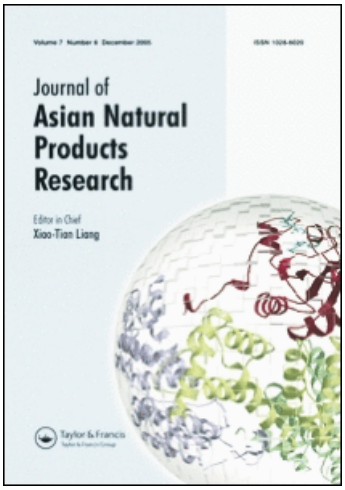

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A new tannin-related compound from the rhizome of *Polygonum bistorta* L.

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A new tannin-related compound named bistortaside A (**1**) and a known compound have been isolated from the rhizome of *Polygonum bistorta* L. A new compound was elucidated as 3-methyl-gallic acid 4-*O*-β-D-(6′-*O*-3″-methyl-galloyl)-glucopyranoside and a known compound was quercetin-3′-*O*-β-D-glucopyranoside (**2**) on the basis of spectroscopic analysis.

Keywords: *Polygonum bistorta*; Polygonaceae; Tannin; Bistortaside A

1. Introduction

Polygonum bistorta L. (Polygonaceae) is widely distributed in Hebei, Liaoning and Inner Mongolia in China [1]. Its rhizomes have been used in Chinese folk medicine to treat dysentery with bloody stools, diarrhoea in acute gastroenteritis, acute respiratory infection with cough; carbuncles, scrofula, aphthous ulcer, haematemesis, epistaxis, haemorrhoidal bleeding and venomous snake bite [2]. It has been reported that this crude drug exhibited several potent pharmacological activities, including antibacterial, anti-inflammatory and anti-mutation activity [3–5]. Previous investigations resulted in the isolation of triterpenoids, flavones and phenolic acids from the rhizome of *P. bistorta* L. [4,6,7]. In present study we found that the BuOH extract from the rhizome of this plant showed an anti-inflammatory effect and a new compound, bistortaside A (**1**) was obtained. Quercetin-3′-*O*-β-D-glucopyranoside (**2**) was gained for the first time from this genus. The structural elucidation of compound **1** is reported in this paper.

2. Results and discussion

Bistortaside A (**1**) was obtained as a pale white, amorphous powder from methanol. It showed positive $FeCl_3$ and Molish reaction. The molecular formula, $C_{22}H_{24}O_{14}$, was determined on

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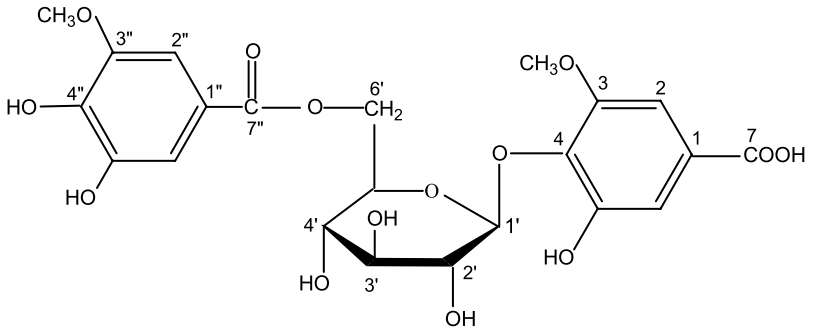

Figure 1. Structure of **1**.

the basis of the quasi-molecular ion peak $[M + Na]^+$ at *m/z* 535.1079 in HRFAB-MS spectrum and by its ^{1}H NMR and ^{13}C NMR spectral data (see figure 1).

The IR spectrum of **1** indicated the presence of hydroxy (ν_{max} 3433 cm^{-1}), carboxyl (ν_{max} 1693 cm^{-1}) and benzene ring (ν_{max} 1601, 1513 cm^{-1}). Its UV spectrum showed the maximum absorption at 214 (4.6), 253 (4.0) and 279 (4.1) nm assignable to galloyl group. The ^{1}H NMR spectrum in DMSO-d_6 gave two methoxyl signals at δ 3.68 (3H, s) and 3.75 (3H, s), two groups of *meta*-related aromatic proton signals at δ 7.01, 7.07 and 7.00, 7.11 as well as glycosyl proton signals at δ 4.84 (1H, d, $J = 7.0$ Hz), 3.51 (1H, m), 4.24 (1H, d d, $J = 11.4$, 5.8 Hz), 4.45 (1H, d, $J = 11.4$ Hz). The ^{13}C NMR spectra showed 22 carbon signals of the two methoxyl carbons (δ 55.9 and 56.2), six carbons of a glycosyl unit (δ 104.4, 74.0, 76.0, 69.9, 74.4, 63.8) and two galloyl carbons (δ 104.9, 105.1, 126.8, 110.8 ($\times$ 2), 119.4, 137.6, 139.6, 145.4, 147.9, 150.2, 152.8, 165.7 and 167.0). Acid hydrolysis of compound **1** indicated the presence of glucose. The ^{1}H NMR and ^{13}C NMR signals of **1** were assigned on the basis of the HMQC and HMBC spectra (table 1). In the HMBC spectrum (figure 2), the signals at δ 4.84 (glu-H-1′) and 9.40 (5-OH) showed long-range correlations with the signal at δ 137.6 (C-4), respectively. Long-range correlations of signals at δ 7.01 (H-2) and 7.07 (H-6) with δ 137.6 (C-4) and 167.0 (C-7) were also observed. So the glycosyl moiety was attached to the C-4 of a gallic acid. In addition, the signals at δ 4.24 (Glu-H-6′), 7.00 (H-2″) and 7.11 (H-6″) showed long-range correlations with the signal at δ 165.7 (C-7″). Thus, another galloyl group was attached to the C-6′ of the glycosyl unit. The two methoxyl signals at δ 3.68, 3.75 showed correlations with C-3 (δ152.8) and C-3″ (δ 147.9), respectively. Thus, the locations of two methoxyl groups were determined. Since the glycosyl was determined as β-type by the coupling constant of anomeric proton at δ 4.84 (1H, d, $J = 7.0$ Hz), the structure of compound **1** was designated as 3-methyl-gallic acid 4-*O*-β-D-(6′-*O*-3″-methyl-galloyl)-glucopyranoside.

3. Experimental

3.1 General experimental procedures

Melting points were measured on a Yanaco MP-S3 micro-melting pointmeter and are uncorrected. UV spectra were recorded on a Shimadzu UV-260 UV–Vis spectrophotometer and IR spectra were taken on a Bruker IR S-55 infrared spectrophotometer. All NMR spectra were recorded on a Bruker ARX-300 instrument with TMS as internal reference. HRFAB-MS was measured on an Autospec Ultima-ETOF mass spectrometer (Micromass, UK).

Table 1. ^{1}H NMR and ^{13}C NMR data of **1.**

Position	δ_C *(DMSO-d_6)*	δ_H *(DMSO-d_6)*	δ_H *(C_5D_5N-d_5)*
1	126.8		
2	105.1	7.01 (1H, br.s)	
3	152.8		
4	137.6		
5	150.2		
6	110.8	7.07 (1H, br.s)	
7	167.0		
3-OCH_3	56.2	3.68 (3H, s)	
5-OH		9.40	
$1'$	104.2	4.84 (1H, d, $J = 7.0$ Hz)	5.45 (1H, d, $J = 6.7$ Hz, H-$1'$)
$2'$	74.0		4.27 (1H, m, H-$2'$)
$3'$	76.0		4.29 (1H, m, H- $3'$)
$4'$	69.9		4.19 (1H, m, H-$4'$)
$5'$	74.4	3.51 (1H, m)	4.19 (1H, m, H-$5'$)
$6'$	63.8	4.24 (1H, dd, $J = 11.4$, 5.8 Hz), 4.45 (1H, d, $J = 11.4$ Hz)	4.97 (1H, dd, $J = 5.1$, 11.6 Hz, H-$6'$), 5.21 (1H, d, $J = 11.6$ Hz, H-$6'$)
$1''$	119.4		
$2''$	104.9	7.00 (1H, br.s)	
$3''$	147.9		
$4''$	139.6		
$5''$	145.4		
$6''$	110.8	7.11 (1H, br.s)	
$7''$	165.7		
$3''$-OCH_3	55.9	3.75 (3H, s)	
$4''$-OH		9.18 (1H, br.s)	
$5''$-OH		9.40 (1H, br.s)	

The optical rotation was measured on a Perkin-Elmer 241 polarimeter at 20°C. Column chromatographic separations were carried out using Polyamide (Taizhou Luqiao Biochemical Corporation, Zhejiang, China) and Sephedex LH-20 (Pharmacia).

3.2 Plant material

The plant material was purchased from Liaoning Province Materia Medica Corporation, China, and identified as *Polygonum bistorta* L. by Professor Yun-zhen Guo of Shenyang

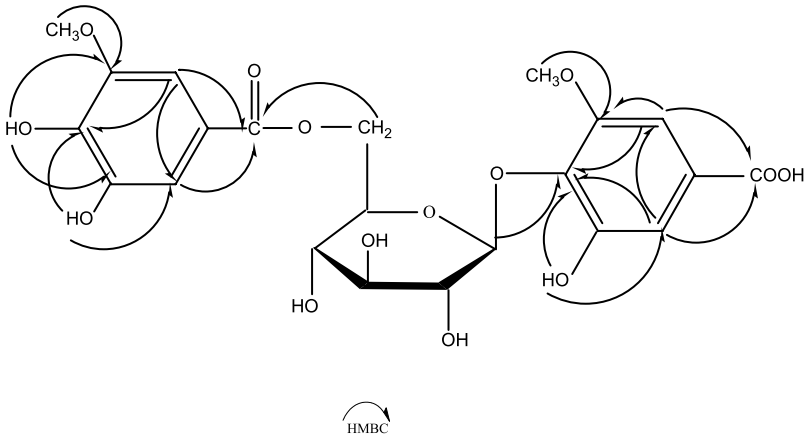

Figure 2. Key HMBC correlations of **1**.

Pharmaceutical University, China. A voucher specimen is deposited at the Herbarium of the Shenyang Pharmaceutical University, China.

3.3 Extraction and isolation

The dried rhizome powder (10 kg) of *Polygonum bistorta* L. was refluxed three times with 95% EtOH and concentrated *in vacuo* to give a crude extract (1580 g). The whole extract was suspended in water and partitioned with $CHCl_3$, EtOAc and n-BuOH, successively. Part of the BuOH extract (227 g) was subjected to polyamide chromatography and eluted with $CHCl_3$/MeOH (from 100:1 to 1:1) and six fractions were obtained. Fraction 3 ($CHCl_3$/MeOH 100:20) was further purified by Sephadex LH-20 chromatography with $CHCl_3$/MeOH (3:7) to yield bistortaside A (**1**) (35 mg) and quercetin-3′-*O*-β-D-glucopyranoside (**2**) (12 mg).

3.3.1 Bistortaside A (1). $C_{22}H_{24}O_{14}$, an amorphous pale white powder, mp: 154–155°C. $[\alpha]_D$ −53 (*c* 0.9, MeOH); UV (MeOH) λ_{max} (nm) (log ϵ): 214 (4.6), 253 (4.0), 279 (4.1); IR ν_{max} (KBr) (cm^{-1}): 3433, 1693, 1600, 1513; ^{1}H NMR (DMSO-d_6 300 MHz), ^{13}C NMR (DMSO-d_6 75 MHz) and ^{1}H NMR (C_5D_5N-d_5 300 MHz) of glycosyl data: see table 1. HRFAB-MS *m/z* 535.1079 (calcd For $C_{22}H_{24}O_{14}Na$ 535.1064) $[M + Na]^+$.

Hydrolysis of **1**: A solution of compound **1** (6 mg) in 2 ml of 2 N HCl was stirred for 24 h at 60°C. The reaction mixture was cooled to room temperature, and extracted with EtOAc three times. The water solution was adjusted to pH 9.0 with 0.05 N NaOH, reacted at room temperature for 12 h, and was neutralized with 2 N HCl.

3.3.2 Quercetin-3′-*O*-β-D-glucopyranoside (2). ^{1}H NMR (DMSO-d_6, 300 MHz) and ^{13}C NMR (DMSO d_6, 75 MHz) data are consistent with literature values [8].

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