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BICYCLOOCTANOID, CARINATONE AND MEGAPHONE TYPE NEOLIGNANS FROM *OCOTEA POROSA**

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Key Word Index—*Ocotea porosa*; Lauraceae; neolignans; bicyclo[3.2.1]octanoid neolignans; carinatone type neolignans; megaphone type neolignans.

Abstract—Four new neolignans were isolated from the wood of *Ocotea porosa*. Two isomers, belonging to the bicyclo[3.2.1]octanoid 7.3′,8.1′-type, differed most conspicuously by the *endo*- or *exo*-relationship of their aryl/methoxyenone units. One of the other two compounds belonged to the megaphone 8.1′-coupled type and the other to the carinatone type. Biosynthesis of the latter may also have initially involved 8.1′-coupling of propenyl- and allylphenols, followed by rearrangement of the allyl from 1′ to 5′.

INTRODUCTION

Ocotea porosa (Nees et Mart. ex Nees) L. Barroso (family Lauraceae), named 'imbuia' [2], is one of the most important timbers of southern Brazil. Its major micromolecular constituent **1a** (porosin) is accompanied by some additional minor neolignans, **1b**, **1c** (porosin-B), **2**, **3**, **4a**, **5a**, **5b**, and **6** (licarin-B) [3]. This list can now be extended to include **7** (burchellin), previously isolated from *Aniba* [4] and *Magnolia* [5] species, **8**, previously isolated from *Aniba* [6] and *Duguetia* [7] species, **9a** (guianin) previously isolated from *Aniba* species [8] as well as the novel compounds **9b**, **10a**, **11a** and **12a**. The existence of **8** in *Duguetia* needs confirmation since so far no other neolignan has been isolated from Annonaceae. The nomenclature and numbering of the neolignans discussed in this report follow the rules outlined in a review [9].

RESULTS AND DISCUSSION

The molecular formulas of the novel compounds, $C_{20}H_{22}O_5$ (**9b**, **10a**), $C_{20}H_{20}O_5$ (**11a**) and $C_{21}H_{26}O_5$ (**12a**), were determined by a combination of low resolution mass spectrometry and C and H counts from NMR spectra. Consideration of the nature and number of ether functions revealed by the ^{1}H NMR spectrum allowed expansions of these formulas to $C_{18}H_{17}O_2(OMe)(O_2CH_2)$ (**9b**, **10a**), $C_{18}H_{14}O(OMe)(O_2CH_2)$ (**11a**) and $C_{18}H_{17}O_2(OMe)_3$ (**12a**). Analysis of SFORD ^{13}C NMR spectra led to further definitions: $Me(CH_2)_2(CH)_9C_5(CO)(OH)(OMe)(O_2CH_2)$ (**9b**, **10a**), $Me(CH_2)_2(CH)_7C_7(CO)(OH)(OMe)(O_2CH_2)$ (**11a**) and $Me(CH_2)_3(CH)_8C_4(CO)_2(OMe)_3$ (**12a**). The new compounds are thus again most probably oxidative dimers of propenyl- and allylphenols, i.e. neolignans.

Oxidation with Jones' reagent of the isomers **9b** and **10a** led, in both cases, to cyclopentanone derivatives (ν_{max} 1760 cm^{-1}), **13** and **14**, respectively. In the neolignan group of natural products this is evidence for bicyclo [3.2.1] octane skeletons. The relative stereochemistry of **9a** and **9b** versus **10a** was assigned by inspection of the ^{13}C NMR spectra. In the former pair of compounds the same molecular face is occupied by the one-carbon bridge and the C-methyl (C-9: δ 17.55±0.15), while in **10a** these groups occupy opposite faces (C-9: δ 13.0). In all three cases the C-Me and the aryl groups keep a *trans*-relationship (δ 1.04±0.14) [10].

The ^{1}H NMR spectra of guianin (**9a**) and of **9b** are very similar and comparable with the spectrum of **10a** (Table 1). The major spectral difference between **9a** and **9b** refers to H-2′, H-3′ and H-6′ coupling. In the case of **9a** no coupling is observed in this system, while in the case of **9b** H-2′ is coupled to the vicinal H-3′ (J=4.5 Hz) on one side and to the *W*-related H-6′ (J=2 Hz) on the other. These facts can be explained solely in terms of the opposite location of H-2′ in **9a** (guianin) and **9b** (2′-epiguianin).

The occurrence of W-coupling involving H-2′, observed in the ^{1}H NMR spectrum of **9b** and confirmed by double resonance experiments, requires the presence of a proton at the β-position of the enone (δ 5.88). Hence, the singlet at δ 6.1 in the spectrum of **9a** may also refer to H-6′. Indeed oxidation of both compounds leads to **13** (δ 6.24 for H-6′) and all three compounds are thus characterized as α-methoxyenones.

Another useful piece of evidence, based on the NMR frequency of the vinylic proton, concerns its *endo*- or *exo*-relation with respect to the aryl group. For each given constitutional type the former situation leads to H-6′ signals at lower field. Thus H-6′ signals at δ6.10 (**9a**) and 5.88 (**9b**) versus 5.64 (**10a**) indicate *endo*- versus *exo*-situations; and H-6′ signals at 6.24 (**13**) versus 5.67 (**14**) again indicate respectively, *endo*- versus *exo*- situations.

*Part LXXXVI in the series 'The Chemistry of Brazilian Lauraceae'. For Part LXXXV see ref. [1]. Based on the Doctorate thesis presented by M.G. de C. to Universidade de São Paulo (1986).

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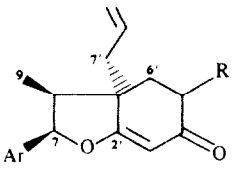
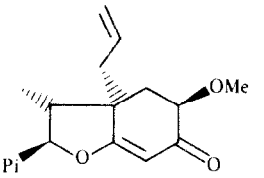
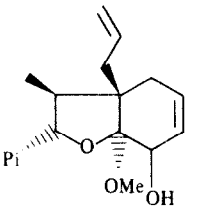


1a Ar = Ve; R = β-OMe
1b Ar = Pi; R = α-OMe
1c Ar = Pi; R = β-OMe





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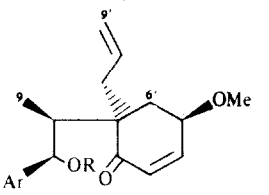

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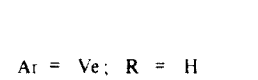
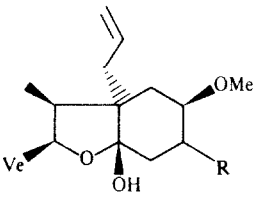
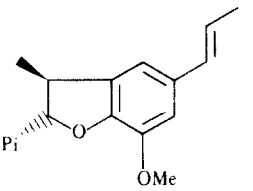


4a Ar = Ve; R = H
4b Ar = Ve; R = Ac
4c Ar = Tp; R = H
4d Ar = Tp; R = Ac



5a R = α-OH
5b R = β-OH
5c R = α-OAc



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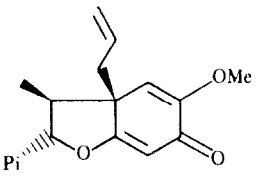

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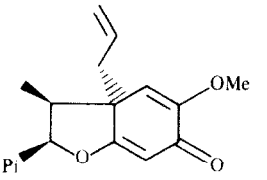


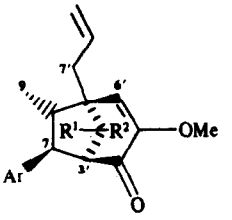
8

Other examples of compounds with *endo*- or *exo*- configurations can be found in the literature [8, 10].

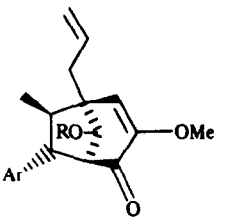
Compound **11a** was recognized to be a piperonyl analogue of the veratryl compound carinatone (**11b**) [11]. As in **11b** the allyl substituted ring of **11a** carries two *meta*-related aromatic protons (δ6.59, 6.67, two *d*, $J = 2$ Hz) and a methoxyl, the ^{13}C NMR signal of which (δ55.9) reveals vicinality to no more than one unsubstituted carbon. However in contradiction to the model, the hydroxyl and allyl groups of **11a** must be vicinal. The *ortho*-hydroxyl causes a γ-effect on the benzylic carbon of the allyl (δ 33.7 for **11a** vs 40.0 in **11b**) and acetylation of this hydroxyl causes a 0.13 ppm diamagnetic shift of the signal due to the benzylic protons. Finally neither hydroxyl nor allyl can be *ortho*-related to the C-C bridge that unites the two phenylpropanoid moieties. It is such an *ortho*-hydroxyl that produces a γ-effect on C-8 of carinatone (δ 47.3 for **11a** vs 39.8 for **11b**). The unusual oxygenation pattern of **11a** suggests the occurrence of a rearrangement (**15**→**16**→**11a**) in its biosynthesis.

The ORD curve for (*S*)-(−)-carinatone (**11b**) shows a negative Cotton effect at 276 nm and a positive Cotton effect at 307 nm. Compound **11a**, with a nearly identical ORD curve, must equally show the (8*S*)-configuration.

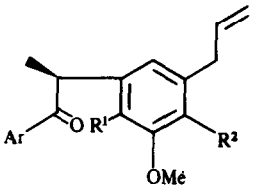
Compound **12a** differs from oxidized megaphone **12b** [12] only with respect to the nature of the aryl group, a veratryl in **12a** and a tri-*O*-methylpyrogallyl in **12b**. The ^{13}C NMR spectrum of the model **12b** has not been recorded. Thus the carbon sequences C-1 to C-9 in carinatone (**11b**) and C-1′ to C-9′ in megaphone (**4c**) were selected as models, performing their role with success (Table 2). The prominent mass spectral features of **12a**, *m/z* 358 $[M]^+$, 194 $[C_6H_3(OMe)_2COEt]^+$, 165 $[C_6H_3(OMe)_2CO]^+$ and of **12b**, *m/z* 388 $[M]^+$, 224



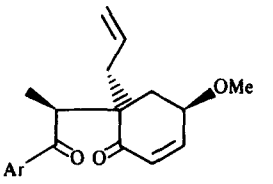
9a Ar = Pi; R^1 = OH; R^2 = H
9b Ar = Pi; R^1 = H; R^2 = OH
9c Ar = Pi; R^1 = H; R^2 = Ac



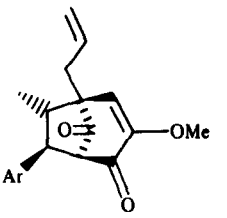
10a Ar = Pi; R = H
10b Ar = Pi; R = Ac



11a Ar = Pi; R^1 = H; R^2 = OH
11b Ar = Ve; R^1 = OH; R^2 = H
11c Ar = Pi; R^1 = H; R^2 = OAc



12a Ar = Ve
12b Ar = Tp



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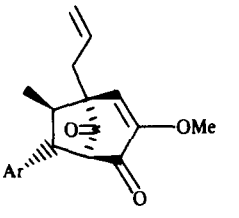

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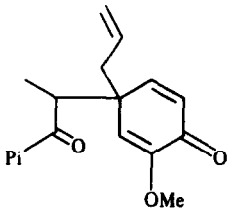

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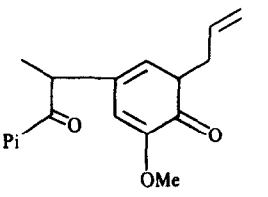

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$[C_6H_2(OMe)_3COEt]^+$, $195[C_6H_2(OMe)_3CO]^+$, are again comparable. Finally, the absolute configuration of megaphone (**4c**) has been established by X-ray crystallography. Thus the absolute configurations not only of megaphone's oxidation product **12b** ($[\alpha_D] = -32.8°$), but also of **12a** ($[\alpha]_D = -29.6°$) are as shown.

Compounds **5a** and **5b** have been isolated previously from *Ocotea porosa*. Acetylation by acetic anhydride–pyridine at room temperature led to the acetate **5c** and to the megaphone type neolignan **4a**, respectively [3]. These reactions were now repeated at reflux temperature. Compound **5a** again gave **5c**, but **5b** gave the acetate **4b**. Megaphone (**4c**) was reported to yield **4d** in an analogous reaction [12].

EXPERIMENTAL

Isolation of the constituents. Trunk wood of *Ocotea porosa*, collected at the Forest Reserve of Instituto Botânico (São Paulo, SP) was dried and pulverized. The powder (0.7 kg) was extracted successively with petrol and CH_2Cl_2. The solvents were evapd giving resp. residues *A* (6.6 g) and *B* (13 g). A was partitioned with C_6H_{14}–MeOH 90%. Both solns were evapd giving resp. residues *C* (3.5 g) and *D* (2.2 g). *C* was composed of aliphatic material present also in most other fractions described below. *D* and *B* were united. The mixture was submitted to dry CC (300 g silicagel deactivated with 10% H_2O, development with $CHCl_3$). The extruded column was divided into 23 equal portions, subsequently extracted with $CHCl_3$. Evapn of the solvent gave

Table 1. NMR data of bicyclo[3.2.1]octanoid neolignans ($CDCl_3$, δ values, multiplicities, J in Hz in parentheses)

H	**9a** [8] 220 MHz	**9b** 300 MHz	**10a** 300 MHz	**13** 80 MHz	**14** 80 MHz
2	6.51 *s*	6.51 *d* (1.5)	7.07 *d* (2)	6.46 *d* (2)	6.55 *d* (2)
6	6.53 *d* (8)	6.52 *dd* (8.5,1.5)	6.75 *dd* (8,2)	6.55 *dd* (8,2)	6.6 *dd* (8,2)
5	6.66 *d* (8)	6.66 *d* (8.5)	6.68 *d* (8)	6.68 *d* (8)	6.70 *d* (8)
O_2CH_2	5.82 *s*	5.87 *s*	5.91 *s*	5.90 *s*	5.93 *s*
8′	5.75–5.92	5.99 *m*	5.86 *ddt*	5.7–6.17 *m*	5.75–6.1 *m*
6′	6.10 *s*	5.88 *d* (2)	5.64 *s*	6.24 *s*	5.57 s
9′	5.13–5.32	5.27 *dm* (17.5)	5.21 *dq* (17.5,2)	5.33 *m*	5.25 *m*
9′		5.24 *dm* (10.5)	5.12 *ddt* (10,2,1)	5.17 *m*	5.09 *m*
2′	3.98 *s*	4.16 *dd* (4.5,2)	4.01 *br s*	—	—
OMe	3.62 *s*	3.64 *s*	3.65 *s*	3.66 *s*	3.71 *s*
3′	3.19 *d* (7)	3.24 *dd* (7,4.5)	2.97 *br s*	3.87 *d* (7)	3.52
OH			2.55 *br s*		
7′	2.64 *dd* (14,7)	2.50 *dd* (14.5,8.5)	2.53 *ddt* (14,7.5,1.5)	2.44 *d* (12)	2.52 *d* (9)
7′		2.42 *dd* (14.5,8.5)	2.39 *dd* (14,7.5)		
7	3.35 *d* (7)	3.03 *dd* (7,6)	2.46 *br dd* (8,1.5)	3.1 *dd* (7,5.5)	2.55 *d* (7)
8	2.22 *dq* (7)	2.37 *qd* (7,6)	2.37 *dq* (8,7)	2–2.8 *m*	2.1 *m*
9	1.23 *d* (7)	1.18 *d* (7)	0.95 *d* (7)	1.12 *d* (6)	1.04 *d* (6)

Double resonance experiments. **9b**: H-9→H-8 *d* (6); H-2′→H-3′ *d* (7) and H-6′ (*s*); H-3′→H-2′ *d* (2) and H-7 *d* (6); H-7→H-8 *q* (7) and H-3 *d* (4.5); H-8′→H-9′ *d* (2), H-9′ *d* (2), H-7′ *d* (14.5) and H-7′ *d* (14.5); H-7′, H-7′→H-8′ *dd* (17.5, 10.5), H-9′ *dd* (17.5, 2) and H-9′ *dd* (10.5, 2). **10a**: H-9→H-8 *d* (8); H-2′→H-3′ *d* (1.5) and sharpens the H-7 *dd*; H-3′→H-7 *d* (8) and sharpens the H-2′ *s*; H-8′→H-7′ *dt* (14, 1.5), H-7′ *br d* (14) and affects 2 H-9′.

Table 2. NMR data of megaphone type neolignans and of model compounds ($CDCl_3$, δ values, multiplicities, J in Hz in parentheses)

	^{1}H NMR		^{13}C NMR		
	60 MHz	100 MHz	20 MHz		
Position	**12a**	**12b** [12]	**12a**	**11b** [11]	**4c** [12]
1	—	—	129.6 *s*	127.6	
2	7.50 *d* (2)	7.18 *s*	110.5 *d*	109.5	
3	—	—	148.6 *s*	148.8	
4	—	—	152.7 *s*	153.0	
5	6.90 *d* (8)	—	109.8 *d*	110.2	
6	7.60 *dd* (8,2)	7.18 *s*	122.4 *d*	123.3	
7	—	—	202.2 *s*	199.6	
8	4.2–4.5	4.04 *q* (7.5)	41.9 *d*	39.8	
9	1.21 *d* (8)	1.18 *d* (7.6)	11.9 *q*	17.9	
1′			49.9 *s*		52.3
2′	—	—	201.2 *s*		193.4
3′	5.95 *d* (10)	5.96 *d* (10.2)	132.7 *d*	132.0	132.0
4′	6.95 *d* (10)	6.93 *dd* (10,2,2.2)	147.6 *d*		149.9
5′	4.05 *d* (10)	4.3 *m*	73.0 *d*		71.0
6′	2.93 *dd* (10,12) 2.1–2.6	2.1–2.5	38.8 *t*		37.7
7′	2.1–2.6	2.1–2.5	34.6 *t*		36.2
8′	5.5–5.9	4.04 *q* (7.5)	128.3 *d*		128.7
9′	5–5.4	5.09, 5.22	118.1 *t*		119.1
OMe	3.42 *s*	3.46 *s*	55.8 *q*	55.9	55.8
	3.84 s	3.90 *s*	55.7 *q*	55.9	
	3.88 *s*	3.90 *s*	55.7 *q*		
		3.90 *s*			

residues which were submitted to prep. TLC (silica gel) and, when applicable, to crystallization. Thus fr. 1 (965 mg) gave **9a** (40 mg); fr. 2 (510 mg) gave **9b** (14 mg) and **6** (108 mg); frs 3–8 (940 mg) gave **1b** (91 mg), **1c** (100 mg), **1a** (102 mg), **7** (103 mg), **10a** (234 mg) and **11a** (161 mg); fr. 9 (902 mg) gave **8** (53 mg) and **1c** (23 mg); fr. 10 (301 mg) gave **1a** (186 mg), **1b** + **1c** (93 mg) and

10a (25 mg); frs 11–14 (1.6 g) gave **1a** (390 mg) and impure **1a**; frs 15+16 (916 mg) gave **12a** (92 mg) and **1a**+**1b**; fr. 17 (551 mg) gave **1a**+**1b**+**12a**; frs 18–22 (2.5 g) gave **5a** (476 mg), impure **5a** and **5b** (93 mg); fr. 23 (3.5 g) gave **5a**+**5b** and a mixture. Acetylation of this mixture and subsequent chromatography of the product gave **5c** (140 mg) and **4b** (152 mg).

Three of the new compounds (**9b**, **10a**, **12a**) were obtained as viscous oils. Their recognition, in repeated separations, relied on comparison of chromatographic behaviour (see above) of the compounds and several known compagnion substances (**1a**, **1b**, **1c**, **5a**, **5b**, **6**, **7**, **8**, **9a**).

(7S, 8S,1'S, 2'S, 3'S)-$\Delta^{5',8'}$-2'-*Hydroxy*-5'-*methoxy*-3,4-*methylenedioxy*-4'-*oxo*-7.3',8.1'-*neolignan* (**9b**). Viscous oil. UV λ_{max}^{MeOH} nm: 234, 274 (ε 8900, 8600). IR ν_{max}^{film} cm^{-1}: 3420 (O—H), 1690 (C=O), 1620, 1490, 1440 (Ar). ^{1}H NMR: Table 1. ^{13}C NMR (20 MHz, $CDCl_3$) δ: 194.3 (*s*, C-4'), 151.7 (*s*, C-5'), 147.4 (*s*, C-3), 146.1 (*s*, C-4), 134.2 (*d*, C-8'), 132.9 (*s*, C-1), 121.0 (*d*, C-6), 119.2 (*d*, C-6'), 118.6 (*t*, C-9'), 108.2 (*d*, C-2), 107.8 (*d*, C-5), 100.6 (*t*, O_2CH_2), 80.7 (*d*, C-2'), 62.6 (*d*, C-3'), 54.7 (*q*, OMe), 50.1 (*d*, C-7), 48.9 (*s*, C-1'), 45.4 (*d*, C-8), 36.7 (*t*, C-7'), 17.7 (*q*, C-9). MS *m/z* (rel. int.): 342 $[M]^+$ (80), 271 (17), 180 (27), 162 (100), 149 (35), 135 (32), 121 (20). CD (*c* 3.4 mg/100 ml MeOH): $[\theta]_{315}^{max}$ −45 800. *Acetate* (**9b** 30 mg, Ac_2O 1 ml, pyridine 1 ml, 24 hr, room temp, purification by silica gel TLC, gave **9c** 30 mg), viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.67 (*d*, *J* = 8.5 Hz, H-5), 6.52 (*dd*, *J* = 8.5, 1.5 Hz, H-6), 6.51 (*d*, *J* = 1.5 Hz, H-2), 6.02 (*m*, H-8'), 5.92 (*d*, *J* = 2 Hz, H-6'), 5.88 (*s*, O_2CH_2), 5.24 and 5.22 (2 H-9'), 5.17 (*dd*, *J* = 4.5, 2 Hz, H-2'), 3.66 (*s*, OMe), 3.39 (*dd*, *J* = 7, 4.5 Hz, H-3'), 3.15 (*dd*, *J* = 7, 6 Hz, H-7), 2.45 and 2.34 (2H-7'), 2.42 (*qd*, *J* = 7, 6 Hz, H-8), 2.00 (*s*, AcO), 1.23 (*d*, *J* = 7 Hz, H-9). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.6 (*s*, C-4'), 170.6 (*s*, AcO), 151.8 (*s*, C-5'), 147.8 (*s*, C-3), 146.6 (*s*, C-4), 133.6 (*d*, C-8'), 132.3 (*s*, C-1), 121.2 (*d*, C-6), 119.4 (*d*, C-6'), 118.9 (*t*, C-9'), 108.4 (*d*, C-2), 108.2 (*d*, C-5), 101.0 (*t*, O_2CH_2), 80.8 (*d*, C-2'), 59.4 (*d*, C-3'), 55.0 (*q*, OMe), 50.3 (*d*, C-7), 47.8 (*s*, C-1'), 45.1 (*d*, C-8), 36.9 (*t*, C-7'), 21.0 (q, AcO), 18.0 (*q*, C-9).

(7R, 8R, 1'S, 2'R, 3'S)-$\Delta^{5',8'}$-2'-*Hydroxy*-6'-*methoxy*-3,4-*methylenedioxy*-4'-*oxo*-7.3',8.1'-*neolignan* (**10a**). Viscous oil. UV λ_{max}^{MeOH} nm: 238, 262, (ε 9200, 8700). IR ν_{max}^{film} cm^{-1}: 3420 (O—H), 1690 (C=O), 1620, 1490, 1440 (Ar). ^{1}H NMR: Table 1. ^{13}C NMR (20 MHz, $CDCl_3$) δ: 195.7 (*s*, C-4'), 151.1 (*s*, C-6'), 147.4 (*s*, C-3), 145.7 (*s*, C-4), 136.0 (*s*, C-1), 134.5 (*d*, C-8'), 121.6 (*d*, C-6), 120.9 (*d*, C-5'), 117.3 (*t*, C-9'), 108.9 (*d*, C-5), 107.4 (*d*, C-2), 100.4 (*t*, O_2CH_2), 78.8 (*d*, C-2'), 63.4 (*d*, C-3'), 55.0 (*s*, C-1'), 54.9 (*q*, OMe), 53.9 (d, C-7), 48.0 (*d*, C-8), 37.0 (*t*, C-7'), 13.0 (*q*, C-9). MS *m/z* (rel. int.): 342 $[M]^+$ (100), 271 (35), 179 (85), 162 (55), 149 (38), 135 (35), 121 (22). CD (*c* 3.4 mg/100 ml MeOH): $[\theta]_{312}^{max}$ −56 700. *Acetate* (**10a** 53 mg, Ac_2O 1.5 ml, pyridine 1.5 ml, 24 hr, room temp, purification by silica gel TLC, gave **10b** 40 mg), viscous oil. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1710 (C=O), 1600, 1490, 1450 (Ar). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.82 (*d*, *J* = 2 Hz, H-2), 6.71 (*d*, *J* = 8 Hz, H-5), 6.67 (*dd*, *J* = 8, 2 Hz, H-6), 5.93 (*s*, O_2CH_2), 5.80 (*m*, H-8'), 5.65 (*s*, H-6'), 5.14 and 5.13 (*m*, 2H-4'), 5.10 (*br s*, H-2'), 3.66 (*s*, OMe), 2.99 (*br s*, H-3'), 2.54 (*dd*, *J* = 8, 1.5 Hz, H-7), 2.40 (*m*, 2H-7', H-8), 2.16 (*s*, AcO), 0.99 (*d*, *J* = 7 Hz, 3H-9). MS *m/z* (rel. int.): 384 $[M]^+$ (80), 324 (73), 297 (23), 271 (20), 179 (70), 175 (20), 162 (100), 149 (98), 135 (60), 121 (30).

(8*S*)-$\Delta^{8'}$-4'-*Hydroxy*-3'-*methoxy*-3,4-*methylenedioxy*-7-*oxo*-8.1',7':1'→5'-neolignan (**11a**). Colourless crystals, mp 103–105° (petrol–Me_2CO). UV λ_{max}^{MeOH} nm: 230, 278, 312 (ε 5400, 1900, 1800). IR ν_{max}^{KBr} cm^{-1}: 3400 (O—H), 1670 (C=O), 1610, 1490, 1440 (Ar). ^{1}H NMR (100 MHz, $CDCl_3$) δ: 7.55 (*dd*, *J* = 8, 2 Hz, H-6), 7.42 (*d*, *J* = 2 Hz, H-2), 6.76 (*d*, *J* = 8 Hz, H-5), 6.67 (*d*, *J* = 2 Hz, H-6') 6.59 (*d*, *J* = 2 Hz, H-2'), 5.98 (*s*, O_2CH_2), 6.2–5.7 (*m*, H-8'), 5.56 (*s*, OH), 5.1–4.9 (*m*, 2H-9'), 4.47 (*q*, *J* = 7 Hz, H-8), 3.84 (*s*, OMe), 3.37 (*d*, *J* = 6 Hz, 2H-7'), 1.48 (*d*, *J* = 7 Hz, 3H-9). ^{13}C NMR (20 MHz, $CDCl_3$) δ: 198.6 (*s*, C-7), 151.3 (*s*, C-4'), 148.1 (*s*, C-3), 146.5 (*s*, C-4'), 142.2 (*s*, C-3'), 136.4 (*d*, C-8'), 132.7 (*s*, C-1'), 131.1' (*s*, C-1), 125.9 (*s*, C-5'), 124.8 (*d*, C-6), 121.7 (*d*, C-5), 115.4 (*t*, C-9'), 108.6 (*d*, C-6'), 107.5 (*d*, C-2, C-2'), 101.6 (*t*, O_2CH_2), 55.9 (*q*, OMe), 47.3 (*d*, C-8), 33.7 (*t*, C-7'), 19.6 (*q*, C-9). MS *m/z* (rel. int.): 340 $[M]^+$ (12), 191 (100), 149 (65), 121 (10). CD (*c* 3.4 mg/100 ml MeOH): $[\theta]_{307}^{max}$ +16 300, $[\theta]_{270}^{max}$ −10 500. *Acetate* (**11a** 22 mg, Ac_2O 1 ml, pyridine 1 ml, 24 hr, room temp, purification by silica gel TLC, gave **11c** 22 mg), IR ν_{max}^{film} cm^{-1}: 1760 (C=O), 1670 (C=O), 1600, 1490, 1440 (Ar). ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.54 (*dd*, *J* = 8, 2 Hz, H-6), 7.40 (*d*, *J* = 2 Hz, H-2), 6.76 (*d*, *J* = 8 Hz, H-5), 6.72 (*br s*, H-2', H-6'), 5.98 (*s*, O_2CH_2), 6.0–5.6 (*m*, H-8'), 5.1–4.9 (*m*, 2H-9'), 4.54 (*q*, *J* = 7 Hz, H-8), 3.78 (*s*, OMe), 3.24 (*d*, *J* = 6 Hz, 2H-7'), 2.28 (*s*, AcO), 1.50 (*d*, *J* = 7 Hz, 3H-9). MS *m/z* (rel. int.): 382 $[M]^+$ (5), 340 (14), 191 (65), 149 (100), 121 (11).

(8S, 1'R, 5'R)-$\Delta^{3,8'}$-3,4,5'-*Trimethoxy*-7,2'-*dioxo*-8.1'-*neolignan* (**12a**). Viscous oil. $[\alpha]_D$ = −29.6° (*c* 1.0, $CHCl_3$). UV λ_{max}^{MeOH} nm: 236, 274, 302 (ε 23 000, 21 900, 12 800). IR ν_{max}^{film} cm^{-1}: 1670 (C=O), 1600, 1500, 1450 (Ar). ^{1}H and ^{13}C NMR: Table 2. MS *m/z* (rel. int.): 358 $[M]^+$ (5), 194 (60), 165 (100). CD (*c* 3.6 mg/100 ml, MeOH): $[\theta]_{333}^{max}$ −1720, $[\theta]_{295}^{max}$ +680, $[\theta]_{244}^{max}$ +1400.

(7S, 8S, 1'S, 3'S)-$\Delta^{5',8'}$-5'-*Methoxy*-3,4-*methylenedioxy*-2',4'-*dioxo*-7.3',8.1'-*neolignan* (**13**). 12 mg in Me_2CO, Jones' reagent, extraction with $CHCl_3$, purification by silica gel TLC, gave **13** 5 mg, viscous oil. IR ν_{max}^{film} cm^{-1}: 1760 (C=O), 1690 (C=O), 1600, 1500, 1450 (Ar). ^{1}H NMR: Table 1. MS *m/z* (rel. int.): 340 $[M]^+$ (82), 299 (13), 271 (31), 175 (35), 162 (100), 149 (65), 135 (45).

(7R, 8R, 1'S, 3'S)-$\Delta^{5',8'}$-6'-*Methoxy*-3,4-*methylenedioxy*-2',4-*dioxo*-7.3',8.1'-*neolignan* (**14**). 14 mg in Me_2CO, Jones' reagent, extraction with $CHCl_3$, purification by silica gel TLC, gave **14** 7 mg, viscous oil. IR ν_{max}^{film} cm^{-1}: 1760 (C=O), 1680 (C=O), 1600, 1490, 1440 (Ar). ^{1}H NMR: Table 1. MS *m/z* (rel. int.): 340 $[M]^+$ (79), 325 (12), 299 (28), 271 (25), 175 (40), 162 (100), 149 (93), 135 (50).

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