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Fitoterapia 79 (2008) 574 – 576

FITOTERAPIA

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A new 8-*O*-4' neolignan glycoside from *Tetracentron sinense*

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Received 17 June 2008; accepted 27 June 2008
Available online 11 July 2008

Abstract

A new 8-*O*-4' neolignan glycoside was isolated from the stem bark of *Tetracentron sinense*. Its structure was elucidated as *erythro* 4',5',7, 9, 9′-pentahydroxy-3-methoxy 8-*O*-4′-neolignan 3′-*O*-β-glucopyranoside on the basis of spectral evidence (MS, IR, 1D and 2D NMR).

Keywords: *Tetracentron sincense*; Neolignan; Spectroscopic methods

1. Introduction

Tetracentron sinense is a flowering plant, the sole species in the genus *Tetracentron*. Commonly known as "shuiqing" in China, it is an endangered species [1]. Among its previously investigated chemical components [2], some were reported to be cytotoxic [3]. As a part of our further investigation of this species, a new 8-*O*-4′ type neolignan glycoside (**1**) and seven known phenolics were isolated from the stem bark by column chromatograph and reverse-phase Rp18. In this paper, the isolation and structural elucidation of these compounds are presented.

2. Experimental

2.1. Generals

FAB-MS (negative-ion mode): VG AutoSpec 3000. FTIR: Bio-Rad Merlin. NMR: Bruker AM-400 and DRX-500.

2.2. Plant

T. sinense (Tetracentreae), barks collected in Yongping, Yunnan, China, in June 2001 was taxonomically identified by Prof. Sun Weipang, Kunming Botanic Garden, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan, People's Republic of China, where a voucher specimen (SWB01-152) is deposited.

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doi:10.1016/j.fitote.2008.06.008

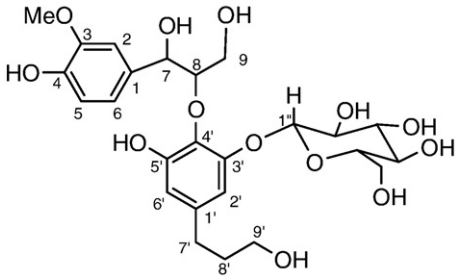

Fig. 1. The structure of compound **1.**

2.3. Extraction and isolation

The powdered barks (5 kg) were extracted with EtOH under reflux. The combined extracts were concentrated in vacuo to yield a dark residue (480 g) which was suspended in water and partitioned with EtOAc and *n*-BuOH. The EtOAc extract (210 g) was subjected to Si-gel CC eluting with a gradient of $CHCl_3$-MeOH giving twenty-one fractions. Fr. 6 (3.5 g) was rechromatographed on Si-gel eluting with $CHCl_3$/acetone (85:15) and then purified on Sephadex LH-20 (MeOH) to yield 4-(3′,4′-methylenedioxyphenyl)-3-methyl-2-butanone (2 mg), 2,3-*trans*-3,4-*cis*-4,5-*trans*-2,5-bis (4-hydroxyphenyl)-3, 4-dimethyltetrahydrofuran (3 mg) and 2,3-*trans*-3,4-*cis*-4,5-*cis*-2, 5-bis (4-hydroxyphenyl)-3, 4-dimethyltetrahydrofuran (3 mg). The BuOH fraction (78 g) was subjected to Si-gel CC eluting with a gradient of $CHCl_3$/MeOH. Among the collected 9 eluates, eluate 2 (1.8 g) was rechromatographed on Si-gel eluting with $CHCl_3$/acetone (85:15). Further purification of the eluate by Sephadex LH-20 (MeOH) yielded *erythro*-1-(4-hydroxyphenyl)-1, 2-propanediol 2-*O*-β-D-glucopyranoside (5 mg) and *cis*-syringin (7 mg). Four subfractions A–F were obtained from

Table 1
^1H and ^{13}C NMR data for **1** (500 MHz and 125 MHz, pyridine-, *J* in Hz, δ in ppm)

C	δH	δC	HMBC (H→C)
1	/	133	/
2	7.51 s	111	1, 3, 4, 6, 7
3	/	148	/
4	/	147	/
5	7.19 *d* (8.0)	116	1, 3, 4
6	7.28 *d* (8.0)	120	2, 4, 7
7	5.96 *d* (2.8)	73	1, 2, 6, 8, 9
8	4.90,m	90	9, 4′
9a	4.70 *dd* (11.3, 7.8)	61	7, 8
9b	4.19 *dd* (11.3, 8.0)		7, 8
1′	/	139	/
2′	7.28 s	109	1′, 3′, 6′, 7′
3′	/	152	/
4′	/	135	/
5′	/	152	/
6′	6.96 s	111	1′, 2′, 5′, 7′
7′	2.80 m	32	1′, 2′, 6′, 8′, 9′
8′	2.03 (m)	35	1′, 7′, 9′
9′	3.82 *t* (6.3)	61	7′, 9′
1′′	5.69 *d* (7.0)	103	3′/5′, 3′′
2′′	4.35 (m)	75	1′′, 3′′, 4′′
3′′	4.34 (m)	78	2′′, 4′′
4′′	4.25 *t* (9.4)	71	3′′, 5′′, 6′′
5′′	4.06 (*m*)	79	3′′, 4′′, 6′′
6′′a	4.53 *d* (9.8)	62	4′′, 5′′
6′′b	4.31 *dd* (11.5, 8.6)		
OMe	3.63 *s*	55	3

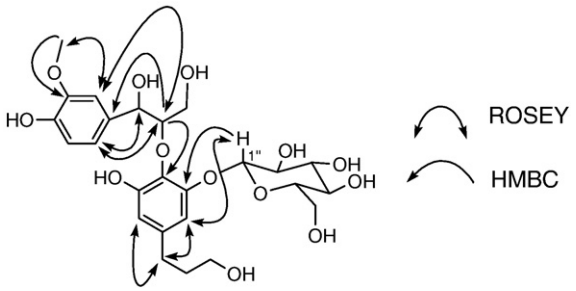

Fig. 2. The Key HMBC and ROSEY correlations of compound **1.**

eluting the eluate 4 (7.2 g) with $CHCl_3$/MeOH (80:20) on Si-gel CC. Purification of sediments from fraction B on RP-18 yielded *trans*-syringin (6 mg), *threo*-guaiacylglycerol 8-*O*-β-D-glucopyranoside (12 mg), and compound **1** (2 mg).

Compound (**1,** Fig. 1), *erythro*-4, 7, 9, 5′, 9′-pentahydroxy-3-methoxy-8-*O*-4′ neolignan-3′-*O*-β-glucopyranoside, white solid, mp 112–115 °C, [α]=−23.2 (*c* 0.6, MeOH). IR bands (KBr) 3600–3100, 1634, 1615, 1575, 1558, 1539, 1519, 1489, 1471, 1418, 1385, 1275, 1156, 1074, 1031 cm^{-1}; negative FAB-MS *m/z*: 633 $[M+Gly-H]^+$ (4), 541 $[M-H]^+$ (69), 265 (26), 219 (21), 127 (35); negative HRFABMS: 541.1907 $[M-H]^+$ calc. for $C_{25}H_{34}O_{13}$ 541.1921. ^1H and ^{13}C NMR spectral data see Table 1.

3. Results and discussion

The molecular formula of $C_{25}H_{34}O_{13}$ was assigned to compound **1** by negative-ion HRFABMS. The ^1H NMR spectrum of **1** showed signals at δ 2.03 (2 H, m), 2.80 (2 H,m), 3.82 (2 H, m), one methoxyl at δ 3.63 (3 H, s), two methine protons at δ 4.90 (1 H, m), 5.96 (1 H, d), another methylene at δ 4.19 (1 H, dd), and 4.70 (1 H, dd), a glucopyranosyl anomeric proton at δ 5.69 (1 H, d, *J* 7.0) and five aromatic protons. From the ^{13}C NMR spectrum, the presence of two C_6–C_3 units and a glucopyranose was suggested; the proton and carbon signals were assigned from the ^1H ^1H COSY, HMQC and HMBC spectral data: see (Table 1).

In the HMBC, the correlations (Fig. 2) between glucopyranosyl H-1′′ and C-3′, H-8 and C-4′ were observed. The proton signal at δ 3.63 (OMe) was correlated with a C-signal at 152.6). These correlations were confirmed by the NOE spectrum, and correlations between H-2 and methoxyl protons, H-2′ and the glucopyranosyl anomeric proton were observed). Thus, **1** was a 8-*O*-4′ neolignan 3′-*O*-β-glucopyranoside.

On the basis of the possible staggered conformers with intramolecular hydrogen bonding of the benzylic hydroxyl and aryloxyl groups, the large and small *J* values for H-7 and H-8 of 8-*O*-4′ neolignan diastereoisomers correspond to the *threo* form and *erythro* form, respectively [4]. The small coupling constant ($J_{7,8}$=2.8) showed that compound **1** has relative *erythro*-configuration. Therefore, the structure of **1** was established as *erythro*-4, 5′, 7, 9, 9′-pentahydroxy-3-methoxy-8-*O*-4′ neolignan-3′-*O*-β-glucopyranoside.

Acknowledgments

This work was financially supported by the National Natural Science Foundation (20702055) and the Yunnan Natural Science Foundation (2006C0045Q). The authors are grateful to the analytical group of the Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences for measuring NMR, MS and IR data.

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