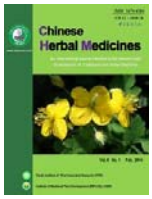

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Letter

A New Secoiridoid Glycoside from *Swertia cincta*

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ABSTRACT

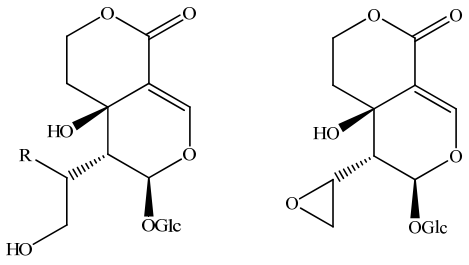
Objective To study the chemical constituents of *Swertia cincta*. **Methods** Preparative liquid chromatography was employed. The structures of the compounds were elucidated by spectroscopic analysis. **Results** Three secoiridoid glycosides were isolated from *S. cincta* and identified as 8-methoxyl-eustomorusside (**1**), secoiridoids eustomorusside (**2**), and eustomoside (**3**). **Conclusion** Compound **1** is a new secoiridoid glycoside. Compounds **2** and **3** are isolated from this plant for the first time.

Key words

Gentianaceae; preparative liquid chromatography; 8-methoxyl-eustomorusside; secoiridoid glycoside; *Swertia cincta*

1. Introduction

Swertia cincta Burk., belonging to the genus *Swertia* L. (Gentianaceae) (Editorial Board of Flora of China, 1988), is one of the oldest medicinal herbs in China, used for the treatment of liver disorders. More than 30 compounds have been isolated from the plant (Yang et al, 2012; Geng et al, 2012; Li et al, 2012), and the major constituents were secoiridoid glycosides (Brahmachari et al, 2004). In this paper, the isolation and structure elucidation of a new secoiridoid glycoside named 8-methoxyl-eustomorusside, together with two known secoiridoids, eustomorusside (**2**) and eustomoside (**3**), were reported (Emmanuel et al, 1990) (Figure 1).



1 R=OCH_3 **2** R=OH **3**

Figure 1 Structures of compounds 1—3

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2. Materials and methods

2.1 General instruments

The UV spectra were measured with a Shimadzu UV–2401PC Spectrometer. The IR spectra were measured with Shimadzu IR–435 Spectrometer. Optical rotations were run with Jasco–20 Polarimeter. The HR-ESI-MS data were taken on JMS–T100 CS Accu TOF LC/MS Spectrometer. The ^{1}H-NMR, ^{13}C-NMR, DEPT, HMQC, and HMBC spectra were measured with Bruker AV–400 III Spectrometer. Prep-HPLC separations were carried out with Agilent 1100 system, equipped with an Agilent DAD Detector and a prep-LC-C_{18} column (40 mm × 200 mm, 6 μm). ODS (100 mesh, YMC AA12S50) was used for column chromatography.

2.2 Plant materials

The dried whole plants of *Swertia cincta* Burk. were collected from Ailao Mountain (Yuxi, Yunnan) in October 2009, and identified by Dr. Li-pan Yang in Yunnan University of Traditional Chinese Medicine (Kunming, China). A voucher specimen (No. 0601007) was deposited in Key Laboratory of Ethnic Medicine Resources Chemistry, State Ethnic Affairs Commission & Ministry of Education, School of Chemistry and Biotechnology, Yunnan University of Nationalities.

2.3 Extraction and isolation

The dried whole plants of *S. cincta* (4.5 kg) were powdered and extracted with ultrasonic (80% MeOH) at room temperature. After evaporation, the residue (880 g) was suspended in water and extracted with CH_2Cl_2. The solvents were evaporated to afford CH_2Cl_2 extract (368 g) and water layer (510 g). The water layer was isolated by macroporous resin [H_2O-MeOH (100:0, 50:50, 30:70, 0:100)] chromatography to afford four fractions. The residue (156 g) was chromatographed on a reverse silica gel column (Agilent Eclips XDB-C_{18}, 250 mm × 21.2 mm) eluted with MeOH-H_2O (3:7) to afford four fractions. Fr. 1 was purified with ODS column CH_3CN-H_2O (5:95) and MeOH-H_2O (20:80) solvent systems, and compounds **1** (15 mg), **2** (20 mg), and **3** (25 mg) were obtained.

3. Results and discussion

Compound **1**: amorphous powder, $[\alpha]_D^{19}$ –87º (*c* 0.070, MeOH), UV λ_{max}: 236 nm (MeOH). The IR spectrum indicated the presence of OH (3430 cm^{-1}), CH_3 (2925 cm^{-1}), and CO groups (1700 cm^{-1}). Its molecular formula was determined as $C_{17}H_{26}O_{12}$ by HRESI-MS (*m/z* 422.1415), ^{1}H-NMR, and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum in CD_3OD showed the signals due to two methines [δ 2.51 (1H, d, J = 6.4 Hz, H-9), δ 3.76 (1H, m, H-8)], a methoxyl group [δ 3.37 (3H, s)], an oxymethylene [δ 4.84 (1H, br dd, J = 12.8, 10.4 Hz, H-7a), 4.40 (1H, ddd, J = 10.8, 7.2, 3.6 Hz, H-7b)], a methylene [δ 2.20 (1H, ddd, J = 13.6, 8.0, 5.2 Hz, H-6a), 2.00 (1H, brd, J = 14.0 Hz, H-6b)], an acetal methane [δ 5.98 (1H, s) H-1)], and an intra-annular vinyl group [δ 7.61 (1H, s, H-3)]. Furthermore, an anomeric proton signal [δ 4.66 (1H, d, J= 8.0 Hz, H-1′)] was recognized. The coupling constant of an anomeric proton indicated that the glycosyl linkage was of β-configuration. The ^{13}C-NMR spectrum (CD_3OD) showed the presence of 17 carbons (Table 1), including a carbonyl group δ 168.4 (C-11), and a β-*D*-glucopyranosyl group δ 62.6 (C-6′), 71.4 (C-4′), 74.5 (C-2′), 77.9 (C-3′), 78.5 (C-5′), and 100.1 (C-1′).

Table 1 ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) data of compound 1 in CD_3OD

No.	δ_C	δ_H (J)
1	96.4	5.98 (1H, s)
3	154.7	7.61 (1H, s)
4	109.9	–
5	64.7	–
6	33.3	2.20 (1H, ddd, 13.6, 8.0, 5.2 Hz)
		2.00 (1H, br d, 14.0 Hz)
7	65.9	4.84 (1H, br dd,12.8, 10.4 Hz)
		4.40 (1H, ddd, 10.8, 7.2, 3.6 Hz)
8	69.0	3.76 (1H, m)
9	50.6	2.51 (1H, d, 6.4 Hz)
10	75.5	3.40−3.60 (2H, m)
11	168.0	–
1'	100.1	4.66 (1H, d, 8.0 Hz)
2'	74.5	3.20 (1H, d, 8.8 Hz)
3'	77.9	3.3-3.45b
4'	71.4	3.3-3.45b
5'	78.5	3.3-3.45b
6'	62.6	3.90 (1H, dd, 11.7, 4.4 Hz)
		3.71(1H, dd, 14.4, 9.6 Hz)
OCH_3	59.3	3.37 (3H, s)

The HMBC spectrum of compound 1 showed cross-peaks between H-7 (δ 4.84 and 4.40) and C-11 and C-5, respectively. H-6 (δ 2.20 and 4.00) exhibited the correlations with C-4, H-3 (δ 7.61) showed cross-peaks with C-5, H-1 (δ 5.98) exhibited the correlations of C-3 and C-8, and H-9 (δ 2.51) showed cross-peaks with C-10. In addition, the ^{1}H-^{1}H COSY spectrum showed the correlations between H-6 and H-7, H-1 and H-9, H-8 and H-9, H-8 and H-10. The planar structure of compound **1** was deduced by ^{1}H-^{1}H COSY and HMBC spectra (Figure 2). From the above data, compared with the reported data of eustomorusside (Emmanuel et al, 1990), there is one more other group than methoxyl group at C-8. Thus the structure of compound **1** was determined as 8-methoxyl-eustomorusside, a new secoiridoid. The known compounds **2** and **3** were identified on the basis of their optical rotation values, NMR, and MS date as eustomorusside (**2**) and eustomoside (**3**).

Compound **2**: amorphous powder, $C_{16}H_{24}O_{12}$. ^{1}H-NMR (400 MHz, C_5D_5N) δ: 2.26 (1H, d, J = 14.0 Hz, H-9), 2.50 (1H, ddd, J = 15.0, 13.0, 6.5 Hz, H-6a), 3.14 (1H, d, J = 4.2, 2.4 Hz, H-6b), 3.90−4.10 (3H, m, H-8, H-10ab), 4.45 (1H, dd,

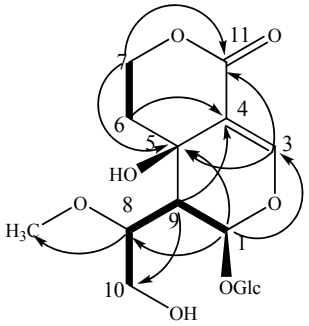

Figure 2 ^{1}H-^{1}H COSY (bold lines) and HMBC (full-line arrows) correlations for compound 1

J = 11.5, 4.0 Hz, H-7b), 4.98 (1H, dd, *J* = 12, 11.0 Hz, H-7a), 5.29 (1H, d, *J* = 8.0 Hz, H-1'), 6.71 (1H, s, H-1), 7.95 (1H, s, H-3). ^{13}C-NMR (100 MHz, C_5D_5N) *δ*: 167.4 (C-11), 154.5 (C-3), 112.8 (C-4), 101.2 (C-1'), 98.1 (C-1), 80.9 (C-5'), 80.3 (C-3'), 76.5 (C-2'), 73.2 (C-4'), 72.2 (C-8), 66.9 (C-5), 66.8 (C-7), 66.7 (C-10), 64.2 (C-6'), 51.9 (C-9), 35.0 (C-6). Compound **2** was identified as eustomorusside by comparison of the physical, ^{1}H-NMR, and ^{13}C-NMR data with the reported data (Emmanuel et al, 1990).

Compound **3**: amorphous powder, $C_{16}H_{22}O_{11}$. ^{1}H-NMR (400 MHz, CD_3OD) *δ*: 2.02 (1H, ddd, *J* = 15.0, 8.0, 2.0 Hz, H-6b), 2.30 (1H, ddd, *J* = 15.0, 13.0, 6.5 Hz, H-6a), 2.72 (1H, m, H-8), 2.78 (1H, dd, *J* = 4.8, 2.4 Hz, H-10b), 2.87 (1H, dd, *J* = 9.2, 4.8 Hz, H-10a), 3.94 (1H, dd, *J* = 10.4, 6.0 Hz, H-6'b), 3.90 (1H, dd, *J* = 10.4, 2.0 Hz, H-6'a), 4.45 (1H, dd, *J* = 11.5, 4.0 Hz, H-7b), 4.52 (1H, dd, *J* = 12, 4.0 Hz, H-7a), 4.68 (1H, d, *J* = 8.0 Hz, H-1'), 5.92 (1H, s, H-1), 7.68 (1H, s, H-3). ^{13}C-NMR (100 MHz, CD_3OD) *δ*: 168.0 (C-11), 154.8 (C-3), 108.8 (C-4), 100.4 (C-1'), 97.5 (C-1), 78.5 (C-5'), 77.7 (C-3'), 74.3(C-2'), 71.5 (C-4'), 66.0 (C-7), 65.0 (C-5) 62.7 (C-6'), 50.9 (C-8), 50.6 (C-9), 46.2 (C-10), 33.4 (C-6). Compound **3** was identified as eustomoside by comparison of the physical, ^{1}H-NMR, and ^{13}C-NMR data with the reported data (Emmanuel et al, 1990).

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