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The Constituents of *Eucommia ulmoides* OLIV. II. Isolation and Structures of Three New Lignan Glycosides

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Three new lignan glycosides were isolated from the bark of *Eucommia ulmoides* OLIV. (Eucommiaceae). Their structures were established as (−)-olivil 4′,4″-di-*O*-*β*-D-glucopyranoside (**1**), (+)-1-hydroxypinoresinol 4′,4″-di-*O*-*β*-D-glucopyranoside (**2**) and (+)-medioresinol 4′-*O*-*β*-D-glucopyranoside (named eucommin A) (**3**), based on chemical evidence and spectroscopic studies. A known lignan glycoside, (+)-syringaresinol *O*-*β*-D-glucopyranoside (**4**) was also isolated.

Keywords——*Eucommia ulmoides*; lignan; (−)-olivil 4′,4″-di-*O*-*β*-D-glucopyranoside; (+)-1-hydroxypinoresinol 4′,4″-di-*O*-*β*-D-glucopyranoside; eucommin A; (+)-medioresinol 4′-*O*-*β*-D-glucopyranoside; (+)-syringaresinol *O*-*β*-D-glucopyranoside; ^{13}C-NMR

In a previous paper,[1] one of the authors reported the isolation of (+)-pinoresinol di-*O*-*β*-D-glucopyranoside (I), (+)-medioresinol di-*O*-*β*-D-glucopyranoside (II), liriodendrin [(+)-syringaresinol di-*O*-*β*-D-glucopyranoside] (III) and (+)-pinoresinol *O*-*β*-D-glucopyranoside (IV) from the air-dried bark of *Eucommia ulmoides* OLIV. (Eucommiaceae) (Japanese name: Tochu). As a continuation of our investigation on the constituents of this crude drug, this paper describes the isolation of three new lignans **1**, **2**, **3** and a known lignan **4**, 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.

A thin-layer chromatogram (TLC) of these lignan glycosides is shown in Fig. 1.

Glycoside **1** was isolated as a white powder (EtOH), $C_{32}H_{44}O_{17}$, mp 157 °C, $[\alpha]_D^{25}$ +65° (water), which gave peaks at *m/z* 740 ($M^+ + K + 1$) and 724 ($M^+ + Na + 1$) on field desorption mass spectrometry (FD-MS). The infrared (IR) spectrum of **1** suggested the presence of hydroxyl groups (3400 cm^{-1}) and aromatic rings (1600 and 1510 cm^{-1}). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** showed signals at δ 3.76 (6H, s) due to two aromatic methoxyl groups and at δ 6.64—7.16 (6H, m) due to aromatic protons.

Hydrolysis of **1** with *β*-glucosidase gave an aglycone (**1a**) as a white powder, $C_{20}H_{24}O_7$, mp 117—120 °C, $[\alpha]_D^{25}$ −57.3° (pyridine), which gave a peak at *m/z* 376.1535 (M^+) on high-resolution MS. **1a** was identified as (−)-olivil[2,3] by comparison of the *Rf* value of TLC, ultraviolet (UV), IR, MS, ^{1}H-NMR, carbon-13 nuclear magnetic resonance (^{13}C-NMR) and $[\alpha]_D$ data with those of an authentic sample.

The presence of glucose in the hydrolysate was detected by gas chromatography (GC).

Acetylation of **1** with acetic anhydride-pyridine gave a decaacetate (**1b$_1$**) and a nonaacetate (**1b$_2$**). Compound **1b$_1$** was isolated as a white powder, mp 85—87 °C, $[\alpha]_D^{23}$ −27.4° ($CHCl_3$), which gave a peak at *m/z* 1143 ($M^+ + Na$) on FD-MS. The ^{1}H-NMR spectrum of **1b$_1$** showed signals at δ 1.62 (3H, s), δ 2.04 and 2.08 (27H, each s) due to ten alcoholic acetyl groups and δ 3.82 (6H, s) due to two aromatic methoxyl groups. Compound **1b$_2$** was isolated as a white powder, mp 90—91 °C, $[\alpha]_D^{23}$ −34.7° ($CHCl_3$), whose IR spectrum showed the presence of a hydroxyl group (3496 cm^{-1}). The ^{1}H-NMR spectrum of **1b$_2$** showed

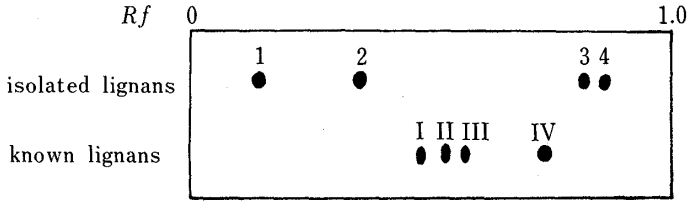
signals at δ 2.04 and 2.08 (27H, each s) due to nine alcoholic acetyl groups. It seems that **1b**$_1$ is completely acetylated, and **1b**$_2$ has a tertiary alcoholic group, but neither **1b**$_1$ nor **1b**$_2$ has any phenolic acetyl groups. These results suggested that **1** is (−)-olivil di-*O*-glucoside and that two glucose moieties are attached to two phenolic groups of the aglycone at the C-4′ and C-4″ positions.

Glycoside **2** was isolated as a white powder, $C_{32}H_{42}O_{17}$, mp 199.7 °C, $[\alpha]_D^{18}$ −55.8° (water), which gave a peak at *m/z* 721 ($M^+ + Na$) on FD-MS. The IR spectrum of **2** showed the presence of hydroxyl groups (3432 cm^{-1}) and aromatic rings (1598 and 1516 cm^{-1}). The ^{1}H-NMR spectrum of **2** showed signals at δ 3.66 (6H, s) and at δ 6.80—7.16 (6H, m), due to two aromatic methoxyl groups and aromatic protons, respectively.

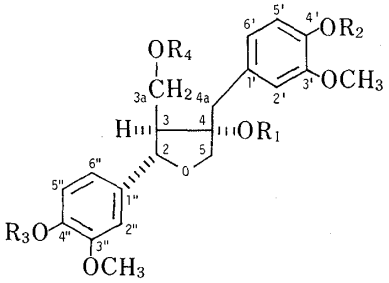
Hydrolysis of **2** with β-glucosidase gave an aglycone (**2a**) as an amorphous powder, $[\alpha]_D^{19}$ +21° ($CHCl_3$), which was identified as (+)-1-hydroxypinoresinol[3] by comparison of the UV, IR, ^{1}H-, ^{13}C-NMR, MS and $[\alpha]_D$ data with those of an authentic sample. The presence of glucose in the hydrolysate was detected by GC.

Acetylation of **2** with acetic anhydride-pyridine gave a nonaacetate (**2b**$_1$) and an octaacetate (**2b**$_2$). Compound **2b**$_1$ was isolated as colorless needles (EtOH), mp 181—182 °C, $[\alpha]_D^{19}$ −4.7° ($CHCl_3$), whose ^{1}H-NMR spectrum showed signals at δ 1.68 (3H, s), δ 2.04 and 2.08 (24H, each s) due to nine alcoholic acetyl groups and at δ 3.82 (6H, s) due to two aromatic methoxyl groups. Compound **2b**$_2$ was isolated as a white powder, mp 192—193 °C, $[\alpha]_D^{19}$ −7.2° ($CHCl_3$), whose IR spectrum showed the presence of a hydroxyl group (3464 cm^{-1}). The ^{1}H-NMR spectrum of **2b**$_2$ showed signals at δ 2.04 and 2.08 (24H, each s) due to eight alcoholic acetyl groups. Thus, it seems that **2** has a tertiary alcoholic group. The above results suggest that **2** is (+)-1-hydroxypinoresinol di-*O*-glucoside and that two glucose moieties are attached to two phenolic groups of the aglycone (**2a**) at the C-4′ and C-4″ positions.

Thus, glycosides **1** and **2** were considered to be (−)-olivil 4′,4″-diglucoside and (+)-1-hydroxypinoresinol 4′,4″-diglucoside, respectively. The positions of glucose linkages in **1** and **2** were investigated as follows. As shown in Table I, the ^{13}C-NMR signals of **1** at 132.0, 137.3, 148.0 and 148.5 were assigned to C-1′, C-1″, C-3′ and C-3″, respectively. The shifts of corresponding carbons in going to **1** from **1a** were +2.9 (C-1′ and C-1″), +1.2 (C-3′) and

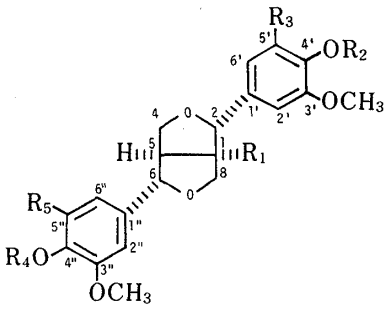


TLC plate: Silicagel 60F_{254}
developer: $CHCl_3$: MeOH : water = 70 : 30 : 5
Fig. 1. TLC of Lignans



1: $R_1 = R_4 = H$, $R_2 = R_3 = glc$
1a: $R_1 = R_2 = R_3 = R_4 = H$
1b$_1$: $R_1 = R_4 = Ac$, $R_2 = R_3 = glc(Ac)_4$
1b$_2$: $R_1 = H$, $R_4 = Ac$, $R_2 = R_3 = glc(Ac)_4$

Chart 1



2: $R_1=OH$, $R_2=R_4=glc$, $R_3=R_5=H$
2a: $R_1=OH$, $R_2=R_3=R_4=R_5=H$
2b$_1$: $R_1=OAc$, $R_2=R_4=glc(Ac)_4$, $R_3=R_5=H$
2b$_2$: $R_1=OH$, $R_2=R_4=glc(Ac)_4$, $R_3=R_5=H$
3: $R_1=R_4=R_5=H$, $R_2=glc$, $R_3=OCH_3$
3a: $R_1=R_2=R_4=R_5=H$, $R_3=OCH_3$
3b: $R_1=R_5=H$, $R_2=glc(Ac)_4$, $R_3=OCH_3$, $R_4=Ac$
4: $R_1=R_4=H$, $R_2=glc$, $R_3=R_5=OCH_3$
4a: $R_1=R_2=R_4=H$, $R_3=R_5=OCH_3$
4b: $R_1=H$, $R_2=glc(Ac)_4$, $R_3=R_5=OCH_3$, $R_4=Ac$

Chart 2

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

	1	**1a**	$\Delta\delta$ (**1**—**1a**)	**1b$_2$**	**2**	**2a**	$\Delta\delta$ (**2**—**2a**)	**2b$_2$**
C-1					91.1	91.0		91.2
C-2	82.8	83.1		83.2	86.8	87.1		86.6
C-3	60.7	60.4		57.2				
C-3a	58.9	58.8		61.9				
C-4	80.2	80.4		80.0	70.3	70.2		70.4
C-4a	38.7	38.8		38.7				
C-5	76.1	76.1		75.8	60.8	60.9		61.0
C-6					85.2	85.5		85.0
C-8					75.0	74.9		74.9
C-1′	132.0	129.1	+2.9	133.6	131.2	128.1	+3.1	133.3
C-1″	137.3	134.4	+2.9	138.4	135.5	132.4	+3.1	137.6
C-2′	111.3	111.1	+0.2	115.6	112.9	112.5	+0.4	113.1
C-2″				111.6	111.2	110.9	+0.3	111.3
C-3′	148.0	146.8	+1.2	149.0	148.5	146.9	+1.6	149.2
C-3″	148.5	147.2	+1.3	149.5	149.0	147.5	+1.5	149.9
C-4′	144.8	144.6	+0.2	144.2	146.0	146.0	0	145.1
C-4″	145.4	145.4	0	145.0				
C-5′	115.1	114.7	+0.4	117.8	115.1	114.6	+0.5	117.4
C-5″	114.9		+0.2	117.6	115.7	115.2	+0.5	118.3
C-6′	122.1	122.4	−0.3	122.3	119.8	120.2	−0.4	119.8
C-6″	118.5	119.0	−0.5	118.6	118.4	118.9	−0.5	118.3
OCH_3	55.7	55.6		55.9	55.9	55.8		56.1
Glc-1′	100.4		$OCOCH_3$	20.2	100.5		$OCOCH_3$	20.3
Glc-1″								20.4
Glc-2′	73.1		$OCOCH_3$	168.7	73.3		$OCOCH_3$	168.8
Glc-2″				169.0				169.1
Glc-3′	76.7			169.3	76.8			169.4
Glc-3″				169.6				169.7
Glc-4′	69.7			169.9	69.8			
Glc-4″								
Glc-5′	76.7				77.0			
Glc-5″								
Glc-6′	60.7				60.8			
Glc-6″								

+1.3 ppm (C-3″), which indicated that the two glucosyl groups in **1** were linked to the C-4′ and C-4″ carbons.[3,4] Similarly, the shift differences of the corresponding carbons of **2** from **2a** were +3.1 (C-1′ and C-1″), +1.6 (C-3′) and +1.5 ppm (C-3″), which indicated that two

TABLE II. ^{13}C-NMR Chemical Shifts and *O*-Glucosylation Shifts (in DMSO-d_6)

	3	**3a**	$\Delta\delta$ (**3**—**3a**)	**4**	**4a**	$\Delta\delta$ (**4**—**4a**)
C-1	53.6	53.6		53.6	53.8	
C-5	53.8	53.7				
C-4	71.1	71.0		71.2	71.1	
C-8	71.3					
C-2	85.1	85.2		85.3	85.3	
C-6		85.3		85.1		
C-1′	134.1	131.6	+2.5	134.1	131.5	+2.6
C-1″	132.3	132.3		131.4		
C-2′	104.5	104.0	+0.5	104.4	103.9	+0.5
C-2″	110.7	110.6		104.0		
C-3′	152.7	148.0	+4.7	152.6	147.9	+4.7
C-3″	147.6	147.5		148.0		
C-4′	137.3	135.1	+2.2	137.2	135.0	+2.2
C-4″	146.0	146.0		135.1		
C-5′	152.7	148.0	+4.7	152.6	147.9	+4.7
C-5″	115.2	115.2		148.0		
C-6′	104.5	104.0	+0.5	104.4	103.9	+0.5
C-6″	118.7	118.6		104.0		
OCH_3	55.8	55.8		56.1	56.1	
	56.5	56.1		56.5		
Glc-1′	103.0			102.9		
Glc-1″						
Glc-2′	74.3			74.2		
Glc-2″						
Glc-3′	76.5			76.5		
Glc-3″						
Glc-4′	70.1			70.1		
Glc-4″						
Glc-5′	77.1			77.1		
Glc-5″						
Glc-6′	61.1			61.1		
Glc-6″						

glucose moieties in **2** were also attached to two phenolic groups of the aglycone (**2a**) at the C-4′ and C-4″ positions, respectively. Furthermore, the ^{13}C-NMR chemical shifts of the glucosyl carbons in **1** and **2** indicated that each glucosyl group was in β-D-pyranosyl form.

From the above results, **1** and **2** were established as (−)-olivil 4′,4″-di-*O*-β-D-glucopyranoside and (+)-1-hydroxypinoresinol 4′,4″-di-*O*-β-D-glucopyranoside, respectively.

Glycoside **4** was isolated as a white powder, mp 187.7 °C, $[\alpha]_D^{18}$ −5.1° (MeOH), which gave peaks at *m/z* 603 ($M^+ + Na$) and 580 (M^+) on FD-MS. The IR spectrum of **4** showed the presence of hydroxyl groups (3428 cm^{-1}) and aromatic rings (1598 and 1520 cm^{-1}). The ^{1}H-NMR spectrum of **4** showed signals at δ 3.66 (12H, s) due to four aromatic methoxyl groups and δ 6.60 and 6.65 (4H, each s) due to aromatic protons.

Hydrolysis of **4** with β-glucosidase gave an aglycone (**4a**) as an amorphous, $[\alpha]_D^{19}$ +22.7° ($CHCl_3$), whose ^{1}H-, ^{13}C-NMR and IR data and TLC behavior were identical with those of (+)-syringaresinol.[1] The presence of glucose in the hydrolysate was detected by GC.

Acetylation of **4** with acetic anhydride–pyridine gave a pentaacetate (**4b**) as an amorphous powder, whose ^{1}H-NMR spectrum showed signals at δ 1.98 (12H, s) due to four alcoholic acetyl groups and δ 2.24 (3H, s) due to a phenolic acetyl group.

^{1}H- and ^{13}C-NMR spectra of **4** (Table II) were identical with those of (±)-syringaresinol

O-β-D-glucopyranoside,[5] which was isolated from the bark of *Magnolia officinalis* (Magnoliaceae).

Thus, **4** was established as (+)-syringaresinol *O*-β-D-glucopyranoside.

A new glycoside, named eucommin A (**3**) was isolated as a white powder (EtOH), mp 162.8 °C, $[\alpha]_D^{18}$ +20.4° (MeOH), which gave a peak at *m/z* 574 ($M^+ + Na + 1$) on FD-MS. The IR spectrum of **3** showed the presence of hydroxyl groups (3424 cm^{-1}) and aromatic rings (1596 and 1516 cm^{-1}). The ^{1}H-NMR spectrum of **3** showed signals at δ 3.65 (9H, s) and δ 6.60—6.92 (5H, m), due to three aromatic methoxyl groups and aromatic protons, respectively.

Hydrolysis of **3** with β-glucosidase gave an aglycone (**3a**) as an amorphous powder, $[\alpha]_D^{19}$ +62.5° ($CHCl_3$), whose ^{1}H-, ^{13}C-NMR, IR and MS data and TLC behavior were identical with those of (+)-medioresinol.[1] The presence of glucose in the hydrolysate was detected by GC.

Acetylation of **3** with acetic anhydride–pyridine gave a pentaacetate (**3b**) as a white powder (EtOH), mp 131 °C, whose ^{1}H-NMR spectrum showed signals at δ 1.98 (12H, s) due to four alcoholic acetyl groups and at δ 2.24 (3H, s) due to a phenolic acetyl group.

Thus, eucommin A (**3**) was considered to be (+)-medioresinol monoglucoside. The position of the glucose linkage was determined as follows. As shown in Table II, the ^{13}C-NMR chemical shifts of the carbon atoms of the guaiacyl group in **3** were identical with those of the corresponding carbon atoms in **3a**. On the other hand, the shifts of carbon atoms of the syringyl group in **3** were identical with those of the corresponding carbons of the 4-*O*-β-D-glucopyranosylsyringyl group in **4**.

These results led us to the conclusion that **3** was (+)-medioresinol 4′-*O*-β-D-glucopyranoside.

Experimental

All melting points are uncorrected. The following instruments were used: melting point, Mitamura micro-melting point apparatus or 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; electron impact (EI)-MS, Hitachi RMU-7L; FD-MS, JEOL-01-SG2; NMR spectra, JEOL-FX-90-Q (^{1}H-NMR, 89.55 MHz; ^{13}C-NMR, 22.5 MHz) with tetramethylsilane (δ = 0) as internal reference. The abbreviations used for NMR data are as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

Kieselgel 60 F_{254} (Merck) precoated TLC plates were used for TLC. The spots were detected by spraying the plate with 20% H_2SO_4 and by heating. Silica gel (Wako gel C-300, Wako Pure Chemical), polyamide C-200 (Wako Pure Chemical) and Diaion HP-20 (Nippon Rensui Co.) were used for column chromatography. TSK gel HW-40 (Toyo Soda) 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 to a small volume under reduced pressure, then suspended in water. This suspension was extracted with EtOAc (3 l × 2) and then with *n*-BuOH (3 l × 2), successively. The aqueous layer was evaporated under reduced pressure, then diluted with water (5 l). The aqueous solution was subjected to column chromatography (Diaion HP-20), eluting with water (5 l), 30% MeOH (5 l), 50% MeOH (10 l) and then 100% MeOH (15 l) successively. The 50% MeOH eluate was concentrated and subjected to silica gel chromatography, eluting with $CHCl_3$–MeOH–water (80 : 20 : 3, 70 : 30 : 5). The fractions were monitored by TLC using $CHCl_3$–MeOH–water (70 : 40 : 8) as a developer. The fractions showing TLC spots at *Rf* 0.38 (**2**) and 0.26 (**1**) were each collected and purified by silica gel chromatography and gel filtration on TSK gel HW-40 with 50% MeOH, yielding **1** (0.3 g) and **2** (0.5 g). The *n*-BuOH extract was concentrated and subjected to silica gel chromatography, eluting with $CHCl_3$–MeOH (20 : 1, 10 : 1). The fractions were monitored by TLC using $CHCl_3$–MeOH–water (80 : 20 : 3) as a developer. The fractions showing TLC spots at *Rf* 0.42 (**3**) and 0.46 (**4**) were each collected and purified by silica gel chromatography and gel filtration on TSK gel HW-40 with 50% MeOH, yielding **3** (0.4 g) and **4** (0.75 g).

(−)-Olivil 4′,4″-Di-*O*-β-D-glucopyranoside (1)——A white powder (from MeOH), mp 157 °C, $[\alpha]_D^{25}$ +65° (*c* = 1.0, water). UV λ_{max}^{MeOH} nm: 217, 278. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1600, 1510 (aromatic ring). FD-MS add. NaI *m/z*: 740 ($M^+ + K + 1$), 724 ($M^+ + Na + 1$), 561; add. none *m/z*: 376 ($M^+ - 2 \times C_6H_{11}O_5 + 2$). ^{1}H-NMR (in DMSO-$d_6$) δ : 3.76

(6H, s, $2\times OCH_3$), 6.64—7.16 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol 4′,4″-Di-*O*-β-D-glucopyranoside (2)——A white powder (from EtOH), mp 199.7 °C, $[\alpha]_D^{18}$ −55.8° (c=3.85, water). UV λ_{max}^{MeOH} nm: 228, 276. IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1598, 1516 (aromatic ring). FD-MS add. NaI m/z: 721 (M^++Na), 559 ($M^+-C_6H_{11}O_5$+Na+1), 372 ($M^+-2\times C_6H_{11}O_5$). ^{1}H-NMR (in DMSO-d_6) δ: 2.80—3.04 (1H, m, C_5-H), 3.66 (6H, s, $2\times OCH_3$), 6.80—7.16 (6H, m, arom. H). ^{13}C-NMR: Table I.

Eucommin A (3)——A white powder (from EtOH), mp 162.8 °C, $[\alpha]_D^{18}$ +20.4° (c=2.40, MeOH). UV λ_{max}^{MeOH} nm: 228.5, 280. IR ν_{max}^{KBr} cm^{-1}: 3424 (OH), 1596, 1516 (aromatic ring). FD-MS add. NaI m/z: 574 (M^++Na+1), 389 ($M^+-C_6H_{11}O_5$+2). ^{1}H-NMR (in DMSO-d_6) δ: 3.65 (9H, s, $3\times OCH_3$), 3.64—4.27 (4H, m, C_4-H, C_8-H), 6.60—6.92 (5H, m, arom. H). ^{13}C-NMR: Table II.

(+)-Syringaresinol *O*-β-D-Glucopyranoside (4)——A white powder (from EtOH), mp 187.7 °C, $[\alpha]_D^{18}$ −5.1° (c=3.85, MeOH). UV λ_{max}^{MeOH} nm: 228, 271.5. IR ν_{max}^{KBr} cm^{-1}: 3428 (OH), 1598, 1520 (aromatic ring). FD-MS add. NaI m/z: 603 (M^++Na), 580 (M^+). ^{1}H-NMR (in DMSO-d_6) δ: 3.64—4.27 (4H, m, C_4-H, C_8-H), 3.66 (12H, s, $4\times OCH_3$), 6.60, 6.65 (4H, each s, arom. H on syringyl ring). ^{13}C-NMR: Table II.

Enzymatic Hydrolysis of 1—4——Glycoside **1** (200 mg) was hydrolyzed with β-glucosidase (100 mg, Miles Laboratories) in acetate buffer (0.1 N HOAc–0.1 M NaOAc = 1 : 2, pH 5.0) for 3 d at 37 °C. The reaction mixture was extracted with Et_2O (50 ml × 2) and the residue obtained from the organic phase was chromatographed on silica gel. Elution with $CHCl_3$–MeOH (20 : 1) gave a pure aglycone (**1a**, 20 mg). The aqueous layer was evaporated under reduced pressure and gave the residue. This residue was trimethylsilylated with TMS-PZ (Tokyo Kasei) and left for 10 min. 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.

Glycosides **2**—**4** (each 100 mg) were each hydrolyzed in the same way as described for **1** and gave the aglycones (**2a**, **3a** and **4a**, respectively). The presence of glucose in the hydrolysates of **2**—**4** was detected by GC in the same way as described for **1**.

(−)-Olivil (1a)——A white powder (from MeOH), mp 117—120 °C, $[\alpha]_D^{25}$ −57.3° (c=0.61, pyridine), UV λ_{max}^{MeOH} nm: 231, 282. IR ν_{max}^{KBr} cm^{-1}: 3368 (OH), 1606, 1516 (aromatic ring). High-resolution MS m/z: 376.1535 (M^+, $C_{20}H_{24}O_7$, 4%), 358.1443 (M^+-H_2O, 5%), 196.0746 ($C_{10}H_{12}O_4$, 37%), 181.0824 ($C_{10}H_{13}O_3$, 77%), 137.0604 ($C_8H_9O_2$, 100%). FD-MS m/z: 377 (M^++1), 376 (M^+). ^{1}H-NMR (in DMSO-d_6) δ: 3.75 (6H, s, $2\times OCH_3$), 6.52—7.08 (6H, m, arom. H). ^{13}C-NMR: Table I.

(+)-1-Hydroxypinoresinol (2a)——An amorphous powder, $[\alpha]_D^{19}$ +21° (c=32.2, $CHCl_3$). 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, $2\times OCH_3$), 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.

(+)-Medioresinol (3a)——An amorphous powder, $[\alpha]_D^{19}$ +62.5° (c=1.0, $CHCl_3$). UV λ_{max}^{MeOH} nm: 231.5, 280. IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1616, 1520 (aromatic ring). ^{1}H-NMR (in $CDCl_3$) δ: 2.9—3.20 (2H, m, C_1-H, C_5-H), 3.80—4.40 (4H, m, C_4-H, C_8-H), 3.88 (9H, s, $3\times OCH_3$), 4.64—4.80 (2H, m, C_2-H, C_6-H), 6.57 (2H, s, arom. H on syringyl ring), 6.72—6.96 (3H, m, arom. H on guaiacyl ring). ^{13}C-NMR: Table II.

(+)-Syringaresinol (4a)——An amorphous powder, $[\alpha]_D^{19}$ +22.7° (c=7.7, $CHCl_3$). UV λ_{max}^{MeOH} nm: 237, 273. IR ν_{max}^{KBr} cm^{-1}: 3428 (OH), 1614, 1520 (aromatic ring). ^{1}H-NMR (in $CDCl_3$) δ: 3.00—3.20 (2H, m, C_1-H, C_5-H), 3.80—4.20 (4H, m, C_4-H, C_8-H), 3.90 (12H, s, $4\times OCH_3$), 4.67 (2H, d, J=4 Hz, C_2-H, C_6-H), 6.58 (4H, s, arom. H). ^{13}C-NMR: Table II.

Acetylation of Glycoside 1——Glycoside **1** (200 mg) was acetylated with acetic anhydride–pyridine in the usual way at room temperature. The crude acetate was subjected to silica gel chromatography, eluting with $CHCl_3$–MeOH (20 : 1). The fractions were monitored by TLC using $CHCl_3$–MeOH (20 : 1) as a developer. The fractions showing TLC spots at Rf 0.62 (**1b**$_1$) and 0.52 (**1b**$_2$) were each collected and purified by silica gel chromatography, yielding **1b**$_1$ (40 mg) and **1b**$_2$ (80 mg).

(−)-Olivil 4′,4″-Di-*O*-β-D-glucopyranoside Decaacetate (1b$_1$)——A white powder (from EtOH), mp 85—87 °C, $[\alpha]_D^{23}$ −27.4° (c=0.64, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1758 (C=O), 1600, 1514 (aromatic ring). FD-MS add. NaI m/z: 1143 (M^++Na), 1101 (M^+-COCH_2+Na), 1059 ($M^+-2\times COCH_2$+Na), 331. ^{1}H-NMR (in $CDCl_3$) δ: 1.62 (3H, s, tertiary alcoholic $OCOCH_3$), 2.04, 2.08 (27H, each s, 9 × alcoholic $OCOCH_3$), 3.82 (6H, s, $2\times OCH_3$), 6.50—7.50 (6H, m, arom. H).

(−)-Olivil 4′,4″-Di-*O*-β-D-glucopyranoside Nonaacetate (1b$_2$)——A white powder (from EtOH), mp 90—91 °C, $[\alpha]_D^{23}$ −34.7° (c=3.24, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3496 (OH), 1758 (C=O), 1598, 1514 (aromatic ring). ^{1}H-NMR (in $CDCl_3$)δ: 2.04, 2.08 (27H, each s, 9 × alcoholic $OCOCH_3$), 6.60—7.28 (6H, m, arom. H). ^{13}C-NMR: Table I.

Acetylation of Glycoside 2——Glycoside **2** (150 mg) was treated in the same way as described for **1**. The fractions were monitored by TLC using $CHCl_3$–MeOH (20 : 1) as a developer, and the fractions showing TLC spots at Rf 0.63 (**2b**$_1$) and 0.53 (**2b**$_2$) were each collected and purified by silica gel chromatography, yielding **2b**$_1$ (40 mg) and **2b**$_2$ (75 mg).

(+)-1-Hydroxypinoresinol 4′,4″-Di-*O*-β-D-glucopyranoside Nonaacetate (2b$_1$)——Colorless needles (from EtOH),

mp 181—182 °C, $[\alpha]_D^{19}$ −4.7° (c=26.4, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O), 1600, 1516 (aromatic ring). ^{1}H-NMR (in $CDCl_3$) δ: 1.68 (3H, s, tertiary alcoholic $OCOCH_3$), 2.04, 2.08 (24H, each s, alcoholic $OCOCH_3$), 3.82, 3.86 (6H, each s, 2×OCH_3), 6.80—7.20 (6H, m, arom. H).

(+)-1-Hydroxypinoresinol 4′,4″-Di-*O*-β-D-glucopyranoside Octaacetate ($2b_2$)——A white power (from EtOH), mp 192—193 °C, $[\alpha]_D^{19}$ −7.2° (c=25.7, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3464 (OH), 1758 (C=O), 1632, 1518 (aromatic ring). ^{1}H-NMR (in $CDCl_3$), δ: 2.04, 2.08 (24H, each s, 8×alcoholic $OCOCH_3$), 3.85 (6H, s, 2×OCH_3) 6.80—7.24 (6H, m, arom. H). ^{13}C-NMR: Table I.

Acetylation of Glycoside 3 and 4——Glycosides **3** (100 mg) and **4** (100 mg) were acetylated in the same way as described for **1** to give pentaacetates, **3b** (50 mg) and **4b** (45 mg), respectively.

Eucommin A Pentaacetate (3b)——A white powder (from EtOH), mp 131 °C, IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O), 1596, 1506 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.98 (12H, s, 4×alcoholic $OCOCH_3$), 2.24 (3H, s, phenolic $OCOCH_3$), 3.76, 3.78 (9H, each s, 3×OCH_3), 6.66—7.12 (5H, m, arom. H).

(+)-Syringaresinol *O*-β-D-Glucopyranoside Pentaacetate (4b)——An amorphous powder. IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O), 1604, 1508 (aromatic ring). ^{1}H-NMR (in DMSO-d_6) δ: 1.98 (12H, s, 4×alcoholic $OCOCH_3$), 2.24 (3H, s, phenolic $OCOCH_3$), 3.76 (12H, s, 4×OCH_3), 6.66, 6.72 (4H, each s, arom. H).

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