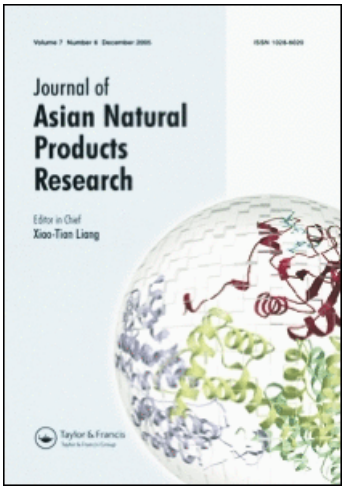

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Note

Two new compounds from *Glycyrrhiza glabra*

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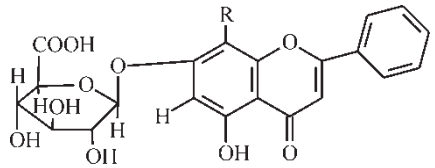
Two new flavonosides have been isolated from the roots of *Glychirriza glabra* and identified as 5,8-dihydroxy-flavone-7-*O*-β-D-glucuronide, glychionide A, and 5-hydroxy-8-methoxyl-flavone-7-*O*-β-D-glucuronide, glychionide B.

Keywords: Glucuronide; Flavonoside; *Glycyrrhiza glabra*; Glychionide A; Glychionide B

1. Introduction

Glycyrrhizae radix is one of the important crude drugs used in traditional Chinese medicine, and its constituents have been well investigated. Most of the over 200 compounds that have been separated from *Glycyrrhiza genus* [1,2] belong to flavonoids and triterpene glycosides, with 133 flavone compounds having been reported [3]. While searching for immune-activating constituents of *Glycyrrhiza glabra*, two new flavone compounds have been isolated and identified as 5,8-dihydroxy-flavone-7-*O*-β-D-glucuronide, named glychionide A (**1**), and 5-hydroxy-8-methoxyflavone-7-*O*-β-D-glucuronide, named glychionide B (**2**). This paper deals with their isolation and structure elucidation.



1 R = OH; **2** R = OCH_3

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2. Results and discussion

Compound **1**, yellow powder, mp 216–217°C; HR-NFAB-MS showed a $[M - 1]^-$ at *m/z* 445.0775, corresponding to a molecular formula of $C_{21}H_{18}O_{11}$. ^{1}H NMR data show mono-substituted benzene signals at δ 8.06 (2H, d, 7.0 Hz), 7.60 (2H, d, 7.0 Hz), 7.59 (1H, m) and two singlets at δ 7.01 (1H,s), 6.95 (1H, s) and a sugar anomeric proton signal at δ 5.23 (1H, d, $J = 7.5$ Hz, glc1-H). ^{13}C NMR data show 14 aromatic carbon signals and one carbonyl signal at δ 183.0 and a group of sugar carbon signals. These data suggest a flavonoside with no substitution in the B ring. UV spectra at λ_{max} 267, 318 nm suggest that there is no substitution at the 3-position. The two singlets at δ 7.01 (1H, s) and 6.95 (1H, s) indicate that one is in A ring and another belongs to C ring. UV (MeOH) spectra differ from UV ($AlCl_3$/HCl) spectra, suggesting a hydroxy at the 5-position, which was confirmed by the ^{1}H NMR signal at δ 12.50 (1H, s). This hydroxy proton is correlated with the carbon that is connected with the proton at δ 7.01 (1H, s). Thus, the proton at δ 7.01 (1H, s) is at the 6-position of the A ring. The ^{13}C NMR data shows another carboxyl group signal at δ 170.6, suggesting that the sugar moiety could be a glucuronic acid, which was confirmed by HMBC correlations between 5″-H at δ 4.05 and C-6″ at δ 170.6 (figure 1). Therefore, the structure of compound **1** was established as 5,8-dihydroxy-flavone-7-*O*-β-D-glucuronide.

Compound **2**, yellow powder, mp 226–227°C; HR-NFAB-MS shows a $[M - 1]^-$ at *m/z* 459.0928, corresponding to a molecular formula of $C_{22}H_{20}O_{11}$. The ^{1}H and ^{13}C NMR spectra of compound **2** were very similar to that of **1**. ^{1}H NMR also shows mono-substituted benzene signals at δ 8.06 (2H, d, 7.0 Hz), 7.60 (2H, d, 7.0 Hz), 7.59 (1H, m), two singlets at δ 7.03 (1H, s), 6.68 (1H, s), and a sugar anomeric proton signal at δ 5.23 (1H, d, $J = 7.5$ Hz, glc1-H). In addition, it has a methoxyl signal at δ 3.87 (3H, s). The ^{13}C NMR spectrum of **2** shows 14 aromatic carbon signals, one carbonyl signal (δ 182.82), and a group of sugar carbon signals; it also has a methoxyl signal at δ 61.8. Thus we concluded it could be the same kind of compound as **1**, and by comparison with **1** the spectral data of **2** was assigned (table 1). On the basis of HMBC correlation, the methoxyl group is linked to the 8-position of the flavone

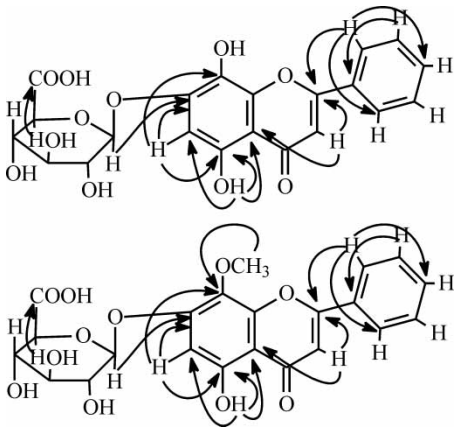

Figure 1. Key HMBC correlations of compounds **1** and **2**.

Table 1. ^{1}H and ^{13}C NMR data of **1** and **2**.

	1		***2***	
Position	δ_C	δ_H	δ_C	δ_H
2	164.1		164.1	
3	105.0	6.95 (s)	105.7	6.68 (s)
4	183.0		182.8	
5	147.2		156.4	
6	94.1	7.01 (s)	99.1	7.03 (s)
7	151.7		156.4	
8	131.0		132.7	
9	149.7		149.7	
10	106.5		105.8	
1′	131.2		131.1	
2′, 6′	126.7	8.06 (d, 7.0)	126.9	8.06 (d, 7.0)
3′, 5′	129.6	7.60 (m)	129.6	7.60 (m)
4′	132.5	7.59 (m)	132.7	7.59 (m)
Glu A 1″	100.5	5.23 (d, 7.5)	100.1	5.23 (d, 7.5)
2″	73.2		73.3	
3″	75.6		75.6	
4″	71.8		71.7	
5″	75.8	4.05 (d, 9.0)	75.8	3.97 (d, 9.0)
6″	170.6		170.6	
OCH_3			61.8	3.87 (s)

moiety and the structure of **2** was established as 5-hydroxy-8-methoxyl-flavone-7-*O*-β-D-glucuronide (figure 1).

3. Experimental

3.1 General experimental procedures

Melting points were measured on an X_4 micromelting point apparatus and are uncorrected. ^{1}HNMR, ^{13}CNMR, ^{1}H—^{1}H COSY, DEPT, HMQC and HMBC spectra were recorded in DMSO-d_6 with a Bruker Am-500 spectrometer. MS spectra were recorded on a FAB-MS instrument. For column chromatography, silica gel (Marine Chemical Plant, Qing Dao) and Sephadex LH-20, RP-18 (Chemical reagent Factory, Tian Jin) were used.

3.2 Plant material

The roots of *Glycyrrhiza glabra* were collected in Jingtai county of Gansu province in July, 2000, and identified by Professor Runeng Zhao, of the Pharmaceutical Department of Lanzhou Medical College. A voucher specimen has been deposited in the Herbarium of Pharmaceutical Department, Medical College of the Chinese People Armed Police Force, Tianjin, China.

3.3 Extraction and isolation

The powered roots of the plant (8 kg) were extracted with 95% EtOH at room temperature. The extract was concentrated under reduced pressure and diluted with H_2O. The aqueous solution was extracted with petroleum ether and EtOAc and n-BuOH

respectively. The n-BuOH extract (150 g) was absorbed onto D 101 macroporus resin column, eluted with H_2O. The H_2O-eluted fractions (32 g) were subjected to repeated chromatography on an Rp-18 silica-gel column, eluting with H_2O, 20%, 40%, 60% MeOH, and on a Sephadex LH-20 column, eluting with 10% MeOH, to give compounds **1** (30 mg) and **2** (21 mg).

3.4 Identification

Compound **1** is a yellow powder, mp 216–217°C; HR-NFAB-MS: $[M - 1]^-$ *m/z* 445.0775 (calcd for $C_{21}H_{18}O_{11}$, 445.0776); UV λ_{max} (MeOH) (nm): 267, 318; ($AlCl_3$) 272, 299, 362; ($AlCl_3$/HCl) 272, 299, 363; (NaOMe) 282, 323; (NaOAc) 270, 323; (NaOAc/H_3BO_3) 269, 323; IR (KBr) ν(cm^{-1}): 3401, 3069, 1722, 1655, 1583, 1504; ^1H and ^{13}C NMR see table 1.

Compound **2** is a yellow powder, mp 226–227°C. HR-NFAB-MS: $[M - 1]^-$ *m/z* 459.0928 (calcd for $C_{22}H_{20}O_{11}$, 459.0932); UV λ_{max} (MeOH) (nm): 262, 315; ($AlCl_3$) 268, 299, 357; ($AlCl_3$/HCl) 268, 299, 357; (NaOMe) 282, 320; (NaOAc) 266, 318; (NaOAc/H_3BO_3) 266, 318; IR (KBr) ν(cm^{-1}): 3403, 3072, 1721, 1651, 1583, 1507, ^1H and ^{13}C NMR see table 1.

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