

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

(Received 3 November 1997)

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. © 1998 Elsevier Science Ltd. All rights reserved

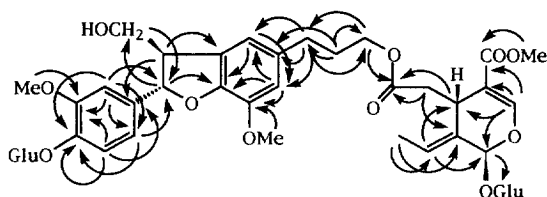
INTRODUCTION

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**.

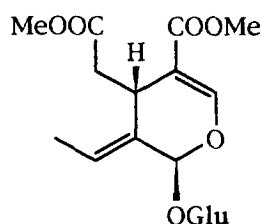
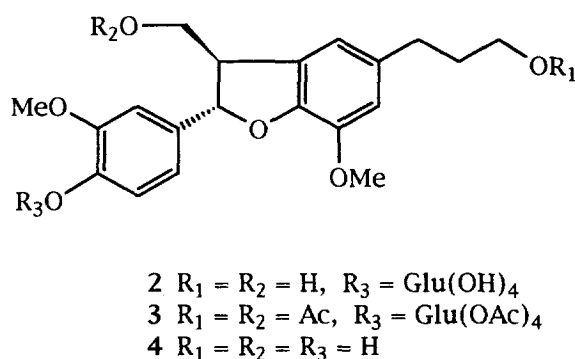
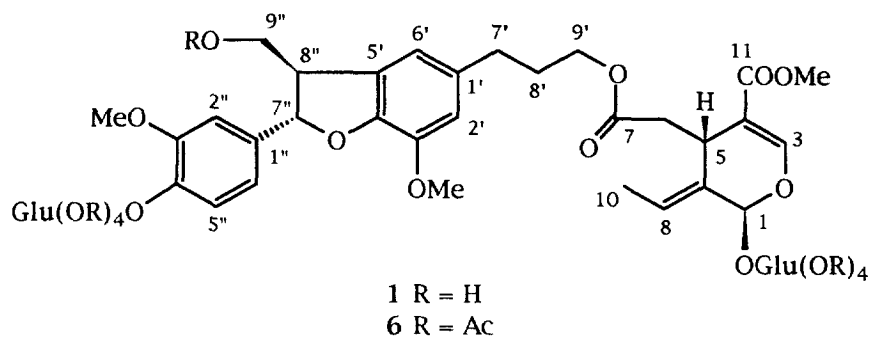
RESULTS AND DISCUSSION

Jasurolignoside (**1**), $[\alpha]_D^{25} -140^\circ$ (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 func-

tions. 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.



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 $[\text{M} + \text{Na}]^+$. 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**.

Jasuroignoside (**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 jasuroside A–G, in *J.*

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

H	1 (CD ₃ OD)	δ ($J = \text{Hz}$) 2 (CD ₃ OD)	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

^1H , ^{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-H₂O (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-H₂O (1:1) to yield jasurolognoside (**1**, 115 mg).

Jasurolognoside (1). Amorphous solid. $[\alpha]_{\text{D}}^{25} -140^\circ$ (MeOH, *c* 0.11). CD nm (θ) 229 ($-3.68 \text{ E}+05$), 268 ($-1.53 \text{ E}+04$), 292 ($+2.22 \text{ E}+04$). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 233 (4.02), 278 (3.27). IR $\nu_{\text{max}}^{\text{neat}}$ 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. ^1H and ^{13}C NMR: Tables 1 and 2. FABMS m/z : 931 $[\text{M}+\text{Na}]^+$; negative FABMS m/z : 907 $[\text{M}-\text{H}]^-$.

Jasurolognoside nonaacetate. Acetylation (Ac_2O -Pyridine; 2:1; room temp.) of **1** (15 mg) gave, after work-up and purification (silica gel) jasurolognoside nonaacetate (12 mg) as a solid. $[\alpha]_{\text{D}}^{25} -115.3^\circ$ (MeOH, *c* 0.15). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 234 (4.01), 277 (3.30). IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1} : 3023, 2954, 2852, 1754, 1708, 1633, 1513, 1452, 1367, 1303, 1226, 1164, 1070, 1039, 981, 908, 856, 815. FABMS m/z : 1311 $[\text{M}+\text{Na}+2\text{H}]^+$. ^1H 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	1 (CD_3OD)	δ (ppm) 2 (CD_3OD)	4 (CDCl_3)
1	95.3 <i>d</i>	—	—
3	155.3 <i>d</i>	—	—
4	109.6 <i>s</i>	—	—
5	32.1 <i>d</i>	—	—
6	41.3 <i>t</i>	—	—
7	173.5 <i>s</i>	—	—
8	124.9 <i>d</i>	—	—
9	130.8 <i>s</i>	—	—
10	13.8 <i>q</i>	—	—
11	168.8 <i>s</i>	—	—
COOMe	52.1 <i>q</i>	—	—
1'	136.4 <i>s</i>	137.2 <i>s</i>	135.4 <i>s</i>
2'	114.4 <i>d</i>	114.3 <i>d</i>	112.4 <i>d</i>
3'	145.5 <i>s</i>	145.4 <i>s</i>	144.2 <i>s</i>
4'	147.8 <i>s</i>	147.7 <i>s</i>	146.6 <i>s</i>
5'	129.8 <i>s</i>	129.7 <i>s</i>	127.7 <i>s</i>
6'	118.2 <i>d</i>	118.2 <i>d</i>	115.9 <i>d</i>
7'	33.0 <i>t</i>	33.0 <i>t</i>	34.6 <i>t</i>
8'	31.8 <i>t</i>	35.9 <i>t</i>	32.0 <i>t</i>
9'	65.3 <i>t</i>	62.4 <i>t</i>	62.3 <i>t</i>
1''	138.5 <i>s</i>	138.5 <i>s</i>	133.1 <i>s</i>
2''	111.3 <i>d</i>	111.4 <i>d</i>	108.8 <i>d</i>
3''	151.1 <i>s</i>	151.1 <i>s</i>	147.1 <i>s</i>
4''	147.7 <i>s</i>	147.6 <i>s</i>	145.6 <i>s</i>
5''	118.1 <i>d</i>	118.1 <i>d</i>	114.2 <i>d</i>
6''	119.5 <i>d</i>	119.5 <i>d</i>	119.4 <i>d</i>
7''	88.7 <i>d</i>	88.6 <i>d</i>	87.9 <i>d</i>
8''	55.8 <i>d</i>	55.8 <i>d</i>	53.8 <i>d</i>
9''	65.2 <i>t</i>	65.2 <i>t</i>	63.9 <i>t</i>
3'-OMe	57.0 <i>q</i>	57.0 <i>q</i>	56.0 <i>q</i>
3''-OMe	56.9 <i>q</i>	56.9 <i>q</i>	56.0 <i>q</i>
1-gl	101.0 <i>d</i>	—	—
1-g2	75.0 <i>d</i>	—	—
1-g3	78.6 <i>d</i>	—	—
1-g4	71.6 <i>d</i>	—	—
1-g5	78.1 <i>d</i>	—	—
1-g6	63.0 <i>t</i>	—	—
4''-gl	102.9 <i>d</i>	102.9 <i>d</i>	—
4''-g2	74.9 <i>d</i>	75.0 <i>d</i>	—
4''-g3	78.3 <i>d</i>	78.3 <i>d</i>	—
4''-g4	71.5 <i>d</i>	71.5 <i>d</i>	—
4''-g5	78.0 <i>d</i>	78.0 <i>d</i>	—
4''-g6	62.6 <i>t</i>	62.6 <i>t</i>	—

**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 $\times$ 4, 2.06 $\times$ 2, 2.07 $\times$ 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 $\times$ 2, 20.7 $\times$ 3, 20.6 $\times$ 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 jasurologinoside (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 $\text{MeOH-H}_2\text{O}$ (1:1), to give urolignoside (**2**, 35 mg).

Urolignoside (2). Amorphous solid. $[\alpha]_D^{25}$ –43.6° (MeOH, *c* 0.15). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 235 (4.03), 278 (3.37). $\nu_{\text{max}}^{\text{neat}}$ 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 [$\text{M} + \text{Na}$] $^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Urolignoside 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 $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 235 (4.03), 280 (3.50). IR $\nu_{\text{max}}^{\text{neat}}$ 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 $\times$ 4, 2.06 $\times$ 2, 2.07 $\times$ 3 (27H, *s*, OAc), 2.03, 2.04, 2.05 $\times$ 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*, C-G5''), 61.9 (*t*, C-G6''), 21.0, 20.8, 20.7, 20.6, 20.5 $\times$ 2 (*q*, COCH_3), 169.3, 169.4, 170.3, 170.6, 170.7, 171.1, (*s*, COCH_3). FABMS *m/z*: 797 [$\text{M} + \text{Na}$] $^+$.

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 $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 235 (4.05), 280 (3.30). IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1} : 3400, 2919, 2850, 1604, 1515, 1496, 1461, 1452, 1272, 1209, 1139, 1124, 1029, 852, 808. FABMS m/z : 383 $[\text{M} + \text{Na}]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Acknowledgements—The authors thank the National Science Council, Republic of China (NSC 86-2732-B-110-002, awarded to Y.C.S.) for financial support. Prof. Tian-Shung Wu, Department of Chemistry, National Cheng Kung University, is acknowledged for his help in providing CD spectra.

REFERENCES

1. Tanahashi, T., Takenaka, Y. and Nagakura, N., *J. Nat. Prod.*, 1997, **60**, 514.
2. Tanahashi, T., Shimada, A., Nagakura, N., Inoue, K., Ono, M., Fujita, T. and Chen, C.-C., *Chem. Pharm. Bull.*, 1995, **43**, 729.
3. Tanahashi, T., Nagakura, N., Inoue, K. and Inouye, H., *Tetrahedron Lett.*, 1988, **29**, 1793.
4. Tanahashi, T., Nagakura, N., Inoue, K., Inouye, H. and Shingu, T., *Chem. Pharm. Bull.*, 1987, **35**, 5032.
5. Ross, S. A., El-Sayyad, S. M., Ali, A. A. and El-Keltawy, N. E., *Fitoterapia*, 1982, **53**, 91.
6. Shen, Y. C. and Hsieh, P. W., *J. Nat. Prod.*, 1997, **60**, 453.
7. Shen, Y. C. and Hsieh, P. W., *Phytochemistry*, 1997, **46**, 1197.
8. Ikouno, Y., Yanagida, S., Shimono, M., Shintomi, Ito, Y. and Yang, C. S., *Phytochemistry*, 1993, **32**, 1573.
9. Achenbach, H., Grob, J., Dominguez, X. A., Cano, G., Star, J. V., Brussolo, L. D. C., Munoz, G., Salgado, F. and Lopez, L., *Phytochemistry*, 1993, **32**, 1573.
10. Yuasa, K., Ide, T., Otsuka, H., Ogimi, C., Hirata, E., Takushi, A. and Takeda, Y., *Phytochemistry*, 1997, **45**, 611.