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FURTHER LIGNOIDS FROM *VIROLA SEBIFERA**

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Key Word Index—*Virola sebifera*, Myristicaceae, fruits, furofuran lignans, dibenzylbutane neolignans, dimethyldiarylbutanol, tetralin neolignans, naphthalene neolignans, dimeric neolignan

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Abstract—From the fruits of *Virola sebifera* 2,3-dibenzylbutanes were isolated together with tetralin and naphthalene neolignans 2,3-Dimethyl-4-piperonyl-4-veratrylbutan-1-ol, a further constituent, probably arises by a retro-Friedel–Crafts reaction from a tetralin neolignan An additional component was identified as a dimeric neolignan

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INTRODUCTION

The fruits of *Virola sebifera* Aubl have been found to contain four dibenzylbutyrolactone lignans [2], eight 4-aryltetralin-1-one [1, 3] and three 3-arylindan-1-one [1] neolignans The present paper describes the isolation from the same plant of further lignans (**1a**, **1b**) and neolignans (**2**, **3**, **4**, **5**, **6a**, **6b**, **7**) In order to facilitate comparisons among the different compounds numbering of neolignans follows the biogenetic rules outlined in a review [4]

RESULTS AND DISCUSSION

The lignans were identified by spectral analysis, including ^{1}H and ^{13}C NMR, as well as mass spectrometry with *epi*-eudesmin (**1a**) and with fargesin (**1b**) [5, 6]

The formula of compound **2**, $C_{22}H_{30}O_5$, was deduced by ^{1}H NMR which indicates the presence of a 1,4-disubstituted 2,3-dimethylbutan-1-ol and of two veratryl units Indeed, the base peak of the mass spectrum at *m/z* 167 testifies strongly for the existence of a dimethoxybenzyl alcohol unit As expected, even in the presence of a trace of acid **2** gives a dehydration product $C_{22}H_{28}O_4$ This proved to be identical with the isolate **5** The negative Cotton effect at 290 nm [7] and the *trans*-diaxial relationship of H-7′ and H-8′ ($J = 8$ Hz) establish the identity of **5** either with (−)-galbuline (7′*S*, 8′*S*, 8′*R*) or with (+)-isogalbuline (7′*S*, 8′*S*, 8′*S*) [8] The published ORD curve of the former and of **5** are not superimposable and this compound can thus only be identical with (+)-isogalbuline Its precursor **2** must hence have the configuration shown

The formula of compound **3**, $C_{21}H_{22}O_6$, was deduced by trivial spectral analysis, including Eu(fod)$_3$ induced ^{1}H NMR shifts necessary to remove the two methine signals from the methoxyl region As expected, even in the presence of a trace of acid **3** gives a dehydration product, $C_{21}H_{20}O_5$, the mass and ^{1}H NMR spectra of which are consistent only with structure **8** Compound **3** $[\alpha]_D^{25} = -30\ 5°$, and the dimethyl ether of dihydroguaiaretic acid **9**, $[\alpha]_D^{25} = -77°$ [9], are both laevorotatory Since the replacement on a chiral carbon of a benzyl by a benzoyl substituent causes inversion of optical rotation [10], **3** must have the 8*R*,8′*R*-configuration shown

The base peak at *m/z* 271 in the mass spectrum of compound **4**, $C_{21}H_{26}O_5$, suggests the presence of a piperonyl-veratryl-methine moiety The ^{1}H NMR spectrum indeed contains all the corresponding signals Addition of Eu(fod)$_3$ is necessary to separate the originally superimposed carbinolic and benzylic proton signals The doubly benzylic methine is represented by a doublet ($\delta 3\ 55$, $J = 11\ 5$ Hz) The relevance of this evidence, as well as of all further chemical shifts and couplings, is interpreted by means of one of the possible Newman projections (**10**) As expected for a primary alcohol, acetylation causes a paramagnetic shift of 0 43 ppm of the doublet ($J = 7$ Hz) assigned to the two carbinolic protons

Compound **6a**, $C_{21}H_{18}O_5$, is an aldehyde (^{1}H NMR $\delta 10\ 17$, *s*) which by air oxidation is converted into **6b**, $C_{21}H_{18}O_6$, the corresponding carboxylic acid ($\delta 13\ 77$) The structures of these compounds become obvious upon ^{1}H NMR spectral comparison chiefly with **6c** [11], but also with **11** and **12** [12] The chemical shift of H-7 in **6a** and **6b** ($\delta 7\ 76$) is comparable with the corresponding value for **6c** ($\delta 7\ 48$) and **11** ($\delta 7\ 72$), but not with the value observed for **12** ($\delta 8\ 31$) Thus the methyls, and not the carbonyl functions of **6a** and **6b**, occupy position 8 Besides, methyls at 8′ would be expected to be shielded by the *ortho*-aryls as in **6c** ($\delta 2\ 16$) This does not occur with the methyls at 8 of **6a**, **6b** ($\delta 2\ 40$) and **6c** ($\delta 2\ 46$) Finally, the methoxyls, rather than the methylenedioxy group, are located on the naphthalene system on account of the differential shielding $\Delta\delta_{OMe}$ 0 27 for **6a** and **6b**, 0 22 for **6c**

A sample of the model compound **6c** was prepared by sequential LiAlH$_4$-reduction of the naturally occurring hydroxytetralone **16a** [3] and TsOH-aromatization of the resulting diol **16b** to the naphthalene derivative (**6c**) A good knowledge of the spectral properties of this compound proved to be important in the structural elucidation of **7**

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*Part 22 in the series "The Chemistry of Brazilian Myristicaceae" For Part 21 see ref [1] Taken from part of the Doctorate thesis presented by L M X L to the Universidade de São Paulo (1983)

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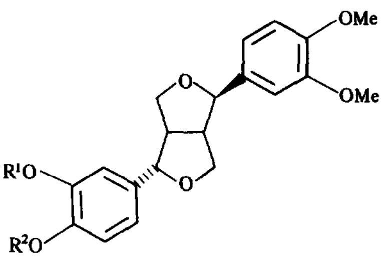
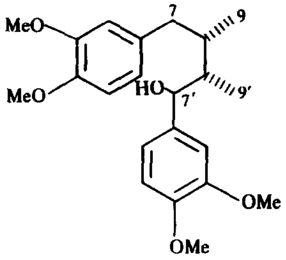


1a R¹——R² = CH₂
1b R¹ = R² = Me



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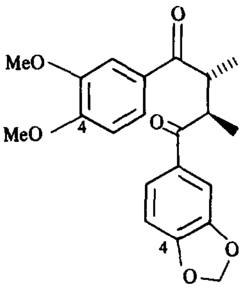

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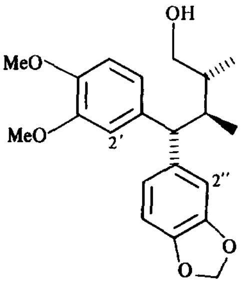

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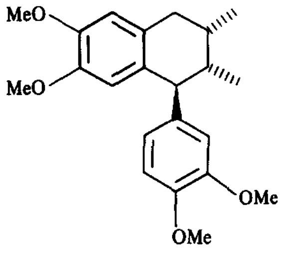

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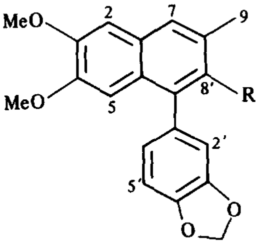
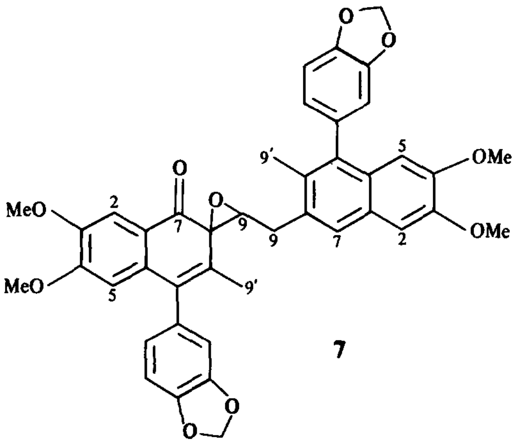


R
6a CHO
6b CO_2H
6c Me

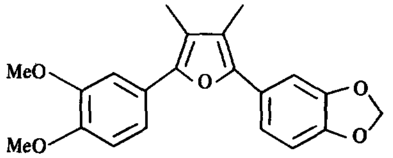
Number and chemical shifts of ^{1}H and ^{13}C NMR signals suggested **7** to be a dimeric neolignan Indeed these spectra showed features closely reminiscent of **13**, an additional isolate of the same plant material [1] and of **6c** [11] Only the C-9 methyls of **13** and of **6c** are not represented by signals in the NMR spectra of **7** (Tables 1 and 2) This compound must contain instead a methylene (δ2 3–3, *m*, 2H, δ19 5, *t*, 1C) and a methine (δ1 96, *ca d*, *J* = 5 Hz, 1H, δ83 0, *d*, 1C) The chemical shifts are consistent with the benzylic nature of the former and the inclusion in an epoxide of the latter Assuming the comparison with model compounds to be sound, the linkage of the two units must involve the CH_2CH moiety as shown in **7**

Three additional groups of evidence are consistent with this deduction Initially, reaction of **7** and $LiAlH_4$ gave a product (**14**) the NMR data of which (Tables 1 and 2) indicate reduction to have taken place at the carbonyl and the epoxide functions More importantly, in contradistinction to **7**, the HR mass spectrum showed a $[M]^+$, its *m/z* value 704 180 is compatible, as expected, with the formula $C_{42}H_{40}O_{10}$

The HR mass spectrum of **7** and **13** share a prominent peak at *m/z* 353 to which structure **15** can be assigned,



7



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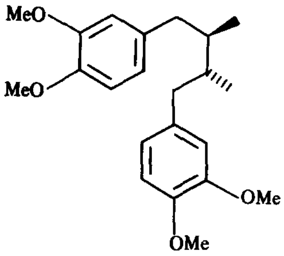

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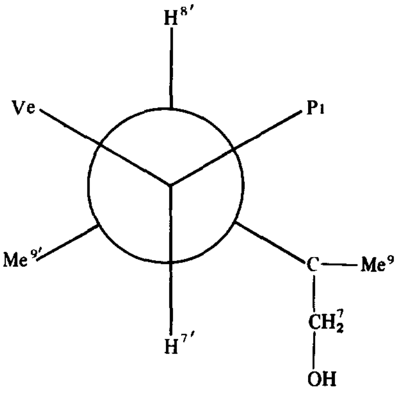


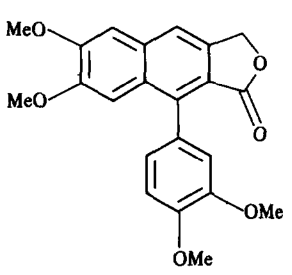
10

H^7, H^8	$J = 7$ Hz
H^8, H^9	$J = 7$ Hz
H^8, $H^{8'}$	$J = 2$ Hz
$H^{7'}$, $H^{8'}$	$J = 11.5$ Hz
$H^{8'}$, $H^{9'}$	$J = 7$ Hz

while the analogous spectra of 7 and 6c share a series of prominent peaks at *m/z* 189, 176 and 165

The Eu(fod)$_3$ induced ^{1}H NMR shifts for 7 are minimal for the two groups of 2,5,6-protons The phenyl ring thus cannot be substituted by an *ortho*-dimethoxy unit which, contrarily to the methylenedioxy unit, associates strongly with the reagent [13] as evidenced by their $\Delta\delta$ values as well as the $\Delta\delta$ values of their protonic entourage The highest $\Delta\delta$ value for an aromatic proton is given by H-2, additional evidence for its vicinality to the carbonyl

The isolation of the dibenzylbutane derivates **2** and **3** opens the question if tetralin (e g **5**), hydroxytetralin (e g **8**), tetralone (e g **13**) and naphthalene (e g **6**) neolignans, previously reported to occur also in other plant species [4], are artifacts This, however, is considered to be improbable on account of the concomitant presence in *V sebifera* of the 4,4-diarylbutan-1-ol **4**, which is very clearly derived from a tetralin by a *retro*-Friedel–Crafts condensation, and the dimeric neolignan **7**, which is clearly derived from a tetralone and a naphthalene by oxidative



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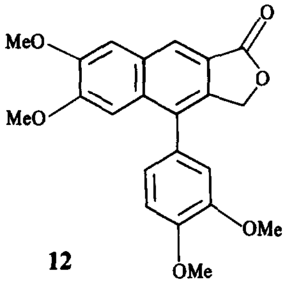

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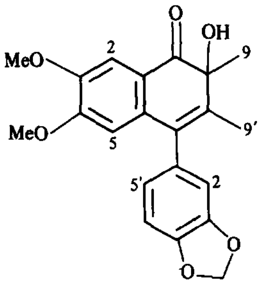

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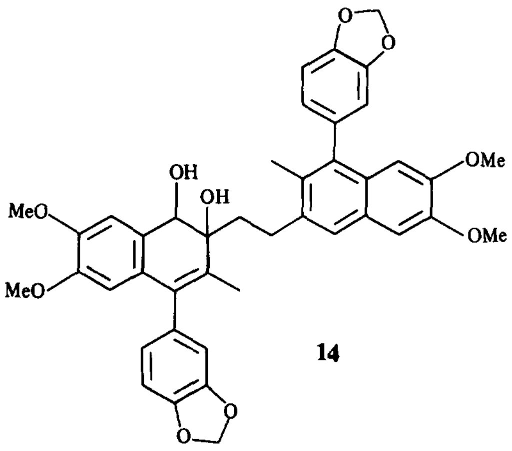

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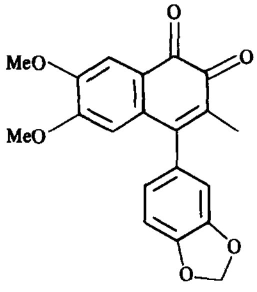

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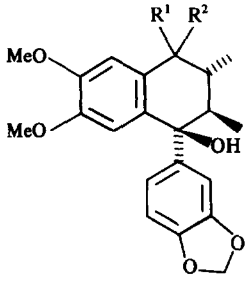

16a $R^1 = R^2 = O$
16b $R^1 = H, R^2 = OH$

condensation Such reactions would hardly be expected to occur during the isolation process

EXPERIMENTAL

Isolation of constituents Isolation of compounds **1a**, **1b**, **2**, **3**, **4**, **5**, **6a**, **6b** and **7** is described in full in a previous paper [1] in which the compounds appear marked by the same numbers with an appended asterisk, **1a***, **1b***, **2***, etc

(8S,7'S,8'S)-7'-*Hydroxy*-3,4,3',4'-*tetramethoxy*-8 8'-*neolignan* (**2**) Oil ($[M]^+$ found 374 189, $C_{22}H_{30}O_5$ requires 374 209) IR ν_{max}^{film} cm^{-1} 3520, 1600, 1590, 1510, 1450, 1420, 1250, 1150, 1030 ^{1}H NMR (60 MHz, $CDCl_3$) δ6 9–6 3 (*m*, 6 ArH), 3 84, 3 82, 3 76 (3*s*, resp 1, 1 and 2 OMe), 4 38 (*d*, J = 8 Hz, H-7'), *ca* 2 4, 2–1 2 (2 *m*, 2H each), 1 00 and 0 79 (2*d*, J = 7 Hz, 2 Me) ^{13}C NMR (20 MHz, $CDCl_3$) δ133 9, 136 9 (2*s*, C-1, C-1'), 111 0, 109 5 (2*d*, C-2, C-2'), 149 0, 149 2 (2*s*, C-3, C-3'), 147 2, 147 5 (2*s*, C-4, C-4'), 113 3, 110 9 (2*d*, C-5, C-5'), 121 0, 119 2 (2*d*, C-6, C-6'), 41 4 (*t*, C-7), 77 8 (*d*, C-7'), 35 3, 41 6 (2*d*, C-8, C-8'), 14 5, 9 6 (2*q*, C-9, C-9'), 55 8, 55 7 (2*s*, 4 OMe) MS *m/z* (rel int) 374 (6), 219 (13), 178 (12), 168 (11), 167 (100), 165 (4), 151 (30), 139 (40), 137 (4)

(8R,8'R)-3,4-*Dimethoxy*-3',4'-*methylenedioxy*-7,7'-*dioxo*-8 8'-

Table 1 ^{1}H NMR data (δ, J in Hz in brackets) of model neolignans (**13**, **6c**) and dimeric neolignans (**7**, **14**) (60 MHz, $CDCl_3$)

H	**13**	**7** tetralin	**14** unit	**6c**	**7** naphthalene	**14** unit
2	7 50 *s*	7 63 *s*	C	7 06 *s*	B	C
5	6 26 *s*	6 33 *s*	6 23 *s*	6 77 *s*	B	C
7	—	—	5 46 *s*	7 48 *s*	7 51 *s*	7 53 *s*
9	1 58 *s*	2 3–2 5 ~ *d* (5)	2 3–3	2 46 *s*	2 6–3	2 3–3
2′	A	B	C	6 76 *d* (1 4)	B	C
5′	A	B	C	6 95 *d* (7 8)	B	C
6′	A	B	C	6 71 *dd* (7, 8, 1 4)	B	C
9′	1 86 *s*	1 96 *s*	1 66 *s*	2 16 *s*	2 10 *s*	2 08 *s*
OMe	3 73 *s*	3 76 *s*	3 66 *s*	3 79 *s*	3 76 *s*	3 73 *s*
OMe	3 96 *s*	3 94 *s*	3 94 *s*	4 01 *s*	4 00 *s*	4 03 *s*
O_2CH_2	6 03 *s*	6 08 *s*	5 96 *s*	6 05 *s*	6 02 *s*	6 00 *s*

A (6 5–7 1), B (6 6–7 2), C (6 4–7) signals located within the indicated band envelopes

Table 2 ^{13}C NMR data (δ) of model neolignans (**13**, **6c**) and dimeric neolignans (**7**, **14**) (20 MHz, $CDCl_3$)

C	**13**	**7** tetralin	**14** unit	**6c**	**7** naphthalene	**14** unit
1	123 1 *s*	124 1 *s*	127 7 *s*	127 5 *s*	129 1 *s*	129 3 *s*
2	105 1 *d*	105 8 *d*	105 9 *d*	105 9 *d*	108 4 *d*	108 4 *d*
3	147 0 *s*	149 2 *s*	148 5 *s*	148 8 *s*	148 4 *s*	148 6 *s*
4	148 2 *s*	154 2 *s*	148 3 *s*	148 9 *s*	148 4 *s*	148 6 *s*
5	109 1 *d*	109 0 *d*	114 6 *d*	105 7 *d*	108 2 *d*	108 4 *d*
6	142 1 *s*	141 2 *s*	133 0 *s*	127 8 *s*	128 7 *s*	128 8 *s*
7	203 7 *s*	199 3 *s*	75 1 *d*	126 0 *d*	124 0 *d*	123 9 *d*
8	101 3 *s*	100 8 *s*	83 0 *s*	133 4 *s*	134 8 *s*	133 0 *s*
9	29 2 *q*	83 0 *d*	22 7 *t*	20 9 *q*	19 5 *t*	20 9 *t*
1′	131 9 *s*	132 6 *s*	137 7 *s*	134 6 *s*	134 8 *s*	134 5 *s*
2′	108 1 *d*	108 6 *d*	108 4 *d*	108 4 *d*	109 2 *d*	108 4 *d*
3′	147 7 *s*	148 0 *s*	147 8 *s*	147 8 *s*	147 7 *s*	147 8 *s*
4′	146 8 *s*	147 0 *s*	146 4 *s*	146 5 *s*	146 6 *s*	146 4 *s*
5′	108 7 *d*	111 4 *d*	111 3 *d*	110 7 *d*	112 5 *d*	110 7 *d*
6′	122 0 *d*	123 0 *d*	118 4 *d*	123 3 *d*	123 1 *d*	123 4 *d*
7′	130 2 *s*	130 6 *s*	128 5 *s*	131 5 *s*	132 2 *s*	131 0 *s*
8′	154 7 *s*	154 2 *s*	149 3 *s*	136 9 *s*	134 8 *s*	133 5 *s*
9′	14 8 *q*	15 4 *q*	16 5 *q*	17 3 *q*	17 0 *q*	17 1 *q*
OMe	55 9 *q*	55 9 *q*	56 0 *q*	55 6 *q*	55 7 *q*	55 7 *q*
OMe	56 1 *q*	56 2 *q*	56 2 *q*	55 7 *q*	55 9 *q*	56 2 *q*
O_2CH_2	101 2 *t*	101 2 *t*	101 0 *t*	101 0 *t*	101 0 *t*	100 4 *t*

neolignan (**3**) Amorphous solid, $[\alpha]_D^{25} = -30\ 5°$ ($CHCl_3$) ($[M]^+$ found 370 180; $C_{21}H_{22}O_6$ requires 370 142) IR ν_{max}^{KBr} cm^{-1} 1670, 1600, 1500, 1440, 1420, 1350, 1250 UV λ_{max}^{MeOH} nm 304, 273, 232 (ε17 800, 19 400, 37 200) ^{1}H NMR (60 MHz, $CDCl_3$) δ7 40, 7 36 (2*d*, $J = 2$ Hz, H-2, H-2′), 6 83, 6 76 (2*d*, $J = 8$ Hz, H-5, H-5′), 7 61, 7 53 (2*dd*, $J = 8, 2$ Hz, H-6, H-6′), 5 92 (*s*, O_2CH_2), 4–3 7 (*m*, H-8, H-8′), 3 88, 3 83 (2*s*, 2 OMe), 1 4–1 1 (*m*, 3H-9, 3H-9′) ^{13}C NMR (20 MHz, $CDCl_3$) δ129 4, 131 2 (2*s*, C-1, C-1′), 110 9, 110 4 (2*d*, C-2, C-2′), 149 1, 148 3 (2*s*, C-3, C-3′), 153 4, 149 2 (2*s*, C-4, C-4′), 108 4, 108 0 (2*d*, C-5, C-5′), 123 2, 124 7 (2*d*, C-6, C-6′), 202 4 (*s*, C-7, C-7′), 43 6 (*d*, C-8, C-8′), 16 0, 15 6 (*q*, C-9, C-9′), 101 9 (*t*, O_2CH_2), 56 0 (*q*, 2 OMe) MS m/z (rel int) 370 (7), 194 (19), 178 (20), 166 (8), 165 (100), 149 (48), 137 (6), 121 (11), 107 (5)

2,3-Dimethyl-4-piperonyl-4-veratrylbutan-1-ol (**4**) Oil IR ν_{max}^{film} cm^{-1} 3450, 1590, 1504, 1485, 1245, 1145, 1042 ^{1}H NMR (60 MHz, $CDCl_3$) δ7–6 6 (*m*, 6 ArH), 3 7–3 4, 3–1 1 (2 *m*, 2H each, 0 73, 0 66 (2*d*, $J = 7$ Hz, 2 Me) ^{13}C NMR (20 MHz, $CDCl_3$) δ136 8, 138 6 (2*s*, C-1′, C-1″), 111 4, 107 8 (2*d*, C-2, C-2″), 148 8, 147 2 (2*s*, C-3, C-3′), 147 4, 145 4 (2*s*, C-4, C-4′), 111 4, 107 8 (2*d*, C-5′, C-5″), 119 5, 120 6, (2*s*, C-6, C-6″), 66 5 (*t*, C-1), 35 6 (*d*, C-2), 35 6 (*d*, C-3), 55 5 (*d*, C-4), 9 3 (*q*, Me-2), 11 5 (*q*, Me-3), 100 5 (*t*, O_2CH_2), 55 7, 55 6 (2*s*, 2 OMe) MS m/z (rel int) 358 (7), 272 (19), 271 (100)

(8S,7′S,8′S)-3,4,3′,4′-*Tetramethoxy*-6 7′,8 8′-*neolignan* [(+)-isogalbuline, **5**] Mp 120–123° (MeOH), lit [14] mp 100–101 5° ($[M]^+$ found 356 206, $C_{22}H_{28}O_4$ requires 356 199) UV λ_{max}^{MeOH} nm 220, 285 (ε3500, 2300) IR ν_{max}^{KBr} cm^{-1} 1605, 1590, 1510, 1470–1445, 1260–1220 ^{1}H NMR see ref [15] ^{13}C NMR

(20 MHz, $CDCl_3$) δ129 2, 139 2 (2*s*, C-1, C-1′), 112 2, 110 5 (2*d*, C-2, C-2′), 148 9, 147 1 (2*s*, C-3, C-3′), 148 5, 147 1 (2*s*, C-4, C-4′), 110 5, 112 4 (2*d*, C-5, C-5′), 132 6 (*s*, C-6), 122 0 (*d*, C-6′), 39 1 (*t*, C-7), 35 6 (*d*, C-8), 20 0 (*q*, C-9), 54 3 (*d*, C-7′), 43 8 (*d*, C-8′), 17 2 (*q*, C-9′), 55 9, 55 8 (2*q*, 4 OMe) MS [8] ORD (MeOH) $[\phi]^{tr}_{260}$ +8200, $[\phi]^{pk}_{270}$ +14600, $[\phi]^{tr}_{290}$ +9950, $[\phi]^{pk}_{300}$ +11750 CD (MeOH) $[\theta]^{max}_{260}$ +2150, $[\theta]^{max}_{290}$ −1070 Compound **5** was also produced when **2** was kept in $CDCl_3$ soln overnight

3,4-*Dimethoxy-3′,4′-methylenedioxy-9′-oxo-*$\Delta^{7\ 8,7\ 8}$*-6,7′,8 8′-neolignan* (**6a**) ($[M]^+$ found 350 119, $C_{21}H_{18}O_5$ requires 350 115) IR ν^{KBr}_{max} cm^{-1} 1715, 1605, 1500, 1425, 1350, 1250, 1215, 1020 ^{1}H NMR (60 MHz, $CDCl_3$) δ7 76 (*s*, H-7), 7 00 (*d*, *J* = 8 Hz, H-5′), 6 69 (*dd*, *J* = 8, 2 Hz, H-6′), 6 9–6 6 (*m*, H-2, H-5, H-2′), 6 10 (*s*, O_2CH_2), 4 03, 3 76 (2*s*, 2OMe), 2 40 (*s*, Me), 10 17 (*s*, CHO)

9′-Hydroxy-3,4-dimethoxy-3′,4′-methylenedioxy-9′-oxo-$\Delta^{7\ 8\ 7\ 8}$*-6 7′,8 8′-neolignan* (**6b**) Yellow, mp 173–175° (MeOH) ($[M]^+$ found 366 110, $C_{21}H_{18}O_6$ 366 110) IR ν^{KBr}_{max} cm^{-1} 3100–3000, 1684, 1600, 1504–1450, 1350, 1300–1220, 1165, 1125, 1042, 943 ^{1}H NMR (60 MHz, $CDCl_3$) with the exception of the signal at δ10 17 replaced by 13 77 (*s*, CO_2H) identical to **6a** MS *m*/*z* (rel int) 366 (100), 365 (6), 351 (5), 336 (4), 321 (4), 307 (6), 306 (5), 293 (10), 279 (4), 278 (4), 277 (4), 265 (5), 189 (5), 165 (14), 149 (7)

3,4-*Dimethoxy-3′,4′-methylenedioxy-*$\Delta^{7,8\ 7\ 8}$*-6 7′,8 8′-neolignan* (**6c**) Yellow, mp and lit [11] mp 188–190° (MeOH) ($[M]^+$ found 336 135, $C_{21}H_{20}O_4$ requires 336 136) UV see ref [11] ^{1}H NMR see Table 1 [11] ^{13}C NMR see Table 2 MS *m*/*z* (rel int) 336 (49), 306 (10), 292 (16), 291 (100), 275 (13), 263 (63), 248 (31), 220 (14), 202 (19), 191 (15), 190 (15), 189 (42), 176 (22), 165 (31), 153 (40), 152 (20), 139 (35), 124 (27), 109 (23), 101 (15) Compound **6c** was obtained by sequential reduction of **16a** ($LiAlH_4$, THF) and aromatization of the resulting **16b** (TsOH, C_6H_6, reflux) [3]

Dimeric neolignan (**7**) Yellow, mp 164–165° (MeOH). $[\alpha]^{25}_D$ = −10 3° ($CHCl_3$) UV λ^{MeOH}_{max} nm 223, 255, 290 (ε47 900, 77 550, 25 650) IR ν^{KBr}_{max} cm^{-1} 1690, 1600, 1500, 1464, 1440, 1360, 1295, 1227, 1170, 1124, 1115, 1045, 943, 885, 864, 813, 758 ^{1}H NMR Table 1 ^{13}C NMR (Table 2) MS *m*/*z* (rel int) 700 (< 1), 403 (< 1), 364 (< 1), 363 (< 1), 362 (< 1), 352 (100), 351 (34), 350 (24), 349 (< 1), 338 (1), 336 (1), 335 (2), 323 (1), 265 (9), 189 (10), 176 (10), 165 (20) *Hydrogenation product* (**7** in THF + $LiAlH_4$ → **14**) Yellow, mp 154–156° (MeOH) ($[M]^+$ found 704 260; $C_{42}H_{40}O_{10}$ requires 704 262) IR ν^{KBr}_{max} cm^{-1} 3500, 1600, 1500, 1480, 1470, 1450, 1430, 1380, 1350, 1220, 1160, 1120, 1040, 935, 880 ^{1}H NMR see Table 1 ^{13}C NMR See Table 2 MS *m*/*z* (rel int) 704 (< 1), 703 (3), 366 (< 1), 364 (1), 354 (1), 353 (7), 352 (52), 351 (100), 338 (18), 336 (22), 335 (2), 323 (8), 265 (6)

3,4-*Dimethyl-2-piperonyl-3-veratrylfuran* (**8**). Mp 166–169° (MeOH) UV λ^{MeOH}_{max} nm 310, 280, 230 (ε5800, 7050, 10 750) IR ν^{KBr}_{max} cm^{-1} 1600, 1500, 1440, 1260. ^{1}H NMR (60 MHz, $CDCl_3$) δ7 5–6 8 (*m*, 6 ArH), 6 00 (*s*, O_2CH_2), 3 96, 3 94 (2*s*, 2 OMe), 2 20 (*s*, 2 Me) MS *m*/*z* (rel int) 352 (5), 165 (24), 149 (22), 137 (5), 121 (6) Compound **8** was obtained by adding to a soln of **3** (67 mg) in $CHCl_3$ (1 ml) drops of HCl After standing overnight the soln was refluxed (30 min) and evapd The residue, submitted to TLC (silica gel, petrol–EtOAc, 9 1), gave **8** (4 mg)

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