Nine New Secoiridoid Glucosides from *Jasminum nudiflorum*

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Phytochemical study of the leaves of *Jasminum nudiflorum* has led to the isolation of nine new secoiridoid glucosides, jasnudiflosides F—L (1—7), nudifloside D (8) and isooleoacteoside (9). The structures of these compounds were elucidated on the basis of chemical and spectroscopic evidence.

Key words *Jasminum nudiflorum*; Oleaceae; secoiridoid glucoside; isooleoacteoside; cyclopentanoid monoterpene

The flowers and leaves of *Jasminum nudiflorum* LINDL. belonging to the Oleaceae have been used as remedies for inflammatory swelling, purulent eruptions, bruises, and traumatic bleeding in China.[1)] Previous phytochemical investigation resulted in the isolation of caffeic glycoside esters.[2)] We have recently investigated the leaves and stems of this plant and isolated eight new oleoside-type secoiridoid glucosides with a cyclopentanoid monoterpene unit.[3)] In continuation of this study, we have now reexamined the constituents of the leaves of *J. nudiflorum* and isolated nine further new glucosides **1**—**9** as well as the known compounds oleoside 11-methyl ester (**10**),[4)] jasnudiflosides A (**11**), B, C (**12**), D, and E, nudiflosides B and C, syringin,[5)] acteoside (**13**),[6)] and poliumoside.[7)] The structure elucidation of these new glucosides, which we have named jasnudiflosides F—L (**1**—**7**), nudifloside D (**8**), and isooleoacteoside (**9**), is reported.

Jasnudifloside F (**1**) was isolated as an amorphous powder. The high-resolution SI mass spectrum (HR-SI-MS) of **1** established the composition to be $C_{27}H_{42}O_{13}$. It exhibited IR bands at 3406 (OH), 1733 (COO), and 1712 and 1632 (C=C–COO) cm^{-1} and ^{1}H-NMR (Table 1) signals common to secoiridoid glucosides with an oleoside 11-methyl ester (**10**) unit [H-3 at δ 7.53 (s), H-1 at δ 5.93 (br s), H-1′ at δ 4.82 (d, J=8.0 Hz), H-8 at δ 6.12 (qd, J=7.0, 1.0 Hz), H_3-10 at δ 1.74 (dd, J=7.0, 1.0 Hz), OMe at δ 3.72 (s)]. The ^{1}H-NMR spectrum, moreover, displayed additional signals for two secondary methyl groups at δ 0.98 and 0.99 (each d), two pairs of oxymethylene protons at δ 3.92 and 4.18 and at δ 3.38 and 3.59, and a methine group bearing a hydroxyl group at δ 4.04, suggesting the presence of a triol (**14**) moiety as in jasnudifloside A (**11**).[3a)] This was confirmed by the fact that compound **1** was subjected to alkaline hydrolysis and the resulting triol was esterified with (*R*)-2-methoxy-2-trifluoromethylphenylacetic acid ((*R*)-MTPA) to yield **15**, which was identified with an (*R*)-MTPA ester derived from **11**.[3a)] The downfield shift of H_2-7″ and C-7″ in **1**, relative to the corresponding signals in **14**, showed that in **1** the C-7 carboxyl group of the oleoside 11-methyl ester moiety was linked to the C-7″ hydroxyl group of the triol moiety. This was further supported by the ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC) interactions between H_2-7″ and C-7 (δ 173.3). Thus the structure of jasnudifloside F was characterized as **1**.

Jasnudifloside G (**2**) was isomeric with **1**. It was evident from its ^{1}H- and ^{13}C-NMR spectral features that **2** consisted of an oleoside 11-methyl ester unit and a triol (**14**) moiety like **1**. The structural difference between **1** and **2** could be accounted for only by the point of ester linkage. The signals of H-5″ and C-5″ resonated in a lower field, compared with the corresponding signals of triol (**14**), demonstrating acylation of the hydroxyl groups at C-5″ in **2**. The ester linkage was further confirmed using the HMBC technique. Final confirmation was obtained by partial methanolysis of jasnudifloside A (**11**) to **2**. Accordingly, the structure of **2** was assigned to jasnudifloside G.

The ^{1}H- and ^{13}C-NMR spectral features of jasnudifloside H (**3**) resembled those of jasnudifloside A (**11**), the differences being the absence of signals due to a carbomethoxyl group. Methylation of **3** with CH_2N_2–Et_2O gave **11**, while methanolysis of **3** afforded oleoside dimethyl ester (**16**) and a carboxylic acid (**17**). These results led us to formulate the structure of jasnudifloside H as shown.

Jasnudifloside I (**4**) was also isolated as an amorphous powder, with molecular formula $C_{26}H_{38}O_{12}$. The ^{1}H- and ^{13}C-NMR spectral features of **4** were very similar to those of jasnudifloside C (**12**),[3a)] except for the absence of signals for an oleoside 11-methyl ester (**10**) unit and chemical shifts of the proton and carbon signals around C-7″. The upfield shifts of H_2-7″ and C-7″ and downfield shifts of C-2″ of **4** relative to the corresponding signals of **12** demonstrated that the hydroxyl group at C-7″ was intact in **4**. These findings suggest that **4** is a derivative of **12** missing an oleoside 11-methyl ester (**10**) moiety at C-7″. This was confirmed by partial methanolysis of **12** to yield **4** along with oleoside dimethyl ester (**16**). Accordingly, structure **4** was assigned to jasnudifloside I.

Jasnudifloside J (**5**) was recognized as an isomer of **4** from its HR-SI-MS measurement. Its ^{1}H- and ^{13}C-NMR spectra demonstrated that **5** possessed an oleoside 11-methyl ester unit and a triol (**14**) moiety as in **4**. The absolute configurations of the triol moiety were ascertained by nuclear Overhauser enhancement and exchange spectroscopy (NOESY) correlations between H-3″ and H-1″, H-5″ and between H_3-6″ and H-2″. The sites of ester linkage were determined by the HMBC interactions between H_2-10″ and C-11 and between H_2-7″ and C-7. Thus the structure of jasnudifloside J was characterized as **5**.

The NMR spectral features of jasnudiflosides K (**6**) and L (**7**) resembled those of jasnudiflosides F (**1**) and A (**11**), respectively. A significant difference in their ^{1}H-NMR spectra was that **6** and **7** revealed additional signals ascribable to a β-glucosyl unit [**6**: δ 4.24 (d, J=7.5 Hz); **7**: δ 4.23 (d, J=7.5 Hz)]. The ^{13}C-NMR spectra of **6** and **7** also showed a set of signals assigned to a second terminal β-glucopyranosyl unit.

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Table 1. ^{1}H-NMR Spectral Data for **1**—**8** in CD_3OD

H	**1**	**2**	**3**	
			a part	b part
1	5.93 br s	5.96 br s	5.95 br s	5.95 br s
3	7.53 s	7.53 s	7.53 s	7.50 s
5	3.99 dd (9.0, 4.5)	4.01 dd (9.0, 4.5)	4.00 dd (9.0, 4.5)	4.00 dd (9.0, 4.5)
6	2.49 dd (14.0, 9.0)	2.50 dd (14.0, 9.0)	2.50 dd (14.0, 9.0)	2.54 dd (14.0, 9.0)
	2.72 dd (9.0, 4.5)	2.70 dd (14.0, 4.5)	2.73 dd (14.0, 4.5)	2.73 dd (14.0, 4.5)
8	6.12 qd (7.0, 1.0)	6.11 br q (7.0)	6.10 br q (7.0)	6.13 br q (7.0)
10	1.74 dd (7.0, 1.0)	1.75 dd (7.5, 1.5)	1.76 dd (7.0, 1.5)	1.74 dd (7.0, 1.0)
OMe	3.72 s	3.72 s	3.72 s	—
1′	4.82 d (8.0)	4.80 d (8.0)	4.810[a] d (7.5)	4.805[a] d (8.0)
2′	3.28—3.44 m	3.28—3.36 m	3.27—3.29 m	3.27—3.29 m
3′		3.40 t (9.0)	3.40[b] t (10.0)	3.41[b] t (9.0)
4′,5′		3.28—3.36 m	3.27—3.29 m	3.27—3.29 m
6′	3.67 dd (11.5, 6.0)	3.65 dd (11.5, 6.0)	3.65[c] dd (12.0, 6.0)	3.67[c] dd (12.0, 6.0)
	3.89 dd (11.5, 1.0)	3.88 dd (11.5, 2.0)	3.89[d] dd (12.0, 2.0)	3.91[d] dd (12.0, 2.0)
1″	1.78 m	2.02 m	1.95 m	
2″	1.85 m	1.66 m	1.83 m	
3″	1.68 m	1.74 m	1.78 m	
4″	1.55 m	1.60 ddd (13.5, 6.5, 4.5)	1.61—1.67 m	
	1.95 m	2.02 m	2.07 ddd (14.5, 9.5, 5.5)	
5″	4.04 q (5.0)	5.00 q (4.5)	5.02 br q (5.0)	
6″	0.99 d (8.5)	0.94 d (7.0)	0.94 d (7.0)	
7″	3.92 dd (11.5, 6.0)	3.52 dd (11.0, 5.5)	3.95 dd (11.5, 5.0)	
	4.18 m	3.60 dd (11.0, 4.0)	3.95 dd (11.5, 5.0)	
8″	1.67 m	1.66 m	1.61—1.67 m	
9″	0.98 d (8.5)	0.98 d (6.5)	0.99 d (7.0)	
10″	3.38 m	3.30 m	3.59 dd (11.0, 4.0)	
	3.59 dd (11.0, 4.0)	3.59 dd (11.0, 4.0)	4.20 dd (11.0, 4.0)	

Table 1. (Continued)

H	**4**	**5**	**6**	
1	5.85 br s	5.91 br s	5.94 br s	
3	7.42 s	7.46 s	7.53 s	
5	3.99 dd (9.0, 4.0)	4.00 dd (12.0, 4.0)	4.00 dd (9.5, 5.0)	
6	2.37 dd (13.0, 4.0)	2.30 dd (12.5, 12.0)	2.51 dd (14.0, 9.5)	
	2.45 dd (13.0, 9.0)	2.49 dd (12.5, 4.0)	2.72 dd (14.0, 5.0)	
8	6.06 qd (7.0, 1.0)	6.08 br q (7.0)	6.12 br q (7.5)	
10	1.83 dd (7.0, 1.0)	1.82 dd (7.0, 1.0)	1.75 dd (7.0, 1.5)	
OMe	—	—	3.72 s	
1′,1‴	4.80 d (7.5)	4.80 d (8.0)	4.81 d (8.0)	4.24 d (7.5)
2′,2‴	3.26—3.29 m	3.27 m	3.26—3.34 m	3.17 dd (9.0, 7.5)
3′,3‴	3.40 t (9.0)	3.40 t (9.0)	3.41 t (9.0)	3.26—3.34 m
4′,5′,4‴,5‴	3.26—3.29 m	3.28—3.36 m	3.26—3.34 m	
6′,6‴	3.88 dd (11.5, 2.0)	3.63 dd (12.0, 6.5)	3.66[e] dd (12.0, 5.5)	3.67[e] dd (12.0, 5.5)
	3.88 dd (11.5, 2.0)	3.90 dd (12.0, 2.0)	3.86[f] dd (12.0, 2.0)	3.90[f] dd (12.0, 2.0)
1″	1.85 m	1.69 m	1.71 m	
2″	1.71 m	1.85 m	1.82 m	
3″	1.82 m	2.20 m	1.73 m	
4″	1.91 m	1.35 ddd (13.5, 8.5, 2.5)	1.54 ddd (13.5, 7.5, 4.5)	
	2.06 d (4.0)	2.15 m	1.90 m	
5″	4.91 m	4.03 m	4.04 q (4.5)	
6″	1.01 d (7.0)	1.00 d (6.5)	0.91 d (7.0)	
7″	3.65 m	4.07 d (4.0)	3.95 dd (11.5, 6.0)	
	3.65 m	4.07 d (4.0)	4.20 dd (11.5, 4.5)	
8″	2.03 d (4.0)	2.15 m	1.84 m	
9″	0.98 d (7.0)	0.96 d (7.0)	1.00 d (6.0)	
10″	4.14 dd (11.5, 4.0)	4.29 dd (12.0, 10.5)	3.56 dd (9.0, 5.0)	
	4.29 dd (11.5, 9.0)	4.00 dd (12.0, 3.0)	3.76 dd (9.0, 7.0)	

Table 1. (Continued)

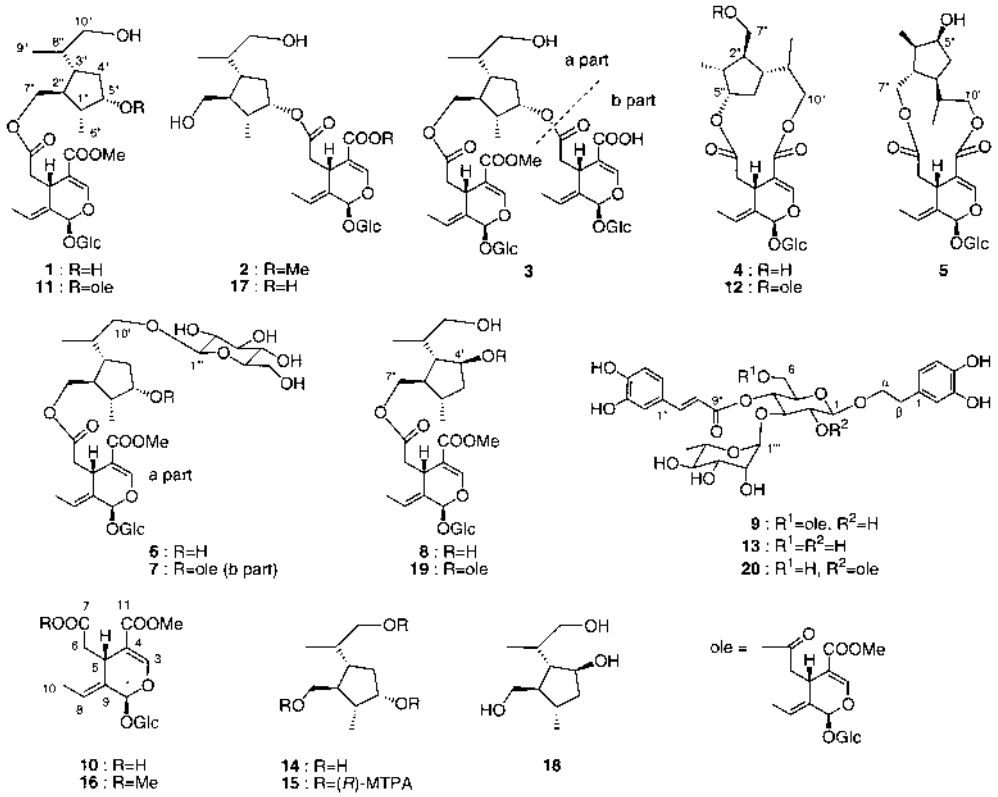
H	7			8
	a part	b part		
1	5.95 br s	5.99 br s		5.94 br s
3	7.53 s	7.54 s		7.53 s
5	4.00 m	4.00 m		4.01 dd (9.0, 4.5)
6	2.52 dd (14.0, 9.0)	2.54 dd (14.0, 9.0)		2.48 dd (14.5, 9.0)
	2.71 dd (14.0, 4.5)	2.73 dd (14.0, 5.0)		2.73 dd (14.5, 4.5)
8	6.11 br q (7.0)	6.12 br q (7.0)		6.12 br q (7.0)
10	1.75 dd (7.0, 1.0)	1.76 dd (7.0, 1.0)		1.75 dd (7.5, 1.5)
OMe	3.72 s	3.73 s		3.72 s
1′,1‴	4.81 d (7.5)	4.81 d (7.5)	4.23 d (7.5)	4.81 d (7.5)
2′,2‴	3.21—3.28 m	3.21—3.28 m	3.17 dd (9.0, 7.5)	3.32—3.40 m
3′,3‴	3.41 t (9.0)	3.41 t (9.0)	3.21—3.28 m	3.41 t (9.5)
4′,5′,4‴,5‴	3.21—3.28 m	3.21—3.28 m		3.32—3.40 m
6′,6‴	3.65[g] dd (12.0, 6.0)	3.66[g] dd (12.0, 6.0)	3.67[g] dd (12.0, 6.0)	3.67 dd (12.0, 5.5)
	3.90[h] dd (12.0, 2.0)	3.91[h] dd (12.0, 2.0)	3.84[h] dd (12.0, 2.0)	3.89 dd (12.0, 2.0)
1″	1.94 m			2.01 m
2″	1.91 m			1.59 m
3″	1.91 m			1.59 m
4″	1.65 m			4.04 m
	2.00 m			1.44 ddd (14.5, 9.0, 5.5)
5″	5.03 br q (4.5)			1.78 m
6″	0.93 d (6.5)			1.03 d (6.5)
7″	4.00 m			3.93 dd (10.5, 6.5)
	4.21 dd (11.0, 2.0)			4.17 dd (10.5, 4.5)
8″	1.91 m			1.72 m
9″	1.00 d (6.5)			0.97 d (7.0)
10″	3.51 m			3.40 dd (11.0, 7.5)
	3.70 m			3.57 dd (11.0, 5.5)

Values in parentheses are coupling constants in Hz. *a*—*h*) Assignments may be interchangeable.

Table 2. ^{13}C-NMR Spectral Data for **1**—**8** in CD_3OD

C	1	2	3		4	5	6		7			8
			a part	b part					a part	b part		
1	94.9	95.3	94.7	95.0	95.2	95.0	94.9		94.8[c]	95.3[c]		95.0
3	155.1	155.2	154.7[a]	155.2[a]	153.3	153.5	155.2		155.2[c]	155.3[c]		155.2
4	109.3	109.4	109.4	109.4	111.4	110.6	109.4		109.4	109.4		109.4
5	32.0	31.9	32.1[a]	32.2[a]	31.7	32.5	32.1		32.0[c]	32.2[c]		32.0
6	41.2	41.5	41.2	41.6	44.1	44.1	41.3		41.3[c]	41.7[c]		41.3
7	173.3	173.0	173.1	173.4	173.9	173.9	173.5		173.1	173.5		173.3
8	124.7	124.8	124.4	124.0	123.5	123.6	124.7		124.0[c]	124.8[c]		124.8
9	130.6	130.8	130.7	131.2	132.5	132.0	130.7		130.8	130.8		130.7
10	13.7	13.8	13.4[a]	13.9[a]	13.2	13.1	13.9		13.7[c]	13.9[c]		13.7
11	168.5	168.7	168.6	168.6	168.8	168.7	168.6		168.6	168.6		168.7
OMe	51.9	51.2	52.0	—	—	—	52.0		52.0	52.0		51.9
1′,1‴	100.6	100.9	100.5[a]	100.8[a]	100.9	100.8	100.6	104.4	100.5[c]	100.9[c]	104.6	100.7
2′,2‴	74.7	74.8	74.8[a]	74.9[a]	74.8	74.8	74.8	75.2	74.8	74.8	75.1	74.8
3′,3‴	77.8	78.0	78.0	78.0	78.0	78.0	77.9	77.9	77.9[c]	77.9[c]	78.0[c]	78.0
4′,4‴	71.5	71.6	71.6[a]	71.7[a]	71.6	71.6	71.7[b]	71.6[b]	71.7	71.7	71.7	71.5
5′,5‴	78.4	78.5	78.5[a]	78.7[a]	78.5	78.6	78.5[b]	78.2[b]	78.5[c]	78.6[c]	78.2[c]	78.5
6′,6‴	62.8	62.9	62.9[a]	63.0[a]	62.8	62.8	62.9[b]	62.8[b]	63.0[c]	63.0[c]	62.8[c]	62.8
1″	43.2	41.1	41.7		41.7	43.9	43.3		41.8			36.5
2″	47.8	51.9	48.2		53.9	43.7	47.5		47.8			48.9
3″	43.0	41.9	42.6		45.6	41.0	43.3		43.2			54.8
4″	36.9	35.2	35.4		32.2	39.3	37.1		35.0			76.4
5″	75.7	80.0	80.0		82.6	74.1	75.5		80.2			43.9
6″	14.0	14.5	14.2		13.3	12.4	13.7		14.0			20.6
7″	68.1	64.8	67.2		63.4	66.3	67.9		67.0			69.1
8″	40.7	41.3	41.1		37.6	36.0	38.1		38.1			39.4
9″	16.6	16.2	16.3		19.2	13.3	16.9		16.9			15.2
10″	66.4	66.6	66.5		68.1	68.0	74.2		74.2			67.0

a—*c*) Assignments may be reversed horizontally.



This unit could be determined to be attached at C-10″ of the triol moiety in each case by the glycosylation shift observed for C-10″ [**6**: $\Delta\delta$ +7.8 ppm; **7**: $\Delta\delta$ +7.7 ppm] and C-8″ [**6**: $\Delta\delta$ −2.6 ppm; **7**: $\Delta\delta$ −3.0 ppm] and by HMBC interaction between H-1‴ and C-10″. Thus jasnudiflosides K (**6**) and L (**7**) were formulated as shown.

Nudifloside D (**8**) was recognized as another isomer of jasnudifloside F (**1**) from its HR-SI-MS measurement. Its ^{1}H- and ^{13}C-NMR spectra showed signals due to a monoterpene unit in addition to a set of signals corresponding to oleoside 11-methyl ester, implying a structural similarity of **8** to **1**. However, detailed two-dimensional NMR experiments with **8** demonstrated that the cyclopentanoid monoterpene unit in **8** differed from **14** but was the same triol **18** as in nudifloside A (**19**).[3b] HMBC experiments with **8**, where ^{3}J interactions were observed from the H_2-7″ to C-7 carbon, as well as comparison of ^{13}C-NMR spectral data of **8** with those of **18** and **19**, showed that the hydroxyl group at C-7″ was esterified with the C-7 carboxyl group of the oleoside 11-methyl ester (**10**) unit. Therefore the structure of nudifloside D was determined to be **8**.

Compound **9** was analyzed for $C_{46}H_{58}O_{25}$ from its HR-SI-MS measurement. Its ^{1}H-NMR spectrum displayed, in addition to the signals of an oleoside 11-methyl ester (**10**) unit, signals assigned to α-rhamnose [H-1‴ at δ 5.19 (br s), H_3-6‴ at δ 1.09 (d, J=6.5 Hz)], β-glucose [H-1′ at δ 4.34 (d, J=8.0 Hz)], *trans*-caffeoyl [an aromatic AMX spin system at δ 6.78, 6.96, 7.05, a pair of *trans*-olefinic protons at δ 6.26 and 7.60 (each d, J=16.0 Hz)], and 3,4-dihydroxyphenethyl [an aromatic AMX spin system at δ 6.56, 6.67, and 6.68, and an ABX_2 system of a OCH_2CH_2Ar moiety at δ 3.75, 3.90, and 2.79] groups. These findings, together with UV maxima at 222, 234, 291, and 333 nm, implied that compound **9** was an ester of oleoside 11-methyl ester (**10**) with acteoside (**13**), which was also isolated from this plant material. Comparison of the ^{13}C-NMR spectral data of **9** with those of **13** and oleoacteoside (**20**)[8] demonstrated that the hydroxyl group at C-6′ in the glucose moiety of acteoside was acylated in the structure of **9**. The HMBC spectrum of **9** revealed a correlation of C-7‴ with H-6′ (δ 4.05), suggesting that the C-7‴ carboxyl group of the oleoside 11-methyl ester unit was esterified with the 6′-hydroxyl group of the acteoside unit. Base on these data, compound **9** was characaterized as illustrated in the figure and designated as isooleoacteoside.

Experimental

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. SI-MS and HR-SI-MS were obtained with a Hitachi M-4100 mass spectrometer. For SI-MS, glycerol was used as the matrix. The NMR experiments were performed with Varian VXR-500 and Varian Gemini-300 spectrometers, with tetramethylsilane (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.

Isolation of Glucosides The source of plant material was described in a previous publication.[3] Dried leaves of *J. nudiflorum* (350 g) were extracted with hot MeOH. After concentration, the extract (61.4 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 0.9 g ($CHCl_3$), 20.5 g (*n*-BuOH) and 24.4 g (H_2O). The *n*-BuOH–soluble fraction was chromatographed on a Wakogel LP-40C_{18} (Wako Pure Chemical Industries, Osaka, Japan) column. Elution with MeOH–H_2O mixtures of the increasing MeOH content gave 10 fractions. Fraction I (H_2O effluent, 1.02 g) was further purified by a combination of preparative TLC ($CHCl_3$–MeOH, 7 : 3 or *n*-BuOH–AcOH–H_2O, 4 : 1 : 0.5) and preparative HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 3 : 2) to give syringin (35.2 mg), oleoside 11-methyl ester (**10**) (14.5 mg), acteoside (**13**) (91 mg), and poliumoside (106 mg). Fractions II—X were also purified by preparative TLC ($CHCl_3$–MeOH, 3 : 2 or *n*-BuOH–AcOH–H_2O,

4 : 1 : 0.5) and preparative HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 3 : 2 or 1 : 1 or 2 : 3 or MeCN–H_2O, 1 : 4 or 2 : 3). Fraction II (0—1% MeOH effluent, 1.05 g): syringin (11.1 mg), **13** (113 mg), poliumoside (193 mg), jasnudifloside F (**1**) (31.5 mg), jasnudifloside I (**4**) (23.6 mg), jasnudifloside D (26.0 mg); fraction III (1—4% MeOH effluent, 0.64 g): poliumoside (201 mg), jasnudifloside K (**6**) (4.2 mg), **1** (112 mg), jasnudifloside J (**5**) (4.2 mg), **4** (7.2 mg), nudifloside C (10.9 mg), jasnudifloside D (10.5 mg); fraction IV (4—7% MeOH effluent, 0.50 g): poliumoside (5.7 mg), **6** (3.7 mg), **1** (54.3 mg), jasnudifloside G (**2**) (20.7 mg), **5** (1.0 mg), **4** (5.3 mg), nudifloside D (**8**) (6.1 mg), nudifloside C (12.4 mg), jasnudifloside D (13.4 mg); fraction V (7—10% MeOH effluent, 0.58 g): poliumoside (12.1 mg), **6** (3.8 mg), **2** (2.7 mg), **1** (54.5 mg), **4** (37.2 mg), **8** (3.8 mg), nudifloside C (8.9 mg), jasnudifloside A (**11**) (13.7 mg); fraction VI (15% MeOH effluent, 0.67 g): poliumoside (14.4 mg), **6** (3.5 mg), **2** (13.9 mg), **1** (58.5 mg), jasnudifloside H (**3**) (35.6 mg), isooleoacteoside (**9**) (3.0 mg), jasnudifloside L (**7**) (13.2 mg), **8** (14.0 mg), **11** (60.6 mg); fraction VII (20% MeOH effluent, 0.79 g): **3** (21.7 mg), **9** (8.6 mg), **1** (4.8 mg), **7** (33.3 mg), **8** (4.9 mg), **11** (53.6 mg), jasnudifloside C (**12**) (8.5 mg); fraction VIII (30% MeOH effluent, 1.73 g): an aliquot (701 mg) of the fraction was purified to give **7** (2.1 mg), **11** (255 mg), **12** (26.0 mg); fraction IX (30—40% MeOH effluent, 2.45 g): an aliquot (971 mg) of the fraction was purified to give **7** (1.7 mg), **11** (437 mg), **12** (215 mg), nudifloside B (11.0 mg); fraction X (40—50% MeOH effluent, 1.21 g): **3** (13.8 mg), **11** (525 mg), **12** (32.2 mg), jasnudifloside B (157 mg).

Jasnudifloside F (**1**): Colorless amorphous powder, $[\alpha]_D^{28}$ −145° (c=0.52, MeOH). UV λ_{max}^{MeOH} nm (log ε): 235 (4.07). IR ν_{max}^{KBr} cm^{-1}: 3406, 1733, 1712, 1632, 1078. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H_3-6″→C-5″, H_3-9″→C-10″, H_2-7″→C-7, H_2-6→C-7, OMe→C-11; SI-MS m/z 573 [M−H]$^-$, 411, 341; HR-SI-MS m/z 573.2557 [M−H]$^-$ (Calcd for $C_{27}H_{41}O_{13}$, 573.2549).

Jasnudifloside G (**2**): Colorless amorphous powder, $[\alpha]_D^{23}$ −161° (c=0.89, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3400, 1731, 1709, 1632, 1078, 818. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H_3-6″→C-5″, H_3-9″→C-8″, H_2-10″→C-8″, H-5″→C-7, H_2-6→C-7, OMe→C-11; SI-MS m/z 573 [M−H]$^-$, 411, 341; HR-SI-MS m/z 573.2567 [M−H]$^-$ (Calcd for $C_{27}H_{41}O_{13}$, 573.2549).

Jasnudifloside H (**3**): Colorless amorphous powder, $[\alpha]_D^{24}$ −183° (c=1.02, MeOH). UV λ_{max}^{MeOH} nm (log ε): 235 (4.35). IR ν_{max}^{KBr} cm^{-1}: 3400, 1731, 1707, 1636, 1078, 818. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H-1″→C-7″, H_3-6″→C-1″, 2″, 5″, H-7″ (δ 3.92)→C-7a, H_3-9″→C-3″, 8″, H_2-10″→C-8″, H_2-6a→C-7a, H_2-6b→C-7b; SI-MS m/z 945 [M−H]$^-$, 783, 421; HR-SI-MS m/z 945.3573 [M−H]$^-$ (Calcd for $C_{43}H_{61}O_{23}$, 945.3606).

Jasnudifloside I (**4**): Colorless amorphous powder, $[\alpha]_D^{26}$ −186° (c=0.39, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236 (4.00). IR ν_{max}^{KBr} cm^{-1}: 3397, 1725, 1705, 1622, 1074. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H_3-6″→C-2″, 5″, H-5″→C-7, H_2-10″→C-11, H_2-6→C-7; SI-MS m/z 541 [M−H]$^-$, 421, 379; HR-SI-MS m/z 541.2283 [M−H]$^-$ (Calcd for $C_{26}H_{37}O_{12}$, 541.2286).

Jasnudifloside J (**5**): Colorless amorphous powder, $[\alpha]_D^{23}$ −189° (c=0.17, MeOH). UV λ_{max}^{MeOH} nm (log ε): 237 (4.04). IR ν_{max}^{KBr} cm^{-1}: 3406, 1732, 1713, 1624, 1074, 822. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H_3-6″→C-5″, H-7″ (δ 4.07)→C-7, H-10″ (δ 4.29)→C-11, H_2-6→C-7; SI-MS m/z 541 [M−H]$^-$, 421, 379; HR-SI-MS m/z 541.2305 [M−H]$^-$ (Calcd for $C_{26}H_{37}O_{12}$, 541.2286).

Jasnudifloside K (**6**): Colorless amorphous powder, $[\alpha]_D^{24}$ −135° (c=0.55, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236 (4.09). IR ν_{max}^{KBr} cm^{-1}: 3394, 1730, 1707, 1636, 1078, 818. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H_3-6″→C-1″, 2″, 5″, H_2-7″→C-7, H-10″ (δ 3.56)→C-8″, 1‴, H-1‴→C-10″, H_2-6→C-7; SI-MS m/z 735 [M−H]$^-$, 573, 503, 471; HR-SI-MS m/z 735.3091 [M−H]$^-$ (Calcd for $C_{33}H_{51}O_{18}$, 735.3077).

Jasnudifloside L (**7**): Colorless amorphous powder, $[\alpha]_D^{24}$ −173° (c=0.73, MeOH). UV λ_{max}^{MeOH} nm (log ε): 237 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3419, 1734, 1717, 1636, 1076, 818. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. Significant HMBC correlations: H-1″→C-7″, H-5″→C-7b, H_3-6″→C-1″, 2″, 5″, H_2-7″→C-7a, H_3-9″→C-3″, 8″, H_2-10″→C-8″, 1‴, H-1‴→C-10″, H_2-6a→C-7a, H_2-6b→C-7b; SI-MS m/z 1121 [M−H]$^-$, 959, 889; HR-SI-MS m/z 1121.4304 [M−H]$^-$ (Calcd for $C_{50}H_{73}O_{28}$, 1121.4291).

Nudifloside D (**8**): Colorless amorphous powder, $[\alpha]_D^{24}$ −161° (c=0.41, MeOH). UV λ_{max}^{MeOH} nm (log ε): 237 (4.08). IR ν_{max}^{KBr} cm^{-1}: 3397, 1731, 1709, 1632, 1078, 818. ^{1}H- and ^{13}C-NMR, see Tables 1 and 2. ^{1}H–^{1}H shift correlation spectrscopy (COSY) correlations: H-1″↔H-2″, H-1″↔H_2-5″, H-1″↔H_3-6″, H-2″↔H-3″, H-2″↔H-7″, H-3″↔H-4″, H-4″↔H_2-5″, H-8″↔H_3-9″, H-8″↔H_2-10″; Significant HMBC correlations: H-1″→C-7″, H-4″→C-8″, H_3-6″→C-1″, 2″, 5″, H_2-7″→C-7, H_3-9″→C-3″, 8″, H_2-6→C-7, OMe→C-11; SI-MS m/z 573 [M−H]$^-$, 411, 341; HR-SI-MS m/z 573.2570 [M−H]$^-$ (Calcd for $C_{27}H_{41}O_{13}$, 573.2549).

Isooleoacteoside (**9**): Colorless amorphous powder, $[\alpha]_D^{23}$ −124° (c=0.28, MeOH). UV λ_{max}^{MeOH} nm (log ε): 222 (3.98), 234 (4.29), 291 (4.28), 333 (4.60). IR ν_{max}^{KBr} cm^{-1}: 3406, 1731, 1705, 1634, 1609, 1520, 1285, 1074, 814. ^{1}H-NMR δ (CD_3OD): 1.09 (3H, d, J=6.5 Hz, H_3-6‴), 1.67 (3H, dd, J=7.0, 1.5 Hz, H_3-10⁗), 2.45 (1H, dd, J=14.5, 8.5 Hz, H-6⁗), 2.71 (1H, dd, J=14.5, 4.0 Hz, H-6⁗), 2.79 (2H, br t, J=7.5 Hz, H_2-β), 3.60—3.70 (1H, m, H-6⁗), 3.67 (3H, s, OMe), 3.74—3.80 (1H, m, H-α), 3.80—3.90 (1H, m, H-6⁗), 3.90 (1H, m, H-α), 3.98 (1H, dd, J=8.5, 4.0 Hz, H-5⁗), 4.05 (1H, dd, J=12.0, 3.0 Hz, H-6′), 4.18 (1H, dd, J=12.0, 5.0 Hz, H-6′), 4.34 (1H, d, J=8.0 Hz, H-1′), 4.82 (1H, d, J=7.5 Hz, H-1⁗), 5.19 (1H, br s, H-1‴), 5.90 (1H, br s, H-1⁗), 6.05 (1H, br q, J=7.0 Hz, H-8⁗), 6.26 (1H, d, J=16.0 Hz, H-8″), 6.56 (1H, dd, J=8.0, 2.0 Hz, H-6), 6.67 (1H, d, J=8.0 Hz, H-5), 6.68 (1H, d, J=2.0 Hz, H-2), 6.78 (1H, d, J=8.5 Hz, H-5″), 6.96 (1H, dd, J=8.5, 2.0 Hz, H-6″), 7.05 (1H, d, J=2.0 Hz, H-2″), 7.48 (1H, s, H-3⁗), 7.60 (1H, d, J=16.0 Hz, H-7″). ^{13}C-NMR δ (CD_3OD): 13.7 (C-10⁗), 18.5 (C-6‴), 31.4 (C-5⁗), 36.7 (C-β), 41.2 (C-6⁗), 52.0 (OMe), 62.8 (C-6⁗), 64.3 (C-6′), 70.5×2 (C-4′, C-5‴), 71.5 (C-4⁗), 72.1 (C-2‴), 72.4 (C-α), 72.5 (C-3‴), 73.1 (C-5′), 73.9 (C-4‴), 74.8 (C-2⁗), 76.2 (C-2′), 78.0 (C-3⁗), 78.3 (C-5⁗), 81.3 (C-3′), 95.3 (C-1⁗), 100.9 (C-1⁗), 103.1 (C-1‴), 104.7 (C-1′), 109.4 (C-4⁗), 114.6 (C-2″), 115.2 (C-8″), 116.4 (C-5″), 116.6 (C-2), 117.2 (C-5), 121.3 (C-6), 123.3 (C-6″), 125.0 (C-8⁗), 127.6 (C-1″), 130.6 (C-9⁗), 131.4 (C-1), 144.2 (C-3), 146.2 (C-4), 146.9 (C-4″), 148.3 (C-7″), 150.0 (C-3″), 155.1 (C-3⁗), 168.2 (C-9″), 168.7 (C-11⁗), 173.4 (C-7⁗). Significant HMBC correlations: H-α (δ 3.75)→C-1′, H_2-6′→C-7⁗, H_2-6⁗→C-7⁗, H-1‴→C-3′, OMe→C-11⁗; SI-MS m/z 1009 [M−H]$^-$, 959, 421; HR-SI-MS m/z 1009.3139 [M−H]$^-$ (Calcd for $C_{46}H_{57}O_{25}$, 1009.3191).

Alkaline Hydrolysis of 1 Followed by Esterification with (*R*)-MTPA A solution of **1** (5.5 mg) in 0.5 M NaOH (0.7 ml) was stirred for 4 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 give triol **8** (2.6 mg). To a solution of **8** in dry CH_2Cl_2 (1 ml) were added (*R*)-MTPA (3.0 mg), DMAP (1 mg), and DCC (4 mg), and the mixture was stirred for 4 h at room temperature. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$, and then washed and dried. The organic layers were concentrated *in vacuo*, and the resulting residue was purified by successive preparative TLC (*n*-hexane–Et_2O, 1 : 1), to give an ester (6.5 mg) identified as **15** (^{1}H-NMR).

Partial Methanolysis of 11 A solution of **11** (56.6 mg) in 0.1 M NaOMe (4 ml) was stirred for 26.5 h at room temperature. The reaction mixture was neutralized with Amberlite IR-120 (H^+ form) and concentrated *in vacuo.* The resulting residue was separated by preparative TLC ($CHCl_3$–MeOH, 9 : 1) to give a mixture (26.4 mg) of oleoside dimethyl ester and triol, and a glucosidic fraction (30.8 mg). The latter was further purified by preparative HPLC (μBondasphere 5μC18-100 Å, MeCN–H_2O, 3 : 7) to afford **2** (19.0 mg) ([α]$_D^{22}$ −162°, ^{1}H-NMR).

Methylation of 3 To a solution of **3** (6.2 mg) in MeOH (1 ml) was added CH_2N_2–Et_2O until the solution showed a persistent yellow color. The reaction mixture was concentrated and dried *in vacuo* to give **11** (1.5 mg) ([α]$_D^{22}$ −194°, ^{1}H-NMR).

Partial Methanolysis of 3 A solution of **3** (7.3 mg) in 0.1 M NaOMe (1 ml) was stirred for 20 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–AcOH, 6 : 4 : 0.01) to give **16** (1.8 mg) and **17** (2.4 mg). **17**: ^{1}H-NMR δ (CD_3OD): 0.93 (3H, d, J=7.0 Hz, H_3-6″), 0.98 (3H, d, J=6.5 Hz, H_3-9″), 1.75 (3H, dd, J=7.0, 1.0 Hz, H_3-10), 1.94—2.60 (2H, m, H-1″, H-2″), 2.45 (1H, dd, J=14.0, 9.0 Hz, H-6), 2.81 (1H, dd, J=14.0, 4.0 Hz, H-6), 3.50—3.62 (4H, m, H_2-7″, H_2-10″), 3.65 (1H, dd, J=12.0, 4.0 Hz, H-6′), 3.88 (1H, dd, J=12.0, 2.0 Hz, H-6′), 4.03 (1H, ddd, J=9.0, 4.0, 2.0 Hz, H-5′), 4.80 (1H, d, J=7.5 Hz, H-1′), 4.98 (1H, br q, J=5.0 Hz, H-5″), 5.89 (1H, br s, H-1), 6.07 (1H, br q, J=7.0 Hz, H-8), 7.40 (1H, s, H-3). HR-SI-MS m/z 559.2403 [M−H]$^-$ (Calcd for $C_{26}H_{39}O_{13}$, 559.2392).

Partial Methanolysis of 12 A solution of **12** (20.8 mg) in 0.1 M NaOH (1 ml) was stirred for 24 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) and preparative HPLC (μBondasphere 5μC18-100 Å, MeOH–H_2O, 1 : 1). to give **16** (4.6 mg) and **4** (8.3 mg).

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