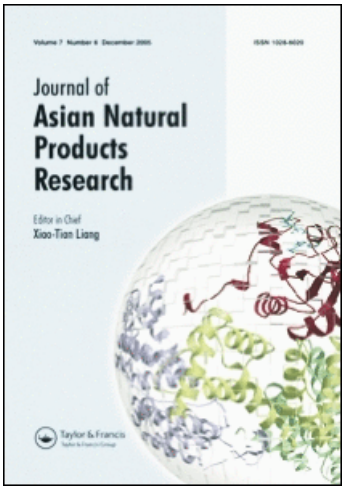

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TWO NEW FLAVONE GLYCOSIDES FROM *VALERIANA JATAMANSI*

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From the rhizomes and roots of *Valeriana jatamansi* Jones, two new flavone glycosides, acacetin 7-*O*-β-sophoroside (**1**), and acacetin 7-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-sophoroside (**2**), have been isolated together with fifteen known compounds. Their structures were determined by spectroscopic and chemical means.

Keywords: *Valeriana jatamansi*; Acacetin 7-*O*-(6″-*O*-α-L-Rhamnopyranosyl)-β-sophoroside; Valerianaceae; Acacetin 7-*O*-β-Sophoroside

INTRODUCTION

Valeriana jatamansi Jones, an annual herb distributed in the southwestern area of China, is known in Chinese folk medicine to have tranquilizing hypnotic and antiviral activities [1]. Previous phytochemical studies on this plant revealed the presence of sesquiterpenoids valerianannoids A–C [1] and essential oils [2]. Recently, we reported the isolation of 15 valeriana-type iridoids [3]. In continuation of the chemical investigation on this species, two new flavone glycosides, acacetin 7-*O*-β-sophoroside (**1**) and acacetin 7-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-sophoroside (**2**), have been isolated together with 15 known compounds (Fig. 1). The structural elucidation of these compounds is reported here.

RESULTS AND DISCUSSION

Compound **1** was obtained as a yellow amorphous powder. Its HRESIMS showed a pseudo-molecular ion $[M - H]^-$ at *m/z* 607.1658, indicating a molecular formula of $C_{28}H_{32}O_{15}$. This was supported by ^{13}C NMR and DEPT spectra, which showed 26 resonance lines consisting of one methyl, two methylenes, 15 methines, and eight quaternary carbons. The IR spectrum of compound **1** showed strong absorption bands at 3426 (OH), 1663

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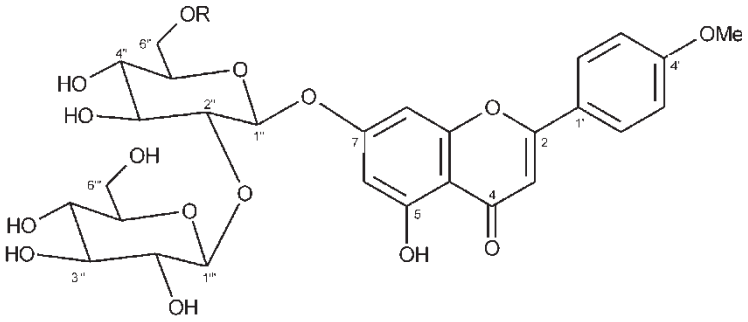

FIGURE 1 Chemical structure of compounds **1** and **2**.

(α,β-unsaturated C═O), 1610, 1580, 1489 (C═C, aromatic), and a broad band at 1160–1000 cm^{-1}, indicating its glycosidic nature. The presence of a singlet at δ 6.94 in the ^1H NMR spectrum and UV absorption bands at 270 and 325 nm suggested that it was a flavonoid [4,5]. Upon acid hydrolysis of **1**, acacetin and glucose were identified by TLC. Acacetin was also identified by UV and ^1H NMR spectroscopy [6]. The ^1H and ^{13}C NMR spectra of **1** showed the presence of an acacetin moiety [4,5] and two sugar residues [7,8]. A ^{13}C NMR signal at δ 163.4 was assigned to C-7, on the basis of its long-range $^{13}C-^1H$ correlations observed in a HMBC experiment with the two ^1H NMR signals at δ 6.46 (1H, d, $J = 2.0$ Hz, H-6) and 6.80 (1H, d, $J = 2.0$ Hz, H-8). The C-7 signal showed a three-bond correlation with the anomeric proton of a glucosyl unit at δ 5.36 (1H, d, $J = 7.2$ Hz). The anomeric proton of the second glucosyl residue at δ 4.67 (1H, d, $J = 7.6$ Hz) showed a long-range correlation with a ^{13}C NMR signal at δ 82.4, corresponding to a proton at δ 3.54 in the HMQC spectrum. The latter signal showed a $^1H-^1H$ correlation, observed in the DQF-COSY experiment, with the anomeric proton at δ 5.36, assigned to H-1″ of the first glucosyl moiety. Therefore, glycosidation of the first glucose at the C-2″ position became evident. 2D NMR allowed the assignment of all ^1H and ^{13}C NMR signals of the two glucosyl moieties (Table I). The β-configuration of two anomeric carbons was evident from the coupling constants of H-1″ ($J = 7.2$ Hz) and H-1‴ ($J = 7.6$ Hz) observed in the ^1H NMR spectrum [9]. These showed the presence of a 7-sophorosyl residue. The ^1H and ^{13}C NMR signals of the 7-sophorosyl residue were the same as those of a flavonoid sophoroside described in the literature [7,8,10–12]. Therefore, compound **1** was identified as acacetin 7-*O*-β-sophoroside.

Compound **2** was as a yellow amorphous powder. Upon acid hydrolysis of **2**, acacetin, glucose, and rhamnose were identified by TLC. Acacetin was also identified by UV and ^1H NMR spectroscopy [6]. The UV and IR spectra of **2** were similar to those of compound **1**. The molecular formula, $C_{34}H_{42}O_{19}$, was inferred from the HRESIMS ($[M-H]^-$ *m/z* 753.2246), and it was supported by ^{13}C NMR and DEPT spectroscopy. The ^1H and ^{13}C NMR spectra of **2** showed the presence of an acacetin moiety [4,5], a rhamnosyl unit, and two glucosyl residues [7,8]. Its ^1H, ^{13}C NMR and 2D NMR spectra showed the presence of an acacetin 7-*O*-β-sophoroside unit, as found for **1** (Table I). When the ^{13}C NMR data of **2** were compared with those of **1**, the effects of glycosylation of the 6″-OH, the downfield shift of C-6″ (δ 60.6 → 66.0) and the upfield shift of C-5″ (δ 77.0 → 75.6) were observed [7]. Of course, the ^{13}C NMR signal at δ 75.6 was assigned to C-5″, based on its long-range $^{13}C-^1H$ correlation to H-1″ (δ 5.32). The attachment of a rhamnosyl group at C-6 of the first glucosyl moiety was shown by the anomeric proton signal at δ 4.33 (1H, brs) [4,13–16]. The observation of the long-range correlation between the anomeric proton at δ 4.33 and C-6″ (δ 66.0) in the HMBC spectrum supported this result. The ^1H and ^{13}C NMR signals of

TABLE I ^{1}H and ^{13}C NMR data of compounds **1** and **2** (DMSO-d_6)

	1		***2***	
Position	^{13}C	^{1}H	^{13}C	^{1}H
2	164.0		164.0	
3	103.7	6.94(s)	103.9	6.93 (s)
4	182.0		182.1	
5	161.1		161.4	
6	99.6	6.46 (d, 2.0)	99.7	6.45 (d, 1.9)
7	163.4		163.1	
8	94.7	6.80 (d, 2.0)	94.7	6.79 (d, 1.9)
9	157.0		157.2	
10	104.9		105.5	
1′	122.6		122.7	
2′,6′	128.3	8.04 (d, 8.2)	128.4	8.05 (d, 8.2)
3′,5′	115.0	7.16 (d, 8.2)	114.9	7.15 (d, 8.2)
4′	162.5		162.5	
5-OH		12.92 (s)		12.90 (s)
4′-OMe	55.7	3.87 (s)	55.6	3.86 (s)
1″	98.3	5.36 (d, 7.2)	98.0	5.32 (d, 7.1)
2″	82.4	3.54 (m)	82.2	3.47 (m)
3″	76.6	3.55 (m)	76.4	3.46 (m)
4″	69.7	3.16 (m)	69.7	3.15 (m)
5″	77.0	3.18 (m)	75.6	3.24 (m)
6″	60.6	3.34, 3.56 (m)	66.0	3.23, 3.64 (m)
1‴	104.0	4.69 (d, 7.6)	103.9	4.62 (d, 7.6)
2‴	74.0	3.12 (m)	74.2	3.08 (m)
3‴	76.7	3.24 (m)	76.4	3.21 (m)
4‴	69.7	3.21 (m)	70.1	3.19 (m)
5‴	77.5	3.16 (m)	77.4	3.17 (m)
6‴	60.7	3.55, 3.64 (m)	60.7	3.52, 3.62 (m)
1⁗			100.4	4.33 (brs)
2⁗			70.3	3.22 (m)
3⁗			70.0	3.37 (m)
4⁗			71.8	3.08 (m)
5⁗			68.2	3.23 (m)
6⁗			17.7	0.96 (d, 6.2)

the 7-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-sophoroside residue were the same as those of a flavonoid-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-sophoroside described in the literature [12]. All of these data demonstrated that compound **2** was acacetin 7-*O*-(6″-*O*-α-L-rhamnopyranosyl)-β-sophoroside.

Eleven of the known compounds were identified by comparing their physical and spectral data with literature values, namely, linarin [4,13–16], acacetin 7-*O*-β-D-glucopyranoside [4,5], apigenin 7-*O*-β-D-glucopyranoside [17], kaempferol 3-*O*-β-rutinoside [18], rutin [18], kaempferol 3-*O*-β-D-glucopyranoside [18], quercetin 3-*O*-β-D-glucopyranoside [18], kaempferol [19], quercetin [19], daucosterol [20,21], and *trans*-caffeic acid [22–24]. In addition, four known substances were identified by comparison of spectral data with those of authentic samples: *trans-p*-coumaric acid, β-sitosterol, behenic acid, and nonadecyl alcohol.

EXPERIMENTAL

General Experimental Procedures

Melting points were determined on an Electrothermal 9200 micro melting point apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer model 241

polarimeter. UV and IR spectra were measured on a Shimadzu UV-1601 instrument and on a Perkin–Elmer 983 spectrometer, respectively. All NMR spectra were run on a Bruker DRX-400 instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C, using standard pulse sequences. Chemical shifts are reported on the δ scale in parts per million, downfield from TMS. Carbon multiplicities were determined from DEPT-135 and DEPT-90 experiments. All 2D NMR spectra were recorded using pulsed field gradients. $^{1}H-^{1}H$ correlations were observed in double quantum filtered (DQF) COSY and TOCSY experiments. One-bond $^{13}C-^{1}H$ correlations were observed in a HMQC experiment. Long-range $^{13}C-^{1}H$ correlations were observed in HMBC experiments. ESIMS spectra were obtained on a PE Biosystems Mariner System 5140 LC/MS spectrometer. Column chromatography was performed on Si gel (Marine Chemical Factory, Qingdao, China), Sephadex LH-20 (Pharmacia), and RP-18 (Shimadzu). Other conditions were as previously described [25].

Plant Material

The roots and rhizomes of *Valeriana jatamansi* Jones were collected from Sichuan Province, and the plant was identified by Dr Chunfeng Qiao, Department of Pharmacognosy, School of Pharmacy, Fudan University, Shanghai. After collection, the bulbs were allowed to dry at ambient temperature for about one week, and were then crushed and immediately extracted. A voucher specimen (No. SIOC-Bio-200103801) is deposited in the State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai.

Extraction and Isolation

The dried and crushed roots and rhizomes of *V. jatamansi* Jones (7.5 kg) were extracted 5 × with light petroleum at room temperature for 24 h each time; the solvent was removed under reduced pressure. The residue was extracted 5 × with EtOAc at room temperature for 24 h each time. The light petroleum extract (370.8 g) was subjected to silica-gel column chromatography, eluting with n-hexane–EtOAc (100:1) followed by stepwise addition of EtOAc to give β-sitosterol (60 g), behenic acid (55 mg), and nonadecyl alcohol (100 mg). The EtOAc extract (480.5 g) was subjected to silica-gel column chromatography, eluting with CH_2Cl_2–MeOH (100:1) followed by stepwise addition of MeOH to yield 14 fractions. Fraction 8 (32.5 g) was subjected to silica gel (CH_2Cl_2–MeOH, 5:1), and was purified by HPLC (RP_{18}, 4 μm, 254 nm, MeOH–1% acetic acid, 20:80) to give **1** (5 mg), **2** (6 mg), linarin (7 mg), acacetin 7-*O*-β-D-glucopyranoside (17 mg), apigenin 7-*O*-β-D-glucopyranoside (20 mg), kaempferol 3-*O*-β-rutinoside (18 mg), rutin (11 mg), kaempferol 3-*O*-β-D-glucopyranoside (14 mg), and quercetin 3-*O*-β-D-glucopyranoside (20 mg). Similarly, fraction 6 (40.7 g) was subjected to silica gel (CH_2Cl_2–MeOH, 9:1) to give kaempferol (17 mg), quercetin (15 mg), daucosterol (2.0 g), *trans-p*-coumaric acid (40 mg), and *trans*-caffeic acid (80 mg).

Compound **1**. Yellow amorphous powder; mp 197–198°C; UV (MeOH) λ_{max} (nm): 270, 325; IR (KBr) ν_{max} (cm^{-1}): 3426, 1663, 1610, 1580, 1573, 1489, 1444, 1415, 1365, 1307, 1268, 1265, 1165, 1135, 1087, 836; ^{1}H and ^{13}C NMR (DMSO-d_6) see Table I; HRESIMS (negative mode, MeOH) *m/z* 607.1658 $[M - H]^-$ (calcd for $C_{28}H_{31}O_{15}$, 607.1662).

Compound **2**. Yellow amorphous powder; mp 176–177°C; UV (MeOH) λ_{max} (nm): 270, 324; IR (KBr) ν_{max} (cm^{-1}): 3435, 1662, 1609, 1582, 1574, 1492, 1447, 1411, 1365, 1308, 1268, 1263, 1160, 1133, 1089, 838; ^{1}H and ^{13}C NMR (DMSO-d_6) see Table I; HRESIMS (negative mode, MeOH) *m/z* 753.2246 $[M - H]^-$ (calcd for $C_{34}H_{41}O_{19}$, 753.2241).

Acid Hydrolysis of 1 and 2

A solution of each compound (**1** and **2**) in 6% HCl (5 mL) was heated for 3 h. Each reaction mixture was extracted with EtOAc. The EtOAc fraction (aglycon) and the aqueous fraction (sugars) were concentrated to dryness for identification.

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