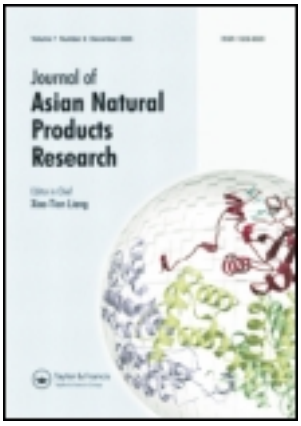

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Structural elucidation of a new flavone from *Sarcopyramis nepalensis*

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A novel flavone, named 4′-methoxy-3′,5,7-trihydroxy-8-(1″-(3‴,4‴,5‴-trihydroxyphenyl)ethyl)flavone (**1**), was isolated from *Sarcopyramis nepalensis*, along with two known compounds syringaresinol (**2**) and aralidioside (**3**). Their structures were established by the spectroscopic analysis, especially by 2D NMR. All of the three compounds were isolated from the plant for the first time.

Keywords: *Sarcopyramis nepalensis*; flavone; 4′-methoxy-3′,5,7-trihydroxy-8-(1″-(3‴,4‴,5‴-trihydroxyphenyl)ethyl)flavone; Melastomataceae

1. Introduction

Sarcopyramis nepalensis Wall. (Melastomataceae), is a kreoherb locally known as 'Fengguidoucao' for its flowers shaped like a cup, and distributed throughout the southern area of China. This plant is used in traditional Chinese medicine for the treatment of acute auriginous hepatitis, cough with lung heat, rheumatic arthralgia, antitussis, snake bite, and edema, especially in Fujian and Taiwan Provinces [1–3]. The hepatoprotective effect of the water extract of *S. nepalensis* has been demonstrated previously [4]. However, no reports were available on the phytochemistry investigation of *S. nepalensis*. Herein, we report the isolation and characterization of a new flavone, named 4′-methoxy-3′,5,7-trihydroxy-8-(1″-(3‴,4‴,5‴-trihydroxyphenyl)ethyl)flavone (**1**), and two known compounds, including syringaresinol (**2**) and aralidioside (**3**) from *S. nepalensis*.

2. Results and discussion

Compound **1** was obtained as yellow crystals with mp 168.0–170.1°C, and was positive to the $FeCl_3$ reagent and HCl–Mg reaction. Positive HR-ESI-MS gave a quasi-molecular ion peak at *m/z* 453.1191 $[M + H]^+$, corresponding to a molecular formula of $C_{24}H_{20}O_9$, which indicated 15 degrees of unsaturation. The ^{13}C NMR and DEPT spectra of **1** showed 22 carbon signals, including 1 carbonyl group (δ_C 176.0), 12 sp^2 quaternary carbons with eight linked to an oxygen atom, 7 tertiary carbon atoms (six sp^2 carbons and one sp^3 carbon), and 2 methyl carbon atoms (including one oxygenated methyl). Detailed analysis of the ^1H NMR spectrum of **1** revealed six hydroxyls at δ 12.30 (1H, br s, 5-OH), 8.34 (1H, br s, 4‴-OH), 8.13 (1H, br s, 7-OH), 8.03 (2H, br s, 3‴,5‴-OH), 7.73 (1H, br s, 3′-OH); seven protons bound to sp^2-type carbon atoms, including two singlets at δ 6.83 (1H), 6.41 (1H), three doublets at δ 7.59 (1H, $J = 2.7$ Hz), 6.94 (1H, $J = 7.8$ Hz),

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6.73(2H, $J = 2.5$ Hz), one double–doublet at δ 7.66 (1H, $J = 7.8$, 2.7 Hz); sp^3-type oxygenated methyl protons at δ 3.75 (3H, s), sp^3-type methine proton at δ 4.92 (1H, q, $J = 7.3$ Hz), and sp^3-type methyl protons at δ 1.77 (3H, d, $J = 7.3$ Hz).

From above results, **1** was predicted to be a 5, 7, 8, 3′, 4′-substituted flavone. Both ^{1}H and ^{13}C NMR signals of **1** were assigned by 2D homo- and heteronuclear NMR experiments, as shown in Table 1.

Careful analysis of the HSQC spectrum of **1** revealed the following correlations: C-3 at δ_C 103.8 with H-3 at δ_H 6.83, 98.3 (C-6) with δ_H 6.41 (H-6), 110.5 (C-2′) with δ_H 7.59 (H-2′), 115.1 (C-5′) with δ_H 6.94 (H-5′), 122.4 (C-6′) with δ_H 7.66 (H-6′), 55.4 (—OCH_3) with δ_H 3.75 (—OCH_3), 32.2 (C-1″) with δ_H 4.92 (H-1″), 18.3 (C-2″) with δ_H 1.77 (H-2″), and 114.9 (C-2‴ and C-6″) with δ_H 6.73 (H-2‴ and H-6‴). In the ^{1}H–^{1}H COSY experiment, H-5′ was correlated with H-6′, and H-1″ with H-2″. The HMBC cross peaks 5-OH (δ_H 12.30)/C-5 (δ_C 159.4), 4‴-OH(δ_H 8.34)/C-4‴(δ_C 136.4), 7-OH(δ_H 8.13)/C-7(δ_C 161.5), 5‴-OH(δ_H 8.03)/C-5‴(δ_C 144.7), and 3′-OH(δ_H 7.73)/C-3′(δ_C 147.3) corroborated the connectivity of the six hydroxyl groups. The HMBC correlation between OCH_3 at δ_H 3.75 and C-4′ at δ_C 148.7 indicated that the methoxyl group was located at C-4′. The connection of C-8 substituent was provided by the HMBC correlations of H-1″ (δ_H 4.92) with C-7 (δ_C 161.5), C-8 (δ_C 110.9), C-9 (δ_C 154.5), C-2″ (δ_C 18.3), and C-1‴ (δ_C 135.7), H-2″ (δ_H 1.77) with C-1″

Table 1. ^{1}H (400 MHz), ^{13}C (100 MHz), and 2D NMR spectral data of compound **1** (acetone-d_6).

Position	δ_C	δ_H (J, Hz)	^{1}H–^{1}H COSY (H—H)
2	161.5		
3	103.8	6.83 (s)	
4	176.0		
5	159.4		
6	98.3	6.41 (s)	
7	161.5		
8	110.9		
9	154.5		
10	114.1		
1′	122.7		
2′	110.5	7.59 (d, $J = 2.7$ Hz)	
3′	147.3		
4′	148.7		
5′	115.1	6.94 (d, $J = 7.8$ Hz)	H-6′
6′	122.4	7.66 (dd, $J = 7.8$, 2.7 Hz)	H-5′
4′-OCH_3	55.4	3.75 (s)	
1″	32.2	4.92 (q, $J = 7.3$ Hz)	H-2″
2″	18.3	1.77 (d, $J = 7.3$ Hz)	H-1″
1‴	135.7		
2‴	114.9	6.73 (d, $J = 2.5$ Hz)	
3‴	144.7		
4‴	136.4		
5‴	144.7		
6‴	114.9	6.73 (d, $J = 2.5$ Hz)	
5-OH		12.30 (br s)	
7-OH		8.13 (br s)	
3′-OH		7.73 (br s)	
3‴,5‴-OH		8.03 (br s)	
4‴-OH		8.34 (br s)	

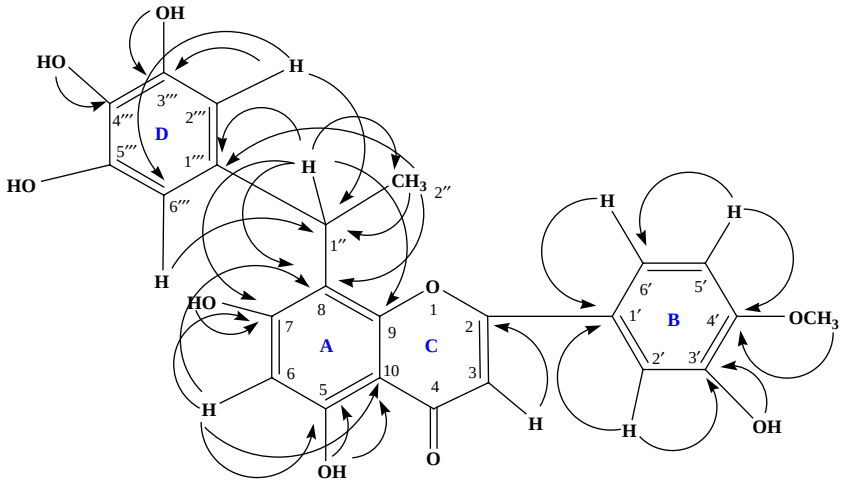

Figure 1. Selected HMBC correlations of compound **1**.

(δ_C 32.2), C-8 (110.9), and C-1‴ (135.7), and of H-2‴ (δ_H 6.73) with C-3‴ (δ_C 144.7), C-6‴ (δ_C 114.9), C-1″ (δ_C 32.2), as shown in Figure 1.

From the evidence described above, the structure of **1** was established as 4′-methoxy-3′,5,7-trihydroxy-8-(1″-(3‴,4‴,5‴-trihydroxyphenyl)ethyl)flavone.

Compounds **2** and **3** were identified as syringaresinol and aralidioside by comparison of their physical and spectral data with those reported in the literature [5,6].

3. Experimental

3.1 General experimental procedures

Melting points were determined on the X_4 apparatus and are uncorrected. The optical rotations were measured on a Perkin-Elmer 241 polarimeter. The UV spectrum was measured on a Shimadzu UV-2401PC spectrophotometer. IR spectra were recorded on a Perkin-Elmer 683 spectrometer. HR-ESI-MS spectra were measured on a VG Auto Spec-3000 ESI-MS spectrometer. ^{1}H NMR and ^{13}C NMR spectral data were recorded on a Bruker-400 spectrometer. TLC was performed on silica gel (Qingdao Marine Chemical, Inc., Qingdao, China). Column chromatography (CC) was carried out on silica gel (100–200 mesh, Qingdao Marine Chemical, Inc.), Diaion HP-20 (Mitsubishi Chemical Co., Tokyo, Japan), Sephadex LH-20 (GE Healthcare Co., Uppsala, Sweden), and ODS (Nacalaitesque Co., Tokyo, Japan).

3.2 Plant material

The whole plants of *S. nepalensis* Wall were obtained from the Medicinal Materials Market of Zhangzhou, Fujian Province, China, and identified by Prof. Jiachun Chen, Tongji Medical College, Huazhong University of Science and Technology. A voucher specimen has been deposited at the herbarium of the School of Pharmacy (TJ 2006070911 dated 9 July 2006).

3.3 Extraction and isolation

The whole plants of *S. nepalensis* Wall (10 kg) were ground, shattered, and exhaustively extracted using 95% ethanol (6 × 15 L × 7 days each) at room temperature and the solvent was removed under reduced pressure to yield a residue (3.0 kg), which was divided into petroleum ether (815 g), ethyl acetate (812 g),

n-butanol (238 g), and water-soluble subfractions (1135 g). The ethyl acetate soluble subfraction was subjected to CC over silica gel, eluted with chloroform–methanol (10:0 and 10:1), and the chloroform fraction was further chromatographed over Sephadex LH-20. The elution was carried out with MeOH–H_2O (1:1), collecting 50 fractions of 50 ml each. The fractions 11–23 showing similar TLC profiles were combined and designated as Fraction A (41 mg). Fraction A was chromatographed over ODS and eluted with H_2O–MeOH (7:3), collecting 15 fractions of 20 ml each. The last six fractions provided a semi-pure compound (15 mg). These were combined and subjected to preparative HPLC using solvent system MeOH–H_2O (1:1) (flow rate 3 ml/min) to obtain compound **1** (6.5 mg). The *n*-butanolic subfraction was dissolved in water and column chromatographed over Diaion HP-20, eluting successively with H_2O and 50% methanol. The fraction eluted with 50% methanol was concentrated and sequentially chromatographed on a silica gel column, eluted with chloroform–methanol–water (8.5:1.5:0.15, 8:2:0.2, and 7:3:0.3) to afford three fractions (I–III). Fraction I (51 g) was further chromatographed over Sephadex LH-20. The elution was carried out with MeOH–H_2O (1:1), collecting 30 fractions of 50 ml each. Fractions 8–17 showing similar TLC profiles were combined and designated as Fraction B (63 mg). Fraction B was chromatographed over ODS and eluted with H_2O–MeOH (4:6), collecting 20 fractions of 20 ml each. Fractions 3–9 provided a mixture of compounds **2** and **3** (28 mg). These were combined and subjected to preparative HPLC using solvent system MeOH–H_2O (1:1) (flow rate 3 ml/min) to afford compounds **2** (12.4 mg) and **3** (7.3 mg).

*3.3.1 4′-Methoxy-3′,5,7-trihydroxy-8-(1″-(3‴,4‴,5‴-trihydroxyphenyl)ethyl))-flavone (**1**)*

Yellow crystals, mp 168.0–170.1°C; $[\alpha]_D^{20}$ −11.6°(c 0.11, MeOH); UV (MeOH) $\lambda_{max}(\log \varepsilon)$: 265 (4.26), 371 (3.52) nm; IR (KBr) ν_{max} cm^{-1}: 3367, 2911, 2842, 1607, 1437, 1063; ^1H and ^{13}C NMR spectral data, see Table 1; HR-ESI-MS (pos.): *m/z* 453.1191 $[M + H]^+$ (calcd for $C_{24}H_{21}O_9$, 453.1186).

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