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NEOLIGNANS FROM FRUITS OF *OCOTEA VERAGUENSIS*

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Key Word Index—*Ocotea veraguensis*; Lauraceae; fruits; isolation; neolignans; bicyclooctanoids; benzofuranoid.

Abstract—A total of 12 neolignans, 11 bicyclooctanoids and one benzofuranoid were isolated from fruit parts of *Ocotea veraguensis*. Seven of the bicyclooctanoids were new; most had 2′-*O*-acetyl functional groups. The major seed and seed coat neolignans had 3,4-methylenedioxyphenyl substituents at C-7, while the fruit pulp contained mainly di- and trimethoxyphenyl groups at this position.

INTRODUCTION

Ocotea veraguensis (Lauraceae) is a common evergreen shrub to small tree in the dry forest of Santa Rosa National Park, northwestern lowland Guancaste Province, Costa Rica (0–350 m elevation). It is involved in a number of interesting plant–animal interactions in this habitat, where it is the only native lauraceous plant. The fruits are swallowed entire by large frugivorous birds such as trogons (e.g. *Trogon elegans*), and then the large seeds (1–2 g) are regurgitated after the gizzard has stripped off the fruit pulp. Such seeds, or those that have fallen from the tree, are not harvested by the spiny pocket mouse (*Liomys salvini*, Heteromyidae); this small rodent is an extremely common seed predator that harvests many other species of seeds from the forest litter in the forest where *O. veraguensis* is common. *L. salvini* rejects the seeds of *O. veraguensis* as food in the laboratory, usually preferring to starve to death rather than eat them (if the seeds are consumed, the rodent loses weight as fast as if it were eating no food) [D. H. Janzen, unpublished], and it is clear that the seeds contain one or more chemicals that are toxic or repellent to the mouse. On the other hand, larger seed predators such as agoutis (*Dasyprocta punctata*), pacas (*Agouti paca*) and peccaries (*Dicotyles tayassu*) readily prey on *O. veraguensis* seeds in Santa Rosa [W. Hallwachs, personal communication]; they grind them up entire, with or without the seed coat and fruit pulp attached.

On the other hand, in Santa Rosa the larvae of the weevil *Heilipus draco* Fabr. (Curculionidae) develop only in the seeds of *O. veraguensis*; the larvae feed on the seed contents, one to a seed. This is the only species of insect that feeds on *O. veraguensis* seeds in Santa Rosa. It is clear that this weevil larva is not deterred by the chemicals that deter *L. salvini*. In addition, it is quite likely that the weevil's restriction to *O. veraguensis* as a host plant in Santa Rosa is based in major part on its ability to overcome the chemical defences of the seed, defences that protect it from the mouse (a small vertebrate) but not from larger vertebrates. It is widely believed that lauraceous seeds are free of seed predation [1]. While this is obviously not the case with *O. veraguensis*, the above comments strongly suggest the presence of some relatively toxic compounds in *O. veraguensis* seeds.

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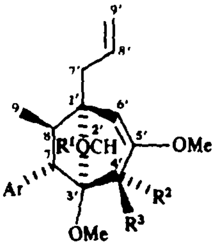
RESULTS AND DISCUSSION

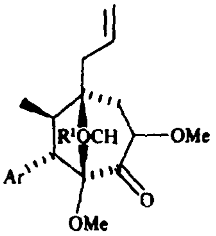
All of the neolignans found (a total of 12) were of the bicyclo[3.2.1]octanoid type except for a single benzofuranoid. The benzofuranoid, **8**, was previously known [2] as were the bicyclooctanoids **1a**, **1c** and **5a**. The remainder are new compounds with most representing structural variations of the neolignans reported [3] from the stem bark. Particularly interesting was the preponderance of 2′-*O*-acetyl derivatives and the relative distribution of structures among the fruit parts. The major neolignans of the seed and seed coat were **1a** and **1b**, while those of the fruit pulp were **2a** and **3a**. The levels of **1a** and **1b** in the seed coat were four times those in the seed, and twice the levels of **2a** and **3a** in the fruit pulp. Hence, methylenedioxy derivatives were concentrated in the seed materials, while methoxylated compounds were the major fruit pulp components.

Neolignan **1c** was previously prepared from **1a** and ^{1}H NMR data reported [4]. It had apparently been isolated earlier [5] from an *Aniba* species, along with **5a**, although in this report the stereochemistry of **1c** and **5a** was incorrectly drawn.

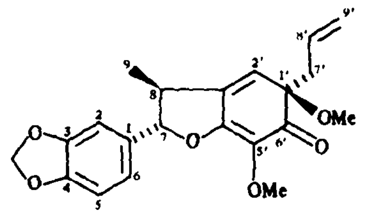
Structures were assigned by high resolution fast atom bombardardment mass spectrometry and ^{1}H NMR spectroscopy in comparison with literature data for **1a**, since a standard could not be obtained, and by an exchange of spectra with the Waterman group [3]. Table 1 gives the comparative NMR data for **1a** and four typical bicyclooctanoids, all containing 7*S*-piperonyl (3,4-methylenedioxyphenyl) substituents. The other bicyclooctanoids differ from those of Table 1 only in the pattern of substitution on the C-7 aromatic ring, which was easily assignable from the NMR spectra; these data are in the Experimental.



1a Ar = 3,4 - methylenedioxyphenyl: R^1 = Ac, R^2 = R^3 = =O
1b Ar = 3,4 - methylenedioxyphenyl; R^1 = Ac, R^2 = H, R^3 = OH
1c Ar = 3,4 - methylenedioxyphenyl; R^1 = H, R^2 = R^3 = =O
2a Ar = 3,4 - dimethoxyphenyl; R^1 = Ac, R^2 = R^3 = =O
2b Ar = 3,4 - dimethoxyphenyl; R^1 = Ac, R^2 = H, R^3 = OH
3a Ar = 3,4,5 - trimethoxyphenyl; R^1 = Ac, R^2 = R^3 = =O
4a Ar = 4,5 - methylenedioxy - 3 - methoxyphenyl; R^1 = Ac, R^2 = R^3 = =O



5a Ar = 3,4 - methylenedioxyphenyl, R^1 = Ac
5c Ar = 3,4 - methylenedioxyphenyl; R^1 = H
6a Ar = 3,4 - dimethoxyphenyl; R^1 = Ac
7c Ar = 3 - hydroxy - 4 - methoxyphenyl; R^1 = H



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Compounds in the **1–4** series have the 1'*S*,3'*R* configuration, while those in the **5–7** series have the 1'*R*,3'*S* configuration. This was determined by comparison of the NMR spectra with those of the literature [4, 6]. The **1a–6a** series have 2'-*O*-acetyl and 4'-carbonyl groups, **1b** and **2b** have 2'-*O*-acetyl and 4'-*β*-OH groups, while **1c** and **5c–7c** have 2'-OH and 4'-carbonyl functions. The presence of the 2'-OAc groups was established by the singlet three proton resonance in the 2.2–2.3 ppm region and shift of the normal H2' singlet at 3.99 ppm to 5.2–5.4 ppm. When a carbonyl group is present at C4', the signal for H6' is a singlet near 5.7 ppm for the **1–4** series and at 6.1 ppm for the **5–7** series. Replacement of the carbonyl with a C4' *β*-OH shifts the signal of H6' to 4.44 ppm (e.g. in **1b**) and the new H4' appears at 4.86 ppm. Had the OH, H configuration been the opposite at C4', the H4' resonance would have been near 4.3 ppm instead [3]. The desacetyl analogue of **1b** as well as the alcohol of opposite configuration were both found in the stem bark [3] and these assignments were confirmed by NOE experiments [3]. The NOE data also confirmed the C7–C8 *trans* stereochemistry.

Keys to distinguishing the **1–4** from the **5–7** series are the chemical shifts of the H7 resonance, the H6' resonance and that for the methyl at C8. In the **1–4** series, H7 is at *ca* 2.6 ppm, H6' is at 5.7 and the methyl at 0.8–0.9 ppm, while in the **5–7** series these resonances appear at 3.3, 6.2 and 1.25–1.28 ppm, respectively.

Animal feeding experiments on fruit parts and their extracts will be conducted in order to determine whether the neolignans are important in the toxicity of the seed.

EXPERIMENTAL

The ^1H NMR spectra were taken in $CDCl_3$ at 270 MHz and are reported in ppm from TMS; *J* values are in Hz. The IR spectra were recorded after evaporating a $CHCl_3$ soln on NaCl plates. Low resolution EIMS were obtained at 70 eV, direct probe insert, at 120–140°.

Extraction and isolation. Fruit of *O. veraguensis* (Meissn.) Mez was collected on June 21, 1985 in Santa Rosa National Park, Guanacaste, Costa Rica, at an elevation of 300 m and identified by D. Whitehead. A voucher specimen is maintained by D.H.J. Seeds (500 g), seed coat (100 g) and dried fruit pulp (200 g) were

Table 1. ^{1}H NMR data for selected neolignans

Proton	Compound 1a	1b	1c	5a	5c
H2	6.96 (1H, *d*, *J* = 0.7)	6.95 (1H, *d*, *J* = 1.3)	6.97* (*s*)	6.54 (*d*, *J* = 0.7)	6.55 (*d*, *J* = 1.6)
H-5	6.65 (1H, *d*, *J* = 8)	6.69 (1H, *d*, *J* = 7.3)	6.704* (*s*)	6.68 (*d*, *J* = 8)	6.67 (*d*, *J* = 8.3)
H-6	6.70 (1H, *dd*, *J* = 8, 0.7)	6.74 (1H, *dd*, *J* = 7.3, 1.3)	6.701* (*s*)	6.52 (*dd*, *J* = 8, 0.7)	6.52 (*dd*, *J* = 8.3, 1.6)
O–CH_2–O	5.93 (2H, *d*, *J* = 4.6)	5.91 (2H, *dd*, *J* = 5.8, 1.4)	5.94 (2H, *d*, *J* = 1.8)	5.89 (2H, *d*, *J* = 0.5)	5.89 (2H, *s*)
2′-OAc	2.28	2.26		2.24	
H7	2.59 (1H, *d*, *J* = 8)	In 2.1–2.6 *m*	In 2.3–2.7 *m*	3.30 (*d*, *J* = 7)	3.33 (*d*, *J* = 6.9)
H8	In 2.32–2.5 *m*	In 2.1–2.6 *m*	In 2.3–2.7 *m*	In 2.25–2.50 *m*	2.23 (1H, *m*)
H9	0.90 (3H, *d*, *J* = 6.3)	0.83 (3H, *d*, *J* = 6.6)	0.89 (3H, *d*, *J* = 6)	1.25 (3H, *d*, *J* = 6)	1.28 (3H, *d*, *J* = 7)
H2′	5.40 (1H, *s*)	5.20 (1H, *s*)	3.99 (1H, *s*)	5.32 (1H, *s*)	3.98 (1H, *s*)
H3′					
H4′		4.86 (1H, *s*)			
H5′					
H6′	5.68 (1H, *s*)	4.44 (1H, *s*)	5.67 (1H, *s*)	6.15 (1H, *s*)	6.12 (1H, *s*)
H7′	In 2.32–2.50 *m*	In 2.1–2.6 *m*	In 2.3–2.7 *m*	In 2.25–2.50 *m*	2.40/2.76 (*dd*, *J* = 6.6, 2)
H8′	5.80 (1H, *m*)	5.80 (1H, *m*)	5.88 (1H, *m*)	5.82 (1H, *m*)	5.88 (1H, *m*)
H9′ *trans*	5.15 (1H, *dd*, *J* = 15.8, < 1)	5.03 (1H, *dd*, *J* = 17.7, < 1)	5.23 (1H, *dd*, *J* = 18.6, 1.4)	5.22 (1H, *dd*, *J* = 18, < 1)	5.30 (1H, *dd*, *J* = 17, 1.7)
H9′ *cis*	5.14 (1H, *dd*, *J* = 11.2, < 1)	5.04 (1H, *dd*, *J* = 10.8, < 1)	5.15 (1H, *dd*, *J* = 9.9, 1.3)	5.21 (1H, *dd*, *J* = 12, < 1)	5.21 (1H, *dd*, *J* = 9, 1.7)
1′-OMe					
2′-OMe					
3′-OMe	3.22	3.15	3.30	3.27	3.41
5′-OMe	3.68	3.63	3.68	3.68	3.67
6′-OMe					

*Interchangeable.

subjected separately to the following extraction procedure. Ground material was extracted with EtOH by percolation with stirring. The EtOH was concd to a syrup and MeOH added to ppt fats. Addition of MeOH and repeated cooling in a freezer was carried out until no additional ppt formed. Each alcoholic extract was diluted to a known vol. with MeOH–H_2O (3:2). An aliquot was removed and evapd to dryness in order to estimate the wt of each extract: seeds 34 g, seed coats 6.5 g, fruit pulp 58 g. The aq. alcohol was then partitioned between hexane, $CHCl_3$ and EtOAc. Analysis by ^{1}H NMR showed the neolignans to be concd in the $CHCl_3$ solns: seed 1.5 g, seed coats 0.68 g, fruit pulp 1.2 g.

Neolignans from seeds. One-half of the $CHCl_3$ extract was subjected to flash chromatography (silica gel) with a gradient of 3:2–2:3 of toluene–EtOAc. Fractions 5–19 (of 27) contained neolignans and were combined based on TLC and NMR analysis. Pure neolignans were then obtained by prep. TLC (silica gel) with hexane–EtOAc (1:0–1:1 gradient) and prep. TLC (silica gel) by double development with toluene–EtOAc (5:1) and (5:3).

Neolignans from seed coats. One-half of the $CHCl_3$ extract was separated by prep. TLC as above, with further purifications by prep. HPLC (ODS column; MeOH–H_2O, 6:4).

Neolignans from fruit pulp. One-third of the $CHCl_3$ extract was separated on a centrifugal prep. TLC plate (silica gel, 2 mm) developed with a hexane–EtOAc gradient (1:0–1:1). Fractions containing neolignans were further separated by prep. TLC as above.

Results of the isolations were as follows:

	% in seeds*	% in seed coat	% in fruit pulp
1a	0.004	0.024	0.005
1b	0.005	0.020	None
1c	0.002	0.001	0.001
2a	0.002	0.002	0.010
2b	0.001	0.004	0.001
3a	Trace	0.001	0.009
4a	0.001	Trace	0.001
5a	Trace	None	None
5c	None	Trace	None
6a	None	Trace	None
7c	0.001	None	None
8	0.001	None	None

*Without seed coat.

(7*S*,8*R*,1′*S*,2′*S*,3′*R*)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′-dimethoxy-3,4-methylenedioxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**1a**). 19.8 mg (seed), 9.5 mg (fruit pulp), 23.5 mg (seed coat) EIMS *m/z* $[M]^+$ 414, 373, 210, 181, 162. IR ν_{max} cm^{-1}: 1750, 1706, 1618. ^{1}H NMR see Table 1.

(7*S*,8 *R*,1′*S*,2′*S*,3′*R*,4′*S*)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′-dimethoxy-4′-hydroxy-3,4-methylenedioxy-1′,2′,3′,4-tetrahydro-7.3′,8.1′-neolignan* (**1b**). 26.4 mg (seed), 20.3 mg (seed coat). Found $[M+1]^+$ 417.1907, $C_{23}H_{28}O_7$ requires $[M+1]^+$ 417.1913. EIMS *m/z*, $[M]^+$ 416, 375, 315, 210, 162. IR ν_{max} cm^{-1}: 3500, 1742, 1652, 1492: ^{1}H NMR see Table 1.

(7*S*,8*R*,1′*S*,2′*S*,3′*R*)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′,3,4-tetramethoxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**2a**). 9.9 mg (seed), 19.4 mg (fruit pulp), 2.3 mg (seed coat). Found $[M]^+$ 430.19916 $C_{24}H_{30}O_7$ requires $[M]^+$ 430.19915. EIMS *m/z*: $[M]^+$ 430, 389, 210, 181, 178. ^{1}H NMR: 6.83 (3H, *m*, H2, 5, 6); 5.82 (1H, *m*, H8′); 5.69 (1H, *s*, H6′), 5.42 (1H, *s*, H2′), 5.16 (1H, *dd*, *J* = 15.9, < 1, H9′ *trans*); 5.15 (1H, *dd*, *J* = 11.0, < 1, H9′ *cis*); 3.88 (3H, *s*, 3-OMe); 3.86 (3H, *s*, 4-OMe); 3.69 (3H, *s*, 5′-OMe); 3.23 (3H, *s*, 3′-OMe); 2.62 (1H, *d*, *J* = 8.5, H7); 2.57–2.30 (3H, *m*, H7′, H8); 2.27 (3H, *s*, 2′-OAc); 0.91 (3H, *d*, *J* = 6.6, H9).

7*S*,8*R*,1′*S*,2′*S*,3′*R*,4′*S*)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′,3,4-tetramethoxy-4′-hydroxy-1′,2′,3′,4′-tetrahydro-7.3′,8.1′-neolignan* (**2b**). 3.9 mg (seed), 2 mg (fruit pulp), 4.3 mg (seed coat). Found $[M+1]^+$ 433.2209 $C_{24}H_{32}O_7$ requires $[M+1]^+$ 433.226. EIMS *m/z*: $[M]^+$ 432, 391, 331, 210, 178. ^{1}H NMR: 6.95 (1H, *d*, *J* = 1.4, H2); 6.86 (1H, *dd*, *J* = 5, 1.4, H6); 6.78 (1H, *d*, *J* = 5, H5); 5.80 (1H, *m*, H8′); 5.23 (1H, *s*, H2′); 5.05 (1H, *dd*, *J* = 10.7, < 1, H9′ *cis*); 5.04 (1H, *dd*, *J* = 10.7, < 1, H9′ *trans*); 4.87 (1H, *s*, H4′); 4.46 (1H, *s*, H6′); 3.89 (3H, *s*, 3-OMe); 3.86 (3H, *s*, 4-OMe); 3.64 (3H, *s*, 5′-OMe); 3.15 (3H, *s*, 3′-OMe), 2.43–2.10 (4H, *m*, H7, H8, H7′); 2.25 (3H, *s*, 2′-OAc); 0.83 (3H, *d*, *J* = 7.0, H9).

(7*S*,8*R*,1′*S*,2′*S*,3′*R*)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′,3,4,5-pentamethoxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**3a**). 2 mg (seed), 16.9 mg (fruit pulp), 1.1 mg (seed coat). Found $[M+1]^+$ 461.2175 $C_{25}H_{32}O_8$ requires $[M+1]^+$ 461.2175. EIMS *m/z*: $[M]^+$ 460, 210, 208. ^{1}H NMR: 6.55 (2H, *s*, H2, 6); 5.80 (1H, *m*, H8′); 5.68 (1H, *s*, H6′); 5.44 (1H, *s*, H2′); 5.15 (1H, *dd*, *J* = 15, 0.8, H9′ *trans*); 5.14 (1H, *dd*, *J* = 13, 0.8, H9′ *cis*); 3.85 (6H, *s*, 3,5-OMe); 3.83 (3H, *s*, 4-OMe); 3.69 (3H, *s*, 5′-OMe); 3.24 (3H, *s*, 3′-OMe); 2.59 (1H, *d*, *J* = 8.7, H7); 2.57–2.30 (3H, *m*, H7′, H8); 2.27 (3H, *s*, 2′-OAc); 0.92 (3H, *d*, *J* = 6.7, H9).

(7S,8R,1′S,2′S,3′R)-$\Delta^{8'}$-*Acetoxy-3′,5′,3-trimethoxy-4,5-methylenedioxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3,′8.1′-neolignan* (**4a**). 6.5 mg (seed), 1.9 mg (fruit pulp), trace (seed coat). Found $[M]^+$ 444.1784 $C_{24}H_{28}O_8$ requires $[M]^+$ 444.1784. EIMS *m/z* $[M]^+$ 444, 210, 192, 181. ^{1}H NMR: 6.65 (1H, *d*, *J* = 1.5, H2*); 6.38 (1H, *d*, *J* = 1.5, H6*); 5.94 (2H, *dd*, *J* = 4, 1, O_2CH_2); 5.82 (1H, *m*, H8′); 5.67 (1H, *s*, H6′); 5.40 (1H, *s*, H2′); 5.15 (1H, *dd*, *J* = 15, 0.8, H9′ *trans*); 5.14 (1H, *dd*, *J* = 13, 0.8, H9′ *cis*); 3.88 (3H, *s*, 5-OMe); 3.68 (3H, *s*, 5′-OMe); 3.24 (3H, *s*, 3′-OMe); 2.56 (1H, *d*, *J* = 8, H7); 2.51–2.30 (3H, *m*, H8, H7′); 2.27 (3H, *s*, 2′-OAc); 0.91 (3H, *d*, *J* = 6.4, H9).

(7S,8R,1′S,2′S,3′R)-$\Delta^{8'}$-3′,5′]-*Dimethoxy-2′-hydroxy-3,4-methylenedioxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**1c**). 8 mg (seed), 1.4 mg (seed coat), 1.5 mg (fruit pulp). EIMS *m/z*: $[M]^+$ 372, 331, 210, 162. ^{1}H NMR see Table 1.

(7S,8R,1′R,2′R,3′S)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′-dimethoxy-3,4-methylenedioxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**5a**). < 1 mg (seed). Found $[M+1]^+$ 415.1759 $C_{23}H_{26}O_7$ requires $[M+1]^+$ 415.17567. EIMS *m/z*: $[M]^+$ 414, 373, 210, 162. IR, ν_{max} cm^{-1}: 1745, 1700, 1615, 1500, 1488. ^{1}H NMR see Table 1.

(7S,8R,1′R,2′R,3′S)-$\Delta^{8'}$-3′,5′-*Dimethoxy-2′-hydroxy-3,4-methylenedioxy-1′,2′3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**5c**). Trace (seed coat). EIMS *m/z*: $[M]^+$ 372, 210, 162. ^{1}H NMR see Table 1.

(7S,8R,1′R,2′R,3′S)-$\Delta^{8'}$-2′-*Acetoxy-3′,5′,3,4-tetramethoxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**6a**). 6 mg (fruit pulp). EIMS *m/z*: $[M]^+$ 430, 389, 210, 178. ^{1}H NMR: 6.74 (1H, *d*, *J* = 8.8, H5); 6.59 (1H, *d*, *J* = 1.9, H2); 6.58 (1H, *dd*, *J* = 8.8, 1.9, H6); 6.17 (1H, *s*, H6′); 5.80 (1H, *m*, H8′); 5.34 (1H, *s*, H2′); 5.22 (1H, *dd*, *J* = 15, < 1, H9′ *trans*); 5.21 (1H, *dd*, *J* = 12, < 1, H9′ *cis*); 3.82 (3H, *s*, H3 or 4*); 3.81 (3H, *s*, H4 or 3*); 3.68 (3H, *s*, 5′-OMe); 3.35 (1H, *d*, *J* = 6.6, H7); 3.28 (3H, *s*, 3′-OMe); 2.5–2.3 (3H, *m*, H8, H7′); 2.25 (3H, *s*, 2′-OAc); 1.27 (3H, *d*, *J* = 7, H9).

(7S,8R,1′R,2′R,3′S)-$\Delta^{8'}$-2′,4-*Dihydroxy-3,3′,5′-trimethoxy-1′,2′,3′,4′-tetrahydro-4′-oxo-7.3′,8.1′-neolignan* (**7c**). 6 mg (seed). Found $[M+1]^+$ 375.1803, $C_{21}H_{26}O_6$ requires $[M+1]^+$ 375.18076. EIMS *m/z*: $[M]^+$ 374, 333, 210, 164. IR, ν_{max}, cm^{-1}: 3450, 1685, 1615, 1512. ^{1}H NMR: 6.77 (1H, *d*, *J* = 8, H5); 6.59 (1H, *d*, *J* = 1.8, H2); 6.52 (1H, *dd*, *J* = 8, 1.8, H6); 6.13 (1H, *s*, H6′); 5.85 (1H, *m*, H8′); 5.30 (1H, *dd*, *J* = 17, 1.7, H9′ *trans*); 5.21 (1H, *dd*, *J* = 9, 1.7, H9′ *cis*); 3.99 (1H, *s*, H2′); 3.82 (3H, *s*, 3-OMe); 3.67 (3H, *s*, 5′-OMe); 3.41 (3H, *s*, 3′-OMe); 3.32 (1H, *d*, *J* = 6.5, H7); 2.76 (1H, *dd*, *J* = 6.7, 2, H7′a or b*); 2.42 (1H, *dd*, *J* = 6.7, 2, H7′b or a*); 2.50 (1H, *m*, H8); 1.28 (3H, *d*, *J* = 7, H9).

(7S,8S,1′R)-$\Delta^{8'}$-1′,6′-*Dihydro-1′,5′-dimethoxy-3,4-methylenedioxy-6′-oxo-7.0.4′,8.3′-neolignan* (**8**). 3 mg (seed). Found $[M+1]^+$ 371.1487; $C_{21}H_{22}O_6$ requires $[M+1]^+$ 371.1416. EIMS *m/z*: $[M]^+$ 370, 340, 329, 207, 162. IR ν_{max}, cm^{-1}: 2920, 1655, 1612, 1500, 1488. ^{1}H NMR: 6.86 (1H, *dd*, *J* = 8.0, 1.6, H6); 6.83 (1H, *d*, *J* = 8.0, H5); 6.83 (1H, *d*, *J* = 1.6, H2); 6.00 (2H, *s*, O_2CH_2); 5.70 (1H, *ddt*, *J* = 17, 10, H8′); 5.20 (1H, *dd*, *J* = 10, 2.2, H9′ *cis*); 5.09 (1H, *dd*, *J* = 17, 2.2, H9′ *trans*); 5.05 (1H, *d*, *J* = 8.6, H7); 3.85 (3H, *s*, 5′-OMe); 3.14 (3H, *s*, 1′-OMe); 3.09 (1H, *dq*, *J* = 8.6, 6.7, H8); 2.50 (2H, *dd*, *J* = 14, 7.1, H7′); 1.34 (3H, *d*, *J* = 6.7, H9). All in agreement with the lit. [3].

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