[Chem. Pharm. Bull.]
31(9)2993—2997(1983)

The Constituents of *Eucommia ulmoides* OLIV. I. Isolation of (+)-Medioresinol Di-*O*- β -D-glucopyranoside

TAKESHI DEYAMA

Central Research Laboratories, Yomeishu Seizo Co., Ltd.,
2132-37, Naka-minowa, Minowa-cho, Kami-ina,
Nagano 399-46, Japan

(Received December 6, 1982)

A new lignan diglycoside was isolated from the bark of *Eucommia ulmoides* OLIV. (Eucommiaceae) and its structure was established as (+)-medioresinol di-*O*- β -D-glucopyranoside (**1**) by means of chemical and spectral studies. (+)-Pinoresinol di-*O*- β -D-glucopyranoside (**2**), liriiodendrin (**3**) and (+)-pinoresinol *O*- β -D-glucopyranoside (**4**) were also isolated.

Keywords—*Eucommia ulmoides*; lignan; (+)-medioresinol di-*O*- β -D-glucoside; (+)-pinoresinol di-*O*- β -D-glucoside; (+)-pinoresinol *O*- β -D-glucoside; liriiodendrin; ^{13}C -NMR

A new lignan glycoside, (+)-medioresinol di-*O*- β -D-glucopyranoside (**1**), was isolated together with three known lignans, (+)-pinoresinol di-*O*- β -D-glucopyranoside (**2**),^{1,2} liriiodendrin[(+)-syringaresinol di-*O*- β -D-glucopyranoside] (**3**)³ and (+)-pinoresinol *O*- β -D-glucopyranoside (**4**),¹ from the bark of *Eucommia ulmoides* OLIV. (Japanese name: Tochu) (Eucommiaceae), which is one of the longest-known tonic herbs in China.⁴ The extraction and separation were carried out as described in the experimental section.

Glycoside **2** was isolated as a white powder, $\text{C}_{32}\text{H}_{42}\text{O}_{16}$, $[\alpha]_{\text{D}}^{22} -24.1^\circ$ (MeOH), whose molecular weight was observed at m/z 705 ($\text{M}^+ + \text{Na}$) and 721 ($\text{M}^+ + \text{K}$) on field desorption-mass spectrometry (FD-MS). Glycoside **2** was identified as (+)-pinoresinol di-*O*- β -D-glucopyranoside^{1,2} by comparison of thin layer chromatography (TLC) behavior and the proton nuclear magnetic resonance (^1H -NMR), carbon-13 nuclear magnetic resonance (^{13}C -NMR) and infrared (IR) spectral data with those of an authentic sample. Furthermore, hydrolysis of **2** with β -glucosidase gave an aglycone (**2b**), colorless oil, which was identified as (+)-pinoresinol^{1,5} by comparison of the ^1H -NMR, IR, MS and $[\alpha]_{\text{D}}$ data with those of an authentic sample.

Glycoside **3** was isolated as colorless needles, $\text{C}_{34}\text{H}_{46}\text{O}_{18}$, mp 258°C , $[\alpha]_{\text{D}}^{22} 0^\circ$ (pyridine), whose molecular weight was observed at m/z 765 ($\text{M}^+ + \text{Na}$) on FD-MS. Glycoside **3** was identified as liriiodendrin³ by comparison of the ^1H -, ^{13}C -NMR and IR spectral data with those of an authentic sample. Furthermore, hydrolysis of glycoside **3** with β -glucosidase gave an aglycone (**3b**), colorless needles, which was identified as (+)-syringaresinol⁵ by comparison of the ^1H -NMR, IR, MS and $[\alpha]_{\text{D}}$ spectral data with those of an authentic sample.

Glycoside **4** was isolated as amorphous, $\text{C}_{26}\text{H}_{32}\text{O}_{11}$, $[\alpha]_{\text{D}}^{22} +8.0^\circ$ (MeOH), whose molecular weight was observed at m/z 544 ($\text{M}^+ + 1 + \text{Na}$) and 560 ($\text{M}^+ + 1 + \text{K}$) on FD-MS. Glycoside **4** was identified as (+)-pinoresinol *O*- β -D-glucopyranoside¹ by comparison of TLC and IR spectral data with those of an authentic sample. Furthermore, the acetate of **4** was studied. Acetylation of **4** with acetic anhydride-pyridine gave a pentaacetate (**4a**) as colorless needles, which was identified as (+)-pinoresinol *O*- β -D-glucopyranoside pentaacetate¹ by comparison of IR spectral data with those of an authentic sample.

Glycoside **1** moved intermediately between **2** and **3** on TLC. Glycoside **1** was isolated as colorless needles, $\text{C}_{33}\text{H}_{44}\text{O}_{17}$, mp 222°C , $[\alpha]_{\text{D}}^{22} -9.1^\circ$ (pyridine), whose molecular weight was

observed at m/z 734 ($M^+ - 1 + Na$) and 750 ($M^+ - 1 + K$) on FD-MS. The ultraviolet (UV) spectrum of **1**, which showed absorption maxima at 225 and 275 nm, was similar to those of **2**, **3** and **4**. The IR spectrum of **1** suggested the presence of aromatic ring (1595 and 1510 cm^{-1}). The ^1H -NMR spectrum of **1** showed signals at δ 7.60–6.98 (3H, m) and 6.60 (2H, s), due to aromatic protons and at 3.78 (9H, s), due to aromatic methoxy groups.

Acetylation of **1** with acetic anhydride-pyridine gave an octaacetate (**1a**) as colorless

- 1** : $R_1 = R_3 = \text{Glc}$, $R_2 = \text{H}$, $R_4 = \text{OMe}$
1a : $R_1 = R_3 = \text{Glc}(\text{Ac})_4$, $R_2 = \text{H}$, $R_4 = \text{OMe}$
1b : $R_1 = R_2 = R_3 = \text{H}$, $R_4 = \text{OMe}$
2 : $R_1 = R_3 = \text{Glc}$, $R_2 = R_4 = \text{H}$
2a : $R_1 = R_3 = \text{Glc}(\text{Ac})_4$, $R_2 = R_4 = \text{H}$
2b : $R_1 = R_2 = R_3 = R_4 = \text{H}$
3 : $R_1 = R_3 = \text{Glc}$, $R_2 = R_4 = \text{OMe}$
3a : $R_1 = R_3 = \text{Glc}(\text{Ac})_4$, $R_2 = R_4 = \text{OMe}$
3b : $R_1 = R_3 = \text{H}$, $R_2 = R_4 = \text{OMe}$
4 : $R_1 = R_2 = R_4 = \text{H}$, $R_3 = \text{Glc}$

Chart 1

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

Carbon	1	2	3	4	1a	2a	3a	2b	3b
C-1	53.6	53.7	53.6	53.7	53.7	53.8	53.7	53.7	53.8
5				53.5					
4, 8	71.2	71.1	71.4	71.0	71.2	71.1	71.3	71.0	71.1
2	85.0	84.8	85.0	85.1	84.9	84.7	84.9	85.2	85.3
6	84.8			84.9	84.7				
C-1'	135.2	135.3	134.0	132.3	137.5	137.5	133.2	132.4	131.5
1''	133.9			135.4	133.2				
2'	110.7	110.7	104.4	110.6	111.0	111.0	103.5	110.6	103.9
2''	104.3			110.8	103.5				
3'	145.9	145.9	152.6	146.0	145.1	145.0	152.6	146.0	147.9
3''	152.6				152.6				
4'	149.0	149.0	137.1	147.5	149.9	149.9	138.4	147.6	135.0
4''	137.1			149.1	138.4				
5'	115.5	115.6	152.6	115.2	118.1	118.1	152.6	115.2	147.9
5''	152.6			115.6	152.6				
6'	118.2	118.2	104.4	118.6	118.2	118.2	103.5	118.6	103.9
6''	104.3			118.2	103.5				
OCH_3	55.8	55.8	56.5	55.7	56.0	56.0	56.2	55.8	56.1
	56.4			55.9	56.2				
glc-1'	100.4	100.4	102.8	100.4					
1''	102.9								
2'	73.2	73.2	74.2		$\text{O}\text{C}\text{O}\text{CH}_3$				
					$\begin{cases} 169.7 \\ 169.4 \\ 169.1 \\ 168.8 \end{cases}$	$\begin{cases} 169.8 \\ 169.4 \\ 169.2 \\ 168.8 \end{cases}$	$\begin{cases} 169.7 \\ 169.4 \\ 169.1 \\ 168.8 \end{cases}$		
2''	74.2			73.3					
3'	77.0	76.9	76.5	76.8					
3''	76.5								
4'	69.7	69.7	70.0		$\text{O}\text{C}\text{O}\text{CH}_3$				
4''	70.0			70.0	20.3	20.3	20.3		
5'	76.8	76.8	77.1	77.0					
5''	77.0								
6'	60.8	60.8	61.0						
6''	60.9			60.7					

needles, $C_{49}H_{60}O_{25}$, mp $168^{\circ}C$, whose molecular weight was observed at m/z 1071 ($M^{+} + Na$) on FD-MS. The 1H -NMR spectrum of **1a** showed the presence of eight alcoholic acetyl groups at δ 2.20 and 1.98 (24H, each s), and aromatic protons at δ 7.12–6.76 (3H, m) and at 6.66 (2H, s).

Hydrolysis of **1** with β -glucosidase gave an aglycone (**1b**) as a white powder, $[\alpha]_D^{22} + 37^{\circ}$ ($CHCl_3$), whose 1H -NMR, IR and MS spectral data were identical with those of (+)-medioresinol.⁵ The presence of glucose in the hydrolysate was detected on TLC and gas chromatography (GC).

Thus, glycoside **1** was concluded to be (+)-medioresinol diglucoside. The position of the glucose linkage was determined as follows. The chemical shifts of C-1' and C-1'' atoms of lignans are sensitive both to change in substituents on the aromatic ring and to their stereochemistry.⁶ As to the chemical shifts of epipinoresinol *O*- β -D-glucopyranoside, Chiba *et al.*⁶ reported a value of 135.4 ppm for C-1 atoms of equatorial guaiacyl groups linked to C-4-*O*- β -D-glucosyl groups. For glycoside **2**, the chemical shift of C-1' is 135.3 ppm, which is essentially identical with the above value. The chemical shift of C-1'' of glycoside **3**, which has a syringyl group linked to the C-4''-*O*- β -D-glucosyl group, is 134.0 ppm. The shifts of the C-1' and C-1'' atoms of glycoside **1** are 135.2 and 133.9 ppm, respectively. Comparison of the chemical shifts of **1**, **2** and **3** confirmed that **1** is (+)-medioresinol di-*O*- β -D-glucopyranoside. This is the first reported isolation of **1** as a natural product.

Sih *et al.*² reported the hypotensive activity of **2**, and Tempesta *et al.*³ reported activity of **3** in the P-388 lymphocytic leukemia (PS) test system. Pharmacological studies of **1** and further investigation of the constituents of *Eucommia ulmoides* OLIV. are in progress.

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 EPI-G2; GC, Hitachi 063 with a hydrogen flame ionization detector; EI-MS, Hitachi RMU-7L; FD-MS, JEOL-01-SG2; 1H - and ^{13}C -NMR spectra, JEOL-FX-90-Q with tetramethylsilane ($\delta=0$) as an internal reference.

Silica gel 60 F_{254} (Merck) and Cellulose F (Merck) precoated TLC plates were used for TLC. The spots were detected by spraying the plates with anisaldehyde- H_2SO_4 solution (anisaldehyde 2 ml, H_2SO_4 1 ml, EtOH 23 ml) for lignans, and diphenylamine-aniline- H_3PO_4 solution (diphenylamine 2 g, aniline 2 ml, acetone 100 ml, 80% H_3PO_4 10 ml) for glucose.

The abbreviations used for NMR data are as follows: s, singlet; d, doublet; t, triplet.

Isolation—The air-dried bark of *Eucommia ulmoides* OLIV. (5 kg) was chopped and extracted twice with hot MeOH. The MeOH solution was evaporated to a small volume under reduced pressure, then diluted with water and filtered. The filtrate was extracted with $CHCl_3$ -MeOH-water (1:1:1). The upper phase was concentrated and the residue was extracted with EtOAc. The aqueous solution was applied to a charcoal column (for chromatography, Wako) and eluted successively with water (20 l), water-EtOH (95:5, 15 l), water-EtOH (4:1, 3 l), water-EtOH (1:1, 3 l), EtOH (3 l) and $CHCl_3$ -MeOH-water (1:2:1, 4 l). The final eluate was concentrated and the residue was subjected to column chromatography, eluting with $CHCl_3$ -MeOH (9:1, 4:1, 2:1). The fractions were monitored by TLC using $CHCl_3$ -MeOH-water (70:30:5) as a developer. The fractions showing a TLC spot at R_f 0.30 (**2**), 0.37 (**1**), 0.41 (**3**) and 0.71 (**4**) were collected respectively and purified by silica gel chromatography and gel filtration on TSK-GEL HW-40 (Toyo Soda) with MeOH, yielding **1** (0.25 g), **2** (0.50 g), **3** (0.30 g) and **4** (0.24 g).

(+)-Medioresinol Di-*O*- β -D-glucopyranoside (1**)**—Colorless needles (from EtOH), mp $222^{\circ}C$, $[\alpha]_D^{22} - 9.1^{\circ}$ ($c=0.1$, pyridine). UV λ_{max}^{MeOH} nm: 225, 275. IR ν_{max}^{KBr} cm^{-1} : 3400 (OH), 1595, 1510 (aromatic ring). FD-MS m/z : 750 ($M^{+} - 1 + K$, 30%), 734 ($M^{+} - 1 + Na$, 100%). 1H -NMR (in $DMSO-d_6$) δ : 7.60–6.98 (3H, m, arom. H on guaiacyl ring), 6.60 (2H, s, arom. H on syringyl ring), 3.78 (9H, s, $3 \times OCH_3$).

(+)-Medioresinol Di-*O*- β -D-glucopyranoside Octaacetate (1a**)**—**1** was acetylated with acetic anhydride-pyridine in the usual way. The crude acetate was purified by silica gel chromatography with $CHCl_3$ -MeOH (20:1), and recrystallized from EtOH as colorless needles, mp $168^{\circ}C$. IR ν_{max}^{KBr} cm^{-1} : 1750 (C=O), 1600, 1510 (aromatic ring). FD-MS m/z : 1071 ($M^{+} + Na$, 75%), 718 ($M^{+} - 331 + 1$, 60%), 331 (95%), 289 ($331 - CH_2O$, 100%). 1H -NMR (in $DMSO-d_6$) δ : 7.12–6.76 (3H, m, arom. H on guaiacyl ring), 6.66 (2H, s, arom. H on syringyl ring), 3.76 (9H, s, $3 \times OCH_3$), 2.02, 1.98 (24H, each s, $8 \times OCOCH_3$).

Enzymatic Hydrolysis of **1**—**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 2 d at 37 °C. The reaction mixture was extracted with Et₂O (50 ml × 2) and the residue obtained from the organic phase was chromatographed on silica gel. Elution with CHCl₃-MeOH (20 : 1) gave a pure aglycone (**1b**, 20 mg). The aqueous layer was evaporated to dryness, and the residue was spotted on a precoated TLC plate (Cellulose F, Merck) and developed with EtOAc : pyridine : HOAc : water = 5 : 5 : 1 : 3. The plate was sprayed with diphenylamine-aniline-H₃PO₄ solution (diphenylamine 2 g, aniline 2 ml, acetone 100 ml and 80% H₃PO₄ 10 ml) and heated at 80 °C. The yellow spot at *R*_f 0.33 was identified as glucose by comparison with an authentic sample.

(+)-Medioresinol (1b)—White powder (from EtOH), $[\alpha]_D^{22} + 37^\circ$ ($c=0.1$, CHCl₃) [lit.⁵] $[\alpha]_D + 57^\circ$ (CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3450 (OH), 1610, 1515 (aromatic ring). EI-MS *m/z*: 388 (M⁺, 100%), 357 (M⁺ - OCH₃, 8%), 167 (25%), 151 (45%), 137 (28%). ¹H-NMR (in CDCl₃) δ : 6.96–6.80 (3H, m, arom. H on guaiacyl ring), 6.58 (2H, s, arom. H on syringyl ring), 4.80–4.64 (2H, m, H_{2,6}), 4.40–3.80 (4H, m, H_{4,8}), 3.20–3.00 (2H, m, H_{1,5}). ¹H-NMR, MS and IR data of **1b** were identical with those of (+)-medioresinol.

(+)-Pinoresinol Di-O-β-D-glucopyranoside (2)—White powder (from EtOH), $[\alpha]_D^{22} - 24.1^\circ$ ($c=0.1$, MeOH) [lit.²] $[\alpha]_D^{25} - 27.3^\circ$ (H₂O). UV $\lambda_{\max}^{\text{MeOH}}$ nm: 227, 278. IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3400 (OH), 1600, 1510 (aromatic ring). FD-MS *m/z*: 721 (M⁺ + K, 25%), 705 (M⁺ + Na, 100%). ¹H-NMR (in DMSO-*d*₆) δ : 7.12–6.78 (6H, m, arom. H on guaiacyl ring), 3.78 (6H, s, 2 × OCH₃). The TLC, ¹H-, ¹³C-NMR, $[\alpha]_D$ and IR data of **2** were identical with those of (+)-pinoresinol di-O-β-D-glucopyranoside.

Enzymatic Hydrolysis of 2—**2** (200 mg) was hydrolyzed in the same way as described for **1** to give a pure aglycone (**2b**, 20 mg) and glucose. Glucose was detected in the same way as described above.

(+)-Pinoresinol (2b)—Colorless oil, $[\alpha]_D^{20} + 51^\circ$ ($c=0.1$, CHCl₃) [lit.¹] $[\alpha]_D^{21} + 61.6^\circ$ (CHCl₃). IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3400 (OH), 1610, 1510 (aromatic ring). EI-MS *m/z*: 358 (M⁺, 100%), 163 (26%), 151 (80%), 137 (27%), 69 (59%). ¹H-NMR (in CDCl₃) δ : 6.92–6.80 (6H, m, arom. H on guaiacyl ring), 4.73 (2H, d, *J* = 5 Hz, H_{2,6}), 4.36–3.64 (4H, m, H_{4,8}), 3.87 (6H, s, 2 × OCH₃), 3.2–3.0 (2H, m, H_{1,5}). The ¹H-NMR, MS and IR data were identical with those of (+)-pinoresinol.

Liriodendrin (3)—Colorless needles (from water), mp 258 °C, $[\alpha]_D^{22} 0^\circ$ ($c=0.1$, pyridine) [lit.³] mp 265–266 °C, $[\alpha]_D^{25} - 12.1^\circ$ (pyridine). UV $\lambda_{\max}^{\text{H}_2\text{O}}$ nm: 227, 272. IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3400 (OH), 1595, 1505 (aromatic ring). FD-MS *m/z* add. NaI: 765 (M⁺ + Na, 23%), 394 (100%); add. none: 418 (M⁺ - 2 × C₆H₁₁O₅ + 2, 100%). ¹H-NMR (in DMSO-*d*₆) δ : 6.64 (4H, s, arom. H on syringyl ring), 3.78 (12H, s, 4 × OCH₃). Anal. Calcd for C₃₄H₄₆O₁₈: C, 54.98; H, 6.24. Found: C, 54.76; H, 6.25.

Liriodendrin Octaacetate (3a)—**3** was acetylated in the same way as described for **1a** to give octaacetate (**3a**), colorless needles (from EtOH), mp 119.3 °C (lit.³) mp 121–124 °C. IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 1750 (C=O), 1600, 1505 (aromatic ring). FD-MS *m/z* add. NaI: 1101 (M⁺ + Na, 100%); add. none: 1078 (M⁺, 15%), 747 (M⁺ - 331, 70%), 331 (100%). ¹H-NMR (in DMSO-*d*₆) δ : 6.66 (4H, s, arom. H on syringyl ring), 3.76 (12H, s, 4 × OCH₃), 2.00 (24H, s, 8 × OCOCH₃).

Enzymatic Hydrolysis of 3—**3** was hydrolyzed in the same way as described for **1** to give an aglycone (**3b**) and glucose. Glucose was detected as described above.

(+)-Syringaresinol (3b)—Colorless needles, mp 183.5 °C, $[\alpha]_D^{20} + 44.0^\circ$ ($c=0.1$, CHCl₃) [lit.⁵] mp 171–173 °C, $[\alpha]_D + 19.0^\circ$ (CHCl₃). High-resolution EI-MS *m/z*: 418.1620 [M⁺ (C₂₁H₂₆O₈), 100%], 388.1325 (M⁺ - OCH₃, 30%). ¹H-NMR (in CDCl₃) δ : 6.60 (4H, s, arom. H on syringyl ring), 4.61 (2H, d, *J* = 4 Hz, H_{2,6}), 4.27–3.64 (4H, m, H_{4,8}), 3.87 (12H, s, 4 × OCH₃), 3.18–2.92 (2H, m, H_{1,5}). The ¹H-NMR, MS and IR data of **3b** were identical with those of (+)-syringaresinol.

(+)-Pinoresinol O-β-D-Glucopyranoside (4)—Amorphous, $[\alpha]_D^{22} + 8.0^\circ$ ($c=0.1$, MeOH) [lit.¹] $[\alpha]_D^{20} + 8.6^\circ$ (EtOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm: 227, 278. IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 3400 (OH), 1600, 1510 (aromatic ring). FD-MS *m/z*: 1064 (2M⁺ + 1 + Na, 55%), 560 (M⁺ + 1 + K, 15%), 544 (M⁺ + 1 + Na, 100%). *R*_f: 0.35 (Silica gel 60F₂₅₄, CHCl₃: EtOH = 4 : 1). TLC behavior and IR spectral data were identical with those of (+)-pinoresinol O-β-D-glucopyranoside.

(+)-Pinoresinol O-β-D-Glucoside Pentaacetate (4a)—Amorphous, IR $\nu_{\max}^{\text{KBr}}$ cm⁻¹: 1760 (C=O), 1610, 1510 (aromatic ring). *R*_f: 0.52 (Silica gel 60F₂₅₄, CHCl₃: EtOAc = 1 : 1). TLC behavior and IR spectral data of **4a** were identical with those of (+)-pinoresinol O-β-D-glucoside pentaacetate.

Detection of Glucose by GC from Glycosides 1, 2 and 3—Glucose in **1**, **2** and **3** was also detected as glucitol acetate by GC. **1** (10 mg) was hydrolyzed with 10% H₂SO₄ (1 ml) for 1 h and then cooled. The reaction mixture was extracted with Et₂O and the aqueous layer was passed through an Amberlite IRA-45 column, which was washed with water. The eluate was concentrated under reduced pressure, then treated with NaBH₄ (5 mg) and stirred for 1 h at room temperature. The reaction mixture was passed through an IR-120 (H⁺) column, which was washed with water. The eluate was concentrated to dryness. H₃BO₃ was removed by codistillation with MeOH. The residue was acetylated with acetic anhydride (1 ml) and pyridine (1 ml) at 100 °C for 1 h. The reaction mixture was diluted with water and then concentrated. The presence of 1,3,5,6-tetra-O-acetyl-2,4-di-O-methyl-glucitol [*t*_R (min) 16.3] in this residue was detected by GC. Conditions: column, 1.5% OV-17 3 mm × 1 m; column temperature, 200 °C; carrier gas, N₂, 30 ml/min; injection temperature, 280 °C.

2 and **3** were treated in a similar way and glucitol acetate was detected.

Acknowledgement The author is grateful to Prof. S. Nishibe, Faculty of Pharmaceutical Science, Higashi Nippon Gakuen University, for supplying (+)-pinoresinol di-*O*- β -D-glucopyranoside, (+)-pinoresinol *O*- β -D-glucopyranoside pentaacetate and spectra of lignans.

Thanks are also due to Dr. R. Irie, Faculty of Agriculture, Shinshu University, for measurement of NMR spectra, to Dr. K. Takabe, Faculty of Engineering, Shizuoka University, for measurement of mass spectra, and to Dr. M. Aoyama, Hokkaido Forest Products Research Institute, for supplying the spectra of medioresinol.

References and Notes

- 1) Private communication from Prof. S. Nishibe; M. Chiba, S. Hisada and S. Nishibe, *Shoyakugaku Zasshi*, **32**, 194 (1978); *idem, ibid.*, **33**, 150 (1979).
- 2) (+)-Pinoresinol di-*O*- β -D-glucoside was reported to be the major antihypertensive principle of *Eucommia ulmoides* OLIV., C. J. Sih, P. R. Ravikumar, Fu-Chih Huang, C. Buckner and H. Whitelock, Jr., *J. Am. Chem. Soc.*, **98**, 5412 (1976).
- 3) M. S. Tempesta and R. B. Bate, *J. Org. Chem.*, **45**, 1327 (1980).
- 4) Hong-Yen Hsü, "The Studies of Chinese Herb Medicine," Chinese Herb Medicine Committee, National Health Administration, Republic of China, 1972, p. 203.
- 5) S. Omori and A. Sakakibara, *Mokuzai Gakkaishi*, **20**, 388 (1974); H. Fujimoto and T. Higuchi, *ibid.*, **23**, 405 (1977); Byung Ho Hwang and A. Sakakibara, *ibid.*, **25**, 647 (1979).
- 6) M. Chiba, S. Hisada, S. Nishibe and H. Thieme, *Phytochemistry*, **19**, 335 (1980); A. Pelter and R. S. Ward, *Tetrahedron*, **32**, 2783 (1976).