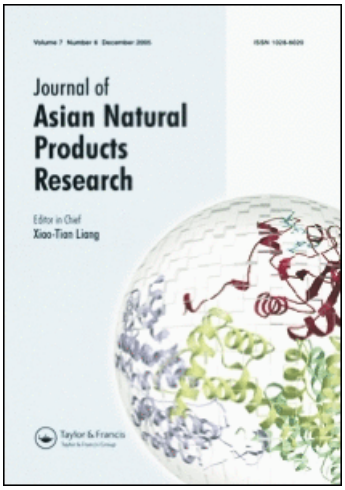

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Note: Xanthone glycosides from Swertia franchetiana

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Note

Xanthone glycosides from *Swertia franchetiana*

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A new xanthone glycoside (**1**) has been isolated from *Swertia franchetiana* together with five known xanthone glycosides. Their structures were elucidated as 7-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-1,7,8-trihydroxy-3-methoxyxanthone (**1**), 7-*O*-[α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl]-1,7,8-trihydroxy-3-methoxyxanthone (**2**), 8-*O*-β-D-glucopyranosyl-1,3,5,8-tetrahydroxyxanthone (**3**), 1-*O*-β-D-glucopyranosyl-1-hydroxy-3,7,8-trimethoxyxanthone (**4**), 1-*O*-[β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyl]-1-hydroxy-2,3,5-trimethoxyxanthone (**5**) and 1-*O*-[β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyl]-1-hydroxy-3,5-dimethoxyxanthone (**6**) on the basis of spectroscopic evidence.

Keywords: *Swertia franchetiana*; Gentianaceae; Xanthone glycoside; 7-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-1,7,8-trihydroxy-3-methoxyxanthone

1. Introduction

The genus *Swertia* (family Gentianaceae) contains about 170 species, of which 79 are distributed throughout China [1]. About 20 species of this genus have been used in Chinese traditional medicine to treat hepatic, choleric and inflammatory diseases [2,3]. The plant *Swertia franchetiana* H. Smith, distributed in the southwestern part of China, is used in Tibetan medicine for hepatitis and cholecystitis [4]. Previous investigations on this plant have led to the isolation of various xanthones, xanthone glycosides and flavonoid glucosides [5–8]. In this investigation, six xanthone glycosides were isolated from the whole plant. Compound **1** is a new xanthone dixylopyranoside, and compounds **2–5** were isolated from this plant for the first time. We report here the isolation and structure elucidation of **1**.

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2. Results and discussion

The n-BuOH-soluble part of the MeOH crude extracts of the whole plant of *Swertia franchetiana* was subjected to polyamide column chromatography, eluted gradiently with H_2O–EtOH. The 40% EtOH eluate was separated by silica-gel column chromatography and preparative HPLC to afford **1**.

Compound **1** was obtained as a yellow powder and its molecular formula $C_{24}H_{26}O_{14}$, was established by APCI mass spectrometry (539.4 $[M + H]^+$, 537.6 $[M - H]^-$) and elemental analysis. Its UV spectrum in MeOH (λ_{max} 235, 260, 327 and 390 nm) is characteristic of a xanthone with a 1,3,7,8-tetraoxygenated pattern [9]. The IR spectrum of **1** showed hydroxyl groups (3418 cm^{-1}), a hydrogen-bonded ketone (1663, 1635 cm^{-1}), and an aromatic ring (1606, 1575, 1505 cm^{-1}). The APCIMS spectra of **1** showed quasi-molecular ion peaks and fragment ion peaks at *m/z* 539.4 $[M + H]^+$, 407.4 $[M + H - 132]^+$, 275.2 $[M + H - 132 \times 2]^+$ and 537.6 $[M - H]^-$, 405.4 $[M - H - 132]^-$, 273.2 $[M - H - 132 \times 2]^-$ in positive and negative mode respectively. The loss of two *m/z* 132 units indicate the presence of two pentosyls, and the ion signals at *m/z* 275.2 and 273.2 corresponding to the aglycone moiety suggest a tetraoxygenated xanthone aglycone (one methoxy and three hydroxyl groups). Acid hydrolysis of **1** by the usual method afforded xylose. The ^1H NMR spectrum showed two carbonyl chelated hydroxyl signals at δ 11.87 and 11.60 (C-1 and C-8 hydroxyl group), four aromatic protons containing two *ortho*-coupled at δ 7.56, 7.13 (each 1H, d, $J = 8.8$ Hz), and two *meta*-coupled at δ 6.56, 6.36 (each 1H, d, $J = 2.1$ Hz), two anomeric proton signals at δ5.11 (1 H, d, $J = 6.8$ Hz), 4.55 (1H, d, $J = 7.2$ Hz), and one methoxyl signal at δ 3.88 (3H, s). The ^{13}C NMR and DEPT-135 spectra of **1** exhibited ten aliphatic carbon signals due to two pentosyl moieties, thirteen carbon signals corresponding to the xanthone skeleton. Thus, **1** should be a 1,3,7,8-tetraoxygenated xanthone dixylosyl glycoside. The positions of the methoxyl group and the sugar moiety were confirmed through HMBC spectrum. In the HMBC spectrum of **1**, the C–H correlation between the methoxyl protons at δ 3.88 and C-3 (δ 167.08) indicate that the methoxyl group should be at C-3. The anomeric proton signal at δ 5.11 is correlated to C-7 of the aglycone (δ 139.35), which accords with the attachment of the sugar moiety to the oxygen at C-7. The correlation between anomeric proton (δ 4.55) of one xylose and C-2 signal (δ 81.35) of the other xylose suggests that two xylosyl units are connected by a $1 \rightarrow 2$ pattern. The configurations of two xylose residues were deduced to be both β from the *J* values (6.8, 7.2 Hz respectively) of two anomeric protons. According to the above evidence, compound **1** was identified as 7-*O*-[β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl]-1,7,8-trihydroxy-3-methoxyxanthone (figure 1).

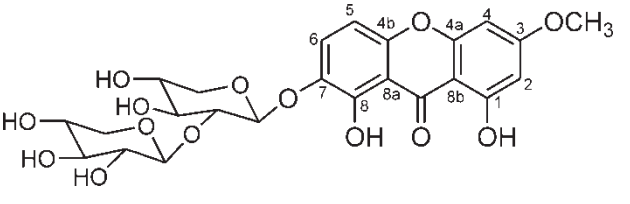

Figure 1. Structure of compound **1**.

Compound **2** was obtained as a yellow powder and its UV and IR spectra were very similar to those of **1**. By comparing MS and NMR spectra of **1** and **2**, it can be deduced that **2** possesses the same aglycone as **1** and a different sugar moiety. The APCIMS signals of **2** at *m/z* 551.6 $[M - H]^-$, 405.4 $[M - H - 146]^-$, 273.4 $[M - H - 146 - 132]^-$ suggest a rhamnosyl-xylosyl moiety, which was further confirmed by acid hydrolysis. **2** was identified as 7-*O*-[α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranosyl]-1,7,8-trihydroxy-3-methoxyxanthone by comparing its spectral data with literature values [10] and its ^{1}H and ^{13}C NMR signal assignments were corrected by 2D NMR data (table 1). To our knowledge, primeverosyl and gentiobiosyl residues are very common in xanthone disaccharide glycosides from the Gentianaceae family, while dixylosyl and rhamnosyl-xylosyl glycosides like **1** and **2** have rarely been reported from this family [11].

Compounds **3**–**6** were identified by comparing their physical and spectral data with literature values: 8-*O*-β-D-glucopyranosyl-1,3,5,8-tetrahydroxyxanthone (**3**) [12], 1-*O*-β-D-glucopyranosyl-1-hydroxy-3,7,8-trimethoxyxanthone (**4**) [13], 1-*O*-[β-D-xylopyr-

Table 1. ^{1}H and ^{13}C NMR data of **1** and **2** (in DMSO-d_6)[a].

	1		***2***	
No.	^1H	^{13}C	^1H	^{13}C
1		161.9		161.8
2	6.36d (2.1)	97.3	6. 40d (2.1)	97.4
3		167.1		167.2
4	6.56d (2.1)	92.9	6.62d (2.1)	93.0
4a		157.5		157.6
4b		150.3		150.3[b]
5	7.13d (8.8)	106.0	6.97d (9.2)	105.9
6	7.56d (8.8)	125.7	7.55d (9.2)	126.2
7		139.4		139.1
8		149.8		150.3[b]
8a		107.6		107.5
8b		101.9		101.8
9		183.8		184.2
3-OMe	3.88s	56.3	3.88s	56.3
1-OH	11.88s			
8-OH	11.60s			
1′	5.11d (6.8)	100.5	5.08d (7.6)	99.9
2′	3.59t (7.2)	81.4	3.55t (8.0)	76.4
3′	3.49m[b]	75.2	3.46mb	77.1
4′	3.50m[b]	68.9	3.73mb	70.4[b]
5′	a: 3.27m[b]	65.3	a: 3.22m[b]	65.6
	b: 3.81dd (4.0, 12.0)		b: 3.78dd (4.0, 12.0)	
1″	4.55d (7.2)	104.6	5.16s	100.4
2″	3.06m[b]	74.1	3.37m[b]	69.5
3″	3.18m	75.9	3.37m[b]	70.4[b]
4″	3.30m[b]	69.5	3.16m[b]	71.9
5″	a: 3.27m[b]	65.7	3.86m[b]	68.4
	b: 3.65dd (5.0, 11.2)			
6″			1.08d (6.0)	17.9
OH[c]	3′-OH: 5.19d (3.2)		5.35	
	4′-OH: 5.48d (2.8)		5.12	
	2″-OH:5.31d (2.8)		4.66	
	3″-OH: 5.02d (4.8)		4.60	
	4″-OH: 4.98d (4.8)		4.47	

[a] Signals were assigned by means of COSY, HSQC and HMBC spectra (*J* Hz).
[b] Overlapped signals.
[c] OH signals of both sugar units.

anosyl-(1→6)-β-D-glucopyranosyl]-1-hydroxy-2,3,5-trimethoxyxanthone (**5**) [14] and 1-*O*-[β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyl]-1-hydroxy-3,5-dimethoxyxanthone (**6**) [6].

3. Experimental

3.1 General experimental procedures

Melting points were obtained using an XT-4 melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO P-1020 polarimeter. The spectra were recorded with the following instruments: IR, Perkin-Elmer 983 G spectrometer; NMR, Bruker DRX 400, 400 MHz for ^{1}H and 100 MHz for ^{13}C with TMS as internal standard; APCIMS, Finnigan TSQ MS/MS spectrometer equipped with an atmospheric pressure chemical ionization interface. Analytical HPLC, Waters 2690, PDA detector (Waters 996), Hypersil ODS-2 (5 μm) column (250 mm × 4 mm i.d.); preparative HPLC, Waters Delta Prep 4000, PDA detector (Waters 996), Superiorex ODS (5 μm) column (250 mm × 20 mm i.d., Shiserdo). Polyamide (30–60 mesh, Shanghai Chemical Co.), Silica gel (200–300 mesh, Qingdao Marine Chemical Co.) and Sephadex LH-20 (Pharmacia).

3.2 Plant material

Whole plants of *Swertia franchetiana* were collected from Qinghai Province, China, in September 2001. The plant was identified by Professor Shangwu Liu (Northwest Plateau Institute of Biology, Chinese Academy of Sciences, Xining 810001, China) and a voucher specimen has been deposited in our laboratory.

3.3 Extraction and isolation

Air-dried whole plants (12.5 kg) were ground and percolated with MeOH at room temperature to exhaustion. The combined extracts were concentrated *in vacuo* to yield 2.9 kg of residue, which was suspended in water and extracted successively with light petroleum, $CHCl_3$, EtOAc and n-BuOH. Parts of the n-BuOH extracts (200 g) were subjected to a polyamide column (10 × 85 cm) and eluted with H_2O, 20%, 40%, 60% and 95% EtOH. The 40% EtOH eluate (25.8 g) was chromatographed over silica gel (1.2 kg), eluted with $CHCl_3$–MeOH gradiently (9:1–6:4) and monitored by HPLC to yield 35 fractions. Fractions 16–22 were combined and subjected to preparative HPLC over ODS with 60% MeOH–H_2O as a mobile phase at a flow rate of 20 ml min^{-1} to furnish **1** (55 mg) and **2** (64 mg). Fractions 16–17 were concentrated to give a yellow powder, which was purified by Sephadex LH-20 (MeOH) column chromatography to yield **3** (1.5 g). The 20% EtOH eluate (10.5 g) was subjected to Si gel ($CHCl_3$–95% EtOH, 9:1–1:1) and Sephadex LH-20 (MeOH) chromatography to give compounds **4** (75 mg), **5** (115 mg) and **6** (45 mg).

3.3.1 7-*O*-[β-D-Xylopyranosyl-(1→2)-β-D-xylopyranosyl]-1,8-dihydroxy-3-methoxyxanthone (1). Yellow powder, mp 243–245°C. $[\alpha]_D^{25}$ −20.3 (*c* 0.88, DMSO); UV (MeOH) λ_{max} (nm): 235, 260, 327, 390; IR (KBr) ν_{max} (cm^{-1}): 3418, 2922, 1663,

1635, 1606, 1575, 1405, 1277, 1240, 1211, 1010, 1057, 813, 696; Positive APCI-MS *m/z*: 539.4 $[M + H]^+$, 407.4 $[M + H - Xyl]^+$, 275.2 $[M + H - Xyl \times 2]^+$; negative APCI-MS *m/z*: 537.6 $[M - H]^-$, 405.4 $[M - H - Xyl]^-$, 273.2 $[M - H - Xyl \times 2]^-$. Elemental analysis: C, 53.35; H, 4.83 (calcd for $C_{24}H_{26}O_{14}$: C, 53.83; H, 4.87%). ^1H and ^{13}C NMR data: see table 1.

3.3.2 7-*O*-[α-L-Rhamnopyranosyl-(1→2)-β-D-xylopyranosyl]-1,8-dihydroxy-3-methoxyxanthone (2). Yellow powder, mp 233–235°C. $[\alpha]_D^{25}$ −47.5 (*c* 0.57, DMSO); UV (MeOH) λ_{max} (nm): 234, 260, 329, 390; IR (KBr) ν_{max} (cm^{-1}): 3415, 2930, 1662, 1630, 1603, 1490, 1320, 1072, 1041, 1021, 895, 811; Positive APCIMS *m/z*: 553.5 $[M + H]^+$, 407.3 $[M + H - Rha]^+$, 275.2 $[M + H - Rha\text{-}Xyl]^+$; negative APCI-MS *m/z*: 551.5 $[M - H]^-$, 405.4 $[M - H - Rha]^-$, 273.2 $[M - H - Rha\text{-}Xyl]^-$. ^1H and ^{13}C NMR data: see table 1.

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