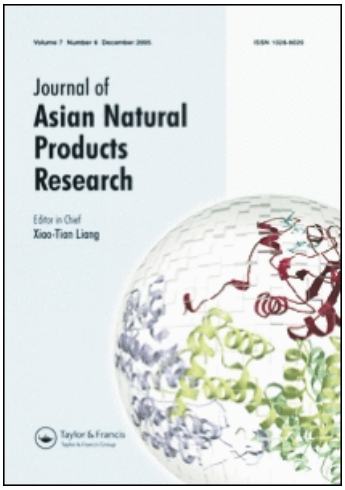

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Flavonoids from *Camptosorus sibiricus* Rupr.

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Three new flavonol glycosides, kaempferol-3-*O*-(6-*trans*-caffeoyl)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside (**1**), kaempferol-3-*O*-(6-*trans*-caffeoyl)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside (**2**), and kaempferol-3-*O*-(6-*trans*-p-coumaroyl)-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside (**3**), were isolated from the aerial part of *Camptosorus sibiricus*. Their structures were elucidated by spectroscopic methods, including 2D NMR spectral techniques.

Keywords: *Camptosorus sibiricus*; Flavonol glycoside; Camsibriside A; Camsibriside B; Camsibriside C

1. Introduction

Camptosorus sibiricus is a Chinese herbal medicine widely distributed in North China that has activity in the dilatation of blood vessels. The total flavonoids with activities of dilatation of blood vessels from this plant have been reported in the literature [1]. In this paper, we describe the isolation and structure elucidation of three new flavonol glycosides, compounds **1**–**3**, from the aerial part of *C. sibiricus*.

2. Results and discussion

The *n*-BuOH fraction of the ethanolic extract from the aerial part of *Camptosorus sibiricus* was chromatographed successively on silica gel column, Sephadex LH-20 and RP-HPLC (ODS) to give compounds **1**–**3**.

Compound **1**, a yellow amorphous solid, showed molecular formula of $C_{36}H_{36}O_{19}$ determined from its HRMS, ^{1}H NMR (table 1) and ^{13}C NMR (table 2). The ESI-MS spectrum gave a $[M + H]^+$ peak at *m/z* 773 and fragment ions at *m/z* 449 and 287. The UV spectrum of **1** showed absorption maxima at 331 and 254 nm, indicating the presence of substituted aromatic rings and α,β unsaturated ketone in the molecule [2]. The ^{1}H NMR

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Table 1. ^{1}H NMR (300 MHz) spectral data for compounds **1**–**3**.

	Compounds (δ, DMSO-d_6)[a]		
No. of atom	***1***	***2***	***3***
6	6.18 (1H, br. S)	6.45 (1H, d, 1.5)	6.41 (1H, d, 2.0)
8	6.36 (1H, br. S)	6.68 (1H, d, 1.6)	6.67 (1H, d, 2.0)
2′,6′	8.05 (2H, d, 9.0)	8.07 (2H, d, 8.7)	8.01 (2H, d, 8.9)
3′,5′	6.91 (2H, d, 9.0)	6.91 (2H, d, 8.9)	6.94 (2H, d, 8.9)
1″	5.70 (1H, d, 6.9)	5.67 (1H, d, 6.7)	5.70 (1H, d, 7.0)
1‴	4.70 (1H, d, 7.5)	4.70 (1H, d, 7.6)	4.70 (1H, d, 7.6)
6‴a	4.18 (1H, dd, 11.7, 5.3)	4.19 (1H, dd, 11.5, 5.0)	4.19 (1H, dd, 11.9, 5.8)
6‴b	4.31 (1H, d, 10.9)	4.30 (1H, d, 11.0)	4.32 (1H, d, 10.7)
1⁗		5.05 (1H, d, 7.2)	5.04 (1H, d, 7.3)
α	6.00 (1H, d, 15.0)	6.00 (1H, d, 15.9)	6.07 (1H, d, 15.9)
β	7.31 (1H, d, 15.0)	7.30 (1H, d, 15.8)	7.37 (1H, d, 15.9)
2	6.91 (1H, br. s)	6.90 (1H, br. S)	7.29 (1H, d, 8.6)
3			6.73 (1H, d, 8.6)
5	6.70 (1H, d, 9.0)	6.70 (1H, d, 8.3)	6.73 (1H, d, 8.6)
6	6.75 (1H, d, 9.0)	6.75 (1H, d, 8.3)	7.29 (1H, d, 8.6)

[a] Coupling constants (*J* in Hz) are given in parentheses.

(300 MHz, DMSO-d_6) spectrum (table 1) showed a typical pattern of a kaempferol aglycon together with signals ascribable to sugar moieties and acyl residue. The two anomeric protons arising from the sugar moieties at δ 5.70 (1H, d, $J = 6.9$ Hz) and 4.70 (1H, d, $J = 7.5$ Hz), correlated respectively with signals at 98.2 and 104.4 in the HMQC spectrum. The ^{1}H NMR spectrum also showed the presence of a caffeoyl residue (table 1). ^{1}H–^{1}H COSY together with the HMBC experiment allowed to identify the spin systems of each sugar residue. In particular the lower field shifts of C-2″ (δ 83.2) together with H-6‴ δ 4.18, 4.31) and C-6‴ (δ 63.6) suggested the substitution pattern of glycosyl and acyl moieties. The HMBC experiment indicated correlations between δ 5.70 (H-1″) and 133.0 (C-3); δ 4.70 (H-1‴) and 83.2 (C-2″); δ 4.31 and 4.18 (H-6‴) and 166.5 (COO). Chemical shifts, multiplicity of the signal, the coupling constant and the correlations in the ^{1}H NMR (table 1) and ^{13}C NMR (table 2), and 2D NMR spectra indicated the presence of two glucopyranosyl moieties with β-configuration at the anomeric carbon and a *trans*-caffeoyl substitution at the terminal glucose. On the basis of all these results the structure of compound **1** (figure 1) was established as Kaempferol 3-*O*-(6-*trans*-caffeoyl)-β-D-glucopyranosyl (1 → 2)-β-D-glucopyranoside [3–6], named camsibriside A.

Compound **2** was assigned to the formula of $C_{42}H_{46}O_{24}$ by HRMS. The ^{1}H NMR (table 1) and ^{13}C NMR (table 2) spectra of **2** were similar to those of **1** except for signals of another sugar and ring-A of the kaempferol aglycon. The lower field shifts of H-6 (δ 6.45) and H-8 (δ 6.68) signals and the anomeric proton at δ 5.05 (1H, d, $J = 7.2$ Hz) suggested the presence of β-D-glucopyranosyl at C-7. HMBC correlations between δ 5.67 (H-1″) and 133.2 (C-3); 4.70 (H-1‴) and 83.4 (C-2″); 5.05 (H-1⁗) and 162.7 (C-7); 4.30 and 4.19 (H-6⁗) and 166.5 (COO) were also similar to those of 1. From these results, the structure of 2 (figure 1) was concluded as Kaempferol-3-*O*-(6-*trans*-caffeoyl)-β-D-glucopyranosyl (1 → 2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside, named camsibriside B.

Finally the molecular formula of compound **3** was determined as $C_{42}H_{46}O_{23}$ from HRMS. NMR and other spectroscopic data were nearly identical with those of **2**; the only difference was that a *trans-p*-coumaroyl group appeared in **3** instead of the *trans*-caffeoyl in **2**. In conclusion, the structure of the new compound **3** (figure 1) was determined to be

Table 2. ^{13}C NMR (75 MHz) spectral data for compounds **1**–**3**.

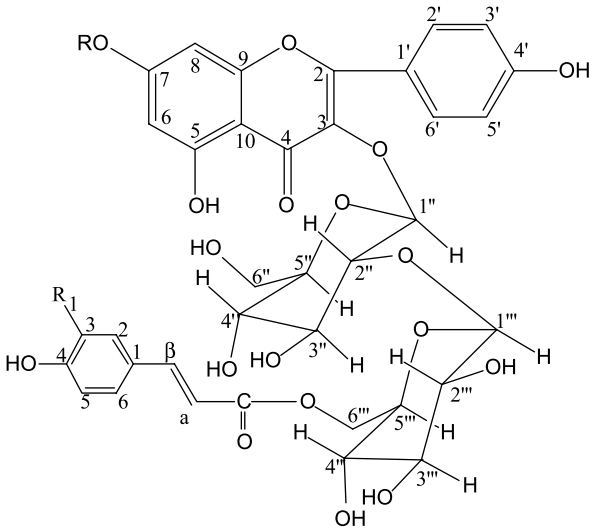
	Compounds (δ, DMSO-d_6)		
No. of atom	***1***	***2***	***3***
2	155.6	155.	155.9
3	133.0	133.2	133.2
4	177.5	177.7	177.6
5	161.3	160.9	160.9
6	98.8	99.3	99.3
7	164.5	162.7	162.7
8	93.8	94.4	94.4
9	156.4	156.2	156.2
10	103.9	105.7	105.6
1′	121.0	120.7	120.7
2′, 6′	131.0	131.1	131.1
3′, 5′	115.3	115.4	115.4
4′	160.1	160.3	160.3
1″	98.2	98.0	98.0
2″	83.2	83.4	83.6
3″	76.6	76.6	76.5
4″	69.9	69.7	69.9
5″	77.5	77.6	77.5
6″	60.6	60.7	6.06
1″	104.4	104.5	104.6
2″	74.2	74.2	74.2
3″	76.4	76.3	76.3
4″	69.7	69.7	69.7
5″	74.2	74.6	74.6
6″	63.6	63.5	63.6
1″		99.8	99.9
2″		73.2	73.2
3″		76.6	76.5
4″		69.7	69.7
5″		77.2	77.2
6″		60.7	60.7
C═O	166.5	166.5	166.5
α	113.7	113.6	113.7
β	145.6	145.1	144.6
1	125.5	125.4	124.9
2	115.1	115.0	130.1
3	145.2	145.6	115.7
4	148.6	148.5	159.9
5	115.7	115.7	115.7
6	121.1	121.1	130.1

kaempferol-3-*O*-(6-*p*-coumaroyl)-β-D-glucopyranosyl (1 → 2)-β-D-glucopyranoside-7-*O*-β-D-glucopyranoside, named camsibriside C.

3. Experimental

3.1 General experimental procedures

Melting points (uncorrected) were measured on a Yanaco-hot-stage and are uncorrected. The UV–vis spectra were performed on a Shimadzu UV-260 instrument. NMR spectra were recorded on Bruker-ARX-300 spectrometer, using TMS as an internal standard. ESI-MS was performed on Finnigan LCQ mass spectrometer. HRESIMS was performed on QSTAR LCQ mass spectrometer. The optical rotation was measured on Perkin-Elmer 241 polarimeter.



1 R=H , R_1=OH

2 R=β-D-glucopyranosyl , R_1=OH

3 R=β-D-glucopyranosyl , R_1=H

Figure 1. **1** R = H, R_1 = OH. **2** R = β-D-glucopyranosyl, R_1 = OH. **3** R = β-D-glucopyranosyl, R_1 = H.

HPLC separations were performed on a Shim-pack PREP-ODS column (216 × 25 mm) equipped with Shimadzu SPD-6A UV spectrophotometric detector and a Shimadzu LC-6AD series pumping system.

3.2 Plant material

The aerial part of *Camptosorus sibiricus* was collected in Beining city, Liaoning Province, China, in July 2002, and identified by Professor Qishi Sun of Shenyang Pharmaceutical University. A voucher specimen (No.20020701) is deposited at the herbarium of the Research Department of Natural Medicine, Shenyang Pharmaceutical University.

3.3 Extraction and isolation

The air-dried aerial part (2.0 kg) of *C. sibiricus* was extracted with 70% ethanol and successively partitioned three times by EtOAc and *n*-BuOH solvent to give 20.0 g and 43.0 g residues, respectively. The *n*-BuOH extract was chromatographed on silica gel column using $CHCl_3$/MeOH as eluent to obtain fraction 3 (100:31). Fraction 3 was submitted on Sephadex LH-20 using MeOH as eluent to get the part of total flavonol glycoside, which was isolated on RP-HPLC with a ODS column (216 × 25 mm, flow rate 5 ml/min) with MeOH/H_2O (40:60) to yield respectively **1** (32.0 mg) (t_R = 53.8 min), **2** (17.0 mg) (t_R = 39.2 min) and **3** (16.0 mg) (t_R = 36.4 min).

3.3.1 Compound 1. Amorphous yellow powder, mp 196–198°C; $[\alpha]_D^{20}$ −46.0 (*c* 0.032, MeOH); UV: λ_{max} (MeOH) 267, 331 nm; ^{1}H and ^{13}C NMR spectral data (DMSO-d_6):

tables 1 and 2; HRESIMS: *m/z* 772.1859, (calcd for $C_{36}H_{36}O_{19}$, 772.1851); ESI-MS *m/z*: 773 $[M + H]^+$, 449 $[M - (glc + caffeoyl) + H]^+$, 287 $[M - (glc + glc + caffeoyl) + H]^+$.

3.3.2 Compound 2. Amorphous yellow powder, mp 185–187°C; $[\alpha]_D^{20}$ −68.8 (*c* 0.275, MeOH); UV: λ_{max} (MeOH) 267, 331 nm; ^1H and ^{13}C NMR spectral data (DMSO-d_6): tables 1 and 2; HRMS: *m/z* 934.2371 (calcd for $C_{42}H_{46}O_{24}$, 934.2379); ESI-MS *m/z*: 935 $[M + H]^+$, 449 $[M - (glc + glc + caffeoyl) + H]^+$, 287 $[M - (glc + glc + glc + caffeoyl) + H]^+$.

3.3.3 Compound 3. Amorphous yellow powder, mp 191–193°C; $[\alpha]_D^{20}$ −54.0 (*c* 0.067, MeOH); UV: λ_{max} (MeOH) 268, 315 nm; ^1H and ^{13}C NMR spectral data (DMSO-d_6): tables 1 and 2; HRMS: *m/z* 918.2438 (calcd for $C_{42}H_{46}O_{23}$, 918.2430); ESI-MS *m/z*: 919 $[M + H]^+$, 449 $[M - (glc + glc + coumaroyl) + H]^+$, 287 $[M - (glc + glc + glc + coumaroyl) + H]^+$.

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