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ScienceDirect
Chinese Chemical Letters 19 (2008) 696–698
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Chemical constituents from *Schisandra sphenanthera*

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Accepted 3 December 2007

Abstract

The chemical constituents of the stems of *Schisandra sphenanthera* are described for the first time. This investigation has resulted in the isolation of a new phenolic glycoside (**1**), along with seven known compounds. The structure of **1** was assigned by using spectroscopic techniques, including 2D NMR spectra.

Keywords: *Schisandra sphenanthera*; Phenolic glycoside; 4,6-Dihydroxyphenyl-1-butanone-2-β-D-*O*-glucopyranoside

The fruits of *Schisandra sphenanthera* Rehd. et Wils (Schisandraceae) are used as an antitussive, tonic and sedative agent under the name of Wuweizi in Chinese traditional medicine together with the fruits of *Schisandra chinensis* Baill [1]. Seventeen lignans, schisantherins A–E [2,3], deoxyshizandrin [4], ganschisandrin [5], chicanine [6], schidandrone [7], benzoylgomisin Q, tigloylgomisin P, *dl*-wulignan [8], benzoylgomisin U, tigloylgomisin O [9], *d*-epigalbacin [10], episahisandrone [11] and schisanol [12], have been isolated from the fruit of *S. sphenanthera*. However, the chemical components of the leaves and stems of the titled plant were not reported until now. Since 2003, the systematic research on the chemical constituents of the leaves and stem of the genus *Schisandra* conducted in our group led to the discovery of a series of novel nortriterpenoids with a diversity of highly oxygenated structures biogenetically related to cycloartane [13–21]. In the course of our continuing investigation on this genus, a new phenolic glycoside (**1**), together with seven known ones, cycloart-23-ene-3,25-diol (**2**) [22], kadsuric acid (**3**) [23], 8-hydroxy-2-methyl-1,4-naphthoquinone (**4**) [24], catechin (**5**) [25], methyl-3,4-dihydroxybenzoate (**6**) [26], 3β-hydroxyl-5α,8α-epidioxyergosta-6,22-diene (**7**) [27] and 7-oxositosterol (**8**) [28], was isolated from the stems of *S. sphenanthera* (Fig. 1). This paper described the isolation and structure elucidation of **1**.

A 70% aqueous acetone extract of the stems (4.5 g) of *S. sphenanthera* was suspended in H_2O and partitioned successively with EtOAc. The EtOAc layer (32 g) was absorbed on 50 g of silica gel and chromatographed on a prepacked (300 g) silica gel column, eluting stepwise with $CHCl_3$–Me_2CO (1:0 → 0:1). The $CHCl_3$–Me_2CO (9:1)

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1001-8417/$ – see front matter
doi:10.1016/j.cclet.2007.12.038

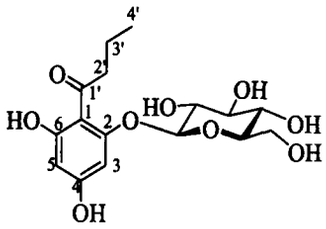

Fig. 1. Structure of compound **1**.

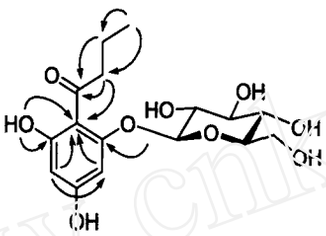

Fig. 2. Key HMBC correlations for **1**.

eluate was subjected to column chromatography over MCI-gel CHP-20P (MeOH–H_2O 9:1), RP-18 Si gel (MeOH–H_2O 7:3) and silica gel ($CHCl_3$–MeOH 8:2) to yield compound **1** (30 mg).

Compound **1** was obtained as a yellow powder, $[\alpha]_D^{18.5}$ −18.04 (*c* 0.19, MeOH). The FAB$^-$-MS spectrum showed a quasi-molecular ion peak at *m/z* 357 with 100% intensity, comparable with the molecular formula $C_{16}H_{22}O_9$, and was confirmed by its HR-FAB$^-$-MS ([M−H]$^+$, *m/z* 357.1188) and ^{1}H NMR and ^{13}C NMR data. The IR spectrum showed important absorption bands at ν_{max} 3474 (br, OH), 1631, 1602 and 1456 cm^{-1} (aromatic). The UV spectrum exhibited strong absorption [λ_{max} 223 nm (log ε 4.09), 283 nm (log ε 4.07)] due to the existence of conjugated system.

The NMR spectroscopic data suggested that **1** was a phenolic glycoside. The ^{1}H NMR spectrum (Table 1) contained a set of *meta*-coupled protons assignable to a 1,2,4,6-tetrasubtituted phenyl group (δ 6.37, 6.63, d, each 1H, *J* = 2.0 Hz), a propyl group (δ 3.54, t, 2H, *J* = 7.3 Hz; 2.43, m, 2H; and 1.32, t, 3H, *J* = 7.3 Hz) and an anomeric proton (δ 5.46, d, 1H, *J* = 7.3 Hz). This was in sound agreement with the ^{13}C NMR spectrum, which showed signals attributable to a ketone at δ 206.4 (C-1′), a glucosyl moiety (δ 62.5, 71.2, 74.4, 77.9, 78.3, 101.7), a 1,2,4,6-tetrasubtituted benzene ring (δ 95.1, 97.9, 106.2, 162.1, 165.2, 167.7) and a propyl (δ 14.1, 18.5, 46.6) group. As required by its molecular formula, two hydroxyls should be present.

HMBC correlations (Fig. 2) between two methylenes of the propyl group (H-2′ and H-3′) and the ketone indicated the presence of a butanone group. The position of the butanone moiety was secured from the HMBC cross peak between H-2′ and C-1. The β-orientation of the glucose was determined from coupling constant of the anomeric proton (*J* = 7.3 Hz) and the linkage was located at the 2-*O*-position of the benzene ring according to the HMBC correlation

Table 1
NMR spectral data for **1** in CD_3COCD_3

No.	δ_H (mult, *J*, Hz)	δ_C	No.	δ_H (mult, *J*, Hz)	δ_C
1		106.2 s	4′	1.32 t (7.3)	14.1 q
2		162.1 s	1″	5.46 d (7.3)	101.7 d
3	6.63 d (2.0)	95.1 d	2″	3.81–4.00 m	74.4 d
4		165.2 s	3″	3.81–4.00 m	77.9 d
5	6.37 d (2.0)	97.9 d	4″	3.81–4.00 m	71.2 d
6		167.7 s	5″	3.81–4.00 m	78.3 d
1′		206.4 s	6″	4.29 br d (11.8)	62.5 t
2′	3.54 t (7.3)	46.6 t		4.10 dd (5.6, 11.8)	
3′	2.43 m	18.5 t	6-OH	14.2 s	

Data were recorded on Bruker DRX-400 MHz spectrometer, chemical shifts (δ) are in ppm.

from H-1″ to C-2. The presence of the β-D-glucopyranosyl moiety was supported by the ^{13}C NMR data and further confirmed by the acid hydrolysis of **1**, which resulted in a release of glucose identified by HPTLC comparisons of the hydrolyzate with an authentic sugar sample. A HMBC correlated peak of 6-OH with C-1 and C-6 indicated the hydroxyl was located at C-6, thus another hydroxyl was connected to C-4. This was consistent with the inequivalent chemical shifts of the three oxygenated aromatic carbons at δ_C 162.1, 165.2 and 167.7. Therefore, the structure of **1** was elucidated and represented a new phenolic glucoside, and named 4,6-dihydroxyphenyl-1-butanone-2-β-D-*O*-glucopyranoside.

Seven known compounds were identified as cycloart-23-ene-3,25-diol (**2**), kadsuric acid (**3**), 8-hydroxy-2-methyl-1,4-naphthoquinone (**4**), catechin (**5**), methyl-3,4-dihydroxybenzoate (**6**), 3β-hydroxyl- 5α,8α-epidioxyergosta-6,22-diene (**7**) and 7-oxositosterol (**8**), respectively, by comparison of their spectroscopic data (^1H NMR, ^{13}C NMR, and MS) with those reported in the literature. Compounds **4** and **8** were obtained from the family Schisandraceae for the first time.

Acknowledgments

The work was supported by grants from the National Natural Science Foundation of China (No. 20402016), the Young Academic and Technical Leader Raising Foundation of Yunnan Province (No. 2005py01-32), the Foundation of Excellent Ph.D. Dissertation of Chinese Academy of Sciences (No. O0602551221), and the Program for New Century Excellent Talents on University (No. NCET-06-0824).

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