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Chromone acyl glucosides and an ayanin glucoside from *Dasiphora parvifolia*

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ABSTRACT

Two new chromone acyl glucosides, 5-hydroxy-7-*O*-(6-*O*-*p*-*cis*-coumaroyl-β-D-glucopyranosyl)-chromone (**1**) and 5-hydroxy-7-*O*-(6-*O*-*p*-*trans*-coumaroyl-β-D-glucopyranosyl)-chromone (**2**), and a new flavonoid glucoside, ayanin 3′-*O*-β-D-glucopyranoside (**3**) were isolated from aerial parts of *Dasiphora parvifolia*, together with flavonoid glycosides (**4**–**10**), catechins (**11**, **12**), and hydrolysable tannins (**13**, **14**). The chemical structures of these compounds were elucidated on the basis of spectroscopic data. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity and the hyaluronidase inhibitory activity of these compounds were evaluated.

1. Introduction

Dasiphora parvifolia (Fisch.) Juz. (synonym: *Potentilla parvifolia* Fisch.) (Rosaceae) is a traditional herbal medicine of Mongolia (Batkhuu et al., 2005) and China (Xiao and Mayanagi, 1993). The aerial parts of this plant are used for the treatment of skin diseases, breast cancer, and edema. *D. parvifolia* was relegated to the genus *Potentilla*, previously. Many species of *Potentilla* are known as medicinal plants, and flavonoids and tannins were reported as important constituents of these plants (Tomczyk et al., 2008). To the best of our knowledge, there are few reports on the secondary metabolites from *D. parvifolia*. Herein, we report the isolation of two new chromone acyl glucosides (**1**, **2**) and a new flavonoid glucoside (**3**), together with 11 known compounds (**4**–**14**).

In order to identify the effective compounds in *D. parvifolia* that may be related to activities in traditional medicine, we evaluated radical scavenging activity using 1,1-diphenyl-2-picrylhydrazyl (DPPH) and hyaluronidase inhibitory activity of the extracts and isolates (**1**–**14**) from *D. parvifolia*.

2. Results and discussion

An acetone–H_2O extract of aerial parts of *D. parvifolia* was dissolved in H_2O and extracted with Et_2O. The H_2O extract was chromatographed on an ODS column and HPLC to obtain acyl chromone glucosides (**1** and **2**), flavonoid glycosides (**3**–**10**), catechins (**11**, **12**), and hydrolysable tannins (**13**, **14**) (Fig. 1). The known compounds **4**–**14** were identified based on spectroscopic data as kaempferol-3-*O*-β-D-glucopyranoside (**4**) (Kazuma et al., 2003), quercetin-3-*O*-β-D-glucopyranoside (**5**) (Kazuma et al., 2003), quercetin -3-*O*-β-D-(6″-*O*-galloyl)glucopyranoside (**6**) (Braca et al., 2003), quercetin-3-*O*-β-D-(6″-*O*-galloyl)galactopyranoside (**7**) (Braca et al., 2003) kaempferol-3-*O*-β-D-(6″-*O*-*p*-*trans*-coumaroyl)glucopyranoside (**8**) (Tsukamoto et al., 2004), kaempferol-3-*O*-β-D-(6″-*O*-*p*-*cis*-coumaroyl)glucopyranoside (**9**) (Tsukamoto et al., 2004), potentilin A (**10**) (Kazuma et al., 2003), catechin-(7,8-*bc*)-4*b*-(3,4-dihydroxyphenyl)-dihydro-2(3*H*)-pyranone (**11**) (Foo, 1987), geranin A (**12**) (Calzada et al., 1999), 1,2,4,6-tetra-*O*-galloyl-β-D-glucopyranoside (**13**) (Saijo et al., 1990), and 1,2,3,4,6-penta-*O*-galloyl-β-D-glucopyranoside (**14**) (Latza et al., 1996). These compounds were isolated for the first time from this plant. On the other hand, compounds **4**, **5**, **8**–**10**, and **14** were obtained from *Chamaerhodos* plants (Rosaceae) in our previous study (Selenge et al., 2013).

Compound **1** was determined to have the molecular formula $C_{24}H_{22}O_{11}$ by HRFABMS (*m/z* 487.1248, calcd for $C_{24}H_{23}O_{11}$, 487.1240). In the ^{1}H NMR spectrum (Table 1), AA′BB′ pattern

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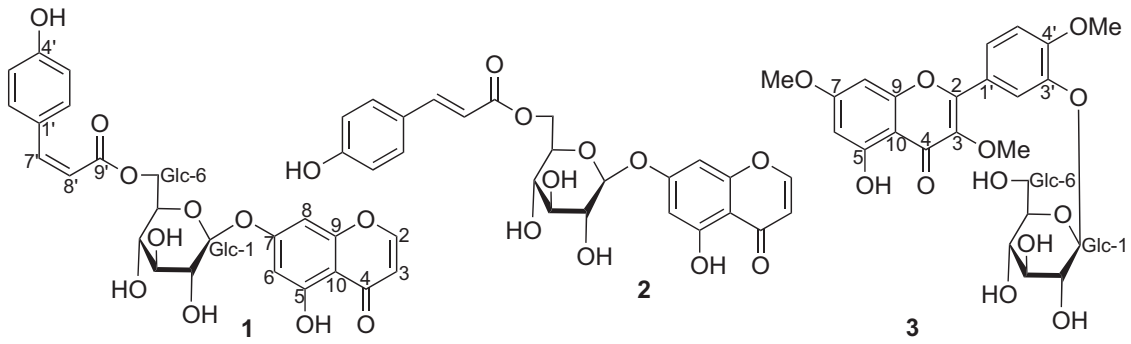

Fig. 1. Structure of compounds **1**–**3**.

resonances at δ_H 7.49 (2H, d, J = 8.5 Hz, H-2′ and 6′) and 6.61 (2H, d, J = 8.5 Hz, H-3′ and 5′), three sets of aromatic/olefinic resonances [δ_H 6.79 (1H, d, J = 13.0 Hz, H-7′), 5.80 (1H, d, J = 13.0 Hz, H-8′); 7.97 (1H, d, J = 6.0 Hz, H-2), 6.18 (1H, d, J = 6.0 Hz, H-3); 6.45 (1H, d, J = 2.0 Hz, H-6), 6.59 (1H, d, J = 2.0 Hz, H-8)], an anomeric resonance at δ_H 5.02 (1H, d, J = 7.0 Hz, H-Glc-1), and oxygenated methylene proton resonances at δ_H 4.43 (2H, m, H-Glc-6) were observed. The AA′BB′ system protons and the coupling constant between H-7′ and 8′ were characteristic of a *p-cis*-coumaroyl moiety (Murata et al., 2008). In the ^{13}C NMR spectrum (Table 1), resonances corresponding to the *p-cis*-coumaroyl (δ_C 127.4, 133.7, 115.8, 160.0, 145.1, 116.0, and 168.1), glycosyl (δ_C 101.5, 74.7, 77.9, 71.9, 75.8, and 64.2), and aglycone (δ_C 158.4, 111.9, 183.6, 163.1, 101.2, 164.6, 96.2, 159.4, and 108.5) moieties were observed. The proton/carbon resonances of the aglycone and the glycosyl were similar to those of 5,7-dihydroxychromone-7-glucoside (Simon et al., 1994) except for the resonances around Glc-6. The HPLC sugar analysis after acid hydrolysis of **1** (Tanaka et al., 2007) and the coupling constant of H-Glc-1 (Murata et al., 2008) suggested that the glycosyl moiety was β-D-glucopyranosyl. In the NOE spectrum (Fig. 2), H-Glc-1 was correlated with H-6 and H-8. The H-Glc-6 and C-Glc-6 were shifted to lower fields than that of 5,7-dihydroxychromone 7-glucoside, which showed that **1** had *p-cis*-coumaroyl as the acyl moiety at C-Glc-6. The HMBC correlations, including between H-Glc-6 and C-9′, supported this conclusion (Fig. 2). These results established that **1** was 5-hydroxy-7-*O*-(6-*O*-*p-cis*-coumaroyl-β-D-glucopyranosyl)-chromone.

Compound **2** was determined to have the molecular formula $C_{24}H_{22}O_{11}$ by HRFABMS (m/z 487.1237, calcd for $C_{24}H_{23}O_{11}$, 487.1240). The ^{1}H NMR and ^{13}C NMR data were similar to those of **1** except for resonances corresponding to a *p*-coumaroyl group. The coupling constant between olefinic protons [δ_H 7.59 (1H, d, J = 16.0 Hz, H-7′), 6.35 (1H, d, J = 16.0 Hz, H-8′)] suggested that the presence of a *p-trans*-coumaroyl group. As the *trans* isomer of **1**, compound **2** was determined to be 5-hydroxy-7-*O*-(6-*O*-*p-trans*-coumaroyl-β-D-glucopyranosyl)-chromone.

Compound **3** was determined to have the molecular formula $C_{24}H_{26}O_{12}$ by HRFABMS (m/z 507.1505, calcd for $C_{24}H_{27}O_{12}$,

Table 1
^{1}H NMR and ^{13}C NMR spectroscopic data for compounds **1**–**3**.

Position	Compound **1**[a]		Compound **2**[a]		Compound **3**[b]	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2	7.97, d (6.0)	158.4	7.69, d (6.0)	158.5		155.3
3	6.18, d (6.0)	111.9	6.13, d (6.0)	112.0		138.3
4		183.6		183.6		178.1
5		163.1		163.2		160.9
6	6.45, d (2.0)	101.2	6.52, d (2.0)	101.2	6.33, d (2.0)	97.8
7		164.6		164.8		165.2
8	6.59, d (2.0)	96.2	6.64, d (2.0)	96.2	6.78, d (2.0)	92.6
9		159.4		159.4		156.3
10		108.5		108.5		105.2
1′		127.4		127.3		122.1
2′	7.49, d (8.5)	133.7	7.42, d (8.5)	131.2	7.82, d (2.5)	115.1
3′	6.61, d (8.5)	115.8	6.80, d (8.5)	117.0		146.3
4′		160.0		161.4		151.5
5′	6.61, d (8.5)	115.8	6.80, d (8.5)	117.0	7.18, d (8.5)	112.3
6′	7.49, d (8.5)	133.7	7.42, d (8.5)	131.2	7.78, dd (8.5, 2.5)	123.2
7′	6.79, d (13.0)	145.1	7.59, d (16.0)	146.9		
8′	5.80, d (13.0)	116.0	6.35, d (16.0)	115.1		
9′		168.1		168.9		
Glc-1	5.02, d (7.0)	101.5	5.03, d (7.0)	101.5	4.96, d (7.5)	100.5
Glc-2	3.49, overlap	74.7	3.49, overlap	74.7	3.30, overlap	73.2
Glc-3	3.49, overlap	77.9	3.49, overlap	77.9	3.30, overlap	76.8
Glc-4	3.33, overlap	71.9	3.38, dd (9.5, 9.0)	72.0	3.18, m	69.7
Glc-5	3.74, m	75.8	3.82, m	76.0	3.39, overlap	77.3
Glc-6	4.43, m	64.2	4.33, dd (12.0, 8.0)	64.7	3.49, dd (12.0, 6.5)	60.8
			4.57, dd (12.0, 2.5)		3.72, dd (12.0, 5.5)	
5-OH					12.60, s	
3-OMe					3.82, s	59.8
7-OMe					3.85, s	56.1
4′-OMe					3.87, s	55.8

[a] CD_3OD.
[b] DMSO-d_6.