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NEOLIGNAN GLUCOSIDES FROM *JASMINUM UROPHYLLUM*

YA-CHING SHEN,*† PEI-WEN HSIEH† and YAO-HAUR KUO‡

† Institute of Marine Resources, National Sun Yat-sen University, 70 Lein-Hai Road, Kaohsiung, Taiwan, Republic of China; ‡ National Research Institute of Chinese Medicine, Taipei, Taiwan, Republic of China

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Key Word Index—*Jasminum urophyllum*; Oleaceae; lignan glucosides, jasurolignoside; urolignoside.

Abstract—A novel neolignan-secoiridoid glucoside, jasurolignoside, and a new neolignan, urolignoside, have been isolated from *Jasminum urophyllum*. Their structures were elucidated on the basis of 2D-NMR and chemical methods.

INTRODUCTION

The genus *Jasminum* is notable for its ability to biosynthesize novel secoiridoid glucosides [1, 2]. Additionally, some species are reported to contain flavonoids and lignan-secoiridoid glucosides [3–5]. *Jasminum urophyllum*, an evergreen shrub, is distributed over the mountains of central Taiwan and is quite rich in secoiridoid glucosides. To investigate the chemotaxonomy of this plant, a phytochemical investigation was undertaken. Its constituents were found different from those of *J. lanceolarium* indicating two different taxa. In previous papers, we reported the structural elucidation of seven new secoiridoid glucosides isolated from the whole plants of *J. urophyllum* [6, 7]. Continued investigation of the *n*-butanol-soluble fraction has resulted in the isolation of a novel neolignan-secoiridoid glucoside, jasurolignoside (**1**), and a new neolignan, urolignoside (**2**). This paper describes the structural elucidation of **1** and **2**.

RESULTS AND DISCUSSION

Jasurolignoside (**1**), $[\alpha]_D$ −140° (MeOH), was obtained as a pale yellow solid. The molecular formula $C_{43}H_{56}O_{21}$ was established from the quasimolecular ions (*m/z* 931 $[M+Na]^+$ and *m/z* 907 $[M-H]^-$) in the positive and negative FAB mass spectra, respectively, and also by DEPT spectra. The UV maxima (233 and 278 nm) and IR bands (3435, 1693, 1502 and 1463 cm^{-1}) suggested that **1** contained a carbomethoxy enol ether and aromatic rings, in addition to hydroxyl functions. In the ^1H NMR spectrum (Table 1), **1** showed typical signals attributable to oleoside methyl ester. In addition, two aromatic methoxyl singlets (δ 3.82, 3.87), five aromatic protons (δ 7.14 *d*, J = 8.4 Hz; δ 7.03 *d*, J = 1.5 Hz; δ 6.93 *dd*, J = 8.4, 1.5 Hz; δ 6.73 *s* and δ 6.72 *s*), and a spin-system of $CH_2CH_2CH_2O$ (δ 2.64 *t*, J = 7.5 Hz; δ 1.92 *m*; δ 4.05 *m*) were also observed. Acetylation of **1** gave **6**, which showed a quasi-molecular ion at *m/z* 1311 in the FAB mass spectrum and nine acetyl singlets in the ^1H NMR spectrum. The structure of compound **1** was determined by extensive 2D-NMR studies, such as COSY, HMQC and HMBC. These helped us to assign each proton and carbon signal in the ^1H and ^{13}C NMR (Table 2) spectra of **1**. The location of methoxyl groups were thus determined at the C-11, 3′ and 3″ positions. Correlations between the C-7 carbonyl and H-9′ and between C-4′ and H-7″ were verified by HMBC (Fig. 1). Alkaline hydrolysis of **1** provided **2** and oleoside, which was methylated to give **5**. The ^{13}C NMR spectrum (Table 2) of **2** exhibited C-9′ at δ 62.4 relative to δ 65.3 in **1**, indicating a hydroxyl group at the C-9′ position in **2**. Hydrolysis of **2** using β-glucosidase yielded compound **4**, the ^1H NMR spec-

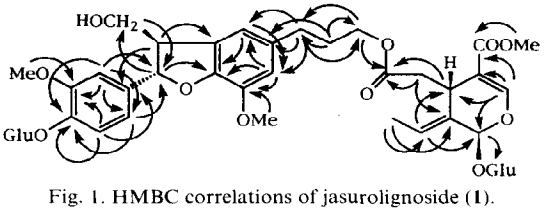
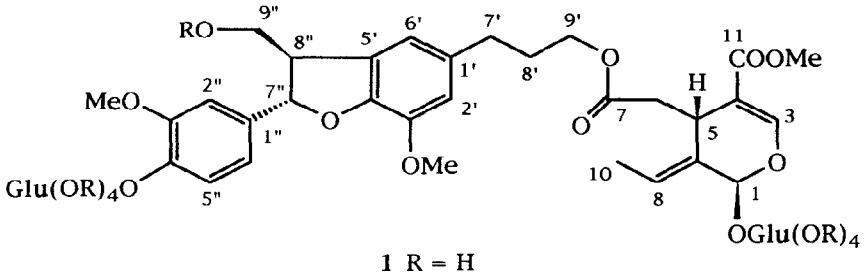
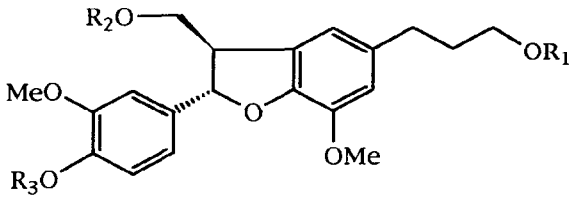


Fig. 1. HMBC correlations of jasurolignoside (**1**).

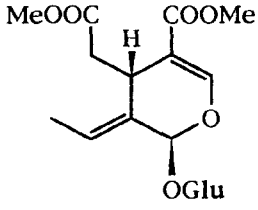
* Author to whom correspondence should be addressed.



1 R = H
6 R = Ac



2 $R_1 = R_2 = H$, $R_3 = Glu(OH)_4$
3 $R_1 = R_2 = Ac$, $R_3 = Glu(OAc)_4$
4 $R_1 = R_2 = R_3 = H$



5

trum (Table 1) of which showed H-5″ at higher field (δ 6.90) than that (δ 7.14) of **2** due to a glucosyl shift. This finding located the second *O*-glucosyl moiety at the C-6″ position. The stereochemistry of **1** was determined by comparison of the spectral data with those of reported compounds [8–10], together with hydrolysis of **1**. The CD curve of **1** exhibited a negative Cotton effect at 229 and 268 nm, and a positive one at 292 nm, similar to common 2-phenyldihydrobenzofuranpropanol-type neolignans [9]. This provided evidence that **1** has the 7″*S*,8″*R*-configuration.

Urolignoside (**2**) was obtained as a pale yellow solid from the less polar fraction. It showed spectral data identical to those of a product from the alkaline hydrolysis of **1**. Upon acetylation, **2** yielded a hexaacetate (**3**), the mass spectrum of which exhibited a quasi-molecular ion at *m/z* 797 $[M+Na]^+$. Because the stereochemistry of **1** had been established as 7″*S* and 8″*R*, the configuration at the corresponding chiral centres of **2** were the same as those of **1**.

Jasurolignoside (**1**) represents a new type of structure, in which a neolignan is connected to a secoiridoid glucoside via an ester function. The discovery of compounds **1** and **2**, together with jasurosides A–G, in *J.*

Table 1. ^{1}H NMR spectral data (300 MHz) for compounds **1**, **2** and **4**

H	δ (J = Hz) **1** (CD_3OD)	**2** (CD_3OD)	**4** ($CDCl_3$)
1	5.95 (1H, *s*)	—	—
3	7.53 (1H, *s*)	—	—
5	4.00 (1H, *m*)	—	—
6	2.72 (1H, *dd*, 4.8, 14)	—	—
	2.49 (1H, *dd*, 9, 14)	—	—
8	6.11 (1H, *q*, 7.2)	—	—
10	1.71 (3H, *d*, 7.2)	—	—
COOMe	3.70 (3H, *s*)	—	
2′	6.72 (1H, *s*)	6.71 (1H, *s*)	6.68 (1H, *s*)
6′	6.73 (1H, *s*)	6.73 (1H, *s*)	6.68 (1H, *s*)
7′	2.64 (2H, *t*, 7.5)	2.62 (2H, *t*, 7.5)	2.68 (2H, *t*, 7.5)
8′	1.92 (2H, *m*)	1.81 (2H, *m*)	1.89 (2H, *m*)
9′	4.05 (2H, *m*)	3.56 (2H, *t*, 6.3)	3.70 (2H, *t*, 6.3)
2″	7.03 (1H, *d*, 1.5)	7.03 (1H, *d*, 1.8)	6.94 (1H, *s*)
5″	7.14 (1H, *d*, 8)	7.14 (1H, *d*, 8)	6.90 (1H, *d*, 8)
6″	6.93 (1H, *dd*, 1.5, 8)	6.93 (1H, *dd*, 1.8, 8)	6.76 (1H, *d*, 8)
7″	5.55 (1H, *d*, 5.7)	5.55 (1H, *d*, 6.0)	5.55 (1H, *d*, 7.5)
8″	3.45 (1H, *m*)	3.40 (1H, *m*)	3.63 (1H, *m*)
9″	3.75 (2H, *m*)	3.75 (2H, *m*)	3.96 (2H, *m*)
1-gl	4.80 (1H, *d*, 7.8)	—	—
4″-gl	4.85 (1H, *d*, 7.8)	4.87 (1H, *d*, 7.8)	—
OMe	3.87 (3H, *s*)	3.86 (3H, *s*)	3.89 (3H, *s*)
OMe	3.83 (3H, *s*)	3.83 (3H, *s*)	3.87 (3H, *s*)

urophyllum is significant from a chemotaxonomic point of view.

EXPERIMENTAL

General

^{1}H, ^{13}C NMR, DEPT, COSY, HMQC and HMBC experiments: Varian FT-300, Bruker AM 300 and Varian FT-400 spectrometers.

Plant material

Jasminum 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

Fractionation of the EtOH extract of leaves and stems (1.5 kg) was carried out according to Ref. [7]. The *n*-BuOH-sol. fr. (30 g) was applied to a LH-20 column (750 g) and eluted with MeOH to give a residue (18 g). This was chromatographed on a silica gel column (180 g) and eluted with $CHCl_3$–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. C was chromatographed on a RP-C18 column (200 g) and eluted with MeOH–H_2O (1:4, 500 ml; 2:3, 500 ml; 1:1, 900 ml) to yield 9 frs. Fr. C3 was purified by CC (silica gel, 25 g) and eluted with $CHCl_3$–MeOH (5:1) to yield urolignoside (**2**, 495 mg). Fr. C6 (529 mg) was separated by a CC (silica gel, 20 g) developed with the same solvent mixture as fr. C3 and further purified by a reverse-phase CC (RP-C18) using MeOH–H_2O (1:1) to yield jasurolignoside (**1**, 115 mg).

Jasurolignoside (**1**). Amorphous solid. $[\alpha]_D^{25}$ −140° (MeOH, *c* 0.11). CD nm (θ) 229 (−3.68 E+05), 268 (−1.53 E+04), 292 (+2.22 E+04). UV λ_{max}^{MeOH} nm (log ε): 233 (4.02), 278 (3.27). IR ν_{max}^{neat} cm^{-1}: 3435, 2952, 2923, 2852, 1633, 1513, 1502, 1463, 1450, 1440, 1384, 1351, 1305, 1265, 1213, 1160, 1143, 1099, 1076, 1045, 890, 852, 769. ^{1}H and ^{13}C NMR: Tables 1 and 2. FABMS *m/z*: 931 $[M+Na]^+$; negative FABMS *m/z*: 907 $[M-H]^-$.

Jasurolignoside nonaacetate. Acetylation (Ac_2O–Pyridine; 2:1; room temp.) of **1** (15 mg) gave, after work-up and purification (silica gel) jasurolignoside nonaacetate (12 mg) as a solid. $[\alpha]_D^{25}$ −115.3° (MeOH, *c* 0.15). UV λ_{max}^{MeOH} nm (log ε): 234 (4.01), 277 (3.30). IR ν_{max}^{neat} cm^{-1}: 3023, 2954, 2852, 1754, 1708, 1633, 1513, 1452, 1367, 1303, 1226, 1164, 1070, 1039, 981, 908, 856, 815. FABMS *m/z*: 1311 $[M+Na+2H]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.72 (1H, *s*, H-1), 7.47 (1H, *s*, H-3), 4.00 (1H, *m*, H-5), 2.44 (1H, *dd*, J = 9, 14.6 Hz, H-6a), 2.76 (1H, *dd*, J = 4.2, 14.6 Hz, H-6b), 6.01 (1H, *q*, J = 6.9 Hz, H-8), 1.75 (3H, *d*, J = 6.9 Hz, H-10), 3.73 (3H, *s*, COOMe), 6.63 (1H, *s*, H-2′), 6.65 (1H, *s*, H-6′), 2.61 (2H, *t*, J = 7.2 Hz, H-7′), 1.91 (2H, *m*, H-8′), 4.02 (2H, *m*, H-9′), 6.96 (1H, *d*, J = 1.5 Hz, H-2″), 7.08 (1H, *d*, J = 8.4 Hz, H-5″), 6.89 (1H, *dd*,

Table 2. ^{13}C NMR spectral data (75.4 MHz)* for compounds **1**, **2** and **4**

C	δ (ppm) **1** (CD_3OD)	**2** (CD_3OD)	**4** ($CDCl_3$)
1	95.3 *d*	—	—
3	155.3 *d*	—	—
4	109.6 *s*	—	—
5	32.1 *d*	—	
6	41.3 *t*	—	—
7	173.5 *s*	—	—
8	124.9 *d*	—	—
9	130.8 *s*	—	—
10	13.8 *q*	—	—
11	168.8 *s*	—	—
COOMe	52.1 *q*	—	—
1′	136.4 *s*	137.2 *s*	135.4 *s*
2′	114.4 *d*	114.3 *d*	112.4 *d*
3′	145.5 *s*	145.4 *s*	144.2 *s*
4′	147.8 *s*	147.7 *s*	146.6 *s*
5′	129.8 *s*	129.7 *s*	127.7 *s*
6′	118.2 *d*	118.2 *d*	115.9 *d*
7′	33.0 *t*	33.0 *t*	34.6 *t*
8′	31.8 *t*	35.9 *t*	32.0 *t*
9′	65.3 *t*	62.4 *t*	62.3 *t*
1″	138.5 *s*	138.5 *s*	133.1 *s*
2″	111.3 *d*	111.4 *d*	108.8 *d*
3″	151.1 *s*	151.1 *s*	147.1 *s*
4″	147.7 *s*	147.6 *s*	145.6 *s*
5″	118.1 *d*	118.1 *d*	114.2 *d*
6″	119.5 *d*	119.5 *d*	119.4 *d*
7″	88.7 *d*	88.6 *d*	87.9 *d*
8″	55.8 *d*	55.8 *d*	53.8 *d*
9″	65.2 *t*	65.2 *t*	63.9 *t*
3′-OMe	57.0 *q*	57.0 *q*	56.0 *q*
3″-OMe	56.9 *q*	56.9 *q*	56.0 *q*
1-gl	101.0 *d*	—	—
1-g2	75.0 *d*	—	—
1-g3	78.6 *d*	—	—
1-g4	71.6 *d*	—	—
1-g5	78.1 *d*	—	—
1-g6	63.0 *t*	—	—
4″-gl	102.9 *d*	102.9 *d*	—
4″-g2	74.9 *d*	75.0 *d*	—
4″-g3	78.3 *d*	78.3 *d*	—
4″-g4	71.5 *d*	71.5 *d*	—
4″-g5	78.0 *d*	78.0 *d*	—
4″-g6	62.6 *t*	62.6 *t*	—

*s = C, d = CH, t = CH_2, q = CH_3. Multiplicities and assignment made by DEPT, HMQC and HMBC.

J = 1.5, 8.4 Hz, H-6″), 5.47 (1H, *d*, J = 6.9 Hz, H-7″), 3.75 (1H, *m*, H-8″), 4.29 (1H, *m*, H-9″a), 4.44 (1H, *dd*, J = 5.4, 11, H-9″b), 5.00–5.25 (1H, *m*, H-G1), 4.93 (1H, *m*, H-G1″), 3.89 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 2.03 × 4, 2.06 × 2, 2.07 × 3 (27H, *s*, OAc). ^{13}C NMR (CD_3OD, 75.4 MHz): δ 93.7 (*d*, C-1), 153.0 (*d*, C-3), 108.7 (*s*, C-4), 30.5 (*d*, C-5), 40.0 (*t*, C-6), 170.5 (*s*, C-7), 124.7 (*d*, C-8), 128.1 (*s*, C-9), 13.6 (*q*, C-10), 166.7 (*s*, C-11), 51.5 (*q*, $COOCH_3$), 134.9 (*s*, C-1′), 112.6 (*d*, C-2′), 144.1 (*s*, C-3′), 146.1 (*s*, C-4′), 127.0 (*s*, C-5′), 116.1 (*d*, C-6′), 32.0 (*t*, C-7′), 30.3 (*t*, C-8′), 63.9 (*t*, C-9′), 137.3 (*s*, C-1″), 110.6 (*d*, C-2″), 150.7 (*s*, C-3″), 145.9 (*s*, C-4″), 118.4 (*d*, C-5″), 120.1 (*d*, C-6″), 87.8 (*d*, C-7″), 50.7 (*d*, C-8″), 65.4 (*t*, C-9″), 56.1 (*q*, C3′-OCH_3), 56.0 (*q*, C3″-OCH_3), 97.0 (*d*, C-G1), 71.0 (*d*, C-G2), 72.5 (*d*, C-G3), 68.2 (C-G4), 72.2 (*d*, C-G5), 61.8 (*t*, C-G6), 100.8 (*d*, C-G1″), 71.2 (*d*, C-G2″), 72.6 (*d*, C-G3″), 68.4 (*d*, C-G4″), 72.0 (*d*, C-G5″), 61.9 (*t*, C-G6″), 20.9, 20.8 × 2, 20.7 × 3, 20.6 × 3 (*q*, $COCH_3$), 169.1, 169.2, 169.3, 169.4, 170.2, 170.7, 170.5, 170.2, 170.1 (*s*, $COCH_3$).

Alkaline hydrolysis of jasuroligniside (**1**)

Hydrolysis (0.5 M NaOH, 2 ml; room temp.) of **1** (100 mg) and usual work-up, provided a residue, which was separated by a prep. RP-C18 TLC using MeOH–H_2O (1:1), to give urolignoside (**2**, 35 mg).

Uroligniside (**2**). Amorphous solid. $[\alpha]_D^{25}$ −43.6°C (MeOH, c 0.15). UV λ_{max}^{MeOH} nm (log ε): 235 (4.03), 278 (3.37). ν_{max}^{neat} cm^{-1}: 3399, 2925, 2879, 1641, 1604, 1513, 1494, 1452, 1427, 1351, 1330, 1265, 1213, 1139, 1074, 1043, 902, 854, 809. FABMS m/z: 545 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Uroligniside hexaacetate (**3**). Acetylation (Ac_2O–Pyridine 1:1, room temp.) of **2** (16 mg) after work-up and purification by prep. TLC (silica gel, $CHCl_3$–Me_2CO, 15:1) gave urolignoside hexaacetate (**3**, 12 mg) as a solid. $[\alpha]_D^{25}$ −8.6° (MeOH, c 0.2). UV λ_{max}^{MeOH} nm (log ε): 235 (4.03), 280 (3.50). IR ν_{max}^{neat} cm^{-1}: 2952, 2852, 1737, 1604, 1500, 1461, 1450, 1427, 1365, 1218, 1141, 1120, 1035, 908, 856, 811. ^1H NMR ($CDCl_3$): δ 6.65 (1H, *s*, H-2′), 6.64 (1H, *s*, H-6′), 2.64 (2H, *t*, J = 7.5 Hz, H-7′), 1.95 (2H, *m*, H-8′), 4.09 (2H, *t*, J = 6.6 Hz, H-9′), 6.95 (1H, *d*, J = 1.5 Hz, H-2″), 7.09 (1H, *d*, J = 8.1 Hz, H-5″), 6.87 (1H, *dd*, J = 1.5, 8.1 Hz, H-6″), 5.47 (1H, *d*, J = 6.9 Hz, H-7″), 3.74 (1H, *m*, H-8″), 4.27 (2H, *m*, H-9″), 4.93 (1H, *d*, J = 7.8 Hz, 4″-G1), 3.89 (3H, *s*, OMe), 3.80 (3H, *s*, OMe) 2.03 × 4, 2.06 × 2, 207 × 3 (27H, *s*, OAc), 2.03, 2.04, 2.05 × 2, 2.07, 2.08 (18H, *s*, OAc). ^{13}C NMR ($CDCl_3$): δ 135.1 (*s*, C-1′), 112.8 (*s*, C-2′), 144.2 (*s*, C-3′), 146.2 (*s*, C-4′), 127.0 (*s*, C-5′), 116.2 (*d*, C-6′), 30.6 (*t*, C-7′), 32.0 (*t*, C-8′), 63.7 (*t*, C-9′), 137.4 (*s*, C-1″), 110.7 (*d*, C-2″), 150.8 (*s*, C-3″), 146.0 (*s*, C-4″), 118.4 (*d*, C-5″), 120.1 (*d*, C-6″), 87.8 (*d*, C-7″), 50.7 (*d*, C-8″), 65.5 (*t*, C-9″), 56.1 (*q*, C3′-OCH_3), 56.0 (*q*, C3″-OCH_3), 100.8 (*d*, C-G1″), 71.2 (*d*, C-G2″), 72.6 (*d*, C-G3″), 68.4 (*d*, C-G4″), 72.0 (*d*, CG5″), 61.9 (*t*, C-G6″), 21.0, 20.8, 20.7, 20.6, 20.5 × 2 (*q*, $COCH_3$), 169.3, 169.4, 170.3, 170.6, 170.7, 171.1, (*s*, $COCH_3$). FABMS m/z: 797 $[M+Na]^+$.

Hydrolysis of urolignoside (**2**)

To a soln of urolignoside (12 mg) in 0.1 M acetate buffer (1 ml) was added β-glucosidase (1.6 mg). The reaction mixt. was allowed to stir for 2.5 h at 37° and then extracted with $CHCl_3$ to yield compound **4**. $[\alpha]_D^{25}$ −14.3° (MeOH, c 0.2). CD nm (θ) 226 (−3.56

E+0.3), 241 (+1.56 E+0.4), 291 (+7.82 E+03). UV λ_{max}^{MeOH} nm (log ε): 235 (4.05), 280 (3.30). IR ν_{max}^{neat} cm^{-1}: 3400, 2919, 2850, 1604, 1515, 1496, 1461, 1452, 1272, 1209, 1139, 1124, 1029, 852, 808. FABMS *m/z*: 383 $[M+Na]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

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