′-*neolignan* (**4b**). Oil, $C_{21}H_{24}O_6$ by NMR C and H counts and MS. $\nu_{\max}^{\text{Film}}$ cm^{-1}: 1650, 1525, 1500, 1450, 1235. MS (*m/e*): 372 (5%) M$^+$, 342 (20), 331 (50), 303 (55), 271 (23), 241 (20), 239 (23), 213 (15), 211 (30), 209 (23), 190 (30), 181 (40), 167 (46), 165 (50), 162 (100), 149 (90), 135 (100), 121 (50). *Dihydro*-**4b**. Hydrogenation of **4b** in $CHCl_3$ over Pd/C and purification of the product by TLC gave oil. MS (*m/e*): 374 (7%) M$^+$, 304 (23), 298 (21), 273 (12), 221 (13), 179 (21), 162 (100), 167 (30), 165 (50), 161 (32), 153 (39), 131 (41).

^{13}C *NMR comparison of* **4b/4c** [8]. (25.2 MHz, $CDCl_3$) δ 129.8/128.3 (*s*, C-1), 106.2/108.6 (*d*, C-2), 147.8/148.8 (*s*, C-3), 147.8/148.5 (*s*, C-4), 108.2/110.9 (*d*, C-5), 118.7/117.8 (*d*, C-6), 87.4/87.2 (*d*, C-7), 42.8/42.5 (*d*, C-8), 11.6/11.6 (*q*, C-9), 48.7/50.2 (*s*, C-1′), 167.0/183.4 (*t*, C-2′), 166.6/100.1 (respectively *s*, *d*; C-3′), 192.3/196.6 (*s*, C-4′), 77.3/76.8 (*s*, C-5′), 32.2/32.0 (*s*, C-6′), 39.8/39.0 (*t*, C-7′), 132.7/132.5 (*d*, C-8′), 119.8/119.8 (*t*, C-9′), —/55.9 (*s*, 2 OMe-3,4), 101.1/— (*t*, O_2CH_2-3,4).

$\Delta^{8'}$-*2′,4′-Dihydroxy-3,3′,5′-trimethoxy-4,5-methylenedioxy-1′,2′,3′,4′,5′,6′-hexahydroneolignan* (**5a**). Oil (Found: M$^+$ 406.1981; $C_{22}H_{30}O_7$ requires: M$^+$ 406.1992). $\nu_{\max}^{\text{Film}}$ cm^{-1}: 3550, 1650, 1530, 1460, 1440, 1140, 1100, 1070. MS (*m/e*): 406 (6%) M$^+$; 192 (13), 167 (13), 165 (23), 149 (10), 135 (16), 121 (46), 119 (100), 117 (100). Oxidation of **5a** in Me_2CO by Jones reagent and purification of the product by column chromatography (Si gel, C_6H_6–EtOAc, 3 : 2) gave an oil, $\nu_{\max}^{\text{Film}}$ cm^{-1}: 1780 (C=O-2′), 1750 (C=O-4′), 1660, 1140, 1100. *Dihydro*-**5a**, obtained by catalytic hydrogenation as above. ^{1}H NMR: no $CH{=}CH_2$ bands. MS (*m/e*): 408 (60%) M$^+$. *Acetate of dihydro*-**5a** (**5a**, Ac_2O, C_5H_5N, 48 hr, room temp.). ^{1}H NMR (60 MHz, $CDCl_3$): δ 5.0 (*d*, $J = 6.5$ Hz, H-4′), 2.12 (*s*, OAc-4′). MS (*m/e*): 450 (14%) M$^+$. *Diacetate of dihydro*-**5a**, (**5a** Ac_2O, C_5H_5N, 18 hr, reflux). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.2 and 2.1 (2*s*, OAc-2′,OAc-4′). MS (*m/e*): 492 (35%) M$^+$.

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