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Two new phenylpropanoid glycosides from *Sanguisorba officinalis*

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Abstract

Two new phenylpropanoid glycosides, 9-*O*-[6-*O*-acetyl-*β*-D-glucopyranosyl]-4-hydroxycinnamic acid (**1**) and 8-*O*-*β*-D-glucopyranosyl-(R)-(+)-3,4,8-trihydroxy methyl phenylpropionate (**2**) were isolated from the 80% EtOH extract of the roots of *Sanguisorba officinalis*. Their structures were characterized by spectroscopic analysis and chemical method, including 1D NMR, 2D NMR, and HR-ESI-MS. Compounds **1** and **2** exhibited the moderate antimicrobial activities against all Gram-positive and Gram-negative bacteria tested.

Keywords: *Sanguisorba officinalis*; Rosaceae; Phenylpropanoid glycosides; NMR techniques

Sanguisorba officinalis L. (Rosaceae), a perennial plant, distributes widely in northern districts of China [1]. In China, Korea, and Japan, this plant has been used for the treatment of inflammatory and metabolic disease such as diarrhea, chronic intestinal infections, duodenal ulcers, and bleeding [2,3]. Previous studies reported the isolation of triterpenoids, triterpenoid glycosides, and a series of hydrolysable tannins which were reported as characteristic constituents of *S. officinalis* and are considered to be partially responsible for the therapeutic effects of this herbal drug [4–6]. The chemical investigate of the 80% EtOH extract of the dry fronds of *S. officinalis* had led to the isolation of two new phenylpropanoid glycosides (Fig. 1). This paper deals with the isolation and structural elucidation of the new compounds on the basis of extensive 1D and 2D NMR (COSY, HMQC, HMBC, and NOESY) analyses. Furthermore, the two new phenylpropanoid glycosides were *in vitro* evaluated for their antimicrobial activities against two Gram-positive and three Gram-negative bacteria.

The dried roots of *S. officinalis* were collected in the suburb of Qujing, Yunnan province of China, in October 2010 and identified by one of the authors (X. Mao). A voucher specimen (20101001) is deposited in the Herbarium of the College of Biological Resources and Environment Science, Qujing Normal University, Qujing, Yunnan Province, China.

The roots (5 kg) of *S. officinalis* were extracted with 80% EtOH (10 L ×3). After removal of EtOH under reduced pressure, the aqueous brownish syrup (1 L) was partitioned with AcOEt to afford AcOEt extract (42 g). AcOEt soluble extract was subjected to chromatography over SiO_2 column, eluting with gradient $CHCl_3$/MeOH to afford fractions 1–8. Fraction 5 (9.0 g) was chromatographed on a MCI gel column eluted with MeOH/H_2O (from 60% to 95%) to

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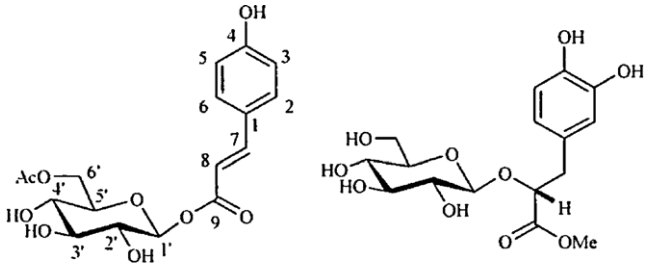

1 2

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

yield 3 subfractions, 5A–5C. Subfraction 5B (1.6 g) was separated by repeated column chromatography (CC) over Sephadex LH-20 (MeOH), silica gel, and then preparative HPLC (MeOH/H_2O 40% to 70%), yielding **1** (27.1 mg) and **2** (29.7 mg).

Compound **1** was obtained as a white amorphous solid. Its molecular formula was established as $C_{17}H_{20}O_9$ with 8 degrees of unsaturation by HRESIMS (*m/z* 367.1025 $[M-H]^-$, calcd. for $C_{17}H_{19}O_9$, 367.1029). The ^{13}C NMR (125 MHz, CD_3OD) data of **1** (Table 1) displayed the presence of one carboxyl group [δ_C 166.6 (s)], one Ac group [δ_C 172.2 (s) and 20.4 (q)], and eight olefinic carbons arising from a phenyl and a disubstituted double bond [δ_C 145.9, 115.0 (d, each 1H)]. The ^1H NMR (600 MHz, CD_3OD) spectrum showed four aromatic protons at δ_H 7.60 (d, 2H, J = 8.2 Hz), 6.95 (d, 2H, J = 8.2 Hz) arising from a 1,4-disubstituted benzene ring, two olefinic protons at δ_H 7.65 (d, 1H, J = 16.0 Hz) and 6.30 (d, 1H, J = 16.0 Hz) for a disubstituted *trans* double bond. These spectroscopic data indicated the characteristic signals of one phenylpropanoid glycoside. The sugar moiety was identified as a β-glucopyranosyl unit by the coupling constant of the anomeric proton [δ_H 4.32 (d, 1H, J = 8.0, glc H-1′)] and similarity of their NMR data with literature data (Table 1) [7]. The HMBC between the anomeric proton of the glucopyranosyl unit and C-9 (δ_C 166.6) of the aglycone (Fig. 2). The C-6′ location of the AcO group

Table 1
^1H and ^{13}C NMR data of compounds **1** and **2** (^1H: 600 MHz; ^{13}C: 125 MHz, in CD_3OD).

	1		**2**		**3**	
	δ_C	δ_H (mult., J in Hz)	δ_C	δ_H (mult., J in Hz)	δ_C	δ_H (mult., J in Hz)
1	127.0 (s)	–	129.8 (s)	–	130.2 (s)	–
2	116.7 (d)	7.60 (d, 8.2)	118.3 (d)	6.72 (d, 2.5)	117.9 (d)	6.69 (d, 2.5)
3	131.2 (d)	6. 95 (d, 8.2)	147.2 (s)	–	146.5 (s)	–
4	160.3 (s)	–	145.8 (s)	–	145.5 (s)	–
5	131.2 (d)	6. 95 (d, 8.2)	117.2 (d)	6. 68 (d, 8.2)	116.7 (d)	6. 66 (d, 8.2)
6	116.7 (d)	7.60 (d, 8.2)	122.8 (d)	6.57 (dd, 8.2, 2.5)	122.4 (d)	6.55 (dd, 8.2, 2.5)
7	145.9 (d)	7.65 (d, 16.0)	39.0 (t)	2.82, 2.94 (dd, 12.6,7.8)	41.5 (t)	2.81, 2.93 (dd, 12.6, 7.8)
8	115.0 (d)	6.30 (d, 16.0)	77.2 (d)	3.88 (d, 7.8)	73.7 (d)	4.26 (d, 7.8)
9	166.6 (s)	–	176.6 (s)	–	176.3 (s)	–
O-glc						
1′	106.8 (d)	4.32 (d, 8.0)	103.9 (d)	4.28 (d, 8.0)		
2′	75.8 (d)	3.20 (m)	74.2 (d)	3.17 (m)		
3′	78.1 (d)	3.38 (m)	76.9 (d)	3.40 (m)		
4′	73.0 (d)	3.28 (m)	70.6 (d)	3.28 (m)		
5′	75.2 (d)	3.38 (m)	77.0 (d)	3.36 (m)		
6′	64.8 (t)	4.26 (dd, 13.0, 6.6) 4.31 (dd, 13.0, 6.6)	61.9 (t)	3.82 (dd, 13.0, 7.0) 3.62 (dd, 13.0, 7.0)		
OMe	–	–	52.7 (q)	3.68 (s)	52.5 (q)	3.69 (s)
C=O	172.2 (s)	–	–	–		
Me	20.4 (q)	2.02 (s)	–	–		

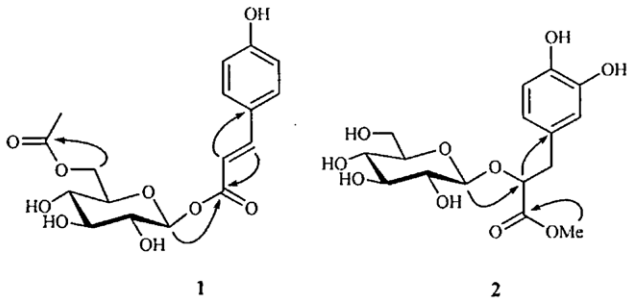

Fig. 2. Key HMBC correlations of compounds **1** and **2**.

Table 2
Antimicrobial and antifungal activities (zones of inhibition/and MIC mmol/L, $n = 3$) of compounds **1**–**14**.

	S. aureus	*S. epidermidis*	*E. coli*	*K. pneumoniae*	*S. dysenteriae*
1	16/2.02	15/2.24	17/1.97	16/2.84	15/2.54
2	17/2.31	15/1.99	16/2.47	17/2.90	15/2.01
Netilmicin	21/0.003	25/0.003	24/0.008	25/0.006	23/0.010

in the glucopyranosyl unit was confirmed by HMBC of H-6′ (δ_H 4.31 and 4.26) with the CO C-atom (δ_C 172.2) of the AcO group. Accordingly, the structure of **1** was established as 9-*O*-[6-*O*-acetyl-*β*-D-glucopyranosyl]-4-hydroxycinnamic acid.

Compound **2** was obtained as a white amorphous powder. The HR-ESI-MS displayed a *quasi*-molecular ion peak at *m*/*z* 373.1133 $[M-H]^-$ (calcd. for $C_{16}H_{21}O_{10}$, 373.1135) corresponding to a molecular formula $C_{16}H_{22}O_{10}$ for **2**. The ^{13}C NMR and DEPT spectra (125 MHz, CD_3OD) of **2** showed resonances characteristic of one phenylpropanoid, one hexosyl unit, and one OMe group (Table 1). The ^1H NMR spectrum (600 MHz, CD_3OD) of **2** showed resonances for a set of ABX-type signals [δ_H 6.72 (d, 1H, $J = 2.5$ Hz, H-2), 6.68 (d, 1H, $J = 8.2$ Hz, H-5), 6.57 (dd, 1H, $J = 8.2$, 2.5 Hz, H-6)], indicating a 1,3,4-trisubstituted benzene ring. In addition, one oxygenated methane coupled with one methylene proton [δ_H 2.82 and 2.94 (dd, each 1H, $J = 12.6$, 7.8 Hz), H-7] appeared at δ_H 3.88 for H-8. Acid hydrolysis of **2** with 1 mol/L HCl in dioxane–H_2O (1:1) gave **2a** and D-glucose as the carbohydrate components. The NMR data (Table 1) and optical rotation $\{[\alpha]_D^{23.3} + 6.1$ ($c = 0.46$, MeOH)$\}$ of **2a** are in good agreement with those of (R)-(+)-3,4,8-trihydroxymethyl phenylpropionate ($C_{10}H_{12}O_5$) reported in the literature [8]. The sugar moiety was identified as a *β*-glucopyranosyl unit by the coupling constant of the anomeric proton [δ_H 4.28 (*d*, $J = 8.0$, glc H-1′)] and its NMR data (Table 1) [7]. The *β*-glucopyranosyl unit was positioned at C-8, and the methoxyl at C-9 respectively, based on the HMBC correlations of the anomeric proton signal of sugar moiety with C-8, and of the methoxyl signal (δ_H 3.88) with C-9 (Fig. 2). Consequently, compound **2** was unambiguously determined as 8-*O*-*β*-D-glucopyranosyl-(R)-(+)-3,4,8-trihydroxymethylphenylpropionate.

Compounds **1** and **2** were tested for their antimicrobial activities against two Gram-positive bacteria: *Staphylococcus aureus* and *Staphylococcus epidermidis* and three Gram-negative bacteria: *Escherichia coli*, *Klebsiella pneumoniae*, and *Shigella dysenteriae.* Antimicrobial activities was evaluated by the disc diffusion method by measuring the zone of inhibitions and the minimum inhibitory concentration (MIC) values were also determined [9]. Standard antibiotic netilmicin was used in order to control the sensitivity of the tested bacteria. The results (Table 2) showed that **1** and **2** exhibited moderate antimicrobial activities, with MIC value of 1.97–2.84 mmol/L and 1.99–2.90 mmol/L respectively.

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