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The Constituents of *Eucommia ulmoides* OLIV. III. Isolation and Structure of a New Lignan Glycoside

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A new lignan glycoside was isolated from the bark of *Eucommia ulmoides* OLIV. (Eucommiaceae) and its structure was established as (+)-1-hydroxypinoresinol 4''-*O*-*β*-D-glucopyranoside (**1**) on the basis of chemical evidence and spectroscopic studies. An isomer of **1**, (+)-1-hydroxypinoresinol 4'-*O*-*β*-D-glucopyranoside (**2**), was also isolated, together with (±)-*erythro*-, and (±)-*threo*-guaiacylglycerol (**3** and **4**), (+)-cyclo-olivil (**5**) and (−)-olivil (**6**).

Keywords——*Eucommia ulmoides*; lignan; (+)-1-hydroxypinoresinol 4''-*O*-*β*-D-glucopyranoside; (+)-1-hydroxypinoresinol 4'-*O*-*β*-D-glucopyranoside; (±)-guaiacylglycerol; (+)-cyclo-olivil; (−)-olivil; ^{13}C-NMR

In a previous paper,[1] we reported the isolation of (−)-olivil 4',4''-di-*O*-*β*-D-glucopyranoside, (+)-1-hydroxypinoresinol 4',4''-di-*O*-*β*-D-glucopyranoside (**7**), eucommin A [(+)-medioresinol 4'-*O*-*β*-D-glucopyranoside (**8**)] and (+)-syringaresinol *O*-*β*-D-glucopyranoside (**9**) from the air-dried bark of *Eucommia ulmoides* OLIV. (Eucommiaceae), which is one of the longest-known tonic herbs in China. As a continuation of our investigation on this crude drug, this paper describes the isolation of a new lignan glycoside, (+)-1-hydroxypinoresinol 4''-*O*-*β*-D-glucopyranoside (**1**), together with a known lignan glycoside, (+)-1-hydroxypinoresinol 4'-*O*-*β*-D-glucopyranoside (**2**) and four other known compounds, (±)-*erythro*-guaiacylglycerol (**3**), (±)-*threo*-guaiacylglycerol (**4**), (+)-cyclo-olivil (**5**) and (−)-olivil (**6**), and the elucidation of their structures on the basis of chemical evidence and spectroscopic analysis.

The extraction and separation were carried out as described in the experimental section.

Fraction A was obtained as an amorphous, which showed a spot at *Rf* 0.22 on thin layer chromatography (TLC) with $CHCl_3$–MeOH–water (80:20:3) as a developer. The field desorption mass spectrum (FD-MS) of A gave peaks at *m/z* 537 ($M^+ + 1$) and *m/z* 375 ($M^+ - C_6H_{10}O_5 + 1$). Hydrolysis of A with *β*-glucosidase gave the aglycone (**10**) as an amorphous powder, $[\alpha]_D^{19}$ +21° (MeOH). Compound **10** was identified as (+)-1-hydroxypinoresinol by comparison of the ultraviolet (UV), infrared (IR), proton nuclear magnetic resonance (^{1}H-NMR), carbon-13 nuclear magnetic resonance (^{13}C-NMR) and $[\alpha]_D$ data with those of an authentic sample.[1,2] The presence of glucose in the hydrolysate was detected by gas chromatography (GC). Thus, fraction A was considered to be (+)-1-hydroxypinoresinol monoglucoside. As shown in Fig. 1, fraction A was separated into two peaks by high-performance liquid chromatography (HPLC) with a reversed-phase column. Peaks 1 and 2 were each isolated and purified by preparative HPLC, yielding **1** and **2**.

A new lignan glycoside (**1**) was isolated as an amorphous, $[\alpha]_D^{18}$ −28.8° (MeOH). The IR spectrum of **1** showed the presence of hydroxyl groups (3420 cm^{-1}) and aromatic rings

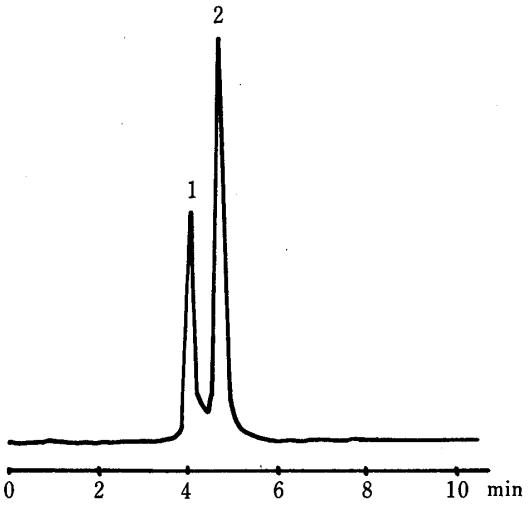


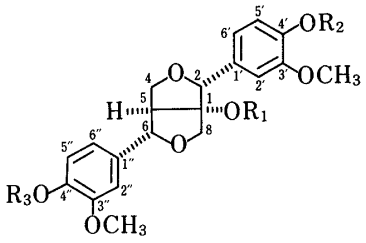
Fig. 1. High-Performance Liquid Chromatogram of Fraction A

Column, Hitachi #3056 (4 × 150 mm); eluent, CH_3CN–water (15:85, v/v); flow rate, 1.0 ml/min; detection, UV at 270 nm.

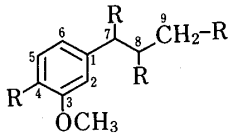
(1608 and 1518 cm^{-1}). The ^{1}H-NMR spectrum of **1** showed signals at δ 3.75 and 3.77 (each s) due to two aromatic methoxyl groups, and at δ 6.65—7.20 (m) due to six aromatic protons. Acetylation of **1** with acetic anhydride–pyridine gave a hexaacetate (**1a**) and a pentaacetate (**1b**). Compound **1a** was isolated as an amorphous, the ^{1}H-NMR spectrum of which showed signals at δ 1.61 (s) due to a tertiary alcoholic acetyl group, at δ 1.96 (3H, s) and 2.00 (9H, s) due to four alcoholic acetyl groups and at δ 2.24 (s) due to a phenolic acetyl group. Compound **1b** was isolated as an amorphous. The IR spectrum of **1b** suggested the presence of a hydroxyl group (3480 cm^{-1}). The ^{1}H-NMR spectrum of **1b** showed signals at δ 1.96 (3H, s) and 2.00 (9H, s) due to four alcoholic acetyl groups, and at 2.24 (s) due to a phenolic acetyl group. The above results suggested that **1** is (+)-1-hydroxypinoresinol monoglucoside and that a glucose moiety is attached to a phenolic group of the aglycone (**10**) at the C-4′ or C-4″ position. The position of the glucose linkage in **1** was investigated as follows. As shown in Table I, the ^{13}C-NMR signals of the carbon atoms of the 4′-free guaiacyl group in **1** were identical with those of the corresponding atoms in **10**.[1-3] On the other hand, the signals of the aromatic carbon atoms of the 4″-*O*-β-D-glucopyranosylguaiacyl group in **1** were identical with those of the corresponding atoms in **7**.[1] The shifts of corresponding carbons in going to **1** from **10** were +2.9 (C-1″) and +1.4 ppm (C-3″), which indicated that the glucosyl group in **1** was linked to the C-4″ position.[1,4] The molecular optical rotation values (M_D) of **1** and **10** are −156° and +81°, respectively. The difference, ΔM_D (**1** M_D − **10** M_D), is −237°, which shows that the D-glucopyranosyl moiety is linked in β-form.[5] Furthermore, the ^{13}C-NMR signals of the glucose moiety in **1** were consistent with β-form.[6] From the above results, **1** was established to be (+)-1-hydroxypinoresinol 4″-*O*-β-D-glucopyranoside. This is the first reported isolation of **1**.

Glycoside **2** was isolated as an amorphous, $[\alpha]_D^{18}$ −25.2° (MeOH). Acetylation of **2** with acetic anhydride–pyridine gave a hexaacetate (**2a**) and a pentaacetate (**2b**). Compound **2a** was obtained as a white powder (EtOH), mp 103.2 °C, and **2b** was obtained as an amorphous. The IR and ^{1}H-NMR spectra of **2a** and **2b** were very similar to those of **1a** and **1b**. Compounds **2** and **2a** were identified as (+)-1-hydroxypinoresinol 4′-*O*-β-D-glucopyranoside and (+)-1-hydroxypinoresinol 4′-*O*-β-D-glucopyranoside hexaacetate, respectively, by comparison with authentic samples.[3]

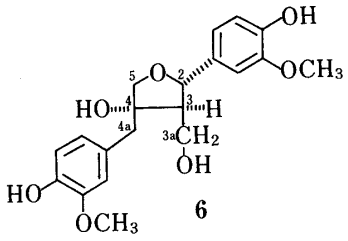
Fraction B was obtained as a syrup, $[\alpha]_D^{28}$ 0° (MeOH). Acetylation of B with acetic anhydride–pyridine gave an amorphous powder, which showed two spots at *Rf* 0.31 (**3a**) and 0.27 (**4a**) on TLC with *n*-hexane–ether (1:1) as a developer. Compounds **3a** and **4a** were identified as (±)-*erythro*-guaiacylglycerol tetraacetate and (±)-*threo*-guaiacylglycerol tetraacetate, respectively, by comparison (IR and ^{1}H-NMR) with authentic samples.[7,8]



1: $R_1=R_2=H$, $R_3=Glc$
1a: $R_1=R_2=Ac$, $R_3=Glc(Ac)_4$
1b: $R_1=H$, $R_2=Ac$, $R_3=Glc(Ac)_4$
2: $R_1=R_3=H$, $R_2=Glc$
2a: $R_1=R_3=Ac$, $R_2=Glc(Ac)_4$
2b: $R_1=H$, $R_2=Glc(Ac)_4$, $R_3=AC$
7: $R_1=H$, $R_2=R_3=Glc$
10: $R_1=R_2=R_3=H$



3: R=OH, *erythro*
4: R=OH, *threo*
3a: R=OAc, *erythro*
4a: R=OAc, *threo*



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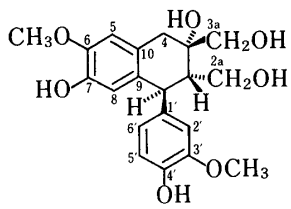

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Chart 1

TABLE I. ^{13}C-NMR Chemical Shifts (in DMSO-d_6)

	1	**2**	**10**	**7**	$\Delta\delta$ **(1—10)**	$\Delta\delta$ **(2—10)**	**1a**	**1b**	**2a**	**2b**
C-1	91.0	91.1	91.1	91.1			96.9	91.2	96.8	91.1
C-5	60.8	60.8	60.9	60.8			58.1	60.9	58.2	60.9
C-4	70.2	70.3	70.2	70.3			71.7	70.4	71.8	70.4
C-8	74.7	74.7	74.9	75.0			73.7	74.7	74.0	74.7
C-2	87.1	86.9	87.1	86.8			85.9	86.5	85.7	86.5
C-6	85.1	85.4	85.5	85.2			83.8	84.8	84.0	84.8
C-1′	127.9	131.1	128.1	131.2		+3.0	135.5	136.2	132.5	133.2
C-1″	135.3	132.3	132.4	135.5	+2.9		136.3	137.5	138.6	138.5
C-2′	112.3	112.5	112.5	112.9		0	113.0	112.1	113.6	112.7
C-2″	110.9	110.7	110.9	111.2	0		111.1	111.0	110.6	110.5
C-3′	146.8	148.3	146.9	148.5		+1.4	150.1	150.0	149.1	149.1
C-3″	148.9	147.5	147.5	149.0	+1.4		149.7	149.8	150.7	150.7
C-4′	145.9	146.0	146.0	146.0		0	138.9	138.5	145.4	145.1
C-4″					−0.1		145.2	145.0	139.4	140.5
C-5′	114.5	114.7	114.6	115.1		+0.1	118.1	118.2	117.3	117.3
C-5″	115.3	115.1	115.2	115.7	+0.1				117.9	117.9
C-6′	120.1	119.8	120.2	119.8		−0.4	122.0	121.6	120.7	119.7
C-6″	118.3	118.8	118.9	118.4	−0.6		118.3	119.5	122.6	122.5
OCH_3	55.6	55.6	55.7	55.9						
	55.7	55.7								
Glc 1	100.1	100.3		100.5						
Glc 2	73.2	73.2		73.3		$OCOCH_3$	20.2	20.2	20.2	20.2
Glc 3	76.9	76.9		76.8			20.3			
Glc 4	69.7	69.7		69.8						
Glc 5	76.9	76.9		77.0			168.3	168.4	168.4	168.5
Glc 6	60.8	60.8		60.8			168.7	168.9	168.7	168.9
							168.9	169.1	168.9	169.2
						$OCOCH_3$	169.2	169.4	169.2	169.5
							169.5	169.8	169.4	169.8
							169.8		169.8	

Compounds **5** and **6** were identified as (+)-cyclo-olivil and (−)-olivil, respectively, by comparison (IR, ^{1}H-, ^{13}C-NMR) with authentic samples.[2,9]

Experimental

All melting points are uncorrected. The following instruments were used; melting point, Mettler FP-61; optical rotation value, JASCO DIP-4; UV spectra, Hitachi 200-20; IR spectra, Hitachi 270-30; GC, Hitachi 063 with a hydrogen flame ionization detector; HPLC, Hitachi 638 with a UV detector; EI-MS, Hitachi RMU-7L; FD-MS, JEOL 01-SG2; ^{1}H-NMR spectra, JEOL JNM-FX-90; ^{13}C-NMR spectra, JEOL JNM-FX-60, with tetramethylsilane ($\delta=0$) as an internal reference. The abbreviations used for NMR data are as follows: s, singlet; d, doublet; dt, doublet-triplet; t, triplet; m, multiplet.

Precoated TLC plates (Silica gel 60 F_{254}, Merck) were used for TLC. The spots were detected by spraying the plates with 20% H_2SO_4 and by heating. Silica gel (Wako gel C-300, Wako Pure Chemical Co.), polyamide C-200 (Wako Pure Chemical Co.) and Diaion HP-20 (Nippon Rensui Co.) were used for column chromatography. TSK gel HW-40 (Toyo Soda Co.) was used for gel filtration.

Isolation——The air-dried bark of *Eucommia ulmoides* Oliv. (10 kg, commercial crude drug produced in China) was chopped and extracted with hot water (20 l × 3). The extract was filtered and the filtrate was evaporated under reduced pressure to a small volume, which was suspended in water. This suspension was extracted with EtOAc (3 l × 2) and then with *n*-BuOH (3 l × 2), successively. The *n*-BuOH extract was evaporated under reduced pressure, then the residue was taken up in water (2 l) and filtered. The filtrate was subjected to chromatography (Diaion HP-20), eluting with water (2 l), 10%, 50% MeOH (each 3 l) and then 100% MeOH (4 l), successively. The 10% MeOH eluate was concentrated and subjected to silica gel chromatography, eluting with $CHCl_3$–MeOH–water (100 : 10 : 1, 90 : 10 : 1, 80 : 20 : 3, 70 : 30 : 5). The fractions were monitored by TLC with $CHCl_3$–MeOH–water (80 : 20 : 3) as a developer. The fractions showing a TLC spot at *Rf* 0.29 were collected and purified by silica gel chromatography and gel filtration on TSK gel HW-40 with MeOH, yielding fraction B (0.2 g). The 50% MeOH eluate was concentrated and subjected to silica gel chromatography, eluting with $CHCl_3$–MeOH–water (100 : 10 : 1, 80 : 20 : 3). The fractions were monitored in the same way as described for B. The fractions showing a TLC spot at *Rf* 0.22 were collected and purified by repeated silica gel chromatography and gel filtration on TSK gel HW-40 with MeOH–water (1 : 1), yielding fraction A (0.3 g), which was separated into two peaks (**1** and **2**) by HPLC. Conditions: column, Hitachi gel #3056, 4 mm × 15 cm; eluent, CH_3CN–water (1 : 9); flow rate, 1 ml/min; detector, UV detector (270 nm). Compounds **1** and **2** were each collected by repeated HPLC under the above conditions, yielding **1** (30 mg) and **2** (60 mg). The 100% MeOH eluate was concentrated. The concentrate showed spots at *Rf* 0.22 (fraction A), 0.36 [(+)-pinoresinol *O*-*β*-D-glucopyranoside],[10] 0.42 (**8**), 0.43 (**5**), 0.44 (**9**) and 0.52 (**6**) on TLC with $CHCl_3$–MeOH–water (80 : 20 : 3) as a developer, and was subjected to silica gel chromatography with $CHCl_3$–MeOH (10 : 1). The fractions showing TLC spots at *Rf* 0.43 (**5**) and 0.52 (**6**) were each collected and purified by silica gel chromatography and on TSK gel HW-40, yielding **5** (0.1 g) and **6** (0.2 g).

Fraction A (1 and 2)——Amorphous, FD-MS *m/z*: 537 ($M^+ + 1$), 375 ($M^+ - C_6H_{10}O_5 + 1$). IR ν_{max}^{KBr} cm^{-1}: 3396 (OH), 1604, 1514 (aromatic ring).

Enzymatic Hydrolysis of Fraction A——Fraction A (100 mg) was hydrolyzed with *β*-glucosidase (50 mg, Sigma) in acetate buffer (0.1 N HOAc–0.1 M NaOAc = 1 : 1, pH = 5.0) for 1 d at 37 °C. The reaction mixture was extracted with Et_2O (50 ml × 2) and the residue obtained from the Et_2O layer was chromatographed on silica gel. Elution with $CHCl_3$–MeOH (20 : 1) gave a pure aglycone (**7**, 30 mg). The aqueous layer was evaporated under reduced pressure to give a residue. This residue was trimethylsilylated with TMS-PZ (Tokyo Kasei Co.) and left for 10 min, then the reaction mixture was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water and concentrated. The presence of trimethylsilylated *α*-glucose [t_R (min) 4.8] and *β*-glucose [t_R (min) 6.9] in this residue was detected by GC. Conditions: column, 1.5% OV-17, 3 mm × 1.5 m; column temperature, 200 °C; carrier gas, N_2, 30 ml/min; injection temperature, 220 °C.

(+)-1-Hydroxypinoresinol (**10**): Amorphous powder, $[\alpha]_D^{19}$ +21° ($c=1.0$, $CHCl_3$). UV λ_{max}^{MeOH} nm: 232, 281. IR ν_{max}^{KBr} cm^{-1}: 3416 (OH), 1606, 1520 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 2.80—3.04 (1H, m, C_5-H), 3.46—4.08 (3H, m, C_{4a}-H, C_8-H), 3.66 (6H, s, 2 × OCH_3), 4.20—4.48 (1H, m, C_{4e}-H), 4.52 (1H, s, C_2-H), 4.76 (2H, d, $J=5$ Hz, C_6-H), 6.60—7.04 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol 4″-*O*-*β*-D-Glucopyranoside (1)——Amorphous, $[\alpha]_D^{18}$ −28.8° ($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm: 228.5, 278. IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1608, 1518 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 3.75, 3.77 (6H, each s, 2 × OCH_3), 6.65—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol 4′-*O*-*β*-D-Glucopyranoside (2)——Amorphous, $[\alpha]_D^{18}$ −25.2° ($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm: 228.5, 279. IR ν_{max}^{KBr} cm^{-1}: 3416 (OH), 1606, 1518 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 3.76 (6H, s, 2 × OCH_3), 6.70—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

Acetylation of 1——**1** (20 mg) was acetylated with acetic anhydride–pyridine. The crude acetate was subjected to silica gel chromatography, with benzene–EtOAc (2 : 1) as a developer. The fractions were monitored by TLC with benzene–EtOAc (1 : 1) as a developer. The fractions showing TLC spots at *Rf* 0.25 (**1a**) and *Rf* 0.13 (**1b**) were each collected, yielding **1a** (3.6 mg) and **1b** (5.6 mg).

(+)-1-Hydroxypinoresinol 4″-*O*-*β*-D-Glucopyranoside Hexaacetate (**1a**): Amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 1758, 1230 ($OCOCH_3$), 1610, 1516 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.61 (3H, s, tert. alcoholic $OCOCH_3$),

1.96, 2.00 (3H, 9H, each s, 4 × alcoholic $OCOCH_3$), 2.24 (3H, s, phenolic $OCOCH_3$), 3.76 (6H, s, 2 × OCH_3), 6.70—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol 4″-*O*-β-D-Glucopyranoside Pentaacetate (**1b**): Amorphous. IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1758, 1228 ($OCOCH_3$), 1608, 1514 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.96, 2.00 (3H, 9H, each s, 4 × alcoholic $OCOCH_3$), 2.24 (3H, s, phenolic $OCOCH_3$), 3.76 (6H, s, 2 × OCH_3), 6.70—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

Acetylation of 2——**2** (50 mg) was acetylated and the crude acetate was treated in the same way as described for **1a** and **1b**, yielding **2a** (*Rf* 0.27, 23 mg) and **2b** (*Rf* 0.15, 21 mg).

(+)-1-Hydroxypinoresinol 4′-*O*-β-D-Glucopyranoside Hexaacetate (**2a**): A white powder (EtOH), mp 103.2 °C. IR ν_{max}^{KBr} cm^{-1}: 1760, 1226 ($OCOCH_3$), 1610, 1516 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.64 (3H, tert. alcoholic $OCOCH_3$), 1.96, 2.00 (3H, 9H, each s, 4 × alcoholic $OCOCH_3$) 2.24 (3H, s, phenolic $OCOCH_3$), 3.73, 3.79 (6H, each s, 2 × OCH_3), 6.85—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol 4′-*O*-β-D-Glucopyranoside Pentaacetate (**2b**): Amorphous. IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1760, 1226 ($OCOCH_3$), 1608, 1514 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.97, 2.02, (3H, 9H, each s, 4 × alcoholic $OCOCH_3$), 2.24 (3H, s, phenolic $OCOCH_3$), 3.73, 3.79 (6H, each s, 2 × OCH_3), 6.85—7.20 (6H, m, arom. H). ^{13}C-NMR: Table I.

(±)-*erythro*- and (±)-*threo*-Guaiacylglycerol (Fraction B; 3 and 4)——Colorless syrup, $[\alpha]_D^{27}$ 0° (*c*=2.24, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1608, 1520 (aromatic ring). MS *m/z*: 214 (M^+), 196 ($M^+ - H_2O$), 167, 152, 137, 125, 97, 85.

Acetylation of Fraction B——Fraction B (0.2 g) was acetylated with acetic anhydride–pyridine. The crude acetate was subjected to silica gel chromatography with *n*-hexane–Et_2O (2 : 1). The fractions were monitored by TLC with *n*-hexane–Et_2O (1 : 1) as a developer. The fractions showing spots at *Rf* 0.31 (**3a**) and at 0.27 (**4a**) were each collected, yielding **3a** (60 mg) and **4a** (150 mg).

(±)-*erythro*-Guaiacylglycerol Tetraacetate (**3a**): Amorphous, $[\alpha]_D^{27}$ −2.5° (*c*=2.02, MeOH). IR ν_{max}^{KBr} cm^{-1}: 1754, 1224 ($OCOCH_3$), 1608, 1514 (aromatic ring). ^{1}H-NMR (in $CDCl_3$) δ: 2.02, 2.11, 2.16 (9H, each s, 3 × alcoholic $OCOCH_3$), 2.29 (3H, s, phenolic $OCOCH_3$), 3.83 (3H, s, OCH_3), 4.24 (2H, d, *J*=4.83 Hz, C_9-H), 5.38 (1H, dt, *J*=5.71, 4.83 Hz, C_8-H), 6.00 (1H, d, *J*=5.71 Hz, C_7-H), 6.86—7.05 (3H, m, arom. H). ^{13}C-NMR (in $CDCl_3$): 55.9 (OCH_3), 61.6 (9), 72.3, 72.7 (8, 7), 111.2 (2), 119.3 (5), 122.8 (6), 134.6 (1), 140.0 (4), 151.2 (3).

(±)-*threo*-Guaiacylglycerol Tetraacetate (**4a**): Colorless prisms (EtOH), mp 115.6 °C, $[\alpha]_D^{27}$ −7.0° (*c*=3.14, MeOH). IR ν_{max}^{KBr} cm^{-1}: 1768, 1224 ($OCOCH_3$), 1608, 1514 (aromatic ring). ^{1}H-NMR (in $CDCl_3$) δ: 2.04, 2.06, 2.08 (9H, each s, 3 × alcoholic $OCOCH_3$), 2.29 (3H, s, phenolic $OCOCH_3$), 3.83 (3H, s, OCH_3), 4.15—4.40 (1H, m, C_9-H_e), 5.25—5.55 (1H, m, C_8-H), 5.95 (1H, d, *J*=7.48 Hz, C_7-H), 6.90—7.10 (3H, m, arom. H). ^{13}C-NMR (in $CDCl_3$): 56.0 (OCH_3), 62.1 (9), 72.3, 73.4 (8, 7), 111.4 (2), 119.7 (5), 123.1 (6), 134.7 (1), 140.3 (4), 151.5 (3).

(+)-Cyclo-olivil (5)——A white powder (EtOH), mp 165 °C, $[\alpha]_D^{25}$ +50.0° (*c*=1.0, MeOH). UV λ_{max}^{MeOH} nm: 228, 283. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1604, 1516 (aromatic ring). MS *m/z*: 376 (M^+), 358 ($M^+ - H_2O$), 340 ($M^+ - 2 \times H_2O$), 327, 309, 297, 265. ^{1}H-NMR (in MeOH-d_4) δ: 1.80—2.06 (1H, m, C_2-H), 2.58 (1H, d, *J*=17 Hz, C_4-H_a), 3.20 (1H, d, *J*=17 Hz, C_4-H_e), 3.73, 3.76 (6H, each s, 2 × OCH_3), 6.16—6.85 (5H, m, arom. H).

(−)-Olivil (6)——A white powder (EtOH), mp 120 °C, $[\alpha]_D^{25}$ −25.2° (*c*=2.5, MeOH). UV λ_{max}^{MeOH} nm: 231, 282. IR ν_{max}^{KBr} cm^{-1}: 3368 (OH), 1606, 1516 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 3.75 (6H, s, 2 × OCH_3), 6.52—7.08 (6H, m, arom. H).

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