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Lignans and Neolignans From Stems of *Piper Wightii*[1]

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Abstract: Studies of the petroleum ether extract of the stems of *Piper wightii* Miq. resulted in the isolation of three novel 2'-oxo-8.1'- and 4'-oxo-8.5'-neolignan with unusual structures, namely 4',5'-dimethoxy-3,4-methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan (6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one) (1), *iso*-4',5'-dimethoxy-3,4-methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan (*iso*-6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one) (**2**) and 1',2'-dimethoxy-3,4-methylenedioxy-4'-oxo-$\Delta^{2',5',8'}$-8.5'-lignan (2-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-4,5-dimethoxy-4-(2-propenyl)-2,5-cyclohexadien-1-one) (**3**) together with one novel tetrahydrofuran lignan, rel-(7*S*,8*S*,7'*S*,8'*S*)-3',4'-dimethoxy-3,4-methylenedioxy-8.8',7.O.7'-lignan (2*S*,3*S*,4*S*,5*S*)-5-[5-(3,4-dimethoxyphenyl)-3,4-dimethyl-2-tetrahydrofuranyl]-1,3-benzodioxol) (**4**). The structures were elucidated on the basis of spectroscopic data (^{1}H-, 2D- and ^{13}C NMR, NOE, UV, IR and MS). Additionally, two known neolignans, rel-(7*S*,8*R*,3'*R*,1'*S*)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$-8.3',7.O.2'-lignan (fargesone A, **5**) and rel-(7*S*,8*R*,3'*R*,1'*R*)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$-8.3',7.O.2'-lignan (fargesone B, **6**) were isolated for the first time from *P. wightii*.

INTRODUCTION

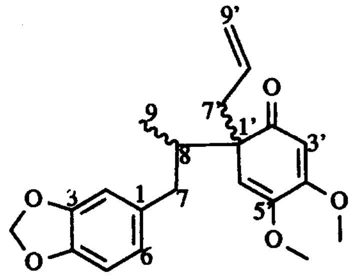
Previous work on *Piper* species during our ongoing project dealing with the isolation of potential insecticides, led to the isolation of a variety of compounds like a wax ester,[2] amides,[3] alkaloids,[4] flavonoids,[3] crotepoxide,[2] lignans and neolignans.[5-7] Our initial investigation of the petroleum ether (PE) extract of the stems and the methanolic extract of the fruits of *Piper wightii* has uncovered several neolignans and lignans.[6] We now wish to report the isolation of further components from the PE ether extract of stems: three new neolignans, 4',5'-dimethoxy-3,4-methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan (6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one) (**1**), *iso*-4',5'-dimethoxy-3,4-

methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan (*iso*-6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one) (**2**) and 1',2'-dimethoxy-3,4-methylenedioxy-4'-oxo-$\Delta^{2',5',8'}$-8.5'-lignan (2-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-4,5-dimethoxy-4-(2-propenyl)-2,5-cyclohexadien-1-one) (**3**) together with one new α,α'-diaryl-β,β'-dimethyltetrahydrofuran lignan, rel-(7*S*,8*S*,7'*S*,8'*S*)-3',4'-dimethoxy-3,4-methylenedioxy-8.8',7.O.7'-lignan (2*S*,3*S*,4*S*,5*S*)-5-[5-(3,4-dimethoxyphenyl)-3,4-dimethyl-2-tetrahydrofuranyl]-1,3-benzodioxol) (**4**), all present in the plant as minor constituents. The biogenetic nomenclature and numbering of neolignans follow the rules outlined in a review[8] and in parentheses the systematic names are given. The occurrence of 2'-oxo-8.1' type neolignans (**1** and **2**) in the plant kingdom has been reported only once,[9] and **3** represents a completely new 4'-oxo-8.5' type neolignan. The same extract also yielded two known benzofuranoid neolignans, rel-(7*S*,8*R*,3'*R*,1'*S*)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$-8.3',7.O.2'-lignan (fargesone A, **5**) and rel-(7*S*,8*R*,3'*R*,1'*R*)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$-8.3',7.O.2'-lignan (fargesone B, **6**).[10]

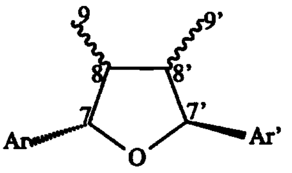
RESULTS AND DISCUSSION

Repeated column chromatography of the petroleum ether extract of the stems of *P. wightii* on silica gel and neutral aluminum oxide followed by preparative TLC on silica gel coated glass plates yielded three new neolignans, **1**, **2** and **3** and one new lignan **4** along with two known neolignans, **5** and **6**. The deduced structures in case of new compounds are mainly based on spectroscopic investigations. The known compounds (**5** and **6**) were identified by comparison of their spectroscopic data with those reported.[10]

Compound **1** is optically active. Its molecular formula, $C_{21}H_{24}O_5$, was determined by HRMS ($[M]^+$ 356.1629, Calcd. 356.1624) in combination with hydrogen and carbon counts from NMR. IR and UV spectra of compound **1** suggested the presence of a conjugated carbonyl group and a benzene ring. ^1H NMR showed the benzene ring to be a piperonyl function (Pi) by giving signals at δ 5.91(2H, s), 6.55(1H, dd, J = 7.8 and 1.4), 6.63 (1H, d, J = 1.4) and 6.70 (1H, d, J = 7.8). The ^1H NMR spectrum of **1** also showed the presence of an allyl moiety resonating at δ 2.46 (1H, dd), 2.75 (1H, dd), 4.94-5.05 (2H, m) and 5.53-5.59 (1H, m). The presence of the allyl moiety was confirmed by the ^1H-^1H COSY NMR spectrum and also by an M-41 peak in the mass spectrum. That the allyl group is attached to a sp^3-hybridized carbon atom was indicated by the low chemical shift of the allylic-CH_2 protons.[11,12] The ^1H NMR spectrum of **1** further revealed the presence of a methyl group resonating at δ 0.69 (d, J = 6.1), a methine proton at δ 2.12 (m) and two double-doublets at δ 2.07 and 2.94 each integrating for one proton. In the ^1H-^1H COSY spectrum, the doublet at δ 0.69 showed coupling with the multiplet at δ 2.12 which in turn couples with the signals at δ 2.07 and 2.94. Additionally, the signals at δ 2.07 and 2.94 showed mutual coupling. This indicates the presence of a CH_3-CH-CH_2- moiety in compound **1**. The ion at m/z 135 in the MS spectrum of **1** indicates the presence of a Pi-CH_2- moiety and the ion at m/z 162 probably comes from the Pi-CH_2-CH=CH_2 moiety. Along with these moieties, the ^1H NMR spectrum of **1** also revealed the presence of two methoxy groups resonating at δ 3.75 and 3.80,

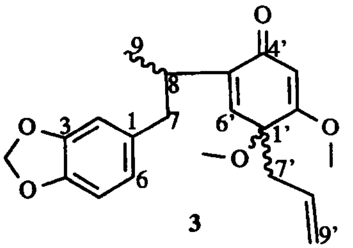


1+2

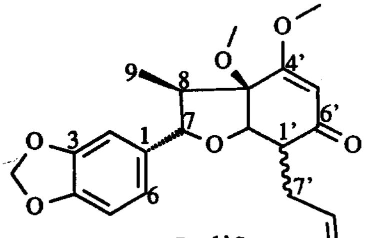


	Ar	Ar'	C*-7	C*-8	C*-7'	C*-8'
4	Pi	Ve	*S*	*S*	*S*	*S*
8	Ve	Ve	*S*	*S*	*S*	*S*
9	Pi	Ve	*S*	*S*	*R*	*R*

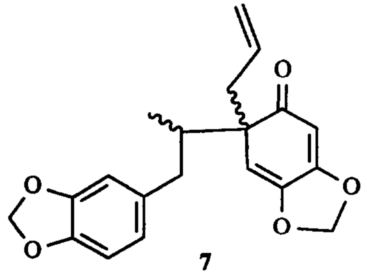
Pi = Piperonyl, Ve = Veratryl
*Relative Stereochemistry



3



5 1'*S*
6 1'*R*



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indicating their attachment to sp^2-hybridized carbon atoms[12,13] and two singlets at δ 5.19 and 5.50. On the basis of the above spectral data we propose the structure of **1** to be 4',5'-dimethoxy-3,4-methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan. The position of two methoxy groups was confirmed by NOE experiments. Irradiation of the 4'- and 5'-OCH_3 groups gave NOE on H-3'(9.1%) and H-6'(14.7%), respectively. Similarly, irradiation of 3'-H and 6'-H gave NOE on 4'-OCH_3 (3.6%) and 5'-OCH_3 (4.4%), respectively. Green and Wiemer[9] has recently isolated a similar neolignan **7** being different from **1** (and **2**) only by having a methylenedioxy group instead of the two methoxy groups in the dienone ring. They have established the structure of **7** and its carbon assignments on the basis of selective INEPT and HMQC experiments along with ^1H- and ^{13}C NMR. The ^1H- and ^{13}C NMR data of our compound is comparable with the published data of **7**. The configurations of the two asymmetric centers has not been established.

Compound **2** is optically active. It gave Mass, ^1H-, ^{13}C NMR, UV and IR spectral data very similar to those of **1**. The only significant differences observed were the chemical shifts of the protons α to the asymmetric centers: H-9, H_a-7, H-8, H_a-7', H_b-7'and H_b-7 resonate at δ 0.69, 2.07, 2.12, 2.46, 2.75 and 2.94, respectively in **1** and at δ 0.88 (3H, d), 2.03 (1H, dd), 2.29-2.47 (2H, m) and 2.55-2.68 (2H, m) in **2**. This suggests that compound **2** is a 8,1'-stereoisomer of **1** having the structure *iso*-4',5'-dimethoxy-3,4-methylenedioxy-2'-oxo-$\Delta^{3',5',8'}$-8.1'-lignan.

Compound **3** is optically active. In the HRMS spectrum, the $[M]^+$ peak at m/z 356.1633 (Calcd. 356.1624) and the hydrogen and carbon counts by NMR indicated the molecular formula to be $C_{21}H_{24}O_5$. The mass fragmentation pattern observed in the EIMS spectrum was almost identical to the fragmentation pattern of compounds **1** and **2** which indicated **3** to be a neolignan with a closely related carbon skeleton. IR and UV spectra of compound **3** suggested the presence of a conjugated carbonyl group, and a piperonyl function was evident from the ^1H NMR spectrum (5.87, 2H, $-OCH_2O-$; 6.57-6.69, 3H, Ar-H). Pi-CH_2-CH-CH_3 and allyl groups were shown in the same way as discribed for **1**. The chemical shifts of the two methoxy groups, δ 2.95 and 3.76, indicated that they are attached to sp^3- and sp^2-carbon atom,[14] respectively. On basis of the above data we propose the structure of **3** to be 1',2'-dimethoxy-3,4-methylenedioxy-4'-oxo-$\Delta^{2',5',8'}$-8.5'-lignan. The position of the 1'- and 2'-OCH_3 groups were confirmed by NOE experiments. Irradiation of 2'-OCH_3 gave 10.7% NOE on H-3'and irradiation of 1'-OCH_3 gave 1.4% NOE on H-6'. This structure was supported by the ^{13}C NMR spectrum. Stereochemical assignments of the two asymmetric centres in **3** could not be made on the basis of ^1H NMR experiments.

Compound **4** is optically active. Its molecular formula, $C_{21}H_{24}O_5$, was determined by HRMS ($[M]^+$ 356.1633, Calcd. 356.1624) in combination with hydrogen and carbon counts from NMR. The ^1H NMR spectrum of **4** exhibited two secondary methyl groups resonating at δ 1.02 (d, J = 5.9) and 1.03 (d, J = 5.9), a multiplet at δ 1.78 integrating for two protons and two doublets at δ 4.57 (J = 9.1) and 4.59 (J = 9.1). The remaining peaks in the ^1H NMR spectrum of **4** suggested the presence of a piperonyl and a veratryl function which were also indicated by the IR and UV spectra. The ^1H NMR spectrum was very similar to those of

Table 1. Comparison of ^1H NMR data(δ) of **4** with those of galbelgin and machilin G.

Lignan	Me	Me-C-H	Ar-C-H	Ar	$-OCH_2O-$	OMe
Compound **4**	1.02(3H,d,J=5.9)	1.78(2H,m)	4.57(1H,d,J=9.1)	6.76-6.97(6H,m)	5.93(2H,s)	3.86(3H,s)
	1.03(3H,d,J=5.9)		4.59(1H,d,J=9.1)			3.90(3H,s)
Galbelgin **8**[15]	0.99(3H,d,J=6.0)	1.75(2H,m)	4.58(1H,d,J=9.0)	6.80-7.00(6H,m)		3.85(6H,s)
	1.10(3H,d,J=6.0)		4.61(1H,d,J=9.0)			3.89(6H,s)
Machilin G **9**[16]	1.02(3H,d,J=6.7)	2.30(2H,m)	4.46(1H,d,J=6.9)	6.80-6.99(6H,m)	5.95(2H,s)	3.88(3H,s)
	1.03(3H,d,J=6.7)		4.47(1H,d,J=6.9)			3.90(3H,s)

All δ-values are relative to TMS; spectra of **4**, galbelgin and machilin G were recorded in $CDCl_3$ at 250-, 400-, and 60 MHz, respectively.

galbelgin (**8**)[15] and machilin G (**9**)[16], considering that galbelgin (**8**) contains two veratryl functions instead of a piperonyl and a veratryl function. Thus, we propose the structure of **4** to be 3',4'-dimethoxy-3,4-methylenedioxy-8.8',7.O.7'-lignan. This was confirmed by ^{13}C NMR data and mass fragmentation pattern, the latter being in agreement with reported data for lignans of this class.[17] The relative stereochemistry of **4** can be elucidated by comparison of the ^1H NMR data with those reported for galbelgin (**8**) and machilin G (**9**) (Table 1). The ^1H NMR data for the tetrahydrofuran ring protons of **4** correspond very closely to those of galbelgin (**8**) which has all of its substituents in the *trans* configuration.

A lignan structure with the stereochemistry of machilin G (**9**) is eliminated on the basis of the low chemical shift (δ 2.30) of the protons on the methyl bearing carbon atoms. Thus, the structure of **4** is assigned as rel-(7*S*,8*S*,7'*S*,8'*S*)-3',4'-dimethoxy-3,4-methylenedioxy-8.8',7.O.7'-lignan.

EXPERIMENTAL

IR spectra were recorded (KBr pellet or film) on a Perkin-Elmer 1720 FT-IR spectrophotometer and UV spectra on a Shimadzu UV 160 A spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC-250 or a Varian Unity 500 spectrometer at 250 or 500 and 62.9 or 125 MHz, respectively. Coupling constants (J) are in Hz. EIMS and HRMS were recorded on a Varian MAT 311A mass spectrometer at 70 ev. Optical rotations were recorded on a Perkin-Elmer 141 polarimeter. Silica-gel 60 (230-400 mesh, art 9385, Merck) and neutral aluminum oxide was used for flash CC. Analytical TLC was performed on Merck silica gel 60 F_{254} plates. Spots were visualised by UV light or by spraying with 10% concentrated H_2SO_4 in ethanol (v/v) followed by heating at around 120°C for a few minutes. Preparative TLC was performed either on silica gel 60 $PF_{254+366}$ or on Merck preparative kieselgel 60 F_{254}. Compound **4** turned pink when heated after H_2SO_4 spraying.

Plant material. Stems of the plant *P. wightii* Miq. were collected from Doddabetta, Ooty (Tamil Nadu, India) in November 1990. Voucher specimens have been deposited in the herbarium of Botanical Survey of India (BSI), Southern Circle, TNAU campus, Coimbatore (Tamil Nadu, India).

Extraction and isolation. Crushed and dried stems (1.35 Kg) of *P. wightii* were extracted successively in a soxhlet apparatus with petroleum ether, dichloromethane and methanol. The dark brown petroleum ether extract (21 g) was flash column chromatographed with a gradient solvent system of petroleum ether and ethyl acetate, increasing the concentration of ethyl acetate stepwise and forty seven fractions were collected. Fractions 25 to 36 (eluted with 35 to 45% ethyl acetate in petroleum ether) were pooled (7.0 g) as they were found by TLC to be a complex mixture and again fractionated into twenty one fractions on a neutral aluminum oxide column with a gradient solvent system of petroleum ether and dichloromethane, increasing the concentration of dichloromethane stepwise. Repetitive preparative TLC of fractions 14-17 (eluted with 30% dichloromethane in petroleum ether) in a solvent system of ethyl acetate/petroleum ether and ethyl acetate/benzene yielded **1**, **2** and **3**. Preparative TLC of fraction 11 (eluted with 25% dichloromethane in petroleum ether) in a solvent system of 10% ethyl acetate in petroleum ether yielded **4**. Similarly, repetitive preparative TLC of fraction 13 (eluted with 10% dichloromethane in petroleum ether) on a silica gel 60 $PF_{254+366}$ and Merck kieselgel 60 F_{254} preparative plate in a solvent system of ethyl acetate / petroleum ether and ethyl acetate / benzene yielded a diastereomeric pair of known neolignans, **5** and **6**.[10]

4’,5’-Dimethoxy-3,4-methylenedioxy-2’-oxo-$\Delta^{3',5',8'}$*-8.1’-lignan (6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one)* (**1**). White gummy solid (25 mg); $C_{21}H_{24}O_5$ (M^+ 356.1629, Calcd. 356.1624); $[\alpha]_D^{24}$ -2.26 (c 1.03, $CHCl_3$); IR ($CHCl_3$) cm^{-1}. 1722, 1657, 1626, 1582, 1504, 1490, 1455, 1442, 1407, 1246, 1230, 1209, 1188, 1086 and 1042; UV ($CHCl_3$) nm. 248, 289 and 312(sh); ^1H NMR (500 MHz): δ 0.69 (3H, d, J = 6.1, H-9), 2.07 (1H, dd, J = 13.1 and 11.8, H_a-7), 2.12 (1H, m, H-8), 2.46 (1H, dd, J = 12.0 and 7.0, H_a-7’), 2.75 (1H, dd, J = 12.0 and 7.0, H_b-7’), 2.94 (1H, dd, J = 11.8 and 2.0, H_b-7), 3.75 (3H, s, CH_3O-4’), 3.80 (3H, s, CH_3O-5’), 4.94-5.05 (2H, m, H-9’), 5.19 (1H, s, H-3’), 5.50 (1H, s, H-6’), 5.53-5.59 (1H, m, H-8’), 5.91 (2H, s, $-OCH_2O-$), 6.55 (1H, dd, J = 7.8 and 1.4, H-6), 6.63 (1H, d, J = 1.4, H-2) and 6.70 (1H, d, J = 7.8, H-5); ^{13}C NMR (62.9 MHz): δ 13.8 (C-9), 36.9 (C-7), 42.9 (C-7’), 44.7 (C-8), 55.3, 56.2, 56.3 (CH_3O-4’, CH_3O-5’, C-1’), 100.6 ($-OCH_2O-$), 102.8 (C-3’), 107.9 (C-6’), 109.3, 109.8 (C-2, C-5), 117.6 (C-9’), 121.8(C-6), 133.0 (C-8’), 134.4 (C-1), 145.6 (C-5’), 147.4, 148.0 (C-3, C-4), 166.3 (C-4’) and 202.4(C-2’); EIMS, m/z (% rel. int.): 356 (M^+, 7), 315 (14), 284 (1), 221 (2), 194 (100), 179 (14), 163 (10), 162 (12), 135 (60), 105 (7), 79 (3), 77 (8), 69 (2) and 51 (2).

Iso-4’,5’-dimethoxy-3,4-methylenedioxy-2’-oxo-$\Delta^{3',5',8'}$*-8.1’-lignan (iso-6-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-3,4-dimethoxy-6-(2-propenyl)-2,4-cyclohexadien-1-one)* (**2**). Pale yellow oil (8.5 mg); $C_{21}H_{24}O_5$ (M^+ 356.1626, Calcd. 356.1624); $[\alpha]_D^{24}$ -14.8 (c 0.3, $CHCl_3$); IR (KBr) cm^{-1}. 1733, 1662, 1635, 1611, 1582, 1504, 1490, 1443, 1407, 1373, 1246, 1221, 1170, 1089 and 1039; UV ($CHCl_3$) nm. 245 and 288; ^1H NMR (250 MHz): δ 0.88 (3H, d, J = 6.9, H-9), 2.03 (1H, dd, J = 13.1 and 11.3, H_a-7), 2.29-2.47 (2H, m, H-8 & H_a-7’), 2.55-2.68 (2H, m, H_b-7 & H_b-7’), 3.79 (3H, s, CH_3O-4’), 3.84 (3H, s, CH_3O-5’), 4.90-5.05 (2H, m, H-9’), 5.27 (1H, s, H-3’), 5.57 (1H, s, H-6’), 5.48-5.60 (1H, m, H-8’), 5.92 (2H, s, $-OCH_2O-$), 6.55 (1H, dd, J = 7.8 and 1.3, H-6), 6.62 (1H, d, J = 1.3, H-2) and 6.70 (1H, d, J = 7.8, H-5); ^{13}C NMR (62.9 MHz): δ 12.6 (C-9), 38.3 (C-7), 43.5 (C-7’), 44.6 (C-8), 55.3, 56.3, 56.5 (CH_3O-4’, CH_3O-5’, C-1’), 100.6 ($-OCH_2O-$), 103.0 (C-3’), 107.7 (C-6’), 109.0, 109.5 (C-2, C-5), 117.6 (C-9’), 121.9 (C-6), 132.8 (C-8’), 134.6 (C-1), 145.5 (C-5’), 148.2, 148.9 (C-3, C-4), 166.8 (C-4’) and 203.5 (C-2’); EIMS, m/z (% rel. int.): 356 (M^+, 19), 315 (37), 284 (2), 271 (2), 194 (50), 162 (10), 153 (10), 149 (16), 135 (100), 103 (12), 99 (14), 85 (36), 83 (44), 73 (55), 55 (34), 43 (89), 41 (30), 29 (22) and 28 (15).

1’,2’-Dimethoxy-3,4-methylenedioxy-4’-oxo-$\Delta^{2',5',8'}$*-8.5’-lignan (2-[2-(1,3-benzodioxol-5-yl)-1-methylethyl]-4,5-dimethoxy-4-(2-propenyl)-2,5-cyclohexadien-1-one)* (**3**). Yellow viscous oil (5 mg); $C_{21}H_{24}O_5$ (M^+ 356.1633, Calcd. 356.1624); $[\alpha]_D^{24}$ -22.7 (c 0.25, $CHCl_3$); IR (film) cm^{-1}. 2928, 1737, 1663, 1631, 1611, 1504, 1490, 1442, 1371, 1246, 1221, 1170, 1089 and 1039; UV ($CHCl_3$) nm. 248 and 286; ^1H NMR (250 MHz): δ 1.07 (3H, d, J = 6.9, H-9), 2.43-2.61 (2H, m, H-7'), 2.58 (1H, dd, J = 13.7 and 11.3, H_a-7), 2.82 (1H, dd, J = 13.7 and 6.8, H_b-7), 2.95 (3H, s, CH_3O-1'), 3.17 (1H, m, H-8), 3.76 (3H, s, CH_3O-2'), 4.90 (2H, m, H-9'), 5.34 (1H, m, H-8'), 5.65(1H, s, H-3'), 5.87 (2H, s, -OCH_2O-), 6.09 (1H, s, H-6') and 6.57-6.69 (3H, m, Ar-H); ^{13}C NMR (62.8 MHz): δ 19.6 (C-9), 33.7 (C-7), 41.3 (C-7'), 42.9 (C-8), 52.3 (CH_3O-1'), 55.7 (CH_3O-2'), 77.2 (C-1'), 100.6 (-OCH_2O-), 105.3 (C-3'), 107.8 (C-2), 109.4 (C-5), 119.0 (C-9'), 121.9 (C-6), 130.9 (C-8'), 134.2 (C-1), 140.0 (C-6'), 145.8(C-3), 146.0 (C-5'), 147.6 (C-4), 171.9 (C-2') and 186.8 (C-4'); EIMS, m/z (% rel. int.): 356 (M^+, 16), 316 (7), 315 (35), 284 (2), 221 (2), 194 (7), 193 (6), 162 (5), 153 (9), 135 (100), 105 (5), 77 (12), 51 (3), 41 (3) and 28 (3).

Rel-(7S,8S,7'S,8'S)-3',4'-dimethoxy-3,4-methylenedioxy-8.8',7.O.7'-lignan(2S,3S,4S,5S)-5-[5-(3,4-dimethoxyphenyl)-3,4-dimethyl-2-tetrahydrofuranyl]-1,3-benzodioxol) (**4**). Colourless viscous oil (3 mg); $C_{21}H_{24}O_5$ (M^+ 356.1633, Calcd. 356.1624); $[\alpha]_D^{24}$ -41.7 (c 0.15, $CHCl_3$); IR ($CHCl_3$) cm^{-1}. 1515, 1505, 1489, 1463, 1445, 1247, 1163, 1141, 1102 and 1031; UV ($CHCl_3$) nm. 245 and 283; ^1H NMR see Table 1; ^{13}C NMR (125.7 MHz): δ 13.80, 13.82 (C-9, C-9'), 50.83, 51.16 (C-8, C-8'), 55.90, 55.91 (CH_3O-3', CH_3O-4'), 88.25, 88.31 (C-7, C-7'), 100.93 (-OCH_2O-), 106.51, 107.94 (C-2, C-2'), 109.30, 110.91 (C-5, C-5'), 118.67, 119.70 (C-6, C-6'), 134.80, 136.57 (C-1, C-1'), 146.99, 147.70, 148.57, 148.11 (C-3, C-4, C-3', C-4'); EIMS, m/z (% rel. int.): 356 (M^+, 76), 344 (5), 271 (5), 206 (Ar^1CH-$CH(Me)$-$CHMe^+$, 72), 194 ($Ar^1COCH_2Me^+$, 16), 190 ($ArCH$-$CH(Me)$-$CHMe^+$, 100), 178 ($Ar^1CH{=}CHMe^+$ or $ArCOCH_2Me^+$, 47), 175 (43), 166 ($Ar^1CH{=}O^+$, 12), 165 (Ar^1CO^+, 34), 162 ($ArCH{=}CHMe^+$, 23), 151 (20), 150 ($ArCH{=}O^+$, 14), 149 ($ArCO^+$, 32), 146 (29), 135 (18), 117 (11), 91 (14), 83 (16), 69 (22), 57 (28), 43 (28), 28 (75) and 18 (73).

Rel-(7S,8R,3'R,1'S)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$*-8.3',7.O.2'-lignan (fargesone A,* **5**). Colourless viscous oil (7.9 mg); $[\alpha]_D^{24}$ -132.8 (c 0.27, $CHCl_3$) (lit[10] $[\alpha]_D$ -150, c 1.1, $CHCl_3$). IR, UV, ^1H and ^{13}C NMR and EIMS spectra were identical with those reported.[10]

Rel-(7S,8R,3'R,1'R)-3',4'-dimethoxy-3,4-methylenedioxy-6'-oxo-$\Delta^{4',8'}$*-8.3',7.O.2'-lignan (fargesone B,* **6**). Colourless viscous oil (3 mg); $[\alpha]_D^{24}$ -103.2 (c 0.12, $CHCl_3$) (lit[10] $[\alpha]_D$ -196, c 1.0, $CHCl_3$). IR, UV, ^1H and ^{13}C NMR and EIMS spectra were identical with those reported.[10]

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