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Bergenin glycosides from *Rodgersia aesculifolia*

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ABSTRACT

Phytochemical investigation on *Rodgersia aesculifolia* afforded twenty-three compounds, including three bergenin glycosides, previously unknown in nature, together with twenty known compounds. Their structures were elucidated by the extensive use of 1D and 2D NMR experiments, along with IR and HRESIMS spectra. This is the first report of bergenin glycosides from nature.

Introduction

Rodgersia genus, which belongs to Saxifragaceae family, is composed of 5 species and 3 variations all over the world. In China, there are about 4 species and 3 variations in *Rodgersia*, which are mainly distributed in West China (Pan, 1992). Previous studies have indicated that tannins, monoterpenoids and polyphenols are the main constituents in this genus (Liu et al., 1995). Some plants of this genus are used as traditional medicines which have antibacterial, anti-virus, antalgic, anti-inflammatory, hemostatic, antirheumatic and antitussive activities (Hu et al., 2007). The rhizomes of *Rodgersia aesculifolia* Batal. are called "ChengGanQi" or "SuoGuDan", one of "QiYao" in Shaanxi province (Guo et al., 2003). In Chinese traditional medicine, the rhizomes possess the effects of clearing heat and removing toxicity, hemostasis, antidiarrheal, invigorating the circulation of blood, regulating menstruation and curing rheumatism. They have been used for the treatment of dysentery, bleeding, throat swelling and pain, traumatic injury, rheumatoid arthritis and gastritis (Guo et al., 2003; Min et al., 2007; Zhang et al., 2005).

Previous phytochemical work on *R. aesculifolia* has led to reports of flavonoids, diterpene lactones, steroids and other compounds (Li et al., 2011; Liu et al., 1995; Shen et al., 1987; Yuan et al., 1994). Among them, bergenin is well known as a principal component and displays potent biological activities of anti-inflammatory, preventing cough and treating stomach hyperacidity and ulcers (Yu et al., 2009; Yuan et al., 1994). Herein described are the isolation and structural elucidation of three new bergenin glycosides (**1**–**3**) (Fig. 1), together with twenty known compounds including three bergenin derivatives (**4**–**6**), seven monoterpene disaccharide glycosides (**7**–**13**), five flavonoids (**14**–**18**) and five other compounds (**19**–**23**) from the title plant.

Results and discussion

Phytochemical investigation on the rhizomes of *R. aesculifolia* afforded twenty-three compounds, including three new bergenin glycosides (**1**–**3**), along with twenty known compounds (**4**–**23**), of which bergenin (**4**) was isolated as the main component.

Compound **1** was obtained as a white amorphous powder and its molecular formula was assigned as $C_{19}H_{24}O_{13}$, deduced from the HRESIMS *m/z* 483.1127 $[M+Na]^+$, as well as its ^1H and ^{13}C NMR spectroscopic data. The IR spectrum of **1** showed absorptions at 3397 cm^{-1} and 1685 cm^{-1}, ascribable to hydroxyl and carbonyl moieties. Full assignments of all the individual protons and carbons (Table 1) were ascertained from a combined analysis of ^1H NMR, ^{13}C NMR, COSY, DEPT, HSQC, HMBC and NOESY data. The ^{13}C NMR (with DEPT) spectrum showed signals for five non-protonated aromatic carbons at δ_C 150.9 (C-8), δ_C 148 (C-10), δ_C 140.6 (C-9), δ_C 118.0 (C-6a) and δ_C 115.7 (C-10a), and one protonated aromatic carbon at δ_C 109.4 (C-7), together with one carbonyl carbon at δ_C 163.3 (C-6). And one aromatic methoxyl was

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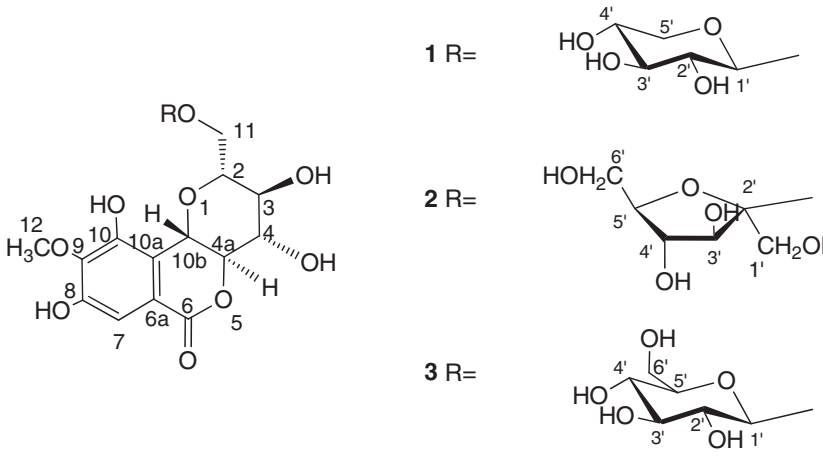

Fig. 1. Structures of compounds **1**–**3**.

Table 1
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectroscopic data for Compounds **1** (DMSO-d_6), **2** (CD_3OD) and **3** (CD_3OD).[a]

Position	**1**		**2**		**3**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2	3.68–3.73	79.7	3.73–3.82	79.6	3.91–3.92	79.2
3	3.23–3.26	70.4	3.47 t-like	70.1	3.44 m	70.5
4	3.60–3.67	73.5	3.73–3.82	73.6	3.80–3.89	73.7
4a	3.97 t-like	79.6	4.07	79.5	4.05–4.09 m	79.5
6		163.3		163.9		163.9
6a		118.0		117.6		117.6
7	6.98 s	109.4	7.08 s	109.2	7.09 s	109.1
8		150.9		150.4		150.4
9		140.6		140.4		140.8
10		148		147.5		147.5
10a		115.7		115.4		115.7
10b	4.95 d (10)	72.0	4.92 d (10.2)	72.2	5.00 d (10.5)	72.0
11a	3.60–3.67	68.8	3.73–3.82	61.1	3.80–3.89	69.3
11b	4.05 d (10.05)		4.17–4.19		4.25 dd (11.5, 1.8)	
12OCH_3	3.76 s	59.7	3.90 s	59.0	3.90 s	59.0
Sugar	Xylose		Fructose		Glucose	
1′a	4.19 d (7.55)	104.1	3.61–3.70	60.7	4.3 d (7.7)	103.2
1′b			3.61–3.70			
2′	3.0 t (7.9)	73.2		103.5	3.24–3.30	73.2
3′	3.12 t (8.7)	76.5	4.17–4.19	76.9	3.32–3.39	76.2
4′	3.23–3.26	69.5	4.04	74.7	3.24–3.30	69.7
5′a	3.68–3.73	65.7	3.73–3.82	81.4	3.32–3.39	76.3
5′b	3.06 t (10.85)		3.61–3.70			
6′a			3.73–3.82	62.1	3.80–3.89	60.9
6′b			3.61–3.70		3.64–3.68 m	

[a] Full assignments of the protons and carbons were accomplished by analysis of COSY, HSQC and HMBC spectra, chemical shifts are in ppm and coupling pattern and coupling constants (J in Hz) are in parentheses. Overlapped signals were given without designating multiplicity.

revealed by the signals at δ_H 3.76 (3H, s) and δ_C 59.7. The proton singlet at δ_H 6.98 (1H, s) suggested the presence of a *penta*-substituted benzene ring. In the NOESY plot, the correlations of H-10b with H-2 and H-4 and correlations of H-3 with H-4a were in accordance with the configurations of C-2, C-3, C-4, C-4a, and C-10b as shown in Fig. 2. The structure of the aglycone of **1** was determined to be bergenin (Wang et al., 2005; Wei et al., 2013). The anomeric proton signal at δ_H 4.19 (d, J = 7.55 Hz) in the ^{1}H NMR spectrum and the carbon signal at δ_C 104.1 in the ^{13}C NMR spectrum indicated one sugar unit in **1**. The signals at δ_C 104.1, 73.2, 76.5, 69.5, 65.7 in the ^{13}C NMR spectra of **1**, established that the sugar was a xylose moiety (Beninger and Hosfield, 1998), with the β-configuration of the xylose determined from the coupling

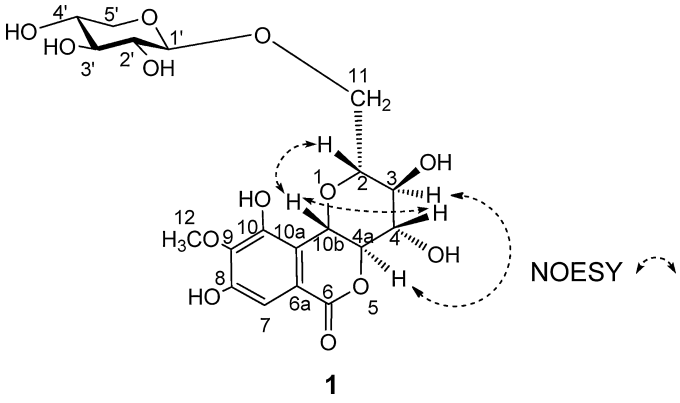

Fig. 2. Selected NOESY (H → H) correlations of **1**.

constant (7.55 Hz) of the anomeric proton signal in the ^{1}H NMR spectrum.

When the ^{13}C NMR spectrum of bergenin (Wang et al., 2005; Wei et al., 2013) was compared with that of **1**, the signal due to C-11 was shifted downfield by 7.7 ppm, suggested that the β-D-xylopyranosyl moiety was located at C-11, which was confirmed by the HMBC correlations (Fig. 3) between C-11 (δ_C 68.8) of the aglycone and H-1′ (δ_H 4.19) of xylose. Accordingly, the structure of the new bergenin glycoside **1** was fully established to be 11-β-D-xylopyranosyl-bergenin.

Compound **2** was obtained as a light yellow amorphous powder. On the basis of HRESIMS (m/z 513.1241 $[M+Na]^+$) and ^{13}C NMR, DEPT spectra, its molecular formula was deduced to be $C_{20}H_{26}O_{14}$.

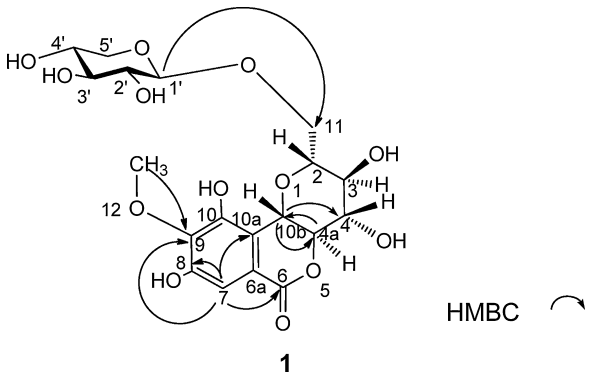

Fig. 3. Selected HMBC (H → C) correlations of **1**.