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Lignans from *Trachelospermum asiaticum* (Tracheolospermum . II)[1]

FUMIKO ABE and TATSUO YAMAUCHI*

Faculty of Pharmaceutical Sciences, Fukuoka University, 8–19–1 Nanakuma, Jonan-ku, Fukuoka 814–01, Japan

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Lignans of *Trachelospermum asiaticum* were isolated from the polar fraction of the methanol percolate, and the structures were determined. Trachelosiaside (matairesinol 5′-*C*-β-D-glucoside) was isolated as the first naturally occurring *C*-glucoside of lignan. Glucosides of dihydrodehydrodiconiferyl alcohol and bisdihydrosiringenin were obtained as minor components, along with many glucosides and gentiobiosides of arctigenin, matairesinol, trachelogenin, and nortrachelogenin.

Keywords——*Trachelospermum*; Apocynaceae; lignan; lignan *C*-glucoside; matairesinol *C*-glucoside; trachelosiaside; dibenzylbutyrolactone type lignan; dihydrodehydrodiconiferyl alcohol; bisdihydrosiringenin; lignan *O*-gentiobioside

Seven lignans were isolated from *Trachelospermum asiaticum* NAKAI (Apocynaceae), and their structures were established by Nishibe *et al.*[2] In the course of our studies on the constituents of Apocynaceae plants, we described the isolation and structure determination of teikaside A, a bisdesmosidic glycoside of 5α-pregn-6-en-3β, 17α, 20α-triol, from the same species.[1] This paper deals with the isolation of matairesinol *C*-glucoside, along with *O*-gentiobiosides of matairesinol and trachelogenin, and *O*-glucosides of dihydrodehydrodiconiferyl alcohol and bisdihydrosiringenin.

When the MeOH percolate of the caules was extracted with benzene and $CHCl_3$, the

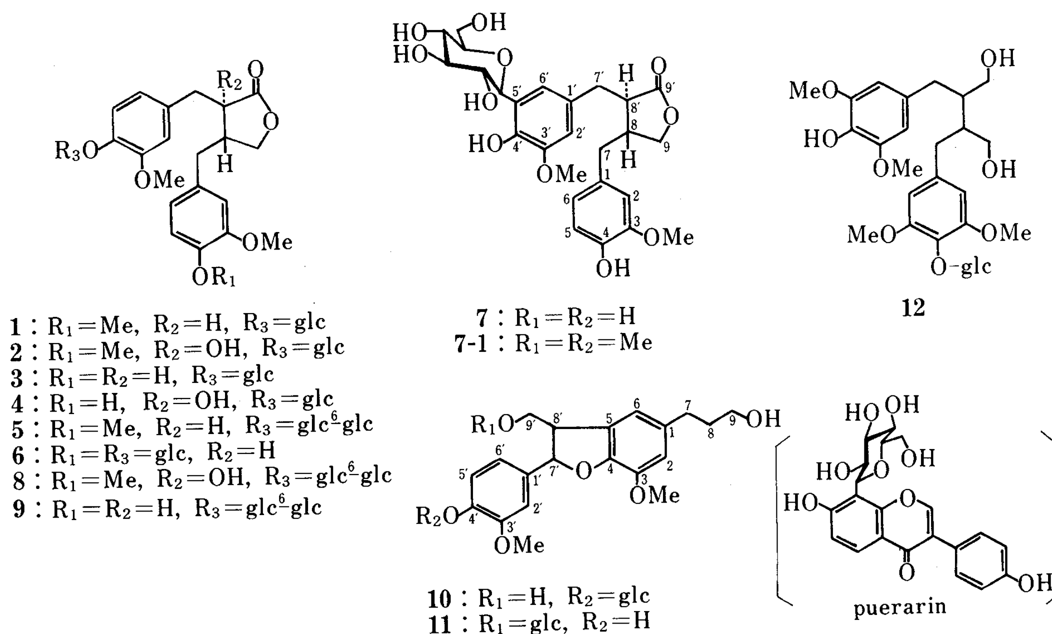

Chart 1

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water layer showed many spots of lignans, as well as triterpene glycosides.[3] The water layer was fractionated on a polystyrene column and a silica gel column, and some fractions were subjected to droplet counter-current chromatography (DCCC), and high-performance liquid chromatography (HPLC). Lignans were numbered for convenience as lignan-**1** to lignan-**12** (**1** to **12**, respectively) as shown in Chart 1.

Among them, six lignan glucosides, arctiin (**1**), tracheloside (**2**), matairesinoside (**3**), nortracheloside (**4**), gentiobiosyl arctigenin (**5**), and 4-*O*-glucosyl matairesinoside (**6**), have already been found in this plant,[2] and **5** was obtained in the highest yield (0.2%) among the

TABLE I. ^{1}H Chemical Shifts of **7** and Related Compounds, δ (ppm) from TMS in Pyridine-d_5 (J/Hz Parentheses)

	1	**1-1**	**3**	**7**	**7-1**	**7-2**
H-2	6.75 (d, 2)	6.75 (d, 2)	6.77 (d, 2)	6.79 (d, 2)	6.77 (d, 2)	6.90 (d, 2)
H-5	6.91 (d, 8)	6.89 (d, 8)	7.17 (d, 8)	7.23 (d, 8)	7.03 (d, 8)	7.24 (d, 8)
H-6	6.72 (dd, 8, 2)	6.72 (dd, 8, 2)	6.71 (dd, 8, 2)	6.77 (dd, 8, 2)	6.80 (dd, 8, 2)	6.72 (dd, 8, 2)
H-2′	7.00 (d, 2)	6.98 (d, 2)	7.01 (d, 2)	6.98 (d, 2)	7.02 (d, 2)	7.01 (d, 2)
H-5′	7.54 (d, 8)	7.20 (d, 8)	7.54 (d, 8)			
H-6′	6.86 (dd, 8, 2)	6.91 (dd, 8, 2)	6.88 (dd, 8, 2)	7.41 (d, 2)	7.34 (d, 2)	7.30 (d, 2)
H-7	2.5—2.9	2.4—2.9	2.5—2.8	2.40 (dd, 14, 9) 2.74 (dd, 14, 6)	2.44 (dd, 14, 8) 2.72 (dd, 14, 6)	2.6—2.9
H-7′	3.03 (dd, 14, 6) 3.08 (dd, 14, 6)	3.06 (dd, 14, 7) 3.14 (dd, 14, 6)	3.06 (d, 6)	2.96 (dd, 14, 7) 3.13 (dd, 14, 5)	2.97 (dd, 14, 6) 3.08 (dd, 14, 5)	2.98 (dd, 14, 7) 3.16 (dd, 14, 5)
H-8,8′	2.5—2.9	2.4—2.9	2.5—2.8	2.6—2.8	2.6—2.8	2.6—2.9
H-9	3.93 (t, 8) 4.20 (dd, 8, 7)	3.92 (t, 8) 4.18 (dd, 9, 8)	3.92 (t, 8) 4.19 (dd, 9, 7)	3.83 (t, 8) 4.03 (t, 8)	3.82 (t, 8) 4.00 (t, 8)	3.92 (t, 9) 4.22 (t, 9)
–OCH_3 (–OAc)	3.76 3.79 3.80	3.77 (×2) 3.76	3.75 3.80	3.74 3.84	3.77, 3.78 3.83, 4.00	3.71, 3.80 (1.91, 1.98 2.04, 2.05 2.27, 2.29)
H_{glc}-1	5.61 (d, 8)		5.63 (d, 7)	5.56 (d, 9)	5.34 (d, 9)	5.24 (d, 10)
H_{glc}-2				4.47 (t, 9)	4.43 (t, 9)	5.81 (dd, 10, 9)
H_{glc}-3						5.88 (t, 9)
H_{glc}-4						5.60 (dd, 10, 9)
H_{glc}-5				4.14 (m)	4.14 (m)	4.2 (m)
H_{glc}-6						4.34 (dd, 12, 2) 4.56 (dd, 12, 5)

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TABLE II. ^{13}C Chemical Shifts of Lignans, δ (ppm) from TMS in Pyridine-d_5

	3	7	pue.[e]	8	9	10	11	12
C-1	129.8	129.8		132.5	129.8	129.9	129.4	132.0
C-2	113.1	113.2		113.6	113.2	113.7	111.0	107.6
C-3	146.9	146.8		147.2	146.8[a]	144.6	144.6	149.0
C-4	148.7	148.7[a]		148.6	148.7	147.6	148.0	135.8
C-5	116.6[a]	116.7		112.9	116.6[b]	136.2	136.2	149.0
C-6	121.8	122.0		121.3	121.9	117.5	117.7	107.6
C-1′	132.7	129.0		130.6	132.7	136.9	133.5	134.4
C-2′	114.4	112.5		115.3	114.2	111.3	113.9	107.9
C-3′	146.9	145.4		147.2	146.9[a]	147.2	147.1	153.5
C-4′	150.0	148.6[a]		150.1	150.1	150.2	148.7	138.4
C-5′	116.5[a]	128.0		116.8	117.0[b]	116.5	116.4	153.5
C-6′	122.3	122.2		123.9	122.6	118.9	119.6	107.9
C-7	38.0	38.1		31.8	38.1	32.6	35.8	36.3[a]
C-8	41.7	41.8		44.1	41.6	36.0	32.6	44.4[c]
C-9	71.4	71.2		70.9	71.5	61.5	61.4	61.3[b]
C-7′	34.6	35.2		41.7	34.7	87.9	88.3	36.5[a]
C-8′	46.6	46.8		76.7	46.6	55.1	52.2	44.0[c]
C-9′	178.9	179.0		179.3	179.0	64.4	71.7	61.1[b]
$-OCH_3$	56.0 (×2)	56.0		56.0 (×2)	56.0	55.9	55.8	56.4 (×2)
		56.1		56.1	56.1	56.3	56.2	56.5 (×2)
C_{glc}-1	102.5	77.4	75.7	102.6	102.6	102.3	105.0	105.4
C_{glc}-2	74.9	76.2	73.1	74.7	74.8	74.9	75.1	76.1
C_{glc}-3	78.8[b]	80.6	80.5	78.4	78.4	78.8[a]	78.6	78.6[d]
C_{glc}-4	71.3	72.3	71.8	71.0	71.1	71.2	71.6	71.6
C_{glc}-5	78.5[b]	82.9	83.2	77.5	77.7	78.5[a]	78.6	78.3[d]
C_{glc}-6	62.4	63.3	62.7	69.7	69.7	62.4	62.7	62.7
C_{glc}-1′				105.4	105.2			
C_{glc}-2′				75.2	75.3			
C_{glc}-3′				78.4	78.4			
C_{glc}-4′				71.7	71.7			
C_{glc}-5′				78.4	78.4			
C_{glc}-6′				62.3	62.7			

a—d) Signal assignments marked *a*), *b*), *c*) or *d*) in each column may be reversed. *e*) pue. = puerarin. Chemical shifts of the aglycone moiety are omitted.

lignans.

In the proton nuclear magnetic resonance (^1H-NMR) spectrum of arctigenin, the aglycone of **1** (**1-1**), and high-field shift of H-5′ was observed in comparison with that of **1**. Since H-2′ and H-6′ were assignable on the basis of *p*- and *o*-couplings with H-5′, the assignment of all the protons in the two benzene rings of **1** was established by two-dimensional ^1H–^1H chemical shift correlation spectroscopy (COSY) (Table I). The ^1H-chemical shifts of matairesinoside (**3**) were in good agreement with those of **1**, except for H-5, which showed a low-field shift of 0.26 ppm due to C_4-OH.

Lignan **7** was isolated from the mixture with **4** by HPLC on a preparative scale. On the basis of the electron impact (EI)-mass spectrum (MS) and fast atom bombardment (FAB)-MS of **7**, the molecular formula was considered to be $C_{26}H_{32}O_{11}$, the same as that of **3**. The amount of component sugar was therefore one mole, and one anomeric proton was observed at δ 5.56 (d, $J=9$ Hz). In the ^1H-NMR spectrum of **7**, the signals of protons of one of the benzene rings (H-2, H-5, and H-6) and of two methoxyl groups were found at almost the same chemical shifts as those of **3**. In the remaining benzene ring, two protons at δ 6.98 and δ 7.41 showed *m*-coupling with each other ($J=2$ Hz) and were assigned to H-2′ and H-6′,

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respectively. On methylation with CH_2N_2, **7** afforded a tetra-*O*-methylate (**7**-1), confirming the presence of two phenolic hydroxyl groups. These *m*-coupled protons were also seen in **7-1** and the component sugar was considered to be attached at C-5′. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **7**, the signals of carbons due to the lactone ring and one benzene ring were almost identical with those of **3**, while one quaternary carbon was observed at δ 128.0, which was ascribable to C-5′.

The facts that all of the hydroxyl groups of the sugar moiety were found to be equatorial on the basis of the ^{1}H–^{1}H COSY spectrum of **7**-acetate (**7**-2), and that the anomeric proton peak of **7** at δ 5.56 (d, J=9 Hz) corresponds to the anomeric carbon peak at unusually high field (δ 77.4) in the ^{1}H–^{13}C COSY spectrum, are also consistent with the *C*-β-D-glucoside structure. C_{glc}-1 and C_{glc}-2(δ 76.2) in **7** were observed at slightly low field in comparison with those of puerarin (δ 75.7 and 73.1, respectively), probably due to the absence of one of the two C–O bonds adjacent to the carbon bearing the glucose in puerarin. The structure of **7** was thus established as matairesinol 5′-*C*-β-D-glucoside, and named trachelosiaside.

On enzymic hydrolysis, **8** afforded trachelogenin, and **9** afforded matairesinol. Since the component sugars of **8** and **9** were identified as gentiobiose from the ^{1}H- and ^{13}C-NMR spectra, the structures were determined to be trachelogenin 4′-*O*-β-gentiobioside and matairesinol 4′-*O*-β-gentiobioside, respectively.

Lignan **10**, $C_{26}H_{34}O_{11}$, seemed to be a phenolic monoglucoside, on the bases of the anomeric proton peak at δ 5.65 and the ^{13}C-NMR spectrum. The aglycone (**10**–1), obtained by enzymic hydrolysis, showed the presence of two primary alcohols. A 2H triplet peak at δ 3.92 (J=6 Hz) was coupled with a 2H multiplet peak at δ 2.09, which was further coupled with benzyl methylene protons at δ 2.88 (t, J=8 Hz), so that one of the primary alcohols seemed to be an *n*-propanol moiety. The methylene protons (δ 4.21, 4.28) on the remaining primary alcohol were coupled with a proton at δ 3.96 (m) which was also coupled with a methine proton at δ 6.06 (d, J=7 Hz), and **10**-1 was considered to be dihydrodehydrodiconiferyl alcohol. In the ^{13}C-NMR spectrum of **10**, a low-field shift was observed at C-1′(+3.0) as well as the glycosylation shift at C-4′(+1.4) in comparison with that of **10**-1, indicating that the glucosyl linkage is at the C-4′-hydroxyl group in **10**. The negative optical rotation value ($[\alpha]_D$ −3.2°) suggests that **10**-1 may have the same stereoisomeric structure as that obtained by Takemoto *et al.* ($[\alpha]_D$ −4.9°),[4a] or by Satake *et al.* ($[\alpha]_D$ −8.5°)[4b] rather than that obtained by Lundgren *et al.* ($[\alpha]_D$ +4.7°),[4c] although the absolute configurations have not been determined. Lignan **11**, $C_{26}H_{34}O_{11}$, also afforded the same aglycone as **10**. Since the component sugar was characterized as a β-linked glucose, and the glycosylation shift was observed at C-9′ in the ^{13}C-NMR spectrum, **11** is considered to be the 9′-*O*-β-D-glucoside of **10**-1.[4b]

In the ^{1}H-NMR spectrum of **12**, two protons of each benzene ring were found, each as a singlet, as well as the protons of two methoxyl groups, suggesting **12** to be a lignan with two 3,4,5-trisubstituted benzene moieties. One glucose seemed to be attached to the *p*-hydroxyl group of one of the benzene rings with β-linkage (H_{glc}-1: δ 5.67, d, J=7 Hz; C_{glc}-1: δ 105.4). The presence of two methine and four methylene groups was shown by pairs of doublets (δ 44.4, 44.0), triplets (δ 36.5, 36.3), and triplets (δ 61.3, 61.1), the latter of the triplets being assignable to the primary carbinyl groups. The structure of **12** was therefore considered to be bisdihydrosiringenin, as shown in Chart 1. The aglycone of **12** (**12**-1) retained positive optical rotation ($[\alpha]_D$ +32.5°), indicating that **12**-1 is not the *meso*-compound.

To the authors' knowledge, **7** is the first *C*-glucoside of lignan to be reported. Although most of the twelve lignans from this plant are of dibenzylbutyrolactone-type, dihydrodehydrodiconyferyl alcohol-type and bisdihydrosiringenin-type lignans are present in small amounts. Their absolute configurations are to be investigated.

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Experimental

The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL GX-400 spectrometer in pyridine-d_5. Chemical shifts are given in δ values referred to internal tetramethylsilane, and the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and dd = doublet of doublets. MS were recorded on a JEOL D-300-FD spectrometer. HPLC was run with a Waters model ALC 200, equipped with a Nova-Pack C_{18} column and eluted with CH_3CN in H_2O (16—24%). The following solvent systems were used for silica gel column chromatography, thin-layer chromatography (TLC), and DCCC: solv. 1. $CHCl_3$–MeOH–H_2O (bottom layer); solv. 2. EtOAc–MeOH–H_2O (top layer); solv. 3. benzene–acetone. For TLC, Silica gel 60 F_{254} (Merck) was used. Detection was done under ultraviolet (UV) light and by charring the plate after spraying it with 10% H_2SO_4.

Extraction——*Trachelospermum asiaticum* was cultivated in the medicinal plant garden of Fukuoka University and harvested in May, 1985. After air-drying in the shade, the caules (12 kg) were powdered and percolated with MeOH. The percolate was concentrated to 3 l and diluted with 3 l of H_2O. The mixture was filtered and the filtrate was defatted with benzene (ext. 7 g) and $CHCl_3$(180 g). The water layer was again concentrated to 3 l, then passed through an MCI gel (Mitsubishi CHP-20) column, which was eluted stepwise with H_2O containing increasing concentrations of MeOH. The fractions eluted with 40% (ext. 80 g), 50% (ext. 100 g), 60% (ext. 84 g), and 70% MeOH (ext. 33 g) afforded lignans as well as triterpene glucosides (trachelosperins).[3] Each fraction was subjected to silica gel column chromatographies with solv. 1 and 2, and ODS-column (Fuji gel) chromatography with CH_3CN in H_2O. The lignans in some fractions were duplicated and the fractions showing similar features on TLC were combined. The major lignan, **5**, was obtained as crystals (*ca.* 21 g) from the 40%, 50%, and 60% MeOH fractions by silica gel column chromatography with solv. 1 (7 : 3 : 1—7 : 3 : 0.8), followed by crystallization from MeOH. The following lignans were finally obtained, besides **5**: **1**, 8.4 g; **2**, 2.2 g; **3**, 140 mg; **4**, 30 mg; **6**, 70 mg; **7**, 500 mg; **8**, 40 mg; **9**, 320 mg; **10**, 70 mg; **11**, 50 mg; **12**, 100 mg. The separation of **7** from accompanying **4** could not be achieved by column chromatography, and isolation was carried out by HPLC with 20% CH_3CN. When the mixture of **7** and **4** was subjected to enzymic hydrolysis with cellulase (Sigma Chem. Co.), followed by silica gel column chromatography, **7** was isolated. The mixture of **8** and **9** was subjected to DCCC with solv. 1 (4 : 6 : 5, ascending), and each component was isolated.

Trachelosiaside (7)——A solid, $[\alpha]_D^{27}$ $-12.1°$ (c = 1.1, MeOH). FAB-MS m/z: 520 (M^+, $C_{26}H_{32}O_{11}$). On methylation of **7** (20 mg) in MeOH (1 ml) with CH_2N_2 in ether, a methylate (**7**-1) was obtained as a solid, $[\alpha]_D^{27}$ $-12.6°$ (c = 1.6, MeOH). FAB-MS m/z: 548 (M^+), EI-MS m/z: 548.225, Calcd for $C_{28}H_{36}O_{11}$: 548.226. Acetylation of **7** (50 mg) with pyridine and Ac_2O at room temperature gave a hexaacetate (**7**-2), $[\alpha]_D^{25}$ $-34.6°$ (c = 2.2, MeOH), EI-MS m/z: 772.256, Calcd for $C_{38}H_{44}O_{17}$: 772.258.

Trachelogenin *β*-Gentiobioside (8)——A solid, $[\alpha]_D^{28}$ $-70.0°$ (c = 2.0, MeOH). FAB-MS m/z: 735 (M^+ + Na, $C_{33}H_{44}O_{17}$). ^{1}H-NMR: 7.69 (1H, d, J = 8 Hz, H-5′), 7.19 (1H, dd, J = 8, 2 Hz, H-6′), 7.14 (1H, d, J = 2 Hz, H-2′), 6.94 (1H, d, J = 8 Hz, H-5), 6.92 (1H, d, J = 2 Hz, H-2), 6.88 (1H, dd, J = 8, 2 Hz, H-6), 5.55 (1H, d, J = 8 Hz, H_{glc}-1), 5.04 (1H, d, J = 8 Hz, H_{glc}-1″), 3.82, 3.78, 3.76 (3H each s, –OMe), 3.61, 3.30 (1H each, d, J = 13 Hz, H-7′), 3.21 (1H, dd, J = 14, 5 Hz, H-7a), 2.93 (1H, dd, J = 14, 10 Hz, H-7b), 2.77 (1H, m, H-8). Acetylation by the usual method gave a heptaacetate (**8**-1), which was crystallized from MeOH to give prisms, mp 194—196 °C, $[\alpha]_D^{26}$ $-35.9°$ (c = 1.2, MeOH), FAB-MS m/z: 1029 (M^+ + Na, $C_{47}H_{58}O_{24}$). *Anal.* Calcd for $C_{47}H_{58}O_{24}$: C, 56.06; H, 5.81. Found: C, 56.06; H, 5.58. Hydrolysis of 8 (20 mg) in 20% EtOH with cellulase at 38 °C for 20 h gave the aglycone, which was proved to be trachelogenin by TLC in comparison with an authentic sample (solv. 1, 7 : 2 : 1; solv. 3, 2 : 1).

Matairesinol 4′-*O*-Gentiobioside (9)——A solid, $[\alpha]_D^{26}$ $-54.7°$ (c = 0.68, MeOH). FAB-MS m/z: 705 (M^+ + Na, $C_{32}H_{42}O_{16}$). ^{1}H-NMR: 7.67 (1H, d, J = 8 Hz, H-5′), 7.18 (1H, d, J = 8 Hz, H-5), 7.01 (1H, dd, J = 8, 2 Hz, H-6′), 6.96 (1H, d, J = 2 Hz, H-2′), 6.77 (1H, d, J = 2 Hz, H-2), 6.71 (1H, dd, J = 8, 2 Hz, H-6), 5.55 (1H, d, J = 7 Hz, H_{glc}-1), 5.07 (1H, d, J = 8 Hz, H_{glc}-1″), 4.18, 3.94 (1H each, t, J = 9 Hz, H-9), 3.82, 3.75 (3H each, s, –OMe), 3.05, 3.00 (1H each, dd, J = 14, 6 Hz, H-7′). Acetylation in the usual manner gave an octaacetate (**9**-1) as prisms, mp 110—113 °C, FAB-MS m/z: 1041 (M^+ + Na, $C_{48}H_{58}O_{24}$). *Anal.* Calcd for $C_{48}H_{58}O_{24}$: C, 56.58; H, 5.74. Found: C, 56.59; H. 5.64. Hydrolysis of **9** (20 mg) in 20% EtOH with cellulase gave the aglycone, which was proved to be matairesinol by TLC in comparison with an authentic sample (solv. 1, 7 : 2 : 1; solv. 3, 2 : 1).

Dihydrodehydrodiconiferyl Alcohol 4′-*O*-*β*-D-Glucoside (10)——A solid, $[\alpha]_D^{27}$ $-34.6°$ (c = 1.4, MeOH). FAB-MS m/z: 545 (M^+ + Na, $C_{26}H_{34}O_{11}$). ^{1}H-NMR: 7.52 (1H, d, J = 8 Hz, H-5′), 7.33 (1H, d, J = 2 Hz, H-2′), 7.19 (1H, dd, J = 8, 2 Hz, H-6′), 7.05, 6.92 (1H each, d, J = 1 Hz, H-6, 2), 6.05 (1H, d, J = 6 Hz, H-7′), 5.65 (1H, d, J = 7 Hz, H_{glc}-1), 3.93 (2H, t, J = 6 Hz, H-$9_{a,b}$), 3.89 (1H, m, H-8′), 3.85, 3.62 (3H each, s, –OMe), 2.88 (2H, t, J = 8 Hz, H-$7_{a,b}$), 2.09 (2H, m, H-$8_{a,b}$). Enzymic hydrolysis of **10** (100 mg) in 20% EtOH (5 ml) was carried out with cellulase in the usual manner. The aglycone was extracted with BuOH and the extract was purified on a silica gel column with solv. 3 (4 : 1) to give the aglycone (**10**-1) (50 mg), $[\alpha]_D^{26}$ $-3.2°$ (c = 1.9, acetone). EI-MS m/z: 360.157. Calcd for $C_{20}H_{24}O_6$: 360.157. ^{1}H-NMR: 7.33 (1H, d, J = 2 Hz, H-2′), 7.25 (1H, dd, J = 8, 2 Hz, H-6′), 7.20 (1H, d, J = 8 Hz, H-5′), 7.07, 6.93 (1H each d, J = 1 Hz, H-6, 2), 6.06 (1H, d, J = 7 Hz, H-7′), 4.28 (1H, dd, J = 11, 5 Hz, H-$9'_a$), 4.21 (1H, dd, J = 11, 7 Hz, H-$9'_b$), 3.96 (1H, m, H-8′), 3.92 (2H, t, J = 6 Hz, H-$9_{a,b}$), 3.84, 3.64 (3H each, s, –OMe), 2.88 (2H, t, J = 8 Hz, H-$7_{a,b}$), 2.09 (2H, m, H-$8_{a,b}$). ^{13}C-NMR: 133.9 (C-1′), 110.8 (C-2′), 147.3 (C-3′), 148.8 (C-4′), 116.5 (C-5′), 119.7 (C-6′).

Dihydrodehydrodiconiferyl Alcohol 9′-*O*-Glucoside (11)——A solid, $[\alpha]_D^{25}$ $-15.5°$ (c = 2.0, MeOH). FAB-MS m/z:

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545 (M^++Na, $C_{26}H_{34}O_{11}$). ^{1}H-NMR: 7.37 (1H, d, J=2 Hz, H-2′), 7.25 (1H, dd, J=8, 2 Hz, H-6′), 7.14 (1H, d, J=8 Hz, H-5′), 7.09, 6.92 (1H each, d, J=1 Hz, H-6, 2), 5.97 (1H, d, J=6 Hz, H-7′), 4.97 (1H, d, J=7 Hz, H_{glc}-1), 3.92 (2H, t, J=6 Hz, H-$9_{a,b}$), 3.83, 3.66 (3H each, s, -OMe), 2.88 (2H, t, J=8 Hz, H-$7_{a,b}$). Hydrolysis of **11** in 20% EtOH with cellulase gave the aglycone ($[\alpha]_D^{24}$ −3.1° (c=0.9, MeOH)), which was identical with **10**-1 on TLC (solv. 1, 7:2:1; solv. 3, 2:1).

8,8′-Bisdihydrosiringenin Glucoside (12)——Prisms from MeOH, mp 125—127 °C, $[\alpha]_D^{27}$ −11.8° (c=3.1, MeOH). FAB-MS m/z: 607 (M^++Na, $C_{28}H_{40}O_{13}$). *Anal.* Calcd for $C_{28}H_{40}O_{13} \cdot 2H_2O$: C, 54.18; H, 7.15. Found: C, 54.02; H, 7.01. ^{1}H-NMR: 6.77, 6.74 (2H each, s, H-2, 6; H-2′, 6′), 5.67 (1H, d, J=7 Hz, H_{glc}-1), 3.76, 3.71 (6H each, s, -OMe). Hydrolysis of **12** (30 mg) with cellulase in the usual manner gave the aglycone as a solid, $[\alpha]_D^{25}$ +32.5° (c=0.2, MeOH). EI-MS m/z: 422.196, Calcd for $C_{22}H_{30}O_8$: 422.194.

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