

## Two new prenylflavonoids from *Epimedium sutchuenense*

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Received 17 December 2008

### Abstract

Two new prenylflavonoids, named sutchuenmedin A (1) and sutchuenmedin B (2), were isolated from the 70% EtOH extract of *Epimedium sutchuenense*. Their structures were determined from spectral analysis.

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**Keywords:** *Epimedium sutchuenense*; Flavonoids; Sutchuenmedin A; Sutchuenmedin B

*Epimedium* plants are widely distributed in China with about 30 species, many of which are used as traditional Chinese medicine “yinyanghuo” with tonic, anti-rheumatic and aphrodisiac effects [1]. Up to now, many researches were focused on the flavonoid compounds in *Epimedium* plants. In which, prenylflavonoids are the major constituents and also an important chemotaxonomic marker [2–6]. To our knowledge, there was no report of chemical constituents on *Epimedium sutchuenense* Franch. As the continuation of research on flavonoid constituents of *Epimedium* plants, we reported herein the isolation and structure elucidation of two new prenylflavonoids, named sutchuenmedin A (1) and sutchuenmedin B (2), from *E. sutchuenense*.

The roots of *E. sutchuenense* (15 kg) were extracted with 70% EtOH. After removal of the solvent in vacuo, the residue was suspended in water and fractionated with  $\text{CHCl}_3$ , EtOAc and n-BuOH, successively. The n-BuOH fraction (110 g) was further separated on silica gel, Sephadex LH-20 and polyamide chromatography to give compounds 1 (9.3 mg) and 2 (11.2 mg).

Compound 1 was obtained as yellow powder and gave a positive reaction with Mg–HCl reagent. Acid hydrolysis of 1 followed by TLC analysis of the hydrolysate and direct comparison with authentic sugars indicated the presence of L-rhamnose. The molecular formula of compound 1 was established as  $\text{C}_{33}\text{H}_{38}\text{O}_{14}$  by (+) ESI-MS, which exhibited quasimolecular ions at  $m/z$  681  $[\text{M}+\text{Na}]^+$  and 659  $[\text{M}+\text{H}]^+$ . The signals at  $\delta$  1.43 (s, 3H), 1.45 (s, 3H), 5.78 (d, 1H,  $J = 10.2$  Hz) and 6.73 (d, 1H,  $J = 10.2$  Hz) in  $^1\text{H}$ -spectrum of compound 1 (Table 1) and  $\delta$  28.2, 78.8, 114.5 and 128.6 in  $^{13}\text{C}$ -spectrum (Table 1) indicated the  $\gamma$ -dimethyl-chromene ring in its structure [2]. This was further confirmed by correlations of H-4'', 5'' ( $\delta$  1.43, 1.45)/C-3'' ( $\delta$  78.8), H-4'', 5'' ( $\delta$  1.43, 1.45)/C-2'' ( $\delta$  128.6), H-2'' ( $\delta$  5.78)/C-3'' ( $\delta$  78.8) and H-1'' ( $\delta$  6.73)/C-3'' ( $\delta$  78.8) in HMBC spectrum (Fig. 1). In  $^1\text{H}$ -spectrum, an  $\text{A}_2\text{X}_2$  coupling system at  $\delta$  7.12 (d, 2H,  $J = 9$  Hz) and 7.92 (d, 2H,  $J = 9$  Hz) was observed, which suggested a *para*-substituted B-ring in structure. The signal at  $\delta$  3.86 exhibited HMBC correlation with  $\delta$  162.0, since H-2', 6' ( $\delta$  7.92) and H-3', 5' ( $\delta$  7.12) also correlated with  $\delta$

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Table 1  
 $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data of compounds **1** and **2** (DMSO- $d_6$ , TMS,  $J_{\text{Hz}}$ ,  $\delta_{\text{ppm}}$ )<sup>a</sup>.

No.	<b>1</b>		<b>2</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
2		157.3		157.5
3		135.2		136.0
4		178.5		179.2
5		159.3		158.8
6	6.26 (s, 1H)	99.7		110.2
7		161.2		158.5
8		105.5	7.04 (s, 1H)	95.0
9		151.0		148.9
10		101.2		107.7
1'		122.4		122.2
2', 6'	7.92 (dd, 2H, 9)	131.0	8.01 (dd, 2H, 9)	131.3
4'		162.0		162.1
3', 5'	7.12 (dd, 2H, 9)	114.6	7.15 (dd, 2H, 9)	114.6
4'-OCH <sub>3</sub>	3.86 (s, 3H)	56.0	3.87 (s, 3H)	56.0
5-OH	12.30	–	12.32	–
1''	6.73 (d, 1H, 10.2)	114.5	7.26 (s, 1H)	100.9
2''	5.78 (d, 1H, 10.2)	128.6		156.4
3''		78.8		132.5
4''	1.45 (s, 3H)	28.2	5.25 (br s, 1H); 5.68 (br s, 1H)	113.8
5''	1.43 (s, 3H)	28.2	2.12 (s, 3H)	19.3
Rha				
1'''	5.40 (br s, 1H)	101.4	5.45 (br s, 1H)	101.4
2'''	4.12 (br s, 1H)	76.0	4.17 (br s, 1H)	76.0
3'''		71.2		71.3
4'''		72.4		72.4
5'''		70.6		70.6
6'''	1.09 (d, 3H, 6)	18.1	1.12 (d, 3H, 6)	18.1
Rha				
1''''	4.88 (br s, 1H)	102.1	4.90 (br s, 1H)	102.1
2''''		70.7		70.7
3''''		71.0		71.0
4''''		71.8		71.8
5''''		69.1		69.3
6''''	0.83 (d, 3H, 6)	18.0	0.84 (d, 3H, 6)	18.0

<sup>a</sup> Run at Bruker ARX-600 instrument, 600 MHz for  $^1\text{H}$  NMR and 150 MHz for  $^{13}\text{C}$  NMR.

162.0, the methoxy group could be attached at C-4' position. In HMBC spectrum, H-6 ( $\delta$  6.26) showed correlations with C-8 (105.5) and C-10 (101.2), H-1'' ( $\delta$  6.73) correlated with C-9 ( $\delta$  151.0), which indicated that the  $\gamma$ -dimethylchromene moiety was fused to C-7 and C-8. The location and sequence of oligosaccharide chains were determined by HMBC experiment, in which, the correlation peaks could be observed between H-1''' ( $\delta$  5.40) and C-3 ( $\delta$  135.2), H-1'''' ( $\delta$  4.88) and C-2''' ( $\delta$  76.0). On the basis of above evidence, the formula **1** for the structure of sutchuenmedin A could be elucidated (Fig. 1).

Compound **2** was isolated as yellow powder and gave the positive reaction with Mg–HCl reagent. The presence of L-rhamnose in the structure was also confirmed by acid hydrolysis and TLC analysis. (+) ESI-MS spectrum of **2** showed quasimolecular ions at  $m/z$  679  $[\text{M}+\text{Na}]^+$ , consistent with a molecular formula of  $\text{C}_{33}\text{H}_{36}\text{O}_{14}$ . In  $^1\text{H}$ -spectrum of compound **2** (Table 1), the signals at  $\delta$  2.12 (s, 3H), 5.25 (br s, 1H), 5.68 (br s, 1H) and 7.26 (s, 1H) suggested the presence of isopropenylfuran group [3], this was confirmed by the cross-peaks between H-5'' ( $\delta$  2.12)/C-3'' ( $\delta$  132.5), C-2'' ( $\delta$  156.4), H-4'' ( $\delta$  5.25, 5.68)/C-2'' ( $\delta$  156.4) and H-1'' ( $\delta$  7.26)/C-2'' ( $\delta$  156.4) in  $^{13}\text{C}$ - (Table 1) and HMBC spectrum (Fig. 1). Meanwhile, the HMBC correlations were also observed between H-1'' ( $\delta$  7.26)/C-6 ( $\delta$  110.2), C-7 ( $\delta$  158.5), H-8 ( $\delta$  7.04)/C-6 ( $\delta$  110.2), C-7 ( $\delta$  158.5), C-10 (107.7), together with the  $\text{A}_2\text{X}_2$  coupling system at  $\delta$  7.15 (d, 2H,  $J = 9$  Hz) and 8.01 (d, 2H,  $J = 9$  Hz) in  $^1\text{H}$ -spectrum and other cross-peaks about oligosaccharide chains in HMBC experiment, the structure of sutchuenmedin B was determined (Fig. 1).

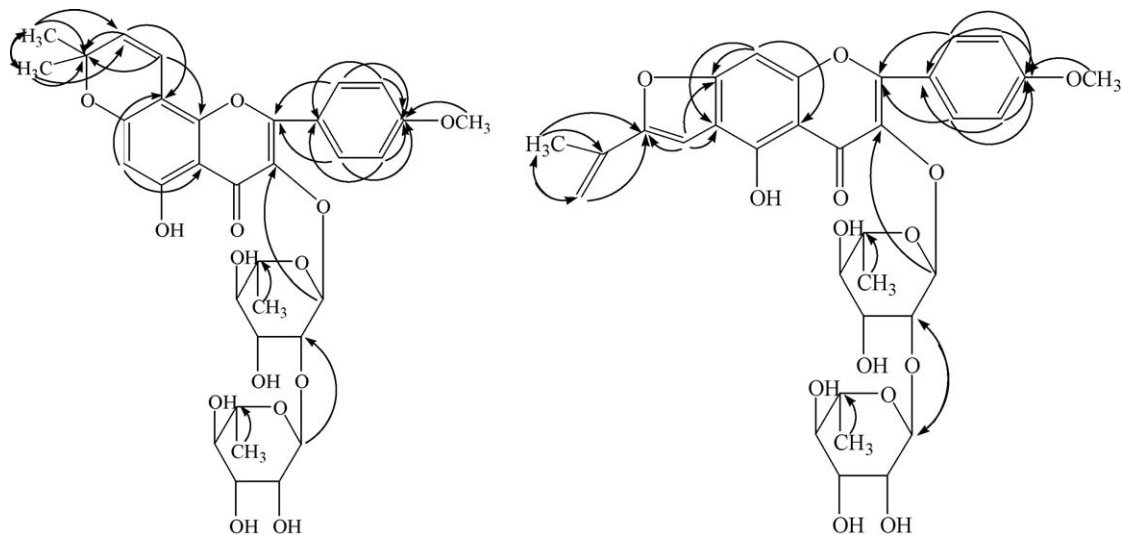


Fig. 1. Structures and key HMBC correlations of compounds **1** and **2**.

## Acknowledgment

This work was financially supported by Young Teacher Grant from Beijing University of Chemical Technology (No. QN0615).

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