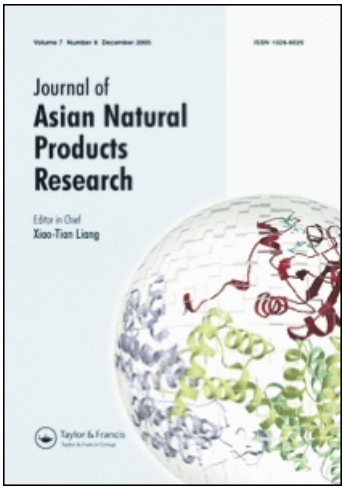

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Two new benzochromone glycosides from the stem of *Berchemia racemosa*

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Two new benzochromone glycosides, rubrofusarin 6-O-α-L-rhamnosyl- (1 → 6)-O-β-D-glucopyranoside (**1**) and demethylflavasperone 10-O-β-D-glucopyranoside (**2**), have been isolated from the stem of *Berchemia racemosa* Sieb. *et* Zucc. (Rhamnaceae). Their structures were elucidated on the basis of spectroscopic evidence.

Keywords: *Berchemia racemosa*; Rhamnaceae; Benzochromone glycosides; Rubrofusarin 6-*O*-α-L-rhamnosyl-(1 → 6)-O-β-D-glucopyranside; Demethylflavasperone 10-O-β-D-glucopyranoside

1. Introduction

Berchemia racemosa Sieb. *et* Zucc. (Rhamnaceae) is widely distributed in the southern part of China. Its root and stem have been used for the treatment of gall stone, liver diseases, neuralgia, and stomach cramp in traditional Chinese medicine [1]. Previous chemical investigation on this species demonstrated the presence of phenol compounds, aromatic glycosides and naphthopyrone glycosides, 2,6-dimethoxy-*p*-benzoquinone, lignans, monoterpene glycosides and flavonoids. Shogo Inoshiri also found that 2,6-dimethoxy-*p*-benzoquinone has strong inhibition on histamine release from rat mast cells [2–5]. In our chemical investigation of *Berchemia racemosa* Sieb. *et* Zucc., two new benzochromone glycosides were isolated from the butanol-soluble fraction of the ethanol extract, namely rubrofusarin 6-*O*-α-L-rhamnosyl-(1 → 6)-*O*-β-D-glucopyranoside (**1**), and demethylflavasperone 10-*O*-β-D-glucopyranoside (**2**). Their structures were elucidated on the basis of spectral evidence (figure 1).

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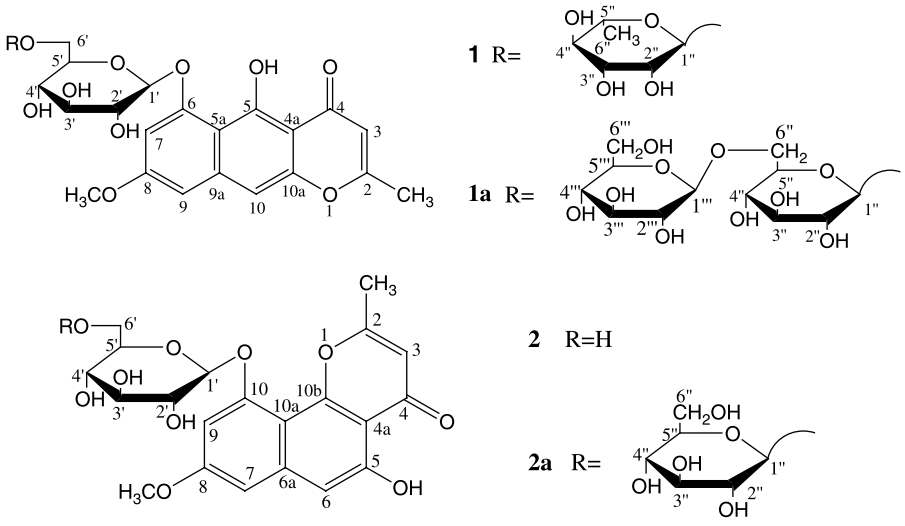

Figure 1. Structures of compounds **1** and **2**.

2. Results and discussion

Compound **1** was obtained as pale yellow flakes and its ESIMS showed two ion peaks at *m/z* 581 $[M + H]^+$ and 603 $[M + Na]^+$. Its molecular formula of $C_{27}H_{32}O_{14}$ was determined by HRFABMS at *m/z* 581.1872 $[M + H]^+$. Its IR spectrum revealed the presence of hydroxyl (3442 cm^{-1}), carbonyl (1657 cm^{-1}), and aromatic rings (1471 and 1583 cm^{-1}). In the ^{1}H-NMR spectrum, two proton signals at δ 6.18 (1H, s, H-3) and 7.18 (1H, s, H-10), two *meta*-coupled doublets at δ 6.72 (1H, d, $J = 2.2$ Hz, H-7) and 6.92 (1H, d, $J = 2.2$ Hz, H-9), a chelated hydroxyl group at δ 14.83 (1H, s, OH-5), and two singlets at δ 3.87 (3H, s, OCH_3), 2.38 (3H, s, CH_3) were observed. Additionally, the ^{1}H-NMR spectrum also showed two anomeric proton signals at δ 4.98 (1H, d, $J = 7.5$ Hz) and 4.52 (1H, s) and one doublet at δ 1.10 (3H, d, $J = 6.5$ Hz). The presence of one rhamnose and one hexose was confirmed by the ^{13}C-NMR spectroscopic data.

The ^{13}C-NMR spectra of **1** showed 27 carbon signals. Except for 12 saccharide carbon signals and a methoxyl signal, the existence of 12 aromatic carbons, a carbonyl carbon and a methyl signal indicated that the aglycone of **1** might be a methyl benzochromone. Furthermore, the ^{1}H-NMR and ^{13}C-NMR spectral data of the aglycone were similar to the corresponding carbon signals of rubrofusarin triglucoside **1a** [6], suggesting that the skeleton of **1** was linetype methyl benzochromone and the methyl group located at C-2. These were also confirmed by HMBC spectrum (figure 2), which showed the correlations of the hydroxyl proton at C-5 with C-5, C-4a and C-5a, H-10 with C-4a, C-5a, C-9, and C-10a, and the methyl protons at C-2 with C-2 and C-3. Additionally, in the ^{13}C-NMR spectrum of sugar moieties**,** besides the carbon signals of α-rhamnose residue, the other 6 carbon signals were at δ 100.9, 73.4, 76.5, 69.9, 75.6, and 66.5. It is obvious that a β-glucose residue existed in **1** combined with the anomeric proton signals at δ 4.98 (1H, d, $J = 7.5$ Hz) in the ^{1}H-NMR spectrum. The correlations of H-1″ of Rha at δ 4.52 with C-6′ of Glc at δ 66.5, H-1′ of Glc at δ 4.98 with C-6 of aglycone at δ 157.6 in the HMBC spectrum confirmed that the α-rhamnose residue was linked to C-6′ of β-glucose, while β-glucose residue was linked to C-6 of aglycone.

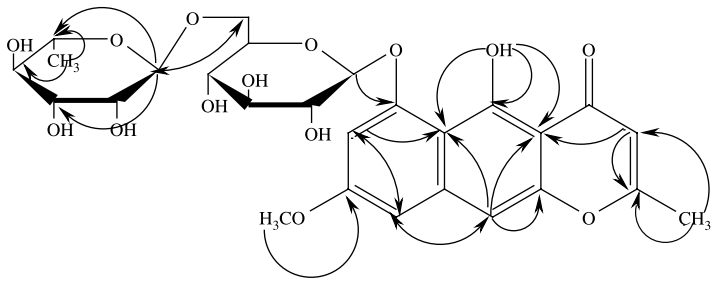

Figure 2. The HMBC correlations of compound **1**.

Therefore, the structure of **1** was identified as rubrofusarin 6-O-α-L-rhamnosyl-(1 → 6)-O-β-D-glucopyranoside.

Compound **2** was obtained as pale yellow needles. The FABMS showed an ion peak at *m/z* 435 $[M + H]^+$, and its molecular $C_{21}H_{22}O_{10}$ was determined by HRFABMS at *m/z* 435.1316. Its IR spectrum revealed the presence of hydroxyl (3411 cm^{-1}), carbonyl (1668 cm^{-1}), and aromatic rings (1468 and 1574 cm^{-1}). The ^{1}H-NMR spectrum of **2** showed two proton singlets at δ 6.93 (1H, s, H-6) and 6.48 (1H, s, H-3), two *meta*-coupled doublets at δ 6.91 (1H, d, $J = 2.0$ Hz, H-7) and 6.71 (1H, d, $J = 2.0$ Hz, H-9), a broad singlet due to a chelated hydroxyl group at δ 12.92 (1H, s), and two singlets at δ 2.52 (3H, s, CH_3) and 3.87 (3H, s, OCH_3). In addition, the ^{1}H-NMR and ^{13}C-NMR spectral data also showed one doublet at δ 5.09 (1H, d, $J = 7.5$ Hz), five proton signals from δ 3.21 to 3.71, and 6 carbon signals at δ 100.5, 73.6, 76.9, 69.6, 77.1, and 60.6, which suggested that the sugar residue was β-glucose.

The ^{13}C-NMR spectrum displayed 21 carbon signals. Except for 6 carbon signals contributed to glucose residue, the other 15 carbon signals similar to **1** suggested that the skeleton of **2** was also a methyl benzochromone. But carefully comparing the ^{1}H-NMR and ^{13}C-NMR spectra of the aglycone in **1** with the corresponding signals of **2**, significant differences were observed in H-3, 5-OH, and Me-2 of ^{1}H-NMR spectrum and C-3, C-4a, and C-5 of ^{13}C-NMR spectrum, especially. Furthermore an angletype benzochromone skeleton in **2**, instead of linetype skeleton in **1**, was suggested by comparing these signals with the known demethylflavasperone gentiobioside **2a** [6]. These were also confirmed by HMBC correlation. While the location of β-glucose residue in **2** can be ascertained to be C-10 by HMBC spectrum, in which the correlations between H-1′ of Glc at δ 5.09 and C-10 of demethylflavasperone at δ 156.2 were observed. Therefore, the structure of compound **2** was shown to be demethylflavasperone 6-O-β-D-glucopyranoside.

3. Experimental

3.1 General experimental procedures

Melting points were determined on Reichert Nr-229 micromelting point apparatus and are uncorrected. The optical rotations were measured on Perkin-Elmer 241 digital polarimeter. IR spectra were recorded on IMPACT 400 with KBr pellets. ^{1}H-NMR (500 MHz), ^{13}C-NMR (125 MHz) and HMBC spectra were performed on INOVA-500 spectrometer with tetramethylsilane (TMS) as internal standard. ESIMS spectra were measured on Agilent 1100 series LC/MSD Trap mass spectrometer (SL). HRFABMS spectra were performed

on AutoSpec Ultima-TOF mass spectrometer. Silica gel (100-200, 200-300 mesh, Qingdao Sea Factory, China) was used for column chromatography (CC) and silica gel GF-254 (Qingdao) for TLC.

3.2 Plant material

Stem of *Berchemia Racemosa* Sieb *et* Zucc. was collected from Jiujiang City of Jiangxi Province, People's Republic of China, in July 2003, and identified by Professor Tan Ceming. A voucher specimen has been deposited in the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China.

3.3 Extraction and isolation

The dried stems of *Berchemia Racemosa* Sieb *et* Zucc. (6.0 kg) were extracted with 95% EtOH at refluxed temperature. The extract was concentrated under reduced pressure

Table 1. ^{13}C-NMR chemical shifts of compounds **1** and **2** (125 MHz in DMSO-d_6, δ, ppm).

C	***1***	***1a***	***2***	***2a***
C-2	168.8	169.0	168.3	168.6
C-3	106.7	106.9	109.2	109.6
C-4	183.7	184.0	182.3	182.6
C-4a	103.6	103.8	108.1	108.3
C-5	161.8	162.1	155.6	155.8
C-5a	107.6	107.9	–	–
C-6	157.6	157.8	104.9	105.2
C-6a	–	–	140.3	140.5
C-7	101.4	101.5	99.5	99.8
C-8	161.1	161.3	161.0	161.4
C-9	99.7	100.0	99.8	100.3
C-9a	140.3	140.5	–	–
C-10	101.1	101.0	156.2	156.3
C-10a	152.4	152.6	104.2	104.4
10b	–	–	155.1	155.4
Me at C-2	20.2	20.4	19.8	20.1
OMe	55.5	55.7	55.4	55.7
Sugar moiety				
C-1′	100.9	101.1	100.5	100.6
C-2′	73.4	73.7	73.6	73.9
C-3′	76.5	76.5	76.9	77.0
C-4′	69.9	69.9	69.6	69.8
C-5′	75.6	75.9	77.1	75.7
C-6′	66.5	68.7	60.6	68.9
C-1″	100.7	102.8	–	103.8
C-2″	70.2	72.4	–	73.8
C-3″	70.7	88.3	–	76.9
C-4″	72.1	68.5	–	70.3
C-5″	68.3	76.3	–	77.2
C-6″	17.8	60.9	–	61.3
C-1‴	–	104.3	–	–
C-2‴	–	74.0	–	–
C-3‴	–	77.1	–	–
C-4‴	–	70.3	–	–
C-5‴	–	76.5	–	–
C-6‴	–	61.3	–	–

and diluted with H_2O. The aqueous solution was extracted with petroleum ether, EtOAc and n-BuOH respectively. The n-BuOH extract (70.0 g) was chromatographed on silica gel column to give 62 fractions. Fraction 13 (1.2 g) was crystallized in MeOH to give compound **1** (34.0 mg). Fraction 11 (2.5 g) was subjected to repeated chromatography on silica gel column eluted with $CHCl_3$-MeOH (12:1) to give compound **2** (4.5 mg).

3.4 Identification

Rubrofusarin 6-O-α-L-rhamnosyl- (1 → 6)-O-β-D-glucopyranoside (**1**), pale-yellow flakes, $[\alpha]_D^{25}$ + 28 (c = 0.1, MeOH). IR (KBr) cm^{-1}: 3442, 2920, 1657, 1628, 1448, 1583, 1414, and 1045. ^{1}H-NMR (500 MHz, DMSO-d_6, ppm) δ: 6.18 (1H, s, H-3), 7.18 (1H, s, H-10), 6.72 (1H, J = 2.2 Hz, H-7), 6.92 (1H, J = 2.2 Hz, H-9), 14.83 (1H, s, OH at C-5), 2.38 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 4.98 (1H, d, J = 7.5 Hz, H-1′ at Glc), 4.52 (1H, s, H-1″ at Rha), 1.10 (3H, d, J = 6.5 Hz, H-6″ at Rha). ^{13}C-NMR (125 MHz, DMSO-d_6, ppm) data see table 1. ESIMS m/z: 581 $[M + H]^+$, 603 $[M + Na]^+$. HRFABMS m/z: 581.1872 $[M + H]^+$ (calcd for $C_{27}H_{33}O_{14}$, 581.1870).

Demethylflavasperone 10-O-β-D-glucopyranoside (**2**), pale-yellow needles, $[\alpha]_D^{25}$ −80 (c = 0.05, MeOH). mp 254°C (in MeOH). IR (KBr) cm^{-1}: 3411, 2916, 2850, 1668, 1622, 1574, 1468, 1379, 1078; ^{1}H-NMR (500 MHz, DMSO-d_6, ppm) δ: 6.48 (1H, s, H-3), 6.93 (1H, s, H-6), 6.91 (1H, d, J = 2.0 Hz, H-7), 6.71 (1H, d, J = 2.0 Hz, H-9), 2.52 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 12.92 (1H, brs, OH at C-5), 5.09 (1H, d, J = 7.5 Hz, Glc H′-1); ^{13}C-NMR (125 MHz, DMSO-d_6, ppm) data see table 1. FABMS m/z: 435 $[M + H]^+$. HRFABMS m/z: 435.1316 $[M + H]^+$ (calcd for $C_{21}H_{23}O_{10}$, 435.1291).

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