Three Secoiridoid Glucosides from *Jasminum nudiflorum*

Takao Tanahashi,*,† Yukiko Takenaka,† Naotaka Nagakura,† and Toyoyuki Nishi‡

Kobe Pharmaceutical University, 4-19-1, Motoyamakita-machi, Higashinada-ku, Kobe 658-8558, Japan, and The Nippon Shinyaku Institute for Botanical Research, 39, Sakanotsuji-cho, Oyake, Yamashina-ku, Kyoto 607-8182, Japan

Received March 26, 1999

Phytochemical study of the leaves and stems of *Jasminum nudiflorum* has led to the isolation of three secoiridoid glucosides, jasnudiflosides A−C (**1**−**3**). The structures of these compounds were elucidated on the basis of chemical and spectroscopic evidence.

Jasminum nudiflorum Lindl. (Oleaceae) is a shrub indigenous to China. Its flowers and leaves have been used as crude drugs in Chinese folk medicine.[1] Previous phytochemical studies of the species resulted in isolation of caffeic glycoside esters.[2] In the course of our chemical studies on the secoiridoid glucosides from oleaceous plants,[3] we have investigated the leaves and stems of *J. nudiflorum*. We report here the isolation and structure elucidation of three glucosides (**1**−**3**), each consisting of oleoside units and a cyclopentanoid monoterpene unit.

Compound **1** was isolated as an amorphous powder. The HRSIMS of **1** established its elemental composition as $C_{44}H_{64}O_{23}$. On conventional acetylation, **1** gave a nonaacetate (**4**) $C_{62}H_{82}O_{32}$. Distinctive ^{1}H NMR spectral features of **1** (see Table 1) indicated that the isolated compound possessed two sets of oleoside 11-methyl ester (**5**) moieties. The ^{1}H NMR spectrum displayed additional signals for two secondary methyl groups (δ 0.93 and 0.99, both d, $J = 7.0$ Hz), two pairs of oxymethylene protons (δ 3.96, 4.21 and δ 3.34, 3.59), and a methine group bearing an acyloxyl group (δ 5.04, td, $J = 5.5$, 4.0 Hz). Its ^{13}C NMR spectrum showed resonances of 10 carbons in addition to the duplicated signals corresponding to the oleoside 11-methyl ester moieties. With the aid of ^{1}H−^{1}H COSY, HMQC, and HMBC experiments, these 10 carbon signals were evaluated as a triol moiety with the same planar structure as triol **6**, also seen as part of jasminin (**7**)[4] and jasmesoside.[5] In the NOESY spectrum of **1**, significant interactions were observed between H-1″ and H-3″, between H-2″ and H-6″, and between H-7″ and H-9″. However, alkaline hydrolysis of **1** afforded a triol and oleoside (**8**), of which the former was not identical to **6**, implying the relative stereochemistry of the triol in **1** to be **9** rather than **6**.

The ^{1}H and ^{13}C NMR spectral features of **1** were in good agreement with those reported for jasuroside A (**10**), which had been isolated from *J. urophyllum* by Shen et al.,[6] except for the assignments of H-2″ and H-3″. The absolute stereochemistry of **10** was deduced solely using its NOESY spectrum. This prompted us to establish the absolute stereochemistry of **1** by chemical evidence. To determine the absolute configuration at C-5″ in triol **9** by a modification of Mosher's method,[7] its (*R*)- and (*S*)-MTPA esters (**11**,**12**) were prepared. The NOESY experiments with **12** confirmed the relative configurations at C-1″, C-2″, C-3″ and C-5″ (Figure 1). The $\Delta\delta$ values of the MTPA derivatives determined the absolute configuration of C-5″ to be *S*, indicating **9** to be the 5″-epimer of triol **6**. This was confirmed when triol **6** derived from jasminin (**7**) was subjected to a Mitsunobu reaction[8] to provide acetate **13**, which differed from acetate **14** but proved identical to the acetate of **9**. Thus, **1** has the structure shown and is named jasnudifloside A.

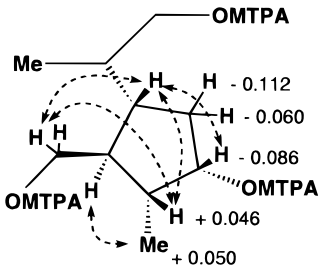


Figure 1. Significant NOESY correlations for **12** and $\Delta\delta$ values of **11** and **12**.

The second glucoside (**2**), named jasnudifloside B, was also isolated as an amorphous powder, with molecular formula $C_{61}H_{86}O_{33}$. The ^{1}H and ^{13}C NMR spectral features of **2** resembled those of **1**, except that **2** demonstrated signals for an additional oleoside 11-methyl ester (**5**) unit. The downfield shift of H-10″ and C-10″ and the upfield shift of C-8″ in **2**, relative to the corresponding signals in **1**, showed that in **2**, the C-7 carboxyl group of the additional oleoside 11-methyl ester moiety was linked to the C-10″ hydroxyl group of the triol moiety. The ^{1}H and ^{13}C NMR signals corresponding to the triol moiety in **2** were coincident with those of **13**, indicating that the stereochemistry of the triol moiety in **2** was the same as in **1**. Accordingly, the structure of **2** was established as shown.

HRSIMS of jasnudifloside C (**3**) established the composition as $C_{43}H_{60}O_{22}$. Its ^{1}H and ^{13}C NMR spectral features (Tables 1 and 2) clearly demonstrated the presence of a triol (**9**) moiety and two oleoside units, of which one contained a methylated carboxyl group. This assumption was supported by hydrolysis of **3**, which afforded oleoside and triol **9**. The pattern of ester linkages was determined by a combination of ^{1}H−^{1}H COSY, HMQC, and HMBC experiments, which allowed assignment of the signals from H-7″ and H-10″ as well as the signals of the carbonyls C-7a, C-7b, C-11a, and C-11b. The HMBC experiments with **3** showed strong interactions between H-7″ and C-7a (δ 173.36), between OMe and C-11a (δ 168.62), and between H-10″ and C-11b (δ 168.78). Accordingly, the structure of jasnudifloside C is **3**.

Oleoside-type secoiridoid glucosides esterified with a cyclopentanoid monoterpene have so far been found only in species of the genus *Jasminum*, that is; *J. mesnyi*,[4,5,9,10]

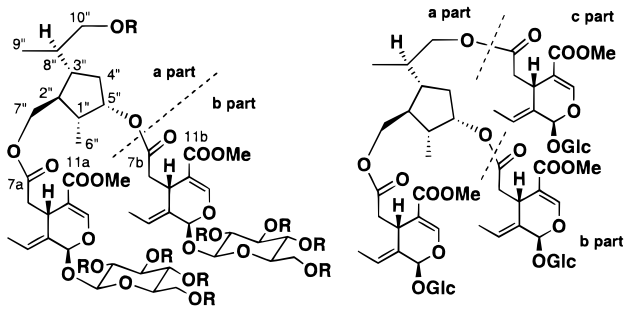
* To whom correspondence should be addressed. Fax:+81-78-441-7546; E-mail: tanahash@kobepharma-u.ac.jp.
† Kobe Pharmaceutical University.
‡ The Nippon Shinyaku Institute for Botanical Research.

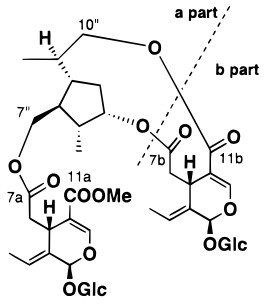
10.1021/np9901175 CCC: $18.00
Published on Web 08/05/1999

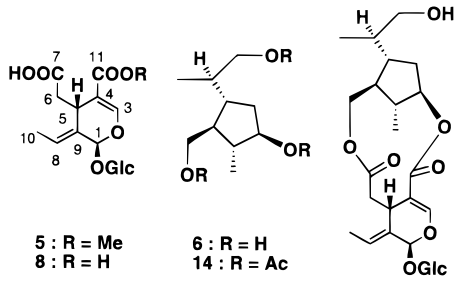
Table 1. ^{1}H NMR Spectral Data for **1**−**4** (500 MHz)[a]

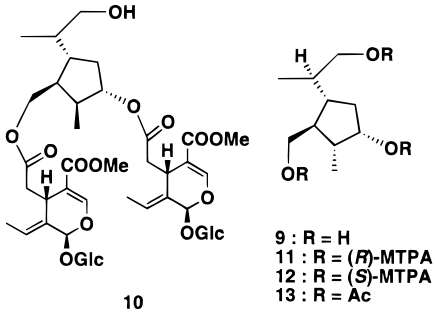
	1[b]		**2**[b,d]			**3**[b]		**4**[c,d]	
H	a part	b part	a part	b part	c part	a part	b part	a part	b part
1	5.96, br s	5.95, br s	5.93, br s	5.95, br s	5.96, br s	5.95, br s	5.87, br s	5.71, br s	5.73, br s
3	7.53, s	7.53, s	7.52, s	7.53, s	7.53, s	7.54, s	7.43, s	7.46, s	7.47, s
5	4.00, dd (9.0, 4.5)	4.00, dd (9.0, 4.5)	3.97−4.03, m	3.97−4.03, m	3.97−4.03, m	4.01, dd (9.5, 4.5)	3.99, dd (9.5, 4.5)	3.97, m	3.97, m
6	2.52, dd (14.0, 9.0)	2.52, dd (14.0, 9.0)	2.49, dd (14.0, 9.0)	2.51, dd (14.0, 9.0)	2.52, dd (14.0, 9.0)	2.54, dd (14.0, 9.0)	2.37, dd (14.0, 4.5)	2.45, dd (15.0, 8.0)	2.47, dd (15.0, 8.5)
	2.73, dd (14.0, 4.5)	2.70, dd (14.0, 4.5)	2.70, dd (14.0, 4.5)	2.72, dd (14.0, 4.5)	2.73, dd (14.0, 4.5)	2.73, dd (14.0, 4.5)	2.45, dd (14.0, 9.5)	2.69, dd (15.0, 4.5)	2.70, dd (15.0, 4.5)
8	6.11, qd (7.0, 1.0)	6.12, qd (7.0, 1.0)	6.10, qd (7.0, 1.0)	6.12, qd (7.0, 1.0)	6.13, qd (7.0, 1.0)	6.13, qd (7.0, 1.0)	6.07, qd (7.0, 1.0)	6.01, br q (7.0)	6.01, br q (7.0)
10	1.75[e], dd (7.0, 1.0)	1.76[e], dd (7.0, 1.5)	1.74, dd (7.0, 1.0)	1.75, dd (7.0, 1.0)	1.76, dd (7.0, 1.0)	1.75, dd (7.0, 1.0)	1.82, dd (7.0, 1.0)	1.75, dd (7.0, 1.5)	1.76, dd (7.0, 1.5)
OMe	3.72, s	3.72, s	3.71, s	3.72, s	3.72, s	3.72, s		3.72, s	3.72, s
1′	4.80, d (8.5)	4.81, d (7.5)	4.80, d (7.5)	4.80, d (8.0)	4.81, d (7.5)	4.81, d (8.0)	4.81, d (8.0)	5.03, d (8.0)	5.04, d (8.0)
2′−4′	3.27−3.41, m	3.27−3.41, m	3.28−3.41, m	3.28−3.41, m	3.28−3.41, m	3.27−3.41, m	3.27−3.41, m	5.03−5.28, m	5.03−5.28, m
5′								3.764, dd (9.5, 4.5, 2.5)	3.765, ddd (9.5, 4.5, 2.5)
6′	3.65[f], dd (12.0, 6.0)	3.66[f], dd (12.0, 6.0)	3.65, dd (12.0, 6.0)	3.66, dd (12.0, 6.0)	3.66, dd (12.0, 6.0)	3.64[h], dd (11.5, 6.0)	3.67[h], dd (12.0, 6.5)	4.00, dd (12.5, 2.5)	4.11, dd (12.5, 2.5)
	3.89[g], dd (12.0, 2.0)	3.90[g], dd (12.0, 2.0)	3.91, dd (12.0, 2.0)	3.87, dd (12.0, 2.0)	3.87, dd (12.0, 2.0)	3.88[i], dd (11.5, 1.5)	3.90[i], dd (12.0, 2.0)	4.31, dd (12.5, 4.5)	4.33, dd (12.5, 4.5)
1″	1.96, m		1.94, m			1.81, m		1.90, m	
2″	1.84, m		1.85, m			1.91, m		1.79, m	
3″	1.81, m		1.85, m			1.81, m		1.71, m	
4″	1.62, ddd (14.0, 5.5, 4.0)		1.64, ddd (14.0, 4.0, 3.0)			2.01, br dd (11.0, 4.5)		1.59, m (14.5, 6.5, 4.0)	
	2.08, ddd (14.0, 9.0, 5.5)		2.09, ddd (14.0, 9.0, 5.0)			2.01, br dd (11.0, 4.5)		2.00, m	
5″	5.04, td (5.5, 4.0)		5.05, td (4.5, 2.0)			4.91, br t (3.5)		5.06, br q (4.5)	
6″	0.93, d (7.0)		0.94, d (7.0)			1.00, d (6.5)		0.90, d (7.0)	
7″	3.96, dd (11.5, 5.0)		3.99, m			4.08, dd (11.5, 4.5)		3.95, m	
	4.21, dd (11.5, 4.0)		4.19, dd (11.0, 3.5)			4.19, dd (11.5, 4.5)		4.10, m	
8″	1.66, ddd (14.0, 7.0, 4.0)		1.90, m			2.08, m		1.85, m	
9″	0.99, d (7.0)		1.00, d (6.5)			0.97, d (7.0)		0.97, d (7.0)	
10″	3.34, m		3.75, dd (11.0, 7.0)			4.12, m (11.5, 3.5)		3.80, dd (11.5, 8.5)	
	3.59, dd (10.0, 4.5)		4.16, dd (11.0, 4.5)			4.34, dd (11.4, 9.0)		4.07, dd (11.5, 4.5)	
Ac								2.025 (×2), 2.031, 2.035, (×2), 2.042 (×2), 2.08, 2.09 s	

[a] Chemical shifts are reported in ppm. Values in parentheses are coupling constants in Hz. [b] Measured in CD_3OD. [c] Measured in $CDCl_3$. [d] All signals due to the oleoside 11-methyl ester units could not be assigned with certainty and may be interchanged horizontally. [e−i] Assignments may be reversed.









J. urophyllum, *J. sambac*,[11,12] and *J. azoricum*.[13,14] The present work gives additional examples of glucosides of this type.

Experimental Section

General Experimental Procedures. The UV spectra were recorded on a Shimadzu UV-240 spectrophotometer and the IR spectra on a Shimadzu FTIR-8200 infrared spectrophotometer. The optical rotations were measured on a JASCO DIP-370 digital polarimeter. CIMS, SIMS, and HRSIMS were obtained with a Hitachi M-4100 mass spectrometer. For SIMS, glycerol or 3-NOBA was used as the matrix. The NMR experiments were performed with Varian VXR-500 and Varian Gemini-300 spectrometers, with TMS as internal standard. HPLC separations were run on a Waters system (600E Multisolvent Delivery System, 486 tunable absorbance detector). TLC was performed on Kieselgel 60F_{254} plates (Merck), and spots were visualized under UV light.

Plant Material. Leaves and stems of *J. nudiflorum* were collected at the Nippon Shinyaku Institute for Botanical Research, Kyoto, Japan. A voucher specimen (KPFY 991) is deposited at the laboratory of Kobe Pharmaceutical University.

Isolation of Glucosides. Dried leaves and stems of *J. nudiflorum* (128 g) were extracted with hot MeOH. After concentration, the extract (20.6 g) was suspended in H_2O and filtered through a Celite layer. The filtrate and washings were combined and extracted successively with $CHCl_3$ and *n*-BuOH, to give three fractions weighing 1.54 g ($CHCl_3$), 6.21 g (*n*-BuOH), and 8.72 g (H_2O). The $CHCl_3$-soluble fraction was chromatographed on a Si gel column, eluting with $CHCl_3$–MeOH mixtures with increasing MeOH content (5–20%). Elution with 10% MeOH–$CHCl_3$ gave three fractions I (152 mg), II (192 mg), and III (639 mg). Fraction II was further purified by preparative HPLC (μBondasphere 5 μC18–100 Å, MeOH–H_2O, 3:2), giving **3** (151 mg). Fraction III was also purified by preparative HPLC (μBondasphere 5 μC18–100 Å, MeOH–H_2O, 3:2) to afford **1** (228 mg), **2** (16.8 mg), and **3** (196 mg).

Jasnudifloside A (1): colorless amorphous powder; $[\alpha]^{20}_D$ −192° (*c* 0.78, MeOH); UV (MeOH) λ_{max} (log ϵ) 237 (4.38) nm; IR (KBr) ν_{max} 3406, 1732, 1709, 1632, 1078 cm^{-1}; ^1H NMR and ^{13}C NMR, see Tables 1 and 2; significant HMBC correlations H-6a (δ 2.73) → C-7a (δ 173.41), H_2-7″ → C-7a, OMe → C-11a/C-11b, H-6b (δ 2.70) → C-7b (δ 172.98), H_3-6″ → C-1″/C-2″, H_2-10″ → C-9″; SIMS *m/z* 959 $[M - H]^-$, 797, 727, 421; HRSIMS *m/z* 959.3771 $[M - H]^-$ (calcd for $C_{44}H_{63}O_{23}$, 959.3762).

Jasnudifloside B (2): colorless amorphous powder; $[\alpha]^{24}_D$ −206° (*c* 0.68, MeOH); UV (MeOH) λ_{max} (log ϵ) 237 (4.56) nm; IR (KBr) ν_{max} 3414, 1732, 1709, 1636, 1078 cm^{-1}; ^1H NMR and ^{13}C NMR, see Tables 1 and 2; significant HMBC correlations OMe → C-11a, C-11b, C-11c; SIMS *m/z* 1345 $[M - H]^-$, 1183, 1114; HRSIMS *m/z* 1345.4984 $[M - H]^-$ (calcd for $C_{61}H_{85}O_{33}$, 1345.4976).

Jasnudifloside C (3): colorless amorphous powder; $[\alpha]^{22}_D$ −238° (*c* 0.31, MeOH); UV (MeOH) λ_{max} (log ϵ) 237 (4.39) nm; IR (KBr) ν_{max} 3400, 1728, 1709, 1630, 1078 cm^{-1}; ^1H NMR and ^{13}C NMR, see Tables 1 and 2; significant HMBC correlations H-3a → C-4a (δ 109.39)/C-11a (δ 168.62), H-6a → C-4a/C-7a (δ 173.36), H_2-7″ → C-7a, OMe → C-11a, H-3b → C-4b (δ 111.27)/C-11b (δ 168.78), H-6b → C-4b/C-7b (δ 173.63), H_3-6″ → C-1″/C-2″/C-5″, H_3-9″ → C-3″/C-8″/C-10″, H_2-10″ → C-11b; SIMS *m/z* 927 $[M - H]^-$, 765, 695; HRSIMS *m/z* 927.3513 $[M - H]^-$ (calcd for $C_{43}H_{59}O_{22}$, 927.3500).

Acetylation of 1. Compound **1** (15.0 mg) was acetylated with Ac_2O–pyridine, and the crude acetate (19.1 mg) was purified by preparative TLC ($CHCl_3$) to yield **4** (18.0 mg) as an amorphous powder: $[\alpha]^{24}_D$ −148° (*c* 1.27, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 235 (4.38) nm; IR (KBr) ν_{max} 1759, 1709, 1635, 1070 cm^{-1}; ^1H NMR and ^{13}C NMR, see Tables 1 and 2; HRSIMS *m/z* 1361.4722 $[M + Na]^+$ (calcd for $C_{62}H_{82}O_{32}Na$, 1361.4690), 1339.4892 $[M + H]^+$ (calcd for $C_{62}H_{83}O_{32}$, 1339.4870).

Alkaline Hydrolysis of 1 and 3. A solution of **1** (50 mg) in 0.5M NaOH (2 mL) was stirred for 18 h at room temperature. The reaction mixture was neutralized with Amberlite IR-120 (H^+ form) and concentrated in vacuo. The resulting residue was purified by preparative TLC ($CHCl_3$–MeOH, 9:1) to **8** (43 mg) and triol **9** (6.5 mg).

Compound 9: syrup; $[\alpha]^{23}_D$ −7.9° (*c* 0.67, MeOH); ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (3H, d, *J* = 6.5 Hz, H_3-9″), 0.99 (3H, d, *J* = 7.0 Hz, H_3-6″), 1.53 (1H, ddd, *J* = 12.5, 7.0, 5.5 Hz, H-4″), 1.66 (3H, m, H-2″, H-3″, H-8"), 1.86 (1H, qt, *J* = 7.0, 6.0 Hz, H-1″), 1.91 (1H, ddd, *J* = 12.5, 8.0, 5.5 Hz, H-4″), 3.37 (1H, dd, *J* = 11.0, 7.0 Hz, H-10″), 3.48 (1H, dd, *J* = 11.5, 5.5 Hz, H-7″), 3.55 (1H, dd, *J* = 11.5, 4.0 Hz, H-7″), 3.60 (1H, dd, *J* = 11.0, 5.0 Hz, H-10″), 4.03 (1H, br q, *J* = 5.5 Hz, H-5″); ^{13}C NMR, see Table 2.

Compound 8: methylated with CH_2N_2–Et_2O and the product identified as oleoside dimethyl ester[15] (^1H NMR).

Table 2. ^{13}C NMR Spectral Data for **1**, **2**, **3**, **4**, **9**, and **13** (125 MHz)

	1[a]		**2**[a,c]			**3**[a]		**4**[b,c]				
C	a part	b part	a part	b part	c part	a part	b part	a part	b part	**9**[b]	**13**[a]	**13**[b]
1	95.22	94.82	94.84	95.21	95.29	94.82	95.16	93.74	93.87			
3	155.18[d]	155.25[d]	155.16	155.19	155.23	155.20	153.26	153.01	153.07			
4	109.42	109.42	109.40	109.41	109.44	109.39	111.27	108.63	108.63			
5	32.15	31.93	31.90	31.93	31.18	32.16	31.66	30.15	30.20			
6	41.52	41.25	41.27	41.27	41.65	41.21	43.90	39.97	40.02			
7	173.41	172.98	173.00	173.29	173.39	173.36	173.63	170.89	171.07			
8	124.79	124.79	124.77	124.77	124.81	124.74	123.60	124.73	124.78			
9	130.84	130.76	130.79	130.83	130.90	130.81	132.30	128.40	128.54			
10	13.73[e]	13.83[e]	13.79	13.82	13.86	13.73	13.23[p]	13.58	13.63			
11	168.64[f]	168.69[f]	168.63	168.63	168.66	168.62	168.78	166.71	166.76			
OMe	51.96[g]	51.98[g]	52.01	52.01	52.01	51.95		51.40	51.44			
1′	100.84	100.54	100.57	100.87	100.90	100.55	100.89	97.02	97.09			
2′	74.84	74.84	74.83	74.83	74.85	74.80[k]	74.87[k]	70.74	70.74			
3′	77.97[h]	78.01[h]	77.98	77.98	78.00	77.98[l]	78.01[l]	72.22	72.27			
4′	71.62[i]	71.69[i]	71.54	71.61	71.71	71.60[m]	71.71[m]	68.29	68.29			
5′	78.54[j]	78.63[j]	78.47	78.50	78.64	78.48[n]	78.66[n]	72.55	72.56			
6′	62.94	62.94	62.86	62.93	63.00	62.78[o]	62.97[o]	61.74	61.80			
1″	41.83		41.86			42.37		40.42		42.32	42.31	40.89
2″	48.11		48.05			50.61		46.75		51.23	48.08	46.64
3″	42.60		43.32			46.31		42.04		42.27	43.75	42.33
4″	35.39		34.95			31.95		33.86		37.02	34.72	33.84
5″	80.06		80.15			82.17		77.79		75.73	79.63	77.67
6″	14.15		13.91			13.20[p]		13.47		14.25	13.67	13.39
7″	67.22		66.83			66.65		66.00		65.42	67.27	66.05
8″	41.07		37.47			37.11		36.18		41.10	37.40	36.01
9″	16.32		16.87			19.21		16.28		16.53	16.61	16.36
10″	66.47		69.14			67.86		67.49		66.70	68.83	67.54
*C*H$_3$CO								20.59[q]	20.72[q]		20.81	20.94[q]
								20.62[q]	20.95		20.85	20.97
								20.67[q]			21.06	
CH$_3$*C*O								169.34	170.54		172.61	170.75
								169.35	170.57		172.93	171.15
								169.40[q]	171.23		172.99	171.17
								170.19[q]				

[a] Measured in CD_3OD. [b] Measured in $CDCl_3$. [c] All carbon signals due to the oleoside 11-methyl ester units could not be assigned with certainty and may be interchanged horizontally. [d−p] Values with the same superscript are interchangeable. [q] Two-carbon signals.

A solution of **3** (52 mg) in 0.5 M NaOH (2 mL) was stirred for 24 h at room temperature. The reaction mixture was worked up in the same way as for **1**, giving oleoside[16] (40.4 mg) and triol **9** (9.9 mg), $[\alpha]^{24}_D$ −6.6° (*c* 0.78, MeOH).

Acetylation of 9. Compound **9** (18 mg) was acetylated with Ac_2O−pyridine and the crude acetate was purified by preparative HPLC (*μ*Bondasphere 5 *μ*C18−100 Å, MeOH−H_2O, 3:2) to yield **13** (7.8 mg).

Compound 13: $[\alpha]^{27}_D$ +3.4° (*c* 0.78, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 0.98 (3H, d, *J* = 7.5 Hz, H$_3$-6″), 0.99 (3H, d, *J* = 6.5 Hz, H$_3$-9″), 1.62 (1H, ddd, *J* = 14.0, 6.5, 3.0 Hz, H-4″), 1.76 (1H, ddt, *J* = 8.5, 8.0, 6.5 Hz, H-3″), 1.86−1.96 (3H, m, H-1″, H-2″, H-8″), 2.055, 2.060, 2.067 (each 3H, s, Ac), 2.07 (1H, ddd, *J* = 14.0, 10.0, 5.5 Hz, H-4″), 3.83 (1H, dd, *J* = 11.0, 7.5 Hz, H-10″), 4.06 (1H, dd, *J* = 11.5, 5.5 Hz, H-7″), 4.10 (1H, dd, *J* = 11.0, 5.0 Hz, H-10″), 4.13 (1H, dd, *J* = 11.5, 4.5 Hz, H-7″), 5.08 (1H, td, *J* = 5.5, 3.0 Hz, H-5″); CIMS *m*/*z* 315 [M + H]$^+$.

***(R)*- and *(S)*-MTPA Esters of 9.** To a solution of **9** (3.8 mg) in dry CH_2Cl_2 (1 mL) were added (*R*)-MTPA acid (7 mg), DMAP (3 mg), and DCC (10 mg), and the whole was stirred for 7 h at room temperature. Then more (*R*)-MTPA acid (20 mg) and DCC (20 mg) were added, and the reaction mixture was stirred for an additional 18 h. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$, and was then washed and dried. The organic layers were concentrated in vacuo, and the resulting residue was purified by successive preparative TLC (Et_2O), column chromatography on Sephadex LH-20 ($CHCl_3$−MeOH, 10:9), and preparative TLC (Et_2O−*n*-hexane, 1:1), giving **11** (11.0 mg).

Compound 11: syrup; ^1H NMR (500 MHz, $CDCl_3$) *δ* 0.779 (3H, d, *J* = 7.0 Hz, H$_3$-9″), 0.865 (3H, d, *J* = 6.5 Hz, H$_3$-6″), 1.546 (1H, ddd, *J* = 14.5, 5.5, 2.5 Hz, H-4″), 1.61−1.72 (3H, m, H-2″, H-3″, H-8″), 1.824 (1H, m, H-1″), 2.008 (1H, ddd, *J* = 14.5, 8.5, 5.0 Hz, H-4″), 3.479, 3.485, 3.506 (each 3H, d, *J* = 1.0 Hz, 3 × OMe), 3.893 (1H, dd, *J* = 12.5, 6.5 Hz, H-10″), 4.128 (1H, dd, *J* = 12.0, 4.5 Hz, H-7″), 4.210 (1H, dd, *J* = 12.5, 3.5 Hz, H-10″), 4.350 (1H, dd, *J* = 12.0, 3.0 Hz, H-7″), 5.274 (1H, td, *J* = 5.0, 2.5 Hz, H-5″), 7.37−7.50 (15H, m, ArH); SIMS *m*/*z* 859 [M + Na]$^+$.

Triol **9** (3.6 mg) was esterified with (*S*)-MTPA acid in the same way described for **11** to yield **12** (11.3 mg).

Compound 12: syrup; ^1H NMR (500 MHz, $CDCl_3$) *δ* 0.812 (3H, d, *J* = 6.5 Hz, H$_3$-9″), 0.915 (3H, d, *J* = 7.0 Hz, H$_3$-6″), 1.434 (1H, ddd, *J* = 15.0, 5.5, 2.5 Hz, H-4″), 1.489 (1H, m, H-8″), 1.560 (1H, m, H-3″), 1.710 (1H, m, H-2″), 1.870 (1H, m, H-1″), 1.948 (1H, ddd, *J* = 15.0, 9.5, 5.0 Hz, H-4″), 3.485, 3.497, 3.531 (each 3H, d, *J* = 1.0 Hz, 3 × OMe), 3.850 (1H, dd, *J* = 11.5, 6.5 Hz, H-10″), 3.962 (1H, dd, *J* = 11.5, 4.0 Hz, H-10″), 4.301 (2H, d, *J* = 3.5 Hz, H$_2$-7″), 5.188 (1H, td, *J* = 5.0, 2.5 Hz, H-5″), 7.42−7.58 (15H, m, ArH); SIMS *m*/*z* 859 [M + Na]$^+$.

Acetylation of 6. Triol **6** (12.8 mg) obtained from jasminin (**7**) by hydrolysis as described by Inoue et al.[5] was acetylated with Ac_2O−pyridine and the crude acetate (15.6 mg) was purified by preparative HPLC (*μ*Bondasphere 5 *μ*C18−100 Å, MeOH−H_2O, 11:9) to yield **14** (8.4 mg): ^1H NMR (300 MHz, $CDCl_3$) *δ* 1.00 (3H, d, *J* = 6.5 Hz, H$_3$-9″), 1.04 (3H, d, *J* = 7.0 Hz, H$_3$-6″), 1.68 (1H, m, H-1″), 1.80−1.94 (5H, m, H-2″, H-3″, H$_2$-4″, H-8″), 2.03, 2.06, 2.07 (each 3H, s, Ac), 3.89 (1H, dd, *J* = 11.0, 6.5 Hz, H-10″), 4.01 (1H, dd, *J* = 11.5, 6.5 Hz, H-7″), 4.04 (1H, dd, *J* = 11.0, 4.5 Hz, H-10″), 4.12 (1H, dd, *J* = 11.5, 5.0 Hz, H-7″), 4.72 (1H, br q, *J* = 4.5 Hz, H-5″).

Mitsunobu Reaction of 6. Triol **6** (57.0 mg), Ph_3P (800 mg), and HOAc (172 *μ*L) were mixed in dry THF (3 mL). Diethyl azodicarboxylate (DEAD; 800 *μ*L) was added dropwise to the solution, and the mixture was kept at room temperature for 6.5 h. Then the same amounts of all reagents were added once more. After an additional 19.5 h, the solution was evaporated in vacuo and the residue purified by preparative TLC ($CHCl_3$−MeOH, 19:1) and preparative HPLC (*μ*Bondas-

phere 5 μC18−100 Å, MeOH−H_2O, 11:9), giving **13** (7.7 mg), $[\alpha]^{27}_D$ +3.0° (*c* 0.62, $CHCl_3$); CIMS *m*/*z* 315 $[M + H]^+$.

Acknowledgment. Thanks are due to Dr. M. Sugiura (Kobe Pharmaceutical University) for ^1H and ^{13}C NMR spectra and to Dr. K. Saiki (Kobe Pharmaceutical University) for MS measurements.

References and Notes

(1) Chiang Su New Medical College, (Eds.) *Zhong-Yao-Dai-Ci-Dian (Dictionary of Chinese Crude Drugs)*; Shanghai Scientific Technologic Publisher: Shanghai, 1978; p 1156.
(2) Andary, C.; Tahrouch, S.; Marion, C.; Wylde, R.; Heitz, A. *Phytochemistry* **1992**, *31*, 885−886.
(3) Tanahashi, T.; Parida; Takenaka, Y.; Nagakura, N.; Inoue, K.; Kuwajima, H.; Chen, C.-C. *Phytochemistry* **1998**, *49*, 1333−1337, and references therein.
(4) Kamikawa, T.; Inoue, K.; Kubota, T.; Woods, M. C. *Tetrahedron* **1970**, *26*, 4561- 4587.
(5) Inoue, K.; Tanahashi, T.; Inouye, H. *Phytochemistry* **1985**, *24*, 1299−1303.
(6) Shen, Y.-C.; Hsieh, P.-W. *J. Nat. Prod.* **1997**, *60*, 453−457.
(7) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092−4096.
(8) Mitsunobu, O.; Eguchi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3427−3430.
(9) Inoue, K.; Fujita, T.; Inouye, H.; Kuwajima, H.; Takaishi, K.; Tanahashi, T.; Nagakura, N.; Asaka, Y.; Kamikawa, T.; Shingu, T. *Phytochemistry* **1991**, *30*, 1191−1201.
(10) He, Z.-D.; Yang, C.-R. *Acta Bot. Yunnan* **1989**, *11*, 55−59.
(11) Tanahashi, T.; Nagakura, N.; Inoue, K.; Inouye, H. *Tetrahedron Lett.* **1988**, *29*, 1793−1796.
(12) Zhang, Y.-J.; Liu, Y.-Q.; Pu, X. Y.; Yang, C.-R. *Phytochemistry* **1995**, *38*, 899−903.
(13) Ross, S. A.; Abdel-Hafiz, M. A.; Ali, A. A. *Egypt. J. Pharm. Sci.* **1986**, *27*, 221−226.
(14) Somanadhan, B.; Wagner Smitt, U.; George, V.; Pushpagadan, P.; Rajasekharan, S.; Duus, J. O.; Nyman, U.; Olsen, C. E.; Jaroszewski, J. W. *Planta Med.* **1998**, *64*, 246−250.
(15) Damtoft, S.; Franzyk, H.; Jensen, S. R. *Phytochemistry* **1992**, *31*, 4197−4201.
(16) Damtoft, S.; Franzyk, H.; Jensen, S. R. *Phytochemistry* **1995**, *40*, 773−784.

NP9901175