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Eight Minor Secoiridoid Glucosides with a Linear Monoterpene Unit from *Jasminum polyanthum*

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Investigation of the crude drug "Ye su xin", the dried flowers of *Jasminum polyanthum*, has led to the isolation of eight new secoiridoid glucosides esterified with a linear monoterpene unit, jaspofoliamosides C—G, jaspogeranosides A and B, and jaspolinaloside B. The structures of these compounds were elucidated on the basis of chemical and spectroscopic evidence.

Key words *Jasminum polyanthum*; Oleaceae; secoiridoid glucoside; jaspofoliamoside; jaspogeranoside; jaspolinaloside

Jasminum polyanthum FRANCH. is an oleaceous shrub indigenous to China. Its dried flowers have long been used as a crude drug "Ye su xin" in Chinese folk medicine.[1] Previous phytochemical studies on this plant resulted in the isolation of verbascoside and several secoiridoid glucosides from the leaves.[2,3] In the course of our chemical studies on the glycosides of oleaceous plants, we have recently investigated the constituents of the dried flowers of the above *Jasminum* species, and reported the structure elucidation of one monomeric, eight dimeric and five trimeric secoiridoid glucosides as well as three secoiridoid glucosides esterified with a linear monoterpene unit.[4—7] Further detailed examination of the minor constituents of the methanolic extract of the same plant material led us to isolate an additional two monomeric and six dimeric secoiridoid glucosides with a linear monoterpene unit. This paper deals with the structure determination of these novel glucosides **1**—**8**.

Compound **1** was isolated as an amorphous powder. The high resolution secondary ion mass spectrum (HR-SI-MS) of **1** established a composition of $C_{27}H_{40}O_{13}$. It exhibited IR bands at 3419 (OH), 1732 (COO), and 1709 and 1636 (C=C–COO) cm^{-1} and ^{1}H-NMR (Table 1) signals common to secoiridoid glucosides with an oleoside 11-methyl ester (**9**) unit [H-3 at δ 7.52, H-1 at δ 5.93 (br s), H-1′ at δ 4.80 (d, J=8.0 Hz), H-8 at δ 6.11 (qd, J=7.0, 1.0 Hz), H_3-10 at δ 1.74 (dd, J=7.0, 1.5 Hz), OMe at δ 3.71 (s)]. The ^{1}H-NMR spectrum, moreover, displayed additional signals for a secondary methyl group at δ 0.96 (d, J=6.5 Hz), a vinyl methyl group at δ 1.82 (d, J=1.0 Hz), a pair of oxygenated methylene protons at δ 4.06 (dt, J=11.0, 6.5 Hz) and 4.12 (dt, J=11.0, 7.0 Hz), and an olefinic proton at δ 6.74 (tq, J=7.0, 1.0 Hz), suggesting a 6,7-dihydrofoliamenthic acid (**10**, 8-hydroxy-2,6-dimethyl-2(E)-octenoic acid) moiety in its structure. The ^{13}C-NMR (Table 2) spectral features were very similar to those of jaspofoliamoside A (**11**), which was previously isolated from the same plant material, except for the absence of signals assignable to a 1-O-acyl-β-glucose moiety. The heteronuclear multiple-bond correlation (HMBC) experiments with **1** revealed the ester linkage of the C-7 carboxyl group of oleoside (**12**) moiety to the hydroxyl group at C-8″, but could not locate the site of the methoxyl group because of the identical frequency of the C-11 and C-1″ resonances. In order to solve this problem, compound **1** was methylated with CH_2N_2–Et_2O to give **1a**. Comparison of the ^{13}C-NMR spectrum of **1a** with that of **1** revealed that the signals assignable to C-1″, C-2″ and C-3″ of the monoterpene unit were shifted by +1.59, +1.06 and +0.80 ppm, respectively, confirming that the newly formed methyl ester was located at C-1″. From these findings, the structure of **1** was established as jaspofoliamoside C.

Compoud **2**, named jaspofoliamoside D, showed spectral data similar to those of **1**. However, its HR-SI-MS exhibited a peak at m/z 553.2279 $(M-H)^-$ consistent with a molecular formula of $C_{27}H_{38}O_{12}$, which was H_2O less than that of **1**. Careful inspection of the ^{1}H- and ^{13}C-NMR spectra of **1** and **2** showed significant differences in the coupling constants of H_2-8″ and the chemical shifts of C-3″, C-4″, C-5″ and C-6″ of the monoterpene unit. These findings, together with the acylation shifts for C-5′ and C-6′ of the oleoside moiety in **2**, implied that the C-1″ carboxyl group of the dihydrofoliamenthic acid moiety was linked to the C-6′ hydroxyl group of the oleoside 11-methyl ester unit to form a lactone ring in jaspofoliamoside D. This was further confirmed by an HMBC cross-peak between H_2-6′ and C-1″ (δ 168.66). Finally, methanolysis of compound **2** gave oleoside dimethyl ester (**13**) and dihydrofoliamenthic acid methyl ester (**14**). Accordingly, compound **2** was formulated as shown.

Glucoside **3**, $C_{44}H_{62}O_{23}$, was also obtained as an amorphous powder. It was evident from its ^{1}H-NMR spectrum that **3** was an ester of oleoside 11-methyl ester (**9**) with jaspofoliamoside C (**1**). Attachment of the C-7 carboxyl group of an additional oleoside 11-methyl ester unit at the C-6′ hydroxyl group of the jaspofoliamoside C moiety was suggested by the downfield shifts of H-5′a and H_2-6′a, when compared with those of **1**. Thus, compound **3** was characterized as jaspofoliamoside E.

Compounds **4** and **5** were recognized as isomers, $C_{50}H_{72}O_{28}$, from their HR-SI-MS. ^{1}H- and ^{13}C-NMR spectral features (Tables 1, 2) demonstrated clearly the presence of a jaspofoliamoside A (**11**) moiety and another oleoside 11-methyl ester unit in each compound. The structural difference between **4** and **5** could be ascribed to the point of ester linkage of the extra oleoside unit, which was discriminated by a combination of ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY), rotating frame nuclear Overhauser effect spectroscopy (ROESY) and HMBC experiments. The HMBC experiments with **4** and **5** showed interactions between H-1′a (**4** and **5**: δ 4.80) and C-1a, between H_2-8″ and C-7a, and between H-1‴ (**4**: δ 5.53; **5**: δ 5.52) and C-1″. Further important HMBC cross-peaks were observed between

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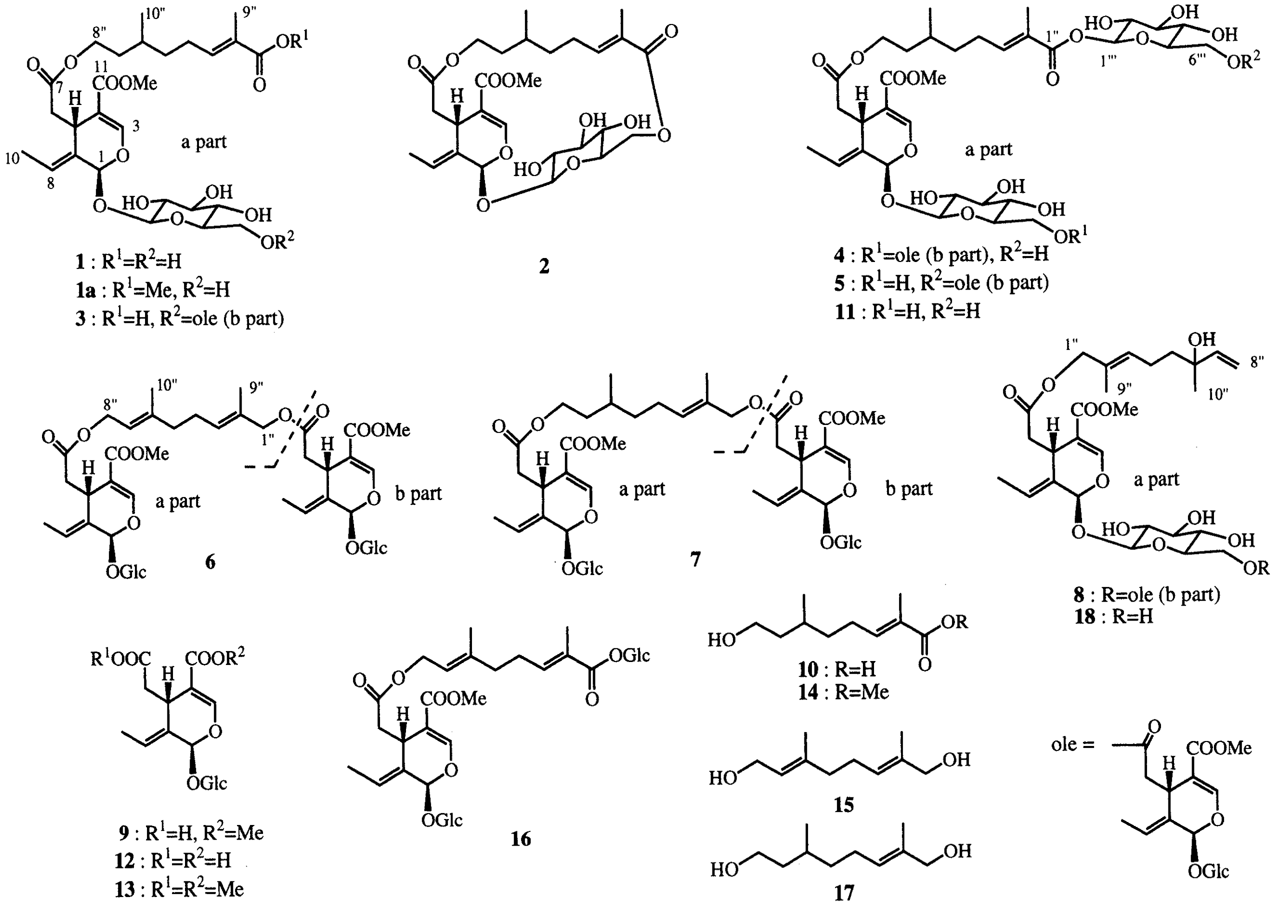

Chart 1

Table 1. ¹H-NMR Spectral Data of Compounds **1**, **1a** and **2**—**8** in CD_3OD (500 MHz)

H	**1**	**1a**	**2**	**3**	
				a part	b part
1	5.93 br s	5.93 br s	5.79 br s	5.85 br s	5.92 br s
3	7.52 s	7.52 s	7.52 s	7.51[a] s	7.53[a] s
5	3.99 dd (9.0, 4.5)	3.99 dd (9.0, 5.0)	4.03 dd (9.0, 4.5)	3.99 dd (9.0, 4.5)	4.01 dd (9.0, 5.0)
6	2.47 dd (14.5, 9.0)	2.47 dd (14.5, 9.0)	2.31 dd (14.5, 9.0)	2.43 dd (14.0, 9.0)	2.47 dd (14.5, 9.0)
	2.70 dd (14.5, 4.5)	2.70 dd (14.5, 5.0)	2.64 dd (14.5, 4.5)	2.70 dd (14.0, 4.5)	2.79 dd (14.5, 5.0)
8	6.11 qd (7.0, 1.0)	6.11 qd (7.0, 1.0)	6.11 qd (7.0, 1.0)	6.10 qd (7.0, 1.5)	6.10 qd (7.0, 1.5)
10	1.74 dd (7.0, 1.5)	1.74 dd (7.0, 1.5)	1.74 dd (7.0, 1.5)	1.739 dd (7.0, 1.5)	1.742 dd (7.0, 1.5)
OMe	3.71 s	3.711 s	3.71 s	3.69[a] s	3.71[a] s
	—	3.710 s	—	—	—
1′	4.80 d (8.0)	4.80 d (8.0)	4.82 d (8.0)	4.81 d (7.5)	4.80 d (8.0)
2′	3.28—3.38 m	3.28—3.34 m	3.34 dd (9.0, 8.0)	3.26—3.42 m	3.26—3.42 m
3′	3.41 t (9.0)	3.40 t (9.0)	3.43 t (9.0)		
4′	3.28—3.38 m	3.28—3.34 m	3.30 t (9.0)		
5′			3.56 ddd (9.0, 6.0, 2.5)	3.53 ddd (9.0, 6.0, 2.5)	
6′	3.66 dd (12.0, 4.5)	3.66 dd (12.0, 6.0)	4.22 dd (12.5, 6.0)	4.20 dd (12.0, 6.0)	3.67 dd (12.0, 6.0)
	3.89 dd (12.0, 2.0)	3.88 dd (12.0, 2.0)	4.55 dd (12.5, 2.5)	4.34 dd (12.0, 2.5)	3.88 dd (12.0, 2.0)
3″	6.74 tq (7.0, 1.0)	6.76 tq (7.5, 1.5)	6.78 tq (7.5, 1.5)	6.69 tq (6.5, 1.0)	
4″	2.20 m	2.24 m	2.23 m	2.20 m	
	2.20 m	2.24 m	2.34 m	2.20 m	
5″	1.32 m	1.32 m	1.34 m	1.43 m	
	1.47 m	1.47 m	1.53 m	1.66 m	
6″	1.60 m	1.60 m	1.53 m	1.58 m	
7″	1.47 m	1.47 m	1.38 m	1.46 m	
	1.70 m	1.69 m	1.67 m	1.66 m	
8″	4.06 dt (11.0, 6.5)	4.06 ddd (11.0, 7.0, 6.0)	3.99 ddd (12.0, 5.5, 4.0)	4.02 ddd (11.0, 7.0, 6.0)	
	4.12 dt (11.0, 7.0)	4.12 dt (11.0, 7.0)	4.16 ddd (12.0, 10.0, 3.0)	4.11 dt (11.0, 7.0)	
9″	1.82 d (1.0)	1.83 d (1.5)	1.84 br s	1.82 d (1.0)	
10″	0.96 d (6.5)	0.95 d (7.0)	0.88 d (6.5)	0.94 d (6.5)	

Table 1. (continued)

H	4		5	
	a part	b part	a part	b part
1	5.85 br s	5.92 br s	5.91 br s	5.93 br s
3	7.52[a] s	7.53[a] s	7.52 s	7.52 s
5	3.99 dd (9.0, 5.0)	4.01 dd (9.0, 5.0)	3.99 dd (9.0, 4.5)	4.00 dd (9.0, 4.0)
6	2.43 dd (14.0, 9.0)	2.47 dd (14.0, 9.0)	2.47 dd (14.0, 9.0)	2.49 dd (14.5, 9.0)
	2.70 dd (14.0, 5.0)	2.78 dd (14.0, 5.0)	2.70 dd (14.0, 4.5)	2.75 dd (14.5, 4.0)
8	6.11 qd (7.0, 1.5)	6.11 qd (7.0, 1.5)	6.09 qd (7.5, 1.0)	6.10 qd (6.5, 1.0)
10	1.743[a] dd (7.0, 1.5)	1.740[a] dd (7.0, 1.5)	1.72 dd (7.5, 1.5)	1.74 dd (6.5, 1.5)
OMe	3.70[a] s	3.72[a] s	3.710[a] s	3.714[a] s
1′	4.80 d (7.5)	4.81 d (7.5)	4.80[a] d (8.5)	4.81[a] d (8.0)
2′	3.30—3.42 m	3.30—3.44 m	3.30—3.44 m	3.30—3.44 m
3′				
4′				
5′	3.54 ddd (9.0, 6.0, 2.0)			
6′	4.20 dd (12.0, 6.0)	3.67[b] dd (12.0, 5.5)	3.66[a] dd (12.0, 5.5)	3.67[a] dd (12.0, 5.5)
	4.34 dd (12.0, 2.0)	3.84[c] dd (12.0, 2.0)	3.89 dd (12.0, 1.0)	3.89 dd (12.0, 1.0)
3″	6.91 tq (7.5, 1.5)		6.92 tq (7.5, 1.5)	
4″	2.25 m		2.27 m	
	2.25 m		2.27 m	
5″	1.32 m		1.30 m	
	1.48 m		1.48 m	
6″	1.56 m		1.60 m	
7″	1.44 m		1.45 m	
	1.66 m		1.70 m	
8″	4.02 ddd (11.0, 7.0. 6.0)		4.06 ddd (11.0, 7.0, 6.5)	
	4.12 dt (11.0, 7.0)		4.13 dt (11.0, 7.0)	
9″	1.87 br s		1.87 br s	
10″	0.94 d (6.0)		0.96 d (7.0)	
1‴	5.53 d (8.0)		5.52 d (7.5)	
2‴	3.42 br t (8.0)		3.30—3.44 m	
3‴	3.30—3.42 m			
4‴				
5‴			3.58 m	
6‴	3.68[b] dd (12.0, 5.5)		4.22 dd (12.0, 5.0)	
	3.88[c] dd (12.0, 2.0)		4.30 dd (12.0, 2.0)	

H	6		7		8	
	a part	b part	a part	b part	a part	b part
1	5.94[a] br s	5.93[a] br s	5.93[a] br s	5.94[a] br s	5.86 br s	5.91 br s
3	7.524[a] s	7.518[a] s	7.52 s	7.52 s	7.51[a] s	7.53[a] s
5	4.00 dd (9.0, 4.5)	3.99 dd (9.5, 4.5)	3.99[a] dd (9.0, 4.5)	4.00[a] dd (9.0, 4.5)	3.99 dd (9.0, 4.5)	4.01 dd (9.0, 4.5)
6	2.48 dd (14.0, 9.0)	2.45 dd (14.0, 9.5)	2.47[a] dd (14.0, 9.0)	2.49[a] dd (14.0, 9.0)	2.45 dd (14.0, 9.0)	2.45 dd (14.0, 9.0)
	2.74 dd (14.0, 4.5)	2.72 dd (14.0, 4.5)	2.71[a] dd (14.0, 4.5)	2.74[a] dd (14.0, 4.5)	2.73 dd (14.0, 4.5)	2.78 dd (14.0, 4.5)
8	6.11 br q (7.0)	6.11 br q (7.0)	6.12 br q (7.0)	6.12 br q (7.0)	6.097 qd (7.0, 1.0)	6.103 qd (7.0, 1.0)
10	1.732[a] dd (7.0, 1.5)	1.730[a] dd (7.0, 1.5)	1.73 dd (7.0, 1.5)	1.74 dd (7.0, 1.5)	1.72 dd (7.0, 1.5)	1.73 dd (7.0, 1.5)
OMe	3.71 s	3.71 s	3.71 s	3.71 s	3.69[a] s	3.71[a] s
1′	4.80 d (7.5)	4.80 d (7.5)	4.80 d (8.0)	4.80 d (8.0)	4.81 d (7.5)	4.80 d (8.0)
2′	3.28—3.34 m	3.28—3.34 m	3.28—3.38 m	3.28—3.38 m	3.30—3.40 m	3.30—3.40 m
3′	3.41 t (9.0)	3.41 t (9.0)	3.41 t (9.0)	3.41 t (9.0)		
4′	3.28—3.34 m	3.28—3.34 m	3.28—3.38 m	3.28—3.38 m		
5′					3.53 ddd (9.0, 6.0, 2.0)	
6′	3.664[a] dd (12.0, 6.0)	3.656[a] dd (12.0, 6.0)	3.66 br dd (12.0, 5.5)	3.66 br dd (12.0, 5.5)	4.17 dd (12.0, 6.0)	3.67 dd (12.0, 6.0)
	3.88 dd (12.0, 2.0)	3.88 dd (12.0, 2.0)	3.88 br d (12.0)	3.88 br d (12.0)	4.35 dd (12.0, 2.0)	3.88 dd (12.0, 2.0)
1″	4.37 br d (12.0)		4.38 br d (12.0)		4.32 br d (12.0)	
	4.48 br d (12.0)		4.49 br d (12.0)		4.47 br d (12.0)	
3″	5.46 tq (7.0, 1.0)		5.48 tq (7.0, 1.0)		5.43 tq (7.0, 1.0)	
4″	2.20 m		2.08 m		2.05 m	
	2.20 m		2.08 m		2.05 m	
5″	2.10 m		1.25 m		1.53 m	
	2.10 m		1.44 m		1.53 m	
6″	—		1.59 m		—	
7″	5.35 tq (7.0, 1.0)		1.44 m		5.91 dd (17.5, 11.0)	
	—		1.70 m		—	
8″	4.54 dd (12.0, 7.0)		4.06 ddd (11.0, 7.0, 6.0)		5.04 dd (11.0, 1.5)	
	4.60 dd (12.0, 7.0)		4.12 dt (11.0, 7.0)		5.21 dd (17.5, 1.5)	
9″	1.66 br s		1.67 br s		1.61 br s	
10″	1.73 br s		0.94 d (6.5)		1.26 s	

Values in parentheses are coupling constants in Hz. *a*) Assignments may be reversed horizontally between a and b parts. *b*, *c*) Assignments may be reversed.

Table 2. ^{13}C-NMR Spectral Data of Compounds **1**, **1a**, **2** and **4**—**7** in CD_3OD (125 MHz)

C	**1**	**1a**	**2**	**4**		**5**		**6**		**7**	
				a part	b part	a part	b part	a part	b part	a part	b part
1	95.15	95.16	94.86	95.19	95.19	95.18	95.23	95.19$^{r)}$	95.16$^{r)}$	95.14$^{w)}$	95.18$^{w)}$
3	155.13	155.12	155.09	155.12	155.21	155.17	155.24	155.19	155.16	155.14$^{x)}$	155.17$^{x)}$
4	109.46	109.47	109.66	109.48$^{b)}$	109.52$^{b)}$	109.47	109.50	109.44	109.41	109.41$^{y)}$	109.44$^{y)}$
5	31.92	31.93	31.95	31.94	31.88	31.82	31.95	31.93	31.93	31.92	31.92
6	41.35	41.35	41.63	41.35	41.47	41.32	41.32	41.30	41.30	41.32	41.32
7	173.32	173.30	173.16	173.07	172.94	173.35	173.08	173.15	173.04	173.31	173.31
8	124.72	124.73	124.36	124.98	124.98	125.00	124.77	124.87$^{s)}$	124.84$^{s)}$	124.74$^{z)}$	124.84$^{z)}$
9	130.76	130.79	130.69	130.62	130.56	130.77	130.57	130.63	130.61	130.66$^{aa)}$	130.72$^{aa)}$
10	13.67	13.67	13.67	13.71$^{c)}$	13.87$^{c)}$	13.72$^{k)}$	13.78$^{k)}$	13.77	13.77	13.72$^{bb)}$	13.74$^{bb)}$
11	168.66	168.65	168.55	168.63$^{d)}$	168.66$^{d)}$	168.67$^{l)}$	168.78$^{l)}$	168.65	168.65	168.64	168.64
OMe	51.93	51.93	51.93	51.99$^{e)}$	52.04$^{e)}$	52.00	52.00	51.97	51.97	51.96	51.96
	—	52.28	—	—	—	—	—	—	—	—	—
1′	100.85	100.86	100.01	100.93	100.93	100.87$^{m)}$	100.91$^{m)}$	100.90$^{t)}$	100.88$^{t)}$	100.85$^{cc)}$	100.88$^{cc)}$
2′	74.82	74.83	75.01	74.69$^{f)}$	74.79$^{f)}$	74.79$^{n)}$	74.83$^{n)}$	74.80	74.80	74.80	74.80
3′	77.99	78.00	77.81	77.86$^{g)}$	78.00$^{g)}$	78.00	78.00	77.97	77.97	77.97	77.97
4′	71.58	71.59	71.61	71.52$^{h)}$	71.52$^{h)}$	71.18$^{o)}$	71.54$^{o)}$	71.56$^{u)}$	71.54$^{u)}$	71.56	71.56
5′	78.51	78.53	75.59	75.51	78.46$^{i)}$	78.45$^{p)}$	78.52$^{p)}$	78.50	78.50	78.49	78.49
6′	62.85	62.86	64.13	64.08	62.39$^{j)}$	62.89$^{q)}$	62.79$^{q)}$	62.85$^{v)}$	62.82$^{v)}$	62.85	62.85
1″	168.66	170.25	168.66	168.17		167.98		71.37		71.56	
2″	127.59	128.65	127.59	128.30		128.25		131.84		131.40	
3″	143.20	144.00	144.19	145.64		145.71		129.88		130.85	
4″	27.12	27.08	26.20	27.31		27.31		26.96		26.12	
5″	36.80	36.69$^{a)}$	35.93	36.60		36.60		39.96		37.54	
6″	30.84	30.79	29.35	30.93		30.91		142.84		30.64	
7″	36.43	36.43$^{a)}$	36.47	36.50		36.43		120.13		36.51	
8″	64.14	64.09	64.08	64.02		64.15		62.54		64.20	
9″	12.66	12.54	12.66	12.54		12.54		14.24		14.21	
10″	19.72	19.70	19.72	19.74		19.71		16.59		19.83	
1‴				95.99		95.85					
2‴				74.03$^{f)}$		73.96$^{n)}$					
3‴				78.18$^{g)}$		78.00					
4‴				71.14$^{h)}$		71.60$^{o)}$					
5‴				78.85$^{i)}$		76.04					
6‴				62.77$^{j)}$		64.72					

a—*cc*) Assignments may be reversed.

the methylene signals (**4**: δ 4.20, 4.34; **5**: δ 4.22, 4.30) and C-7b. The downfield shifted proton signals at δ 4.20 and 4.34 in **4** were assigned to H_2-6′a rather than H_2-6‴ on the basis of a COSY correlation with H-5′a (δ 3.54), which showed a ROESY interaction with H-1′a. On the other hand, the proton signals at δ 4.22 and 4.30 in **5** were assignable to H_2-6‴ with the aid of COSY and ROESY spectra. Consequently, the new compounds were represented by **4** and **5**, and were designated jaspofoliamosides F and G, respectively.

Compound **6** was also isolated as an amorphous powder. Its HR-SI-MS exhibited a molecular ion peak at *m/z* 941.3678 $(M-H)^-$ calculated for $C_{44}H_{61}O_{22}$. The ^{1}H-NMR spectrum of **6** displayed duplicated signals due to two oleoside 11-methyl ester units with additional signals for two vinyl methyl groups at δ 1.66 and δ 1.73 (each br s), two pairs of oxygenated methylene protons at δ 4.37, 4.48 (each br d, $J=12.0$ Hz) and δ 4.54, 4.60 (each dd, $J=12.0$, 7.0 Hz) and two olefinic protons at δ 5.35 and 5.46 (each tq, $J=7.0$, 1.0 Hz). The ^{13}C-NMR spectrum of **6** showed, in addition to the signals ascribable to two oleoside 11-methyl ester units, ten carbon resonances including two methyls, four methylenes (two deshielded by oxygenation), two olefinic methines and two quaternary sp^2 carbons. The carbon signals were evaluated as 10-hydroxygeraniol (**15**) by HMBC and ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) spectra as well as comparison of its ^{13}C-NMR spectral data with the carbon signals due to the monoterpene portion in jaspofoliamoside B (**16**). The *E*-configuration of the olefinic bonds at C-2″ and C-6″ was confirmed by rotating frame nuclear Overhauser effect (ROE) interactions observed between H_3-9″ and H_2-4″ and between H_3-10″ and H_2-8″ in the ROESY spectrum of **6**. The HMBC technique revealed cross-peaks between H_2-1″ (δ 4.37, 4.48) and C-7b and between H_2-8″ (δ 4.54, 4.60) and C-7a, suggesting that each of the C-1″ and C-10″ hydroxyl groups of a 10-hydroxygeraniol moiety was esterified with an oleoside 11-methyl ester unit. Accordingly, compound **6** was formulated as shown and designated jaspogeranoside A.

UV and IR spectral features of compound **7** were analogous to those of jaspogeranoside A (**6**). Its ^{1}H- and ^{13}C-NMR (Tables 1, 2) spectral data, excluding the signals attributable to the monoterpene moiety, were in good agreement with those of **6**. The ^{1}H-NMR spectrum of **7** demonstrated a three-proton doublet at δ 0.94 but lacked the signals for a vinyl methyl group and an olefinic proton such as were observed in **6**. In the ^{13}C-NMR spectrum of **7**, the signals assignable to C-6″ and C-7″ of the monoterpene unit appeared as two sp^3 carbons (δ 30.64, δ 36.51) instead of two sp^2 carbons (δ 142.84, δ 120.13) as in **6**. The *E*-configuration of the olefinic bond at C-2″ was deduced from the ROE cross-peaks between H-1″ and H-3″ and between the vinyl methyl and H_2-4″ observed in the ROESY spectrum of **7**. Thus, it was concluded that the monoterpene unit in **7** should be 10-hydroxycitronellol (**17**). A combination of 2D-NMR experiments allowed us to determine the same ester linkages as in **6** and, thereby, to establish that glucoside **7** was the 6″,7″-dihydro derivative of **6**. Therefore, the structure of jaspogeranoside B is the one given by **7**.

Glucoside **8**, named jaspolinaloside B, was found to have the formula $C_{44}H_{62}O_{22}$ from its HR-SI-MS. Its ^{1}H-NMR spectrum indicated that **8** possessed a jaspolinaloside A (**18**)[8] moiety and an additional oleoside 11-methyl ester unit in its structure. The downfield shift of H_2-6′a (δ 4.17, 4.35) was ascribed to acylation effects, and indicated that the hydroxyl group at C-6′a was linked to the C-7b carboxyl group. Furthermore, the monoterpene unit in **8** was confirmed to be 1-hydroxylinalool as in **18** by ROE interaction. Thus, the structure of jaspolinaloside B was determined to be **8**.

The absolute configuration of the monoterpene unit in the new compounds could not be determined as had been done with jaspofoliamoside A (**11**) and jaspolinaloside A (**18**),[6] owing to a lack of material.

Experimental

General experimental procedures were as described previously.[5]

Plant Material and Isolation of Glucosides The source of plant material and isolation of glucosides are described in previous publications.[4,5] Fraction No. 26 (50% MeOH effluent, 305.8 mg) was further purified by preparative HPLC (μBondasphere 5 μ C18-100 Å, MeOH–H_2O, 11 : 9), giving GI 5 (6.1 mg), jaspolyoleoside A (3.3 mg), **1** (6.1 mg) and **4** (6.6 mg) in order of elution. The following fractions were also purified by preparative HPLC (μBondasphere 5 μ C18-100 Å, MeOH–H_2O, 57 : 43 or MeCN–H_2O, 2 : 3). Fraction No. 27 (50—55% MeOH effluent, 204.0 mg) yielded jaspolyoleoside B (6.2 mg), jaspolyoleoside C (4.4 mg), **1** (9.8 mg) and **5** (7.1 mg); Fraction No. 28 (55% MeOH effluent, 263.7 mg): jaspolyoleoside C (1.8 mg) and **8** (2.5 mg); fraction No. 29 (60% MeOH effluent, 291.6 mg): **2** (8.6 mg), **3** (2.5 mg) and **6** (14.5 mg); fraction No. 30 (60% MeOH effluent, 112.3 mg): **6** (1.3 mg) and **7** (5.9 mg).

Jaspofoliamoside C (**1**): Colorless amorphous powder, $[\alpha]_D^{26}$ $-152°$ (c=0.66, MeOH). UV λ_{max}^{MeOH} nm (log ε): 221 (4.22). IR ν_{max}^{KBr} cm^{-1}: 3419, 1732, 1709, 1636, 1078. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. Significant HMBC correlations: H_2-6→C-7, H_2-8″→C-7. Significant nuclear Overhauser effect (NOE) correlation: H_3-9″→H_2-4″. HR-SI-MS *m/z*: Calcd for $C_{27}H_{39}O_{13}$ $(M-H)^-$: 571.2392. Found: 571.2404.

Jaspofoliamoside D (**2**): Colorless amorphous powder, $[\alpha]_D^{28}$ $-138°$ (c=0.36, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223.5 (4.27). IR ν_{max}^{KBr} cm^{-1}: 3405, 1736, 1709, 1634, 1078. ^{1}H- and ^{13}C-NMR see Tables 1 and 2. Significant HMBC correlations: H-3→C-11, OMe→C-11, H_2-6→C-7, H_2-8″→C-7, H_2-6′→C-1″, H_3-9″→C-1″, H-1′→C-1. Significant NOE correlation: H_3-9″→H_2-4″. HR-SI-MS *m/z*: Calcd for $C_{27}H_{37}O_{12}$ $(M-H)^-$: 553.2286. Found: 553.2279.

Jaspofoliamoside E (**3**): Colorless amorphous powder, $[\alpha]_D^{23}$ $-157°$ (c=0.20, MeOH). UV λ_{max}^{MeOH} nm (log ε): 232.5 (4.33). IR ν_{max}^{KBr} cm^{-1}: 3399, 1734, 1707, 1636, 1078. ^{1}H-NMR: see Table 1. Significant NOE correlation: H_3-9″→H_2-4″. SI-MS *m/z*: 957 $(M-H)^-$, 571. HR-SI-MS *m/z*: Calcd for $C_{44}H_{61}O_{23}$ $(M-H)^-$: 957.3606. Found: 957.3585.

Jaspofoliamoside F (**4**): Colorless amorphous powder, $[\alpha]_D^{25}$ $-148°$ (c=0.43, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.43). IR ν_{max}^{KBr} cm^{-1}: 3407, 1731, 1709, 1636, 1076. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OMe(a)/OMe(b)→C-11a/C-11b, H_2-6a (δ 2.43, 2.70)→C-7a (δ 173.07), H_2-8″→C-7a, H-1′a→C-1a, H_2-6′a (δ 4.20, 4.34)→C-7b (δ 172.94), H_2-6b (δ 2.47, 2.78)→C-7b, H-1‴→C-1″. Significant ROE correlations: H_3-9″→H_2-4″, H-5′a (δ 3.54)→H-1′a (δ 4.80). HR-SI-MS *m/z*: Calcd for $C_{50}H_{71}O_{28}$ $(M-H)^-$: 1119.4134. Found: 1119.4124.

Jaspofoliamoside G (**5**): Colorless amorphous powder, $[\alpha]_D^{28}$ $-153°$ (c=0.32, MeOH). UV λ_{max}^{MeOH} nm (log ε): 230 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3425, 1709, 1632, 1076. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OMe(a)/OMe(b)→C-11a/C-11b, H-1′a→C-1a, H_2-8″→C-7a (δ 173.36), H_2-6‴ (δ 4.22, 4.30)→C-7b (δ 173.08), H-6b (δ 2.75)→C-7b, H-1‴ (δ 5.52)→C-1″. Significant ROE correlations: H_3-9″→H_2-4″, H-5‴ (δ 3.58)→H-1‴. HR-SI-MS *m/z*: Calcd for $C_{50}H_{71}O_{28}$ $(M-H)^-$: 1119.4134. Found: 1119.4173.

Jaspogeranoside A (**6**): Colorless amorphous powder, $[\alpha]_D^{26}$ $-194°$ (c=0.68, MeOH). UV λ_{max}^{MeOH} nm (log ε): 237 (4.33). IR ν_{max}^{KBr} cm^{-1}: 3419, 1732, 1713, 1634, 1076. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OMe(a)/OMe(b)→C-11a/C-11b, H_2-1″→C-7b (δ 173.04), H_2-8″→C-7a (δ 173.14). Significant ROE correlations: H_3-9″→H_2-4″, H_3-10″→H_2-8″. HR-SI-MS *m/z*: Calcd for $C_{44}H_{61}O_{22}$ $(M-H)^-$: 941.3657. Found: 941.3678.

Jaspogeranoside B (**7**): Colorless amorphous powder, $[\alpha]_D^{26}$ $-162°$ (c=0.48, MeOH). UV λ_{max}^{MeOH} nm (log ε): 236.5 (4.26). IR ν_{max}^{KBr} cm^{-1}: 3412, 1734, 1709, 1630, 1078. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. Significant HMBC correlations: H-3a/H-3b→C-11a/C-11b, OMe(a)/OMe(b)→C-11a/C-11b, H_2-1″→C-7b (δ 173.08), H_2-8″→C-7a (δ 173.31). Significant ROE correlations: H-1″ (δ 4.49)→H-3″, H_3-9″→H_2-4″. HR-SI-MS *m/z*: Calcd for $C_{44}H_{63}O_{22}$ $(M-H)^-$: 943.3814. Found: 943.3791.

Jaspolinaloside B (**8**): Colorless amorphous powder, $[\alpha]_D^{26}$ $-128°$ (c=0.16, MeOH). UV λ_{max}^{MeOH} nm (log ε): 235 (4.21). IR ν_{max}^{KBr} cm^{-1}: 3387, 1734, 1709, 1632, 1080. ^{1}H-NMR: see Table 1. Significant ROE correlations: H-1′a→H-5′a, H_2-1″→H-3″, H_3-9″→H_2-4″. HR-SI-MS *m/z*: Calcd for $C_{44}H_{61}O_{22}$ $(M-H)^-$: 941.3657. Found: 941.3637.

Methylation of 1 A solution of **1** (4.6 mg) in MeOH (1 ml) was treated with ethereal CH_2N_2 to give **1a** (4.6 mg). Colorless amorphous powder. ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. HR-SI-MS *m/z*: Calcd for $C_{28}H_{41}O_{13}$ $(M-H)^-$: 585.2549. Found: 585.2554.

Methanolysis of 2 A solution of **2** (0.6 mg) in dry MeOH (1 ml) and 0.1 M NaOMe (1 ml) was stirred for 7 h at room temperature. The reaction mixture was neutralized with AcOH–MeOH and concentrated *in vacuo*. The two main products were identified as oleoside dimethyl ester and dihydrofoliamenthic acid methyl ester, respectively (^{1}H-NMR, HPLC).

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References and Note

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8) Compound **18**, which had been previously designated jaspolinaloside, was renamed jaspolinaloside A in this publication.