Pergamon

PII: S0031-9422(96)00641-3

Phytochemistry, Vol. 44, No. 5, pp. 891–895, 1997

0031-9422/97 $17.00+0.00

THREE SECOIRIDOID GLUCOSIDES FROM *JASMINUM LANCEOLARIUM*

YA-CHING SHEN,* SHAO-LING LIN and CHYH-CHUNG CHEIN

Institute of Marine Resources, National Sun Yat-sen University, 70 Lien-Hai Road, Kaohsiung, Taiwan, R.O.C.

(*Received in revised form* 3 *August* 1996)

Key Word Index—*Jasminum lanceolarium*; Oleaceae; secoiridoid glycosides; jaslanceosides C–E.

Abstract—Three new secoiridoid glycosides, jaslanceosides C–E, in addition to jaslanceosides A and B, 10-hydroxyoleoside dimethyl ester and jasminoside were isolated from the leaves and stems of *Jasminum lanceolarium*. The structures of these compounds were elucidated on the basis of spectral analysis and chemical correlation with known compounds. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

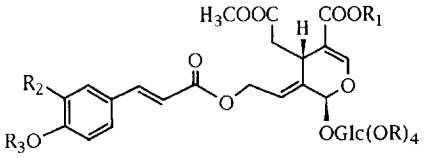
Secoridoid glycosides, the major secondary metabolites in oleaceaous plants, have been investigated extensively in the past few years [1–8]. Of particular interest are those compounds isolated from members of the genus *Jasminum*, which are known for their medicinal application in Chinese folklore [9]. *Jasminum lanceolarium* is a climbing shrub distributed over thickets at low altitudes from south-eastern China to India [10]. Its stems and roots are used in Chinese medicine for the treatment of fever and rheumatic pain. The leaves are also used as an anti-inflammatory agent for the release of pain in the eyes [11]. No previous phytochemical study on this species has been reported. In our study of the chemotaxonomy of the Oleaceae, we examined the *n*-butanol soluble constituents of *J. lanceolarium*, with emphasis on secoiridoid glycosides. Recently, we have reported two new secoirdoids, jaslanceosides A (**1**) and B (**2**), from the leaves and stems of this species [12]. Continued investigation of the *n*-butanol soluble fraction has led to the isolation of three additional new secoiridoids, jaslanceosides C (**3**), D (**4**) and E (**5**). Herein, we report the isolation and structural elucidation of the new compounds **3**–**5**.

RESULTS AND DISCUSSION

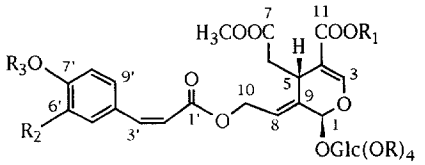
Extensive column and preparative TLC chromatography furnished three new secoiridoid glucosides, jaslanceosides C (**3**), D (**4**) and E (**5**), and the previously isolated jaslanceosides A (**1**) and B (**2**), 10-hydroxyoleoside dimethyl ester (**11**) and jasminoside from the ethanolic extract of fresh leaves and stems of *J. lanceolarium*. Compounds **3**–**5** were elucidated primarily on the basis of spectral analysis and chemical correlation with known compounds.

Jaslanceoside C (**3**), was obtained as a hygroscopic solid. The low resolution FAB–mass spectrum showed a quasi-molecular ion at *m/z* 619 $[M + Na]^+$, consistent with the molecular formula $C_{27}H_{32}O_{15}$. Its UV absorption maxima (299 and 323 nm) and IR bands (1700 and 1640 cm^{-1}) suggested the presence of a ferulic chromophore. The ^1H NMR spectrum of **3** (Table 1) resembled that of **1** and exhibited typical signals from a 10-hydroxyoleoside nucleus. The chemical shifts in the aromatic region in **3** were similar to those of jaslanceoside A (**1**). However, an AX spin system at δ 5.77 *d* and δ 6.84 (J = 13 Hz), relative to the doublets in **1** at δ 6.34 and 7.62 (J = 16 Hz), suggested the presence of a *cis*-6′,7′-disubstituted cinnamoyl moiety in **3**. The ^{13}C NMR spectral data of **3** and **1** match well, except that the chemical shifts at C-2′, C-3′ and C-9′ in the aromatic side-chains showed some differences. Methylation of **3** yielded a dimethyl ether (**6**), which showed two methoxyl singlets (δ 3.86 and 3.62). The chemical shift of H-8′ in **6** was shifted downfield (+0.15 ppm), relative to that of **3**. In addition, the resonance of C-3 was shifted downfield from δ 153.3 in **3** to 155.1 in **6** (Table 2). Upon acetylation, compound **3** gave a pentaacetate (**7**). The location of the phenolic hydroxyl was determined to be at the C-7′ position, due to the upfield shift (−9 ppm) of C-7′ and the downfield shift (+8 ppm) of C-8′ in **7** compared with the corresponding signals of **3** in the ^{13}C NMR spectra. These reactions determined the locations of a 6′-methoxy-7′-hydroxy-*cis*-cin-

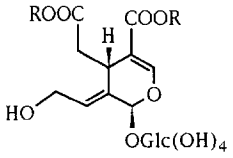
*Author to whom correspondence should be addressed.



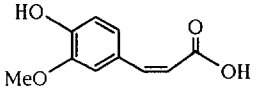
1, R = R_1 = R_3 = H, R_2 = OMe
2, R = R_1 = R_2 = R_3 = H
5, R = R_1 = R_3 = H, R_2 = OH
10, R = R_3 = Ac, R_1 = H, R_2 = OAc
14, R = H, R_1 = R_3 = Me, R_2 = OMe



3, R = R_1 = R_3 = H, R_2 = OMe
4, R = R_1 = R_2 = R_3 = H
6, R = H, R_1 = R_3 = Me, R_2 = OMe
7, R = R_3 = Ac, R_1 = H, R_2 = OMe
8, R = R_2 = H, R_1 = R_3 = Me
9, R = R_3 = Ac, R_1 = R_2 = H



11, R = Me
12, R = H



13

namoyl moiety at C-10 and of a free carboxylic acid at C-11 [13]. An HMBC spectrum of **7** revealed that correlation between the aromatic methoxyl protons (δ 3.85) and the C-6′ (δ 151.4) unambiguously assigned the location of the methoxyl moiety at C-6′ in compound **3**. The stereochemistry of **3** was further determined by observation of the coupling constants of **3** and chemical correlation with known compounds. Alkaline hydrolysis of **3** yielded compound **13** and the secoiridoid glucoside moiety (**12**), which was methylated with CH_2N_2 to furnish the known dimethyl ester (**11**) [14].

Jaslanceoside D (**4**) was obtained as an amorphous powder. The molecular formula $C_{26}H_{30}O_{14}$ was derived from the low resolution FAB-mass and DEPT spectra. The UV absorptions (224 and 298 nm) and the IR bands (1714 and 1644 cm^{-1}) resembled those of **3**. The ^1H and ^{13}C NMR data of **4** were similar to those of **3** except for the aromatic signals in the side-chain. For example, the aromatic ABX spin system in **3** was missing. Instead, a typical A_2B_2 pattern was observed at δ 7.61 and 6.76 (J = 8.5 Hz) in compound **4**. The characteristics of the chemical shifts (δ 5.76 and 6.84) and the coupling constants (J = 12.6 Hz) of H-2′ and H-3′, as well as the symmetric A_2B_2 spin system in **4** clearly indicated that it contains a *cis-p*-coumaroyl moiety [15]. Methylation of **4** yielded compound **8**, which showed two methoxyl singlets similar to those in the ^1H NMR spectrum of **6**. Upon acetylation **4** provided a pentaacetate (**9**). Comparison of the specific rotation and coupling constants of **4** with those of **3** indicated identical stereochemistry for **3** and **4**.

The UV and ^1H NMR spectra of **5** (Table 1) displayed absorptions and signals similar to those of **2**, suggesting a close relationship. Characteristic resonances included signals of a secoiridoid nucleus and of aromatic ABX (δ 6.77, 6.94 and 7.04) and AX (δ 6.25 *d*, 7.55 *d*, J = 15.9 Hz) spin systems, indicating a caffeoyl moiety on the side-chain [16, 17]. The assignment of each proton in **5** was established by a COSY experiment. In the ^{13}C NMR spectrum of **5** (Table 2), signals arising from the secoiridoid nucleus and the caffeoyl group, as well as a β-glycopyranosyl group, also resembled those of **2**, except that the aromatic methoxyl carbon in **2** (δ 56.7) was missing in **5**. Upon acetylation, compound **5** provided a hexaacetate (**10**), the ^1H NMR spectrum of which showed two aromatic acetyl singlets at δ 2.27 and 2.29, and four aliphatic acetyl singlets. Methylation of **5** yielded a trimethyl ether identical with jaslanceoside A dimethyl ether (**14**) [12]. Comparison of the ^1H NMR spectrum of **5** with that of **1** revealed a significant upfield shift for the resonance of H-5 in **5**, indicating that the methoxyl in **1** was replaced by a hydroxyl in **5**. Close comparison of the carbon resonances of **5** with those of **1** also revealed an upfield shift for C-6′, C-7′ and C-9′, and a downfield shift for C-5′ and C-8′. Alkaline hydrolysis of **5** provided caffeoic acid and the known secoridoid (**12**). On the basis of spectral and chemical evidence, compound **5** was established as 10-*O-trans*-caffeoyl-10-hydroxyoleoside-7-methyl ester.

10-Hydroxyoleoside and its methyl derivatives are common iridoids which are considered to be important precursors in the biosynthesis of secoiridoid glucosides in oleaceaous plants [18, 19]. The occurrence of coumaroyl, caffeoyl and feruloyl moieties on the side-chain of 10-hydroxyoleoside is thus of significance in the genus *Jasminum*. Biogenetically, compounds characterized by an exocyclic 8,9-olefinic and 10-hydroxyl functionality, such as jaslanceosides A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**), are derived from 10-hydroxyoleosides. From the viewpoint of chemotaxonomy, it is reasonable that the distribution of jaslanceosides A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**) would be only found in the Oleaceae.

EXPERIMENTAL

General. The ^1H, ^{13}C NMR, COSY and HMBC spectra were recorded on Varian FT-300 and Bruker

Table 1. ^{1}H NMR spectral data (300 MHz, CD_3OD, TMS as internal standard) for compounds **3–5**

	δ (ppm) (*J*, Hz)		
H	**3**	**4**	**5**
1	5.93 *brs*	5.95 *brs*	5.94 *brs*
3	7.46 *s*	7.48 *s*	7.42 *s*
5	4.08 *m*	4.07 *m*	4.10 *m*
6α	2.90	2.90	2.92 *dd* (15.1, 3.6)
6β	2.50	2.52	2.50 *dd* (15.1, 10.5)
8	6.15 *t* (7.0)	6.17 *t* (7.0)	6.14 *t* (6.6)
10	5.95, 4.85	4.95, 4.87	4.92
2′	5.77 *d* (13)	5.76 *d* (12.6)	6.25 *d* (15.9)
3′	6.84 *d* (13)	6.86 *d* (12.6)	7.55 *d* (15.9)
4′			
5′	7.78 *d* (1.8)	7.61 *d* (8.5)	7.04 *d* (2.0)
6′		6.76 *d* (8.5)	
7′			
8′	6.77 *d* (8.4)	6.76 *d* (8.5)	6.77 *d* (8.1)
9′	7.09 *dd* (8.4, 1.8)	7.61 *d* (8.5)	6.94 *dd* (8.1, 2.0)
COOMe	3.65 *s*	3.65 *s*	3.65 *s*
ArOMe	3.85 *s*		
1″	4.81 *d* (7.8)	4.82 *d* (7.8)	4.82 overlap
2″–6″	3.30–3.90 *m*	3.30–3.90 *m*	3.30–3.90 *m*

300-AC spectrometers. Chemical shifts are given in δ (ppm), coupling constants in Hz.

Plant material. Fresh leaves and stems (2.1 kg) of *J. lanceolarium* Roxb. were collected in June 1994, in Tai-chung County, Taiwan. A voucher specimen is kept in the Institute of Marine Resources, National Sun Yat-sen University.

Extraction and isolation. Part of the residue (15 g) obtained from Sephadex LH-20 column as reported in ref. [12] was chromatographed on a silica gel column (250 g) and eluted with the lower layers of the following $CHCl_3$/MeOH/H_2O mixts: 108:27:24; 108:27:16; 108:27:10; 101:27:8; 45:15:4; 13:7:2; each 1 l to give 9 frs, A (0.1 g), B (0.1 g), C (0.3 g), D (1.7 g), E (3 g), F (1.9 g), G (2.3 g), H (0.8 g) and I (0.9 g). Fr. G was re-chromatographed on a silica gel column and eluted with the same solvent system as mentioned above to yield 6 frs. Fr. G4 (0.4 g) was further purified by silica gel CC and eluted with EtOAc/Et_2O (1:1) to give jaslanceosides A (**1**) and C (**3**). Jaslanceosides B (**2**) and D (**3**) were obtained from fr. G5 (0.65 g) using silica gel CC and $CHCl_3$/EtOAc/MeOH (4:2:1). Separation of compounds **1** and **3**, as well as compounds **2** and **4**, were achieved by combination of prep. TLC (silica gel, lower layer of $CHCl_3$/MeOH/H_2O, 13:7:2; C-18, MeOH/H_2O, 1:1).

In another batch of plant material, fr. leaves and stems (2.8 kg) were crushed with EtOH (7 l × 2). The alcoholic extracts were combined and concd *in vacuo* to give an aq. suspension, which was extracted with EtOAc (750 ml). The aq. layer was then exhaustively extracted with *n*-BuOH (100 ml × 5) to yield a *n*-BuOH sol. residue (58 g). This residue was subjected to Sephadex LH-20 CC (1 kg) and eluted with MeOH (12 l) to afford a crude secoiridoid mixt. (42 g). Then, the secoiroid mixt. was chromatographed on a silica gel column (420 g) eluted with the lower layer of $CHCl_3$/MeOH/H_2O (each 2 l) to give frs I (1.5 g) (540:135:120), II (0.4 g) (540:135:80), III (3.8 g) (540:135:50), IV (17.6 g) (505:135:40), V (7 g) (45:15:4), VI (3.1 g) (65:35:10) and VII (2.3 g) (65:35:10). 10-Hydroxyoleoside-7,11-dimethyl ester (**11**) and jasminoside were obtained from fr. IV. Part of fr. VI (180 mg) was purified by prep. TLC (RP-C18, 1 mm thick × 3) developed with H_2O/MeOH (1:1) to yield jaslanceoside E (**5**, 75 mg).

Jaslanceoside C (**3**). Amorphous solid. $[\alpha]_D^{25} -58^0$ (MeOH, *c* 0.25). IR ν_{max}^{KBr} cm^{-1}: 3470, 2930, 1700, 1640, 1530, 1070, 792, 768. UV λ_{max}^{MeOH} nm (log ε): 216 (3.96), 232 (3.86), 299 (3.62), 323 (3.77). ^{1}H and ^{13}C NMR, see Tables 1 and 2. FAB-MS *m/z*: 619 ($C_{27}H_{32}O_{15}$+Na) [M + Na]$^+$. EIMS *m/z* (rel. int.): 390 (1.6), 372 (1.0), 359 (1.2), 342 (0.9), 314 (1.7), 299 (1.2), 285 (1.0), 262 (1.4), 241 (2.8), 231 (1.2), 208 (1.4), 194 (60), 177 (100), 154 (35), 150 (65), 135 (38), 123 (47), 107 (27), 91 (21), 77 (35), 73 (67).

Jaslanceoside C dimethyl ether (**6**). Jaslanceoside A

Table 2. ^{13}C NMR spectral data* (75 MHz, CD_3OD) for compounds **3–6**

	δ (ppm)			
C	**3**	**4**	**5**	**6**
1	94.2 *d*	94.2 *d*	94.0 *d*	94.4 *d*
3	153.3 *d*	153.8 *d*	152.6 *d*	155.1 *d*
4	†	111.2 *s*	†	109.3 *s*
5	33.1 *d*	33.0 *d*	33.1 *d*	32.7 *d*
6	41.2 *t*	41.1 *t*	41.1 *t*	41.0 *t*
7	173.8 *s*	173.7 *s*	173.7 *s*	173.5 *s*
8	123.9 *d*	124.0 *d*	123.8 *d*	124.2 *d*
9	135.0 *s*	134.8 *s*	135.1 *s*	134.3 *s*
10	61.8 *t*	61.7 *t*	61.9 *t*	61.7 *t*
11	169.0 *s*	169.1 *s*	168.9 *s*	168.8 *s*
1′	168.1 *s*	168.2 *s*	168.9 *s*	168.5 *s*
2′	115.1 *d*	116.5 *d*	115.2 *d*	115.0 *d*
3′	145.7 *d*	145.2 *d*	146.8 *d*	145.3 *d*
4′	128.2 *s*	127.7 *s*	127.7 *s*	126.4 *s*
5′	112.0 *d*	133.8 *d*	114.9 *d*	112.1 *d*
6′	150.8 *s*	116.1 *d*	149.6 *s*	150.9 *d*
7′	149.6 *s*	160.2 *s*	147.1 *s*	149.8 *s*
8′	116.4 *d*	116.1 *d*	116.5 *d*	117.4 *d*
9′	126.9 *d*	133.8 *d*	123.0 *d*	124.6 *d*
1″	101.0 *d*	101.0 *d*	100.9 *d*	101.1 *d*
2″	74.8 *d*	74.8 *d*	74.8 *d*	74.8 *d*
3″	78.5 *d*	78.5 *d*	78.4 *d*	78.7 *d*
4″	71.5 *d*	71.5 *d*	71.4 *d*	71.7 *d*
5″	78.0 *d*	78.0 *d*	77.9 *d*	78.1 *d*
6″	62.8 *t*	62.8 *t*	62.7 *t*	62.8 *t*
COOMe	52.9 *q*	52.4 *q*	52.2 *q*	52.1 *q*
				52.5 *q*
ArOMe	56.7 *q*		–	56.5 *q*
				56.7 *q*

* Multiplicities determined by DEPT (*s* = C, *d* = CH, *t* = CH_2, *q* = CH_3).

† Peaks too small to be observed.

(**3**) (12 mg) was treated with excess CH_2N_2 and allowed to react overnight at 0–5°. The reaction mixt. was reduced in vol. under vacuum and purified by prep. TLC (silica gel, 1 mm, developed with lower layer of $CHCl_3$/MeOH/H_2O, 13:7:2) to give **6** (5 mg). ^1H NMR (300 MHz, CD_3OD): δ 5.98 (1H, *brs*, H-1), 7.54 (1H, *s*, H-3), 4.09 (1H, *m*, H-5), 2.83 (1H, *dd*, *J* = 15.3, 4.7 Hz, H-6α), 2.51 (1H, *dd*, *J* = 15.3, 4.7 Hz, H-6β), 6.17 (1H, *t*, *J* = 7.5 Hz, H-8), 5.82 (1H, *d*, *J* = 12.6 Hz, H-2′), 6.89 (1H, *d*, *J* = 12.6 Hz, H-3′), 7.74 (1H, *d*, *J* = 2.1 Hz, H-5′), 6.92 (1H, *d*, *J* = 7.8 Hz, H-8′), 6.86 (1H, *dd*, *J* = 7.8 Hz, H-9′), 3.62 (3H, *s*, 7-COOMe), 3.66 (3H, *s*, 11-COOMe), 3.85 (3H, *s*, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): see Table 2. FABMS *m/z*: 647 $[M + Na]^+$. EIMS *m/z* (rel. int.): 575 (1.8), 545 (1.8), 531 (2.9), 487 (3.5), 443 (4.7), 412 (0.8), 352 (6.9), 284 (3.6), 250 (9.0), 208 $[C_{11}H_{12}O_4]^+$ (90), 191 $[C_{11}H_{11}O_3]^+$ (95), 163 (61), 133 (55), 91 (71), 89 (90).

Jaslanceoside C pentaacetate (**7**). Acetylation (Ac_2O/Py, 2:1, room temp.) of **3** (11 mg) gave after work-up, **7** (10 mg) as a solid. ^1H NMR (300 MHz), $CDCl_3$: δ 5.73 (1H, *brs*, H-1), 7.53 (1H, *s*, H-3), 2.85 (1H, H-6α), 2.42 (1H, H-6β), 6.05 (1H, *t*, *J* = 7.5 Hz, H-8), 5.94 (1H, *d*, *J* = 12.8 Hz, H-2′), 6.87 (1H, *d*, *J* = 12.8 Hz, H-3′), 7.10 (1H, H-5′), 7.10 (1H, H-8′), 7.05 (1H, H-9′), 3.62 (3H, COOMe), 3.85 (3H, *s*, OMe), 2.02, 2.03 (×2), 2.09 (12H, *s*, OAc), 2.32 (3H, *s*, OAc). ^{13}C NMR (75 MHz, $CDCl_3$): δ 92.9 (*d*, C-1), 151.4 (*d*, C-3), 111.3 (*s*, C-4), 29.7 (*d*, C-5), 123.6 (*d*, C-8), 133.3 (*s*, C-9), 168.7 (*s*, C-11), 51.8 (*q*, COOMe), 166.5 (*s*, C-1′), 114.3 (*d*, C-2′), 143.2 (*d*, C-3′), 151.4 (*s*, C-6′), 140.6 (*s*, C-7′), 123.2 (*d*, C-8′), 121.3 (*d*, C-9′), 97.1 (*d*, C-1″), 70.7 (*d*, C-2″), 72.5 (*d*, C-3″), 68.2 (*d*, C-4″), 72.2 (*d*, C-5″), 61.7 (*t*, C-6″), 55.9 (*q*, OMe), 20.6 (×5) (*q*, COMe), 168.7, 169.3, 169.4, 170.1, 170.6 (*s*, COMe). EIMS *m/z* (rel. int.): 331 (1.4), 271 (0.5), 255 (1.0), 215 (1.2), 208 (2.7), 194 (7.4), 169 (10), 150 (14), 115 (11), 93 (19), 84 (27), 43 (100).

Alkaline hydrolysis of jaslanceoside C (**3**). Hydrolysis (0.5 M NaOH, 2 ml; room temp.) of **3** (18 mg) provided, after work-up [2, 3], compound **13** (5 mg) and a secoiridoid glucoside (**11**). The latter was further methylated with CH_2H_2/Et_2O to give **12**, identical (^1H NMR, $[\alpha]_D$ and TLC) with 10-hydroxyoleoside-7,11-dimethylester [3]. *Compound* **13**. ^1H NMR (CD_3OD, 300 MHz): δ 5.80 (1H, *d*, *J* = 13.0 Hz, H-2′), 6.69 (1H, *d*, *J* = 13.0 Hz, H-3′), 7.66 (1H, *d*, *J* = 1.5 Hz, H-5′), 6.74 (1H, *d*, *J* = 7.8 Hz, H-8′), 7.05 (1H, *dd*, *J* = 7.8, 1.5 Hz, H-9′), 3.85 (3H, *s*, OMe). ^{13}C NMR (75 MHz, CD_3OD): δ 171.5 (*s*, C-1′), 115.7 (*d*, C-2′), 141.8 (*d*, C-3′), 128.1 (*s*, C-4′), 111.7 (*d*, C-5′), 149.5 (*s*, C-6′), 150.5 (*s*, C-7′), 116.5 (*s*, C-8′), 126.0 (*d*, C-9′), 56.6 (*q*, OMe).

Jaslanceoside D (**4**). Amorphous powder. $[\alpha]_D^{25}$ −92° (MeOH, *c*, 0.25). IR ν_{max}^{neat} cm^{-1}: 3 376, 2 920, 1 714, 1 644, 1 606, 1 514, 1 258, 1 164, 1 078, 950, 836, 796. UV λ_{max}^{MeOH} nm (log ε): 224 (4.02), 298 (3.77), 312 (3.82). ^1H and ^{13}C NMR, see Tables 1 and 2. FABMS *m/z*: 589 $[C_{26}H_{30}O_{14} + Na]^+$.

Jaslanceoside D dimethyl ether (**8**). Jaslanceoside D (**4**) (13 mg) was treated with excess CH_2N_2 and allowed to react overnight at 0–5°. The reaction mixt. was reduced under vacuum and purified by prep. TLC (silica gel, 1 mm, $CHCl_3$/EtOAc/MeOH, 4:2:1) to give **8** (5 mg). ^1H NMR (300 MHz, CD_3OD): δ 6.0 (1H, *brs*, H-1), 7.54 (1H, *s*, H-3), 2.83 (1H, *dd*, *J* = 15.0, 3.9 Hz, H-6α), 2.52 (1H, *dd*, *J* = 15.0, 9.6 Hz, H-6β), 6.15 (1H, *t*, *J* = 6.6 Hz, H-8), 5.81 (1H, *d*, *J* = 12.6 Hz, H-2′), 6.90 (1H, *d*, *J* = 12.6 Hz, H-3′), 6.90 (2H, H-6′, 8′), 7.52 (2H, H-5′, 7′), 3.63 (3H, *s*, 7-COOMe), 3.66 (3H, *s*, 11-COOMe), 3.82 (3H, *s*, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 94.5 (*d*, C-1), 155.1 (*d*, C-3), 109.3 (*s*, C-4), 32.6 (*d*, C-5), 41.0 (*t*, C-6), 173.4 (*s*, C-7), 124.4 (*d*, C-8), 134.3 (*s*, C-9), 61.6 (*t*, C-10), 168.5 (*s*, C-11), 52.5 (*q*, COOMe), 168.4 (*s*, C-1′), 115.6 (*d*, C-2′), 144.8 (*d*, C-3′), 128.3 (*s*, C-4′), 133.5 (*d*, C-5′), 116.0 (*d*, C-6′), 162.0 (*s*, C-7′), 116.0 (*d*, C-8′), 133.5 (*d*, C-9′), 101.1 (*d*, C-1″), 74.8 (*d*, C-2″), 78.7 (*d*, C-3″), 71.5 (*d*, C-4″), 78.1 (*d*, C-5″), 62.8 (*t*, C-6″), 56.0 (*q*, OMe). FABMS *m/z*: 619 $[M + Na]^+$, 597 $[M + H]^+$.

Jaslanceoside D pentaacetate (**9**). Acetylation

(Ac_2O/Py, 2:1; room temp.) of **4** (16 mg) gave, after work-up, **9** (14 mg) as a solid. ^1H NMR (300 MHz, $CDCl_3$): δ 5.74 (1H, *brs*, H-1), 7.53 (1H, *s*, H-3), 2.83 (1H, H-6α), 2.42 (1H, H-6β), 6.05 (1H, *t*, J = 6.9 Hz, H-8), 5.95 (1H, *d*, J = 12.6 Hz, H-2′), 6.91 (1H, *d*, J = 12.6 Hz, H-3′), 7.08 (2H, *d*, J = 8.7 Hz, H-6′, 8′), 7.52 (2H, *d*, J = 8.7, H-5′, 7′), 3.62 (3H, *s*, COOMe), 2.08, 2.05, 2.03, 2.01 (×2) (15 H, *s*, OAc), 2.31 (3H, *s*, OAc). ^{13}C NMR (75 MHz, $CDCl_3$): δ 92.9 (*d*, C-1), 152.1 (*d*, C-3), 108.2 (*s*, C-4), 30.8 (*d*, C-5), 39.7 (*t*, C-6), 124.2 (*d*, C-8), 133.3 (*s*, C-9), 51.8 (*q*, COOMe), 165.5 (*s*, C-1′), 119.1 (*d*, C-2′), 142.8 (*d*, C-3′), 132.2 (*s*, C-4′), 129.2 (*d*, C-5′), 121.2 (*s*, C-6′), 151.0 (*s*, C-7′), 121.2 (*d*, C-8′), 129.2 (*d*, C-9′), 97.0 (*d*, C-1″), 70.6 (*d*, C-2″), 72.4 (*d*, C-3″), 68.1 (*d*, C-4″), 72.2 (*d*, C-5″), 61.7 (*t*, C-6″), 55.9 (*q*, OMe), 20.6 (×3), 20.8, 21.1 (*q*, COMe), 169.3, 169.4, 170.1, 170.6, 171.3 (*s*, COMe). FAB-MS *m/z*: 799 $[M + Na]^+$. EIMS *m/z* (rel. int.): 331 (4.2), 289 (0.6), 271 (1.2), 255 (0.9), 229 (1.5), 194 (4), 169 (24), 147 (19), 120 (17), 115 (24), 97 (24), 84 (21), 60 (20), 43 (100).

Jaslanceoside E (**5**). Amorphous solid. $[\alpha]_D^{25} -85^\circ$ (MeOH, *c* 0.1). UV λ_{max}^{MeOH} nm (log ε): 221 (4.94), 262 (4.52), 266 (4.53), 332 (3.99). ^1H and ^{13}C NMR: see Tables 1 and 2.

Methylation of jaslanceoside E (**5**). Jaslanceoside E (**5**) (5 mg) was treated with excess CH_2N_2 and allowed to react overnight at 0–5°. The reaction mixt. was reduced under vacuum to give a trimethylate, which showed spectral data (IR, ^1H NMR, MS and $[\alpha]_D$) identical with those of **14** [12].

Jaslanceoside E hexaacetate (**10**). Acetylation (Ac_2O/Py, 2:1, room temp.) of **5** (10 mg) gave, after work-up, **10** as a solid. ^1H NMR (300 MHz, $CDCl_3$): δ 5.81 (1H, *brs*, H-1), 7.53 (1H, *s*, H-3), 2.90 (1H, *m*, H-6α), 2.43 (1H, *m*, 6β), 6.04 (1H, *t*, J = 6.5 Hz, H-8), 6.55 (1H, *d*, J = 16.2 Hz, H-2′), 7.69 (1H, *d*, J = 16.2 Hz, H-3′), 7.43 (1H, *brs*, H-5′), 7.26 (1H, *d*, J = 8.1, H-8′), 7.16 (1H, *d*, J = 8.1, H-9′), 3.64 (3H, *s*, COOMe), 2.05, 2.01 (×2), 1.98 (12 H, *s*, OAc), 2.27, 2.29 (6H, *s*, OAc).

Alkaline hydrolysis of jaslanceoside E (**5**). Hydrolysis (0.5 M NaOH, 2 ml, room temp.) of **5** (10 mg) provided, after work-up, caffeloic acid and a secoiridoid glucoside, identical (^1H NMR, [α] and TLC) with compound **12**.

Acknowledgements—This research was supported by the National Science Council, R.O.C. (grant No. NSC 85-2113-M-110-006). The authors thank Dr Kuo yao haur, National Institute of Chinese Medicine, for providing HMBC data. Ms Ho chao Lein and Yu shiu Ching of NSC southern NMR and MS Instrument Center for the measurement of NMR and MS spectral data are gratefully acknowledged.

REFERENCES

1. Shen, Y.-C. and Chen, C.-H., *Journal of Natural Products*, 1993, **56**, 1905.
2. Shen, Y.-C., Chen, C.-H. and Lee, K.-H., *Phytochemistry*, 1993, **33**, 1531.
3. Shen, Y.-C. and Chen, C.-Y., *Planta Medica*, 1995, **61**, 281.
4. He, Z.-D., Ueda, S., Inoue, K., Akaji, M., Fujita, T. and Yang, C.-R., *Phytochemistry*, 1994, **35**, 177.
5. Dantoft, S., Franzyk, H. and Jensen, S. R., *Phytochemistry*, 1992, **31**, 4197.
6. Shen, Y.-C. and Chen, C.-H., *Journal of the Chinese Chemical Society*, 1994, **41**, 473.
7. Zhang, Y. J., Liu, Y. Q., Pu, X. Y. and Yang, C.-R., *Phytochemistry*, 1995, **38**, 899.
8. Tanahashi, T., Shimada, A., Nagakura, N., Inoue, K., Ono, M., Fujita, T. and Chen, C.-C., *Chemical and Pharmacology Bulletin*, 1995, **43**, 729.
9. Kan, W. S., *Pharmaceutical Botany*, National Research Institute of Chinese Medicine, Taipei, 1981, pp. 442–443.
10. Li, H. L., Liu, T. S., Huang, T. C., Koyama, T. and DeVol, C. E., *Flora of Taiwan*, Vol. IV. Epoch, Taipei, 1981, pp. 138–140.
11. Chiu, N.-Y. and Chang, K.-H., *The Illustrated Medicinal Plants of Taiwan*, Vol. 4. SMC, Taipei, 1995, p. 171.
12. Shen, Y.-C. and Lin, S.-L., *Planta Medica*, in press.
13. Nishimura, H., Sasaki, H., Morota, T., Chin, M. and Mitsuhashi, H., *Phytochemistry*, 1989, **28**, 2705.
14. Inoue, H., Inoue, K., Nishioka, T. and Kaniwa, M., *Phytochemistry*, 1975, **14**, 2029.
15. Bianco, A., Boll, D. and Passacantilli, P., *Gazzetta Chimica Italiana*, 1981, **111**, 91.
16. Sticher, O. and Affi-Yazar, F. U., *Helvetica Chimica Acta*, 1979, **62**, 535.
17. Kikuchi, M., Yamauchi, Y., Tanahashi, Y. and Sugiyama, M., *Yakugaku Zasshi*, 1989, **109**, 366.
18. Murai, F., Tagawa, M., Damtoft, S., Jensen, S. R. and Nielsen, B. J., *Chemistry and Pharmacy Bulletin*, 1984, **32**, 2809.
19. Abe, F., Chen, R.-F. and Yamauchi, T., *Chemistry and Pharmacy Bulletin*, 1988, **36**, 2784.