Four New Secoiridoid Glucosides from *Jasminum urophyllum*

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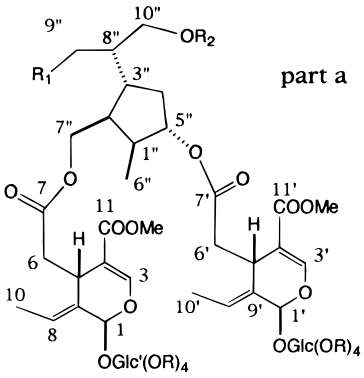
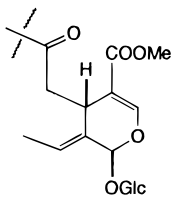
By application of centrifugal partition chromatography, four new secoiridoid glucosides, jasurosides A−D (**1**−**4**), were isolated from the whole plant of *Jasminum urophyllum*. The structures of these compounds, which comprise a di- or trimeric oleoside with an unusual triol or tetrol moiety, have been elucidated on the basis of spectroscopic analysis and chemical methods.

Plants of the genus *Jasminum* are notable for their ability to biosynthesize secoiridoids of novel structure.[1−3] Recently, we reported the separation and structural elucidation of five new secoiridoids named jaslanceosides A−E from *Jasminum lanceolarium* Roxb. (Oleaceae).[4,5] As part of our continued studies on the constituents of oleaceaous plants, a phytochemical investigation of *J. urophyllum* Hemsley has been undertaken. The taxonomic and morphological aspects of plants in the genus *Jasminum* appear to be of some complexity. Thus, the presently investigated species, which was formerly classified as *J. taiwanianum* Masamune, is now referred to as *J. urophyllum* Hemsley.[6,7] This species is a climbing shrub native to Taiwan and mainland China and grows in thickets at low and medium altitudes. The fragrant, white flowers of *J. urophyllum* have a five-lobed calyx and open in June. Although the use of this plant in folk medicine has not yet been documented, the plant has a bitter taste. Herein, we report the isolation and structure elucidation of four new secoiridoids, jasurosides A−D (**1**−**4**), from *J. urophyllum*. All of these compounds contain an unusual triol or tetrol ring system and are di- or trimeric oleoside secoiridoids.



1 R = R_1 = R_2 = H
2 R = R_1 = H, R_2 = A
3 R = R_2 = H, R_1 = OH
4 R = H, R_1 = OH, R_2 = A
5 R = R_2 = Ac, R_1 = H
6 R = R_2 = Ac, R_1 = OAc

A = 

part b

Results and Discussion

The ethanolic extract of *J. urophyllum*, after solvent partition, Sephadex LH-20 column, centrifugal partition chromatography, and preparative TLC furnished purification, the four new isolates, jasurosides A−D (**1**−**4**), of which compounds **1** and **3** are trimeric monoterpenes and compounds **2** and **4** are tetramers.

Jasuroside A (**1**), $[\alpha]_D$ −235° (MeOH), was obtained as an amorphous solid. The negative FABMS of **1** showed a $[M - H]^-$ ion at *m/z* 959, consistent with a molecular formula of $C_{44}H_{64}O_{23}$. The ^{1}H-NMR spectrum of **1** (Table 1) displayed signals for two oleoside methyl ester units and one triol moiety, and the latter exhibited two methyl doublets at δ 0.94 and 0.99. Additional evidence for the structure of **1** was deduced from its COSY spectrum, which revealed not only the couplings between H-10/H-8 and H-5/H-6 but also correlations between each proton in the triol nucleus. The ^{13}C-NMR spectrum of **1** (Table 2) also exhibited signals for two oleoside methyl ester units and one triol moiety. Five methine carbons at δ 80.0 (C-5″), 48.1 (C-2″), δ 41.8 (C-1″), 41.0 (C-8″), and 42.6 (C-3″), three methylene carbons at δ 66.4 (C-10″), 67.2 (C-7″), and δ 35.3 (C-4″), as well as the methyl carbons at δ 14.1 (C-6″) and δ 16.3 (C-9″), were observed in the DEPT and HETCOR spectra, supporting the fact that **1** was a triol-containing secoiridoid. The characteristic carbon signals (C-1″, C-2″, C-5″, and C-6″) in the triol moiety and two methylene carbon signals (C-6, C-6′) at δ 41.5 and 41.2 in the oleoside moiety of **1** excluded jasmoside as a possible structure, because the latter has a C-6 signal at δ 44.0 and the C-1″, C-2″, C-5″, and C-6″ signals appear at δ 44.8, 52.0, 82.5, and 20.8, respectively.[8] Detailed comparison of the ^{13}C-NMR spectrum of **1** with that of molihuaside A revealed that both substances possess the same basic skeleton.[9] However, compound **1** has a molecular weight of 16 mass units less than that of molihuaside A, indicating that the C-8″ hydroxymethyl group of the latter compound was replaced by a methyl group in **1**. In addition, the carbon signals at δ 41.8 (C-1″) and 80.0 (C-5″) of **1** were different from those in molihuaside A, which showed corresponding signals at δ 44.3 and 83.4, respectively. This finding suggested that both the C-1″ methyl and C-5″ protons in **1** have a β-orientation.

Upon acetylation, compound **1** afforded a nonaacetate (**5**). Alkaline hydrolysis of **1** yielded compound **7** and a secoiridoid glucoside (**10**), which was methylated with CH_2N_2 to furnish the known dimethyl ether **11**.[10] A comparison of the ^{13}C-NMR spectra of **7** and **1** deter-

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Table 1. ^{1}H-NMR Spectral Data (CD_3OD, 300 MHz) for Compounds **1**−**4**[a,b]

		2			**4**	
proton(s)	**1**	part a	part b	**3**	part a	part b
1′	5.95 (s)	5.95 (s)	5.96 (s)	5.97 (s)	5.95 (s)	5.97 (s)
3′	7.52 (s)	7.53 (s)	7.52 (s)	7.53 (s)	7.54 (s)	7.55 (s)
5′	4.00 (dd, 3.5, 6.6)	4.00 (dd, 3.9, 8.9)	4.00 (dd, 3.9, 8.9)	4.01 (m)	4.01 (m)	4.01 (m)
6′a	2.52 (dd, 10.5, 6.6)	2.52 (m)	2.52 (m)	2.52 (dd, 11.8, 7.0)	2.56 (m)	2.56 (m)
6′b	2.72 (dd, 10.5, 3.5)	2.72 (m)	2.72 (m)	2.72 (dd, 11.8, 4.2)	2.75 (m)	2.75 (m)
8′	6.11 (q, 5.4)	6.10 (q, 5.4)	6.12 (q, 5.4)	6.13 (q, 5.7)	6.10 (q, 5.4)	6.14 (q, 5.4)
10′	1.74 (d, 5.4)	1.74 (d, 5.4)	1.75 (d, 5.4)	1.75 (d, 5.7)	1.75 (d, 5.4)	1.76 (d, 5.4)
1″	1.95 (m)	1.90 (m)		1.94 (m)	1.90 (m)	
2″	1.82 (m)	1.86 (m)		1.90 (m)	1.90 (m)	
3″	1.84 (m)	1.84 (m)		1.85 (m)	1.85 (m)	
4″a	1.64 (m)	1.64 (m)		1.65 (m)	1.65 (m)	
4″b	2.08 (m)	2.10 (m)		2.06 (m)	2.10 (m)	
5″	5.04 (dd, 3.9, 6.6)	5.10 (m)		5.02 (m)	5.05 (m)	
6″	0.94 (d, 5.1)	0.94 (d, 6.6)		0.94 (d, 6.6)	0.95 (d, 5.4)	
7″a	3.96 (dd, 3.9, 8.6)	4.00 (dd, 3.9, 8.9)		3.90 (m)	3.95 (m)	
7″b	4.21 (m)	4.20 (m)		4.21 (m)	4.21 (m)	
8″	1.65 (m)	1.65 (m)		1.65 (m)	1.65 (m)	
9″	0.99 (d, 5.1)	1.00 (d, 6.3)		3.67 (m) 3.90 (m)	3.67 (m) 3.90 (m)	
10″	3.31 (m)	3.41 (m)		3.40 (m)	3.40 (m)	
	3.59 (m)	3.63 (m)		3.57 (m)	3.59 (m)	
1	5.94 (s)	5.93 (s)		5.94 (s)	5.93 (s)	
3	7.52 (s)	7.53 (s)		7.53 (s)	7.53 (s)	
5	4.00 (dd, 3.3, 6.6)	4.00 (dd, 3.9, 8.9)		4.01 (m)	4.01 (m)	
6a	2.52 (dd, 10.5, 6.6)	2.52 (m)		2.52 (dd, 9.3, 13.8)	2.56 (m)	
6b	2.72 (dd, 10.5, 3.6)	2.72 (m)		2.72 (dd, 4.2, 11.8)	2.75 (m)	
8	6.11 (q, 5.4)	6.10 (q, 5.4)		6.13 (q, 5.7)	6.10 (q, 5.4)	
10	1.74 (d, 5.4)	1.74 (d, 5.4)		1.75 (d, 5.4)	1.75 (d, 5.4)	
OMe	3.72 (s)	3.72 (s)	3.71 (s)	3.72 (s)	3.72 (s)	3.71 (s)
	3.72 (s)	3.72 (s)		3.72 (s)	3.72 (s)	
glc-1	4.80	4.79			4.79	4.82
glc2-glc6	3.30−4.00	3.30−4.00			3.30−4.00	3.30−4.00
glc-1′	4.80	4.79			4.79	4.82
glc2′-glc6′	3.30−4.00	3.30−4.00			3.30−4.00	3.30−4.00

[a] δ in ppm (J in Hz); TMS as internal standard. [b] Assignments determined by COSY and HETCOR.

Table 2. ^{13}C-NMR Spectral Data (CD_3OD, 75.4 MHz) for Compounds **1**−**4**[a,b]

		2			**4**				**2**			**4**	
carbon	**1**	part a	part b	**3**	part a	part b	carbon	**1**	part a	part b	**3**	part a	part b
1	95.2 d	95.3 d		95.3 d	95.2 d		1″	41.8 d	42.0 d		41.8 d	41.8 d	
3	155.2 d	155.3 d		155.4 d	155.2 d		2″	48.1 d	48.2 d		49.4 d	49.6 d	
4	109.4 s	109.5 s		109.5 s	109.4 s		3″	42.6 d	43.4 d		38.9 d	39.3 d	
5	32.1 d	32.0 d		32.2 d	31.9 d		4″	35.3 t	35.5 t		34.7 t	34.5 t	
6	41.5 t	41.7 t		41.6 t	41.5 t		5″	80.0 d	80.2 d		80.2 d	80.0 d	
7	173.4 s	173.4 s		173.5 s	173.3 s		6″	14.1 q	14.0 q		14.1 q	13.9 q	
8	124.7 d	124.9 d		124.9 d	124.9 d		7″	67.2 t	66.9 t		66.7 t	66.5 t	
9	130.8 s	130.9 s		130.9 s	130.8 s		8″	41.0 d	37.6 d		47.7 d	45.0 d	
10	13.8 q	13.9 q		13.9 q	13.9 q		9″	16.3 q	17.0 q		62.0 t	62.7 t	
COOMe	168.7 s	168.7 s		168.8 s	168.6 s		10″	66.4 t	69.3 t		63.0 t	65.7 t	
	51.9 q	52.1 q		52.1 q	52.0 q		glc-1	100.8 d	101.0 d		100.9 d	100.8 d	
1′	94.8 d	94.9 d	95.4 d	94.9 d	94.8 d	95.2 d	glc-2	74.8 d	74.9 d		74.9 d	74.8 d	
3′	155.1 d	155.3 d	155.3 d	155.3 d	155.2 d	155.2 d	glc-3	78.6 d	78.6 d		78.7 d	78.5 d	
4′	109.4 s	109.5 s	109.5 s	109.5 s	109.4 s	109.4 s	glc-4	71.6 d	71.7 d		71.8 d	71.5 d	
5′	31.9 d	32.0 d	32.3 d	32.0 d	31.8 d	32.1 d	glc-5	78.0 d	78.1 d		78.1 d	78.4 d	
6′	41.2 t	41.4 t	41.4 t	41.3 t	41.2 t	41.2 t	glc-6	62.9 t	63.0 t		63.3 t	62.9 t	
7′	172.9 s	173.1 s	173.5 s	173.0 s	172.9 s	173.2 s	glc-1′	100.5 d	100.7 d	101.0 d	100.6 d	100.5 d	100.9 d
8′	124.7 d	124.9 d	124.9 d	124.9 d	124.8 d	124.9 d	glc-2′	74.8 d	74.9 d	74.9 d	74.9 d	74.8 d	74.8 d
9′	130.7 s	130.9 s	131.0 s	130.8 s	130.7 s	130.6 s	glc-3′	78.5 d	78.1 d	78.8 d	78.6 d	78.4 d	78.5 d
10′	13.7 q	13.9 q	14.0 q	13.9 q	13.8 q	13.8 q	glc-4′	71.6 d	71.6 d	71.8 d	71.7 d	71.4 d	71.6 d
COOMe	168.6 s	168.7 s	168.7 s	168.8 s	168.6 s	168.6 s	glc-5′	77.9 d	78.1 d	78.1 d	78.1 d	78.5 d	78.5 d
	51.9 q	52.1 q	52.1 q	52.1 q	52.0 q	52.0 q	glc-6′	62.9 t	63.0 t	63.1 t	63.6 t	62.9 t	62.9 t

[a] Multiplicities determined by DEPT. [b] Assignments made by HETCOR.

mined the sites of attachment of the oleoside to the triol. The downfield shifts of C-2″ and C-4″ as well as the upfield shifts of C-5″ and C-7″ in the triol (**7**) relative to those in **1** suggested that the C-5″ and C-7″ triol hydroxyl groups were connected to oleoside methyl ester units, probably via esterification at the C-7 and C-7′-carboxyl groups.[11] Although the HMBC spectrum (Figure 1) did not show any correlation between C-7′ (δ 172.9) and H-5″ due to the low sensitivity of H-5″ (δ 5.04, dd, J = 3.9, 6.6 Hz), a diagnostic correlation (δ 173.4, δ 3.96) established a structural linkage between C-7 and H-7″. The stereochemistry of **1** was determined on the basis of the results of NOESY experiments and the hydrolysis products of **1**. It was assumed that C-2″

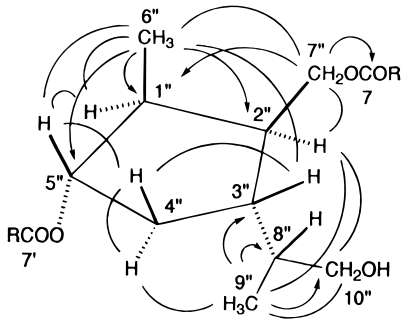
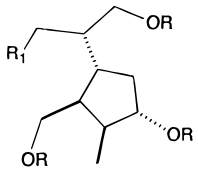
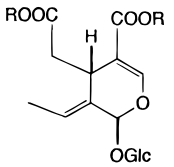


Figure 1. Selective NOESY (curve) and HMBC (hook) observations for jasuroside A (**1**).

and C-3″ have the same configurations as those of jasminine and jasmoside.[11,12] NOESY correlations were



7 R = R_1 = H
8 R = Ac, R_1 = H
9 R = H, R_1 = OH
12 R = Ac, R_1 = OAc



10 R = H
11 R = Me

observed between H-3″, H-5″, H_3-6″, and H_2-7″ and between H-2″, H_3-9″, and H_2-10″ but not between H-2″ and H_3-6″ or between H_3-9″ and H_3-6″. These findings indicated that the H-3″, H-5″, H_3-6″, and H_2-7″ protons were in the β-orientation and that H-2″, H-8″, H_3-9″, and H_2-10″ protons were in an α-disposition, as shown in Figure 1.

Jasuroside B (**2**) was obtained as an amorphous powder, $[\alpha]_D$ −222° (MeOH). A molecular formula of $C_{61}H_{86}O_{33}$ was established for a quasimolecular ion ([M + Na]$^+$) at *m*/*z* 1369 in its FABMS. The UV absorption (236 nm) and the IR bands (3400, 1710, 1632 cm^{-1}) as well as the ^{1}H-NMR spectral data (Table 1) of **2** resembled those of **1**, suggesting that it was a close analogue of **1**. The ^{13}C-NMR spectrum of **2** (Table 2) was superimposable with that of **1** except that three sets of oleoside signals were observed, indicating that the C-10″ hydroxyl was replaced by a third oleoside unit. In addition, the signal of C-10″ was shifted downfield to δ 69.3 in **2** when compared to **1** (δ 66.4). Partial alkaline hydrolysis of **2** gave a product identical with jasuroside A (**1**). On the basis of the result of hydrolysis and close comparison of the specific rotation and coupling patterns of **2** with those of **1**, it was inferred that both compounds have the same stereochemistry.

Jasuroside C (**3**), $[\alpha]_D$ −185° (MeOH), was obtained as an amorphous powder. The molecular formula of $C_{44}H_{64}O_{24}$ was derived from a quasimolecular ion ([M + Na + H]$^+$) at *m*/*z* 1000 in the FABMS of **3**, clearly indicating that the molecule was 16 mass units larger than **1**. The UV (236 nm) and the IR (3396, 1706, 1632 cm^{-1}) spectral data resembled those of **1**, suggesting that it was a similar type of compound. The ^{1}H- and ^{13}C-NMR data of **3** and **1** were also similar except that the C-9″ methyl doublet (δ 0.99) in **1** was absent. Instead, a hydroxymethyl group was observed [δ_H 3.67, 3.90 (H-9″) and δ_C 62.0 (C-9″)] in **3**. This finding was supported by the COSY spectrum of **3**. Acetylation of **3** gave a decaacetate (**6**). On alkaline hydrolysis, compound **3** yielded **10** and a tetrol (**9**). The ^{13}C-NMR spectrum of **9** exhibited the C-1″, C-5″, and C-6″ signals at δ 42.7, 76.1, and 14.2 compared to δ 46.2, 79.6, and 18.6 for a tetrol obtained from the hydrolysis of molihuaside A. Comparison of the ^{13}C-NMR data of **3** with those of **1** revealed upfield shifts for C-3″ (-2.7 ppm) and C-10″ (-4.4 ppm) and a downfield shift for C-8″ (+6.7 ppm), confirming the presence of a C-9″ hydroxyl group. The similar specific rotation and coupling constants of **3** and **1** were suggestive of their identical stereochemistry.

Jasuroside D (**4**), $[\alpha]_D$ −191° (MeOH), which is an isomer of sambacoside,[2] has the molecular formula $C_{61}H_{86}O_{34}$ as deduced from a negative FABMS of **4**. The UV, IR, and ^{1}H-NMR spectra of **4** (Table 1) displayed absorptions and signals similar to those of **2** and **3**, suggesting that it was a close analogue. In the ^{13}C-NMR spectrum of **4** (Table 2), signals arising from the oleoside methyl ester and tetrol moieties also resembled those of **2** and **3**. However, in its EIMS compound **4** was 16 mass units greater than that of **2**, indicating the presence of a hydroxymethyl group (δ_H 3.67, 3.90, H-9″) in **4** compared with a methyl group (δ_H 1.00, C-9″) in **2**. The ^{13}C-NMR data (Table 2) of **4** also supported the structure assigned for this compound. On the basis of the spectral evidence, therefore, compound **4** was established as 9″-hydroxyjasuroside B.

The structures established for compounds **1**−**4** represent new secoiridoid glucosides, which contain di- or trioleoside methyl esters with a cyclopentane ring system. The occurrence of these compounds in a further species in the genus *Jasminum* is therefore of chemotaxonomic significance in the family Oleaceae.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a JASCO DIP-1000 polarimeter. IR and UV spectra were measured on Hitachi T-2001 and Hitachi V-3210 spectrophotometers, respectively. EIMS and FABMS were recorded on a VG Quattro 5022 mass spectrometer. Negative-ion FABMS spectra were taken on a JEOL JMS-SX 102 mass spectrometer. The ^{1}H- and ^{13}C-NMR, DEPT, COSY, HETCOR, and NOESY experiments were recorded on Varian FT-300 and Varian FT-400 spectrometers. The HMBC spectra were taken on a Bruker 300-AC spectrometer.

Plant Material. *J. urophyllum* Hemsley was collected in June 1995, in Te-chi, Tai-chung County, Taiwan. This plant was identified by Dr. Yuen-po Yang, Department of Biology, National Sun Yat-sen University, and a voucher specimen (TP 260-6) has been deposited in the Institute of Marine Resources, National Sun Yat-sen University.

Extraction and Isolation. The fresh whole plant (50 g) was ground and extracted with EtOH (300 mL × 2). The combined EtOH extracts were concentrated to a green tar (7.5 g). After dilution with H_2O (600 mL), the resulting suspension was partitioned with an equal volume of EtOAc. The H_2O-soluble fraction was extracted three times with *n*-BuOH (each 200 mL). The *n*-BuOH-soluble fraction was reduced under vacuum to give a secoiridoid-containing residue (1.6 g), which was

applied to a Sephadex LH-20 column (3 × 34 cm, 100 g) and eluted with MeOH to give a residue (1 g). A portion of the residue (0.8 g) was subjected to centrifugal partition chromatography (descending mode, 700 psi, 800 rpm, flow rate 2 mL/min) using the upper layer of the mixture $CHCl_3$−MeOH−H_2O (43:37:20) as stationary phase and the lower layer as mobile phase (1000 mL) to give seven fractions, I (19 mg), II (26 mg), III (41 mg), IV (174 mg), V (65 mg), VI (43 mg), VII (80 mg). Part of fraction IV (60 mg) was chromatographed on a preparative TLC plate (Si gel, 20 × 20 cm, 1 mm thickness) and developed with the lower layer of the solvent mixture $CHCl_3$−MeOH−H_2O (43:37:20) to yield three bands, A (5 mg), B (28 mg), and C (11 mg). Bands B and C were rechromatographed, respectively, on a reversed-phase preparative TLC plate (C_{18}, 20 × 20 cm, 1 mm thickness) and developed with MeOH and H_2O (1:1) to yield jasuroside A (**1**, 20 mg) and jasuroside B (**2**, 7 mg). Fraction VII was chromatographed on a preparative TLC plate (Si gel, 20 × 20 cm, 1 mm thickness) and developed with the same solvent system mentioned above to yield four bands D (6 mg), E (9 mg), F (21 mg), and G (14 mg). Bands F and G were applied, respectively, to a C_{18} TLC plate using MeOH/H_2O (1:1) as solvent to give jasuroside C (**3**, 12 mg) and jasuroside D (**4**, 9 mg).

Jasuroside A (**1**) was isolated as an amorphous solid: $[\alpha]^{25}_D$ −235° (*c* 0.11, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.58) nm; IR (neat) ν_{max} 3424, 2964, 2916, 1736, 1712, 1636, 1442, 1394, 1308, 1162, 966, 922, 898, 862, 814, 792, 768 cm^{-1}; ^1H and ^{13}C NMR data are listed in Table 1 and 2, respectively; negative FABMS *m/z* $[M - H]^-$ 959.

Jasuroside A Nonaacetate (**5**)**.** Acetylation [Ac_2O−pyridine (2:1), room temperature] of **1** (40 mg) gave **5** (50 mg) as a solid: $[\alpha]^{25}_D$ −83.3° (*c* 0.25, MeOH); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.72 (1H, s, H-1), 5.70 (1H, s, H-1′), 7.46 (2H, s, H-3, H-3′), 4.04 (2H, m, H-5, H-5′), 2.68 (2H, dd, *J* = 14, 3.3 Hz, H-6α, H-6′α), 2.45 (2H, m, H-6*β*, H-6′*β*), 6.00 (2H, q, *J* =7.2 Hz, H-8, H-8′), 1.74 (6H, d, *J* = 7.2 Hz, H-10, H-10′), 3.71 (6H, s, COOMe × 2), 5.01 (1H, m, H-5″), 0.89 (3H, d, *J* = 6.6 Hz, H-6″), 3.95 (1H, m, H-7″a), 4.30 (1H, m, H-7″b), 0.96 (3H, d, *J* = 6.6 Hz, H-9″), 3.77 (1H, m, H-10″), 2.01 × 2, 2.02 × 2, 2.03 × 2, 2.07 × 2, 2.08 (27H, s, OAc); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 93.6 (d, C-1), 152.9 (d, C-3), 108.5 (s, C-4), 30.0 (d, C-5), 39.8 (t, C-6), 169.2 (s, C-7), 124.6 (d, C-8), 128.3 (s, C-9), 13.3 (q, C-10), 166.5 (s, C-11), 51.8 (q, OMe), 93.7 (d, C-1′), 152.9 (d, C-3′), 108.5 (s, C-4′), 30.1 (d, C-5′), 39.9 (t, C-6′), 169.3 (s, C-7′), 124.6 (d, C-8′), 128.4 (s, C-9′), 13.4 (q, C-10′), 166.6 (s, C-11′), 51.3 (q, OMe), 40.3 (d, C-1″), 46.6 (d, C-2″), 36.0 (d, C-3″), 33.7 (t, C-4″), 77.7 (d, C-5″), 13.5 (q, C-6″), 65.8 (t, C-7″), 41.9 (d, C-8″), 16.1 (q, C-9″), 67.3 (t, C-10″), 96.9 (d, glc-1, 1′), 70.6 (d, glc-2, 2′), 72.4 (d, glc-3, 3′), 68.1 (d, glc-4, 4′), 72.1 (d, glc-5, 5′), 61.6 (t, glc-6, 6′), 20.8, 20.7 × 2, 20.6 × 2, 20.5 × 2, 20.4 × 2 (q, $COCH_3$), 169.2 × 2, 169.3 × 2, 170.4 × 2, 170.7 × 2, 170.9, 171.1 (s, $COCH_3$); EIMS (30 eV) *m/z* 702 (1), 477 (1), 405 (1), 331 (30), 271 (8), 225 (10), 207 (6), 193 (9), 180 (13), 169 (100), 145 (8), 133 (10), 109 (32), 97 (70), 81 (4), 69 (4), 43 (43).

Alkaline Hydrolysis of Jasuroside A (**1**). Hydrolysis (0.5 M NaOH, 2 mL; room temperature) of **1** (20 mg) provided after workup as described in previous papers [2,3] a triol (**7**, 4 mg) and a secoiridoid glucoside (**10**). Compound **7**: syrup; $[\alpha]^{25}_D$ −14.7° (*c* 0.34, MeOH); ^1H NMR (CD_3OD, 300 MHz) δ 1.70 (2H, m, H-1″, H-2″), 1.55 (2H, m, H-3″, H-4″a), 1.88 (2H, m, H-4″b, H-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); COSY data (CD_3OD, 300 MHz) [H-1″, H-6″], [H-2″, H-7″], [H-3″, H-4″], [H-4″a, H-4″b], [H-4″, H-5″], [H-8″, H-9″], [H-8″, H-3″], [H-8″, H-10″], [H-10″a, 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* $[M + H]^+$ 189, $[M + Na]^+$ 211.

Acetylation of Triol (**7**). Triol **7** (20 mg) was acetylated (Ac_2O, 0.5 mL, pyridine, 0.5 mL; room temperature) to yield a residue, which was purified on a Si gel column [$CHCl_3$/acetone (10:1), 100 mL)] to give **8** (21 mg) as a syrup; $[\alpha]^{25}_D$ −14.4° (*c* 0.11, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.56, 1.73, 1.87, 1.96−2.10 (6H, m, H-1″, H-2″, H-3″, H-4″, H-8″), 5.05 (1H, m, H-5″), 0.96 (3H, d, *J* = 6.9 Hz, H-6″), 4.05 (1H, m, H-7″a), 4.10 (1H, m, H-7″b), 0.95 (3H, d, *J* = 6.3 Hz, H-9″), 3.80 (1H, dd, *J* =7.2, 10.8 Hz, H-10″a), 4.06 (1H, m, H-10″b), 2.02, 2.03, 2.04 (9H, s, OAc); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 42.3 (d, C-1″), 46.6 (d, C-2″), 40.8 (d, C-3″), 33.8 (t, C-4″), 77.6 (d, C-5″), 13.3 (q, C-6″), 66.0 (t, C-7″), 36.0 (d, C-8″), 16.3 (q, C-9″), 67.5 (t, 10″), 171.1, 171.0, 170.7 (s × 3, $OCOCH_3$), 20.9, 21.0, 21.1 (q × 3, $OCOCH_3$); EIMS (30 eV) *m/z* 255 $[M - OAc]^+$ (1), 211 (2), 194 $[M - 2HOAc]^+$ (3), 169 (2), 152 (13), 134 $[M - 3HOAc]^+$ (100), 121 (45), 119 (56), 105 (29), 97 (15), 93 (35), 81 (10), 69 (5), 55 (5), 43 (41).

Jasuroside B (**2**) was isolated as an amorphous powder: $[\alpha]^{25}_D$ −222° (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.58) nm; IR (neat) ν_{max} 3400, 2932, 1710, 1632, 1442, 1382, 1340, 1306, 1262, 1190, 1162, 1074, 988, 908, 854, 814, 770, 696 cm^{-1}; ^1H- and ^{13}C-NMR data are listed in Tables 1 and 2, respectively; FABMS *m/z* $[M + Na]^+$ 1369.

Partial Alkaline Hydrolysis of 2. A solution of **2** (35 mg) in diethylamine/MeOH (1:200, 2 mL) was heated at 60 °C for 40 h. The reaction mixture after neutralization was evaporated under vacuum and separated on a preparative TLC plate (Si gel, lower layer of $CHCl_3$/MeOH/H_2O, 43:37:20) to yield compound **2** (13 mg) and a product (17 mg), identical with compound **1** ([α], ^1H NMR, R_f).

Jasuroside C (**3**) was isolated as an amorphous powder: $[\alpha]^{25}_D$ −185° (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.58) nm; IR (neat) ν_{max} 3404, 2924, 1710, 1634, 1442, 1386, 1354, 1262, 1192, 1162, 1076, 1044, 924, 902, 814, 768, 720 cm^{-1}; ^1H- and ^{13}C-NMR data are listed in Tables 1 and 2, respectively; FABMS *m/z* $[M + Na + H]^+$ 1000.

Alkaline Hydrolysis of Jasuroside C (3). Hydrolysis (0.5 M NaOH, 10 mL; room temperature, 5 h) of **3** (450 mg) provided a residue after workup as described above, which was chromatographed on a Si gel column (14 g), eluted with $CHCl_3$/MeOH (15:1, 60 mL; 10:1, 60 mL) and MeOH (100 mL), to give a tetrol (**9**, 25 mg) and a secoiridoid glucoside (**10**, 182 mg). Compound **9**: syrup; $[\alpha]^{25}_D$ −14.3° (*c* 0.13, MeOH); ^1H NMR (CD_3OD, 300 MHz) δ 1.70 (2H, m, H-1″, H-2″),

1.65 (1H, m, H-3″), 1.52 (1H, m, H-4″a), 1.87 (1H, m, H-4″b), 1.89 (1H, m, H-8″), 3.96 (1H, m, H-5″), 0.95 (3H, d, J = 6.6 Hz, H-6″), 3.60 (2H, m, H-7″), 3.66 (1H, dd, J = 4.2, 11 Hz, H-9″a), 3.56 (1H, dd, J = 6.6, 11 Hz, H-9″b), 3.49 (1H, dd, J = 5.1, 11 Hz, H-10″a), 3.56 (1H, dd, J = 6.6, 11 Hz, H-10″b); ^{13}C NMR (CD_3OD, 75.4 MHz) δ 42.7 (d, C-1″), 51.1 (d, C-2″), 38.9 (d, C-3″), 37.0 (t, C-4″), 76.1 (d, C-5″), 14.2 (q, C-6″), 65.4 (t, C-7″), 48.3 (d, C-8″), 63.3 (t, C-9″), 62.6 (t, C-10″); EIMS (30 eV) m/z 205 $[M + 1]^+$ (1), 168 $[M - 2H_2O]^+$ (12), 155 (9), 150 $[M - 3H_2O]^+$ (7), 138 (36), 127 (22), 123 (29), 120 (73), 107 (88), 95 (92), 81 (100), 67 (59), 55 (71).

Acetylation of Tetrol 9. Triol **9** (20 mg) was acetylated (Ac_2O, 0.5 mL, pyridine, 0.5 mL; room temperature) to give **12** (21 mg) as a syrup: $[\alpha]^{25}_D$ −7.6° (c 0.1, $CHCl_3$); ^{1}H NMR δ ($CDCl_3$, 300 MHz) 1.90−2.04 (6H, m, H-1″, H-2″, H-3″, H-4″, H-8″), 5.11 (1H, m, H-5″), 0.98 (3H, d, J = 6.6 Hz, H-6″), 4.08 (1H, m, H-7″a), 4.11 (1H, m, H-7″b), 4.05 (2H, m, H-9″), 3.99 (1H, dd, J = 7.2, 11.4 Hz, H-10″a), 4.22 (1H, dd, J = 4.5, 11.4 Hz, H-10″b), 2.04, 2.05, 2.06, 2.07 (12H, s, OAc); ^{13}C NMR δ (75.4 MHz, $CDCl_3$) 38.9 (d, C-1″), 46.8 (d, C-2″), 40.0 (d, C-3″), 33.4 (t, C-4″), 77.6 (d, C-5″), 13.1 (q, C-6″), 65.4 (t, C-7″), 40.8 (d, C-8″), 63.9 (t, C-9″), 62.5 (t, 10″), 171.0, 170.9, 170.8, 170.6 (s × 4, O*C*OCH$_3$), 21.1, 20.9, 20.9, 20.9 (q × 4, OCO*C*H$_3$); EIMS (30 eV) m/z 313 $[M - OAc]^+$ (1), 269 (3), 252 $[M - 2HOAc]^+$ (1), 210 (6), 192 $[M - 3HOAc]^+$ (40), 150 (50), 132 $[M - 4HOAc]^+$ (100), 121 (23), 119 (32), 117 (64), 105 (29), 92 (54), 81 (18), 69 (72), 55 (8), 43 (58).

Jasuroside C Decaacetate (6). Acetylation [Ac_2O−pyridine (1:1), room temperature) of **3** (44 mg) gave **6** (52 mg) as a solid: $[\alpha]^{25}_D$ −114.8° (c 0.12, MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.71 (1H, s, H-1), 5.68 (1H, s, H-1′), 7.44 (2H, s, H-3, H-3′), 4.02 (2H, m, H-5, H-5′), 2.70 (1H, dd, J = 7.5, 4.5 Hz, H-6α), 2.65 (1H, dd, J = 7.5, 4.5 Hz, 6′α), 2.46 (1H, dd, J = 7.5, 1.8 Hz, H-6β), 2.42 (1H, dd, J = 7.5, 1.5 Hz, H-6′β), 5.98 (2H, q, J = 6.9 Hz, H-8, H-8′), 1.73 (6H, d, J = 6.9 Hz, H-10, H-10′), 3.69 (6H, s, COOMe × 2), 5.00 (1H, m, H-5″), 0.89 (3H, d, J = 6.6 Hz, H-6″), 3.95 (1H, m, H-7″a), 4.29 (1H, m, H-7″b), 3.99 (2H, m, H-9″), 3.77 (1H, m, H-10″), 2.00, 2.01, 2.02, 2.04, 2.06 (30H, s, OAc); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 93.8 (d, C-1), 153.0 (d, C-3), 108.5 (s, C-4), 30.1 (d, C-5), 39.8 (t, C-6), 169.4 (s, C-7), 124.6 (d, C-8), 128.5 (s, C-9), 13.1 (q, C-10), 166.7 (s, C-11), 51.4 (q, OMe), 93.7 (d, C-1′), 152.9 (d, C-3′), 108.4 (s, C-4′), 30.1 (d, C-5′), 39.9 (t, C-6′), 169.3 (s, C-7′), 124.7 (d, C-8′), 128.3 (s, C-9′), 13.5 (q, C-10′), 166.6 (s, C-11′), 51.3 (q, OMe), 40.3 (d, C-1″), 46.8 (d, C-2″), 38.5 (d, C-3″), 33.4 (t, C-4″), 77.7 (d, C-5″), 13.5 (q, C-6″), 65.3 (t, C-7″), 40.0 (d, C-8), 63.0 (t, C-9″), 62.3 (t, C-10″), 96.9 (d, glc-1, 1′), 70.7 (d, glc-2, 2′), 72.5 (d, glc-3, 3′), 68.2 (d, glc-4, 4′), 72.2 (d, glc-5, 5′), 61.7 (t, glc-6, 6′), 20.8, 20.7 × 2, 20.6 × 3, 20.5 × 4 (q, CO*C*H$_3$), 170.1 × 3, 170.4, 170.5 × 2, 170.8 × 3, 171.1 (s, *C*OCH$_3$); EIMS (30 eV) m/z 661 (1), 419 (1), 331 (20), 271 (7), 225 (13), 211 (5), 207 (5), 180 (12), 169 (100), 135 (24), 109 (29), 97 (6), 81 (3), 43 (27).

Jasuroside D (4) was isolated as an amorphous powder; $[\alpha]^{25}_D$ −191° (c 0.13, MeOH); UV (MeOH) λ_{max} (log ϵ) 236 (4.56) nm; IR (neat) ν_{max} 3396, 2952, 2888, 1706, 1632, 1544, 1444, 1380, 1344, 1306, 1266, 1208, 1194, 1160, 1076, 1044, 984, 924, 902, 858, 814, 768, 720, 698 cm^{-1}; ^{1}H- and ^{13}C-NMR data are listed in Tables 1 and 2, respectively; negative FABMS m/z $[M - H]^-$ 1362.

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References and Notes

(1) Tanahashi, T.; Nagakura, N.; Kuwajima, H.; Takaishi, K.; Inoue, K.; Inouye, H. *Phytochemistry* **1989**, *28*, 1413−1415.
(2) Tanahashi, T.; Nagakura, N.; Inoue, K.; Inouye, H. *Tetrahedron Lett.* **1988**, *29*, 1793−1796.
(3) Tanahashi, T.; Nagakura, N.; Inoue, K.; Inouye, H.; Shingu, T. *Chem. Pharm. Bull.* **1987**, *35*, 5032−5035.
(4) Shen, Y.-C.; Lin, S.-L. *Planta Med.* **1996**, *62*, 515−518.
(5) Shen, Y.-C.; Lin, S.-L.; Chein, C.-C. *Phytochemistry* **1997**, *44*, 891−895.
(6) Information obtained from an unpublished paper by Dr. Yuen-po Yang, Department of Biology, National Sun Yat-sen University.
(7) Liu, Y.-C.; Lu, F.-Y.; Ou, C.-H. *Trees of Taiwan*; College of Agriculture, National Chung-Shing University; Taichung, Taiwan, Republic of China, 1994; p 607.
(8) Inoue, K.; Tanahashi, T.; Inouye, H. *Phytochemistry* **1985**, *24*, 1299−1303.
(9) Zhang, Y.-J.; Liu, Y.-Q.; Pu, X.-Y.; Yang, C.-R. *Phytochemistry* **1995**, *38*, 899−903.
(10) Chen, H.-Y.; Shen, Y.-C.; Chen, C.-H. *J. Nat. Prod.* **1991**, *54*, 1087−1091.
(11) Inoue, K.; Fujita, T.; Inouye, H.; Kuwajima, H.; Takaishi, K.; Tanahashi, T.; Nagakura, N.; Asaka, Y.; Kamikawa, T.; Shingu, T. *Phytochemistry* **1991**, *30*, 1191−1201.
(12) Kamikawa, T.; Inoue, K.; Kubota, T.; Woods, M. C. *Tetrahedron* **1970**, *26*, 4561−4567.

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