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Constituents of *Craspedolobium schochii*

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Abstract

Nine phenolic compounds, including a new one, were isolated from 70% acetone extract of *Craspedolobium schochii*. The new compound was identified as 3-(3,4-dimethoxy-2-hydroxyphenyl)-7-hydroxy-coumarin (**1**) on the basis of spectroscopic evidence. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Craspedolobium schochii; Phenolics; 3-(3,4-Dimethoxy-2-hydroxyphenyl)-7-hydroxycoumarin

1. Introduction

Craspedolobium schochii Harms (Fabaceae) is not only a unique species of its genus, but also an endemic plant in China, growing in Yunnan, Guangxi and Sichuan provinces. In Chinese folk medicine, the plant has been used for promoting blood circulation, removing blood stasis, tonifying the blood, stopping internal bleeding and eliminating dampness [1]. It is a substitute of *Millettia dielsiana* Harms (named as Jixueteng in China) in Chinese traditional medicine. However, there are no previous studies on its constituents. In search for bioactive constituents from *C. schochii*, we investigated its aerial parts. As a result, one new and eight known phenolics were isolated from the 70% acetone extract by column chromatographies on silica gel, MCI and RP-18. Their structures were elucidated

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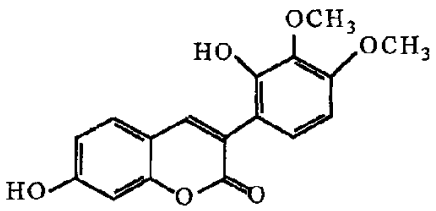
using spectroscopic methods, mainly by NMR experiments. The new compound was identified as 3-(3,4-dimethoxy-2-hydroxyphenyl)-7-hydroxycoumarin (**1**), and the other compounds were naringenin (**2**) [2], genistein (**3**) [3], daidzein (**4**) [4], 3′-hydroxy-5,7,4′,5′-tetramethoxyflavone (**5**) [5], naringenin-6-C-glucoside (**6**) [6], vicenin-2 (**7**) [7], vicenin-3 (**8**) [8], and schaftoside (**9**) [8].



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2. Results and discussion

Compound **1** showed blue fluorescence under 254 nm ultraviolet light. The UV maxima at 205.5, 241 and 338 nm and IR absorptions at 3344 (OH), 1706 (C=O), 1682, 1619, 1580 (C=C) and 1070 (C–O–C) cm^{-1} suggested the presence of aromatic rings and of an α,β-unsaturated lactone. In the NMR spectra, besides two methoxyl signals, only aromatic carbons (8 × C and 6 × CH) and protons were observed. In the ^{13}C-NMR spectrum a carbonyl signal at δ 160.1 (C-2) was also present. This evidence characterized **1** to be a coumarin type compound. The ^{1}H-NMR spectrum revealed the presence of two substituents on the coumarin skeleton, one of them being at the C-3 position because only a singlet at δ 7.79 (H-4) in place of the typical AB system between H-3 and H-4 was observed. The other substituent was at the C-7 position due to the coupling constant between proton signals at δ 7.52 (1H, *d*, *J* 8.5 Hz, H-5), 6.78 (1H, *dd*, *J* 2.2 and 8.5 Hz, H-6), and and 6.73 (1H, *d*, *J* 2.2 Hz, H-8). In addition, one of the two substituents was a phenyl group on which C-2′, C-3′ and C-4′ positions were substituted on account of the proton coupling relationship between δ 6.62 (1H, *d*, *J* 8.3 Hz, 5′-H) and 6.85 (1H, *d*, *J* 8.3 Hz, 6′-H) signals; it should be at C-3 position according to the correlations between proton signal at δ 7.79 (H-4) with the aromatic carbon signal at δ 120.3 (C-1′), and proton signal at δ 6.85 (H-6′) with the carbon signal at δ 121.1 (C-3) in the HMBC spectrum. Moreover, the observed correlations between aromatic proton at δ 7.52 (H-5) with carbon signals at δ 113.1 (C-6) and 160.8 (C-7); 6.78 (H-6) with δ 160.8 (C-7), 129.5 (C-5) and 101.8 (C-8); 6.73 (H-8) with δ 113.1 (C-6) and 160.8 (C-7); δ 6.85 (H-6′) with δ 151.5 (2′, 4′) and 120.3 (C-1′); 6.62

(H-5′) with δ 151.5 (C-4′), 140.6 (C-3′) and 120.3 (C-1′); 3.74 (OCH_3) with δ 140.6 (C-3′), and 3.71 (OCH_3) with δ 151.5 (C-4′) further confirmed that C-7 and C-2′ position were substituted by hydroxyl groups and two methoxyls were at C-3′ and C-4′ positions. Thus, compound **1** was elucidated as 3-(3,4-dimethoxy-2-hydroxyphenyl)-7-hydroxycoumarin.

3. Experimental

3.1. Plant material

Aerial parts of *Craspedolobium schochii* were collected in Luchun county of Yunnan province, in December 1997 and authenticated by Prof. Lin Zhong-Wen at Kunming Institute of Botany, Chinese Academy of Sciences, where the voucher specimen is deposited.

3.2. Extraction and isolation

The air-dried powdered plant (8.5 kg) was extracted with 70% acetone (3 × 19 l) at room temperature for 3 days each time. The extract was concentrated and partitioned with EtOAc and *n*-BuOH to afford the residues Fr.1 (38.5 g) and Fr.2 (339 g), respectively.

Fr.1 (38.5 g) was Si-gel (1.0 kg, 200–300 mesh) CC and eluted with $CHCl_3/CH_3OH$ gradient system (1:0–0:1) to give seven fractions (I–VII). From fraction II, compound **1** (18.6 mg) and **4** (20.0 mg) were isolated by CC on Si-gel (300–400 mesh) eluting with $CHCl_3$/EtOAc (10:1). Fraction III was Si-gel CC with $CHCl_3/CH_3OH$ (20:1) to yield compounds **2** (20.7 mg) and **5** (13.2 mg). Compound **3** (21.1 mg) was obtained from fraction IV by Si-gel CC ($CHCl_3/CH_3OH$, 20:1).

Fr.2 (103 g) was Si-gel (2.0 kg, 200–300 mesh) CC and gradiently eluted with $CHCl_3/CH_3OH$ (5:1–0:1) to give four fractions (A–D). Fraction A was Si-gel CC eluting with $CHCl_3/CH_3OH$ (5:1) to yield compound **6** (58.0 mg). Fraction C was chromatographed on MCI-gel CHP 20P column (CH_3OH/H_2O, 1:0–1:0) to give five subfractions (No. 1–5); from No. 4, following RP-18 CC (CH_3OH/H_2O, 4:6), compound **7** (89.6 mg) was obtained along with a mixture which was Si-gel CC (4.0 μm, $CHCl_3/CH_3OH/H_2O$, 3:2:1) yielding compounds **8** (67.0 mg) and **9** (48.4 mg).

3-(3,4-Dimethoxy-2-hydroxyphenyl)-7-hydroxycoumarin (**1**). $C_{17}H_{14}O_6$, pale yellow needles ($CH_3OH/CHCl_3$), mp 208–210°C; UV max (CH_3OH): 205.5, 241, 338 nm; IR bands (KBr): 3344, 3230, 1706, 1682, 1619, 1580, 1070, 840 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.79 (1H, *s*, H-4), 7.52 (1H, *d*, *J* 8.5 Hz, H-5), 6.78 (1H, *dd*, *J* 8.5, 2.2 Hz, H-6), 6.73 (1H, *d*, *J* 2.2 Hz, H-8), 6.85 (1H, *d*, *J* 8.3 Hz, H-6′), 6.62 (1H, *d*, *J* 8.3 Hz, H-5′), 3.74 (3H, *s*, OC**H**$_3$), 3.71 (3H, *s*, OC**H**$_3$); ^{13}C-NMR (100.4 MHz, DMSO-d_6): 160.1 (*s*, C-2), 121.1 (*s*, C-3), 141.7 (*d*, C-4), 129.5 (*d*, C-5), 113.1 (*d*, C-6), 160.8 (*s*, C-7), 101.8 (*d*, C-8), 154.8 (*s*, C-9), 111.7 (*s*, C-10), 120.3 (*s*, C-1′), 151.5 (*s*, C-2′), 140.6 (*s*, C-3′), 151.5 (*s*, C-4′), 111.2 (*d*, C-5′), 125.0 (*d*, C-6′), 60.3

(q, OCH_3), 60.0 (q, OCH_3); EIMS m/z: 314 $[M]^+$ (100), 297 [M-CH_3 + 2] (47), 285 [M-OCH_3 + 1] (31), 271 (57), 228 (51), 175 (79), 147 (27), 115 (68), 77 (41).

Acknowledgment

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