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NEW COUMARIN GLUCOSIDE FROM *Angelica dahurica*

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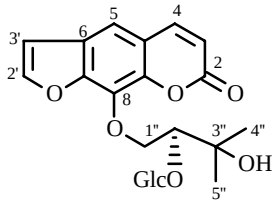
*A new linear furanocoumarin glycoside named dahurin B (**1**) was isolated from the fresh roots and rhizomes of* Angelica dahurica. *The structure of the new compound was elucidated by spectral techniques including ^{1}H NMR, ^{13}C NMR, as well as HSQC, HMBC, and COSY.*

Key words: *Angelica dahurica*, dahurin B, coumarin glycoside, structure elucidation.

The roots and rhizomes of *Angelica dahurica* (Fisch. ex Hoffm.) Benth. et Hook. f. ex Franch. et Sav. cv. Hangbaizhi (Umbelliferae) are important chinese traditional medicines. They have been widely used for the treatment of headache caused by cold, toothache, coryza, vitiligo, acne, freckle, etc. Previous phytochemical work on this plant had only led to the isolation of about 20 coumarins and 3 coumarin glycosides [1–7]. Our research was focus on the water-soluble constituents from fresh material of this plant. Here, we describe the isolation and structure elucidation of the new coumarin glycoside named dahurin B (**1**).

Dahurin B (**1**) was obtained as an optically active yellowish amorphous powder. Its molecular formula $C_{22}H_{26}O_{11}$ was determined on the basis of its ESI-MS (489 $[M+Na]^+$) and confirmed by ^{1}H NMR and ^{13}C NMR data.

Detailed analysis of its ^{1}H NMR, ^{13}C NMR, COSY, HSQC, and HMBC spectra indicated the presence of a linear furanocoumarin glucoside and a 2-methylbutane structural unit; see Table 1.



1

The ^{1}H NMR spectrum of **1** was measured in pyridine-d_5. In the aromatic proton region, there was a pair of doublets at δ 6.37 and 7.65 ppm (d, J = 9.6 Hz), which were identified as the signals of C-3-H and C-4-H of the α-pyrone ring system. A distinct singlet at δ 6.81 ppm was assigned to a single aromatic proton in the coumarin ring. A pair of doublets at δ 7.80 and 6.80 ppm (d, J = 2.2 Hz), which were identical with the signals of C-2′-H and C-3′-H, indicated that **1** was a linear furanocoumarin. Acid hydrolysis of **1** together with the doublet at δ 5.30 ppm (d, J = 7.8 Hz) indicated the presence of a β-D-glucopyranosyl unit. The two singlets at δ 1.69 and 1.67 ppm indicates that there are two methyls in the coumarin structure.

In the aromatic region of the ^{13}C NMR spectrum, the signal at δ 159.55 can be easily assigned to C-2. We can also see the following structural segments: six signals of a glucoside and five signals of a 2-methylbutane structural unit.

We confirm that all chemical shifts of the carbon atoms are connected with the hydrogen proton through HSQC, including C-3, C-4, C-2′, C-3′, singlet proton, carbons in the 2-methylbutane structural unit, and C-1 and C-6 in the sugar skeleton.

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TABLE 1. ^{1}H NMR and ^{13}C NMR as well as HSQC, HMBC, and Cosy Spectral Data for Compound **1** in C_5D_5N (300 MHz, δ, ppm, J/Hz)

Atom	δ_H	δ_C	COSY	HSQC	HMBC
		Aglycon			
2		159.55			
3	6.37 (1H, d, J = 9.58)	114.06	H-4	C-3	C-2,10
4	7.65 (1H, d, J = 9.60)	143.89	H-3	C-4	C-2,5,8,9,10
5	7.31 (1H, s)	112.79			C-4,7,8,9,10,3′
6		125.68			
7		146.90			
8		131.98		C-8	
9		143.30			
10		116.21			
2′	7.80 (1H, d, J = 2.21)	146.55	H-3′	C-2′	C-6,7,3′
3′	6.80 (1H, d, J = 2.22)	106.33	H-2′	C-3′	C-6,7,2′
1_a″	5.12 (1H, dd, J = 4.98, 10.33)	74.01	H-2″	C-1″	C-8,3″
1_b″	5.03 (1H, dd, J = 5.12, 10.33)		H-2″	C-1″	C-8,2″,3″
2″	4.56 (1H, t, J = 5.10)	87.08	H-1″	C-2″	C-4″,5″,g-1
3″		71.60			
4″	1.69 (3H, s)	25.79		C-4″	C-2″, 3″
5″	1.67 (3H, s)	25.06		C-5″	C-2″, 3″
		Glucose			
1	5.30 (1H, d, J = 7.82)	106.08	G-2	G-1	C-2″,g-3
2	4.09 (1H, m)	75.11	C-1,3	G-2	C-g-1, g-3
3	3.71 (1H, m)	77.77	G-2,4	G-3	C-g-4
4	4.24 (1H, m)	70.82	G-3,5	G-4	C-g-3,g-5
5	4.21 (1H, m)	77.37	G-4,6_b	G-5	C-g-4, g-6
6_a	4.47 (1H, dd, J = 2.19, 11.55)	61.90	G-5,6_b	G-6	
6_b	4.38 (1H, dd, J = 5.16, 11.51)		G-5,6_a	G-6	C-g-5

By analysis of the above spectrums, the chemical shifts of C-2, 3, 4 in the α-pyrone ring system has been ascertained. During our investigation of HMBC, such relations were confirmed: δ 116.21 ppm was assigned to C-10 from the correlations of C-3-H to C-2 and δ 116.21 ppm; the position of the glucosyl unit was ascribed to C-2″ from the correlation between the glucoside-1-H and C-2″ signal. We can also assign the singlet proton to C-5 from its strong correlation with C-4 and long range coupling with C-3′. The 2-methylbutane structural unit was assigned to C-8 from the weak correlation between C-8 and C-1″-H.

At present the planar structure of **1** can be ascertained. By comparing the optical rotation values of compound **1** with sec-*O*-β-D-glucopyranosyl-(*R*)-byakangelicin with similar structure [8], the structure of compound **1** can be elucidated as sec-*O*-β-D-glucopyranosyl-(*R*)-heraclenol.

On the basis of the above evidence, compound **1** was assigned to a new compound named dahurin B (**1**).

EXPERIMENTAL

General Methods. ^{1}H NMR and ^{13}C NMR, COSY, HMQC and HMBC spectra: Bruker spectrometers operating at 300 MHz; ESI-MS: Agilent 1100 LC/MSD SL; JASCO P-1020 optical rotation apparatus.

Plant Material. Fresh roots and rhizomes of *Angelica dahurica* (Fisch. ex Hoffm.) Benth. et Hook. f. ex Franch. et Sav. cv. Hangbaizhi, collected from Jiangsu province of PR China in 2004, were taxonomically identified by Prof. Chang-Qi Yuan. A voucher specimen was deposited in Nanjing Botanical Garden Mem. Sun Yat-Sen, Nanjing, Jiangsu, China.

Extraction and Purification. The fresh roots and rhizomes (38.0 kg) were extracted with ethanol at room temperature. After removal of ethanol, the water suspension was re-extracted with petroleum ether, EtOAc, and the obtained aqueous portion was subjected to HP-20 ($H_2O \rightarrow$MeOH). The methanol eluate (70.0 g) was chromatographed on silica gel [$CHCl_3$–MeOH–H_2O

(10:1:0.0→17:3:0.2→4:1:0.1→7:3:0.5)] to furnish four fraction (fractions 1 to 4). Fraction 3 was subjected to ODS column and then Sephadex LH-20 to afford **1** (19.0 mg).

Acid Hydrolysis of Compound. The sample (5 mg) was refluxed with 2N H_2SO_4 (5 ml) at 80 for 4 hours. After neutralization with $Ba(OH)_2$ and extraction with $CHCl_3$, the aqueous supernatant separated from $CHCl_3$-layer was dried and dissolved in DMSO (2 mL), and then extracted with *n*-hexane (2 mL). Reaction of the solution with a hexamethyl-disilazane–trimethylchlorosilane (2:1) mixture with shaking for 15 min yielded the corresponding derivatives. After deposition for 1 hour, the upper solution was detected by GC and compared with authentic sample derivatives under the same conditions.

Shimadzu GC-2010 with ZB-WAX (30 mm × 0.25 mm × 0.25 μm); SPL temperature: 225°; column temperature: 0–2 min 160°, and then rise to 190° with 2.5° per min; split ratio (1:50); total flow: 50.0 mL/min; FID temperature: 250°.

Dahurin B (1), yellow amorphous powder; $[\alpha]_D^{21.7}$ -15.21° (*c* 0.28 MeOH–H_2O 40:60).

IR bands (KBr, ν_{max}, cm^{-1}): 3450, 3060, 2960, 1722, 1600, 1580, 1450, 1250, 1162, 1050, 890, 820.

ESI-MS *m/z*, 489 $[M+Na]^+$, indicates the molecular weight is 466; combined the data of ^1H NMR and ^{13}C NMR, the molecular formula can be deduced as $C_{22}H_{26}O_{11}$.

For ^1H NMR and ^{13}C NMR as well as HSQC, HMBC, and COSY spectral data, see Table 1.

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