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Lignans from Bark of the *Olea* Plants. II[1)]

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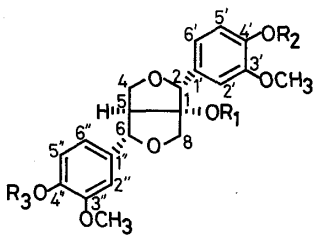
Four new lignans, (+)-1-acetoxypinoresinol-4′-β-D-glucoside (**1**), (+)-1-acetoxypinoresinol-4′-β-D-glucoside 4″-*O*-methyl ether (**2**), (+)-1-hydroxypinoresinol-1-β-D-glucoside (**4**) and (+)-fraxiresinol-1-β-D-glucoside (**5**), and a known lignan, (+)-1-hydroxypinoresinol-4′-β-D-glucoside (**3**), were isolated from the bark of *Olea europaea* L. and the bark of *Olea africana* MILL. (*Olea europaea* L. subsp. *africana* (MILL.) GREEN) (Oleaceae). Their structures were elucidated on the basis of spectroscopic analysis and chemical evidence. The bark of *Olea capensis* L. did not yield any lignan glucosides.

Keywords——*Olea europaea*; *Olea africana*; *Olea capensis*; Oleaceae; lignan; (+)-1-acetoxypinoresinol-4′-β-D-glucoside; (+)-1-acetoxypinoresinol-4′-β-D-glucoside 4″-*O*-methyl ether; (+)-1-hydroxypinoresinol-4′-β-D-glucoside; (+)-1-hydroxypinoresinol-1-β-D-glucoside; (+)-fraxiresinol-1-β-D-glucoside

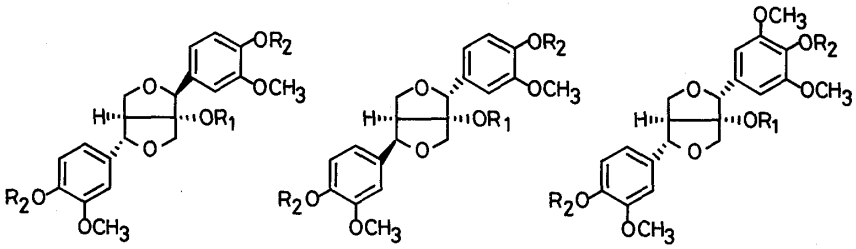
In a previous paper,[1)] we reported the isolation of four new and two known lignans from *Olea* bark. As a continuation of our studies on the constituents of *Olea* bark, this paper deals with the isolation of four new lignans, (+)-1-acetoxypinoresinol-4′-β-D-glucoside (**1**), (+)-1-acetoxypinoresinol-4′-β-D-glucoside 4″-*O*-methyl ether (**2**), (+)-1-hydroxypinoresinol-1-β-D-glucoside (**4**) and (+)-fraxiresinol-1-β-D-glucoside (**5**), along with a known lignan, (+)-1-hydroxypinoresinol-4′-β-D-glucoside (**3**), from both *Olea europaea* L. and *O. africana* MILL. (*O. europaea* L. subsp. *africana* (MILL.) GREEN) (Oleaceae), and their structure elucidation on the basis of spectroscopic analysis and chemical evidence.

The bark of *O. capensis* L. did not yield any lignan glucosides.

The lignan **1** was obtained as colorless needles, $C_{28}H_{34}O_{13} \cdot 1/2H_2O$, mp 183.5—185 °C, $[\alpha]_D^{22}$ +7.9° (ethanol). The infrared (IR) spectrum of **1** suggested the presence of an ester (1735 cm^{-1}) and aromatic rings (1600, 1590 and 1520 cm^{-1}). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** exhibited signals at δ 1.67 (3H, s) due to alcoholic acetoxy protons, at δ 3.87 (6H, s) due to aromatic methoxy protons and at δ 6.67—7.30 (6H, m) due to aromatic protons. The ultraviolet (UV) spectrum of **1** showed absorption maxima at 231 and 279.5 nm. The bathochromic shift of the absorption maxima in the presence of base was very similar to that of (+)-pinoresinol-β-D-glucoside.[2)] The enzymatic hydrolysis of **1** gave compound **1a** and D-glucose. Compound **1a** was identified as (+)-1-acetoxypinoresinol by direct comparison with an authentic sample.[1)] Acetylation of **1** with acetic anhydride–pyridine gave compound **1b** as a colorless syrup, $C_{38}H_{44}O_{18}$, $[\alpha]_D^{20}$ −6.3° (ethanol). The ^{1}H-NMR spectrum of **1b** showed the presence of five alcoholic acetoxy groups (δ 1.67, 2.03 and 2.10), a phenolic acetoxy group (δ 2.33) and two aromatic methoxy groups (δ 3.83 and 3.87). These data suggested that **1** is a monoglucoside of **1a**. As regards the position of the glucose linkage in **1**, carbon-13 nuclear magnetic resonance (^{13}C-NMR) glucosylation shift values[3)] of aromatic carbons in **1** relative to **1a** ($\Delta\delta$ +2.7 at C-1′ and +1.3 at C-3′) indicated that D-glucose is attached to the 4′-*O*-position of **1a**. Methylation of **1** with diazomethane gave



1 : R_1=Ac, R_2=Glc, R_3=H
1a: R_1=Ac, R_2=R_3=H
1b: R_1=Ac, R_2=Glc(Ac)$_4$, R_3=Ac
2 : R_1=Ac, R_2=Glc, R_3=CH_3
2a: R_1=Ac, R_2=H, R_3=CH_3
3 : R_1=H, R_2=Glc, R_3=H
3a: R_1=H, R_2=R_3=H
3b: R_1=H, R_2=R_3=CH_3
4 : R_1=Glc, R_2=R_3=H
4a: R_1=Glc(Ac)$_4$, R_2=R_3=Ac
4b: R_1=Glc, R_2=R_3=CH_3



4c: R_1=R_2=H
4d: R_1=H, R_2=CH_3
4e: R_1=Ac, R_2=H

4f: R_1=Ac, R_2=H
4g: R_1=R_2=H
4h: R_1=H, R_2=CH_3

5 : R_1=Glc, R_2=H
5a: R_1=Glc(Ac)$_4$, R_2=Ac
5b: R_1=Glc, R_2=CH_3
6 : R_1=R_2=H
6a: R_1=H, R_2=CH_3

Chart 1

compound **2**, which was identical with the lignan **2**, isolated as an amorphous powder, $C_{29}H_{36}O_{13}\cdot H_2O$, $[\alpha]_D^{20}$ +9.1° (ethanol). The enzymatic hydrolysis of **2** gave compound **2a** and D-glucose. Compound **2a** was confirmed to be (+)-1-acetoxypinoresinol 4″-*O*-methyl ether by direct comparison with an authentic sample.[1)]

Thus, the structures of **1** and **2** have been established as (+)-1-acetoxypinoresinol-4′-*β*-D-glucoside and (+)-1-acetoxypinoresinol-4′-*β*-D-glucoside 4″-*O*-methyl ether, respectively.

The lignan **3** was obtained as colorless plates, $C_{26}H_{32}O_{12}\cdot 3/2H_2O$, mp 127—129 °C, $[\alpha]_D^{23}$ −9.3° (methanol), whose molecular weight was confirmed by the observation of *m/z* 536 (M^+) on field desorption mass spectra (FD-MS). The enzymatic hydrolysis of **3** gave compound **3a** and D-glucose. Compound **3a** was identified as (+)-1-hydroxypinoresinol by direct comparison with an authentic sample.[1)] The spectral data (IR, UV, ^{1}H-NMR and ^{13}C-NMR) of **3** suggested that **3** is a monoglucoside of **3a**. The lignan **3** was identical with (+)-1-hydroxypinoresinol-4′-*β*-D-glucoside, which was isolated from bark of *Fraxinus mandshurica* RUPR. var. *japonica* MAXIM. (Oleaceae).[2)]

The lignan **4** was obtained as an amorphous powder, $C_{26}H_{32}O_{12}\cdot 5/2H_2O$, mp 179—183 °C, $[\alpha]_D^{23}$ −17.5° (ethanol). The ^{1}H-NMR spectrum of **4** exhibited signals at δ 3.84 (6H, s) due to aromatic methoxy protons and at δ 6.52—7.22 (6H, m) due to aromatic protons. The UV spectrum of **4** showed absorption maxima at 232.3 and 280.5 nm. The bathochromic shift of the absorption maxima in the presence of base was very similar to that of **3a**. Acetylation of **4** with acetic anhydride–pyridine gave compound **4a** as a colorless syrup, $C_{38}H_{44}O_{18}$, $[\alpha]_D^{23}$ −14.2° (chloroform). The ^{1}H-NMR spectrum showed the presence of four alcoholic acetoxy groups (δ 1.95, 2.00 and 2.03), two phenolic acetoxy groups (δ 2.33) and two aromatic methoxy groups (δ 3.86 and 3.89). Methylation of **4** with diazomethane gave compound **4b** as an amorphous powder, $C_{28}H_{26}O_{12}$, $[\alpha]_D^{23}$ −12.3° (methanol). The ^{1}H-NMR spectrum showed the presence of four aromatic methoxy groups (δ 3.77). These data revealed that **4** has two aromatic methoxy groups, four alcoholic and two phenolic hydroxy groups in the structure,

being indicative of pinoresinol-type lignan glycoside. The lignan **4** was resistant to enzymatic hydrolysis. However, the acid hydrolysis of **4** gave compound **4c** as a colorless crystalline powder, $C_{20}H_{22}O_7$, mp 137—140 °C, $[\alpha]_D^{18}$ +60.9° (ethanol), and D-glucose. Methylation of **4c** with diazomethane gave compound **4d** as colorless plates, $C_{22}H_{26}O_7$, mp 163—165 °C, $[\alpha]_D^{17}$ +59.4° (chloroform). The acid hydrolysis of **4b** gave **4d** and D-glucose. The spectral data of **4d** were in good agreement with those of known neogmelinol (**4d**), which is formed in good yield from isogmelinol (**3b**) by acid treatment.[3] Further, the acid treatment of **3a** gave only **4c**. Thus, the structure of **4c** has been elucidated as (+)-1-hydroxy-2-epipinoresinol (**4c**). These results suggested that **4** is a monoglucoside of either **3a** or **4c** in which D-glucose is attached to the 1-*O*-position.

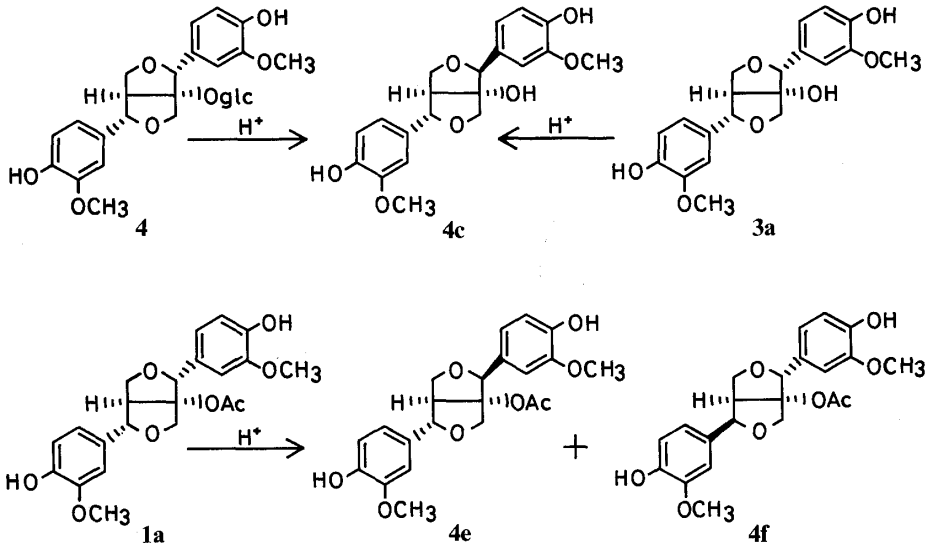


Chart 2

TABLE I. ^{1}H-NMR Chemical Shifts[a] of the 2,6-Diaryl-3,7-dioxabicyclo[3.3.0]octane Ring

	4[b]	1a	3b[c]	4e	4d[c]	4f	4h[c]
C_5-H		3.00—3.57 1H, m	2.80—3.35 1H, m	3.04—3.42 1H, m	2.50—2.80 1H, m	3.18—3.70 1H, m	2.97—3.16 1H, m
C_{4a}-H						3.29, 1H, dd, J=9, 9 Hz	3.31, 1H, dd, J=9, 9 Hz
C_{4e}-H		4.36, 1H (4e) dd, J=8, 9 Hz	4.57, 1H (4e) dd, J=8, 9 Hz	4.03—4.41 2H, m	3.96—4.34 2H, m		4.03, 1H, dd, J=9, 9 Hz
	3.60—4.56 4H, m					4.03—4.23 2H, m	
C_{8a}-H		3.65—4.55 3H, m	3.50—4.36 3H, m	3.58, 1H, d, J=10 Hz	3.46, 1H, d, J=10 Hz	4.58, 1H, d, J=10 Hz	3.68, 1H, d, J=9 Hz
C_{8e}-H				3.67, 1H, d, J=10 Hz	3.62, 1H, d, J=10 Hz		4.20, 1H, d, J=9 Hz
C_2-H	4.98 1H, s	5.08 1H, s	4.87 1H, s	5.13 1H, s	4.70 1H, s	4.70 1H, s	4.56 1H, s
C_6-H	4.73, 1H, d, J=5 Hz	4.77, 1H, d, J=5 Hz	4.90, 1H, d, J=5 Hz	4.47, 1H, d, J=8 Hz	4.44, 1H, d, J=8 Hz	5.11, 1H, d, J=6 Hz	5.33, 1H, d, J=6 Hz

a) The spectra were taken in a 5 mm spinning tube with a Hitachi R-40 spectrometer (90.00 MHz) in $CDCl_3$ with tetramethylsilane (TMS) (δ=0) as an internal reference. *b*) The solvent used in this experiment was CD_3OD. *c*) The same assignments were reported in the literature.[4]

TABLE II. ^{13}C-NMR Chemical Shifts[a)]

	4	4b	1a	3a	4c	4e	4f	4g
C-1	97.3	97.3	96.9	91.0	92.3	98.4	95.9	89.9
C-5	58.7	58.7	58.2	60.8	61.9	58.3	55.0	56.9
C-4	69.9	69.8	69.3	70.2	68.8	68.5	66.7	67.2
C-8	72.5	72.4	73.9	74.7	75.6	73.4	74.5	75.4
C-2	87.6	87.3	86.3	87.1	87.8	86.4	79.3	80.6
C-6	85.2	84.9	84.6	85.4	85.4	82.8	88.4	88.6
C-1′	127.5	129.0	127.6	128.1	128.6	127.7	127.7	127.9
C-1″	131.7	133.3	131.2	132.3	132.0	131.1	128.6	129.5
C-2′	113.8	113.4	113.0	112.3	109.3	110.3	112.7	112.3
C-2″	110.2	109.7	110.7	110.8	110.6	110.6	109.7	109.7
C-3′	146.8	147.9	146.9	146.9	147.1	147.2	146.8	146.8
C-3″	147.8	149.0	147.6	147.5	147.4	147.6	147.3	147.2
C-4′	146.1	148.3	146.4	145.9	145.5	146.0	146.3	145.8
C-4″	146.1	148.3	146.4	145.9	146.1	146.3	145.5	145.2
C-5′	114.4	110.7	114.8	114.5	115.1	115.2	114.7	114.5
C-5″	115.4	112.0	115.3	115.1	115.1	115.2	115.1	115.0
C-6′	121.4	120.9	121.3	120.2	117.5	118.4	121.0	120.1
C-6″	118.6	118.1	118.9	118.8	118.9	118.8	117.7	117.7
OCH_3	55.7	55.5 55.7	55.7	55.6	55.6	55.6	55.6	55.5
$\underline{C}H_3CO$			20.5			21.6	20.5	
$CH_3\underline{C}O$			168.7			170.2	168.5	
Glc-1	98.6	98.6						
Glc-2	73.4	73.2						
Glc-3	77.2	77.1						
Glc-4	69.9	69.8						
Glc-5	77.2	77.1						
Glc-6	60.9	60.9						

a) The spectra were taken in micro cells with a JNM-FX 60 spectrometer (15.00 MHz) in DMSO-d_6 with TMS as an internal reference.

On the other hand, the acid treatment of **1a** gave compound **4e** as an amorphous powder, $C_{22}H_{24}O_8$, $[\alpha]_D^{25}$ +81.2° (chloroform) and compound **4f** as an amorphous powder, $C_{22}H_{24}O_8$, $[\alpha]_D^{25}$ +61.5° (chloroform) in a ratio of *ca.* 1 : 1. The deacetylation of **4e** with ammonia in methanol gave **4c**. The deacetylation of **4f** with ammonia in methanol gave compound **4g** as colorless plates, $C_{20}H_{22}O_7$, mp 156—158°C, $[\alpha]_D^{22}$ +69.7° (chloroform), whose methylation with diazomethane gave known gmelinol (**4h**).[3,4)] Thus, the structures of **4e**, **4f** and **4g** have been elucidated as (+)-1-acetoxy-2-epipinoresinol, (+)-1-acetoxy-6-epipinoresinol and (+)-1-hydroxy-6-epipinoresinol, respectively.

This conversion of isogmelinol-type lignan (equatorial aryl units at C-2 and C-6) into gmelinol-type lignan (equatorial aryl unit at C-2 and axial aryl unit at C-6) is the first reported example, though the reverse transformation is known.[5)]

In order to determine the genuine aglycone of **4**, the chemical shifts of the 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane ring protons, the multiplicity and the coupling constants in the ^{1}H-NMR spectrum of **4** were correlated with those of **1a**, **3b**, **4d**, **4e**, **4f** and **4h** as summarized in Table I. The chemical shifts and coupling constants of the benzylic protons at the C-2 and C-6 positions of **4**, which are readily distinguished as one is a singlet (δ 4.98) and the other is a doublet (δ 4.73, J = 5 Hz), clearly indicated that the aglycone of **4** should be **3a**.

Furthermore, the ^{13}C-NMR spectra of **4** and **4b** were correlated with those of **1a**, **3a**, **4c**,

4e, **4f** and **4g** as summarized in Table II. It was shown that the chemical shifts of the C-2′ and C-6′ carbons in these compounds are not very much affected by 4′-*O*-methylation[6] and are only sensitive to a hydroxy group at the C-1 position and to the stereochemistry of the 2,6-diaryl-3,7-dioxabicyclo[3.3.0]octane ring. That is, the signals of the C-2′ and C-6′ carbons in **1a**, **3a**, **4f** and **4g** are shifted downfield by 1.5—3.5 ppm relative to those of the corresponding carbons of the equatorial unit (δ 110.5 at C-2′ and δ 118.6 at C-6′) in (+)-pinoresinol or (+)-epipinoresinol.[6] On the other hand, the chemical shifts of the C-2′ and C-6′ carbons in **4c** and **4e** are not very much affected by a hydroxy group at the C-1 position and are almost equal to those of the corresponding carbons of the axial guaiacyl unit (δ 109.8 at C-2′ and δ 117.8 at C-6′) in (+)-epipinoresinol.[6] Thus, the chemical shifts of these carbons in **4** (δ 113.8 at C-2′ and δ 121.4 at C-6′) and **4b** (δ 113.4 at C-2′ and δ 120.9 at C-6′), clearly indicated that **4** has an equatorial guaiacyl unit at the C-2 position, so the ^{13}C-NMR spectral data also support the view that the aglycone of **4** is not **4c** but **3a**. In addition, the 6.3 ppm downfield shift at the C-1 carbon of **4** relative to that of **3a** confirmed that D-glucose is attached to the 1-*O*-position of **3a**. The β-linkage of D-glucose in **4** was deduced from the anomeric proton signal (δ 4.36, d, J=8 Hz) in the ^{1}H-NMR spectrum, the ^{13}C-NMR spectral data of the sugar moiety[7] and the molecular optical rotation difference between **4** and **3a** (Table IV). Thus, the structure of **4** has been established as (+)-1-hydroxypinoresinol-1-β-D-glucoside.

The lignan **5** was obtained as an amorphous powder, $C_{27}H_{34}O_{13}\cdot 3/2H_2O$, mp 125—126 °C, $[\alpha]_D^{20}$ −13.6° (methanol). The ^{1}H-NMR spectrum of **5** resembled that of **4** except for the signals of protons assigned to three aromatic methoxy groups (δ 3.78 and 3.82) and five aromatic protons (δ 6.66 and 6.73—7.03). Acetylation of **5** with acetic anhydride–pyridine gave compound **5a** as a colorless syrup, $C_{39}H_{46}O_{19}$, $[\alpha]_D^{24}$ −15.7° (chloroform). The ^{1}H-NMR spectrum showed the presence of four alcoholic acetoxy groups (δ 1.91, 1.93, 1.96 and 2.00), two phenolic acetoxy groups (δ 2.29) and three aromatic methoxy groups (δ 3.80 and 3.85). Methylation of **5** with diazomethane gave compound **5b** as an amorphous powder, $C_{29}H_{38}O_{13}$, mp 95—97 °C, $[\alpha]_D^{25}$ −13.0° (ethanol). The ^{1}H-NMR spectrum showed the presence of five aromatic methoxy groups (δ 3.73, 3.78 and 3.83). These data suggested that **5** bears a marked structural resemblance to **4**. The acid hydrolysis of **5b** gave compound **5c** as a colorless crystalline powder, $C_{23}H_{28}O_8$, mp 118—121 °C, $[\alpha]_D^{25}$ +82.3° (chloroform) and D-glucose. The ^{1}H-NMR and ^{13}C-NMR spectral data of **5c** suggested that **5c** structurally resembles **4h**. Compound **5c** was also obtained by the acid treatment of known (+)-fraxiresinol 4′,4″-di-*O*-methyl ether (**6a**).[2] It is interesting that the acid treatment of **6a** gave the 6-epimer (**5c**), whereas that of **3a** gave the 2-epimer (**4c**). Thus, the structure of **5c** has been elucidated as (+)-6-epifraxiresinol 4′,4″-di-*O*-methyl ether.

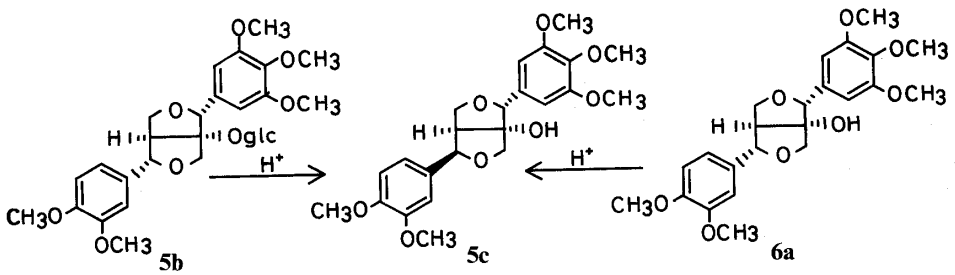


Chart 3

In order to determine the structure of **5**, the ^{13}C-NMR spectra of **5** and **5b** were correlated with those of (+)-fraxiresinol (**6**),[2] **6a** and **5c** as summarized in Table III. These data indicated that **5** is a monoglucoside of **6** in which D-glucose is attached to the 1-*O*-

Table III. ^{13}C-NMR Chemical Shifts[a]

	5	5b	6	6a	5c
C-1	97.1	97.3	91.1	91.2	90.2
C-5	58.7	58.7	60.7	60.8	56.9
C-4	69.9	69.8	70.2	70.3	67.4
C-8	72.4	72.4	74.6	74.6	75.3
C-2	87.6	87.3	87.2	87.0	80.4
C-6	85.2	84.9	85.3	85.0	88.4
C-1′	126.4	132.0	127.1	132.8	132.8
C-1″	131.7	133.3	132.3	133.9	131.8
C-2′	106.9	106.4	105.5	105.0	105.1
C-2″	110.2	109.7	110.8	110.3	109.4
C-3′	147.2	152.0	147.4	152.2	152.2
C-3″	147.7	149.0	147.8	148.7	148.5
C-4′	135.1	136.9	134.9	136.8	136.7
C-4″	146.1	148.3	145.9	148.2	147.6
C-5′	147.2	152.0	147.4	152.2	152.2
C-5″	115.3	111.9	115.1	111.7	111.6
C-6′	106.9	106.4	105.5	105.0	105.1
C-6″	118.6	118.2	118.8	118.4	117.5
OCH_3	55.7	55.5	55.6	55.4	55.4
	56.1	55.7	55.9	55.7	55.7
		55.8		59.8	59.8
		59.8			
Glc-1	98.5	98.5			
Glc-2	73.4	73.2			
Glc-3	77.2	77.1			
Glc-4	69.9	69.8			
Glc-5	77.2	77.1			
Glc-6	60.9	60.9			

a) The spectra were taken in micro cells with a JNM-FX 60 spectrometer (15.00 MHz) in DMSO-d_6 with TMS as an internal reference.

Table IV. Molecular Optical Rotation Differences

	$[\alpha]_D$ (°)	$[M]$ (°)	$\Delta[M]$ (°)
3	−9.3	−49.9	−195.8
3a	+39.0	+145.9	
4	−17.5	−93.8	−239.7
3a	+39.0	+145.9	
5	−13.6	−77.0	−195.4
6	+29.3	+118.4	

position. The β-linkage of D-glucose in **5** was deduced in the same manner as described for **4**. Thus, the structure of **5** has been established as (+)-fraxiresinol-1-β-D-glucoside.

In regard to the biological activity of the isolated lignans, lignan 1 showed high inhibitory activity against cyclic adenosine monophosphate (cAMP)-phosphodiesterase *in vitro* ($IC_{50}(\times 10^{-5}$ M): 4.4).[8] Weinryb *et al.* reported that a considerable number of therapeutic agents used as antipsychotics, antianxiety agents, antihypertensives and so on showed inhibitory effects against phosphodiesterase.[9] Thus, the lignan **1** might possess some pharmacological activity.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. The following instruments were used: optical rotation, Yanaco OR-50D; UV spectra, Shimadzu UV-210; IR spectra, Shimadzu IR-400 and Hitachi 270-30; circular dichroism (CD) curves, Jasco J-40; ^{1}H-NMR spectra, Hitachi R-40 with tetramethylsilane ($\delta=0$) as an internal reference; ^{13}C-NMR spectra, JEOL JNM-FX 60 equipped with a JEC-980 computer; mass spectrum (MS), Hitachi RMU-7L and Shimadzu LKB-9000. The abbreviations used are as follows: s, singlet; d, doublet; m, multiplet; br s, broad singlet; t, triplet; q, quartet; sh, shoulder.

Precoated thin-layer chromatography (TLC) plates, Silica gel 60_{F254} (Merck), were used for TLC and preparative TLC. The spots were detected by spraying the plates with 10% H_2SO_4 soln. and heating. Silica gel (100 mesh, Mallinckrodt) was used for column chromatography.

Isolation——The extraction of dry powdered bark of *Olea europaea* (4.0 kg) collected in December 1979 at Shodoshima Island, Kagawa, Japan, was carried out as described in the previous paper,[1] and 26.5 g of $CHCl_3$ extract and 237.3 g of BuOH extract were obtained. The $CHCl_3$ extract (26.5 g) was subjected to column chromatography, eluting with a $CHCl_3$–EtOH solvent system with gradually increasing proportions of EtOH. The fractions were monitored by TLC developed with $CHCl_3$–EtOH (4 : 1). The fractions (100 ml each) showing a TLC spot at *Rf* 0.30 were concentrated. The residue was purified by preparative TLC using $CHCl_3$–EtOH (4 : 1) and recrystallized from EtOH to give 203.5 mg of **1**.

When treated in the same way as described for **1**, the fractions showing a TLC spot at *Rf* 0.43 gave 220.0 mg of **2**.

The BuOH extract (62.0 g) was subjected to column chromatography, eluting with a $CHCl_3$–EtOH solvent system with gradually increasing proportions of EtOH. The fractions were monitored by TLC developed with the upper layer of $CH_3COC_2H_5$–AcOEt–HCOOH–H_2O–C_6H_6 (4 : 3 : 1 : 1 : 2). The fractions (100 ml each) showing a TLC spot at *Rf* 0.35 were concentrated. The residue was purified by preparative TLC using EtOH–C_6H_{12} (cyclohexane) (1 : 1) to give 44.8 mg of **3**.

When treated in the same way as described for **3**, the fractions showing TLC spots at *Rf* 0.49 and 0.44 gave 200.2 mg of **4** and 124.1 mg of **5**, respectively.

Dry powdered bark (1.0 kg) of *Olea africana* (*Olea europaea* subsp. *africana*) collected in October 1982 at Bloemfontein, Republic of South Africa, was treated in the same manner as described for *Olea europaea*. The $CHCl_3$ extract (2.4 g) gave 546.6 mg of **1** and 50.4 mg of **2**. The BuOH extract (33.4 g) gave 34.6 mg of **3**, 103.4 mg of **4** and 69.2 mg of **5**.

Dry powdered bark (110 g) of *Olea capensis* collected in November 1982 at Cape Town, Republic of South Africa, was treated in the same manner as described for *Olea europaea*. However, neither the $CHCl_3$ extract (0.3 g) nor the BuOH extract (20.4 g) yielded any lignan glucosides.

(+)-1-Acetoxypinoresinol-4′-β-D-glucoside (1)——Colorless needles from EtOH. mp 183.5—185 °C. $[\alpha]_D^{22}$ +7.9° ($c=1.0$, EtOH). UV λ_{max}^{EtOH} nm (log ε): 231 (4.31), 279.5 (3.83). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 254, 280, 292. IR ν_{max}^{KBr} cm^{-1}: 3325 (OH), 1735 (C=O), 1600, 1590, 1520 (arom. C=C). *Anal.* Calcd for $C_{28}H_{34}O_{13}\cdot 1/2H_2O$: C, 57.23; H, 6.00. Found: C, 57.68; H, 5.93. CD ($c=3.727\times10^{-4}$, EtOH) $[\theta]^{20}\times10^{-3}$ (nm): +0.27 (285), −0.77 (265), +6.01 (240), +3.04 (225). ^{1}H-NMR (in CD_3OD) δ: 1.67 (3H, s, alcoholic $OCOCH_3$), 2.77—3.03 (1H, m, C_5-H), 3.87 (6H, s, $2\times OCH_3$), 3.24—4.44 (4H, m, $C_{4,8}$-H), 5.05 (1H, s, C_2-H), 6.67—7.30 (6H, m, arom. H). ^{13}C-NMR (in DMSO-d_6) δ: 97.0 (C-1), 58.2 (C-5), 69.7 (C-4), 73.8 (C-8), 86.2 (C-2), 84.6 (C-6), 130.3 (C-1′), 131.2 (C-1″), 113.0 (C-2′), 110.7 (C-2″), 148.2 (C-3′), 147.5 (C-3″), 146.3 (C-4′), 146.3 (C-4″), 114.6 (C-5′), 115.3 (C-5″), 121.1 (C-6′), 119.0 (C-6″), 20.6 ($\underline{C}H_3CO$), 168.8 ($CH_3\underline{C}O$), 55.6, 55.7 (CH_3O), 99.9 (Glc-1), 73.2 (Glc-2), 76.9 (Glc-3), 69.7 (Glc-4), 76.9 (Glc-5), 60.7 (Glc-6).

Hydrolysis of (+)-1-Acetoxypinoresinol-4′-β-D-glucoside (1) with Emulsin——**2** (32.7 mg) was hydrolyzed with emulsin in the usual way to give **1a** and D-glucose. Compound **1a** was identical with known (+)-1-acetoxypinoresinol.[1]

(+)-1-Acetoxypinoresinol-4′-β-D-glucoside Pentaacetate (1b)——**1** (60 mg) was acetylated with acetic anhydride–pyridine in the usual way. The crude acetate was purified by preparative TLC to give **1b** (108 mg) as a colorless syrup. $[\alpha]_D^{20}$ −6.3° ($c=1.8$, EtOH). UV λ_{max}^{EtOH} nm (log ε): 220 (4.26), 275 (3.75), 279 (3.74). IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O), 1595, 1500 (arom. C=C). MS *m/z*: 788 (M^+, $C_{38}H_{44}O_{18}$). ^{1}H-NMR (in $CDCl_3$) δ: 1.67 (3H, s, alcoholic $OCOCH_3$), 2.03, 2.10 (12H, each s, $4\times$alcoholic $OCOCH_3$), 2.33 (3H, s, phenolic $OCOCH_3$), 3.10—3.55 (1H, m, C_5-H), 3.83, 3.87 (6H, each s, $2\times OCH_3$), 4.10—4.55 (4H, m, $C_{4,8}$-H), 4.82 (1H, d, $J=5$ Hz, C_6-H), 5.08 (1H, s, C_2-H), 6.73—7.27 (6H, m, arom. H).

Methylation of (+)-1-Acetoxypinoresinol-4′-β-D-glucoside (1)——**1** in MeOH was methylated with diazomethane in the usual way. The crude product was purified by preparative TLC using $CHCl_3$–EtOH (4 : 1). The product was identical with **2**.

(+)-1-Acetoxypinoresinol-4′-β-D-glucoside 4″-*O*-Methyl Ether (2)——Amorphous powder, $[\alpha]_D^{20}$ +9.1° ($c=1.6$, EtOH). UV λ_{max}^{EtOH} nm (log ε): 231 (4.22), 279 (3.72). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1730 (C=O), 1605, 1590, 1510 (arom. C=C). *Anal.* Calcd for $C_{29}H_{36}O_{13}\cdot H_2O$: C, 57.04; H, 6.27. Found: C, 57.53; H, 5.97. CD ($c=3.439\times10^{-4}$, EtOH) $[\theta]^{20}\times10^{-3}$ (nm): −0.24 (288), +2.82 (239). ^{1}H-NMR (in CD_3OD) δ: 1.67 (3H, s, alcoholic $OCOCH_3$), 2.75—3.08 (1H, m, C_5-H), 3.87 (9H, s, $3\times OCH_3$), 3.22—4.44 (4H, m, $C_{4,8}$-H), 5.05 (1H, s, C_2-H), 6.77—7.28 (6H, m,

arom. H).

Hydrolysis of (+)-1-Acetoxypinoresinol-4′-β-D-glucoside 4″-*O*-Methyl Ether (2) with Emulsin——**2** (140 mg) was hydrolyzed with emulsin in the usual way to give **2a** and D-glucose. Compound **2a** was identical with known (+)-1-acetoxypinoresinol 4″-*O*-methyl ether.[1]

(+)-1-Hydroxypinoresinol-4′-β-D-glucoside (3)——Colorless plates from EtOH. mp 127—129 °C. $[\alpha]_D^{23}$ −9.3° (c=0.42, MeOH). UV λ_{max}^{EtOH} nm (log ε): 228.0 (4.11), 279.8 (3.66). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 252, 280, 292sh. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1600, 1515 (arom. C=C). *Anal.* Calcd for $C_{26}H_{32}O_{12}\cdot 3/2H_2O$: C, 55.41; H, 6.26. Found: C, 55.39; H, 6.29. CD ($c=3.444\times10^{-4}$, EtOH) $[\theta]^{20}\times10^{-3}$ (nm): −0.59 (271), −1.90 (239), +1.77 (214). FD-MS m/z: 536 (M^+, $C_{26}H_{32}O_{12}$). ^{1}H-NMR (in CD_3OD): 2.96—3.14 (1H, m, C_5-H), 3.80, 3.83 (6H, each s, 2×OCH_3), 3.47—4.58 (4H, m, $C_{4,8}$-H), 4.80 (1H, s, C_2-H), 6.60—6.80 (6H, m, arom. H).

Hydrolysis of (+)-1-Hydroxypinoresinol-4′-β-D-glucoside (3) with Emulsin——**3** (20.7 mg) was hydrolyzed with emulsin in the usual way to give **3a** and D-glucose. Compound **3a** was identical with known (+)-1-hydroxypinoresinol.[1] Compound **3** was identical with known (+)-1-hydroxypinoresinol-4′-β-D-glucoside.[2]

(+)-1-Hydroxypinoresinol-1-β-D-glucoside (4)——Amorphous powder, mp 179—183 °C. $[\alpha]_D^{23}$ −17.5° (c=0.38, EtOH). UV λ_{max}^{EtOH} nm (log ε): 232.3 (4.13), 280.5 (3.69). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 254.5, 292.5. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1610, 1520 (arom. C=C). *Anal.* Calcd for $C_{26}H_{32}O_{12}\cdot 5/2H_2O$: C, 53.69; H, 6.41. Found: C, 53.50; H, 6.11. CD ($c=4.015\times10^{-4}$, EtOH) $[\theta]^{20}\times10^{-3}$ (nm): +2.95 (236), +0.61 (281). MS m/z: 536 (M^+, $C_{26}H_{32}O_{12}$), 374 ($C_{20}H_{22}O_7$). ^{1}H-NMR (in CD_3OD) δ: 3.60—4.56 (4H, m, $C_{4,8}$-H), 3.84 (6H, s, 2×OCH_3), 4.36 (1H, d, J=8 Hz, Glc_1-H), 4.73 (1H, d, J=5 Hz, C_6-H), 4.98 (1H, s, C_2-H), 6.52—7.22 (6H, m, arom. H).

(+)-1-Hydroxypinoresinol-1-β-D-glucoside Hexaacetate (4a)——**4** (50 mg) was acetylated with acetic anhydride–pyridine in the usual way. The crude acetate was purified by preparative TLC using $CHCl_3$–AcOEt (1:1) to give **4a** (40 mg) as a colorless syrup. $[\alpha]_D^{23}$ −14.2° (c=0.94, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 221 (4.16), 274 (3.62), 279.5 (3.60). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 (C=O), 1600, 1505 (arom. C=C). MS m/z: 788 (M^+, $C_{38}H_{44}O_{18}$). ^{1}H-NMR (in $CDCl_3$) δ: 1.95, 2.00, 2.03 (12H, each s, 4× alcoholic $OCOCH_3$), 2.33 (6H, s, 2× phenolic $OCOCH_3$), 3.12—3.51 (1H, m, C_5-H), 3.86, 3.89 (6H, each s, 2×OCH_3), 3.63—4.16 (4H, m, $C_{4,8}$-H), 4.73 (1H, s, C_2-H), 4.86 (1H, d, J=5 Hz, C_6-H), 6.75—7.18 (6H, m, arom. H).

(+)-1-Hydroxypinoresinol-1-β-D-glucoside 4′,4″-Di-*O*-methyl Ether (4b)——**4** (120 mg) in MeOH was methylated with diazomethane in the usual way. The crude product was purified by preparative TLC using $CHCl_3$–EtOH (4:1) to give **4b** (100 mg) as an amorphous powder. $[\alpha]_D^{23}$ −12.3° (c=0.89, MeOH). UV λ_{max}^{EtOH} nm (log ε): 231.4 (4.12), 278.4 (3.63). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1595, 1515 (arom. C=C). MS: Calcd for $C_{28}H_{26}O_{12}$, 564.2204. Obsd., 564.2181. ^{1}H-NMR (in CD_3OD)δ: 3.00—3.17 (1H, m, C_5-H), 3.77 (12H, s, 4×OCH_3), 3.55—4.54 (4H, m, $C_{4,8}$-H), 6.64—7.13 (6H, m, arom. H).

Acid Hydrolysis of (+)-1-Hydroxypinoresinol-1-β-D-glucoside (4)——A solution of **4** (30 mg) in 10% H_2SO_4 soln. (10 ml) was heated on a boiling water bath for 1 h. The oily product that separated was extracted with ether. The ether extract was washed with H_2O, dried over Na_2SO_4 and evaporated to dryness. The residue was crystallized from EtOH to give **4c** (10 mg).

The aqueous layer left after extraction was neutralized with $BaCO_3$ and evaporated to dryness. TLC of this residue (solvent, BuOH–AcOH–H_2O (4:1:1); color reagent, aniline hydrogen phthalate) showed a single spot of D-glucose.

(+)-1-Hydroxy-2-epipinoresinol (4c)——Colorless crystalline powder, mp 137—140 °C. $[\alpha]_D^{18}$ +60.9° (c=0.58, EtOH). UV λ_{max}^{EtOH} nm (log ε): 233.1 (4.12), 281 (3.64). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 262, 305. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 1610, 1510 (arom. C=C). MS: Calcd for $C_{20}H_{22}O_7$, 374.1363. Obsd., 374.1333. ^{1}H-NMR (in $CDCl_3$) δ: 1.71 (1H, br s, alcoholic OH, quenched by addition of D_2O), 2.41—2.71 (1H, m, C_5-H), 3.45 (1H, d, J=10 Hz, C_{8a}-H), 3.64 (1H, d, J=10 Hz, $C_{8\varepsilon}$-H), 3.87 (6H, s, 2×OCH_3), 3.65—4.33 (2H, m, C_4-H), 4.45 (1H, d, J=8 Hz, C_6-H), 4.68 (1H, s, C_2-H), 5.62 (2H, br s, 2× OH, quenched by addition of D_2O), 6.67—7.08 (6H, m, arom. H).

Methylation of (+)-1-Hydroxy-2-epipinoresinol (4c)——**4c** (65 mg) in MeOH was methylated with diazomethane in the usual way. The crude product was purified by preparative TLC and recrystallized from EtOH to give **4d** (56.7 mg) as colorless plates. mp 163—165 °C. $[\alpha]_D^{17}$ +59.4° (c=0.9, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 232 (4.29), 279 (3.81). IR ν_{max}^{KBr} cm^{-1}: 3370 (OH), 1580, 1505 (arom. C=C). MS: Calcd for $C_{22}H_{26}O_7$, 402.1676. Obsd., 402.1686. CD ($c=2.89\times10^{-4}$, EtOH) $[\theta]^{20}\times10^{-3}$ (nm): +4.42 (240), −1.61 (277). ^{1}H-NMR (in $CDCl_3$) δ: 2.33 (1H, s, alcoholic OH, quenched by addition of D_2O), 2.50—2.80 (1H, m, C_5-H), 3.46 (1H, d, J=10 Hz, C_{8a}-H), 3.62 (1H, d, J=10 Hz, $C_{8\varepsilon}$-H), 3.84, 3.86, 3.88 (12H, each s, 4×OCH_3), 3.96—4.34 (2H, m, C_4-H), 4.44 (1H, d, J=8 Hz, C_6-H), 4.70 (1H, s, C_2-H), 6.67—7.04 (6H, m, arom. H).

The properties and spectral data of **4d** were in good agreement with those of neogmelinol given in the literature (mp 163—164 °C, $[\alpha]_D^{25}$ +60°).[3]

Acid Hydrolysis of (+)-1-Hydroxypinoresinol-1-β-D-glucoside 4′,4″-Di-*O*-methyl Ether (4b)——A solution of **4b** (44 mg) in 10% H_2SO_4 soln. (50 ml) was heated on a boiling water bath for 1 h. The oily product that separated was extracted with ether. The ether extract was washed with H_2O, dried over Na_2SO_4 and evaporated to dryness. The residue was crystallized from EtOH to give the product (10 mg). This was identical with neogmelinol (**4d**).

The aqueous layer left after extraction was neutralized with $BaCO_3$ and evaporated to dryness. TLC of this

residue (solvent, BuOH–AcOH–H_2O (4 : 1 : 1); color reagent, aniline hydrogen phthalate) showed a single spot of D-glucose.

Acid Treatment of (+)-1-Hydroxypinoresinol (3a)——**3a** (23 mg) was dissolved in glacial acetic acid (0.9 ml), the solution was cooled, and perchloric acid (5 *gtt.*) was added. After 3 d at room temperature the solution was diluted with water and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution. The solvent was evaporated to yield a dark gum, which was purified by preparative TLC using $CHCl_3$–AcOEt (2 : 1) to give the product (11.7 mg). This was identical with (+)-1-hydroxy-2-epipinoresinol (**4c**).

Acid Treatment of (+)-1-Acetoxypinoresinol (1a)——**1a** (240 mg) was dissolved in glacial acetic acid (8.4 ml), the solution was cooled, and perchloric acid (35 *gtt.*) was added. The solution was treated in the same manner as described for **3a**. A dark gum thus obtained was purified by preparative TLC using $CHCl_3$–AcOEt (2 : 1) to give **4e** (59.2 mg) and **4f** (45.1 mg).

(+)1-Acetoxy-2-epipinoresinol (4e)——Amorphous powder. $[\alpha]_D^{25}$ +81.2° (c=0.99, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 232.2 (4.14), 281.1 (3.73), 286 (3.68)sh. UV $\lambda_{max}^{EtOH+NaOH}$ nm: 254, 295. IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1735 (C=O), 1610, 1515 (arom. C=C). MS: Calcd for $C_{22}H_{24}O_8$, 416.1469. Obsd., 416.1438. ^{1}H-NMR (in $CDCl_3$) δ: 2.17 (3H, s, alcoholic $OCOCH_3$), 3.04—3.42 (1H, m, C_5-H), 3.53 (1H, d, J=10 Hz, C_{8a}-H), 3.67 (1H, d, J=10 Hz, C_{8e}-H), 3.87 (6H, s, 2×OCH_3), 4.03—4.41 (2H, m, C_4-H), 4.47 (1H, d, J=8 Hz, C_6-H), 5.13 (1H, s, C_2-H), 5.66 (2H, br s, 2× phenolic OH, quenched by addition of D_2O), 6.76—7.13 (6H, m, arom. H).

(+)-1-Acetoxy-6-epipinoresinol (4f)——Amorphous powder, $[\alpha]_D^{25}$ +61.5° (c=0.75, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 232.2 (4.11), 281.1 (3.70), 286.5 (3.64)sh. UV $\lambda_{max}^{EtOH+NaOH}$ nm: 254, 295. IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1740 (C=O), 1615, 1520 (arom. C=C). MS: Calcd for $C_{22}H_{24}O_8$, 416.1469. Obsd., 416.1437. ^{1}H-NMR (in $CDCl_3$) δ: 1.73 (3H, s, alcoholic $OCOCH_3$), 3.18—3.70 (1H, m, C_5-H), 3.29 (1H, dd, J=9 and 9 Hz, C_{4a}-H), 3.84, 3.86 (6H, each s, 2×OCH_3), 4.03—4.23 (2H, m, $C_{4e,8}$-H), 4.58 (1H, d, J=10 Hz, C_8-H), 4.70 (1H, s, C_2-H), 5.11 (1H, d, J=6 Hz, C_6-H), 5.66 (2H, br s, 2× phenolic OH, quenched by addition of D_2O), 6.63—7.11 (6H, m, arom. H).

Deacetylation of (+)-1-Acetoxy-2-epipinoresinol (4e) with Ammonia in Methanol——**4e** (19 mg) was deacetylated with ammonia in methanol in the usual way. The crude product was purified by preparative TLC using $CHCl_3$–AcOEt (2 : 1) to give the product (11 mg). This was identical with (+)-1-hydroxy-2-epipinoresinol (**4c**).

Deacetylation of (+)-1-Acetoxy-6-epipinoresinol (4f) with Ammonia in Methanol——**4f** (10 mg) was deacetylated with ammonia in methanol in the usual way. The crude product was purified by preparative TLC using $CHCl_3$–AcOEt (2 : 1) to give **4g** (7.3 mg).

(+)-1-Hydroxy-6-epipinoresinol (4g)——Colorless plates from EtOH, mp 156—158 °C. $[\alpha]_D^{22}$ +69.7° (c=0.1, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 231.0 (3.96), 280.5 (3.55), 286.7 (3.49)sh. UV $\lambda_{max}^{EtOH+NaOH}$ nm: 252.6, 294.7. IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 1658, 1632, 1520 (arom. C=C). MS: Calcd for $C_{20}H_{22}O_7$, 374.1363. Obsd., 374.1342. ^{1}H-NMR (in $CDCl_3$) δ: 1.64 (1H, br s, alcoholic OH, quenched by addition of D_2O), 2.87—3.18 (1H, m, C_5-H), 3.33 (1H, dd, J=9 and 9 Hz, C_{4a}-H), 3.69 (1H, d, J=9 Hz, C_8-H), 3.89 (6H, s, 2×OCH_3), 4.06 (1H, dd, J=9 and 9 Hz, C_{4e}-H), 4.18 (1H, d, J=9 Hz, C_8-H), 4.55 (1H, s, C_2-H), 5.13 (1H, d, J=6 Hz, C_6-H), 5.59 (2H, br s, 2× phenolic OH, quenched by addition of D_2O), 6.63—7.03 (6H, m, arom. H).

Methylation of (+)-1-Hydroxy-6-epipinoresinol (4g)——**4g** (7 mg) in MeOH was methylated with diazomethane in the usual way. The crude product was purified by preparative TLC using AcOEt–$CHCl_3$ (2 : 5) to give **4h** (7 mg).

(+)-1-Hydroxy-6-epipinoresinol 4′,4″-Di-*O*-methyl Ether (4h)——Colorless crystalline powder from AcOEt–ether (1 : 1), mp 151—153 °C. $[\alpha]_D^{23}$ +117.1° (c=0.07, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 230.5 (3.96), 278.9 (3.54), 283.5 (3.51)sh. IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 1660, 1632, 1516 (arom. C=C). MS: Calcd for $C_{22}H_{26}O_7$, 402.1676. Obsd., 402.1655. ^{1}H-NMR (in $CDCl_3$) δ: 2.97—3.16 (1H, m, C_5-H), 3.31 (1H, dd, J=9 and 9 Hz, C_{4a}-H), 3.68 (1H, d, J=9 Hz, C_8-H), 3.86 (12H, s, 4×OCH_3), 4.03 (1H, dd, J=9 and 9 Hz, C_{4e}-H), 4.20 (1H, d, J=9 Hz, C_8-H), 4.56 (1H, s, C_2-H), 5.33 (1H, d, J=6 Hz, C_6-H), 6.60—7.03 (6H, m, arom. H).

The properties and spectral data of **4h** were in good agreement with those of gmelinol given in the literature.[3,4]

(+)-Fraxiresinol-1-β-D-glucoside (5)——Amorphous powder, mp 125—126 °C. $[\alpha]_D^{20}$ −13.6° (c=1.61, MeOH). UV λ_{max}^{EtOH} nm (log ε): 231 (4.04), 280 (3.54). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 257.3, 290. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1610, 1518 (arom. C=C). *Anal.* Calcd for $C_{27}H_{34}O_{13}\cdot 3/2H_2O$: C, 54.63; H, 6.28. Found: C, 54.48; H, 6.12. CD (c=3.993×10^{-4}, EtOH) $[\theta]^{20}\times 10^{-3}$ (nm): +3.27 (234.5), +0.47 (270). MS m/z: 566 (M^+, $C_{27}H_{34}O_{13}$). ^{1}H-NMR (in CD_3OD) δ: 3.03—3.16 (1H, m, C_5-H), 3.78, 3.82 (9H, each s, 3×OCH_3), 3.47—4.10 (3H, m, $C_{4,8}$-H), 4.41 (1H, d, J=8 Hz, Glc_1-H), 4.43 (1H, dd, J=9 and 9 Hz, C_{4e}-H), 6.66 (2H, s, arom. $C_{2',6'}$-H), 6.73—7.03 (3H, m, arom. $C_{2'',5'',6''}$-H).

(+)-Fraxiresinol-1-β-D-glucoside Hexaacetate (5a)——**5** (16 mg) was acetylated with acetic anhydride–pyridine in the usual way. The crude acetate was purified by preparative TLC using $CHCl_3$–AcOEt (1 : 1) to give **5a** (9.8 mg) as a colorless syrup. $[\alpha]_D^{24}$ −15.7° (c=0.16, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 223.1 (4.17), 274.5 (3.52), 279.5 (3.50). IR ν_{max}^{KBr} cm^{-1}: 1760 (C=O), 1610, 1510 (arom. C=C). MS m/z: 818 (M^+, $C_{39}H_{46}O_{19}$). ^{1}H-NMR (in $CDCl_3$) δ: 1.91, 1.93, 1.96, 2.00 (12H, each s, 4× alcoholic $OCOCH_3$), 2.29 (6H, s, 2× phenolic $OCOCH_3$), 3.10—3.46 (1H, m, C_5-H), 3.80, 3.85 (9H, each s, 3×OCH_3), 3.69—4.55 (4H, m, $C_{4,8}$-H), 4.66 (1H, s, C_2-H), 4.88 (1H, d, J=5 Hz, C_6-H), 6.53 (2H, s, arom. $C_{2',6'}$-H), 6.88—7.11 (3H, m, arom. $C_{2'',5'',6''}$-H).

(+)-Fraxiresinol-1-β-D-glucoside 4′,4″-Di-*O*-methyl Ether (5b)——**5** (90 mg) in MeOH was methylated with diazomethane in the usual way. The crude product was purified by preparative TLC using $CHCl_3$–EtOH (4 : 1) to give

5b (53 mg) as an amorphous powder, mp 95—97 °C. $[\alpha]_D^{25}$ −13.0° (c=0.89, EtOH). UV λ_{max}^{EtOH} nm (log ε): 231.0 (4.14), 278.6 (3.52). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1590, 1510 (arom. C=C). FD-MS m/z: 594 (M^+, $C_{29}H_{38}O_{13}$). ^{1}H-NMR (in CD_3OD) δ: 2.97—3.14 (1H, m, C_5-H), 3.73, 3.78, 3.83 (15H, each s, 5×OCH_3), 3.46—4.10 (3H, m, $C_{4,8}$-H), 4.31 (1H, d, J=8 Hz, Glc_1-H), 4.48 (1H, dd, J=9 and 9 Hz, C_{4e}-H), 4.81 (1H, d, J=5 Hz, C_6-H), 6.73 (2H, s, arom. $C_{2',6'}$-H), 6.82—7.10 (3H, m, arom. $C_{2'',5'',6''}$-H).

Acid Hydrolysis of (+)-Fraxiresinol-1-β-D-glucoside 4′,4″-Di-*O*-methyl Ether (5b)——A solution of **5b** (20 mg) in 10% H_2SO_4 soln. (10 ml) was heated on a boiling water bath for 1 h. The oily product that separated was extracted with ether. The ether extract was washed with H_2O, dried over Na_2SO_4 and evaporated to dryness. The residue was crystallized from EtOH to give **5c** (6 mg).

The aqueous layer left after extraction was neutralized with $BaCO_3$ and evaporated to dryness. TLC of this residue (solvent, BuOH–AcOH–H_2O (4 : 1 : 1); color reagent, aniline hydrogen phthalate) showed a single spot of D-glucose.

(+)-6-Epifraxiresinol 4′,4″-Di-*O*-methyl Ether (5c)——Colorless crystalline powder, mp 118—121 °C. $[\alpha]_D^{25}$ +82.3° (c=0.12, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 227.0 (4.14)sh, 276.8 (3.60), 285.2 (3.50)sh. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550 (OH), 1590, 1510 (arom. C=C). MS: Calcd for $C_{23}H_{28}O_8$, 432.1782. Obsd., 432.1782. ^{1}H-NMR (in $CDCl_3$) δ: 1.23 (1H, s, alcoholic OH), 3.01—3.25 (1H, m, C_5-H), 3.30 (1H, dd, J=9 and 9 Hz, C_{4a}-H), 3.72 (1H, d, J=9 Hz, C_8-H), 3.86 (15H, s, 5×OCH_3), 4.04 (1H, dd, J=9 and 9 Hz, C_{4e}-H), 4.22 (1H, d, J=9 Hz, C_8-H), 4.54 (1H, s, C_2-H), 5.18 (1H, d, J=6 Hz, C_6-H), 6.56 (2H, s, arom. $C_{2',6'}$-H), 6.70—7.10 (3H, m, arom. $C_{2'',5'',6''}$-H).

Acid Treatment of (+)-Fraxiresinol 4′,4″-Di-*O*-methyl Ether (6a)——**6a** (24 mg) was dissolved in glacial acetic acid (2.1 ml), the solution was cooled, and perchloric acid (10 *gtt.*) was added. The solution was treated in the same manner as described for **3a**. A dark gum thus obtained was purified by preparative TLC using $CHCl_3$–AcOEt (1 : 2) to give the product (7.2 mg). This was identical with (+)-6-epifraxiresinol 4′,4″-di-*O*-methyl ether (**5c**).

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