Isolation and Characterization of Phenolic Compounds from Magnoliae Cortex Produced in China

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A chemical examination of Magnoliae Cortex produced in China (*Magnolia officinalis* REHD. *et* WILS., Magnoliaceae) has led to the isolation of eighteen new lignans and related compounds [four monoterpenyl-lignans: piperitylmagnolol (3), dipiperitylmagnolol (4), piperitylhonokiol (5) and bornylmagnolol (6); seven lignans: magnaldehydes B(8), C(9), magnolignans A(10), B(11), C(12), D(13) and E(14); three norlignans: magnatriol B(16), magnaldehydes D(17) and E(18); and four dilignans: magnolignans F(19), G(20), H(21) and I(22)], together with randainal (7), randaiol (15), sinapic aldehyde, syringaresinol, syringaresinol 4′-*O*-*β*-D-glucopyranoside and 6′-*O*-methylhonokiol. Their structures were determined by the chemical and spectral methods.

Keywords *Magnolia officinalis*; Magnoliaceae; lignan; piperitylmagnolol; piperitylhonokiol; bornylmagnolol; magnatriol; magnaldehyde; magnolignan; randainal

Magnoliae Cortex, the bark of *Magnolia officinalis* REHD. *et* WILS. (Magnoliaceae) is a Chinese crude drug used as a repression drug for turgescence of the thoreco-abdominal region, and a stomachic.[1)] With regard to the ingredients of the magnoliae species, lignans such as magnolol (**1**)[2)] and honokiol (**2**),[3)] and alkaloids[4)] are known, however, the minor constituents of this crude drug have not yet been surveyed. We have now obtained eighteen new lignans and related compounds together with **1**, **2**, randainal (**7**),[5)] randaiol (**15**),[5)] 1-(4-hydroxy-3-methoxyphenyl)-2-[4-(*ω*-hydroxypropyl)-2-methoxyphenoxy]propane-1,3-diol (**23**),[6)] sinapic aldehyde (**24**), syringaresinol (**25**), syringaresinol 4′-*O*-*β*-D-glucopyranoside (**26**), 6′-*O*-methylhonokiol (**27**).[7)] This paper deals with the structural characterization of the new compounds of monoterpenyl-lignans: piperitylmagnolol (**3**), dipiperitylmagnolol (**4**), piperitylhonokiol (**5**) and bornylmagnolol (**6**); lignans: magnaldehydes B(**8**) and C(**9**), magnolignans A(**10**), B(**11**), C(**12**), D(**13**) and E(**14**); norlignans: magnatriol B(**16**), magnaldehyde D(**17**) and E(**18**); and dilignans: magnolignans F(**19**), G(**20**), H(**21**) and I(**22**).

Monoterpenyl-Lignans Piperitylmagnolol (**3**), colorless viscous oil, $[\alpha]_D$ −146.0° ($CHCl_3$), showed the ultraviolet (UV) absorption [λ_{max}^{MeOH} (ε): 290 nm (8500)] and circular dichroism (CD) spectrum [$\theta]_{max}^{MeOH}$ (nm): $+7.22\times10^3$ (254), $+2.50\times10^3$ (292). It has a molecular formula $C_{28}H_{34}O_2$ (*m/z* 402.257), which is based on its electron impact mass spectrum (EI-MS) and nuclear magnetic resonance (NMR) spectra. It afforded a dimethyl ether (**3a**) on methylation. In the ^{1}H-NMR spectrum of **3**, signals at *δ* 0.80, 0.88 (each 3H, d, *J*=6 Hz), and 1.70 (3H, br s) were assignable to the methyl groups, and signals at *δ* 3.30 (4H, d, *J*=6 Hz), 5.00 (2H, br d, *J*=11 Hz), 5.02 (2H, br d, *J*=18 Hz) and 5.75—6.20 (2H, m) were similar to those of the allyl group in magnolol and five aromatic protons at *δ* 6.79 (m) were observed. The ^{13}C-NMR spectrum (Table I) of **3** revealed the presence of twelve aromatic carbons at *δ* 116.4 (d), 125.0×2 (s), 129.0×2 (d), 129.8 (d), 131.1 (d), 132.0×2 (s), 132.4 (s), 148.9 (s) and 150.8 (s) and two allyl group carbons at *δ* 39.3×2 (t), 115.3×2 (t) and 137.3×2 (d). Moreover, the remaining ten carbon signals indicated the occurrence of three methyl groups at *δ* 16.8, 21.6 and 23.5, a trisubstituted olefinic carbon at *δ* 124.3 (d) and 136.8 (s), three methine carbons at *δ* 27.0, 41.0 and 44.8, and two methylene carbons at *δ* 21.6 and 30.1. From the above evidence, **3** was assumed to be a monoterpenyl magnolol derivative. The monoterpenyl residue consisting of $C_{10}H_{17}$ was suggested by the ^{1}H-NMR spectrum to contain two methyl groups at *δ* 0.80 and 0.88, a trisubstituted olefinic proton at *δ* 5.40 (1H, br s), a methine proton at *δ* 3.60 (1H, m) coupled with the olefinic proton and a methyl group at *δ* 1.70 attached to a double bond. These signals were almost the same as those of a menthane-type monoterpene. Comparison of the ^{13}C-NMR spectra of the substituent in **3** with those of menthane, menthol, limonene and *p*-menth-1-ene (piperityl) moiety of linderatin[8)] revealed that the chemical shifts of the carbon atoms were similar to those of the *p*-menth-1-ene moiety of linderatin. Oxidation of the tetrahydrogenated compound (**3b**), obtained by the mild hydrogenation over Pd–C of **3**, with *m*-chloroperbenzoic acid, yielded a product (**3c**) (Chart 2), whose ^{1}H-NMR spectrum showed an epoxy methine proton signal at *δ* 4.27 (1H, d, *J*=6 Hz) and a benzylic methine proton signal at *δ* 3.02 (1H, dd, *J*=6, 11 Hz) coupled with the epoxy methine proton and C-4″ (*δ* 1.10, 1H, m) methine proton, suggesting the occurrence of a partial structure of *p*-menth-1″-ene-3″,4″-*trans* system (piperityl) for the substituent in **3**, and this result furthermore indicated that the magnolol moiety in **3** was linked at the C-3 carbon atom of the piperityl structure. As regards the bonding location into the magnolol side, the signal of one magnolol unit was shifted by +15.5 ppm at C-5 in the ^{13}C-NMR spectrum. Therefore, the structure of **3** was deduced to be 3″, 4″-*trans*-piperityl-(3″→5)-magnolol. In order to establish this structure involving the configurations at C-3″ and C-4″ on the piperityl moiety in **3**, dimethyltetrahydrate (**3d**), obtained by the methylation and hydrogenation of **3**, was treated with SeO_2 to give an oxidative product (**3e**). Next, **3e** was subjected to reduction with $NaBH_4$ to afford two C-6″-hydroxyl products **3f** and **3g** (Chart 2). Both compounds **3f** and **3g** showed a peak at *m/z* 450 due to M^+ in the EI-MS. Respective signals at *δ* 4.35 (1H, dd, *J*=11, 4 Hz) and 4.04 (1H, br t, *J*=4 Hz) in the ^{1}H-NMR spectra of **3f** and **3g** could be assigned to H-6″. Consequently, **3f** and **3g** could be represented as 6″-equatorial and 6″-axial hydroxyl products, respectively. The configuration at C-6″ of the two epimeric products were determined by the modified Horeau's method[9)] to be *S* for **3f** (6″-equatorial

hydroxyl) and *R* for **3g** (6″-axial hydroxyl). Consequently, the configuration on C-3″ and C-4″ of the piperityl moiety in **3** could be represented as 3 (*S*), 4 (*S*). The structure of **3** was concluded to be as shown in the formula.

Dipiperitylmagnolol (**4**), a white powder, $[\alpha]_D$ −140.0° ($CHCl_3$) showed a maximum absorption band at 290 nm ($\varepsilon = 10200$) in the UV spectrum. The EI-MS of **4** presented a molecular ion peak at *m/z* 538.373, indicating the molecular formula to be $C_{38}H_{50}O_2$. In the ^{1}H-NMR spectrum, the characteristic signals were due to the piperityl groups and substituted magnolol moiety. These spectral data indicated that **4** was a magnolol substituted symmetrically by the two piperityl groups. The ^{13}C-NMR (Table I) signals also indicated the presence of the piperityl moieties and the magnolol moiety di-substituted at C-5 and C-5′ in a symmetrical structure, showing down-field shifts at C-5 and C-5′ carbons (+15.8 ppm) by comparing with those of magnolol. Compound **4** was therefore considered to be dipiperityl-(3″→5 and 3‴→5′)-magnolol. The configurations at C-3″, C-3‴, C-4″ and C-4‴ in **4** were established as *S*, *S*, *S* and *S*, respectively, by reason of a comparative study of the Cotton curves in the CD spectra of **3** and **4** [255 nm (+1.04 × 10^4) and 294 nm (+4.96 × 10^3)]. Therefore, the structure of **4** could be represented as shown in the formula.

Piperitylhonokiol (**5**) was obtained as a colorless viscous oil, $[\alpha]_D$ −97.0° ($CHCl_3$), $C_{28}H_{34}O_2$, showed a maximum absorption at 290 nm in the UV spectrum. In the EI-MS, the same molecular ion peak at *m/z* 402 as that of **3** was obtained, thus **5** was estimated to be an isomer of **3**. The ^{13}C-NMR spectrum (Table I) of **5** exhibited piperityl moiety and honokiol moiety signals, in which the C-5 or C-5′ signal

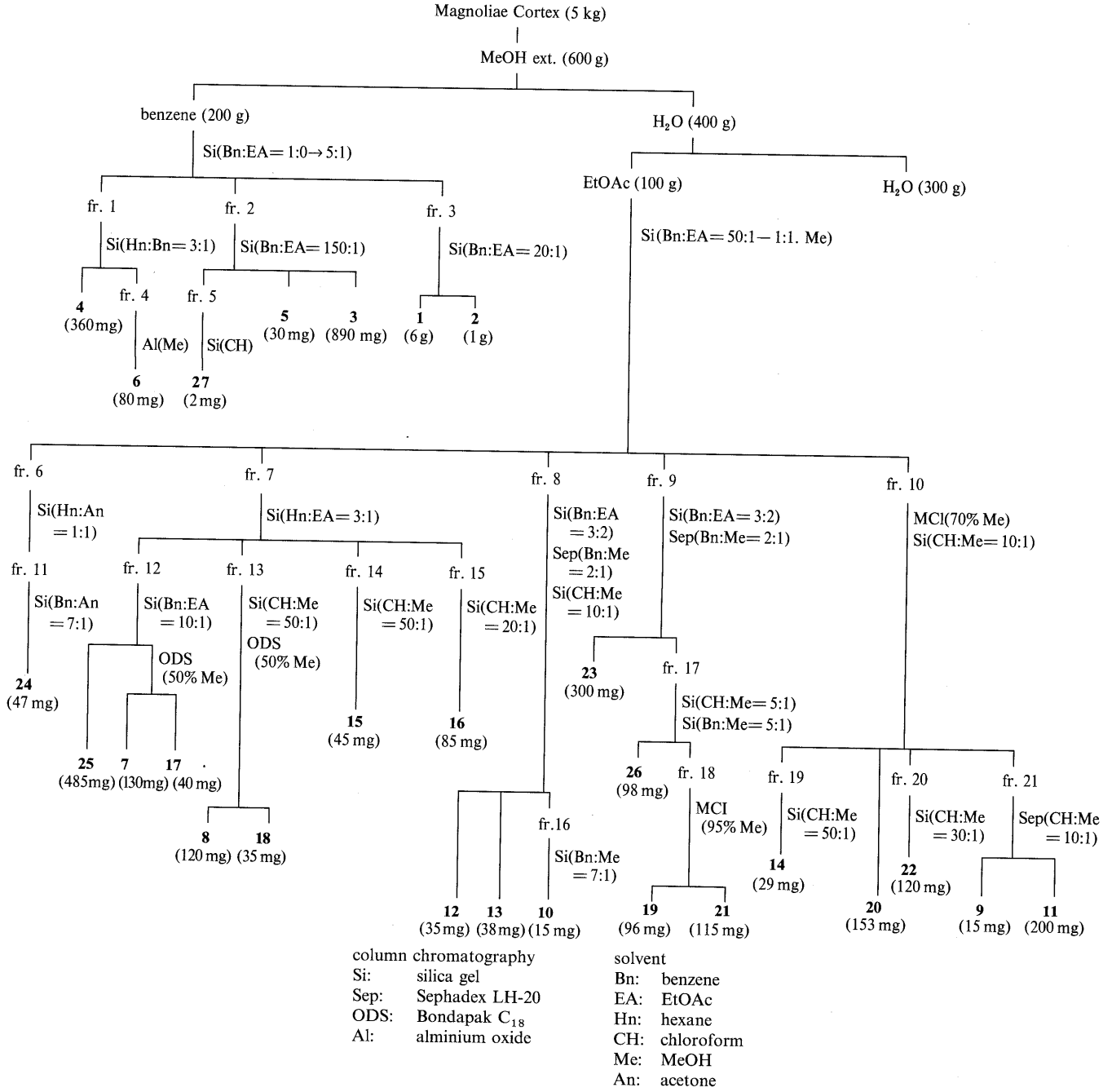


Chart 1. Extraction and Separation of Magnoliae Cortex

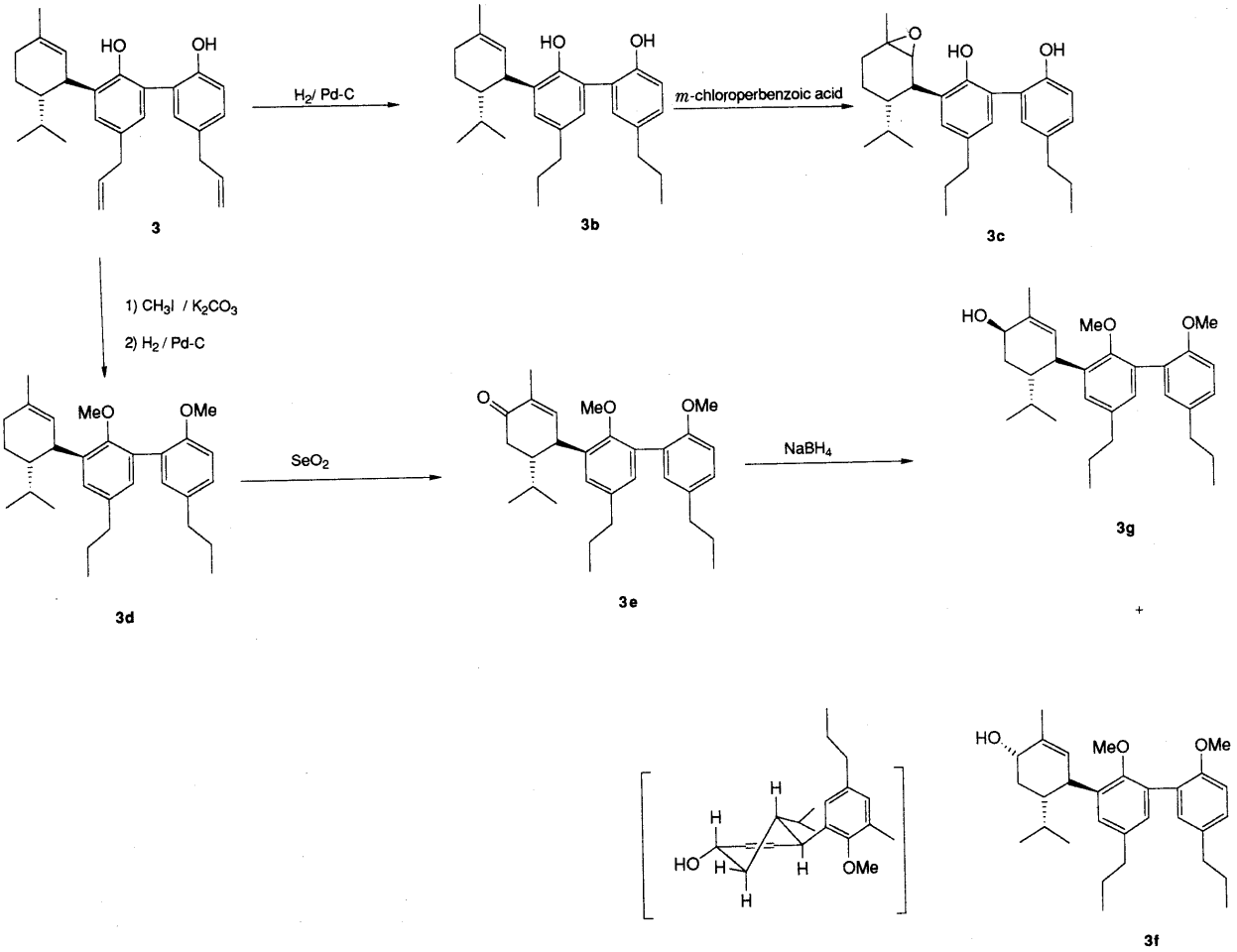
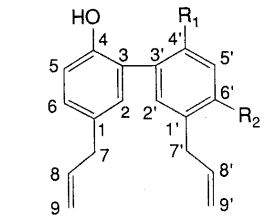
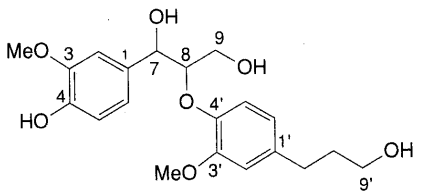


Chart 2

known compounds

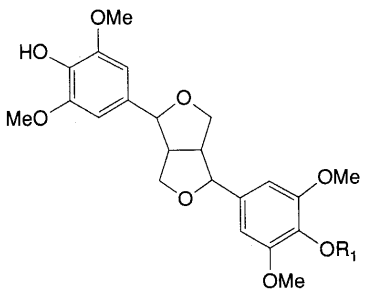


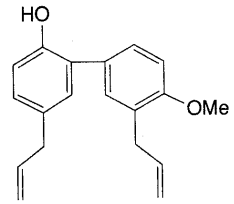
magnolol (1) : R_1= OH, R_2= H
honokiol (2) : R_1= H, R_2= OH

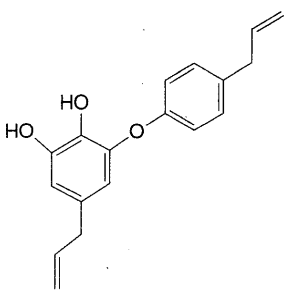


23

sinapic aldehyde (24)



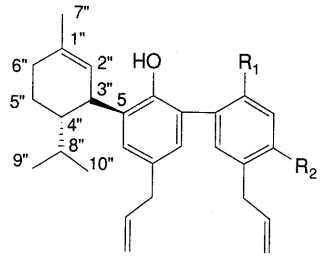




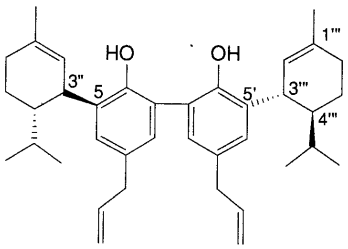
6'-*O*-methylhonokiol (27)

obovatol (29)

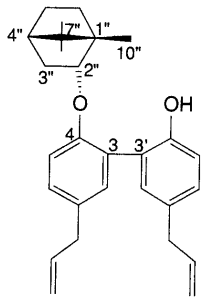
syringaresinol (25) : R_1= H
syringaresinol 4'-*O*-glucopyranoside (26) : R_1= glc



piperitylmagnolol (3) : R_1= OH, R_2= H
piperitylhonokiol (5) : R_1= H, R_2= OH



dipiperitylmagnolol (4)



bornylmagnolol (6)

TABLE I. ^{13}C-NMR Data for **1**, **2**, **3**, **4**, **5**, **6** and Borneol ($CDCl_3$)

	1	2	3	4	5	6	Borneol
C-1	132.9	132.1	132.0[a]	132.0	131.2	133.4	
C-2	131.2	130.7	129.0[b]	129.9	131.4	132.3[a]	
C-3	124.7	126.4	125.0	125.4	125.7	128.0	
C-4	150.8	150.1	148.9	149.5	149.3	153.3	
C-5	116.5	115.3	132.0	132.2	131.0	117.2	
C-6	129.3	130.0	129.0[b]	129.2	129.4	129.1[b]	
C-7	39.5	39.2	39.3	39.5	39.5	39.4	
C-8	137.2	137.4	137.3	137.5	138.0	137.9[c]	
C-9	115.2	115.4	115.3	115.4	115.3	115.7[d]	
C-1′	132.9	127.7	132.4[a]	132.0	128.2	131.9	
C-2′	131.2	128.0	131.1	129.9	128.2	131.0[a]	
C-3′	124.7	129.3	125.0	125.4	130.7	126.6	
C-4′	150.8	128.4	150.8	149.5	128.9	152.0	
C-5′	116.5	116.0	116.4	132.2	116.0	114.7	
C-6′	129.3	153.2	129.8[b]	129.2	153.5	128.9[b]	
C-7′	39.5	34.6	39.3	39.5	35.2	39.4	
C-8′	137.2	135.8	137.3	137.5	136.3	137.4[c]	
C-9′	115.2	116.2	115.3	115.4	116.7	115.3[d]	
C-1″			136.8	136.5	137.0	49.5	49.4
C-2″			124.3	124.8	124.7	87.0	76.9
C-3″			44.8	44.9	44.4	36.7	38.7
C-4″			41.0	40.7	41.4	44.9	45.1
C-5″			21.6	21.6	21.6	26.7	26.0
C-6″			30.1	30.1	30.2	27.8	28.3
C-7″			23.5	23.6	23.5	47.7	47.9
C-8″			27.0	27.6	27.5	19.3	20.2
C-9″			16.8	17.0	16.7	18.9	18.7
C-10″			21.6	21.6	21.6	13.6	13.3
C-1‴				136.5			
C-2‴				124.8			
C-3‴				44.9			
C-4‴				40.7			
C-5‴				21.6			
C-6‴				30.1			
C-7‴				23.6			
C-8‴				27.6			
C-9‴				17.0			
C-10‴				21.6			

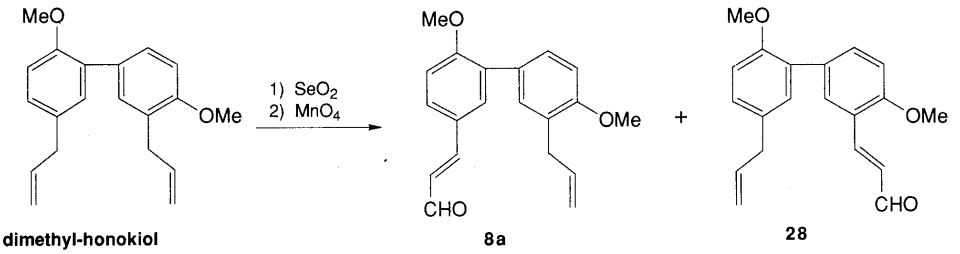
a—d) Assignments are interchangeable in each column.

was shifted to δ 131.0, thus **5** was presumed to be bonding through the C-3″ of the piperityl moiety and C-5 or C-5′ of the honokiol moiety. The proton selective decoupling ^{13}C-NMR spectrum of **5** showed a long-range coupling between the H-3″ proton signal at δ 3.50 and the C-4 carbon signal at δ 149.3, thus **5** was concluded to be linked through C-3″ and C-5. The CD spectrum of **5** showed positive Cotton curves at 248 and 293 nm suggesting configurations at C-3″ and C-4″ to be *S* and *S*, respectively. Therefore, the structure of **5** could be represented as shown in the formula.

Bornylmagnolol (**6**), a colorless viscous oil, $[\alpha]_D$ −7.6° ($CHCl_3$) has a molecular formula, $C_{28}H_{34}O_2$ (*m/z* 402.254) based on its EI-MS, and afforded a monoacetate (*m/z* 444 in EI-MS) on acetylation. The ^{1}H-NMR spectrum of **6** showed three singlets of methyl groups at δ 0.80, 0.83 and 0.87, a signal at δ 4.38 (1H, dd, J=9, 3 Hz) for an axial hydrogen geminal to the ether linkage (this signal showed non-shift on acetylation), two allyl groups signals at δ 3.36 (4H, br d, J=7 Hz), 4.90—5.20 (4H, m) and 5.75—6.23 (2H, m), a hydroxy proton signal at δ 6.28 and six aromatic proton signals at δ 6.79—7.23, which suggested **6** to be a monoterpenyl-magnolol. The ^{13}C-NMR (Table I) signals also indicated the presence of a magnolol moiety and a monoterpenyl moiety, the latter of which consisted of three methyl groups (δ 13.6, 18.9 and 19.3), an oxygenated methine (δ 87.0), three methylenes (δ 26.7, 27.8 and 36.7), a methine (δ 44.9) and two quaternary carbons (δ 47.7 and 49.5). These signals were almost the same as those of borneol except for the C-2 carbon signal, which was shifted down-field by +10.1 ppm. From the above evidence, the chemical structure of **6** was estimated to involve an ether linkage through C-4-OH in magnolol and C-2 in borneol. As regards the configuration of the bornyl moiety, the optical rotation ($[M]_D$ −30.6°) of **6** was compared with that of (−)-borneol methyl ether ($[M]_D$ −82.5°), thus suggesting **6** should be (−)-bornyl group. Consequently, the structure of **6** could be represented as shown in the formula.

Lignans Randainal (**7**) was obtained as pale yellow needles, mp 135—138 °C, showed a molecular ion peak at *m/z* 280 in the EI-MS. The infrared (IR) spectrum showed the presence of a hydroxyl group (3550 cm^{-1}), α,β-unsaturated carbonyl group (1675 and 1625 cm^{-1}) and aromatic group (1605 cm^{-1}). The compound **7** was identified as randainal isolated previously from *Sassafras randaiense*.[5]

Magnaldehyde B(**8**), pale yellow needles, mp 155—158 °C, $C_{18}H_{16}O_3$, showed absorption bands due to a hydroxyl (3550 cm^{-1}), an α,β-unsaturated carbonyl (1675 and 1625 cm^{-1}) and aromatic groups (1605 cm^{-1}) in the IR spectrum. In the EI-MS, the same molecular ion peak at *m/z* 280 as that of **7** was obtained, thus **8** was estimated to be an isomer of **7**. The ^{1}H-NMR spectrum of **8** exhibited two ABX type aromatic signals [δ 6.92, 7.03 (each 1H, d, J=8 Hz, H-5, 5′), 7.33, 7.51 (each 1H, dd, J=8, 2 Hz, H-6, 4′) and 7.37, 7.60 (each 1H, d, J=2 Hz, H-2, 2′)], an allyl



dimethyl-honokiol **8a** **28**

Chart 3

TABLE II. ^{13}C-NMR Data for **7**, **8**, **9**, **10**, **11**, **12**, **13** and **14** (in Acetone-d_6)

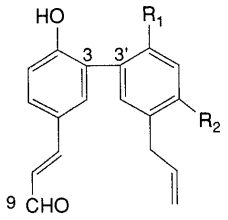
	7	8	9	10	11	12	13	14
C-1	127.7	126.8	127.0[a]	131.9[a]	132.6[a]	130.8[a]	130.9[a]	131.7[a]
C-2	133.6	131.6	130.1[b]	132.4	128.1	131.9[b]	130.3[b]	128.7[b]
C-3	127.0	126.8	128.0[a]	131.0[a]	126.7[b]	128.8	129.0[a]	129.6[c]
C-4	158.1	158.2	158.5	153.0	153.0[c]	153.0	154.8[c]	153.1
C-5	117.7	117.7	117.8	117.2[b]	117.1[d]	115.3[c]	115.4[d]	116.8
C-6	132.2	132.3	133.2[c]	133.3	132.5	131.6[b]	131.7[b]	131.7[d]
C-7	154.8	155.0	155.0	40.0	77.2	39.7	85.1	39.8
C-8	126.3	126.2	126.5	74.1	74.5	74.0	76.7	139.1
C-9	195.2	195.1	195.3	66.5	63.9	66.1	63.5	115.4
C-1′	132.2	129.6[a]	131.2	133.2[a]	135.2[a]	126.5	126.8	132.3[a]
C-2′	130.1	128.9	130.8[b]	130.5	130.9	128.8	129.0[b]	127.4[b]
C-3′	125.5	130.1[a]	125.4[a]	131.9[a]	127.2[b]	130.9[a]	130.8[a]	129.0[c]
C-4′	152.9	129.5	153.2	153.0	154.0[c]	129.3[b]	127.8[b]	131.2[d]
C-5′	116.9	115.4	115.8	117.4[b]	117.4[d]	116.5[c]	116.8[d]	110.1
C-6′	129.8	155.0	133.8[c]	129.8	129.6	154.5	154.6[c]	161.7
C-7′	39.7	34.9	39.5	40.0	40.0	34.9	35.0	92.0
C-8′	138.7	137.9	73.9	139.1	139.1	138.0	138.1	73.8
C-9′	115.6	115.5	66.0	115.5	115.5	115.3	115.5	62.7
OMe							56.7	

a—*d*) Assignments are interchangeable in each column.

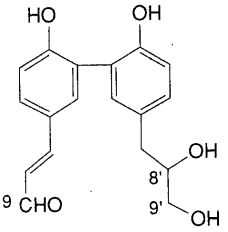
group and an α,β-unsaturated aldehyde group signal [δ 6.75 (1H, dd, $J=16$, 8 Hz, H-8), 7.60 (1H, d, $J=16$ Hz) and 9.62 (1H, d, $J=8$ Hz, H-9)], thus suggesting that **8** was an isomer (honokiol type) of **7**. The ^{13}C-NMR spectrum of **8** exhibited a benzylic methylene signal (δ 34.9) and a terminal vinyl carbon signal (δ 115.5 and 137.9), which were similar with the allyl group signals in the *ortho*-allyl-phenol type, thus suggesting that **8** might be the 9-aldehyde type of honokiol. Treatment of honokiol dimethyl ether with SeO_2 and then with MnO_2 resulted in the formation of two oxidative products (**8a** and **28**) (Chart 3). The physical constants of **8a** agreed well with those of dimethylmagnaldehyde B prepared by methylation. Compound **28** was estimated as the 9′-aldehyde type of honokiol, an isomer of **8a**, by the nuclear Overhauser effect (NOE) experiment. All physical data of **8** were identical with those of the synthetic product.[10] Consequently, the structure of **8** could be represented as shown in the formula.

Magnaldehyde C(**9**), a pale yellow powder, $[\alpha]_D$ −15.5° (MeOH), IR ν_{max}^{KBr} 1655 cm^{-1} (α,β-unsaturated carbonyl), has a molecular ion peak at m/z 314 in the field desorption (FD)-MS. The ^{1}H-NMR spectrum of **9** exhibited signals due to a benzylic methylene [δ 2.65 (1H, dd, $J=14$, 8 Hz) and 2.84 (1H, dd, $J=14$, 5 Hz)], which coupled with an oxygenated methine proton [δ 3.80 (m)], two oxygenated methylene protons [δ 3.56 (m)], an α,β-unsaturated aldehyde group [δ 6.66 (1H, dd, $J=16$, 8 Hz), 7.70 (1H, d, $J=16$ Hz) and 9.62 (1H, d, $J=8$ Hz)] and six aromatic protons [δ 6.97—7.62 (m)]. The ^{13}C-NMR spectrum (Table II) of **9**, indicated distinctions in the two signals at C-8′ and C-9′ in the propyl moiety in comparison with those of **7**.

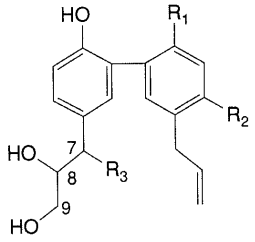
lignans

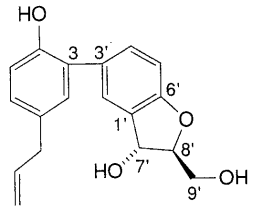


randainal (7) : R_1= OH, R_2= H
magnaldehyde B (8) : R_1= H, R_2= OH



magnaldehyde C (9)

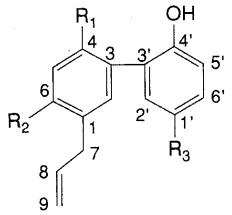




magnolignan A (10) : R_1= OH, R_2=R_3= H
magnolignan B (11) : R_1=R_3= OH, R_2= H
magnolignan C (12) : R_1=R_3= H, R_2= OH
magnolignan D (13) : R_1= H, R_2= OH, R_3= OMe

magnolignan E (14)

norlignans



randaiol (15) : R_1=R_3= OH, R_2= H
magnatriol B (16) : R_1= H, R_2=R_3= OH
magnaldehyde D (17) : R_1= OH, R_2= H, R_3= CHO
magnaldehyde E (18) : R_1= H, R_2= OH, R_3= CHO

The above evidence suggested that the structure of **9** corresponds to that of **7** possessing two hydroxy groups at C-8′ and C-9′. The structure of **9** was thus concluded to be as shown in the formula.

Magnolignan A(**10**), a white powder, $[\alpha]_D$ −0.8° (MeOH) showed a molecular ion peak at m/z 300.134, along with m/z 239 ($M^+ - C_2H_5O_2$), indicating a molecular formula to be $C_{18}H_{20}O_4$ in the EI-MS, and was transformed into a tetraacetate on acetylation. The ^{1}H-NMR spectrum of **10** exhibited a benzylic methylene signal [δ 2.64 (1H, dd, $J=14$, 7 Hz) and 2.80 (1H, dd, $J=14$, 5 Hz)], one oxygenated methine and one oxygenated methylene signal [δ 3.82 (1H, m) and 3.50 (2H, m)], an allyl group signal and six aromatic

proton signals. The above evidence suggested that the structure of **10** was 8,9-dihydroxydihydro-magnolol. The ^{13}C-NMR spectrum (Table II) of **10**, when compared with those of **1** and **9**, indicated that the signals in **10** were nearly the same as those in the *para*-8,9-dihydroxypropyl-phenol moiety of **9** and as those in the *para*-allyl-phenol moiety of magnolol. The structure of **10** was then concluded to be as shown in the formula.

Magnolignan B(**11**), a white powder, $[\alpha]_D$ +0.3° (MeOH), showed a molecular ion peak at *m/z* 316 in the FD-MS, suggesting the one additional oxygen atom on **10**. The ^{1}H-NMR spectrum of **11** displayed an allyl group signal, two ABX-type aromatic proton signals [δ 6.90, 6.92 (each 1H, d, J=8 Hz), 7.07, 7.25 (each 1H, dd, J=8, 2 Hz), 7.11, 7.31 (each 1H, d, J=2 Hz)], a benzylic methine proton signal adjacent to the oxygen [δ 4.65 (d, J=6 Hz, H-7)] and one oxygenated methine and one oxygenated methylene signal [δ 3.70 (1H, m) and 3.52 (2H, m), respectively], suggesting that **11** had a hydroxyl group at C-7 in **10**. This inferential structure was supported with the ^{13}C-NMR data as listed in Table II. Therefore, the structure of **11** could be represented as shown in the formula.

Magnolignan C(**12**), a white powder, $[\alpha]_D$ −6.8° (MeOH), afforded a molecular ion peak at *m/z* 300.138 along with *m/z* 239 ($M^+ - C_2H_5O_2$) in the EI-MS, indicating the molecular formula to be $C_{18}H_{20}O_4$, and was transformed into a tetraacetate (**12a**) on acetylation. The ^{1}H-NMR spectrum of **12** exhibited the presence of an allyl group, a benzylic methylene group [δ 2.65 (1H, dd, J=12, 8 Hz), 2.79 (1H, dd, J=12, 6 Hz), H_2-7], one oxygenated methine and one oxygenated methylene group [δ 3.82 (1H, m) and 3.50 (2H, m)] and six aromatic proton signals. From the spectral data analogous to those of **10**, **12** was estimated to be a honokiol type isomer of **10**. The ^{13}C-NMR spectrum (Table II) of **12**, compared with those of **2** and **9**, the location of the hydroxyl groups were revealed to be at C-8 and C-9 positions in the honokiol skeleton. The structure of **12** could be represented as shown in the formula.

Magnolignan D(**13**), a white powder, $[\alpha]_D$ +3.0° (MeOH), exhibited a molecular ion peak at *m/z* 330.150, providing a molecular formula of $C_{19}H_{22}O_5$, besides strong peaks at *m/z* 300, 269 (base peak, $M^+ - C_2H_4O_2$) and 239 (*m/z* 269 − CH_2O) in the EI-MS. Its ^{1}H-NMR spectrum showed the signals of four protons consisting of an oxygenated benzyl methine signal [δ 4.17 (1H, d, J=7 Hz, H-7)] and one oxygenated methylene and one oxygenated methine signal [δ 3.66 (2H, m) and 4.00 (1H, m)]. Besides the above signals, an aliphatic methoxyl signal (δ 3.21), an allyl group signal and two ABX type aromatic signals [δ 6.89, 6.96 (each 1H, d, J=8 Hz), 7.12, 7.50 (each 1H, dd, J=8, 2 Hz) and 7.42, 7.56 (each 1H, d, J=2 Hz)] were observed. This signal pattern was similar to that of one side in **11**, except for the methoxyl signal. The ^{13}C-NMR spectrum, compared with that of **12**, indicated shifts of +45.4, +2.7 and −2.6 ppm in the *para*-propylphenol type C-7, C-8 and C-9, respectively, supporting that the structure of **13** could be 7-methoxylated **12**. Therefore, the structure of **13** was concluded to be as shown in the formula.

Magnolignan E(**14**), a white powder, $[\alpha]_D$ −2.0° (MeOH), showed a molecular ion peak at *m/z* 298 together with fragment peaks at *m/z* 280 ($M^+ - H_2O$) and 250 (*m/z* 280 − CH_2OH) in the FD-MS. The ^{1}H-NMR spectrum of **14** showed signals ascribable to two mutually coupled methines bearing oxygen [δ 4.53 (dd, J=10, 6 Hz) and 5.28 (m, after D_2O exchange J=4 Hz)], an oxygenated methylene proton [δ 3.75 (2H, d, J=6 Hz)], an allyl group and six aromatic proton signals. On methylation, **14** afforded a monomethyl ether (**14a**) [^{1}H-NMR: δ 3.78 (3H, s)]. On acetylation, **14** yielded a triacetate (**14b**) [EI-MS *m/z*: 424 (M^+)]. The location of the acetyl groups in **14b** was determined by comparing the ^{1}H-NMR spectra with those of **14a**. Signals due to the benzylic methine and terminal methylene appeared at δ 6.11 (1H, d, J=4 Hz, H-7′), and at 4.28 (1H, dd, J=6, 12 Hz, H-9′) and 4.42 (1H, dd, J=5, 12 Hz, H-9′) showing acetylation shifts. Taking the chemical shift of the H-8′ signal into account, the C-7′ and C-8′ position were concluded to be on the dihydrobenzofuran ring, compared with those of **2** and **13**. The ^{13}C-NMR spectrum of **14** exhibited to oxygenated methine carbons (δ 73.8 and 92.0) and one oxygenated methylene carbon (δ 62.7). Moreover, the ^{13}C-NMR spectrum of **14**, compared with that of **2**, indicated shifts of +8.5 and −5.9 ppm at C-6′ and C-5′, respectively, also supporting the above deduced structure. The relative stereochemistry of the two substituents on the dihydrobenzofuran ring was concluded to be *trans*, based on the fact that irradiation of the hydroxymethyl H_2-9′ signal (δ 3.75) caused the enhancement of the benzylic H-7′ signal (δ 5.28) in the NOE experiment of **14**. Therefore, the structure of **14** could be represented as shown in the formula.

Norlignans Randaiol (**15**) showed a molecular peak at *m/z* 242 in the EI-MS. The ^{1}H-NMR spectrum of **15** revealed the presence of an allyl group and two ABX type aromatic protons [δ 6.75, 7.05 (each 1H, dd, J=9, 2 Hz), 6.84, 6.94 (each 1H, d, J=9 Hz) and 6.79, 7.11 (each 1H, d, J=2 Hz)]. The compound **15** was identified as randaiol isolated previously from *Sassafras randaiense*.[5]

Magnatriol B(**16**), pale yellow needles, mp 99—100 °C, showed an absorption maximum at 306 nm (ε=5100) in the UV spectrum. In the EI-MS, the same molecular ion peak at *m/z* 242 ($C_{15}H_{14}O_3$) as that of **15** was obtained, thus **16** was estimated to be an isomer of **15**. The ^{1}H-NMR spectrum of **16** showed signals ascribable to an allyl group and two

Table III. ^{13}C-NMR Data for **15**, **16**, **17** and **18** (in Acetone-d_6)

	15	16	17	18
C-1	132.6	126.7	132.5	130.0
C-2	132.2	128.8	131.1[a]	128.9
C-3	127.2[a]	129.9[a]	125.3	129.3
C-4	152.7[b]	131.5	153.4	130.6
C-5	116.2[c]	115.4[b]	117.1[b]	115.5
C-6	129.7	154.6	130.1	155.1
C-7	39.8	34.6	39.9	34.8
C-8	138.8	137.9	139.0	137.8
C-9	115.7	115.4	115.6	115.5
C-1′	151.6[b]	151.2	130.7	130.5
C-2′	118.2[c]	117.5[c]	134.9	133.2
C-3′	127.9[a]	130.9[a]	127.8	127.0
C-4′	147.3	147.6	160.9	160.5
C-5′	117.4[c]	117.4[c]	117.8[b]	117.2
C-6′	118.1[c]	115.0[b]	132.5[a]	131.6
C-7′			191.2	191.3

a—*c*) Assignments are interchangeable in each column.

ABX type aromatic signals. The ^{13}C-NMR spectrum (Table III) of **16**, when compared with that of **15**, indicated shifts of +24.9, −4.9 and −21.2 ppm at C-6, C-7 and C-4, respectively, and other signals were almost the same pattern. On methylation of **16** it afforded a trimethyl ether, which was then hydrogenated to yield a dihydrotrimethyl ether (**16a**) [EI-MS *m/z*: 286 (M^+)]. In the NOE experiments of **16a**, irradiation on the benzylic methylene (H_2-7) signal at δ 2.76 caused enhancement of the H-2 [δ 7.53 (J=3 Hz)], on the other hand, irradiation on the center of the two methoxyl signals (δ 3.36 and 3.37) caused enhancements of the H_2-7 (δ 2.76), H-5 [δ 6.64 (d, J=9 Hz)] and H-5′ [δ 6.66 (d, J=9 Hz)], and irradiation on the methoxyl signal (δ 3.42) caused enhancements of the H-2′ [δ 7.15 (d, J=3 Hz)] and H-6′ [δ 6.80 (dd, J=9, 3 Hz)]. On the basis of these NOE, the structure of **16** was concluded to be as shown in the formula.

Magnaldehyde D(**17**), pale yellow needles, mp 140—143 °C, showed a molecular ion peak at *m/z* 254.093, indicating the molecular formula to be $C_{16}H_{14}O_3$ in the EI-MS. The ^{1}H-NMR spectrum of **17** revealed the presence of an aldehyde proton signal [δ 9.89 (s)], six aromatic proton signals and an allyl group. The above evidence suggested that the structure of **17** was presumed to be allyl-formyl-dihydroxy-biphenyl. In the ^{13}C-NMR spectrum (Table III), signals due to one allyl group [δ 39.9 (t), 115.6 (t) and 139.0 (d)] of the *ortho*-hydroxy-allyl-phenol type, the twelve aromatic signals and an aldehyde signal [δ 191.2 (d)] were observed. These signals were similar to those of **7**, except for the olefinic carbons at C-7 and C-8 in **7**. Therefore, the structure of **17** was concluded to be as shown in the formula.

Magnaldehyde E(**18**), pale yellow needles, mp 160—162 °C, showed a molecular ion peak at *m/z* 254 in the EI-MS, whose molecular weight was the same as that of **17**, thus **18** was estimated to be an isomer of **17**. To decide the location of hydroxyl, aldehyde and allyl groups on the biphenyl, a comparative investigation of the ^{13}C-NMR spectra (Table III) of **8** and **18** had almost the same chemical shifts, except for the olefinic carbons at C-7 and C-8 in **8**. Therefore, the structure of **18** was concluded to be as shown in the formula.

Dilignans Magnolignan F(**19**) showed a molecular ion peak at *m/z* 564 together with fragment ions at *m/z* 546, 282 and 266 in the FD-MS. In the ^{1}H-NMR spectrum, the signals due to three allyl groups, a benzylic methine [δ 4.64 (d, J=5 Hz)] and twelve aromatic protons were observed, which suggested **19** to be a dimeric lignan. The ^{13}C-NMR spectrum of **19** showed signals due to thirty-six carbons, including three signals [δ 70.2 (t), 74.1 (d) and 74.9 (d)] assignable to C-9″, C-8″ and C-7″, whose signal patterns were similar to those of 7,8,9-trihydroxypropyl moiety in **11**, signals of the magnolol type three allyl group and four oxygenated aromatic carbons. On methylation, **19** afforded a trimethyl ether (**19a**) [^{1}H-NMR: δ 3.68, 3.69, 3.73 (each 3H, s)]. Subsequent acetylation of **19a** yielded a diacetate (**19b**). The ^{1}H-NMR spectrum of **19b** exhibited mutually coupled two methine protons [δ 5.30 (m) and 5.82 (d, J=8 Hz)] connecting to the acetoxyl groups (δ 1.92 and 1.99). Hydrogenation of **19a** over Pd–C afforded a hexahydrogenated derivative (**19c**) [EI-MS *m/z*: 612 (M^+)]. From the above evidence, **19** was assumed to be a dilignan compound possessing an ether bonding between **1** and **11**. To determine the location of the ether bond, oxidation of **19c** with sodium metaperiodate was undertaken to yield two products (**19d** and **19e**) (Chart 4). The product **19d** showed a molecular ion at *m/z* 284 in the EI-MS. The ^{1}H-NMR spectrum of **19d** exhibited signals due to an aldehyde proton [δ 9.91 (s)], two methoxy groups (δ 3.75 and 3.87), a propyl group and two ABX type aromatic protons. The product **19d** was found to be identical with the dimethyldihydrogenated compound of **17**. Another

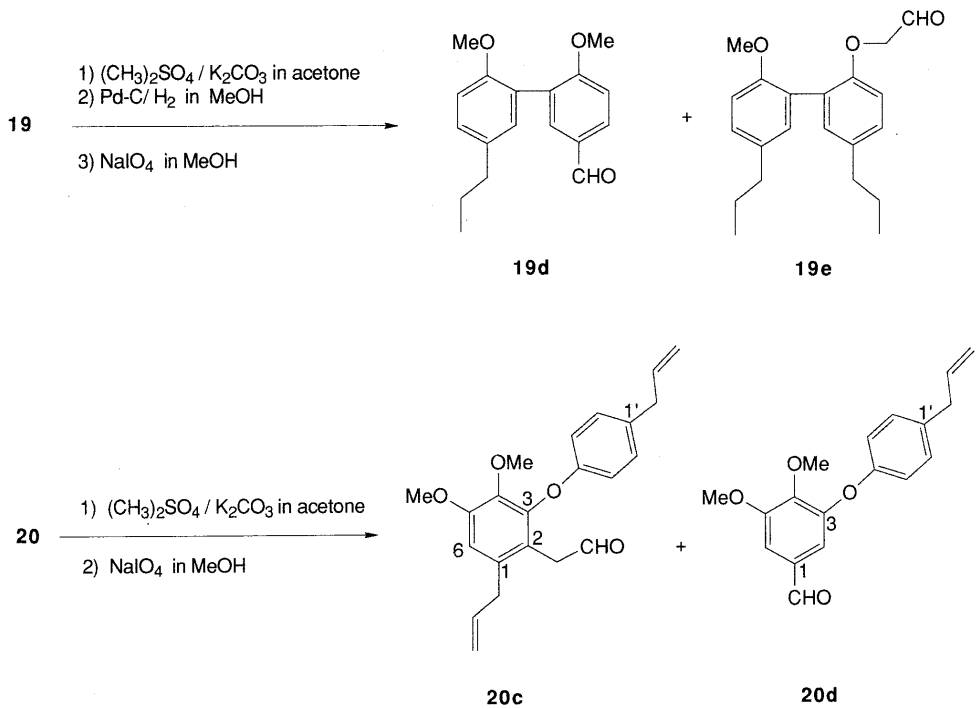
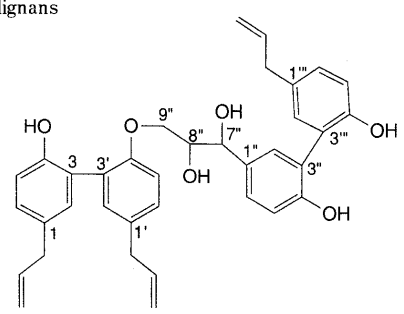
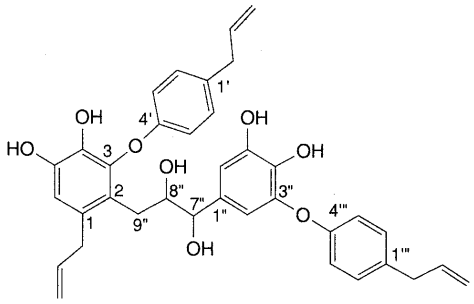


Chart 4

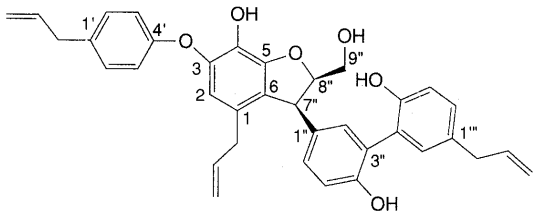
dilignans



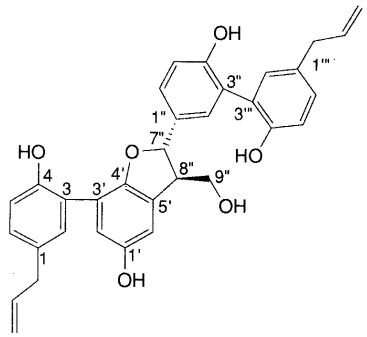
magnolignan F (19)



magnolignan G (20)



magnolignan H (21)



magnolignan I (22)

TABLE IV. ^{13}C-NMR Data for **19**, **20**, **21**, **22** (in Acetone-d_6) and Obovatol (**29** in $CDCl_3$)

	19	29	20	21	22
C-1	132.3[a]	132.5	131.1	126.7[a]	131.8[a]
C-2	129.3[b]	111.3	123.1	114.7	127.1[b]
C-3	127.1[c]	144.7	141.7[a]	144.6	125.3[c]
C-4	153.0[d]	135.1	134.1[b]	134.3[b]	152.6[d]
C-5	117.0[e]	143.8	144.9[a]	149.1	117.1[e]
C-6	132.5	110.9	114.3	127.9[a]	131.5[f]
C-7	39.3	39.6[a]	39.6	36.7	39.7
C-8	138.8[f]	137.4[b]	138.5[c]	137.1	138.7
C-9	115.5[g]	115.8[c]	115.2[d]	115.7	115.6
C-1′	133.2[a]	133.0	133.7	132.4	150.3[d]
C-2′	129.3[b]	129.8	129.7[e]	130.1[c]	116.6[e]
C-3′	126.8	117.9	115.2[f]	117.2	129.5[c]
C-4′	155.0	155.0	156.6[g]	152.8[e]	154.3[d]
C-5′	112.8	117.9	117.2[f]	117.2	121.2
C-6′	132.5	129.8	129.7[e]	130.1[c]	112.0
C-7′	39.3	39.4[a]	39.6	39.7	
C-8′	139.0[f]	137.2[b]	138.5[c]	138.6	
C-9′	115.5[g]	115.7[c]	115.5[d]	115.7	
C-1″	129.5		133.2	126.7[a]	132.4[a]
C-2″	127.9		110.5[h]	129.5[c]	127.1
C-3″	128.8		143.6[a]	127.5[a]	127.1[c]
C-4″	154.1[d]		137.1[b]	153.6[d]	153.0[d]
C-5″	117.4[e]		146.9[a]	117.2	117.2[e]
C-6″	130.8		111.6[h]	129.5[c]	129.8
C-7″	74.9[h]		76.8[i]	48.9	87.5
C-8″	74.1[h]		77.7[i]	89.0	54.5
C-9″	70.2		37.3	63.2	64.2
C-1‴	134.7[a]		133.7	134.3[b]	134.6[a]
C-2‴	129.5[b]		130.0[e]	132.6	129.5[b]
C-3‴	127.5[c]		117.2[f]	130.9	126.6[c]
C-4‴	153.5[d]		157.0[g]	157.6[d]	151.9[d]
C-5‴	117.6[e]		117.2[f]	117.2	117.5[e]
C-6‴	132.5		130.0[e]	132.3	132.2[f]
C-7‴	39.3		39.6	39.7	39.7
C-8‴	139.0[f]		138.7[c]	138.6	138.7
C-9‴	115.7[g]		115.7[d]	115.7	115.6

a—*i*) Assignments are interchangeable in each column.

product (**19e**) showed a molecular ion at *m/z* 326 in the EI-MS. The ^{1}H-NMR spectrum of **19e** exhibited mutually coupled aldehyde and oxygenated methylene signals [δ 9.69 (1H, d, J=1.5 Hz) and 4.45 (2H, d, J=1.5 Hz)], a methoxy signal (δ 3.73), two propyl and six aromatic proton signals. The above evidence suggested that the structure of **19e** was represented as shown in the formula. The structure of **19** was thus estimated to involve the ether bonding through C-9 in **11** and C-4-OH in **1**, and concluded to be as shown in the formula.

Magnolignan G(**20**) showed a molecular peak at *m/z* 596 in the FD-MS. In the ^{1}H-NMR spectrum, the signal due to a benzylic methylene [δ 2.43 (2H, d, J=6 Hz)], a benzylic methine having oxygen [δ 4.22 (d, J=6 Hz)] whose signals were coupled with the oxygenated methine proton [δ 3.77 (1H, m)], three allyl groups and eleven aromatic proton signals were observed, which suggested **20** to be a dimeric lignan. The ^{13}C-NMR spectrum of **20** showed the following signals: thirty-six carbon signals including two signals at δ 76.8 (d) and 77.7 (d) assignable to C-7″ and C-8″ on the propyl moiety, a benzylic methylene signal (δ 37.3), three allyl group signals of the magnolol-type, two *para*-substituted phenoxyl carbons, 1-substituted-3,4,5-trioxybenzene-type carbons and 1,2-di-substituted-3,4,5-trioxybenzene-type carbons. From the above evidence, **20** was assumed to be a dilignan of an obovatol (**29**)[11] and obovatol 7,8-dihydroxy derivative. As regards the bonding location, the signal of an obovatol unit in **20** was shifted by +11.8 ppm at C-2 or C-6, and another unit possessed the C-9″ methylene carbon (δ 37.3), thus indicating that the molecule has a bonding between C-2 (or C-6) and a terminal C-9″ of the propyl unit. On methylation, **20** afforded a tetramethyl ether (**20a**) [^{1}H-NMR: δ 3.53, 3.65, 3.79 and 3.81 (each 3H, s)]. On acetylation, **20** afforded a hexaacetate (**20b**), which showed signals of two aliphatic acetoxyl groups (δ 1.81 and 1.83) and four aromatic acetoxyl groups (δ 2.00,

2.18, 2.21 and 2.28) in the ^{1}H-NMR spectrum. These chemical data were coincident with the above evidence. To determine the bonding location, oxidation of **20a** with sodium metaperiodate was carried out to yield two products (**20c** and **20d**) (Chart 4), **20c** or which showed a molecular ion at *m/z* 352 in the EI-MS. The signal assignable to the ethanal group connected to the benzene ring appeared at δ 3.50 (2H, d, $J=2$ Hz) and 9.46 (1H, t, $J=2$ Hz), in the ^{1}H-NMR spectrum of **20c**. Furthermore, two methoxyl signals (δ 3.62 and 3.81), two allyl groups, two AB type aromatic signals [δ 6.67, 6.98 (each 2H, d, $J=9$ Hz)] and a singlet aromatic signal (δ 6.62) appeared. In the NOE experiment of **20c**, irradiation of the methoxyl signal (δ 3.81) caused the enhancement at the aromatic signal [δ 6.62 (s), H-6] and the methoxyl signal (δ 3.62, C-4-OMe). The structure of **20c** was represented as 3-*O*-(*para*-allyl-phenyl)-1-allyl-2-ethanal-4,5-dimethoxy-3-oxybenze ether. Another product (**20d**) showed a molecular ion at *m/z* 298 in EI-MS. The ^{1}H-NMR spectrum of **20d** exhibited signals due to an aldehyde group [δ 9.77 (s)], two AB and an AX type aromatic signals [δ 6.91, 7.15 (each 2H, d, $J=9$ Hz) and 7.07, 7.24 (each 1H, d, $J=2$ Hz)], an allyl group and two methoxyl groups [δ 3.96 (6H, s)]. In the NOE experiment of **20d**, irradiation on the methoxyl signal (δ 3.96) caused the enhancement at the aromatic H-6 (δ 7.24). Consequently, **20d** was concluded to be 3-*O*-(*para*-allyl-phenyl)-1-formyl-4,5-dimethoxy-3-oxybenzene ether. The above evidence suggested that the bonding location of **20** was through the C-2 of obovatol (**29**) and the C-9 in a 7,8-dihydroxypropyl derivative of obovatol. Therefore, the structure of **20** was concluded to be as shown in the formula.

Magnolignan H(**21**) showed a quasi-molecular ion peak $[M+H]^+$ at *m/z* 563 in the FD-MS, which suggested **21** to be a dilignan. The ^{1}H-NMR spectrum of **21** exhibited signals ascribable to the allyl groups, and eleven aromatic signals including a singlet signal at δ 6.36. Moreover, it showed the following signals: an oxygenated methylene signal [δ 3.51 (d, $J=6$ Hz)], an oxygenated methine [δ 4.78 (m)] and a down-field shifted benzylic methine proton [δ 4.68 (d, $J=9$ Hz)], which could be assigned to H_2-9″, H-8″ and H-7″, respectively, in the dihydrobenzofuran moiety, on the basis of spin-decoupling experiments. The ^{13}C-NMR spectrum (Table IV) disclosed the presence of thirty-six carbon signals including an oxygeneted methylene group [δ 63.2 (t)] and two methine groups [δ 48.9 (d), 89.0 (d)], suggesting the presence of a dihydrobenzofuran ring. Furthermore, it showed the following signals: two allyl group signals of the *para*-allyl-phenol type, an upper-field shifted benzylic methylene (C-7) in one allyl group, twelve aromatic carbons of the mono-substituted obovatol type and twelve aromatic carbons of the magnolol type. Methylation of **21** yielded a trimethyl ether (**21a**). Hydrogenation of **21a** provided a hexahydroganate (**21b**) and subsequent acetylation of **21a** yielded a monoacetate (**21c**). From this evidence, **21** could contain a benzofuran, a primary alcohol, three allyl and three aromatic hydroxyl groups. In the NOE experiments of **21b**, irradiation of a signal at δ 2.16 (2H, m, H_2-7) resulted in the observation of NOE at the signal of H-2 [δ 6.33 (s)] and irradiation of the methoxyl signals at δ 3.67, 3.72 and 3.88 resulted in the enhancement of signals around at δ 6.80—7.12, respectively. From these facts, **21** was assumed to be a dilignan constituted of obovatol (**29**) and magnolignan A (**10**). Careful examination of the ^{1}H-NMR spectrum of **21**, showed that the up-field shift of the H_2-7 signal (δ 2.97) in 3,4,5-trihydroxy-phenyl-allyl moiety could be reasonably explained when the aromatic ring in the other lignan moiety and the H_2-7 are located on the same side, thus indicating that the molecule has a bond between C-6 in obovatol and C-7″ on the dihydroxy-propyl moiety in **10**, and the dihydrobenzofuran ring could be formed around C-6→C-7″→C-8″-O→C-5 positions. The relative stereochemistry of the two substituents on the dihydrobenzofuran ring was concluded to be *cis*, based on the fact that irradiation of the benzylic H-7″ signal (δ 4.58) caused the enhancement of the oxygenated methine H-8″ (δ 5.02) in the NOE experiment in **21b**. Consequently, the structure of **21** was concluded to be as shown in the formula.

Magnolignan I(**22**) exhibited a molecular ion peak at *m/z* 522 in the FD-MS. The ^{1}H-NMR spectrum showed three ABX type aromatic signals [δ 6.86, 6.93, 7.00 (each 1H, d, $J=8.1$ Hz), 7.01, 7.05, 7.33 (each 1H, dd, $J=8.1$, 2.2 Hz), 7.10, 7.19, 7.37 (each 1H, d, $J=2.2$ Hz)], an AX type aromatic signal [δ 6.78, 6.83 (each 1H, d, $J=2.2$ Hz)] shifted toward up-field, and two allyl group signals. Moreover, it showed the following signals: two methine signals [δ 5.63 (1H, d, $J=6.2$ Hz), 3.60 (1H, m)] and a hydroxymethyl signal [δ 3.89 (2H, m)], which could be assigned to H-7″, H-8″ and H_2-9″, respectively, in the dihydrobenzofuran moiety, on the basis of spin-decoupling experiments. The ^{13}C-NMR spectrum of **22** revealed the presence two allyl groups of the magnolol type and four aromatic rings. The carbon signals at δ 54.5 (d), 64.2 (t), 87.5 (d), 112.0 (d), 116.6 (d), 121.2 (s), 129.5 (s), 150.3 (s) and 154.3 (s) were assigned to the moiety of the dihydrobenzofuran ring. That is, their signals disclosed a partial structure, 5-hydroxy-3-hydroxymethyl-2,7-diphenyl-dihydrobenzofuran for **22** by comparing the ^{13}C- and ^{1}H-NMR spectra with those of **15**, leptolepisol C[12] and lappaol A.[13] On methylation under the same condition as for **20**, **22** yielded a tetramethyl ether (**22a**) [^{1}H-NMR δ 3.64, 3.68, 3.73, 3.77 (each 3H, s)]. Hydrogenation of **22a** yielded a tetrahydrogenated derivative (**22b**) and subsequent acetylation of **22b** yielded a monoacetate (**22c**). The ^{1}H-NMR spectrum of **22c** afforded an acetyl methyl signal (δ 2.04), two propyl group signals, two methine of the 3-hydroxymethyl-dihydrobenzofuran type signals [δ 3.79 (1H, m) and 5.43 (1H, d, $J=6.6$ Hz)] and one methylene signal [δ 4.31 (1H, dd, $J=11.0$, 7.7 Hz) and 4.46 (1H, dd, $J=11.0$, 5.8 Hz)] and an AX type and three ABX type aromatic signals. These chemical and spectral data suggested that **22** possessed a bond between C-5′ in **15** and C-8 on the propyl moiety in the 9-hydroxy derivative of magnolol, and the dihydrofuran ring was formed around the C-4′-O→C-7″→C-8″→C-5′ position. The relative stereochemistry of the two substituents on the dihydrobenzofuran ring was concluded to be *trans*, based on the fact that irradiation on the oxygenated benzylic H-7″ signal (δ 5.43) caused the enhancement of the hydroxymethyl signal (H_2-9″, δ 4.31 and 4.46) in the NOE experiment of **22c**. Consequently, the structure of **22** was concluded to be as shown in the formula.

Compounds **3**, **4**, **5** and **6** are unique in respect to having the structures linked by the two parts of monoterpene and neolignan, and are the first reported monoterpenoid-

neolignan. These monomeric and dimeric lignans occur rarely in nature.

Experimental

Melting points were determined with a Yanagimoto micromelting apparatus and are uncorrected. The optical rotation were measured with a JASCO DIP-4 digital polarimeter. The IR and UV spectra were obtained with JASCO IR-G and Hitachi UV-340 spectrometers, respectively. The EI- and FD-MS were measured with a JEOL DX-300 and DX-303. The ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL PS-100 (100 MHz for ^{1}H-NMR), FX-100 (100 MHz for ^{1}H-NMR and 25 MHz for ^{13}C-NMR) and GX-400 (400 MHz for ^{1}H-NMR) spectrometers, chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Column chromatography was carried-out with MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.), Kieselgel 60 (70—230 mesh, Merck), Bondapak C_{18} (Waters) and Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemicals). TLC was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) using benzene–EtOAc (40 : 1) as the developing solvent for the compounds **1**—**6** and benzene–MeOH (5 : 1) as the solvent for the compounds **7**—**22**, and detection was achieved by spraying 10% H_2SO_4 reagent followed by heating, or by irradiating with a UV-lamp (254 nm). Purity was checked by highe performance liquid chromatography (HPLC) (Toso HPLC 803D, UV-8 model II system (280 nm); column, Toso TSK-80TM (ODS, 4.6 mm × 150 mm); solvent, 50—90% MeOH.

Isolation Commercial Magnoliae Cortex (*Magnolia officinalis* REHD *et* WILS.) produced in China (5 kg) was extracted at room temperature with MeOH and its extract was evaporated under reduced pressure to afford a residue (600 g). The MeOH extract was partitioned between H_2O and benzene, and the aqueous layer was extracted with EtOAc (100 g). The benzene extract (200 g) was chromatographed over silica gel (1 kg) using benzene–EtOAc as the solvent to give frs. 1—3, which were further separated by means of various chromatographies on silica gel and alumina afforded compounds **1** (6 g), **2** (1 g), **3** (890 mg), **4** (360 mg), **5** (30 mg), **6** (80 mg) and **27** (2 mg). The EtOAc extract (100 g) was chromatographed over silica gel (500 g) using benzene–EtOAc and MeOH as the solvent to give frs. 1—5. These frs. were subjected to column chromatographies on silica gel, Bondapak C_{18} and Sephadex LH-20 furnished compounds **7** (130 mg), **8** (120 mg), **9** (15 mg), **10** (15 mg), **11** (200 mg), **12** (35 mg), **13** (38 mg), **14** (29 mg), **15** (45 mg), **16** (85 mg), **17** (40 mg), **18** (35 mg), **19** (96 mg), **20** (153 mg), **21** (115 mg), **22** (120 mg), **23** (300 mg), **24** (47 mg), **25** (485 mg) and **26** (98 mg) (Chart 1).

Magnolol (1) ^{1}H-NMR ($CDCl_3$) δ: 3.35 (4H, br d, J=7 Hz, H_2-7, H_2-7′), 5.01 (2H, br d, J=11 Hz, H-9, H-9′), 5.06 (2H, br d, J=18 Hz, H-9, H-9′), 5.94 (2H, ddt, J=18, 11, 7 Hz, H-8, H-8′), 6.81 (2H, d, J=8 Hz), 7.02 (2H, dd, J=8, 2 Hz), 7.07 (2H, d, J=2 Hz).

Honokiol (2) ^{1}H-NMR ($CDCl_3$) δ: 3.27, 3.36 (each 2H, br d, J=7 Hz, H_2-7, H_2-7′), 5.05 (4H; m, H_2-9, H_2-9′), 5.93 (2H, m, H-8, H-8′), 6.74, 6.91 (each 1H, d, J=8 Hz), 6.97, 7.15 (each 1H, dd, J=8, 2 Hz), 7.00, 7.17 (each 1H, d, J=2 Hz).

1-(4-Hydroxy-3-methoxyphenyl)-2-[4-(ω-hydroxypropyl-2-methoxy)-phenoxy]-propane-1,3-diol (23)[6] (7,8-*threo* and *erythro* Mixture) EI-MS m/z: 378 (M^+). UV λ_{max}^{MeOH} nm (ε): 281 (12000). ^{1}H-NMR (acetone-d_6) δ: 1.62—1.97 (2H, m, H-8′), 2.50—3.90 (4H, m, H_2-9, H_2-9′), 3.80 (6H, s, OMe), 4.17—4.40 (1H, m, H-8), 7.91 (1/2H, d, J=4 Hz, H-7), 4.92 (1/2H, d, J=7 Hz, H-7), 6.60—7.15 (6H, m, Ar-H). ^{13}C-NMR (acetone-d_6) δ: 32.1 (C-8′), 35.0 (C-7′), 56.2, 55.5 (OMe × 2), 61.9 (61.1, 61.3) (C-9, C-9′), 73.2 (73.1) (C-8), 85.6 (86.4) (C-7), 111.5 (C-2′), 113.6 (113.4) (C-2), 115.2 (C-5), 118.3 (117.9) (C-5′), 120.3 (C-6), 121.4 (C-6′), 133.8 (133.6) (C-1), 137.2 (C-1′), 146.4 (C-3, C-4), 184.0 (C-3′), 150.9 (150.7) (C-4′).

Sinapic Aldehyde (24) ^{1}H-NMR ($CDCl_3$) δ: 3.90 (6H, s), 6.60 (1H, dd, J=8, 16 Hz), 6.80 (2H, s), 7.37 (1H, d, J=16 Hz), 9.62 (1H, d, J=8 Hz).

Syringaresinol (25) Colorless needles, mp 174—177 °C (benzene–acetone). $[\alpha]_D^{20}$ 0 (c=2.40, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 3.11 (2H, m, H-1, H-5), 3.86 (12H, s), 3.94 (2H, dd, J=9, 4 Hz, H-4, H-8), 4.30 (2H, dd, J=8, 9 Hz, H-4, H-8), 4.76 (2H, d, J=5 Hz, H-2, H-6), 5.83 (2H, s, OH), 6.59 (4H, s, Ar-H).

Syringaresinol 4′-*O*-β-D-Glucopyranoside (26) Colorless needles, mp 192—194 °C ($CHCl_3$). $[\alpha]_D^{19}$ −19.3° (c=1.10, MeOH). FD-MS m/z: 580 (M^+). ^{13}C-NMR (DMSO-d_6) δ: 53.6, 85.1, 71.2, 53.6, 85.4, 71.2 (C-2—8), 131.5, 103.5, 147.8, 134.5, 147.8, 103.9 (C-1′—6′), 137.4, 103.5, 152.5, 133.5, 152.5, 103.9 (C-1″—6″), 102.7, 73.9, 76.1, 69.6, 76.9, 60.7 (glc C-1—6).

6′-*O*-Methylhonokiol (27) ^{1}H-NMR ($CDCl_3$) δ: 3.35, 3.43 (each 2H, br d, J=7 Hz, H_2-7, H_2-7′), 3.88 (3H, s, OMe), 5.00—5.19 (5H, m, H_2-9, H_2-9′, OH), 5.78—6.22 (2H, m, H-8, H-8′), 6.86—7.34 (6H, m, Ar-H).

Piperitylmagnolol (3) Colorless viscous oil, $[\alpha]_D^{26}$ −146.0° (c=1.18, $CHCl_3$). UV λ_{max}^{MeOH} nm (ε): 290 (8500). CD (c=1.77 × 10^{-3}, MeOH) [θ] (nm): +7.22 × 10^3 (254), +2.25 × 10^3 (292). EI-MS m/z: 402.257 (M^+, $C_{28}H_{34}O_2$, requires 402.255). ^{1}H-NMR ($CDCl_3$) δ: 0.80, 0.88 (each 3H, d, J=6 Hz, H_3-9″, 10″), 1.70 (3H, br s, H_3-7″), 1.20—1.80 (4H, m, H-4″, H-8″, H_2-5″), 2.06 (2H, m, H_2-6″), 3.30 (4H, d, J=6 Hz, H_2-7, H_2-7′), 3.60 (1H, m, H-3″), 5.00 (2H, br d, J=11 Hz, H-9, H-9′), 5.02 (2H, br d, J=18 Hz, H-9, H-9′), 5.40 (1H, br s, H-2″), 6.75—6.20 (2H, m, H-8, H-8′), 6.30 (2H, br s, OH), 6.79 (5H, m, H-2, H-2′, H-5′, H-6, H-6′). ^{13}C-NMR: Table I.

Methylation of 3 A mixture of **3** (200 mg), dimethyl sulfate (3 ml) and anhydrous potassium carbonate (5 g) in dry acetone (50 ml) was refluxed for 2 h with stirring. After removal of inorganic salts by filtration, the filtrate was concentrated to a syrup, which was subjected to silica gel chromatography with benzene to afford **3a** (210 mg) as a colorless viscous oil, EI-MS m/z: 430.285 (M^+, $C_{30}H_{38}O_2$, requires 430.287). ^{1}H-NMR ($CDCl_3$) δ: 0.82, 0.90 (each 3H, d, J=6 Hz, H_3-9″, H_3-10″), 1.71 (3H, br s, H_3-7″), 1.40—1.80 (4H, m, H_2-5″, H-4″, H-8″), 2.07 (2H, m, H_2-6″), 3.35 (4H, d, J=6 Hz, H_2-7, H_2-7′), 3.77 (1H, m, H-3″), 3.73 (3H, s, C-4-OMe), 3.81 (3H, s, C-4′-OMe), 5.02 (2H, br d, J=11 Hz, H-9, H-9′), 5.06 (2H, br d, J=18 Hz, H-9, H-9′), 5.48 (1H, br d, J=7 Hz, H-2″), 5.77—6.20 (2H, m, H-8, H-8′), 6.83—7.722 (5H, m, Ar-H).

Partial Hydrogenation of 3 **3** (100 mg) was hydrogenated over 10% Pd–C (25 mg) in MeOH (20 ml) under a hydrogen atmosphere for 1 h. After removal of the catalyst by filtration, the filtrate was evaporated under reduced pressure to give a residue. The residue was purified by silica gel chromatography with benzene to give **3b** (90 mg) as a colorless viscous oil, EI-MS m/z: 406 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.80—1.01 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.40—1.85 (8H, m, H-4″, H-8″, H_2-5″, H_2-8, H_2-8′, H_2-6″), 1.77 (3H, br s, H_3-7″), 2.57 (4H, br t, J=6 Hz, H_2-7, H_2-7′), 3.52 (1H, m, H-3″), 5.49 (1H, br s, H-2″), 6.00 (2H, br s, OH), 6.85—7.15 (5H, m, Ar-H).

Oxydation of 3b with *m*-Chloroperbenzoic Acid A solution of **3b** (90 mg) and *m*-chloroperbenzoic acid (100 mg) in dry $CHCl_3$ was stirred overnight at room temperature. The reaction mixture was evaporated under reduced pressure to give a residue. The residue was purified by silica gel chromatography with benzene–EtOAc (200 : 7) to give **3c** (33 mg), as a white powder, $[\alpha]_D^{20}$ −1.0° (c=3.30, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.80—1.02 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.43 (3H, s, H_3-7″), 1.40—2.10 (10H, m, H-4″, H-8″, H_2-5″, H_2-6″, H_2-8, H_2-8′), 2.59, 2.61 (each 2H, t, J=6 Hz, H_2-7, H_2-7′), 3.02 (1H, dd, J=6, 11 Hz, H-3″), 4.27 (1H, d, J=6 Hz, H-2″), 6.90—7.20 (5H, m, Ar-H), 7.02 (2H, br s, OH).

Partial Hydrogenation of 3a **3a** (550 mg) was hydrogenated in the same way as **3** to yield **3d** (374 mg) as a colorless viscous oil, EI-MS m/z: 434 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.80—1.01 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.71 (3H, br s, H_3-7″), 1.40—1.80 (8H, m, H-4″, H-8″, H_2-5″, H_2-8, H_2-8′), 2.03 (2H, m, H_2-6″), 2.58 (4H, br t, J=6 Hz, H_2-7, H_2-7′), 3.45 (3H, s, C-4-OMe), 3.77 (3H, s, C-4′-OMe), 3.82 (1H, m, H-3″), 5.35 (1H, br s, H-2″), 6.82—7.20 (5H, m, Ar-H).

Oxidation of 3d with Selenium Dioxide A mixture of **3d** (100 mg) and selenium dioxide (200 mg) in dioxane (10 ml) was heated at 80 °C for 5 h with stirring. The reaction mixture was filtered after cooling, diluted with water, and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated under reduced pressure to give a residue, which was purified by silica gel chromatography using hexane–EtOAc (10 : 1) to afford **3e** (25 mg) as a white powder, $[\alpha]_D^{27}$ −109.5° (c=1.49, $CHCl_3$). EI-MS m/z: 448.298 (M^+, $C_{30}H_{40}O_3$, requires 448.297). ^{1}H-NMR ($CDCl_3$) δ: 0.83—1.01 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.83 (3H, br s, H_3-7″), 1.50—1.80 (6H, m, H_2-8, H_2-8′, H-4″, H-8″), 2.20—2.50 (2H, m, H_2-5″), 2.57, 2.59 (each 2H, t, J=6 Hz, H_2-7, H_2-7′), 3.30, 3.77 (each 3H, s, OMe), 4.05 (1H, m, H-3″), 6.61 (1H, br s, H-2″), 6.85—7.20 (5H, m, Ar-H).

$NaBH_4$ Reduction of 3e **3e** (20 mg) was reduced with $NaBH_4$ (50 mg) in MeOH (10 ml) at room temperature for 5 h. The reaction mixture (20 mg) was purified by silica gel chromatography using benzene–EtOAc (30 : 1) to give two products, **3f** (15 mg) and **3g** (1 mg). **3f**: A white powder. $[\alpha]_D^{27}$ −118.8° (c=1.12, $CHCl_3$). EI-MS m/z: 450.313 (M^+, $C_{30}H_{42}O_3$, requires 450.313). ^{1}H-NMR ($CDCl_3$) δ: 0.81—1.01 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.43—1.80 (7H, m, H-4″, H-5″, H-8″, H_2-8, H_2-8′), 1.82 (3H, br s, H_3-7″), 2.16 (1H, m, H-5″), 2.56, 2.58 (each 2H, t, J=6 Hz, H_2-7, H_2-7′), 3.28, 3.75 (each 3H, s, OMe), 3.55 (1H, m, H-3″), 4.35 [1H, dd, J=11, 4 Hz, H-6″ (axial)], 5.38 (1H, br s, H-2″), 6.83—7.17 (5H, m, Ar-H). **3g**: A white powder. EI-MS m/z: 450 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.80—1.01 (12H, m, H_3-9, H_3-9′, H_3-9″, H_3-10″), 1.40—1.80 (7H, m, H-4″, H-5″, H-8″, H_2-8, H_2-8′), 1.80 (3H, br s, H_3-7″), 2.10 (1H, m, H-5″), 2.56, 2.58 (each 2H, t, J=6 Hz, H_2-7, H_2-7′), 3.27, 3.75 (each 3H, s, OMe), 3.78

(1H, m, H-3″), 4.04 [1H, br t, J=4 Hz, H-6″ (equatorial)], 5.48 (1H, br s, H-2″), 6.80—7.20 (5H, m, Ar-H).

Determination of the Configuration (By Modified Horeau's Method) at C-6″ of 3f and 3g **3f** (5 mg) and **3g** (1 mg) in pyridine (10 μl) were each treated with (±)-α-phenylbutylic anhydride (6 μl) and kept in a sealed tube at 40 °C for 2 h. Then, (+)-(*R*)-α-phenylethylamine (6 μl) was added. After 30 min, the mixture was diluted with dry ethyl acetate (100 μl) and a sample was analyzed by gas chromatography (GLC) at 215 °C on a 2 mm × 2 m column packed with 2% OV-17 (N_2 1 kg/cm^2). The relative proportion of the amides of (−)-*R*- and (+)-*S*-phenylbutylic acid was indicated by the peak height. The peak retention indices % were: **3f**, 55 : 45 (6″*S*); **3g**, 51 : 49 (6″*R*).

Dipiperitylmagnolol (4) A white powder. $[\alpha]_D^{21}$ −140.0° (c=0.31, $CHCl_3$). EI-MS m/z: 538.373 (M^+, $C_{38}H_{50}O_2$, requires 538.380), UV λ_{max}^{MeOH} nm (ε): 290 (10200). CD ($c=2.41\times10^{-3}$, MeOH) [θ] (nm): $+1.04\times10^4$ (255), $+4.96\times10^3$ (294). ^{1}H-NMR ($CDCl_3$) δ: 0.83, 0.90 (each 6H, d, J=6 Hz, H_3-9″, H_3-9‴, H_3-10″, H_3-10‴), 1.72 (6H, br s, H_3-7″, H_3-7‴), 1.20—1.90 (8H, m, H-4″, H-4‴, H-8″, H-8‴, H_2-5″, H_2-5‴), 2.05 (4H, m, H_2-6″, H_2-6‴), 3.32 (1H, br d, J=7 Hz, H_2-7, H_2-7′), 3.65 (2H, m, H-3″, H-3‴), 5.02 (2H, br d, J=11 Hz, H-9, H-9′), 5.06 (2H, br d, J=18 Hz, H-9, H-9′), 5.40 (2H, br s, H-2″, H-2‴), 5.99 (2H, ddt, J=18, 11, 7 Hz, H-8, H-8′), 5.93 (2H, s, OH), 6.93 (4H, m, Ar-H). ^{13}C-NMR (Table I).

Methylation of 4 **4** (50 mg) was methylated in the same way as **3** to give a dimethyl ether (50 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 0.81, 0.85 (each 6H, d, J=6 Hz, H_3-9″, H_3-9‴, H_3-10″, H_3-10‴), 1.40—1.85 (8H, m), 1.71 (6H, br s, H_3-7″, H_3-7‴), 2.05 (4H, m, H_2-6″, H_2-6‴), 3.32 (6H, s, OMe), 3.36 (4H, br d, J=7 Hz, H_2-7, H_2-7′), 3.74 (2H, m, H-3″, H-3‴), 5.01 (2H, br d, J=11 Hz, H-9, H-9′), 5.04 (2H, br d, J=18 Hz, H-9, H-9′), 5.24 (2H, br s, H-2″, H-2‴), 5.98 (2H, ddt, J=18, 11, 7 Hz, H-8, H-8′), 6.95 (4H, m, Ar-H).

Piperitylhonokiol (5) Colorless viscous oil. $[\alpha]_D^{24}$ −97.0° (c=0.69, $CHCl_3$). EI-MS m/z: 402.250 (M^+, $C_{28}H_{34}O_2$, requires 402.255). UV λ_{max}^{MeOH} nm (ε): 290 (7800). CD ($c=1.74\times10^{-3}$, MeOH) [θ] (nm): $+4.59\times10^3$ (248), $+2.30\times10^3$ (293). ^{1}H-NMR ($CDCl_3$) δ: 0.83, 0.89 (each 3H, d, J=6 Hz, H_3-9″, H_3-10″), 1.72 (3H, br s, H_3-7″), 1.30—1.90 (4H, m, H-4″, H-8″, H_2-5″), 2.05 (2H, m, H_2-6″), 3.30, 3.42 (each 2H, d, J=7 Hz, H_2-7, H_2-7′), 3.50 (1H, m, H-3″), 4.92—5.30 (4H, m, H_2-9, H_2-9′), 5.12, 5.51 (each 1H, s, OH), 5.41 (1H, br s, H-2″), 5.78—6.25 (2H, m, H-8, H-8′), 6.80—6.93 (3H, m, Ar-H), 7.22 (2H, br s, Ar-H). ^{13}C-NMR (Table I).

Acetylation of 5 A mixture of **5** (7 mg), acetic anhydride (0.5 ml) and pyridine (0.5 ml) was kept standing overnight at room temperature and evaporated under reduced pressure to give a residue, which was subjected to silica gel chromatography with benzene–EtOAc (20 : 1) to afford an acetate (**5a**, 7 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 0.78, 0.86 (each 3H, d, J=6 Hz, H_3-9″, H_3-10″), 1.40—1.75 (4H, m, H-4″, H-8″, H_2-5″), 1.69 (3H, br s, H_3-7″), 2.02 (2H, m, H_2-6″), 1.98, 2.31 (each 3H, s, Ac), 3.28, 3.37 (each 2H, br d, J=7 Hz, H_2-7, H_2-7′), 3.35 (1H, m, H-3″), 4.95—5.20 (2H, m, H-8, H-8′), 5.20 (1H, br s, H-2″), 5.70—6.20 (2H, m, H-8, H-8′), 7.03 (3H, m, Ar-H), 7.24 (2H, m, Ar-H).

Bornylmagnolol (6) Colorless viscous oil. $[\alpha]_D^{26}$ −7.6° (c=1.67, $CHCl_3$). EI-MS m/z: 402.254 (M^+, $C_{28}H_{34}O_2$, requires: 402.255), 266, 137. UV λ_{max}^{MeOH} nm (ε): 290 (8000). ^{1}H-NMR ($CDCl_3$) δ: 0.80, 0.83, 0.87 (each 3H, s, H_3-8″, H_3-9″, H_3-10″), 0.70—2.45 (7H, m, H_2-3″, H_2-5″, H_2-6″, H-4″), 3.36 (4H, br d, J=7 Hz, H_2-7, H_2-7′), 4.38 (1H, dd, J=9, 3 Hz, H-2″), 4.90—5.20 (4H, m, H_2-9, H_2-9′), 5.75—6.23 (2H, m, H-8, H-8′), 6.28 (1H, br s, OH), 6.79—7.23 (6H, m, Ar-H). ^{13}C-NMR (Table I).

Acetylation of 6 **6** (10 mg) was acetylated in the same way as **5** to yield a monoacetate (10 mg) as a white powder. EI-MS m/z: 444.266 (M^+, $C_{30}H_{36}O_3$, requires: 444.266), 308, 266, 137. ^{1}H-NMR (CCl_4) δ: 0.73, 0.82, 0.87 (each 3H, s, H_3-8″, H_3-9″, H_3-10″), 0.70—2.35 (7H, m, H_2-3″, H-4″, H_2-5″, H_2-6″), 1.89 (3H, s, Ac), 3.25, 3.36 (each 2H, br d, J=7 Hz, H_2-7, H_2-7′), 4.18 (1H, dd, J=3, 9 Hz, H-2″), 4.85—5.15 (2H, m, H_2-9, H_2-9′), 5.70—6.17 (2H, m, H-8, H-8′), 6.62 (1H, d, J=8 Hz, H-5), 6.90—7.11 (5H, m, Ar-H).

Randainal (7)[5] Pale yellow needles, mp 135—138 °C ($CHCl_3$). UV λ_{max}^{MeOH} nm (ε): 330 (28000), 373 (26000). EI-MS m/z: 280.110 (M^+, $C_{18}H_{16}O_3$, requires: 280.109). IR $\nu_{max}^{CHCl_3}$ (cm^{-1}): 3550 (OH), 1675, 1625 (α,β-unsaturated aldehyde), 1605 (aromatic ring). ^{1}H-NMR (acetone-d_6) δ: 3.35 (2H, d, J=7 Hz, H_2-7′), 4.60 (2H, br, OH), 5.02 (1H, br d, J=10 Hz, H-9′), 5.06 (1H, br d, J=18 Hz, H-9′), 5.98 (1H, ddt, J=18, 10, 7 Hz, H-8′). 6.65 (1H, dd, J=16, 8 Hz, H-8), 6.92—7.13 (4H, m, Ar-H), 7.58 (1H, d, J=8 Hz, Ar-H), 7.60 (1H, d, J=2 Hz, Ar-H), 7.62 (1H, d, J=16 Hz, H-7), 9.61 (1H, d, J=8 Hz, H-9). ^{13}C-NMR (Table II).

Magnaldehyde B (8) Pale yellow needles, mp 155—158 °C ($CHCl_3$). UV λ_{max}^{MeOH} nm (ε): 284 (40000), 324 (33000). EI-MS m/z: 280.109 (M^+, $C_{18}H_{16}O_3$, requires: 280.109), IR $\lambda_{max}^{CHCl_3}$ (cm^{-1}): 3550 (OH), 1675, 1625 (α,β-unsaturated aldehyde), 1605 (aromatic ring). ^{1}H-NMR (acetone-d_6) δ: 3.44 (2H, d, J=7 Hz, H_2-7′), 3.46 (2H, br s, OH), 5.00 (1H, br d, J=11 Hz, H-9′), 5.11 (1H, br d, J=18 Hz, H-9′), 6.07 (1H, ddt, J=18, 11, 7 Hz, H-8′), 6.75 (1H, dd, J=16, 8 Hz, H-8), 6.92, 7.03 (each 1H, d, J=8 Hz, H-5, H-5′), 7.33, 7.51 (each 1H, dd, J=8, 2 Hz, H-6, H-4′), 7.37, 7.60 (each 1H, d, J=2 Hz, H-2, H-2′), 7.60 (1H, d, J=16 Hz, H-7), 9.62 (1H, d, J=8 Hz, H-9). ^{13}C-NMR (Table II).

Methylation of 8 **8** (12 mg) was methylated in the same way as **3** to yield a dimethyl ether (**8a**) (5 mg) as a pale yellow powder. ^{1}H-NMR ($CDCl_3$) δ: 3.42 (2H, d, J=7 Hz, H_2-7′), 3.87, 3.88 (each 3H, s, OMe), 5.65 (1H, br d, J=11 Hz, H-9′), 5.08 (1H, br d, J=18 Hz, H-9′), 6.04 (1H, ddt, J=18, 11, 7 Hz, H-8′), 6.64 (1H, dd, J=16, 8 Hz, H-8), 7.45 (1H, d, J=16 Hz, H-7), 6.87—7.50 (6H, m, Ar-H), 9.67 (1H, d, J=8 Hz, H-9).

Oxidation of Honokiol Dimethyl Ether A mixture of honokiol dimethyl ether (200 mg) and selenium dioxide (110 mg) in dioxane (5 ml) was heated at 90 °C for 1.5 h. It was filtered after cooling, diluted with water, and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with 10% aqueous sodium bicarbonate, then with water and dried over anhydrous sodium sulfate. The organic solvent was evaporated under reduced pressure to give a residue. Next, an active manganese dioxide (50 mg) was added to a solution of the residue (35 mg) in $CHCl_3$ (10 ml) and the mixture was stirred at room temperature overnight. After removal of the inorganic by filtration, the filtrate was concentrated to a syrup, which was subjected to silica gel chromatography with hexane–EtOAc (10 : 1) to afford two products [**8a** (4 mg) and **28** (3 mg)]. **28**: Pale yellow powder. ^{1}H-NMR ($CDCl_3$) δ: 3.37 (2H, d, J=7 Hz, H_2-7), 3.80, 3.94 (each 3H, s, OMe), 5.06 (1H, br d, J=11 Hz, H-9), 5.13 (1H, br d, J=18 Hz, H-9), 6.18 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.81 (1H, dd, J=8, 16 Hz, H-8′), 6.95—7.80 (6H, m, Ar-H), 7.89 (1H, d, J=16 Hz, H-7′), 9.70 (1H, d, J=8 Hz, H-9′).

Magnaldehyde C(9) A pale yellow powder. $[\alpha]_D^{29}$ −15.5° (c=1.50, MeOH). FD-MS m/z: 314 (M^+), 337 $[M+Na]^+$. IR $\lambda_{max}^{CHCl_3}$ (cm^{-1}): 3500 (OH), 1655, 1622 (α,β-unsaturated aldehyde), 1600 (aromatic ring). ^{1}H-NMR (acetone-d_6) δ: 2.65 (1H, dd, J=14, 8 Hz, H-7′), 2.84 (1H, dd, J=14, 5 Hz, H-7′), 3.56 (2H, m, H-9′), 3.80 (1H, m, H-8′), 6.66 (1H, dd, J=16, 8 Hz, H-8), 6.97—7.20 (4H, m, Ar-H), 7.62 (2H, m, Ar-H), 7.70 (1H, d, J=16 Hz, H-7), 9.62 (1H, d, J=8 Hz, H-9). ^{13}C-NMR (Table II).

Magnolignan A(10) A white powder. $[\alpha]_D^{17}$ −0.8° (c=1.50, MeOH). EI-MS m/z: 300.134 (M^+, $C_{18}H_{20}O_4$, requires: 300.136), 282 (M^+-H_2O), 269 (M^+-CH_2OH), 239 ($M^+-C_2H_5O_2$). UV λ_{max}^{MeOH} nm (ε): 256 (18000), 293 (18600). ^{1}H-NMR (acetone-d_6) δ: 2.64 (1H, dd, J=14, 7 Hz, H-7), 2.80 (1H, dd, J=14, 5 Hz, H-7), 3.35 (2H, br d, J=7 Hz, H_2-7′), 3.50 (2H, m, H-9), 3.82 (1H, m, H-8), 5.01 (1H, br d, J=11 Hz, H-9′), 5.06 (1H, br d, J=18 Hz, H-9′), 6.00 (1H, ddt, J=18, 11, 7 Hz, H-8′), 6.80—7.35 (6H, m, Ar-H). ^{13}C-NMR (Table II).

Acethylation of 10 **10** (5 mg) was acetylated in the same way as **5** to yield a tetraacetate (4 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 2.03, 2.04, 2.07, 2.08 (each 3H, s, Ac), 2.93 (2H, d, J=7 Hz, H_2-7), 3.41 (2H, br d, J=7 Hz, H_2-7′), 3.98 (1H, dd, J=12, 6 Hz, H-9), 4.36 (1H, dd, J=12, 4 Hz, H-9), 5.10 (2H, m, H_2-9′), 5.25 (1H, m, H-8), 5.80—6.20 (1H, m, H-8′), 7.13 (6H, m, Ar-H).

Magnolignan B(11) A white powder. $[\alpha]_D^{28}$ +0.3° (c=2.50, MeOH). FD-MS m/z: 316 (M^+), 254. ^{1}H-NMR (acetone-d_6) δ: 3.35 (2H, br d, J=6 Hz, H_2-7′), 3.52 (2H, m, H_2-9), 3.70 (1H, m, H-8), 4.65 (1H, d, J=6 Hz, H-7), 5.01 (1H, br d, J=11 Hz, H-9′), 5.06 (1H, br d, J=18 Hz, H-9′), 5.99 (1H, ddt, J=18, 11, 6 Hz, H-8′), 6.90, 6.92 (each 1H, d, J=8 Hz), 7.07, 7.56 (each 1H, dd, J=8, 2 Hz), 7.11, 7.31 (each 1H, d, J=2 Hz). ^{13}C-NMR (Table II).

Magnolignan C(12) A white powder. $[\alpha]_D^{22}$ −6.8° (c=0.91, MeOH), EI-MS m/z: 300.138 (M^+, $C_{18}H_{20}O_4$, requires: 300.136). UV λ_{max}^{MeOH} nm (ε): 259 (19400), 293 (17800). ^{1}H-NMR (acetone-d_6) δ: 2.65 (1H, dd, J=12, 8 Hz, H-7), 2.79 (1H, dd, J=12, 6 Hz, H-7), 3.40 (2H, br d, J=6 Hz, H_2-7), 3.50 (2H, m, H_2-9), 3.82 (1H, m, H-8), 4.93 (1H, br d, J=11 Hz, H-9′), 5.08 (1H, br d, J=18 Hz, H-9′), 6.02 (1H, ddt, J=18, 11, 6 Hz, H-8), 6.80—7.37 (6H, m, Ar-H). ^{13}C-NMR (Table II).

Acetylation of 12 **12** (20 mg) was acetylated in the same way as **5** to afford a tetraacetate (19 mg) as a white powder, $[\alpha]_D^{19}$ +2.9° (c=1.88, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.02, 2.04, 2.05, 2.32 (each 3H, s, Ac), 2.94 (2H, d, J=7 Hz, H_2-7), 3.33 (2H, br d, J=6 Hz, H_2-7′), 4.03 (1H, dd, J=12, 6 Hz, H-9), 4.26 (1H, dd, J=12, 4 Hz, H-9), 5.05 (1H, br d, J=11 Hz, H-9′), 5.06 (1H, br d, J=18 Hz, H-9′), 5.23 (1H, m, H-8), 5.91 (1H, ddt, J=18, 11, 6 Hz, H-8′), 6.97—7.30 (6H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 131.2, 129.3, 134.1, 146.6, 122.4, 131.2, 36.5, 71.9, 64.1 (C-1—9), 127.9, 134.5, 135.2, 130.8, 123.0, 148.5, 34.7, 135.7, 116.4 (C-1′—9′), 20.8 × 2, 20.9 × 2, 169.4 × 2, 170.2, 170.6 ($COCH_3$).

Magnolignan D(13) A white powder. $[\alpha]_D^{17}$ +3.0° (c=0.88, MeOH). EI-MS m/z: 330.150 (M^+, $C_{19}H_{22}O_5$, requires: 330.147), 300, 269 $[M-C_2H_4O_2]^+$, 239 $[269-CH_2O]^+$. UV λ_{max}^{MeOH} nm (ε): 259 (14500), 293 (11500). ^{1}H-NMR (acetone-d_6) δ: 3.21 (3H, s, OMe), 3.42 (2H, br d. J=7 Hz, H_2-7'), 3.66 (2H, m, H_2-9), 4.00 (1H, m, H-8), 4.17 (1H, d, J=7 Hz, H-7), 4.94 (1H, br d, J=11 Hz, H-9'), 5.11 (1H, br d, J=18 Hz, H-9'), 6.05 (1H, ddt, J=18, 11, 7 Hz, H-8'), 6.89, 6.96 (each 1H, d, J=8 Hz, H-5, H-5'), 7.12, 7.50 (each 1H, dd, J=8, 2 Hz, H-6, H-4'), 7.42, 7.56 (each 1H, d, J=2 Hz, H-2, H-2').

Acetylation of 13 **13** (10 mg) was acetylated in the same way as **5** to afford a tetraacetate (10 mg) as a white powder, $[\alpha]_D^{17}$ −0.3° (c=1.25, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 2.03×2, 2.10, 2.33 (each s, $COCH_3$), 3.29 (3H, s, OMe), 3.35 (2H, br d, J=7 Hz, H_2-7'), 3.92 (1H, dd, J=12, 7 Hz, H-9), 4.33 (1H, dd, J=12, 4 Hz, H-9), 4.59 (1H, d, J=6 Hz, H-7), 5.08 (2H, m, H_2-9'), 5.26 (1H, ddd, J=7, 6, 4 Hz, H-8), 5.75—6.20 (1H, m, H-8'), 7.02—7.36 (6H, m, Ar-H).

Methylation of 13 **13** (6 mg) was methylated in the same way as **3** to afford a dimethyl ether (3 mg) as a white powder, $[\alpha]_D^{20}$ −2.0° (c=0.20, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 3.26, 3.81, 3.87 (each 3H, s, OMe), 3.42 (2H, br d, J=7 Hz, H_2-7'), 3.53 (1H, dd, J=12, 6 Hz, H-9), 3.62 (1H, dd, J=12, 4 Hz, H-9), 4.10 (1H, d, J=8 Hz, H-7), 4.29 (1H, ddd, J=8, 6, 4 Hz, H-8), 5.05 (1H, br d, J=11 Hz, H-9'), 5.08 (1H, br d, J=18 Hz, H-9'), 6.00 (1H, ddt, J=18, 11, 7 Hz, H-8'), 6.89, 6.92 (each 1H, d, J=8 Hz), 7.20, 7.35 (each 1H, dd, J=8, 2 Hz), 7.25, 7.32 (each 1H, d, J=2 Hz).

Magnolignan E(14) A white powder, $[\alpha]_D^{29}$ −2.0° (c=2.06, MeOH). FD-MS m/z: 298 (M^+), 280, 250. ^{1}H-NMR (acetone-d_6) δ: 3.32 (2H, br d, J=6 Hz, H_2-7), 3.75 (2H, d, J=6 Hz, H_2-9'), 4.53 (1H, dd, J=10, 6 Hz, H-8'), 5.03 (1H, br d, J=11 Hz, H-9), 5.05 (1H, br d, J=18 Hz, H-9), 5.28 (1H, br s, H-7', after D_2O exchange J=4 Hz), 5.98 (1H, ddt, J=18, 11, 6 Hz, H-8), 6.77 (1H, d, J=8 Hz, H-5'), 6.94 (1H, d, J=8 Hz, H-5), 6.96 (1H, dd, J=8, 2 Hz, H-6), 7.42 (1H, dd, J=8, 2 Hz, H-4'), 7.08 (1H, d, J=2 Hz, H-2), 7.56 (1H, d, J=2 Hz, H-2'). NOEs: δ 3.75 (irr)→5.28 (5% NOE); 5.28 (irr)→3.75 (5% NOE), 7.56 (4% NOE).

Methylation of 14 **14** (10 mg) was methylated in the same way as **3** to afford a dimethyl ether (**14a**) (5 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 3.34 (2H, m, H_2-7), 3.78 (3H, s, OMe), 3.60—3.98 (2H, m, H_2-9'), 4.78 (1H, m, H-8'), 5.05 (1H, br d, J=11 Hz, H-9), 5.08 (1H, br d, J=18 Hz, H-9), 5.13 (1H, d, J=6 Hz, H-7'), 5.79—6.12 (1H, m, H-8), 6.83—7.60 (6H, m, Ar-H).

Acetylation of 14 **14** (7 mg) was acetylated in the same way as **5** to afford a triacetate (**14b**) (7 mg) as a white powder. EI-MS m/z: 424 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 2.05 (3H, s, Ac), 2.11 (6H, s, Ac×2), 3.41 (2H, m, H_2-7), 4.28 (1H, dd, J=12, 6 Hz, H-9'), 4.42 (1H, dd, J=12, 5 Hz, H-9'), 4.85 (1H, m, H-8'), 5.08 (1H, br d, J=10 Hz, H-9), 5.10 (1H, br d, J=18 Hz, H-9), 5.82 (1H, m, H-8), 6.11 (1H, d, J=4 Hz, H-7'), 6.86—7.40 (6H, m, Ar-H).

Randaial[5] **(15)** A pale yellow powder. EI-MS m/z: 242.094 (M^+, $C_{15}H_{14}O_3$, requires: 242.094). UV λ_{max}^{MeOH} nm (ε): 298 (5700). ^{1}H-NMR (acetone-d_6) δ: 3.35 (2H, br d, J=7 Hz, H_2-7), 5.01 (1H, br d, J=11 Hz, H-9), 5.06 (1H, br d, J=18 Hz, H-9), 5.99 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.75, 7.05 (each 1H, dd, J=9, 2 Hz, H-6, H-6'), 6.84, 6.94 (each 1H, d, J=9 Hz, H-5, H-5'), 6.79, 7.11 (each 1H, d, J=2 Hz, H-2, H-2'). ^{13}C-NMR (Table III).

Methylation and Hydrogenation of 15 **15** (30 mg) was methylated in the same way as **3** to afford a trimethyl ether (30 mg) as a pale yellow powder. ^{1}H-NMR ($CDCl_3$) δ: 3.40 (2H, br d, J=7 Hz, H_2-7), 3.70, 3.71, 3.88 (each 3H, s, OMe), 5.02 (1H, br d, J=11 Hz, H-9), 5.06 (1H, br d, J=18 Hz, H-9), 6.00 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.65—7.30 (6H, m, Ar-H). The trimethyl ether (30 mg) was hydrogenated over 10% Pd–C (30 mg) in MeOH (20 ml) under a hydrogen atmosphere for 3 h. After removal of the catalyst by filtration, the filtrate was evaporated under reduced pressure. The residue was purified by chromatography over silica gel with benzene–hexane (1:1) to give a dihydrotrimethyl ether (**15a**) (33 mg) as a pale yellow powder. EI-MS m/z: 286 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=8 Hz, H_3-9), 1.50 (2H, m, H_2-8), 2.48 (2H, br t, J=7 Hz, H_2-7), 3.34, 3.35, 3.37 (each 3H, s, OMe), 6.66 (1H, d, J=9 Hz, H-5'), 6.68 (1H, d, J=8 Hz, H-5), 6.83 (1H, dd, J=9, 3 Hz, H-6'), 7.00 (1H, dd, J=8, 2 Hz, H-6), 7.05 (1H, d, J=3 Hz, H-2'), 7.19 (1H, d, J=2 Hz, H-2). NOEs: δ 2.48 (irr)→7.00 (11% NOE), 7.19 (21% NOE); δ 3.34, 3.35, 3.37 (center irr)→6.66 (12% NOE), 6.68 (12% NOE), 6.83 (11% NOE), 7.03 (11% NOE).

Magnatriol B(16) Pale yellow needles, mp 99—100 °C ($CHCl_3$–benzene). EI-MS m/z: 242.094 (M^+, $C_{15}H_{14}O_3$, requires: 242.094). UV λ_{max}^{MeOH} nm (ε): 306 (5100). ^{1}H-NMR (acetone-d_6) δ: 3.40 (2H, br d, J=7 Hz, H_2-7), 5.01 (1H, br d, J=11 Hz, H-9), 5.06 (1H, br d, J=18 Hz, H-9), 6.06 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.65 (1H, dd, J=8, 2 Hz, H-6'), 6.80 (1H, d, J=2 Hz, H-2'), 6.84 (1H, d, J=8 Hz, H-5), 6.96 (1H, d, J=8 Hz, H-5'), 7.28 (1H, dd, J=8, 2 Hz, H-4), 7.33 (1H, d, J=2 Hz, H-2). ^{13}C-NMR (Table III).

Methylation and Hydrogenation of 16 **16** (30 mg) was methylated in the same way as **3** to afford a trimethyl ether (25 mg) as a pale yellow powder. ^{1}H-NMR ($CDCl_3$) δ: 3.41 (2H, br d, J=7 Hz, H_2-7), 3.67, 3.72, 3.79 (each 3H, s, OMe), 5.02 (1H, br d, J=11 Hz, H-9), 5.07 (1H, br d, J=18 Hz, H-9), 6.02 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.67—7.42 (6H, m, Ar-H). The trimethyl ether (25 mg) was hydrogenated in the same way as **15** to give a dihydrotrimethyl ether (**16a**) (25 mg) as a pale yellow powder. EI-MS m/z: 286 [M^+]. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, t, J=7 Hz, H_3-9), 1.61 (2H, m, H_2-8), 2.76 (2H, t, J=7 Hz, H_2-7), 3.36, 3.37, 3.42 (each 3H, s, OMe), 6.64 (1H, d, J=9 Hz, H-5), 6.66 (1H, d, J=9 Hz, H-5'), 6.80 (1H, dd, J=9, 3 Hz, H-6'), 7.15 (1H, d, J=3 Hz, H-2'), 7.51 (1H, dd, J=9, 3 Hz, H-4), 7.53 (1H, d, J=3 Hz, H-2). NOEs: δ 2.76 (irr)→δ 7.53 (20% NOE); δ 3.56, 3.57 (center irr)→δ 2.76 (2% NOE), 6.64 (13% NOE), 6.66 (13% NOE); δ 3.42 (irr)→δ 6.80 (23% NOE), 7.15 (21% NOE).

Magnaldehyde D(17) Pale yellow needles, mp 140—143 °C ($CHCl_3$–benzene). EI-MS m/z: 254.093 (M^+, $C_{16}H_{14}O_3$, requires: 254.094). ^{1}H-NMR (acetone-d_6) δ: 3.38 (2H, br d, J=7 Hz, H_2-7), 5.02 (1H, br d, J=11 Hz, H-9), 5.08 (1H, br d, J=18 Hz, H-9), 6.02 (1H, ddt, J=18, 11, 7 Hz, H-8), 7.00—7.21 (4H, m, Ar-H), 7.77 (1H, dd, J=9, 2 Hz), 7.83 (1H, d, J=2 Hz), 9.89 (1H, s, H-7'). ^{13}C-NMR (Table III).

Magnaldehyde E(18) Pale yellow needles, mp 160—162 °C ($CHCl_3$–benzene). EI-MS m/z: 254.094 (M^+, $C_{16}H_{14}O_3$, requires: 254.094). ^{1}H-NMR (acetone-d_6) δ: 3.46 (2H, br d, J=7 Hz, H_2-7), 5.01 (1H, br d, J=11 Hz, H-9), 5.07 (1H, br d, J=18 Hz, H-9), 6.00 (1H, ddt, J=18, 11, 7 Hz, H-8), 6.92, 7.13 (each 1H, d, J=9 Hz, H-5, H-5'), 7.40, 7.72 (each 1H, dd, J=9, 2 Hz, H-4, H-6'), 7.40, 7.80 (each 1H, d, J=2 Hz, H-2, H-2'), 9.86 (1H, s, H-7'). ^{13}C-NMR (Table III).

Magnolignan F(19) A pale brown powder. $[\alpha]_D^{28}$ −1.5° (c=1.04, MeOH). FD-MS m/z: 564 (M^+), 546, 282, 273, 266, 182. ^{1}H-NMR (acetone-d_6) δ: 3.20—3.40 (6H, m, H_2-7, H_2-7', H_2-7''), 3.80—4.20 (3H, m, H-8'', H_2-9''), 4.64 (1H, d, J=5 Hz, H-7''), 4.85—5.20 (6H, m, H_2-9, H_2-9', H_2-9'''), 5.70—6.20 (3H, m, H-8, H-8', H-8'''), 6.80—7.25 (12H, m, Ar-H). ^{13}C-NMR (Table IV).

Methylation of 19 **19** (20 mg) was methylated in the same way as **3** to afford a trimethyl ether (**19a**, 14 mg) as a pale brown powder. $[\alpha]_D^{20}$ +0.8° (c=1.47, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 3.35 (6H, br d, J=7 Hz, H_2-7, H_2-7', H_2-7'''), 3.68, 3.69, 3.73 (each 3H, s, OMe), 3.90 (3H, m, H-8'', H_2-9''), 4.50 (1H, m, H-7''), 4.85—5.16 (6H, m, H_2-9, H_2-9', H_2-9'''), 5.77—6.18 (3H, m, H-8, H-8', H-8'''), 6.60—7.28 (12H, m, Ar-H).

Acetylation of 19a **19a** (2 mg) was acetylated in the same way as **5** to yield a diacetyl-trimethyl ether (**19b**, 2 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 1.92, 1.99 (each 3H, s, $COCH_3$), 3.30 (6H, m, H_2-7, H_2-7', H_2-7'''), 3.64, 3.72, 3.76 (each 3H, s, OMe), 3.62 (1H, dd, J=11, 4 Hz, H-9''), 4.04 (1H, dd, J=11, 3 Hz, H-9''), 4.85—5.15 (6H, m, H_2-9, H_2-9', H_2-9'''), 5.30 (1H, m, H-8''), 5.82 (1H, d, J=8 Hz, H-7''), 5.78—6.18 (3H, m, H-8, H-8', H-8'''), 6.60—7.15 (12H, m, Ar-H).

Hydrogenation of 19a **19a** (11 mg) was hydrogenated in the same way as **15** to give a hexahydroganate (**19c**, 11 mg) as a white powder. EI-MS m/z: 612 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.95 (9H, m, H_3-9, H_3-9', H_3-9'''), 1.60 (6H, m, H_2-8, H_2-8', H_2-8'''), 2.55 (6H, m, H_2-7, H_2-7', H_2-7'''), 3.62, 3.71, 3.76 (each 3H, s, OMe), 3.65 (1H, dd, J=10, 4 Hz, H-9''), 4.02 (2H, m, H-8'', H-9''), 4.60 (1H, d, J=8 Hz, H-7''), 6.63—7.15 (12H, m, Ar-H).

Periodate Oxidation of 19c A mixture of **19c** (11 mg) and sodium metaperiodate (3 mg) in MeOH (5 ml) was stirred at room temperature for 3 h. The reaction mixture was concentrated to a syrup, which was subjected to silica gel chromatography with hexane–EtOAc (20:1) furnished two products [**19d** (1.5 mg) and **19e** (1.8 mg)]. **19d**: EI-MS m/z: 284 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.95 (3H, t, J=7 Hz, H_3-9), 1.60 (2H, m, H_2-8), 2.57 (2H, t, J=7 Hz, H_2-7), 3.75, 3.87 (each 3H, s, OMe), 6.89, 7.06 (each 1H, d, J=8 Hz, H-5, H-5'), 7.04, 7.78 (each 1H, d, J=2 Hz, H-2, H-2'), 7.17, 7.87 (each 1H, dd, J=8, 2 Hz, H-6, H-6'), 9.91 (1H, s, CHO). **19e**: EI-MS m/z: 326 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.95 (6H, t, J=7 Hz, H_3-9, H_3-9'), 1.61 (4H, m, H_2-8, H_2-8'), 2.44 (4H, m, H_2-7, H_2-7'), 3.73 (3H, s, OMe), 4.45 (2H, d, J=1.5 Hz, O-$\underline{CH_2}$-CHO), 6.72—7.18 (6H, m, Ar-H), 9.69 (1H, d, J=1.5 Hz, O-CH_2-$\underline{CHO}$).

Magnolignan G(20) A pale brown powder. $[\alpha]_D^{29}$ +0.1° (c=1.25, MeOH). FD-MS m/z: 596 (M^+), 578, 446, 298, 289. ^{1}H-NMR (acetone-d_6 + D_2O) δ: 2.43 (2H, d, J=6 Hz, H_2-9''), 3.30 (6H, m, H_2-7, H_2-7', H_2-7'''), 3.77 (1H, m, H-8''), 4.22 (1H, d, J=6 Hz, H-7''), 4.80—5.15 (6H, m, H_2-9, H_2-9', H_2-9'''), 5.68—6.15 (3H, m, H-8, H-8', H-8'''), 6.38 (1H, d, J=2 Hz, H-2''), 6.51—7.08 (10H, m, Ar-H). ^{13}C-NMR (Table IV).

Methylation of 20 **20** (40 mg) was methylated in the same way as **3** to yield a tetramethyl ether (**20a**, 15 mg) as a pale brown powder. $[\alpha]_D^{20}$ +0.8° (c=1.50, $CHCl_3$). ^{1}H-NMR (acetone-d_6) δ: 2.59 (2H, d, J=6 Hz, H_2-9″), 3.30 (6H, m, H_2-7, H_2-7′, H_2-7‴), 3.53, 3.65, 3.79, 3.81 (each 3H, s, OMe), 3.80 (1H, m, H-8″), 4.35 (1H, m, H-7″), 5.02 (6H, m, H_2-9, H_2-9′, H_2-9‴), 5.96 (3H, m, H-8, H-8′, H-8‴), 6.55—7.17 (11H, m, Ar-H).

Acetylation of 20 **20** (17 mg) was acetylated in the same way as **5** to yield a hexaacetate (**20b**, 15 mg) as a white powder. $[\alpha]_D^{25}$ +0.7° (c=1.50, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.81, 1.83, 2.00, 2.18, 2.21, 2.28 (each 3H, s, Ac), 2.76 (2H, d, J=7 Hz, H_2-9″), 3.32 (6H, m, H_2-7, H_2-7′, H_2-7‴), 5.05 (6H, m, H_2-9, H_2-9′, H_2-9‴), 5.34 (1H, td, J=7, 6 Hz, H-8″), 5.65 (1H, d, J=6 Hz, H-7″), 5.88 (3H, m, H-8, H-8′, H-8‴), 6.63—7.17 (11H, m, Ar-H).

Hydrogenation of 20b **20b** (3 mg) was hydrogenated in the same way as **15** to give a hexahydro-hexaacetate (2 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (9H, m, H_3-9, H_3-9′, H_3-9‴), 1.59 (6H, m, H_2-8, H_2-8′, H_2-8‴), 1.79, 1.82, 1.99, 2.17, 2.20, 2.27 (each 3H, s, Ac), 2.53 (6H, m, H_2-7, H_2-7′, H_2-7‴), 2.73 (2H, d, J=7 Hz, H_2-9″), 5.32 (1H, td, J=7, 6 Hz, H-8″), 5.66 (1H, d, J=6 Hz, H-7″), 6.58—7.16 (11H, m, Ar-H).

Periodate Oxidation of 20a A mixture of **20a** (15 mg) and sodium metaperiodate (5 mg) in MeOH (5 ml) was stirred at room temperature for 3 h. The reaction mixture was concentrated to a syrup, which was subjected to silica gel chromatography with hexane–EtOAc (20 : 1) to afford two products [**20c** (3.5 mg) and **20d** (2.8 mg)]. **20c**: EI-MS m/z: 352 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 3.23 (4H, br d, J=6 Hz, H_2-7, H_2-7′), 3.50 (2H, d, J=2 Hz, $\underline{CH_2}$–CHO), 3.62 (3H, s, C-4-OMe), 3.81 (3H, s, C-5-OMe), 5.00 (4H, m, H_2-9, H_2-9′), 5.67—6.06 (2H, m, H-8, H-8′), 6.62 (1H, s, H-6), 6.67 (2H, d, J=9 Hz, H-3′, H-5′), 6.98 (2H, d, J=9 Hz, H-2′, H-6′), 9.46 (1H, d, J=2 Hz, CH_2–$\underline{CHO}$). NOEs: δ 3.81 (irr)→6.62 (28% NOE) and 3.62 (10% NOE), 3.62→3.81 (10% NOE), 3.50→3.23 (9% NOE). **20d**: EI-MS m/z: 298 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 3.37 (2H, br d, J=6 Hz, H_2-7′), 3.96 (6H, s, C-4-OMe, C-5-OMe), 5.05 (1H, br d, J=11 Hz, H-9′), 5.06 (1H, br d, J=17 Hz, H-9′), 5.97 (1H, ddt, J=17, 11, 6 Hz, H-8′), 6.91 (2H, d, J=9 Hz, H-3′, 5′), 7.07 (1H, d, J=2 Hz, H-2), 7.15 (2H, d, J=9 Hz, H-2′, H-6′), 7.24 (1H, d, J=2 Hz, H-6), 9.77 (1H, s, C-1-CHO). NOE: δ 3.96 (irr)→7.24 (18% NOE).

Magnolignan H(21) A pale brown powder, $[\alpha]_D^{28}$ +2.0° (c=2.65, MeOH). FD-MS m/z: 563 $[M+H]^+$, 544, 531, 337, 239. ^{1}H-NMR (acetone-d_6) δ: 2.97 (2H, br d, J=6 Hz, H_2-7), 3.31 (4H, br d, J=6 Hz, H_2-7′, H_2-7‴), 3.51 (2H, d, J=6 Hz, H_2-9″), 4.68 (1H, d, J=9 Hz, H-7″), 4.78 (1H, m, H-8″), 4.75—5.16 (6H, m, H_2-9, H_2-9′, H_2-9‴), 5.46—6.17 (3H, m, H-8, H-8′, H-8‴), 6.36 (1H, s, H-2), 6.80—7.14 (10H, m, Ar-H). ^{13}C-NMR (Table IV).

Methylation of 21 **21** (50 mg) was methylated in the same way as **3** to yield a trimethyl ether (**21a**, 40 mg) as a pale yellow powder. $[\alpha]_D^{28}$ +0.4° (c=4.00, MeOH). ^{1}H-NMR ($CDCl_3$) δ: 2.93 (2H, br d, J=7 Hz, H_2-7), 3.35 (4H, br d, J=7 Hz, H_2-7′, H_2-7‴), 3.58 (2H, m, H_2-9″), 3.67, 3.71, 3.87 (each 3H, s, OMe), 4.59 (1H, d, J=9 Hz, H-7″), 4.78—5.20 (7H, m, H-8″, H_2-9, H_2-9′, H_2-9‴), 5.60 (1H, ddt, J=17, 11, 7 Hz, H-8), 5.75—6.20 (2H, m, H-8′, H-8‴), 6.35 (1H, s, H-2), 6.84—7.19 (10H, m, Ar-H).

Hydrogenation of 21a **21a** (20 mg) was hydrogenated in the same way as **15** to give a hexahydrogenate (**21b**, 18 mg) as a white powder. EI-MS m/z: 610 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 0.71, 0.92, 0.94 (each 3H, t, J=7 Hz, H_3-9, H_3-9′, H_3-9‴), 1.27 (1H, m, H_2-8), 1.62 (4H, m, H-8′, H-8‴), 2.16 (2H, m, H_2-7), 2.55 (4H, br t, J=8 Hz, H_2-7′, H_2-7‴), 3.50 (1H, dd, J=12, 6 Hz, H-9″), 3.69 (1H, dd, J=12, 8 Hz, H-9″), 3.67, 3.73, 3.88 (each 3H, s, OMe), 4.58 (1H, d, J=9 Hz, H-7″), 5.02 (1H, ddd, J=9, 8, 6 Hz, H-8″), 6.33 (1H, s, H-2), 6.80—7.12 (10H, m, Ar-H). NOEs: δ 2.16 (irr)→6.33 (20% NOE), 3.50 (irr)→5.02 (8% NOE), 3.67 (irr)→6.80—7.12 (8% NOE); δ 3.73 (irr)→6.80—7.12 (8% NOE), 3.88 (irr)→6.80—7.12 (3% NOE); δ 4.58 (irr)→5.02 (12% NOE); δ 5.02 (irr)→4.58 (10% NOE).

Acetylation of 21a **21a** (5 mg) was acetylated in the same way as **5** to yield a tetraacetyltrimethyl ether (**21c**, 5 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, Ac), 2.93 (2H, br d, J=7 Hz, H_2-7), 3.35 (4H, br d, J=7 Hz, H_2-7′, H_2-7‴), 3.67, 3.75, 3.90 (each 3H, s, OMe), 4.02 (1H, dd, J=12, 8 Hz, H-9″), 4.13 (1H, dd, J=12, 4 Hz, H-9″), 4.58 (1H, d, J=9 Hz, H-7″), 4.76—5.15 (7H, m, H-8″, H_2-9, H_2-9′, H_2-9‴), 5.61 (1H, ddt, J=18, 11, 7 Hz, H-8), 5.77—6.17 (2H, m, H-8′, H-8‴), 6.35 (1H, s, H-2), 6.85—7.18 (m, 10H, Ar-H).

Magnolignan I(22) A pale brown powder, $[\alpha]_D^{28}$ +2.1° (c=0.97, MeOH), FD-MS m/z: 522 (M^+). ^{1}H-NMR (acetone-d_6, 400 MHz) δ: 3.32 (4H, m, H_2-7, H_2-7‴), 3.60 (1H, m, H-8″), 3.89 (2H, m, H_2-9″), 5.01 (4H, m, H_2-9, H_2-9‴), 5.63 (1H, d, J=6.2 Hz, H-7″), 5.95 (2H, m, H-8, H-8‴), 6.78, 6.83 (each 1H, d, J=2.2 Hz, H-2′, H-6′), 6.86, 6.93, 7.00 (each 1H, d, J=8.1 Hz, H-5, H-5″, H-5‴), 7.01, 7.05, 7.33 (each 1H, dd, J=8.1, 2.2 Hz, H-6, H-6″, H-6‴), 7.10, 7.19, 7.37 (each 1H, d, J=2.2 Hz, H-2, H-2″, H-2‴). ^{13}C-NMR (Table IV).

Methylation of 22 **22** (30 mg) was methylated in the same way as **3** to yield a tetramethyl ether (**22a**, 19 mg) as a white powder. ^{1}H-NMR ($CDCl_3$) δ: 3.33 (4H, br d, J=6 Hz, H_2-7, H_2-7‴), 3.64, 3.68, 3.73, 3.77 (each 3H, s, OMe), 3.60 (1H, m, H-8″), 3.86 (2H, m, H_2-9″), 5.04 (4H, m, H_2-9, H_2-9‴), 5.51 (1H, d, J=7 Hz, H-7″), 5.73—6.17 (2H, m, H-8, H-8‴), 6.77—7.21 (11H, m, Ar-H).

Hydrogenation of 22a **22a** (12 mg) was hydrogenated in the same way as **15** to give a tetrahydrogenate (**22b**, 12 mg) as a white powder. EI-MS m/z: 582 (M^+), 564, 552. $[\alpha]_D^{30}$ +1.7° (c=1.18, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.91, 0.92 (each 3H, t, J=7 Hz, H_3-9, H_3-9‴), 1.65 (4H, m, H_2-8, H_2-8‴), 2.53 (4H, t, J=7 Hz, H_2-7, H_2-7‴), 3.63, 3.68, 3.43, 3.77 (each 3H, s, OMe), 3.60 (1H, m, H-8″), 3.91 (2H, m, H_2-9″), 5.52 (1H, d, J=7 Hz, H-7″), 6.58—7.20 (11H, m, Ar-H).

Acetylation of 22b **22b** (12 mg) was acetylated in the same way as **5** to yield a monoacetate (**22c**, 13 mg) as a white powder. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.92, 0.94 (each 3H, t, J=7.3 Hz, H_3-9, H_3-9‴), 1.61 (4H, m, H_2-8, H_2-8‴), 2.04 (3H, s, Ac), 2.52 (4H, m, H_2-7, H_2-7‴), 3.65, 3.70, 3.76, 3.78 (each 3H, s, OMe), 3.79 (1H, m, H-8″), 4.31 (1H, dd, J=11.0, 7.7 Hz, H-9″), 4.46 (1H, dd, J=11.0, 5.8 Hz, H-9″), 5.43 (1H, d, J=6.6 Hz, H-7″), 6.77 (1H, d, J=2.3 Hz, H-6′), 6.81 (1H, d, J=2.3 Hz, H-2′), 6.84, 6.86 (each 1H, d, J=8.4 Hz, H-5, H-5‴), 6.92 (1H, d, J=8.4 Hz, H-5″), 7.01, 7.17 (each 1H, d, J=2.2 Hz, H-2, H-2‴), 7.26 (1H, d, J=2.2 Hz, H-2″), 7.09, 7.10 (each 1H, dd, J=8.4, 2.2 Hz, H-6, H-6‴), 7.35 (1H, dd, J=8.4, 2.2 Hz, H-6″). NOEs: δ 4.31 (irr)→3.79 (22% NOE), 5.43 (22% NOE), 6.77 (3% NOE); δ 4.46 (irr)→3.79 (16% NOE), 5.43 (5% NOE); δ 5.43 (irr)→4.31 (9% NOE), 4.46 (4% NOE), 7.26 (12% NOE), 7.35 (10% NOE).

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