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Four new constituents from *Taraxacum mongolicum*

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Abstract

Two new flavone glycosides, isoetin-7-*O*-β-D-glucopyranosyl-2′-*O*-α-L-arabinopyranoside (**1**) and isoetin-7-*O*-β-D-glucopyranosyl-2′-*O*-α-D-glucopyranoside (**2**), a new lignan, mongolicumin A (**3**), and a new guaianolide, mongolicumin B (**4**) were isolated from the aerial part of *Taraxacum mongolicum*. Their structures were elucidated mainly by spectral analyses.

Keywords: Flavone glycoside; Lignan; Sesquiterpene; *Taraxacum mongolicum*

The genus *Taraxacum* has about 2000 species worldwide with 70 species scattered in China, which contains mainly sesquiterpenes [1], triterpenoids [2] and flavonoids [3]. However, only pieces of phytochemical investigations specifically on *Taraxacum mongolicum* have been traced [4]. To thoroughly clarify the components of this popular Chinese herbal medicine, the plant was chemically investigated and four new compounds (**1–4**) were isolated (Fig. 1).

The aerial parts of *T. mongolicum* (5.0 kg) were purchased at Bozhou, Anhui Province in January 2001. The plant material was extracted with MeOH (50 L × 7 d × 3). The extracts were then combined and evaporated under reduced pressure to afford brown syrup (420 g). The syrup was subjected to repeated chromatography over Sephadex LH-20 and silica gel columns to afford 14.0 mg of **1**, 11.0 mg of **2**, 17.0 mg of **3**, and 9.0 mg of **4**, respectively.

Compound **1** was obtained as yellow amorphous powder. The HRESIMS of **1** showed a quasimolecular ion peak $[M+H]^+$ at *m/z* 597.1831, indicating a molecular formula of $C_{26}H_{28}O_{16}$ (calc. for $M+H$ 597.1848). The UV absorptions of **1** at 258 and 357 nm were typical characteristics of flavonoid. Using common shift reagents, UV spectral data suggested that **1** was a flavonoid with 5-OH and adjacent hydroxyl groups at ring B.

Furthermore, acid hydrolysis of **1** and subsequent workup yielded glucose, arabinose from the water layer. The comparison of their TLC characteristic and specific optical rotations suggested the presence of a D-glucose and L-arabinose in the molecule. Moreover, the obtained aglycone, isoetin, was identified by comparing its UV and ^{1}H NMR spectra with the authentic sample [5]. The ^{1}H NMR spectrum of **1** (Table 1) showed doublets at δ 6.44 (H-6) and 6.72 (H-8), as well as three singlets at δ 7.31, 7.16 and 6.77. In addition, two doublets at δ 5.08 (1H, H-1″, J = 8.0 Hz) and δ 4.87 (1H, H-1‴, J = 6.0 Hz) were assigned to the anomeric protons of the sugar moieties, which were correlated with

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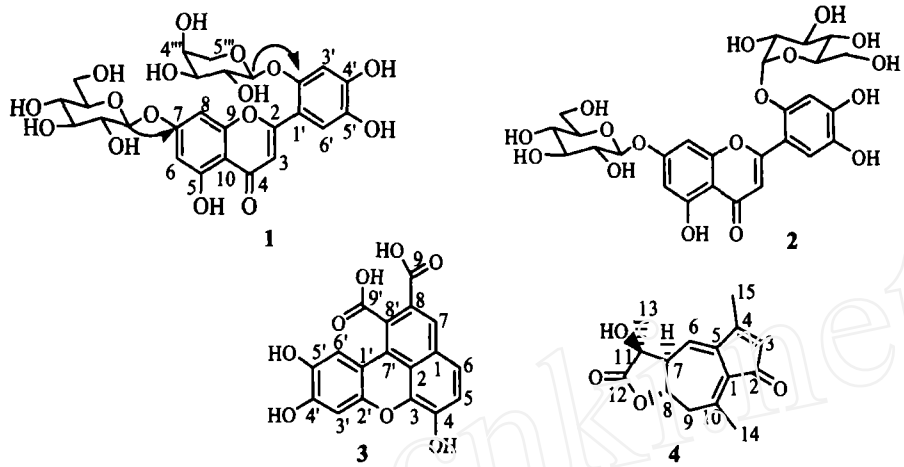

Fig. 1. Structures of compounds 1–4 and key HMBC correlations of compound 1.

the carbon resonances at δ 100.0 and 101.3, respectively. Comparing with those in the aglycone, the H-6, H-8 and H-3′ signals of **1** were apparently downfield shifted suggesting these protons might be located at the *ortho* positions of the glycosylated hydroxyl groups. Furthermore, the HMBC experiment showed correlations between δ 5.08 (H-1″) and δ 163.1 (C-7), δ 4.37 (H-1‴) and δ 150.4 (C-2′). This pointed out the presence of the sugar residues at C-7 and C-2′, respectively (Fig. 1). Moreover, the β-configuration of the glucose and α-configuration of the arabinose in **1** could be deduced from the diagnostic coupling patterns of the two anomeric protons and the corresponding carbon resonances in the NMR spectrum [6]. Thus, **1** was identified as isoetin-7-*O*-β-D-glucopyranosyl-2′-*O*-α-L-arabinopyranoside.

Table 1
NMR data of compounds **1** and **2**[a] [^{1}H, 400 MHz and ^{13}C, 100 MHz, δ ppm]

Position	**1** (DMSO-d_6)		**2** (DMSO-d_6)	
	δ_C	δ_H	δ_C	δ_H
2	161.8		161.8	
3	108.9	7.16 (1H, s)	108.9	7.11 (1H, s)
4	182.4		182.2	
5	161.4		161.3	
6	99.5	6.44 (1H, d, J = 2.0 Hz)	99.5	6.45 (1H, d, J = 2.0 Hz)
7	163.1		163.0	
8	94.7	6.72 (1H, d, J = 2.0 Hz)	94.7	6.73 (1H, d, J = 2.0 Hz)
9	157.9		157.2	
10	105.4		105.4	
1′	110.6		110.4	
2′	150.4		150.4	
3′	104.4	6.77 (1H, s)	104.7	6.80 (1H, s)
4′	150.4		150.4	
5′	140.6		140.5	
6′	114.8	7.31 (1H, s)	114.7	7.31 (1H, s)
1″	100.0	5.08 (1H, d, J = 8.0 Hz)	100.1	5.08 (1H, d, J = 8.0 Hz)
2″	73.3		73.3	
3″	76.6		76.5	
4″	69.7	3.20–3.60 (6H, m)	69.7	3.20–3.60 (6H, m)
5″	77.3		77.3	
6″	60.8		60.8	
1‴	101.8	4.87 (1H, d, J = 6.0 Hz)	101.3	4.91 (1H, brs)
2‴	72.5		73.5	
3‴	70.7		76.9	
4‴	67.3	3.20–3.60 (5H, m)	69.7	3.20–3.60 (6H, m)
5‴	65.4		77.3	
6‴			60.8	

[a] Assignments were established by DEPT, HMQC and HMBC.

Table 2
NMR data of compounds **3** and **4**[a] [^{1}H, 400 MHz and ^{13}C, 100 MHz, δ ppm]

Position	**3** (DMSO-d_6)		Position	**4** (DMSO-d_6)	
	δ_C	δ_H		δ_C	δ_H
1	125.8		1	126.8	
2	123.3		2	194.6	
3	136.7		3	131.2	6.16 (1H, s)
4	141.8		4	146.5	
5	120.0	7.25 (1H, d, J = 8.8 Hz)	5	162.9	
6	121.4	7.46 (1H, d, J = 8.8 Hz)	6	118.3	6.04 (1H, d, J = 2.4 Hz)
7	128.4	8.05 (1H, s)	7	52.8	2.99 (1H, dd, J = 9.6, 2.4 Hz)
8	126.2		8	74.9	4.39 (1H, td, J = 9.6, 9.6, 4.8 Hz)
9	167.8		9	43.9	3.20 (1H, d, J = 11.2 Hz)
					3.01 (1H, d, J = 11.2 Hz)
1′	109.7		10	139.5	
2′	146.4		11	74.8	
3′	103.9	6.62 (1H, s)	12	178.4	
4′	148.6		13	18.8	1.31 (3H, s)
5′	142.1		14	21.1	2.37 (3H, s)
6′	112.5	7.40 (1H, s)	15	14.1	2.19 (3H, s)
7′	123.0				
8′	127.3				
9′	171.6				

[a] Assignments were established by DEPT, HMQC and HMBC.

The molecular formula of compound **2** was assigned as $C_{27}H_{30}O_{17}$ based on its ESIMS, ^{1}H and ^{13}C NMR spectral data (Table 1). Close similarities could be observed in the spectral data of the aglycon portions of compounds **1** and **2**. However, the ^{1}H NMR spectrum of **2** revealed that one anomeric proton appeared at δ 4.91 (brs, 1H, H-1‴), which showed slight difference with that of **1**. By comparison of its ^{1}H, ^{13}C NMR spectral data and its specific optical rotation with those of reported values [7], the two sugars of **2** were both identified as glucoses, one with a β-D-configuration and the other with an α-D-configuration. Furthermore, the locations of the two glucopyranoses were established by HMBC correlations between δ 5.08 (H-1″) and δ 163.0 (C-7), δ 4.91 (H-1‴) and δ 150.4 (C-2′). Therefore, compound **2** was identified as isoetin-7-*O*-β-D-glucopyranosyl-2′-*O*-α-D-glucopyranoside.

Compound **3** was isolated as red amorphous powder. The molecular formula of **3**, $C_{18}H_{10}O_8$, was deduced by the analyses of its ESIMS, as well as ^{1}H and ^{13}C NMR spectral data (Table 2). Comprehensive analysis of the NMR spectra indicated that **3** consisted of 18 sp^2 carbons including 5 aromatic methines, 5 oxygen-bearing aromatic carbons and 2 carboxyl groups. The ^{1}H NMR spectrum of **3** exhibited close similarities of an arylnaphthalene, rufescidride [8]. However, the ESIMS of **3** disclosed its molecular weight appeared at *m/z* 353 $[M - H]^+$, 18 mass units higher than that of rufescidride. Moreover, the TLC status of **3** and its diagnostic IR absorptions at 1721 and 3400 cm^{-1} indicated that it might be a hydrolyzed derivative of rufescidride. The structure of **3** was therefore determined as shown in Fig. 1.

The structure of compound **4** was established by comparing its mass, ^{1}H and ^{13}C NMR spectral data with those of taraxacin [9]. It could be found that the olefinic signals of C-7 (δ 154.7) and C-11 (δ 124.3) of taraxacin were absent in the ^{13}C NMR spectrum of **4**. Instead, signals for a methine (δ 52.8) and an oxygenated quaternary carbon atom (δ 74.8) were observed. The Me-13 singlet of **4** shifted upfield to δ 1.31 while an additional double doublet (H-7) at δ 2.99 was observed in the ^{1}H NMR spectrum of **4**, which further supported the absence of the double bond between C-7 and C-11 and the presence of a tertiary-hydroxyl group at C-11 in **4** (Table 2). The β-orientation of H-8 could be assigned based on the large coupling constant ($J_{7,8}$ = 9.6 Hz) between H-7α and H-8. Moreover, the α-orientation of Me-13 could be deduced based on the NOE correlation between H-7 and Me-13 in the NOESY experiment of **4**.

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