

Three Secoiridoid Glucosides from *Jasminum nudiflorum*

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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 C₄₄H₆₄O₂₃. On conventional acetylation, **1** gave a nonacetate (**4**) C₆₂H₈₂O₃₂. Distinctive ¹H NMR spectral features of **1** (see Table 1) indicated that the isolated compound possessed two sets of oleoside 11-methyl ester (**5**) moieties. The ¹H 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 acyloxy group (δ 5.04, td, J = 5.5, 4.0 Hz). Its ¹³C 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 ¹H–¹H 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 jasmesome.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 ¹H and ¹³C 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

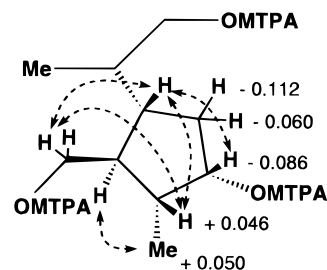


Figure 1. Significant NOESY correlations for **12** and $\Delta\delta$ values of **11** and **12**.

confirmed when triol **6** derived from jasminin (**7**) was subjected to a Mitsunobu reaction⁸ 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.

The second glucoside (**2**), named jasnudifloside B, was also isolated as an amorphous powder, with molecular formula C₆₁H₈₆O₃₃. The ¹H and ¹³C 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 ¹H and ¹³C 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 C₄₃H₆₀O₂₂. Its ¹H and ¹³C 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 ¹H–¹H 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}

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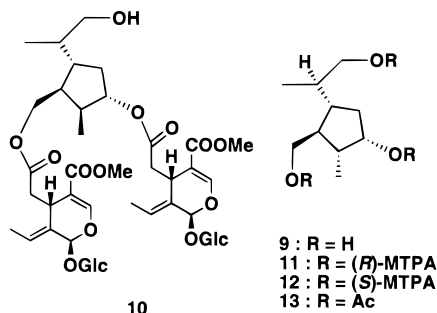
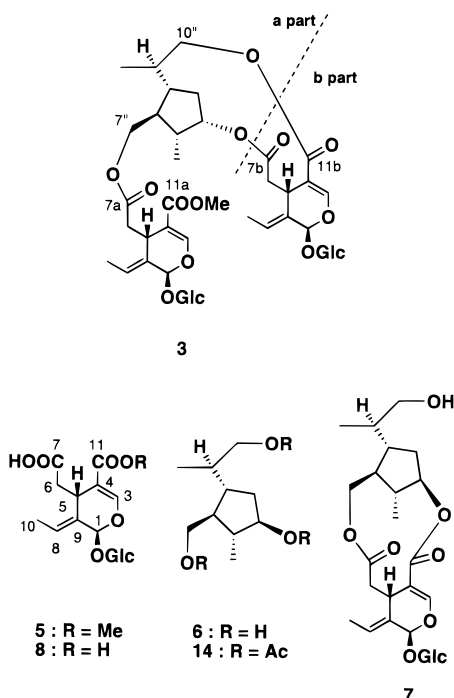
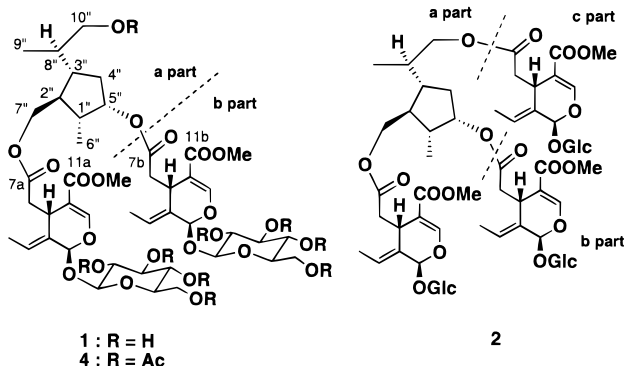
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Table 1. ¹H NMR Spectral Data for **1–4** (500 MHz)^a

H	1^b		2^{b,d}			3^b		4^{c,d}	
	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' 5' }	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 3.764, dd (9.5, 4.5, 2.5)	5.03–5.28, m 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 CD₃OD. ^c Measured in CDCl₃. ^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

Multisolvant Delivery System, 486 tunable absorbance detector). TLC was performed on Kieselgel 60F₂₅₄ 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 H₂O and filtered through a Celite layer. The filtrate and washings were combined and extracted successively with CHCl₃ and *n*-BuOH, to give three fractions weighing 1.54 g (CHCl₃), 6.21 g (*n*-BuOH), and 8.72 g (H₂O). The CHCl₃-soluble fraction was chromatographed on a Si gel column, eluting with CHCl₃-MeOH mixtures with increasing MeOH content (5–20%). Elution with 10% MeOH-CHCl₃ gave three fractions I (152 mg), II (192 mg), and III (639 mg). Fraction II was further purified by preparative HPLC (μ Bondasphere 5 μ C18–100 Å, MeOH-H₂O, 3:2), giving **3** (151 mg). Fraction III was also purified by preparative HPLC (μ Bondasphere 5 μ C18–100 Å, MeOH-H₂O, 3:2) to afford **1** (228 mg), **2** (16.8 mg), and **3** (196 mg).

Jasnudifloside A (1): colorless amorphous powder; [α]_D²⁰ –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 ¹³C NMR, see Tables 1 and 2; significant HMBC correlations H-6a (δ 2.73) → C-7a (δ 173.41), H₂-7'' → C-7a, OMe → C-11a/C-11b, H-6b (δ 2.70) → C-7b (δ 172.98), H₃-6'' → C-1''/C-2'', H₂-10'' → C-9''; SIMS m/z 959 [M – H]⁻, 797, 727, 421; HRSIMS m/z 959.3771 [M – H]⁻ (calcd for C₄₄H₆₃O₂₃, 959.3762).

Jasnudifloside B (2): colorless amorphous powder; [α]_D²⁴ –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 ¹³C 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 C₆₁H₈₅O₃₃, 1345.4976).

Jasnudifloside C (3): colorless amorphous powder; [α]_D²² –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 ¹³C 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), H₂-7'' → 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), H₃-6'' → C-1''/C-2''/C-5'', H₃-9'' → C-3''/C-8''/C-10'', H₂-10'' → C-11b; SIMS m/z 927 [M – H]⁻, 765, 695; HRSIMS m/z 927.3513 [M – H]⁻ (calcd for C₄₃H₅₉O₂₂, 927.3500).

Acetylation of 1. Compound **1** (15.0 mg) was acetylated with Ac₂O-pyridine, and the crude acetate (19.1 mg) was purified by preparative TLC (CHCl₃) to yield **4** (18.0 mg) as an amorphous powder; [α]_D²⁴ –148° (c 1.27, CHCl₃); UV (EtOH) λ_{\max} (log ϵ) 235 (4.38) nm; IR (KBr) ν_{\max} 1759, 1709, 1635, 1070 cm⁻¹; ¹H NMR and ¹³C NMR, see Tables 1 and 2; HRSIMS m/z 1361.4722 [M + Na]⁺ (calcd for C₆₂H₈₂O₃₂Na, 1361.4690), 1339.4892 [M + H]⁺ (calcd for C₆₂H₈₃O₃₂, 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 (CHCl₃-MeOH, 9:1) to **8** (43 mg) and triol **9** (6.5 mg).

Compound 9: syrup; [α]_D²³ –7.9° (c 0.67, MeOH); ¹H NMR (500 MHz, CDCl₃) δ 0.97 (3H, d, J = 6.5 Hz, H₃-9''), 0.99 (3H, d, J = 7.0 Hz, H₃-6''), 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''); ¹³C NMR, see Table 2.

Compound 8: methylated with CH₂N₂-Et₂O and the product identified as oleoside dimethyl ester¹⁵ (¹H NMR).

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

C	1 ^a		2 ^{a,c}			3 ^a		4 ^{b,c}		9 ^b	13 ^a	13 ^b
	a part	b part	a part	b part	c part	a part	b part	a part	b part			
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
CH 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 CO								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 CD₃OD. ^b Measured in CDCl₃. ^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 oleoside¹⁶ (40.4 mg) and triol **9** (9.9 mg), $[\alpha]_D^{25} -6.6^\circ$ (*c* 0.78, MeOH).

Acetylation of 9. Compound **9** (18 mg) was acetylated with Ac₂O–pyridine and the crude acetate was purified by preparative HPLC (μ Bondasphere 5 μ C18–100 Å, MeOH–H₂O, 3:2) to yield **13** (7.8 mg).

Compound 13: $[\alpha]_D^{27} +3.4^\circ$ (*c* 0.78, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.98 (3H, d, *J* = 7.5 Hz, H₃-6''), 0.99 (3H, d, *J* = 6.5 Hz, H₃-9''), 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 CH₂Cl₂ (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 H₂O and extracted with CHCl₃, and was then washed and dried. The organic layers were concentrated in vacuo, and the resulting residue was purified by successive preparative TLC (Et₂O), column chromatography on Sephadex LH-20 (CHCl₃–MeOH, 10:9), and preparative TLC (Et₂O–*n*-hexane, 1:1), giving **11** (11.0 mg).

Compound 11: syrup; ¹H NMR (500 MHz, CDCl₃) δ 0.779 (3H, d, *J* = 7.0 Hz, H₃-9''), 0.865 (3H, d, *J* = 6.5 Hz, H₃-6''), 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 \times 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, CDCl₃) δ 0.812 (3H, d, *J* = 6.5 Hz, H₃-9''), 0.915 (3H, d, *J* = 7.0 Hz, H₃-6''), 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 \times 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, H₂-7''), 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 Ac₂O–pyridine and the crude acetate (15.6 mg) was purified by preparative HPLC (μ Bondasphere 5 μ C18–100 Å, MeOH–H₂O, 11:9) to yield **14** (8.4 mg): ¹H NMR (300 MHz, CDCl₃) δ 1.00 (3H, d, *J* = 6.5 Hz, H₃-9''), 1.04 (3H, d, *J* = 7.0 Hz, H₃-6''), 1.68 (1H, m, H-1''), 1.80–1.94 (5H, m, H-2'', H-3'', H₂-4'', 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), Ph₃P (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 (CHCl₃–MeOH, 19:1) and preparative HPLC (μ Bondas-

phere 5 μ C18–100 Å, MeOH–H₂O, 11:9), giving **13** (7.7 mg), $[\alpha]_D^{27} + 3.0^\circ$ (*c* 0.62, CHCl₃); CIMS *m/z* 315 [M + H]⁺.

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