

# A New Phenylpropanol Glycoside and Its Five Known Analogues from *Boschniakia rossica*

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**Abstract:** **Objective** To study the constituents in the whole plant of *Boschniakia rossica*. **Methods** The constituents were separated and purified with chromatographic methods. Their structures were elucidated by spectroscopic methods (1D, 2D NMR, UV, IR, and HRESI-TOF-MS) and chemical analyses. **Results** One new phenylpropanol glycoside (**1**) and its five known analogues were obtained from *B. rossica*. They were identified as *trans-p*-coumaryl-(2'-*O*- $\beta$ -D-glucopyranosyl)- $\beta$ -D-glucopyranoside (**1**), salidroside I (**2**), rossicasin A (**3**), *trans-p*-coumaryl alcohol 1-*O*- $\beta$ -glucopyranosyl(1 $\rightarrow$ 4)- $\alpha$ -rhamnopyranosyl(1 $\rightarrow$ 3)- $\beta$ -glucopyranoside (**4**), salidroside (**5**), and acetoside (**6**). **Conclusion** Among the known compounds, compound **2** is firstly isolated from the plants in genus *Boschniakia* C. A. Mey. ex Bongard. Meanwhile, the <sup>13</sup>C-NMR data of 9 and 4' positions in compound **4** are corrected.

**Key words:** acetoside; analogues; *Boschniakia rossica*; rossicasin C; salidroside I

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## Introduction

*Boschniakia rossica* Fedtsch et Flerov. is a parasitic plant in Orobanchaceae growing on the roots of plants in genus *Alnus* B. Ehrh. (Betulaceae) (Jiangsu New Medical College, 1979). It is mainly distributed in Changbai Mountain of China, Fuji Yama of Japan, and the northern mountains of North Korea (Yu and Xin, 1996). As a rare medicinal plant, it shows the effects including invigorating the kidney, strengthening *Yang*, moistening intestines, nourishing body, and lengthening life of human being (Liu and Liang, 2001), so it is called as "Bulaocao" in folk of China. It also shows some pharmacological activities, such as antitumor, anti-inflammatory, antisenile, and immunoregulation (Liang, Bu, and Liu, 2009; Liu and Liang, 2011; Yin, Jin, and Quan, 2011). In our present study on the constituents of *B. rossica*, one new phenylpropanol glycoside together with its five known analogues was obtained. Compound **2** is firstly isolated from the plants in genus *Boschniakia* C. A. Mey. ex Bongard. Meanwhile, the <sup>13</sup>C-NMR data of 9 and 4' positions in compound **4** are corrected.

## Materials and methods

### General

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were determined on a Bruker 500 MHz NMR spectrophotometer (Avance III 500MR) at 500 MHz for <sup>1</sup>H-NMR and 125 MHz for <sup>13</sup>C-NMR with tetramethylsilane (TMS) as an internal standard. Positive- and negative-ion HRESI-TOF-MS spectra were recorded on an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS Spectrometer.

Optical rotations were measured on a Rudolph Autopol® IV Automatic Polarimeter (*l* = 50 mm), IR spectra were recorded on a Varian 640-IR FT-IR Spectrophotometer, and UV spectra were recorded on a Varian Cary 50 UV-Vis Spectrophotometer.

D-101 was purchased from Haiguang Chemical Co., Ltd. (Tianjin, China). Silica gel was obtained from Qingdao Haiyang Chemical Co., Ltd. (48—75  $\mu$ m, China). HPLC was performed on ODS (Cosmosil 5C18-MS-II, Tokyo, Japan; 250 mm  $\times$  20 mm, flow rate 9.0 mL/min), and the eluate was monitored with a UV Detector (Shimadzu RID-10A UV-Vis, Japan).

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Pre-coated TLC plates with Silica gel GF<sub>254</sub> (Tianjin Silida Technology Co., Ltd., China) were used to detect the purity of the isolate achieved by spraying with 10% H<sub>2</sub>SO<sub>4</sub>-EtOH, followed by heating.

#### Plant materials

The whole plant of *Boschniakia rossica* Fedtsch et Flerov. was collected from Changbai Mountain (Jilin, China), and identified by Prof. ZHANG Li-juan at Tianjin University of Traditional Chinese Medicine. The voucher specimen was deposited at Academy of Traditional Chinese Medicine of Tianjin University of Traditional Chinese Medicine (China).

#### Extraction and isolation

The dried whole plant of *B. rossica* (6 kg) was extracted with 75% ethanol-water under reflux. After evaporation in vacuo, the combined 75% ethanol extract (260 g) was dissolved in water (6 L), and further subjected to D-101 resin column chromatography (CC) to obtain the water (F<sub>A</sub> 80 g) and 95% EtOH (F<sub>B</sub> 152 g) fractions, respectively. F<sub>B</sub> (72 g) was subjected to silica gel CC [CHCl<sub>3</sub>-MeOH (100:0→100:5)→CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (10:3:1→7:3:1, lower layer)→MeOH] to give 13 fractions (Fr. 1—13). Fr. 7 (16.4 g) was separated by

preparative HPLC (PHPLC) with MeOH-H<sub>2</sub>O [20% (0—42 min)→35% (42—96 min)→45% (96—148 min)→60% (148—196 min)→100% (196—230 min)] to yield 29 fractions (Fr. 7-1—7-29). Fr. 7-6 (189.2 mg) was purified by PHPLC [CH<sub>3</sub>CN-H<sub>2</sub>O (10:90)] to give compound **5** (54.8 mg). Fr. 7-9 (385.3 mg) was subjected to PHPLC [CH<sub>3</sub>CN-H<sub>2</sub>O (12:88)], and compound **2** (62.4 mg) was obtained. Fr. 10 (6.5 g) was subjected to PHPLC with MeOH-H<sub>2</sub>O [25% (0—16 min)→35% (16—56 min)→45% (56—106 min)→60% (106—112 min)→100% (112—128 min)], and 14 fractions (Fr. 10-1—10-14) were obtained. Fr. 10-4 (265.1 mg) was further separated by PHPLC [CH<sub>3</sub>CN-H<sub>2</sub>O (10:90)] to give compound **1** (23.8 mg). Fr. 10-5 (210.8 mg) was subjected to PHPLC [CH<sub>3</sub>CN-H<sub>2</sub>O (12:88)] to yield six fractions (Fr. 10-5-1—10-5-6). Fr. 10-5-1 (27.6 mg) was subjected to silica gel CC [CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (20:3:1→10:3:1, lower layer)], and to give compounds **3** (8.5 mg) and **4** (11.7 mg). Fr. 10-9 (412.5 mg) was purified by PHPLC [CH<sub>3</sub>CN-H<sub>2</sub>O (17:83)] to give compound **6** (15.3 mg). The structures of the isolated compounds **1**—**6** were shown in Fig. 1.

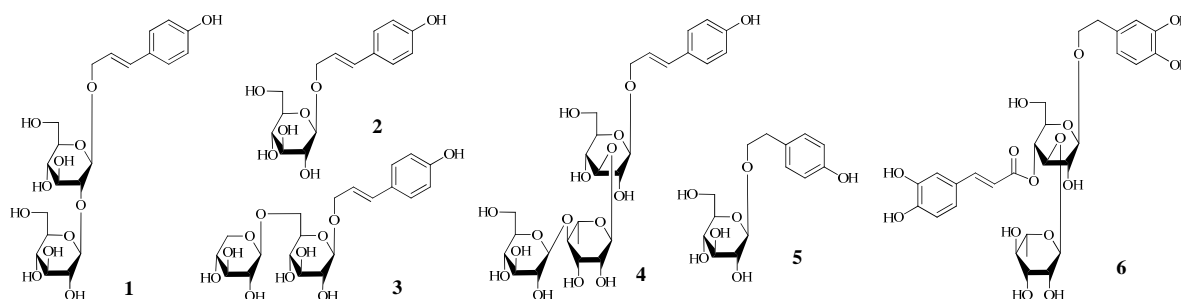


Fig. 1 Structures of compounds **1**—**6** isolated from *B. rossica*

#### Acid hydrolysis of compound **1**

A solution of rossicasin C (2.6 mg) in 1 mol/L HCl (1 mL) was refluxed for 3 h. After cooling, the reaction mixture was extracted with EtOAc. The aqueous layer was subjected to the HPLC analysis under the following conditions, respectively: HPLC column was Kaseisorb LC NH<sub>2</sub>-60-5, 250 mm × 4.6 mm (Tokyo Kasei Co. Ltd., Japan); Detection was carried out on an optical rotation [Chiralyser (IBZ Messtechnik GMBH, Mozartstrasse 14-16 D-30173 Hannover, Germany)]; Mobile phase was CH<sub>3</sub>CN-H<sub>2</sub>O (75:25); Flow rate was 1.0 mL/min. The identification of *D*-glucose in the aqueous layer was carried out by comparison on its retention time (*t<sub>R</sub>*) and

optical rotation with those of authentic *D*-glucose (*t<sub>R</sub>*: 12.3 min, positive optical rotation).

#### Results and discussion

Compound **1**: white powder with negative rotation [ $\alpha$ ]<sub>D</sub><sup>20</sup> −16.5° (MeOH). The IR spectrum indicated the presence of hydroxy (3451 cm<sup>−1</sup>) and an aromatic ring (1461, 1589, and 1608 cm<sup>−1</sup>). Its molecular formula was determined to be C<sub>21</sub>H<sub>30</sub>O<sub>12</sub> by HRESI-TOF-MS (*m/z* 497.1623 [M + Na]<sup>+</sup>). Compound **1** was treated with 1 mol/L HCl liberate *D*-glucose and identified by HPLC (Yoshikawa *et al*, 2007). The <sup>1</sup>H-NMR (C<sub>5</sub>D<sub>5</sub>N, 500 MHz) and <sup>13</sup>C-NMR (C<sub>5</sub>D<sub>5</sub>N, 125 MHz) spectra of

compound **1**, which were assigned by various NMR experiments including  $^1\text{H}$ - $^1\text{H}$  COSY, HSQC, and HMBC spectra (Fig. 2), indicating that there were one *trans*-*p*-coumaryl moiety [ $\delta_{\text{H}}$  4.48 (1H, m, overlapped), 4.70 (1H, dd,  $J = 6.5, 12.0$  Hz), H<sub>2</sub>-9), 6.50 (1H, dt,  $J = 6.5, 16.0$  Hz, H-8), 6.80 (1H, d,  $J = 16.0$  Hz, H-7), 7.12 (2H, d,  $J = 8.5$  Hz, H-3, 5), and 7.51 (2H, d,  $J = 8.5$  Hz, H-2, 6)], and two anomeric protons of sugar moieties [ $\delta_{\text{H}}$  5.01 (1H, d,  $J = 7.5$  Hz, H-1')/ $\delta_{\text{C}}$  102.1 (C-1');  $\delta_{\text{H}}$  5.38 (1H, d,  $J = 7.5$  Hz, H-1'')/ $\delta_{\text{C}}$  106.4 (C-1'')]. The  $^1\text{H}$ - $^1\text{H}$  COSY experiment indicated the presence of the partial structure written in bold lines. In the HMBC spectrum, long-range correlations were observed in the following proton and carbon pairs:  $\delta_{\text{H}}$  5.01 (H-1') and  $\delta_{\text{C}}$  70.4 (C-9);  $\delta_{\text{H}}$  5.38 (H-1'') and  $\delta_{\text{C}}$  84.2 (C-2'). On the basis of above mentioned data, the structure of rossicasin C was elucidated to be *trans*-*p*-coumaryl-(2'-*O*- $\beta$ -*D*-glucopyranosyl)- $\beta$ -*D*-glucopyranoside (**1**).

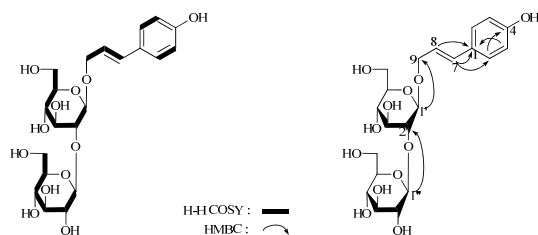


Fig. 2  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC correlations of compound **1**

The physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data of compound **1** were described as following: white powder.  $[\alpha]_{\text{D}}^{25} -16.5^\circ$  (MeOH). UV  $\lambda_{\text{max}}^{\text{MeOH}}$  (nm): 265 (4.38). IR  $\nu_{\text{max}}^{\text{KBr}}$  ( $\text{cm}^{-1}$ ): 1036, 1082, 1340, 1461, 1589, 1608, 3451. HRESI-TOF-MS  $m/z$ : 497.1623  $[\text{M} + \text{Na}]^+$  (calcd. 497.1629 for  $\text{C}_{21}\text{H}_{30}\text{O}_{12}\text{Na}$ ).  $^1\text{H}$ -NMR ( $\text{C}_5\text{D}_5\text{N}$ , 500 MHz)  $\delta$ : 3.88 (1H, m, H-5'), 3.97 (1H, m, H-5''), 4.13 (1H, dd,  $J = 7.5, 8.0$  Hz, H-2''), 4.20 (1H, dd,  $J = 7.5, 8.0$  Hz, H-2'), 4.22 (1H, m, overlapped, H-4', 3''), 4.24 (1H, m, overlapped, H-4''), [4.33, 4.52 (1H each, both m, overlapped, H<sub>2</sub>-6'), 4.34 (1H, m, overlapped, H-3'), [4.38, 4.54 (1H each, both m, overlapped, H<sub>2</sub>-6''), [4.48 (1H, dd,  $J = 6.0, 12.0$  Hz), 4.70 (1H, dd,  $J = 6.0, 12.0$  Hz), H<sub>2</sub>-9], 5.01 (1H, d,  $J = 7.5$  Hz, H-1'), 5.38 (1H, d,  $J = 7.5$  Hz, H-1''), 6.50 (1H, dt,  $J = 6.5, 16.0$  Hz, H-8), 6.80 (1H, d,  $J = 16.0$  Hz, H-7), 7.12 (2H, d,  $J = 8.5$  Hz, H-3, 5), 7.51 (2H, d,  $J = 8.5$  Hz, H-2, 6);  $^{13}\text{C}$ -NMR ( $\text{C}_5\text{D}_5\text{N}$ , 125 MHz)  $\delta$ : 128.8 (C-1), 128.5 (C-2, 6), 116.5 (C-3, 5), 158.8 (C-4), 132.5 (C-7), 123.4 (C-8),

70.4 (C-9), 102.1 (C-1'), 84.2 (C-2'), 78.0 (C-3'), 71.3 (C-4'), 78.4 (C-5'), 62.5 (C-6'), 106.4 (C-1''), 76.6 (C-2''), 78.1 (C-3''), 71.6 (C-4''), 78.7 (C-5''), 62.8 (C-6'').

Compound **2**: white powder. HRESI-TOF-MS  $m/z$ : 335.1099  $[\text{M} + \text{Na}]^+$  (calcd. 335.1101 for  $\text{C}_{15}\text{H}_{20}\text{O}_7\text{Na}$ ).  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ , 500 MHz)  $\delta$ : 3.22–3.40 (4H, m, H-2'–5'), [3.69 (1H, dd,  $J = 5.5, 12.0$  Hz), 3.88 (1H, dd,  $J = 1.5, 12.0$  Hz), H<sub>2</sub>-6'], [4.28 (1H, dd,  $J = 7.0, 12.5$  Hz), 4.49 (1H, dd,  $J = 7.0, 12.5$  Hz), H<sub>2</sub>-9], 4.29 (1H, d,  $J = 8.0$  Hz, H-1'), 6.16 (1H, dt,  $J = 7.0, 16.0$  Hz, H-8), 6.57 (1H, d,  $J = 16.0$  Hz, H-7), 6.73 (2H, d,  $J = 8.5$  Hz, H-3, 5), 7.25 (2H, d,  $J = 8.5$  Hz, H-2, 6);  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}$ , 125 MHz)  $\delta$ : 129.8 (C-1), 128.9 (C-2, 6), 116.4 (C-3, 5), 158.4 (C-4), 134.2 (C-7), 123.4 (C-8), 71.1 (C-9), 103.1 (C-1'), 75.1 (C-2'), 78.1 (C-3'), 71.7 (C-4'), 77.9 (C-5'), 62.8 (C-6'). Compound **2** was identified as salidroside I by comparison of the physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data with the reported data (Mizuno *et al.*, 1990).

Compound **3**: white powder. HRESI-TOF-MS  $m/z$ : 467.1520  $[\text{M} + \text{Na}]^+$  (calcd. 467.1524 for  $\text{C}_{20}\text{H}_{28}\text{O}_{11}\text{Na}$ ).  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ , 500 MHz)  $\delta$ : [3.22 (1H, dd,  $J = 10.5, 11.5$  Hz), 3.89 (1H, dd,  $J = 5.5, 11.5$  Hz), H<sub>2</sub>-5''], 3.25 (2H, m, H-2', 2''), 3.35 (1H, dd,  $J = 9.0, 9.0$  Hz, H-3''), 3.37 (2H, m, H-3', 4'), 3.45 (1H, m, H-5'), 3.52 (1H, td,  $J = 5.5, 10.5$  Hz, H-4''), [3.76 (1H, dd,  $J = 6.0, 11.5$  Hz), 4.12 (1H, dd,  $J = 2.0, 11.5$  Hz), H<sub>2</sub>-6'], [4.31 (1H, ddd,  $J = 1.0, 6.0, 12.5$  Hz), 4.50 (1H, ddd,  $J = 1.0, 6.0, 12.5$  Hz), H<sub>2</sub>-9], 4.37 (1H, d,  $J = 7.0$  Hz, H-1''), 4.38 (1H, d,  $J = 8.0$  Hz, H-1'), 6.19 (1H, dt,  $J = 6.0, 16.0$  Hz, H-8), 6.61 (1H, d,  $J = 16.0$  Hz, H-7), 6.75 (2H, d,  $J = 8.5$  Hz, H-3, 5), 7.28 (2H, d,  $J = 8.5$  Hz, H-2, 6);  $^{13}\text{C}$ -NMR ( $\text{CD}_3\text{OD}$ , 125 MHz)  $\delta$ : 129.8 (C-1), 128.9 (C-2, 6), 116.4 (C-3, 5), 158.5 (C-4), 134.3 (C-7), 123.4 (C-8), 71.3 (C-9), 103.2 (C-1'), 74.9 (C-2'), 78.0 (C-3'), 71.6 (C-4'), 77.1 (C-5'), 69.7 (C-6'), 105.6 (C-1''), 75.0 (C-2''), 77.8 (C-3''), 71.2 (C-4''), 66.9 (C-5''). Compound **3** was identified as rossicasin A by comparison of the physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data with the reported data (Shyr, Tsai, and Lin, 2006).

Compound **4**: brown powder. HRESI-TOF-MS  $m/z$ : 643.2204  $[\text{M} + \text{Na}]^+$  (calcd. 643.2209 for  $\text{C}_{27}\text{H}_{40}\text{O}_{16}\text{Na}$ ).  $^1\text{H}$ -NMR ( $\text{CD}_3\text{OD}$ , 500 MHz)  $\delta$ : 1.32 (3H, d,  $J = 6.5$  Hz, H<sub>3</sub>-6''), 3.20 (1H, dd,  $J = 8.0, 9.0$  Hz, H-2'''), 3.26 (2H, m, H-5', H-5''), 3.28 (1H, m, H-4''), 3.34 (1H, m, H-4'), 3.35 (1H, m, H-2'), 3.37 (1H, dd,  $J = 9.0, 9.0$  Hz, H-3''), 3.50 (1H, dd,  $J = 8.5, 8.5$  Hz,

H-3'), 3.62 (1H, dd,  $J = 9.5, 9.5$  Hz, H-4''), [3.69 (1H, dd,  $J = 5.0, 12.0$  Hz), 3.88 (1H, dd,  $J = 2.0, 12.0$  Hz), H<sub>2</sub>-6''], [3.69 (1H, dd,  $J = 5.0, 12.0$  Hz), 3.84 (1H, dd,  $J = 2.5, 12.0$  Hz), H<sub>2</sub>-6'], 3.94 (1H, m, overlapped, H-3''), 3.96 (1H, m, overlapped, H-2'), 4.08 (1H, m, H-5''), [4.28 (1H, ddd,  $J = 1.0, 6.5, 12.5$  Hz), 4.48 (1H, ddd,  $J = 1.0, 6.5, 12.5$  Hz), H<sub>2</sub>-9], 4.36 (1H, d,  $J = 8.0$  Hz, H-1'), 4.58 (1H, d,  $J = 8.0$  Hz, H-1'''), 5.17 (1H, d,  $J = 1.5$  Hz, H-1''), 6.16 (1H, dt,  $J = 6.5, 16.0$  Hz, H-8), 6.57 (1H, d,  $J = 16.0$  Hz, H-7), 6.73 (2H, d,  $J = 9.5$  Hz, H-3, 5), 7.25 (2H, d,  $J = 9.5$  Hz, H-2, 6);  $^{13}\text{C}$ -NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta$ : 129.8 (C-1), 128.9 (C-2, 6), 116.4 (C-3, 5), 158.5 (C-4), 134.2 (C-7), 123.4 (C-8), 70.3 (C-9), 103.1 (C-1'), 75.8 (C-2'), 84.3 (C-3'), 71.2 (C-4'), 77.9 (C-5'), 62.8 (C-6'), 102.5 (C-1''), 72.3 (C-2'', 3''), 83.5 (C-4''), 68.7 (C-5''), 18.1 (C-6''), 105.7 (C-1'''), 76.1 (C-2'''), 78.3 (C-3'''), 71.6 (C-4'''), 78.1 (C-5'), 62.8 (C-6''). Compound **4** was identified as *trans-p*-coumaryl alcohol 1-*O*- $\beta$ -glucopyranosyl (1 $\rightarrow$ 4)- $\alpha$ -rhamnopyranosyl (1 $\rightarrow$ 3)- $\beta$ -glucopyranoside by comparison of the physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data with the reported data, and the chemical shifts of positions 9 and 4' were corrected [in ref.  $\delta$  70.1 (C-4'), 71.2 (C-9)] (Shyr, Tasi, and Lin, 2006).

Compound **5**: white powder. HRESI-TOF-MS  $m/z$ : 323.1100  $[\text{M} + \text{Na}]^+$  (calcd. 323.1101 for C<sub>14</sub>H<sub>20</sub>O<sub>7</sub>Na).  $^1\text{H}$ -NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta$ : 2.83 (2H, m, H<sub>2</sub>-7), 3.18—3.39 (4H, m, H-2'—5'), 3.70, 4.03 (1H each, both m, H<sub>2</sub>-8), [3.68 (1H, dd,  $J = 5.5, 12.0$  Hz), 3.87 (1H, dd,  $J = 2.0, 12.0$  Hz), H<sub>2</sub>-6'], 4.29 (1H, d,  $J = 7.5$  Hz, H-1'), 6.70 (2H, d,  $J = 8.5$  Hz, H-3, 5), 7.06 (2H, d,  $J = 8.3$  Hz, H-2, 6);  $^{13}\text{C}$ -NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta$ : 130.7 (C-1), 130.9 (C-2, 6), 116.1 (C-3, 5), 156.7 (C-4), 36.3 (C-7), 72.1 (C-8), 104.3 (C-1'), 75.1 (C-2'), 78.1 (C-3'), 71.6 (C-4'), 77.9 (C-5'), 62.7 (C-6'). Compound **5** was identified as salidroside by comparison of the physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data with the reported data (Chu *et al.*, 2011).

Compound **6**: brown powder. HRESI-TOF-MS  $m/z$ : 647.1967  $[\text{M} + \text{Na}]^+$  (calcd. 647.1946 for C<sub>29</sub>H<sub>36</sub>O<sub>15</sub>Na).  $^1\text{H}$ -NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta$ : 1.11 (3H, d,  $J = 6.5$  Hz, H<sub>3</sub>-6''), 2.80 (2H, m, H<sub>2</sub>-7), [3.72, 4.04 (1H each, both m, H<sub>2</sub>-8)], 3.84 (1H, dd,  $J = 8.0, 8.8$  Hz, H-3'), 3.96 (1H, brs, H-2''), 4.38 (1H, d,  $J = 8.0$

Hz, H-1'), 4.94 (1H, dd,  $J = 9.5, 9.5$  Hz, H-4''), 5.21 (1H, brs, H-1''), 6.29 (1H, d,  $J = 16.0$  Hz, H-8'''), 6.57 (1H, dd,  $J = 2.0, 8.0$  Hz, H-6), 6.70 (1H, d,  $J = 2.0$  Hz, H-2), 6.72 (1H, d,  $J = 8.0$  Hz, H-5), 6.70 (1H, d,  $J = 8.0$  Hz, H-5'''), 6.96 (1H, dd,  $J = 1.5, 8.0$  Hz, H-6'''), 7.08 (1H, d,  $J = 2.0$  Hz, H-2''), 7.61 (1H, d,  $J = 16.0$  Hz, H-7''');  $^{13}\text{C}$ -NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta$ : 131.5 (C-1), 116.6 (C-2), 144.5 (C-3), 146.0 (C-4), 117.1 (C-5), 121.3 (C-6), 36.5 (C-7), 72.3 (C-8), 104.1 (C-1'), 75.8 (C-2'), 81.8 (C-3'), 70.4 (C-4'), 76.1 (C-5'), 62.3 (C-6'), 103.0 (C-1''), 72.0 (C-2''), 72.2 (C-3''), 73.7 (C-4''), 70.5 (C-5''), 18.5 (C-6''), 127.6 (C-1'''), 115.3 (C-2'''), 149.6 (C-3'''), 146.7 (C-4'''), 116.4 (C-5'''), 123.3 (C-6'''), 148.0 (C-7'''), 114.7 (C-8'''), 168.3 (C-9'''). Compound **6** was identified as acetoside by comparison of the physical,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR data with the reported data (Fan *et al.*, 2010).

## References

- Chu HB, He WJ, Zhang YM, Ji CJ, Tan NH, 2011. Flavonoids and nor-sesquiterpenes of *Pedicularis densispica*. *China J Chin Mater Med* 36(19): 2672-2675.
- Fan K, Wang P, Zhang XL, Hao SH, Huang S, Wang JQ, 2010. Study on the chemical constituents of *Phlomis younghusbandii*. *J Chin Med Mater* 33(12): 1884-1886.
- Jiangsu New Medical College, 1979. *Dictionary of Chinese Materia Medica*. Shanghai Scientific and Technological Publishers: Shanghai.
- Liang M, Bu XL, Liu Y, 2009. Progress on research of polysaccharides of *Boschniakia rossica*. *Food Drug* 11(9): 65-67.
- Liu JH, Liang ZY, 2001. Progress on research of chemistry and pharmacology of *Boschniakia rossica*. *Spec Wild Economic Animal Plant Res* 4: 55-58.
- Liu Y, Sheng Y, Yuan G, Wang Y, Wei H, Guan M, Pei J, 2011. Purification and physicochemical properties of different polysaccharide fractions from the water extract of *Boschniakia rossica* and their effect on macrophages activation. *Int J Biol Macromol* 49(5): 1007-1011.
- Mizuno, M, Kato M, Hosoi N, Iinuma M, Tanaka T, Kimura A, Ohashi H, Sakai H, Kajita T, 1990. Phenolic compounds from *Salix sachalinensis*. *Heterocycles* 31(8): 1409-1412.
- Shyr MH, Tsai TH, Lin LC, 2006. Rossicasins A, B and rosicaside F, three new phenylpropanoid glycosides from *Boschniakia rossica*. *Chem Pharm Bull* 54(2): 252-254.
- Yin XZ, Jin MH, Quan JS, 2011. *In vitro* antioxidative effect of *Boschniakia rossica*. *Food Sci Technol* 36(1): 157-159.
- Yoshikawa M, Morikawa T, Zhang Y, Nakamura S, Muraoka O, Matsuda H, 2007. Megastigmanes and their glucosides from the whole plant of *Sedum sarmentosum*. *J Nat Prod* 70(4): 575-583.
- Yu Y, Xiu JC, 1996. The rare plant in Changbai Mountain-*Boschniakia rossica*. *China Wild Plant Resour* 3: 21.