

Communication

A New Dicoumarinyl Ether from the Roots of *Stellera chamaejasme* L

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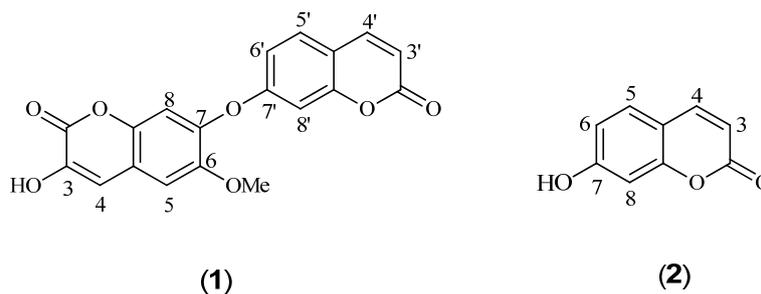
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Abstract: A new dicoumarinyl ether, 3-hydroxy-6-methoxy-7,7'-dicoumarinyl ether (**1**), was isolated from the roots of *Stellera chamaejasme* L, together with the known compound umbelliferone (**2**). Their structures were determined on the basis of spectroscopic techniques, including IR, NMR, and HR-ESI-MS.

Keywords: *Stellera chamaejasme* L; dicoumarinyl ether; 3-hydroxy-6-methoxy-7,7'-dicoumarinyl ether

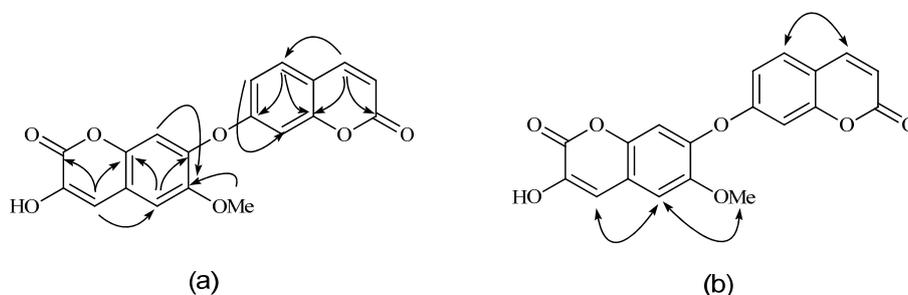
1. Introduction

Stellera chamaejasme L. (*Ruixianglangdu* in Chinese, family Thymelaeaceae), has been used in China as an important traditional medicine for the treatment of scabies, tinea, stubborn skin ulcers, chronic tracheitis, cancer, and tuberculosis [1,2]. Previous phytochemical studies of *S. chamaejasme* showed the presence of groups of biflavonoids, diterpenes, lignans, and coumarins [3–12]. In our continuous studies on the chemical constituents of *S. chamaejasme*, a new bicoumarin, 3-hydroxy-6-methoxy-7,7'-dicoumarinyl ether (**1**, Figure 1) was isolated, together with the known coumarin umbelliferone (**2**). Here, we report the isolation and structure elucidation of the new compound.

Figure 1. Chemical Structures of **1–2**.

2. Results and Discussion

Compound **1** was obtained as a white, amorphous powder. HR-ESI-MS (negative) indicated a molecular formula of $C_{19}H_{12}O_7$ by a pseudo molecular ion peak at m/z 351.0505 $[M-H]^-$. The IR spectrum of **1** displayed absorptions of hydroxyl ($3,448\text{ cm}^{-1}$), α,β -unsaturated lactone ($1,724\text{ cm}^{-1}$), and phenyl ($1,614$, $1,580$, and $1,456\text{ cm}^{-1}$) functionalities. In the $^1\text{H-NMR}$ spectrum, vicinal pairs of signals typical of the H-3' and H-4' protons of an AX system at δ_H 6.31 (1H, d, $J = 9.6\text{ Hz}$, H-3') and 7.96 (1H, d, $J = 9.6\text{ Hz}$, H-4'), were observed, along with an ABX coupling pattern (δ_H 7.68 (1H, d, $J = 8.6\text{ Hz}$, H-5'), 7.10 (1H, dd, $J = 8.6, 2.0\text{ Hz}$, H-6') and 7.06 (1H, d, $J = 2.0\text{ Hz}$, H-8')), suggesting the presence of an 7-oxygenated coumarin moiety, which was further confirmed by the NOESY correlation of H-4' and H-5' (Figure 2).

Figure 2. Key HMBC (a), and key NOESY (b) correlations of compound **1**.

The other unit was deduced to be a 3-hydroxy-6-methoxy-7-substituted- coumarin as follows: H-4 (δ_H 7.80) and H-5 (δ_H 7.24) showed a correlation in the NOESY experiment. Accordingly, cross-peaks between H-4 and C-5 (δ_C 109.9) and between H-5 and C-4 (δ_C 131.5) were evident in the HMBC experiment (Table 1). The correlation between the methoxy protons (δ_H 3.92) and H-5 in the NOESY spectrum indicated that the methoxy group was attached to C-6 (δ_C 146.6), which was further supported by the long-range correlation between the methoxy protons and C-6 in the HMBC spectrum. Compared with the known compound daphnoretin that was isolated from the same plant [13], the resonance of H-8' in **1** was shifted downfield by 0.22 ppm, and the H-8 one shifted upfield by 0.25 ppm, indicating that the two coumarin moieties were connected at C-7 and C-7' via an oxygen bridge, which was further supported by ESIMS/MS experiment of **1**. The daughter ion peaks at m/z 206 and m/z 144 were derived from fission of the C-7'–O bond. Therefore, compound **1** was elucidated as 3-hydroxy-6-methoxy-7,7'-dicoumarinyl ether and named neodaphnoretin. The known compound

was identified as umbelliferone (**2**) by comparison of its ^1H - and ^{13}C -NMR and MS data with published data.

Table 1. NMR data of neodaphnoretin (**1**) in CD_3COCD_3 (600 MHz for ^1H , 150 MHz for ^{13}C).

NO.	δ_{H} Mult ($J = \text{Hz}$)	δ_{C}	HMBC	NO.	δ_{H} Mult ($J = \text{Hz}$)	δ_{C}	HMBC
2		157.8 s		3'	6.31 d (9.6)	115.0 d	2', 10'
3		137.5 s		4'	7.96 d (9.6)	144.4 d	2', 5', 9'
4	7.80 s	131.5 d	2, 3, 5, 9	5'	7.68 d (8.6)	130.6 d	4', 7', 9'
5	7.24 s	109.9 d	4, 6, 7, 9	6'	7.10 dd (8.6, 2.0)	114.3 d	8', 10'
6		146.6 s		7'		161.1 s	
7		151.2 s		8'	7.06 d (2.0)	104.9 d	6', 7'
8	6.90 s	103.7 d	6, 7, 9, 10	9'		156.5 s	10'
9		149.0 s		10'		115.5 s	
10		111.6 s		6-OCH ₃	3.92 s	56.7 q	6
2'		160.7 s					

3. Experimental

3.1. General

Melting points were measured on a Thermal Values analytical microscope and are uncorrected. IR spectra were recorded on a FI-IR 200SXY spectrophotometer (Nicolet, Madison, WI, USA). The high resolution-electrospray ionization-mass spectra (HR-ESI-MS) were acquired with a Micromass Q-TOF mass spectrometer (Waters Corporation, Carlsbad, CA, USA). NMR spectra were measured (^1H at 600 MHz and ^{13}C at 150 MHz) with TMS as the internal standard on a DD2 600 NMR instrument (Agilent, Santa Clara, CA, USA). Silica gel G₂₅₄ and H (Qingdao Sea Chemical Factory, Qingdao, China) were used for TLC and column chromatography, respectively.

3.2. Plant Material

The roots of *S. chamaejasme* were collected in Kunming, Yunnan Province, China, in October, 2010. The plant was identified by Le Cai (Yunnan University). A voucher specimen (LJ-RXLD1008) was deposited with the Zhejiang University City College.

3.3. Extraction and Isolation

Air-dried powdered roots (3.0 kg) of *S. chamaejasme* were extracted exhaustively with 95% aq. EtOH (2 L) at r.t. for four times (7 days for each time). After concentration *in vacuo*, a crude extract (360 g) was obtained, which was suspended in H₂O (1 L), and the suspension was extracted three times successively with petroleum ether, EtOAc and BuOH (1 L). The EtOAc fraction (160 g) was subjected to column chromatography (CC) with a PE/EtOAc gradient system of increasing polarity (9:1, 8:2, 7:3, 6:4, 5:5) as eluent to give six fractions (Fr. 1–6). Fr. 3 was rechromatographed on a SiO₂ column with CHCl₃/MeOH (98:2→95:5) to give compounds **1** (34 mg) and **2** (23 mg).

Neodaphnoretin (**1**) was obtained as white, amorphous powder, mp 133–135 °C, from CHCl₃–MeOH (97:3). IR (KBr) cm⁻¹: 3,448, 1,724, 1,614, 1,580, 1,456; ¹H-NMR (CD₃COCD₃) δ: see Table 1; ¹³C-NMR (CD₃COCD₃) δ: see Table 1; HR-ESI-MS: *m/z* [M–H]⁻ 351.0505 (calcd. for C₁₉H₁₁O₇, 351.0505).

Umbelliferone (**2**) was obtained as colorless crystals, mp 222–224 °C, from MeOH; ¹H-NMR (CD₃OD) δ: 7.83 (1H, d, *J* = 9.4 Hz), 7.44 (1H, d, *J* = 8.5 Hz), 6.79 (1H, dd, *J* = 8.5, 2.0 Hz), 6.70 (1H, d, *J* = 2.0 Hz), 6.17 (1H, d, *J* = 9.4 Hz); ¹³C-NMR (CD₃OD) δ: 162.3, 161.8, 155.8, 144.6, 129.2, 113.1, 111.6, 102.0.

4. Conclusions

A new dicoumarinyl ether, 3-hydroxy-6-methoxy-7,7'-dicoumarinyl ether (**1**) was isolated from the EtOH extract of the roots of *Stellera chamaejasme* L together with the known compound umbelliferone (**2**).

Supplementary Materials

Supplementary materials can be accessed at: <http://www.mdpi.com/1420-3049/19/2/1603/s1>.

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Author Contributions

Xiang-Rong Li and Jie Li organized the study. Qian Shen, and Li-Ting Chen carried out the extraction and isolation. Jie Li and Chen-Hao Bao interpreted the results and helped write the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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Sample Availability: Available from the authors.

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