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Two new phenolic glycosides from the aerial parts of *Androsace umbellata*

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Abstract

Two new phenolic glycosides, 2-hydroxy-4-*O*-β-D-glucopyranosylphenylacetic acid methyl acetate (**1**) and 2-hydroxy-4-*O*-β-D-glucopyranosylphenylacetic acid (**2**) were isolated from the aerial parts of *Androsace umbellata*. Their structures were elucidated by spectral techniques.

Keywords: *Androsace umbellata*; Phenolic glycosides; Phenylacetic acid

Androsace umbellata (Lour.) Merr., which is also named as ''Houlongcao'' and ''Fodingzhu'', belongs to family Primulaceae. It is a perennial plant distributed in many countries such as Korea, Japan, India and China. This plant has been reported possessing detumescence, heat-clearing and detoxicating activities, especially used in the treatment of sore throat as a traditional Chinese medicine [1]. Members of this genus also have been used as contraceptive and abortifacient agents in India [2–4]. Previous phytochemical studies had resulted in triterpenoid saponins from this genus. In order to search for bioactive compounds, we had investigated the chemical constituents of *A. umbellate* [5]. This paper describes the isolation and structural elucidation of two new phenolic glycosides **1** and **2**.

The *n*-butanol part of 75% EtOH extract of the aerial parts of *A. umbellata* was subjected to silica gel column chromatography eluted with $CHCl_3$–MeOH gradient system, then purified by Sephadex LH-20 column chromatography eluted with MeOH to yield compounds **1** and **2**.

Compound **1** was obtained as brownish amorphous powder (MeOH), $[\alpha]_D^{23}$-20 (*c* 0.034, MeOH). UV max (MeOH): 270 nm. The ESI-MS afforded the *quasi*-molecular ion $[M-H]^-$ at *m/z* 343, consistent with a molecular formula of $C_{17}H_{12}O_6$, which was confirmed by the HRESI-MS exhibiting a *quasi*-molecular ion $[M+Na]^+$ at *m/z* 367.0996 (calcd. 367.0999). The IR spectrum (KBr, *ν*) showed absorptions at 3396 cm^{-1} (O–H), 1638 cm^{-1}, 1433 cm^{-1} (phenyl). The ^1H NMR spectrum of **1** displayed the presence of a hydroxyl group (*δ* 9.52), a methylene (*δ* 3.48), a methoxyl

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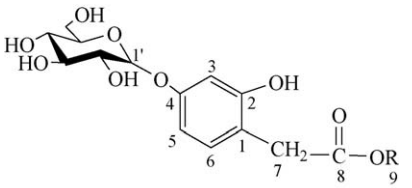
Table 1
^{1}H and ^{13}C NMR data for **1** and **2** (500 and 125 MHz, DMSO-d_6, δ in ppm, J in Hz).

Position	Compound **1**			Compound **2**		
	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
1	114.8	–	H-3, 5, 7, 2-OH	116.0	–	H-3, 5, 7
2	155.9	–	H-3, 6, 7	156.4	–	H-3, 6, 7
3	103.5	6.49, d (2.4)	H-5	103.9	6.48, br s	H-5
4	157.4	–	H-3, 5, 6; H-1′	157.2	–	H-3, 5, 6; H-1′
5	106.5	6.44, dd (2.4, 8.5)	H-3	106.5	6.41, br d (8.0)	H-3
6	131.1	6.98, d (8.5)	H-7	131.0	6.94, d (8.0)	H-7
7	34.3	3.48, s	H-6	36.0	3.37, s	H-6
8	171.8	–	H-7, 9	173.5	–	H-7
9	51.3	3.57, s	–	–	–	–
1′	100.6	4.74, d (7.5)	H-2′, 3′	100.7	4.74, d (7.2)	H-2′, 3′
2′	73.2	3.17, m	H-1′, 3′	73.2	3.17, dd (7.2, 8.0)	H-1′, 3′
3′	76.9	3.21, m	H-2′, 4′	77.0	3.23, br d (8.0)	H-2′, 4′
4′	69.6	3.13, m	H-3′, 5′, 6′	69.7	3.13, m	H-3′, 5′, 6′
5′	76.6	3.25, m	H-6′	76.7	3.20, m	H-6′
6′	60.6	3.69, br d (12.0)	H-4′	60.7	3.68, br d (11.5)	H-4′
		3.50, br d (5.0)			3.49, br d (7.1)	
2-OH	–	9.52, s	–	–	–	–

group (δ 3.57), an anomeric proton (δ 4.74), three aromatic protons [δ 6.49 (d, J = 2.4 Hz), 6.44 (dd, J = 2.4, 8.5 Hz), 6.98 (d, J = 8.5 Hz)] indicating a 1,2,4-substituted pattern for an aromatic ring. The ^{13}C NMR spectrum of compound **1** revealed signals for the corresponding carbon. The full assignments of ^{1}H and ^{13}C NMR signals were accomplished by a combination of ^{13}C DEPT, HMQC and HMBC data (Table 1). Comparison of the ^{1}H and ^{13}C NMR data of compound **1** with **2**, 4-dihydroxyphenylacetic acid methyl ester [6], the structure of compound **1** was proposed to be 2-hydroxy-4-*O*-β-D-glucopyranosylphenylacetic acid methyl acetate, which was supported by HMBC correlations. In the HMBC spectrum, H-7 (δ 3.48), H-9 (δ 3.57) correlated with C-8 (δ 171.8), as well as H-7 (δ 3.48) with C-1 (δ 114.8), C-2 (δ 155.9), C-6 (δ 131.1), implying the position of the linkage of the substituent $-CH_2COOCH_3$ was located at C-1. Furthermore, correlation signal between proton of hydroxyl (δ 9.52) and C-1 (δ 114.8) was observed, suggesting the hydroxyl group located at C-2. In addition, correlations between H-1′ (δ 100.6) and C-4 (δ 157.4) implied that the sugar moitey was connected to C-4. Hydrolysis of **1** yielded D-glucose which was indentified to an authentic sample on HPTLC, and the coupling constant (J = 7.5 Hz) of an anomeric proton of sugar residue indicated that the glucose was β-D-glucopyranose. Thus, compound **1** was determined to be 2-hydroxy-4-*O*-β-D-glucopyranosylphenylacetic acid methyl acetate, it is a new compound (Fig. 1).

Compound **2** was obtained as brownish amorphous powder (MeOH), $[\alpha]_D^{23}$-37.6 (*c* 0.021, MeOH). UV max (MeOH): 270 nm. The ESI-MS dislayed the *quasi*-molecular ion $[M-H]^-$ at *m/z* 329, confirmed by the HRESI-MS exhibiting a *quasi*-molecular ion $[M+Na]^+$ at *m/z* 353.0845 (calcd. 353.0843), indicating a molecular formula of $C_{17}H_{12}O_6$. The IR spectrum (KBr) exhibited absorptions at 3425 (O–H), 1623 cm^{-1}, 1519 cm^{-1} (phenyl). The ^{1}H NMR spectrum of **2** showed signals for a methylene group (δ 3.37), three aromatic protons [δ 6.41 (br d, J = 8.0 Hz)), 6.48 (br s), 6.94 (d, J = 8.0 Hz)] indicating a 1,2,4-substituted pattern for an aromatic ring, an anomeric proton (δ 4.74).



1 R=CH_3
2 R=H

Fig. 1. Structures of compounds **1** and **2**.

By comparing the NMR data of **2** to those of **1**, these two compounds were very similar except for an additional methoxyl group in compound **1**. In the HMBC spectrum, correlation signals between H-7 (δ 3.37) and C-1 (δ 116.0), C-2 (δ 156.4), C-6 (δ 131.0), C-8 (δ 173.5) were observed, implying the group $-CH_2COOH$ was substituted at C-1. Furthermore, in the HMBC spectrum of compound **2**, cross-peaks between H-1′ (δ 4.74), H-3 (δ 6.48), H-5 (δ 6.41), H-6 (δ 6.94) and C-4 (δ 157.2) suggested the sugar residue was connected to C-4. Hydrolysis of **2** afforded D-glucose which was indentified by HPTLC by comparison to an authentic sample. And the coupling constant (J = 7.2 Hz) of an anomeric proton of **2** indicated that the glucose was β-D-glucopyranose. Based on the above results, compound **2** was elucidated as 2-hydroxy-4-*O*-β-D-glucopyranosylphenyl acetic acid, it is a new compound. The full assignments of ^1H and ^{13}C NMR signals were attributed to the combination of DEPT, HMQC, and HMBC experiments (Table 1).

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