Chemical Constituents of Chinese Folk Medicine "Sân Léng", *Sparganium stoloniferum*

Osamu Shirota, Setsuko Sekita, and Motoyoshi Satake*

Division of Pharmacognosy and Phytochemistry, National Institute of Health Sciences, Tokyo 158, Japan

Yan Ni and Hua Weiyi

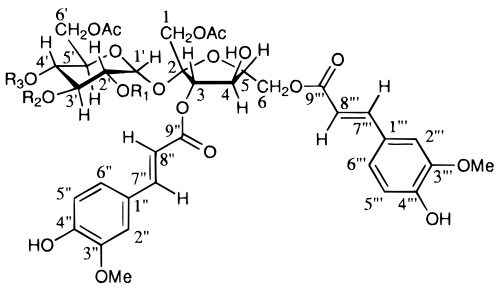
Tianjin Institute of Pharmaceutical Research, Tianjin, China

Received July 3, 1995[⊗]

The isolation and structure elucidation of three phenylpropanoid glycosides (**1**−**3**) along with three known phenylpropanoid glycerides from Chinese folk medicine "Sân Léng" (*Sparganium stoloniferum* Buch.−Hamil.) are described. The structures of these phenylpropanoid glycosides and glycerides were elucidated by a combination of chemical and spectroscopical evidence including 2D-NMR studies.

"Sân Léng" is a Chinese folk medicine which has been using as an emmenagogue, a galactagogue, and an antispasmodic agent.[1,2] It originates from the rhizome of *Sparganium stoloniferum* Buch.−Hamil., *Sparganium simplex* Huds., and *Sparganium stenophyllum* Maxima. (Sparganiaceae) and *Scirpus flaviatilis* (Torr.) A. Gray. or *Scirpus yagara* Ohwi (Cyperaceae).[1,2] To date, only a few studies on the constituents of the genus *Scirpus* and *Sparganium* have been reported.[3,4]

Chemical investigation of *S. stoloniferum* Buch.−Hamil. led us to isolate three novel phenylpropanoid glycosides (**1**−**3**) together with three known phenylpropanoid glycerides, 1,3-*O*-di-*p*-coumaroylglycerol, 1,3-*O*-diferuloylglycerol, and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol. The structures of **1**−**3**, derived from sucrose esterified with two feruloyl groups and four acetyl groups, were elucidated by a combination of several spectroscopic data including 2D-NMR and chemical evidence.



1: R_1 = H, R_2 = Ac, R_3 = Ac

2: R_1 = Ac, R_2 = H, R_3 = Ac

3: R_1 = Ac, R_2 = Ac, R_3 = H

Results and Discussion

A CH_2Cl_2-soluble portion (21 g) of the methanolic extract (364 g) of the rhizome of *S. stoloniferum* Buch.−Hamil. (3.7 kg) was subjected to silica gel column chromatography. The fractions obtained were further separated by Sephadex LH-20 column chromatography and followed by silica gel medium-pressure liquid chromatography (MPLC) to give three phenylpropanoid glycosides (**1**; 0.0003%), (**2**; 0.0039%), (**3**; 0.0003%), and three known phenylpropanoid glycerides, 1,3-*O*-di-*p*-coumaroylglycerol (0.0003%), 1,3-*O*-diferuloylglycerol (0.0003%), and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol (0.0027%).

Compound **1** was obtained as a colorless amorphous solid with elemental composition $C_{40}H_{46}O_{21}$, established by high-resolution MS. The ^{1}H-NMR spectrum suggested that **1** contained two feruloyl moieties, represented by signals of two sets of *trans* olefinic protons [δH 6.33 (1H, d, J = 16.0 Hz), 7.66 (1H, d, J = 16.0 Hz); 6.36 (1H, d, J = 16.0 Hz), 7.72 (1H, d, J = 16.0 Hz)], two sets of 1,3,4-trisubstituted aromatic ring protons [δH 7.04 (1H, d, J = 2.0 Hz), 6.92 (1H, d, J = 8.1 Hz), 7.09 (1H, dd, J = 2.0, 8.1 Hz); 7.13 (1H, d, J = 2.0 Hz), 6.92 (1H, d, J = 8.0 Hz), 7.16 (1H, dd, J = 2.0, 8.0 Hz)], two methoxy groups [δH 3.94 (3H, s), 3.95 (3H, s)], and two phenolic hydroxy groups [δH, 5.90 (1H, s), 5.95 (1H, s)]. Signals in the ^{13}C-NMR spectrum at δC 91.9 (d), 70.8 (d), 73.3 (d), 68.5 (d), 69.0 (d), 62.8 (t); 65.5 (t), 103.3 (s), 80.9 (d), 73.8 (d), 81.4 (d), 63.8 (t) suggested the presence of a disaccharide moiety. Alkaline and acid hydrolysis of **1** gave sucrose and a mixture of glucose and fructose, which were identified by direct comparison with authentic samples on TLC. A characteristic doublet signal with a smaller coupling constant at δH 5.62 (1H, d, J = 3.6 Hz) in the ^{1}H-NMR that was ascribed to the anomeric proton in the α-glucopyranose unit[5,6] also supported the presence of a sucrose moiety in **1**. Furthermore, ^{1}H- and ^{13}C-NMR spectra revealed the presence of four acetyl groups [δH 1.79 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 2.12 (3H, s); δC 20.6 (q), 20.9 (q), 21.1 (q), 21.0 (q), 170.1 (s), 171.0 (s), 171.3 (s), 170.6 (s)] located in the sucrose moiety. The position of bond conjugation of the feruloyl and the acetyl groups on the sucrose was assigned by ^{1}H-detected multiple-bond heteronuclear multiple quantum coherence spectroscopy (HMBC) experiment. This HMBC spectrum enabled the assignments of two feruloyl moieties located at positions 3 and 6 on the fructose unit of sucrose, since the methine proton (δH 5.29) of position 3 and one *trans* olefinic proton (δH 7.72) of position 7″ on a feruloyl moiety gave cross-peaks with the same carbonyl carbon (δC 167.7) and one set of the methylene protons (δH 4.44, 2H) of position 6 and another *trans* olefinic proton (δH 7.66) of position 7‴ with the same carbonyl carbon (δC 167.5).

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

0163-3864/96/3259-0242$12.00/0

Also, the methine and methylene protons of positions 3′ (δH 5.25), 4′ (δH 4.91), and 6′ (δH 4.10, 2H) on the glucose and methylene protons of position 1 (δH 4.29 and 4.40) on the fructose showed cross-peaks with respective acetyl carbonyl carbons (δC 171.3, 170.1, 170.6, and 171.0). Furthermore, significant upfield shift (*ca*. 1.0 ppm) of the methine protons of positions 4 and 2′ in the tetraacetyl derivative of **1** clearly certified that the positions of nonesterified hydroxyl groups on **1** were attached at C-4 and C-2′. On the basis of these spectroscopic data and chemical evidence, the structure of compound **1** was determined to be β-D-(1-*O*-acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-3′,4′,6′-*O*-triacetylglucopyranoside.

Compound **2** obtained as a colorless amorphous solid with the same elemental composition as **1**, $C_{40}H_{46}O_{21}$, was also a phenylpropanoid glycoside. The ^{1}H-NMR spectrum suggested that **2** had the same substructures of two feruloyl moieties [*trans* olefinic protons: δH 6.34 (1H, d, J = 15.9 Hz), 7.66 (1H, d, J = 15.9 Hz); 6.34 (1H, d, J = 15.9 Hz), 7.69 (1H, d, J = 15.9 Hz); 1,3,4-trisubstituted aromatic ring protons: δH 7.05 (1H, br s), 6.91 (1H, d, J = 8.0 Hz), 7.07 (1H, br d, J = 9.6 Hz); 7.11 (1H, br s), 6.91 (1H, d, J = 8.0 Hz), 7.10 (1H, br s); two methoxy groups: δH 3.91 (3H, s), 3.93 (3H, s); and two phenolic hydroxy groups: δH 6.25 (1H, br s) × 2]. As in the case of **1**, compound **2** also had four acetyl groups [δH 1.95 (3H, s), 2.05 (3H, s), 2.12 (3H, s), 2.13 (3H, s)] linked to a sugar. Acid and alkaline hydrolysis followed by TLC indicated that **2** contained a sucrose moiety. Acetylation of both **1** and **2** afforded the identical tetraacetyl derivative, which suggested that **2** was an isomer of **1** in respect to the acetylated positions. The HMBC spectrum of **2** revealed long-range couplings between the oxygenated methine and methylene protons at positions 3 and 6 of the fructose, as well as the *trans* olefinic protons at positions 8″ and 8‴ of two feruloyl groups, and their respective carbonyl carbons (^{1}H/^{13}C/^{1}H: 5.38/167.6/6.34 ppm for the C-3 feruloyl group; 4.13/167.8/6.34 ppm for the C-6 feruloyl group), so these two feruloyl groups were located at C-3 and C-6, equal to **1**. Analogously, couplings between the methyl protons of four acetyl groups, as well as methine and methylene protons at 1, 2′, 4′, and 6′ of the sucrose core and its carbonyl carbon (^{1}H/^{13}C/^{1}H: 1.95/170.7/4.10, 4.24 ppm for the C-1 acetyl group; 2.05/171.0/4.83 ppm for the C-2′ acetyl group; 2.12/171.1/4.87 ppm for the C-4′ acetyl group; 2.13/171.3/4.51 ppm for the C-6′ acetyl group) indicated that the four acetyl groups were at C-1, C-2′, C-4′, and C-6′. These data confirmed that the substantial differences between **2** and **1** were in the interchange of the C-2′ acetyl group and the C-3′ hydroxy group, so the structure of **2** was β-D-(1-*O*-acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-2′,4′,6′-*O*-triacetylglucopyranoside.

Compound **3** was obtained as a colorless amorphous solid, and its elemental composition and the number of components were identical with those in **1** and **2**, namely a sucrose, two feruloyl moieties, and four acetyl groups. Acetylation of **3** gave the identical tetraacetyl derivative as that of **1**, revealing that two feruloyl moieties were in C-3 and C-6 and the differences among them were in acetylated positions. According to the HMBC spectrum, the four acetyl groups were at positions 1, 2′, 3′, and 6′ (^{1}H/^{13}C/^{1}H: 2.12/170.5/4.13, 4.23 ppm for C-1 acetyl group; 2.06/170.6/4.87 ppm for C-2′; 2.08/171.8/5.42 ppm for C-3′; 2.08/171.9/4.35 ppm for C-6′). Consequently, the structure of **3** was determined as β-D-(1-*O*-acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-2′,3′,6′-*O*-triacetylglucopyranoside.

The phenylpropanoid glycerides 1,3-*O*-di-*p*-coumaroylglycerol, 1,3-*O*-diferuloylglycerol, and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol were obtained as colorless amorphous solids and determined by the comparison of spectroscopic and physical data with those described in the literature,[7] respectively.

Complete assignments of the ^{1}H- and ^{13}C-NMR signals of the compounds **1**−**3** are shown in Tables 1 and 2. To our knowledge, these are the first phenylpropanoid esters isolated from the family Sparganiaceae. Although several phenylpropanoid glycosides have been reported recently,[6,8−10] the oligoacetylated type, such as **1**−**3**, is rare.[11−13]

Experimental Section

General Experimental Details. Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-370 digital polarimeter, and the $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. FAB-MS spectra were obtained on a JEOL AX-505H spectrometer. UV and IR spectra were taken with a Hitachi U-2000 spectrophotometer and a JASCO FT/IR-5300 spectrophotometer, respectively. Medium-pressure liquid chromatography (MPLC) was performed with a CIG column system (22 mm i.d. × 300 mm or 22 mm i.d. × 100 mm, Kusano Scientific Co., Tokyo) packed with 10 or 5 μm silica gel. TLC was conducted on precoated Kieselgel 60 F254 (Art. 5715; Merck), and the spots were detected by heating after spraying with 10% H_2SO_4 or with orcinol reagent (orcinol, $FeCl_3$ and H_2SO_4). 1D and 2D ^{1}H- and ^{13}C-NMR spectra were recorded on Varian spectrometers (Gemini 300 and Unity 400) at 298 K. The NMR coupling constants (J) are given in Hz.

Plant Materials. Rhizomes of *S. stoloniferum* Buch.−Hamil. (3.7 kg), commonly known as "Sân Léng", a Chinese folk medicine, were purchased at Tianjin, China, in 1992. The botanical identification was made by Mr. Zhang Tie-jin (Tianjin Institute of Pharmaceutical Research). A voucher specimen has been deposited in the herbarium of Tianjin Institute of Pharmaceutical Research, China, and at the National Institute of Health Sciences, Japan.

Extraction and Isolation. The rhizome (3.7 kg) of *S. stoloniferum* Buch.−Hamil. was milled and extracted with hot MeOH (36 L) to give an extract (364 g), which was partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2-soluble fraction (21.9 g) was subjected to silica gel column chromatography using a CH_2Cl_2−EtOAc gradient (1:0−0:1) followed by EtOAc−MeOH gradient (9:1−0:1) to give 17 fractions (fractions A−Q). Fractions F and G (eluted by 30% EtOAc in CH_2Cl_2) were separately subjected to Sephadex LH-20 column chromatography with an *n*-hexane−CH_2Cl_2−MeOH (4:5:1) solvent system to get 1,3-*O*-di-*p*-coumaroylglycerol, 1,3-*O*-diferuloylglycerol, and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol as amorphous solids. Similarly, fractions J, K, and L (eluted by 50% EtOAc in CH_2Cl_2) gave **1**, **2**, and **3**, respectively. These compounds were further purified

Table 1. ^{1}H-NMR Chemical Shifts (ppm, Number of Protons, Multiplicity, and *J*/Hz) for Compound **1**−**3**[a]

assignment	compd **1**				compd **2**				compd **3**			
fructose												
1-Ha	4.29	1H	d	12.0	4.10	1H	d	9.9	4.13	1H	d	11.8
1-Hb	4.40	1H	d	12.0	4.24	1H	d	9.9	4.23	1H	d	11.8
3-H	5.29	1H	d	7.2	5.38	1H	d	7.7	5.33	1H	d	7.7
4-H	4.50	1H	t	8.6	4.43	1H	t	7.9	4.41	1H	dt	2.5, 7.7
4-OH	3.71	1H	br s		3.90	1H	br s		3.90	1H	d	2.6
5-H	4.26	1H	m	(overlap)	4.25	1H	m	(overlap)	4.27	1H	dd	3.5, 7.4
6-Ha	4.44	2H	d	4.8	4.13	2H	t	7.1	4.44	1H	dd	3.3, 12.1
6-Hb			(overlap)				(overlap)		4.68	1H	dd	6.9, 12.4
1-OAc	2.12	3H	s		1.95	3H	s		2.12	3H	s	
glucose												
1′-H	5.62	1H	d	3.6	5.68	1H	d	3.5	5.67	1H	d	3.6
2′-H	3.71	1H	br m	(overlap)	4.83	1H	dd	3.5, 9.9	4.87	1H	dd	3.6, 10.3
3′-H	5.25	1H	t	9.8	4.10	1H	t	10.0	5.42	1H	t	9.8
4′-H	4.91	1H	t	9.8	4.87	1H	t	9.6	3.49	1H	dt	6.1, 3.0
5′-H	4.27	1H	m	(overlap)	4.23	1H	m	(overlap)	4.17	1H	dd	2.8, 7.0
6′-H	4.10	2H	br d	2.8	4.51	2H	br d	4.7	4.35	2H	br d	4.6
2′-OAc					2.05[b]	3H	s		2.06	3H	s	
2′-OH	2.60	1H	br s									
3′-OAc	2.06	3H	s						2.08[c]	3H	s	
3′-OH					2.85	1H	br s					
4′-OAc	1.79	3H	s		2.12[b]	3H	s					
4′-OH									3.22	1H	d	6.3
6′-OAc	2.04	3H	s		2.13[b]	3H	s		2.08[c]	3H	s	
3-feruloyl												
2″-H	7.13	1H	d	2.0	7.11	1H	br s		7.15	1H	br s	
5″-H	6.92	1H	d	8.0	6.91	1H	d	8.0	6.93	1H	d	7.9
6″-H	7.16	1H	dd	2.0, 8.1	7.10	1H	br d	9.6	7.12	1H	dd	1.7, 7.9
7″-H	7.72	1H	d	16.0	7.69	1H	d	15.9	7.72	1H	d	15.9
8″-H	6.36	1H	d	16.0	6.34	2H	d	15.9	6.39	1H	d	15.9
3″-OMe	3.94	3H	s		3.91	3H	s		3.94	3H	s	
4″-OH	5.90	1H	br s		6.25	1H	br s		6.00	1H	s	
6-feruloyl												
2‴-H	7.04	1H	d	2.0	7.05	1H	br s		7.07	1H	br s	
5‴-H	6.92	1H	d	8.0	6.91	1H	d	8.0	6.92	1H	d	8.0
6‴-H	7.09	1H	dd	2.0, 8.2	7.07	1H	br d	9.6	7.07	1H	dd	1.6, 8.0
7‴-H	7.66	1H	d	16.0	7.66	1H	d	15.9	7.66	1H	d	15.9
8‴-H	6.33	1H	d	16.0	6.34	2H	d	15.9	6.35	1H	d	15.9
3‴-OMe	3.95	3H	s		3.93	3H	s		3.95	3H	s	
4‴-OH	5.95	1H	br s		6.25	1H	br s		5.94	1H	s	

[a] Measurements were performed in $CDCl_3$ at 400 MHz. [b,c] Assignments for values in the same column bearing the same superscript may be reversed.

by silica gel MPLC with *n*-hexane−EtOH (85:15), *n*-hexane−EtOAc (3:7), and/or CH_2Cl_2−MeOH (95:5) solvent systems.

β-D-(1-*O*-Acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-3′,4′,6′-*O*-triacetylglucopyranoside (**1**) was obtained as a colorless amorphous solid (10 mg): mp 86−92 °C; $[\alpha]^{25}_D$ +46.2° (*c* 0.18, $CHCl_3$); UV (MeOH) *λ* max (log *ϵ*) 203 (4.61), 215 (4.50), 234 (4.43), 298 (4.43), 328 (4.60) nm; IR (KBr) *ν* max 3407, 1746, 1632, 1603, 1516, 1431, 1375, 1240, 1159, 1032 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) listed in Table 1; ^{13}C-NMR ($CDCl_3$, 100 MHz) listed in Table 2; positive FAB-MS *m*/*z* $[M]^+$ 862 (2.6), 557 (22), 177 (77); HR FAB-MS (added KI) *m*/*z* $[M + K]^+$ 901.2179 (calcd for $C_{40}H_{46}O_{21}K$, 901.2169).

β-D-(1-*O*-Acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-2′,4′,6′-*O*-triacetylglucopyranoside (**2**) was obtained as a colorless amorphous solid (145 mg): mp 94−100 °C; $[\alpha]^{25}_D$ +36.3° (*c* 0.16, $CHCl_3$); UV (MeOH) *λ* max (log *ϵ*) 204 (4.51), 216 (4.48), 235 (4.42), 300 (4.46), 328 (4.63) nm; IR (KBr) *ν* max 3455, 1746, 1632, 1601, 1516, 1431, 1373, 1240, 1157, 1034 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) listed in Table 1; ^{13}C-NMR ($CDCl_3$, 100 MHz) listed in Table 2; positive FAB-MS *m*/*z* $[M]^+$ 862 (2.5), 557 (23), 177 (73); HR FAB-MS (added KI) *m*/*z* $[M + K]^+$ 901.2152 (calcd for $C_{40}H_{46}O_{21}K$, 901.2169).

β-D-(1-*O*-Acetyl-3,6-*O*-diferuloyl)fructofuranosyl α-D-2′,3′,6′-*O*-triacetylglucopyranoside (**3**) was obtained as a colorless amorphous solid (10 mg): mp 91−97 °C; $[\alpha]^{25}_D$ +53.7° (*c* 0.15, $CHCl_3$); UV (MeOH) *λ* max (log *ϵ*) 204 (4.55), 217 (4.50), 235 (4.52), 300 (4.59), 328 (4.74) nm; IR (KBr) *ν* max 3436, 1744, 1632, 1601, 1516, 1431, 1373, 1246, 1159, 1034 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) listed in Table 1; ^{13}C-NMR ($CDCl_3$, 100 MHz) listed in Table 2; positive FAB-MS *m*/*z* $[M]^+$ 862 (4.6), 557 (30), 229 (22), 177 (78); HR FAB-MS (added KI) *m*/*z* $[M + K]^+$ 901.2180 (calcd for $C_{40}H_{46}O_{21}K$, 901.2169).

Alkaline Hydrolysis of 1−3. Each phenylpropanoid glycoside (*ca*. 0.1 mg) was dissolved in 3% KOH/MeOH and kept at room temperature for 2 h. The reaction mixture was neutralized with 1 N HCl and was subjected to a Sephadex LH-20 column using MeOH as eluant. Sugar-containing fractions were compared with reference sugars on silica gel TLC developed with EtOAc−MeOH−H_2O−acetic acid (6:2:1:1) and $CHCl_3$−MeOH−H_2O (7:3:0.5) and detected by spraying with orcinol reagent (orcinol, $FeCl_3$ and H_2SO_4).

Acid Hydrolysis of 1−3. Each phenylpropanoid glycoside (*ca*. 0.1 mg) was dissolved in 1 N HCl and refluxed for 2 h. The reaction mixture was neutralized with 3% KOH/MeOH and was subjected to a Sephadex

Table 2. ^{13}C-NMR Chemical Shifts (ppm) for compounds **1**−**3**[a]

assignment	compd **1**		compd **2**		compd **3**	
fructose						
C1	65.5	t	64.2	t	63.6	t
C2	103.3	s	103.1	s	103.6	s
C3	80.9	d	78.9	d	79.7	d
C4	73.8	d	73.6	d	74.1	d
C5	81.4	d	80.9	d	81.4	d
C6	63.8	t	62.5	t	64.2	t
1-OAc; CH_3	21.0	q	20.4[c]	q	20.6[f]	q
; C=O	170.6	s	170.7	s	170.5	s
glucose						
C1′	91.9	d	89.5	d	89.8	d
C2′	70.8	d	72.6	d	70.1	d
C3′	73.3	d	69.6	d	72.5	d
C4′	68.5	d	70.9	d	69.5	d
C5′	69.0	d	68.4	d	70.9	d
C6′	62.8	t	63.9	t	63.2	t
2′-OAc; CH_3			20.4[c]	q	20.6[f]	q
; C=O			171.0[d]	s	170.6[g]	s
3′-OAc; CH_3	21.1	q			20.6[f]	q
; C=O	171.3	s			171.8[g]	s
4′-OAc; CH_3	20.6	q	20.6[c]	q		
; C=O	170.1	s	171.1[d]	s		
6′-OAc; CH_3	20.9	q	20.6[c]	q	20.7[f]	q
; C=O	171.0	s	171.3[d]	s	171.9[g]	s
3-feruloyl						
C1″	126.7	s	126.9	s	126.6	s
C2″	110.3	d	109.8	d	109.9	d
C3″	147.1	s	147.3	s	147.2	s
C4″	148.9	s	149.0	s	148.9	s
C5″	115.0	d	115.0	d	114.9	d
C6″	123.9	d	123.9	d	124.0	d
C7″	147.8	d	147.7	d	148.0	d
C8″	113.7	d	113.4	d	113.4	d
C9″	167.7	s	167.6	s	168.2	s
3″-OMe	56.3[b]	q	55.9[e]	q	56.0[h]	q
6-feruloyl						
C1‴	127.0	s	126.6	s	127.1	s
C2‴	109.7	d	109.6	d	109.6	d
C3‴	147.1	s	147.2	s	147.1	s
C4‴	148.5	s	148.6	s	148.5	s
C5‴	115.0	d	115.0	d	114.9	d
C6‴	123.6	d	123.5	d	123.5	d
C7‴	146.3	d	146.3	d	146.3	d
C8‴	114.7	d	114.5	d	114.8	d
C9‴	167.5	s	167.8	s	167.7	s
3‴-OMe	56.3[b]	q	55.9[e]	q	55.9[h]	q

[a] Measurements were performed in $CDCl_3$ at 100 MHz. [b−h] Assignments for values in the same column bearing the same superscript may be reversed.

LH-20 column using MeOH as eluant. Sugar identification was performed as described under alkaline hydrolysis above.

Acetylation of 2. Compound **2** (30 mg) was dissolved in pyridine (0.2 mL) and treated with excess Ac_2O (0.4 mL) at room temperature for 2 days. The reaction mixture was added to cool water and was extracted with CH_2Cl_2. The CH_2Cl_2 extract was subjected to a Sephadex LH-20 column using MeOH, followed by silica gel MPLC using CH_2Cl_2−MeOH (98:2) to give a tetraacetyl derivative of **2** (27.5 mg) as a colorless amorphous solid: mp 75−79 °C; $[\alpha]^{25}_D$ +30.9° (*c* 0.42, $CHCl_3$); UV (MeOH) λ max (log ϵ) 214 (4.49), 233 (4.42), 283 (4.60), 312 (4.36) nm; IR (KBr) ν max 1752, 1638, 1601, 1510, 1422, 1372, 1227, 1154, 1036 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) δH 1.84 (3H, s), 1.96 (3H, s), 2.06 (3H, s), 2.10 (3H, s), 2.12 (3H, s), 2.14 (3H, s), 2.32 (3H, s) × 2, 3.87 (3H, s), 3.91 (3H, s), 4.18 (1H, d, J = 11.5 Hz), 4.19 (2H, br s), 4.26 (1H, d, J = 11.5 Hz), 4.31 (1H, m), 4.37 (1H, br dd, J = 6.8, 10.9 Hz), 4.46 (1H, dd, J = 7.2, 11.8 Hz), 4.55 (1H, dd, J = 4.7, 11.8 Hz), 4.93 (1H, dd, J = 3.6, 10.3 Hz), 5.03 (1H, dd, J = 9.8 Hz), 5.45 (1H, dd, J = 10.3 Hz), 5.53 (1H, dd, J = 6.2 Hz), 5.62 (1H, d, J = 6.2 Hz), 5.70 (1H, d, J = 3.6 Hz), 6.44 (1H, d, J = 15.9 Hz), 6.49 (1H, d, J = 15.9 Hz), 7.06 (1H, d, J = 8.2 Hz) × 2, 7.13 (1H, s), 7.14 (1H, dd, J = 1.0, 8.0 Hz), 7.18 (1H, dd, J = 1.0, 8.2 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δC 20.1 (q), 20.4 (q) × 4, 20.5 (q) × 2, 20.6 (q), 55.9 (q) × 2, 61.9 (t), 63.6 (t), 64.1 (t), 68.3 (d), 68.5 (d), 69.6 (d), 70.1 (d), 75.2 (d), 76.2 (d), 79.2 (d), 90.3 (d), 104.2 (s), 111.5 (d), 111.7 (d), 116.6 (d), 117.5 (d), 121.57 (d), 122.1 (d), 123.4 (d), 123.5 (d), 133.2 (s), 133.4 (s), 141.9 (s), 142.2 (s), 145.4 (d), 146.6 (d), 151.8 (s) × 2, 165.7 (s) × 2, 166.6 (s), 169.0 (s), 169.9 (s), 170.1 (s), 170.2 (s), 170.4 (s), 170.6 (s), 171.0 (s); positive FAB-MS m/z $[M + H]^+$ 1031 (0.9), 988 (6.5), 683 (36), 331 (27), 219 (38), 177 (100), 169 (72); positive FAB-MS (added KI) m/z $[M + K]^+$ 1069 (66), 683 (14), 331 (15), 219 (28), 177 (90), 169 (57).

Acetylation of 1 and 3. Each phenylpropanoid glycoside (*ca*. 2.5 mg) was acetylated in a manner similar to that described for **2**. These acetyl derivatives were identical to the tetraacetyl derivative of **2** by comparison of their ^{1}H-NMR spectra.

1,3-*O*-Di-*p*-coumaroylglycerol was obtained as a colorless amorphous solid (12 mg): mp 178−184 °C; $[\alpha]^{25}_D$ 0° (*c* 0.28, MeOH). Identification was made by comparison to literature data.[7]

1,3-*O*-Diferuloylglycerol was obtained as a colorless amorphous solid (10 mg): mp 47−56 °C; $[\alpha]^{25}_D$ 0° (*c* 0.21, MeOH). Identification was made by comparison to literature data.[7]

1-*O*-Feruloyl-3-*O*-*p*-coumaroylglycerol was obtained as a colorless amorphous solid (100 mg): mp 38−46 °C; $[\alpha]^{25}_D$ −0.9° (*c* 1.26, MeOH). Identification was made by comparison to literature data.[7]

References and Notes

(1) Jiang-su New Medical Academy. *Zhong-yao da-ci-dian*; Shanghai Science and Technology Publisher: Shang-hai, China, 1977; pp 56−58.
(2) Hsu, H.-Y. *Oriental Materia Medica: a concise guide*; The Oriental Healing Arts Institute: Long Beach, CA, 1986; p 485.
(3) Ni, Y.; Kawahara, N.; Sekita, S.; Satake, M. *Abstracts of the 114th Annual Meeting of The Pharmaceutical Society of Japan*; Tokyo, 1994; Vol. 2, p 216.
(4) Miyaiachi, Y.; Matsuura, Y.; Yamaji, S. *Nat. Med.* **1995**, *49*, 24−28.
(5) Binkley, W. W.; Horton, D.; Bhacca, N. S. *Carbohydr. Res.* **1969**, *10*, 245.
(6) Linscheid, M.; Wendisch, D.; Strack, D. *Z. Naturforsch.* **1980**, *35c*, 907−914.
(7) Cooper, R.; Gottlieb, E. H.; Lavie, D. *Phytochemistry* **1978**, *17*, 1673−1675.
(8) Ikeya, Y.; Sugama, K.; Okada, M.; Mitsuhashi, H. *Chem. Pharm. Bull.* **1991**, *39*, 2600−2605.
(9) Shimomura, H.; Sashida, Y.; Adachi, T. *Phytochemistry* **1987**, *26*, 249−251.
(10) Hamburger, M.; Hostettmann, K. *Phytochemistry* **1985**, *24*, 1793−1797.
(11) Shimomura, H.; Sashida, Y.; Mimaki, Y. *Phytochemistry* **1986**, *25*, 2897−2899.
(12) Harrison, J. L.; Sia, G.-L.; Sim, K.-Y.; Tan, T.-W. H.; Connolly, D. J.; Lavaud, C.; Massiot, G. *Phytochemistry* **1995**, *38*, 1497−1500.
(13) Leitão, G. S.; Kaplan, A. C. M.; Monache, D. F. *J. Nat. Prod.* **1994**, *57*, 1703−1707.

NP960160H