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SECOIRIDOID GLUCOSIDES FROM *JASMINUM UROPHYLLUM*

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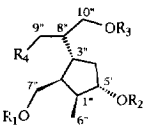
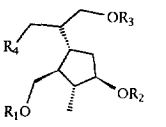
Key Word Index—*Jasminum urophyllum*; Oleaceae; secoiridoid glucosides; jasurosides E, F, G.

Abstract—The three new secoiridoid glucosides, jasurosides E, F and G, have been isolated from the leaves and stems of *Jasminum urophyllum*, and their structures established. © 1997 Elsevier Science Ltd

INTRODUCTION

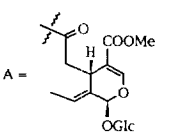
Plants of the genus *Jasminum* are rich in secoiridoid glycosides [1–5]. Some of the species were known for their medicinal applications in Chinese folklore [6]. For example, the flowers of *J. sambac* (L.) Ait. were used for the treatment of diarrhoea, dermatitis and ophthalmitis. The whole plant of *J. hemsleyi* Yamamoto has been used for treating ophthalmitis and weakness. In a phytochemical investigation of *J. urophyllum* Hemsley, we primarily focused on the isolation and structures of secoiridoid glucosides. *J. urophyllum*, an evergreen shrub, is distributed over the mountainous areas of central Taiwan [7]. This species was noted for its morphological similarity to *J. lanceolarium* Roxb. In addition to the different distribution, the leaves of *J. urophyllum* are smaller than those of *J. lanceolarium*. Nevertheless, these two species were mistakenly combined into one species in the past [8]. It seemed worthwhile to attempt to solve this problem by chemotaxonomy. Previously, we reported on the isolation and structural elucidation of jasurosides A–D (**3**–**6**) from whole plants of *J. urophyllum* [9]. Re-investigation of the constituents of this plant has resulted in the isolation of three additional new secoiridoid glycosides together with jasurosides A–C (**3**–**5**) and 10-hydroxyoleoside 7,11 dimethyl ester (**14**) from the *n*-BuOH-soluble layer and jasminoside (**15**) [10, 11] from the EtOAc-soluble layer.

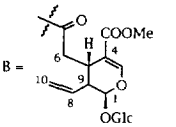


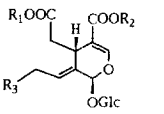


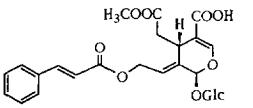
1 R_1 = A, R_2 = R_3 = R_4 = H
2 R_1 = H, R_2 = A, R_3 = R_4 = H
3 R_1 = R_2 = A, R_3 = R_4 = H
4 R_1 = R_2 = R_3 = A, R_4 = H
5 R_1 = R_2 = A, R_3 = H, R_4 = OH
6 R_1 = R_2 = R_3 = A, R_4 = OH
7 R_1 = R_2 = R_3 = R_4 = H

8 R_1 = A, R_2 = H, R_3 = B, R_4 = H
9 R_1 = A, R_2 = R_3 = R_4 = H
10 R_1 = H, R_2 = A, R_3 = R_4 = H
11 R_1 = R_2 = R_3 = R_4 = H
12 R_1 = B, R_2 = R_3 = A, R_4 = OH









13 R_1 = R_2 = R_3 = H
14 R_1 = R_2 = Me, R_3 = OH

15

RESULTS AND DISCUSSION

Fractionation of the ethanolic extracts of the leaves and stems of *J. urophyllum* as described in the Experimental gave three new jasurosides, E (**1**), F (**2**) and G (**8**), and the known jasminoside (**15**) and 10-hydroxyoleoside 7,11 dimethyl ester (**14**). Known compounds were identified by comparing their spectral data (^{1}H, ^{13}C NMR, MS and [α]) with those of authentic samples.

Jasuroside E (**1**) was assigned the molecular formula $C_{27}O_{42}O_{13}$ (FAB-MS, m/z = 597 $[M+Na]^+$). Comparison of the ^{1}H (Table 1) and ^{13}C NMR (Table 2) spectra with those of **3** revealed that it contained a same basic skeleton as **3**. The difference between them was that the ^{13}C NMR data of **1** exhibited only one set of oleoside methyl ester moiety signals c.f. two in **3**. Oleoside methyl ester moiety was placed at C-7″ by

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Table 1. ^{1}H NMR spectral data* (in CD_3OD, 300 MHz), for compounds **1**, **2**, **3** and **8**

			3		**8**	
H	**1**	**2**	A	A	A	B
1	5.94 *s*	5.96 *s*	5.95 *s*	5.94 *s*	5.94 *s*	5.47 *s*
3	7.53 *s*	7.54 *s*	7.52 *s*	7.52 *s*	7.53 *s*	7.48 *s*
5	4.00 *dd* (4.6, 9)	4.00 *dd* (4.4, 9)	4.00 *dd* (3.5, 6.6)	4.00 *dd* (4, 7)	4.00 *m*	3.23 *m*
6	2.50 *dd* (9, 14)	2.43 *dd* (9, 14.4)	2.52 *dd* (10.5, 6.6)	2.52 *dd* (10.5, 7)	2.49 *dd* (9, 14)	2.33 *dd* (9, 16)
	2.72 *dd* (4.6, 14)	2.70 *dd* (4.4, 14.4)	2.72 *dd* (10.5, 3.5)	2.72 *dd* (10.5, 4)	2.73 *dd* (4.8, 14)	2.89 *dd* (6.6, 16)
8	6.12 *q* (7.2)	6.11 *q* (7.2)	6.11 *q* (5.4)	6.11 *q* (5.4)	6.11 *q* (6.6)	5.65 *m*
9						3.88 *m*
10	1.75 *d* (7.2)	1.75 *d* (7.2)	1.74 *d* (5.4)	1.74 *d* (5.4)	1.75 *d* (6.6)	5.24 *m*
1″	1.72 *m*	2.01 *m*	1.95 *m*		1.80 *m*	
2″	1.81 *m*	1.70 *m*	1.82 *m*		1.86 *m*	
3″	1.70 *m*	2.04 *m*	1.84 *m*		1.70 *m*	
4″	1.55 *m*	1.59 *m*	1.64 *m*		1.84 *m*	
	1.96 *m*	1.64 *m*	2.08 *m*		1.96 *m*	
5″	4.04 *m*	5.00 *m*	5.04 *dd* (4, 6.6)		3.98 *m*	
6″	0.98 *d* (5.6)	0.94 *d* (7.2)	0.94 *d* (5.1)		0.99 *d* (6.9)	
7″	4.17 *dd* (4.4, 11)	3.88 *dd* (2, 11)	4.21 *m*		4.17 *m*	
	3.93 *dd* (5.6, 11)	3.66 *dd* (5.8, 11)	3.96 *dd* (4, 8.6)		3.90 *m*	
8″	1.74 *m*	1.73 *m*	1.65 *m*		1.65 *m*	
9″	1.00 *d* (6.8)	0.99 *d* (6.4)	0.99 *d* (5.1)		1.03 *d* (6.3)	
10″	3.41 *m*	3.34 *m*	3.31 *m*		3.41 *m*	
	3.59 *m*	3.52 *m*	3.59 *m*		3.59 *m*	
COOMe	3.72 *s*	3.72 *s*	3.72 *s*	3.72 *s*	3.72 *s*	3.67 *s*
1′	4.81 *d* (8)	4.81 *d* (7.6)	4.80	4.80	4.81 *d* (7.8)	4.60 *d* (7.8)
2′–6′	3.30–3.90 *m*	3.30–3.90 *m*	3.30–4.00 *m*	3.30–4.00 *m*	3.30–3.90	3.30–3.90 *m*

* δ in ppm (J in Hz); TMS as internal standard.

the signal δ_C 68.1 (C-7″) and δ_H 4.17 and 3.93 (H-7″). In addition, the signals of H-5″ (δ 5.04) and C-5″ (δ 80.0) in **3** were upfield shifted to δ 4.04 and δ 75.7, respectively, in **1**. Moreover, the carbon signals of C-1″, 5″ and 6″ (δ 43.2, 75.7 and 14.0) in the triol moiety of **1** were quite different from those in jasmesoside which have the corresponding signals at δ 46.8, 79.7 and 18.4, respectively [12]. It was assumed that both the C-1″ methyl and the C-5″ proton in **1** have a β-orientation relative to α in those of common secoiridoids such as jasmesoside. The assignment of each proton in the triol nucleus of **1** was established by the COSY spectrum.

Upon acetylation compound **1** provided a hexa-acetate, which showed a $[M]^+$ at m/z 826 in the EI mass spectrum. Alkaline hydrolysis of **1** yielded compound **7** and a secoiridoid glucoside (**13**), which was methylated with diazomethane to furnish the known dimethyl ether **14**. The ^{13}C NMR spectra of **7** and **1** also agreed with the site of connection of the oleoside with the triol. The downfield shift (+4.4 ppm) of C-2″ and upfield shift (−2.6 ppm) of C-7″ in the triol (**7**) relative to those in **1**, suggested that the C-7″ hydroxyl group in the triol was attached to the oleoside methyl ester. Because the relative stereochemistry of **3** has been determined by NOESY studies, the chiral centres at the salient carbons of **1** are the same as those of **3** [9].

Jasuroside F (**2**) showed UV absorption (236 nm), IR bands (3400, 1708 and 1633 cm^{-1}) and ^{1}H NMR spectral data (Table 1) similar to those of compound **1** suggesting that it was a close analogue of **1**. Compound **2** gave the same quasi-molecular ion $[M+Na]^+$ at m/z 597 in its FABMS spectrum and was assigned the same molecular formula as **1**. The ^{13}C NMR spectrum of **2** (Table 2) was close to that of **1** except for the signals of C-2″, 5″ and C-7″. The signal of C-5″ at δ 79.9 (c.f. δ 75.7 in **1**) and the signals of C-7″ at δ 64.8 and C-2″ at δ 51.1 (c.f. δ 68.1 and 47.9 in **1**, respectively) indicated the oleoside moiety was located at the C-5″ position. Alkaline hydrolysis of **2** gave products, identical with the hydrolytic products of jasuroside E (**1**). Upon acetylation compound **2** yielded a hexa-acetate, which had a $[M]^+$ at m/z 826. The ^{1}H and ^{13}C NMR data of the hexa-acetate were all in agreement with the structure of **2**. On the basis of the spectral evidence and hydrolytic results, the stereochemistry of **2** was therefore determined.

Jasuroside G (**8**) was assigned the molecular formula $C_{44}H_{64}O_{23}$ (FAB-MS, m/z = 983 $[M+Na]^+$). The UV band at 236 nm and the IR absorption (3399, 1708 and 1633 cm^{-1}) resembled those of **1**–**3**, suggesting a similar analogue. Comparison of the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) of **8** with those of **3** revealed that compound **8** contained a secoxyloganin (unit B, δ 5.24, 134.5 and δ 120.7, H-8, H-10, C-8, C-10) moiety while compound **3** had two oleoside methyl ester (unit A) moieties. In addition, the signals arising

Table 2. ^{13}C NMR spectral data* (CD_3OD, 75.4 MHz) for compounds **1**, **2**, **3** and **8**

			3		**8**	
C	**1**	**2**	part A	part A	part A	part B
1	94.9 *d*	95.2 *d*	95.2 *d*	94.8 *d*	95.0 *d*	97.5 *d*
3	155.1 *d*	155.2 *d*	155.2 *d*	155.1 *d*	155.1 *d*	153.7 *d*
4	109.4 *s*	109.4 *s*	109.4 *s*	109.4 *s*	109.3 *s*	109.9 *s*
5	32.0 *d*	31.9 *d*	32.1 *d*	31.9 *d*	31.9 *d*	29.0 *d*
6	41.2 *t*	41.2 *t*	41.5 *t*	41.2 *t*	41.3 *t*	35.5 *t*
7	173.3 *s*	173.0 *s*	173.4 *s*	172.9 *s*	173.2 *s*	174.3 *s*
8	124.7 *d*	124.7 *d*	124.7 *d*	124.7 *d*	124.7 *d*	134.5 *d*
9	130.7 *s*	130.8 *s*	130.8 *s*	130.7 *s*	130.7 *s*	45.4 *d*
10	13.6 *q*	13.7 *q*	13.8 *q*	13.7 *q*	13.7 *q*	120.7 *t*
COOMe	168.6 *s*	168.5 *s*	168.7 *s*	168.6 *s*	168.6 *s*	168.7 *s*
	51.9 *q*	51.9 *q*	51.9 *q*	51.9 *q*	52.0 *q*	51.8 *q*
1″	43.2 *d*	41.1 *d*	41.8 *d*		46.7 *d*	
2″	47.9 *d*	51.1 *d*	48.1 *d*		48.1 *d*	
3″	43.1 *d*	41.9 *d*	42.6 *d*		42.6 *d*	
4″	37.0 *t*	35.2 *t*	35.3 *t*		37.6 *t*	
5″	75.7 *d*	79.9 *d*	80.0 *d*		79.4 *d*	
6″	14.0 *q*	14.4 *q*	14.1 *q*		18.3 *q*	
7″	68.1 *t*	64.8 *t*	67.2 *t*		68.9 *t*	
8″	40.8 *d*	41.5 *d*	41.0 *d*		37.6 *d*	
9″	16.6 *q*	16.7 *q*	16.3 *q*		16.2 *t*	
10″	66.5 *t*	67.2 *t*	66.4 *t*		68.9 *t*	
g-1	100.6 *d*	100.9 *d*	100.8 *d*	100.5 *d*	100.7 *d*	100.0 *d*
g-2	74.8 *d*	74.7 *d*	74.8 *d*	74.8 *d*	74.6 *d*	74.7 *d*
g-3	78.5 *d*	78.4 *d*	78.6 *d*	78.5 *d*	78.3 *d*	78.4 *d*
g-4	71.5 *d*	71.6 *d*	71.6 *d*	71.6 *d*	71.5 *d*	71.6 *d*
g-5	77.9 *d*	77.9 *d*	78.0 *d*	77.5 *d*	77.9 *d*	78.0 *d*
g-6	62.8 *t*	62.7 *t*	62.9 *t*	62.9 *t*	62.7 *t*	62.9 *t*

* Multiplicities determined by DEPT.

from the cyclopentane moiety were different from those in **3**. Acetylation of **8** yielded a nona-acetate. The structure of compound **8**, which contains a moiety of jasmesoside (**9**), was revealed by detailed comparison of the ^{13}C NMR data of compound **8** with those of jasmesoside (**9**) and that of ester **10** [12]. To prove this assumption, compound **8** yielded **11** on normal alkaline hydrolysis. Comparison of ^{13}C NMR data of **11** with those of **8** revealed downfield shifts for C-10″ (+2.2 ppm) and C-7″ (+2.5 ppm), and upfield shifts for C-2″ (−2.9 ppm) and C-8″ (−3.7 ppm), confirming the ester functions at C-10″ and C-7″ and, of course, a free hydroxy at C-5″. Further, the secoxyloganin unit was determined at C-10″ rather than at C-7″ by comparing the ^{13}C NMR signals of the triol moiety in **8** with those of molihuaside B (**12**) [13]. Although secoxyloganin is very uncommon in Oleaceae, the occurrence of this moiety has been reported in the flowers of *J. sambac* [13]. On partial hydrolysis, **8** provided a compound identical with jasmesoside (**9**) [12]. This finding completely eliminated jasuroside G (**8**) having a moiety of ester **10** from consideration. Also, the results from hydrolysis of **8** suggested that compound **8** has the same stereochemistry as **9**. On the basis of spectral evidence and chemical correlation, compound **8** was established as 10″-*O*-secoxyloganinjasmesoside.

In summary, compounds **1**–**6** and **8** from *J. urophyllum* are di- or tri meric secoiridoid glucosides. The structures of these compounds are quite different from those of jaslanceosides A–E, recently isolated from *J. lanceolarium* [11, 14]. These two species both contain two compounds, jasminoside (**15**) and 10-hydroxyoleoside 7,11 dimethyl ester (**14**), normally found in oleaceaous plants. The above results are in accord with the morphological difference between the two taxa and indicate that they should indeed be treated as two different species.

EXPERIMENTAL

General. EI-MS and FAB-MS: VG Quattro 5022 Mass spectrometer; the ^1H, ^{13}C NMR, DEPT and COSY: Varian FT-300 and Varian FT-400 spectrometers.

Plant material. J. urophyllum Hemsley was collected in June 1995, in Tai-chung County, Taiwan. A voucher specimen (TP 260-6) is deposited in the Institute of Marine Resources, National Sun Yat-sen University.

Extraction and isolation. Fresh leaves and stems (1.5 kg) were ground and extracted with EtOH (31 × 3). The combined EtOH extracts were concd to a green tar (110 g), which was mixed with H_2O (600 ml) to

form a suspension. The suspension was extracted with EtOAc (300 ml × 2) to give the EtOAc-soluble fr. (40 g) and then extracted with *n*-BuOH (300 ml × 3). The *n*-BuOH-soluble fr., after concn *in vacuo* (30 g), was applied on a LH-20 column (750 g) and eluted with MeOH to give a residue (18 g). This residue was chromatographed on a silica gel column (180 g) and eluted with solvent mixt. of $CHCl_3$–MeOH (5:1, 2 l) to give frs A (0.3 g), B (3.3 g), C (5.5 g), D (3.8 g) and E (4.6 g). Fr. B was rechromatographed on an RP-C18 column (200 g) and eluted with solvent mixts of MeOH–H_2O (1:4, 450 ml; 2:3, 450 ml; 1:1, 500 ml) to yield seven frs. Fr. B1 contained 10-hydroxyoleoside 7,11-dimethyl ester (**14**). Part of fr. B4 (150 mg) was subjected to prep. TLC (silica gel, 20 × 20 cm, 1 mm thickness × 3) developed with the lower layer of the solvent mixt. $CHCl_3$–MeOH–H_2O (43:37:20) to yield jasuroside E (**1**, 40 mg) and jasuroside F (**2**, 24 mg) (compound **2** more polar than compound **1**). Fr. B6 yielded jasuroside A (**3**, 330 mg) without purification. Fr. C was chromatographed on a RP-C18 column (200 g) and eluted with solvent mixts; of MeOH–H_2O (1:4, 500 ml; 2:3, 500 ml; 1:1, 900 ml) to yield nine frs. Jasurosides C (**5**, 587 mg), A (**3**, 863 mg) and G (**8**, 53 mg) were obtained directly from frs C5, C7 and C8, respectively. Fr. C9 was sepd by prep. TLC (silica gel, 20 × 20 cm, 1 mm thickness) developed with the lower layer of the solvent mixt. $CHCl_3$–MeOH–H_2O (43:37:20) to yield jasuroside B (**4**, 35 mg) and jasuroside G (**8**, 28 mg). Part (7 g) of the EtOAc-soluble fr. was applied on a LH-20 column (100 g) and eluted with MeOH to give a secoiridoid containing residue (1.4 g). Further sepn of the residue by silica gel column using solvent mixt. of $CHCl_3$/MeOH with increasing polarity yielded jasminoside (**15**, 12 mg).

Jasuroside E (**1**). Isolated as an amorphous solid; $[\alpha]_D^{25}$ −143° (MeOH, *c* 0.2); UV λ_{max}^{MeOH} nm (log ε): 236 (4.04); IR ν_{max}^{neat} cm^{-1}: 3399, 2958, 2884, 1693, 1633, 1513, 1440, 1382, 1305, 1265, 1205, 1160, 991, 854, 815, 769; ^1H and ^{13}C NMR: Tables 1 and 2; FABMS *m/z*: 597 $[M+Na]^+$.

Jasuroside E hexa-acetate. Acetylation (Ac_2O–Pyridine; 1:1; room temp.) of **1** (25 mg) gave Jasuroside E hexa-acetate (21 mg) as a solid. $[\alpha]_D^{25}$ −101° ($CHCl_3$, *c* 0.1); IR ν_{max}^{neat} cm^{-1}: 3018, 2962, 2881, 1737, 1633, 1506, 1436, 1373, 1303, 1230, 1164, 1128, 1070, 1041, 979, 908, 856, 815, 757, 705, 667; ^1H ($CDCl_3$, 300 MHz): δ 5.69 (1H, *s*, H-1), 7.46 (1H, *s*, H-3), 4.00 (1H, *m*, H-5), 2.70 (1H, *dd*, *J* = 14.7, 4.2 Hz, H-6α), 2.43 (1H, *m*, H-6β), 6.00 (1H, *q*, *J* = 7.2 Hz, H-8), 1.74 (3H, *d*, *J* = 7.2 Hz, H-10), 3.71 (3H, *s*, COOMe), 5.05 (1H, *m*, H-5″), 0.95 (3H, *d*, *J* = 6.9 Hz, H-6″), 3.95 (1H, *m*, H-7″a), 4.15 (1H, *m*, H-7″b), 0.97 (3H, *d*, *J* = 7.2 Hz, H-9″), 3.70–3.84 (2H, *m*, H-10″), 5.00–5.16 (3H, *m*, H-1′, 2′, 4′), 5.27 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-3′), 3.78 (1H, *m*, H-5′), 4.13 (1H, *m*, H-6′), 4.31 (1H, *dd*, *J* = 12, 4.7 Hz, H-6′), 2.01, 2.02, 2.04, 2.05 × 2, 2.07, 2.08 (18H, *s*, OAc); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 93.5 (*d*, C-1), 153.0 (*d*, C-3), 108.6 (*s*, C-4), 30.2 (*d*, C-5), 39.9 (*t*, C-6), 170.5 (*s*, C-7), 124.7 (*d*, C-8), 128.2 (*s*, C-9), 13.5 (*q*, C-10), 166.9 (*s*, C-11), 51.4 (*q*, OMe), 40.8 (*d*, C-1″), 46.6 (*d*, C-2″), 42.2 (*d*, C-3″), 33.7 (*t*, C-4″), 77.7 (*d*, C-5″), 13.5 (*q*, C-6″), 67.5 (*t*, C-7″), 36.0 (*d*, C-8″), 16.3 (*q*, C-9″), 66.1 (*t*, C-10′), 96.9 (*d*, C-1′), 70.6 (*d*, C-2′), 72.4 (*d*, C-3′), 68.2 (*d*, C-4′), 72.2 (*d*, C-5′), 61.7 (*t*, C-6′), 21.1, 20.9, 20.7, 20.6, 20.5, 20.4 (*q*, $CO\underline{C}H_3$), 169.3, 169.4, 170.1, 170.7, 171.1, 171.2 (*s*, $\underline{C}OCH_3$). EIMS 30 eV, *m/z* (rel. int.): 826 $[M]^+$ (0.03), 494 (1), 405 (1), 331 (60), 271 (13), 169 (100), 135 (39), 127 (24), 109 (68).

Alkaline hydrolysis of jasuroside E (**1**). Hydrolysis (0.5 M NaOH, 2 ml; room temp.) of **1** (100 mg) and work-up as usual provided a residue, which was sepd by silica gel CC (5 g) using $CHCl_3$–MeOH (10:1) as eluent to give the triol **7** (12 mg) and a secoiridoid glucoside **13** (40 mg). The latter was further methylated with CH_2N_2–Et_2O to give **14**, identical (^1H NMR, [α], and TLC) with oleoside dimethyl ester. Compound **7**, syrup; $[\alpha]_D^{25}$ −14.7° (MeOH, *c* 0.34); ^1H NMR (CD_3OD, 300 MHz): δ 1.70 (2H, *m*, H-1″, 2″), 1.55 (2H, *m*, H-3″, 4″a), 1.88 (2H, *m*, H-4″b, 8″), 4.03 (1H, *m*, H-5″), 0.97 (3H, *d*, *J* = 6.5 Hz, H-6″), 3.55 (2H, *m*, H-7″), 0.99 (3H, *d*, *J* = 5.4 Hz, H-9″), 3.37 (1H, *dd*, *J* = 6.6, 11 Hz, H-10″a), 3.60 (1H, *dd*, *J* = 4.2, 11 Hz, H-10″b); ^{13}C NMR (75.4 MHz, CD_3OD): δ 42.4 (*d*, C-1″), 51.3 (*d*, C-2″), 41.2 (*d*, C-3″), 37.1 (*t*, C-4″), 75.8 (*d*, C-5″), 14.4 (*s*, C-6″), 65.5 (*s*, C-7″), 42.3 (*s*, C-8″), 16.7 (*d*, C-9″), 66.8 (*t*, 10″), FABMS *m/z*: 189 $[M+H]^+$, 211 $[M+Na]^+$.

Jasuroside F (**2**). Isolated as an amorphous powder; $[\alpha]_D^{25}$ −130° (MeOH, *c* 0.1); UV λ_{max}^{MeOH} (log ε) nm: 236 (4.03); IR ν_{max}^{neat} cm^{-1}: 3399, 2927, 2879, 1708, 1633, 1461, 1440, 1382, 1305, 1284, 1205, 1191, 1160, 1078, 991, 943, 921, 854, 817, 771; ^1H and ^{13}C NMR: Tables 1 and 2; FABMS *m/z*: 597 $[M+Na]^+$.

Alkaline hydrolysis of jasuroside F (**2**). Hydrolysis (0.5 M NaOH, 2 ml; room temp.) of **2** (85 mg) and work-up as usual gave two products. One was a triol (10 mg) identical with compound **7** (^1H NMR, ^{13}C NMR, MS, [α], and TLC) and the other was compound **13** (35 mg) identical with oleoside (^1H NMR).

Jasuroside F hexa-acetate. Acetylation (Ac_2O–Pyridine; 1:1; room temp.) of **2** (15 mg) gave Jasuroside F hexa-acetate (15 mg) as a solid. $[\alpha]_D^{25}$ −96° ($CHCl_3$, *c* 0.16); IR ν_{max}^{neat} cm^{-1}: 2962, 2938, 2857, 1737, 1633, 1436, 1369, 1303, 1230, 1164, 1128, 1095, 1070, 1041, 981, 908, 856, 759, 667; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.72 (1H, *s*, H-1), 7.46 (1H, *s*, H-3), 3.98 (1H, *m*, H-5), 2.71 (1H, *dd*, *J* = 14.7, 4.5 Hz, H-6α), 2.45 (1H, *J* = 8.1, 14.7 Hz, H-6β), 6.00 (1H, *q*, *J* = 6.9 Hz, H-8), 1.75 (3H, *d*, *J* = 6.9 Hz, H-10), 3.71 (3H, *s*, COOMe), 5.00 (1H, *m*, H-5″), 0.90 (3H, *d*, *J* = 6.9 Hz, H-6″), 3.90–4.20 (2H, *m*, H-7″), 0.97 (3H, *d*, *J* = 6.9 Hz, H-9″), 3.70–3.84 (2H, *m*, H-10″), 5.00–5.16 (3H, *m*, H-1′, 2′, 4′), 5.27 (1H, *dd*, *J* = 9.3, 9.3 Hz, H-3′), 3.78 (1H, *m*, H-5′), 4.10 (1H, *m*, H-6′), 4.33 (1H, *dd*, *J* = 11.4, 4.8 Hz, H-6′), 2.01, 2.02, 2.03, 2.04, 2.06, 2.08 (18H, *s*, OAc); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 93.7 (*d*, C-1), 153.1 (*d*, C-3), 108.6 (*s*, C-4), 30.1 (*d*, C-5), 40.0 (*t*, C-6), 170.5 (*s*, C-7), 124.8 (*d*, C-8), 128.4

(*s*, C-9), 13.5 (*q*, C-10), 166.7 (*s*, C-11), 51.4 (*q*, OMe), 40.5 (*d*, C-1″), 46.7 (*d*, C-2″), 42.0 (*d*, C-3″), 33.9 (*t*, C-4″), 77.7 (*d*, C-5″), 13.6 (*q*, C-6″), 67.5 (*t*, C-7″), 36.1 (*d*, C-8″), 16.2 (*q*, C-9″), 66.0 (*t*, C-10″), 97.0 (*d*, C-1′), 70.7 (*d*, C-2′), 72.5 (*d*, C-3′), 68.2 (*d*, C-4′), 72.2 (*d*, C-5′), 61.8 (*t*, C-6′), 20.9, 20.7 × 2, 20.6 × 2, 20.5, (*q*, $CO\underline{C}H_3$), 169.3, 169.4, 170.2, 170.9, 171.0, 171.1 (*s*, $\underline{C}OCH_3$); EIMS 30 eV, *m/z* (rel. int.): 826 $[M]^+$ (0.02), 478 (1), 331 (33), 223 (24), 178 (51), 165 (86), 135 (81), 109 (50), 98 (27), 43 (100).

Jasuroside G (**8**). Isolated as an amorphous powder; $[\alpha]_D^{25}$ −116° (MeOH, *c* 0.2); UV λ_{max}^{MeOH} (log ε) nm: 236 (4.58); IR ν_{max}^{neat} cm^{-1}: 3408, 2930, 1710, 1632, 1442, 1386, 1344, 1306, 1190, 1162, 1078, 1046, 948, 926, 854, 816, 770; ^1H and ^{13}C NMR: Tables 1 and 2; FABMS *m/z*: 983 $[M+Na]^+$.

Jasuroside G nona-acetate. Acetylation (Ac_2O–Pyridine; 1:1; room temp.) of **8** (8 mg) gave a non-acetate (7 mg) as a solid. $[\alpha]_D^{25}$ −90.3° (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 5.71 (1H, *s*, H-1A), 5.27 (1H, *d*, *J* = 3 Hz, H-1B), 7.46 (1H, *s*, H-3A), 7.39 (1H, *d*, *J* = 1.8 Hz, H-3B), 4.00 (1H, *m*, H-5A), 3.16 (1H, *m*, H-5B), 2.71 (1H, *dd*, *J* = 14.1, 4.2 Hz, H-6αA), 2.99 (1H, *dd*, *J* = 16.7, 4.2 Hz, H-6αB), 2.42 (1H, *dd*, *J* = 14.1, 8.7 Hz, H-6βA), 2.28 (1H, *dd*, *J* = 16.7, 9.6 Hz, H-6βB), 6.00 (1H, *q*, *J* = 6.9 Hz, H-8A), 5.41 (1H, *m*, H-8B), 3.64 (1H, *m*, H-9B), 1.75 (3H, *d*, *J* = 6.9 Hz, H-10A), 1.75 (3H, *d*, *J* = 6.9 Hz, H-10A), 5.05 (2H, *m*, H-10B), 3.73 (3H, *s*, COOMe), 3.68 (3H, *s*, COOMe), 5.05 (1H, *m*, H-5″), 0.97 (3H, *d*, *J* = 7.2 Hz, H-6″), 3.85 (1H, *m*, H-7″a), 4.12 (1H, *m*, H-7″b), 1.01 (3H, *d*, *J* = 7.2 Hz, H-9″), 3.47 (1H, *m*, H-10″a), 3.17 (1H, *m*, H-10″b), 5.00–5.30 (8H, *m*, H-1′, 2′, 3′, 4′), 3.78 (2H, *m*, H-5′), 4.13 (2H, *m*, H-6′), 4.32 (2H, *dd*, *J* = 11.4, 4.8 Hz, H-6′), 2.00, 2.03 × 6, 2.09, 2.10 (27H, *s*, OAc); EIMS 30 eV, *m/z* (rel. int.): 920 $[M-7AcOH]^+$ (0.2), 661 (1), 555 (1), 419 (1), 331 (33), 271 (10), 180 (11), 169 (100), 135 (32), 109 (48), 43 (61).

Alkaline hydrolysis of jasuroside G (**8**). Hydrolysis (0.5 M NaOH, 2 ml; room temp.) of **8** (50 mg) provided after work-up as described above triol **11** (4 mg). Compound **11**: syrup, $[\alpha]_D^{25}$ −16.1° (MeOH, *c* 0.34); FABMS *m/z*: 189 $[M+H]^+$, 211 $[M+Na]^+$. ^1H and ^{13}C NMR identical with those reported [12].

Partial alkaline hydrolysis of jasuroside G (**8**). A soln of **8** (15 mg) in diethylamine–MeOH (1:200, 2 ml) was heated at 60° for 40 hr. The reaction mixt. after neutralization, was evapd *in vacuo* and sepd by prep. TLC (silica gel, lower layer of $CHCl_3$–MeOH–H_2O, 43:37:20) to yield compound **8** (12 mg) and a product (1.3 mg) identical with jasmesoside (**9**) ([α], ^1H NMR, MS).

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