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JASPOLYSIDE, A SECOIRIDOID GLYCOSIDE FROM *JASMINUM POLYANTHUM*

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Key Word Index—*Jasminum polyanthum*; Oleaceae; secoiridoid glycoside; jaspolyside.

Abstract—A new secoiridoid glucoside, jaspolyside was isolated from the leaves of *Jasminum polyanthum* along with nine known secoiridoid glycosides: oleoside dimethyl ester, 10-hydroxyoleoside dimethyl ester, oleoside 11-methyl ester, methyl-glucooleoside, 8-epi-kingiside, ligustroside, angustifolioside B, oleuropein, and oleoacetoside. The structure of the new compound has been established on the basis of spectral and chemical methods.

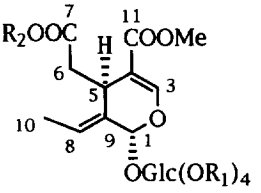
INTRODUCTION

The evergreen *Jasminum* has been extensively investigated in the past few years [1–6]. As part of a study on the secoiridoid glycosides of oleaceaous plants, we have undertaken the investigation of the chemical constituents of *Jasminum polyanthum* Franch. The species with fragrant, white flowers is indigenous to the western area of China and is now cultivated in Taiwan. In a previous paper, we reported on the structural elucidation of secoiridoid glycosides from the leaves of *J. polyanthum* [7]. We now report on the isolation of a new secoiridoid glycoside, jaspolyside (**1**), in addition to nine known secoiridoids: oleoside dimethyl ester, 10-hydroxyoleoside dimethyl ester, oleoside 11-methyl ester (**4**), methyl-glucooleoside, 8-epi-kingiside, ligustroside, angustifolioside B, oleuropein and oleoacetoside, from the ethanolic extract of this plant.

RESULTS AND DISCUSSION

A combination of solvent partition and extensive column chromatography allowed the isolation of jaspolyside (**1**) and nine known secoiridoid glycosides: oleoside dimethyl ester, 10-hydroxyoleoside dimethyl ester, oleoside 11-methyl ester (**4**), methyl-glucooleoside, 8-epi-kingiside, ligustroside, angustifolioside B, oleuropein, and oleoacetoside. The structures of these compounds were identified on the basis of spectral data and comparison with authentic samples.

Jaspolyside (**1**), $[\alpha]_D^{25}$ −53° (MeOH), was obtained as an amorphous solid. Its UV absorption at 234 nm and IR bands at 1720, 1690 and 1640 cm^{-1} suggested the presence of an enol ether system conjugated with a carbonyl chromophore. The ^1H NMR spectrum of compound **1** (Table 1) exhibited signals typical of a secoiridoid nucleus [8], including a hemiacetalic proton H-1 (δ 6.27), two vinylic protons, H-3 and H-8 (δ 7.46, 5.70), an ABX spin system comprising H-6α,β and H-5 (δ 2.90, 2.52 and 3.70). The relationships between the protons in compound **1** was established by a COSY experiment. In the ^{13}C NMR spectrum signals at δ 154.1 (C-3), 125.9 (C-8) and 132.6 (C-9), two carbonyl resonances at δ 176.6 and 168.8, a methoxy



1, $R_1 = R_2 = H$
2, $R_1 = Ac$, $R_2 = H$
3, $R_1 = H$, $R_2 = Me$

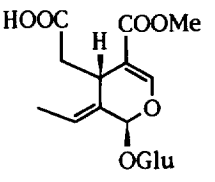


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Table 1. ^{1}H NMR spectral data* (300 MHz, CD_3OD) for compounds **1** and **4**

	1	COSY (**1**)	**4**
1	6.27 *s*		5.94 *brs*
3	7.46 *s*		7.52 *s*
5	3.70 *dd* (8.7, 3.3)	H-6	4.01 *dd* (9.6, 4.2)
6α	2.90 *dd* (15.6, 3.3)	H-5	2.72 *dd* (14.4, 4.2)
6β	2.52 *dd* (15.6, 8.7)	H-5	2.37 *dd* (14.4, 9.6)
8	5.70 *q* (7.2)	H-10	6.12 *q* (7.2)
10	1.79 *d* (7.2)	H-8	1.76 *d* (7.2)
11-OMe	3.69 *s*		3.68 *s*

*TMS as internal standard.

signal at δ 51.8 and a methyl carbon signal at δ 13.5 (C-10), and also signals from a β-glucopyranosyl group, resembled those of oleoside 11-methyl ester and suggested that compound **1** was a stereoisomer of the compound. Acetylation of compound **1** provided a tetraacetate (**2**), which showed four acetyl singlets at δ 2.05, 2.01, 1.96 and 1.92. Upon methylation, compound **1** yielded a dimethyl ester (**3**), indicating a free carboxylic function in **1**. The ^{1}H NMR spectrum of **3** exhibited an additional methoxyl signal (δ 3.64) arising from the C-7 ester group. A ^{1}H NMR spectral comparison of compounds **1** and **4** revealed significant upfield shifts in compound **1** for the resonances of H-8 and H-5, while a downfield shift was observed for the signal of H-1 (Table 1). In addition, the chemical shift of Me-10 remain unchanged, suggesting that the orientation of Me-10 is identical to that of compound **4**. The specific rotation of compound **1** although negative but much smaller than that of compound **4** (−176°, MeOH), indicating that they are diastereoisomers [9]. Close comparison of the carbon resonances of C-4, C-5 and C-6 in compound **1** with those in **4** revealed a downfield shift for C-4 and C-5, and an upfield shift for C-6, suggesting that C-5 is the epimeric carbon atom. Moreover, the chemical shifts of C-1 and C-9 appeared at δ 93.9 and 132.6 in compound **1** relative to δ 95.5 and 130.7 in compound **4**, respectively, indicating that **1** and **4** are also epimeric at C-1. These findings pointed to the structure of compound **1**, which is a new secoiridoid glycoside bearing a carboxylic acid at C-6, an α-H at C-5 and an *O*-glucosyl moiety at C-1 with α orientation. Although we could not explain the reason for the large downfield shift for C-1′ in some 1α-Glc-compounds [9, 10], both the resonances of C-1 and C-1′ in compound **1** and the shift change between these carbons are similar to those reported for 1α-protoplumericin A [11].

This is the first example of the occurrence of a secoiridoid glucoside of this type in the Oleaceae.

EXPERIMENTAL

General. FAB-MS: VG Quattro 5022 mass spectrometer; ^{1}H ^{13}C NMR and COSY Varian FT-300 spectrometer.

Plant material. Leaves of *J. polyanthum* were collected in March 1994, in Tai-chung county, Taiwan. A voucher specimen is kept in Institute of Marine Resources, National Sun Yat-sen University.

Extraction and isolation. Fresh leaves (1.1 kg) of *J. polyanthum* were extracted and fractionated as described previously [7]. After partition between *n*-BuOH and H_2O, the H_2O-soluble fraction (10 g) was chromatographed on a silica gel column (150 g) and eluted with the lower layers of mixtures of $CHCl_3$–MeOH–H_2O of increasing polarity (540:135:120; 540:135:80; 540:135:40; 505:135:40; 450:150:40; 650:350:100, each 1 l) to yield a residue (1.7 g). Further sepn of the residue by C-18 CC (16 g) developed with a mixt. of H_2O and MeOH (gradient, 5:1, 4:1, 3:1, 2:1, 1:1, each 200 ml) yielded compound **1** (15 mg), methyl-glucooleoside (32 mg) and oleoside 11 methyl ester (**4**, 46 mg).

Jaspolyside (**1**). $[\alpha]_D^{24}$: −53° (MeOH, $c = 0.075$); UV λ_{max}^{MeOH} (log ε) nm: 234 (3.68); IR ν_{max}^{neat} cm^{-1}: 3460, 1720, 1690, 1640, 1405, 1105, 930; ^{1}H NMR (CD_3OD): Table 1; ^{13}C NMR (CD_3OD): Table 2; FAB-MS *m/z* rel. int.: 427 ($[M + Na]^+$, 4.0), 386 ($[M - H_2O]^+$, 16), 225 ($[M - Glu]^+$, 5.9), 207 ($[M - Glu - H_2O]$, 10).

Jaspolyside tetraacetate (**2**). Acetylation (Ac_2O–pyridine, 2:1, rt) of compound **1** (5 mg) gave after work-up **2** (4 mg) as a solid; ^{1}H NMR ($CDCl_3$): δ 6.12 (1H, *s*, H-1), 7.42 (1H, *s*, H-3), 3.60 (1H, *m*, H-5), 2.86 (1H, *dd*, J = 15.9, 2.7 Hz, H-6a), 2.55 (1H, *dd*, J = 15.9, 7.8 Hz, H-6b), 5.72 (1H, *q*, J = 6.1 Hz, H-8), 1.73 (3H, *d*, J = 6.1 Hz, H-10), 3.70 (3H, *s*, COOMe), 1.92, 1.96, 2.01, 2.05 (12H, *s*, OAc); ^{13}C NMR (CD_3OD): δ 93.9 (*d*, C-1), 152.6 (*d*, C-3), 30.8 (*d*, C-5), 126.1 (*d*, C-8), 133.1 (*s*, C-9), 13.1 (*q*, C-10), 168.4 (*s*, C-11), 51.7 (*q*, $COOCH_3$), 97.4 (*d*, C-1′), 72.3 (*d*, C-2′), 74.1 (*d*, C-3′), 69.8 (*d*, C-4′), 73.2 (*d*, C-5′), 62.9 (*d*, C-6′),

Table 2. ^{13}C NMR spectral data* (75 MHz) for compounds **1** and **4**

C		**1**‡	**4**†
1	*d*	93.8	95.5
3	*d*	154.1	155.2
4	*s*	112.6	109.8
5	*d*	33.8	32.1
6	*t*	38.2	41.4
7	*s*	176.6	175.4
8	*d*	125.9	125.0
9	*s*	132.6	130.7
10	*q*	13.5	13.8
11	*s*	168.8	168.8
OMe	*q*	51.8	52.0
1′	*d*	100.0	101.1
2′	*d*	74.8	74.9
3′	*d*	78.5	78.5
4′	*d*	71.7	71.6
5′	*d*	78.1	78.1
6′	*t*	62.9	62.9

*Multiplicities determined by DEPT (*s* = C, *d* = CH, *t* = CH_2, *q* = CH_3).
‡Measured in CD_3OD.

20.4, 20.5 (×2), 20.6 (*q*, OAc), 170.7, 171.2, 171.6, 172.2 (*s*, OAc).

Jaspolyside methyl ester (**3**). Compound **1** (5 mg) was treated with an excess of CH_2N_2 overnight at 0–5°. The reaction mixt. was red. under vacuum to give **3** (3.5 mg); ^{1}H NMR ($CDCl_3$): δ 6.25 (1H, *s*, H-1), 7.47 (1H, *s*, H-3), 3.65 (1H, *m*, H-5), 2.89 (1H, *dd*, J = 16, 3 Hz, H-6a), 2.66 (1H, *dd*, J = 16, 7.5 Hz, H-6b), 5.63 (1H, *q*, J = 6.5 Hz, H-8), 1.78 (3H, *d*, J = 6.5 Hz, H-10), 3.69 (3H, *s*, 11-COOMe), 3.64 (3H, *s*, 7-COOMe); ^{13}C NMR (CD_3OD): δ 93.7 (*d*, C-1), 154.2 (*d*, C-3), 106.2 (*s*, C-4), 33.7 (*d*, C-5), 37.7 (*t*, C-6), 174.1 (*s*, C-7), 126.1 (*d*, C-8), 132.3 (*s*, C-9), 13.4 (*q*, C-10), 168.7 (*s*, C-11), 51.8 (*q*, $COOCH_3$), 52.1 (*q*, COOMe), 101.1 (*d*, C-1′), 74.7 (*d*, C-2′), 78.4 (*d*, C-3′), 71.6 (*d*, C-4′), 78.1 (*d*, C-5′), 62.8 (*d*, C-6′).

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