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A NEW COMPOUND FROM *Cymbaria dahurica*

Qing-hu Wang,* Wen-qiang Bao, Bi-li-ge-tu-lan Pa, and Na-ren-chao-ke-tu Han

*A new compound, named cymbadahoside A (**1**), was isolated from the EtOAc extract of* Cymbaria dahurica*. The structure of cymbadahoside A was identified by UV, IR, ESI-MS, and 1D and 2D NMR.*

Keywords: *Cymbaria dahurica*, Orobanchaceae, cymbadahoside A, NMR.

Cymbaria dahurica L. (Orobanchaceae) is a perennial herb, densely covered with white sericeous leaves, making the plant silver gray, which grows up to 20–30 cm high with large yellow flowers. It is found predominantly in hills, gullies, and grasslands of Ximeng, Inner Mongolia. The aerial parts of *C. dahurica* are used as folk medicine for impetigo, toxic liver diseases, skin itch, and vaginal pruritus [1]. Flavonoids [2] and nonglycosidic iridoids [3, 4] have been isolated from this plant. Further phytochemical study of the EtOAc extract from the aerial parts of *C. dahurica* resulted in the isolation of a new compound, named cymbadahoside A (**1**).

Compound **1** was obtained as a white solid. The molecular formula was established as $C_{29}H_{36}O_{15}$ based on the HR-ESI-MS at *m/z* 623.5787 $[M - H]^-$ (calcd 623.5792). The IR spectrum exhibited stretching bands for hydroxyl, carbonyl, and aromatic groups at 3424, 1691, 1586, and 1481 cm^{-1}. The ^1H NMR spectrum of **1** (Table 1) exhibited two olefinic hydrogens at δ 7.61 (1H, d, J = 15.5 Hz, H-7), and 6.30 (1H, d, J = 15.5 Hz, H-8), which were verified by the HMBC correlations (Fig. 1) from H-7 to C-2 (δ 113.7), C-6 (δ 121.8), and C-9 (δ 166.9), and H-8 to C-1 (δ 126.2) and C-9 (δ 166.9). Moreover, the signals of six aromatic protons at δ 6.96 (1H, dd, J = 8.0, 2.0 Hz, H-6), 6.79 (1H, d, J = 8.0 Hz, H-5), and 7.04 (1H, d, J = 2.0 Hz, H-2), and 6.58 (1H, dd, J = 8.0, 2.0 Hz, H-6′), 6.70 (1H, d, J = 2.0 Hz, H-2′), and 6.68 (1H, d, J = 8.0 Hz, H-5′) indicated the presence of two ABC systems. The HMBC correlations observed from H-6 to C-4 (δ 148.4), C-2 (δ 113.7) and C-7 (δ 146.6), from H-5 to C-1 (δ 126.2) and C-3 (δ 145.4), from H-2 to C-4 (δ 148.4), C-6 (δ 121.8), and C-7 (δ 146.6), from H-6′ to C-2′ (δ 115.7), C-4′ (δ 143.3), and C-7′ (δ 35.1), from H-5′ to C-1′ (δ 129.9) and C-3′ (δ 144.7), and from H-2′ to C-4′ (δ 143.3), C-6′ (δ 119.8), and C-7′ (δ 35.1) further supported the presence of two ABC systems.

The ^{13}C NMR signals (Table 1) also proved the presence of one *trans* olefinic group and two trisubstituted aromatic rings. Except for the aglycone carbons, there were 12 carbon signals, which were assigned to the sugar moiety. Acid hydrolysis [5, 6] of compound **1** afforded sugar components identified as D-glucose and L-rhamnose by GC analysis. The anomeric proton appearing at δ 4.39 (1H, d, J = 8.0 Hz, H-1‴) and its corresponding carbon resonating at δ 102.8 (C-1‴) from the HSQC experiment also suggested the presence of a β-D-glucose. The remaining signals at 101.7 (C-1″), 80.9 (C-2″), 70.6 (C-3″), 72.4 (C-4″), 69.0 (C-5″), and 17.0 (C-6″) belong to the L-rhamnose. In the ^1H–^1H COSY spectrum, the mutual couplings observed between H-1″ (δ 5.20) and H-2″ (δ 3.93), H-6″ (δ 1.10) and H-5″ (δ 3.56), H-5″ and H-4″ (δ 3.31), H-4″ and H-3″ (δ 3.58), H-1‴ and H-2‴ (δ 3.41), H-2‴ and H-3‴ (δ 3.85), H-3‴ and H-4‴ (δ 4.89), and H-4‴ and H-5‴ (δ 3.58) also confirmed the presence of a β-D-glucose and L-rhamnose.

The structure of **1** was determined further by long-range correlations of H-1‴ of the β-D-glucose to C-8′ (δ 70.8) of the aglycon, H-1″ (δ 5.20) of the L-rhamnose to C-3‴ (δ 80.2) of the β-D-glucose, and H-2″ (δ 3.93) of the L-rhamnose to C-9 (δ 166.9) of the aglycon. The anomeric configuration in the L-rhamnose was determined as α according to the singlet peak. Thus, the structure of compound **1** was elucidated and named cymbadahoside A.

College of Traditional Mongolian Medicine, Inner Mongolia University for Nationalities, 028000, Tongliao, P. R. China, fax: +86 0475 831424, e-mail: wqh196812@163.com. Published in *Khimiya Prirodnykh Soedinenii*, No. 4, July–August, 2019, pp. 560–561. Original article submitted May 25, 2018.

TABLE 1. ^{1}H and ^{13}C NMR Spectral Assignments of Compound **1** (CD_3OD, δ, ppm, J/Hz)

C atom	δ_C	δ_H	C atom	δ_C	δ_H
1	126.2 (C)	–	7′	35.1 (CH_2)	2.81 (m)
2	113.7 (CH)	7.04 (d, J = 2.0)	8′	70.8 (CH_2)	4.06 (dd, J = 16.0, 8.5)
3	145.4 (C)	–			3.72 (dd, J = 16.0, 8.5)
4	148.4 (C)	–	1″	101.7 (CH)	5.20 (s)
5	115.1 (CH)	6.79 (d, J = 8.0)	2″	80.9 (CH)	3.93 (m)
6	121.8 (CH)	6.96 (dd, J = 8.0, 2.0)	3″	70.6 (CH)	3.58 (m)
7	146.6 (CH)	7.61 (d, J = 15.5)	4″	72.4 (CH)	3.31 (m)
8	113.2 (CH)	6.30 (d, J = 15.5)	5″	69.0 (CH)	3.56 (m)
9	166.9 (C)	–	6″	17.0 (CH_3)	1.10 (d, J = 6.0)
1′	129.9 (C)	–	1‴	102.8 (CH)	4.39 (d, J = 8.0)
2′	115.7 (CH)	6.70 (d, J = 2.0)	2‴	74.8 (CH)	3.41 (t, J = 9.0)
3′	144.7 (C)	–	3‴	80.2 (CH)	3.85 (t, J = 9.0)
4′	143.3 (C)	–	4‴	69.1 (CH)	4.89 (m)
5′	114.8 (CH)	6.68 (d, J = 8.0)	5‴	74.6 (CH)	3.58 (m)
6′	119.8 (CH)	6.58 (dd, J = 8.0, 2.0)	6‴	60.9 (CH_2)	3.64 (m); 3.53 (m)

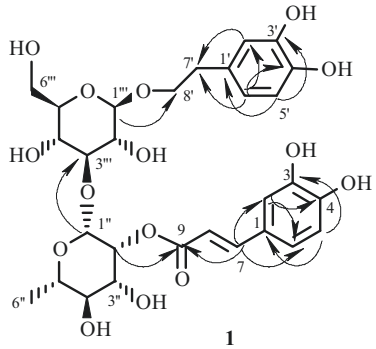

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Fig. 1. Selected HMBC correlations for **1**.

EXPERIMENTAL

General. IR spectra were recorded on a Thermo Nicolet 200 double-beam spectrophotometer. HR-ESI-MS spectra were measured on Waters Xeve C2-S QTOF. The LC system consisted of a LC-20AT pump (Shimadzu, Kyoto, Japan), Shimadzu SPD-20A detector, and Shimadzu CBM-20A software for data processing. ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY, HSQC, and HMBC spectra were recorded in CD_3OD using a 500 Hz Bruker NMR Avance spectrometer.

Plant Material. The aerial parts of *C. dahurica* were collected in Tongliao, Inner Mongolia of China, in June 2016, and identified by Prof. Buhebateer (Inner Mongolia University for Nationalities). A voucher (No. 20160526) has been deposited in the School of Traditional Mongolian Medicine of Inner Mongolia University for Nationalities.

Extraction and Isolation. After extraction with 2000 mL of CH_2Cl_2, the ground-dried aerial parts of *C. dahurica* (2.0 kg) were extracted with EtOAc (5.0 L) under reflux. The EtOAc extract (85.0 g) was separated with $CHCl_3$–CH_3OH (50:1 to 10:1) using silica gel column chromatography to give three fractions (Frs. 1–3). Fraction 3 (760 mg) was isolated by HPLC (CH_3OH–H_2O, 45:55) to give **1** (31 mg).

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