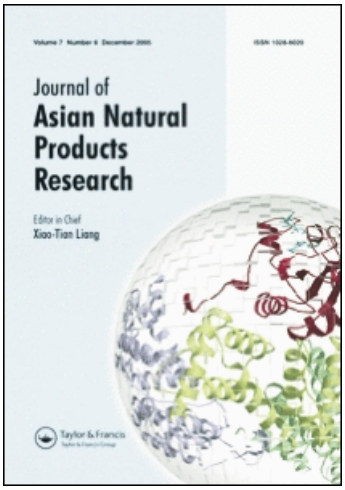

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A NEW COMPOUND FROM *GEUM RIVALE* L.

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A new compound, 1-*O*-methyl-6-*O*-caffeoyl-β-D-glucopyranose (**1**), has been isolated from the aerial part of *G. rivale*, together with five known compounds, cecropiacic acid (**2**), niga-ichgoside (**3**), gallic acid (**4**), 1-*o*-protocatechuoylglucose (**5**), and sucrose (**6**). Their structures were elucidated by spectral methods and chemical reactions.

Keywords: *Geum rivale*; 1-*O*-Methyl-6-*O*-caffeoyl-β-D-glucopyranose; Cecropiacic acid; Niga-ichgoside; Gallic acid; 1-*O*-Protocatechuoylglucose

INTRODUCTION

The *Geum* species are used in traditional Chinese medicine as diuretics and astringents [1,2]. Phytochemical studies on the *Geum japonicum* have revealed the occurrence of triterpenoids and tannins [3–6]. Various bioactivities about these constituents, such as anticoagulant [7], antiviral [8], antifungal [9] and antiinflammatory [10] activities, have been reported in recent years. As part of our studies on naturally occurring antiviral substances, we found that the *n*-BuOH soluble part of the 70% EtOH extract of *Geum rivale* showed significant antiviral activity. Thus, we carried out the isolation and identification of chemical constituents from the *n*-BuOH extract of the title plant. The *n*-BuOH soluble extract was fractionated by Si gel column chromatography, to afford a number of compounds. This paper describes the isolation and structural elucidation of the new compound, 1-*O*-methyl-6-*O*-caffeoyl-β-D-glucopyranose (**1**), along with five known compounds, all of which were obtained from this species for the first time.

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RESULTS AND DISCUSSION

Compound **1** was obtained as an amorphous solid, $[\alpha]_D^{20}$ −18.1(c 0.10, CH_3OH). The HRSIMS spectrum of **1** gave a pseudo-molecular ion at *m/z* 357.1181 $[M + H]^+$ (calcd. 357.1185) corresponding to a molecular formula of $C_{16}H_{20}O_9$. The IR spectrum of **1** implied the presence of a conjugated ester (1694 cm^{-1}) and aromatic ring (1598, 1522 cm^{-1}). The ^{1}H-NMR spectrum (in CD_3OD) of **1** showed three aromatic proton resonances at δ 6.99 (1H, *d*, $J = 1.5$ Hz), 6.72 (1H, *d*, $J = 8.5$ Hz), and 6.88 (1 H, *dd*, $J = 8.5$, 1.5 Hz), which suggested the existence of 1,3,4-trisubstituted phenyl ring, and the three signals were assigned to H-2′, H-5′, H-6′, respectively, based on their chemical shifts and coupling pattern analysis. In addition, the ^{1}H-NMR spectrum of **1** (see Table I), also displayed signals for an AB system at δ 7.52 and 6.25 (each 1H, $J = 15.5$ Hz) corresponding to the H-7′ and H-8′, respectively. The above information revealed the presence of a caffeoyl partial structure in the molecule. A singlet at δ 3.35 (3H, s) in the ^{1}H-NMR spectrum was ascribed to the CH_3 protons.

^{13}C-NMR (Table I) spectrum and DEPT experiments of **1** showed 16 carbon signals: 1 methyl, 1 methylene, 10 methines and 4 quaternary carbons, of which the signals at δ 127.68, 115.11, 146.84, 149.67, 116.50, 123.02, 147.22, 114.88, and 169.15 were attributed to the caffeoyl moiety.

The anomeric proton at δ 4.15 (1H, *d*, $J = 7.5$ Hz) in the ^{1}H-NMR and corresponding carbon signal at δ 105.43 in the ^{13}C-NMR suggested that compound **1** contained a sugar residue. Using ^{1}H–^{1}H COSY NMR experiments, from the anomeric proton H-1, the assignments of H-2 (δ 3.12, m), H-3 (δ 3.26, m) H-4 (δ 3.30, m), H-5 (δ 3.45, m), H-6 (δ 4.28, *dd*, $J = 12.0, 6.0$ Hz; 4.43 *dd*, $J = 12.0, 2.0$ Hz) could be made. The corresponding carbon signals were assigned as δ 105.43 (C-1), 75.02 (C-2), 71.62 (C-3), 77.86 (C-4), 75.44 (C-5), 64.57 (C-6), respectively, by the ^{13}C-H COSY NMR spectrum. These spectral data suggested that the monosaccharide unit was glucose, which was also established by comparison on TLC with standard sugar after hydrolysis. The configuration of the anomeric proton of the glucose was proposed as β on the basis of the coupling constant (7.5 Hz) of the ^{1}H-NMR signal at δ 4.15.

TABLE I ^{1}H and ^{13}C-NMR data of compound **1**

Positions	*^{1}H*	*^{13}C*
1		127.68
2	6.99 *d* (1.5)	115.11
3		146.84
4		149.67
5	6.72 *d* (8.5)	116.50
6	6.88 *dd* (8.5, 1.5)	123.02
7	7.52 *d* (15.5)	147.22
8	6.72 *d* (15.5)	114.82
9		169.15
1′	4.15 *d* (7.5)	105.43
2′	3.12 m	75.02
3′	3.26 m	71.62
4′	3.30 m	77.86
5′	3.45 m	75.44
6′	4.28 *dd* (12.0, 6.0)	64.57
	4.43 *dd* (12.0, 2.0)	
OCH_3	3.35 s	57.31

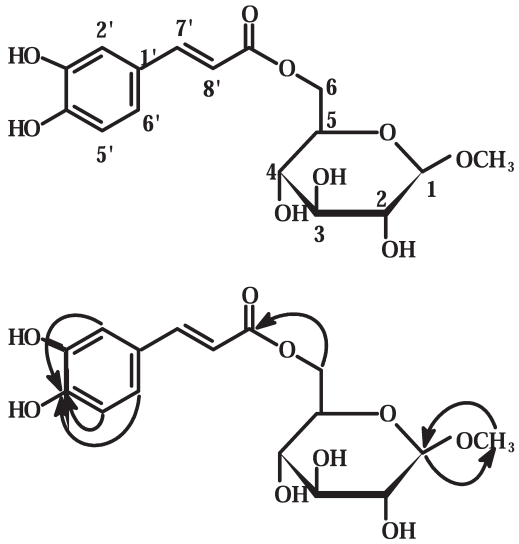

FIGURE 1 Key HMBC correlations for compound **1**.

The respective positions of the substituents were determined using long-range heteronuclear correlations observed by HMBC experiment (see Fig. 1). The correlations showed three bonding coupling from H-1 to methyl carbon, methyl protons to C-1, and H-6 to C-9′, which indicated that the carboxylic C-9′ and methyl were attached to the glucose C-6 and C-1, respectively. Structure of compound **1**, therefore, we assigned as 1-*O*-methyl-6-*O*-caffeoyl-β-D-glucopyranose.

Besides the new compound, other isolated compounds from this plant were identified as cecropiacic acid (**2**) [15], niga-ichgoside (**3**) [11,12], gallic acid (**4**) [13], 1-*O*-protocatechuoylglucose (**5**) [14], and sucrose (**6**) [16] on the basis of spectral evidence, and comparison of physical data with literature values.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined with an XT4-100X micromelting point apparatus and are uncorrected. Specific rotations were obtained on a Perkin–Elmer 683 spectrophotometer. NMR spectra were run on a Bruke AM-500 spectrometer. ESIMS and HRSIMS were recorded on Finnigan TSQ 7000 and Bruke FT-ICR instruments, respectively. Si gel (Hai Yang 200–300 mesh, produced by Qing Dao Hai Yang Chemical Group Company, Qing Dao, People's Republic of China) was used for column chromatography. Precoated Si gel plates (GF_{254}) were used for analytical and preparative TLC.

Plant Material

The dry aerial part of *G. rivale* was collected in Iceland, in August 1999. Prof Paul But identified the plant material, and a voucher specimen has been deposited in the Herbarium of Institute of Chinese Medicine, the Chinese University of Hong Kong.

Extraction and Isolation

The aerial part of *G. rivale* (2 kg) were extracted with hot 70% EtOH (8 l) three times, and the solutions were combined and concentrated *in vacuo*. A suspension of the EtOH extract in H_2O was extracted successively with diethyl ether and *n*-butanol. The combined *n*-BuOH extract (40 g) was analyzed over Si gel (200–300 mesh) eluted with a $CHCl_3$–MeOH gradient solvent system. Fractions with similar R_f values by TLC were evaporated and combined to give 15 fractions. Each fraction was repeatedly subjected to column chromatography over RP-C18 and Sephadex LH-20 eluted with H_2O–EtOH gradient solvent system to give **1** (15 mg), **2** (10 mg), **3** (60 mg), **4** (20 mg), **5** (10 mg), and **6** (100 mg).

1-*O*-Methyl-6-*O*-Caffeoyl-β-D-glucopyranose (**1**). Amorphous solid, mp 163–166°C, $[\alpha]_D^{20}$ − 18.1 (*c* 0.10, MeOH); IR(KBr) ν_{max} 3349, 2943,1694, 1598, 1522, 1447, 1381, 1274, 1183, 1164, 1023, 855, 814 cm^{-1} ^{13}C- and ^{1}H-NMR data see Table I; ESIMS *m/z* 355 $[M - H]^-$. HRSIMS *m/z* 357.1181 $[M + H]^+$.

Acid Hydrolysis Of 1

Compound **1** (5 mg) was refluxed with 3% H_2SO_4 (1 ml) for 3 h. The reaction mixture was extracted with EtOAc. The EtOAc layer was washed and evaporated to dryness. Caffeic acid in the residue was identified by comparison with an authentic sample [on TLC with $CHCl_3$–EtOAC–ACOH (1:1:0.02)]. The aqueous layer was neutralized with 5% NaOH, then filtered. The filtrate showed the presence of glucose [identified by TLC comparison using CH_3–MeOH–H_2O (7:3:0.3), detection with anisaldehyde-H_2 SO_4 reagent].

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