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A NEW FLAVONE GLYCOSIDE FROM THE AERIAL PART OF *Peganum nigellastrum*

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Chemical investigation of the aerial part of Peganum nigellastrum *furnished a new flavone glycoside, and the structure was established by NMR, MS, and DEPT, HSQC, and HMBC as diosmetin 7-*O-β-*D-glucopyranosyl(1→2)-*β*-*D*-glucopyranosyl(1→2)-[*α*-*L*-rhamnopyranosyl(1→6)]-*β*-*D*-glucopyranoside.*

Keywords: *Peganum nigellastrum*, diosmetin 7-*O*-*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl(1→2)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside, flavone glycoside.

Peganum nigellastrum Bge. (Zygophyllaceae) is distributed over Asia and commonly found in the northwest region of China. The plant has been used as a Chinese traditional medicine for rheumatism, abscess, inflammation, and so on [1].

Various compounds have been reported in this plant, including alkaloids, phenylpropanoids, triterpenes, and so on [2–6]. We have studied the chemical constituents of the ethanol extract of the aerial part and obtained a novel flavone glycoside with a tetrasaccharide. Its structure was determined as diosmetin 7-*O*-*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl(1→2)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside (**1**).

The ethanol extract of the aerial part of *P. nigellastrum* was fractionated on silica gel with petroleum, ethyl acetate, and methanol. Isolation and purification were achieved using a combination of TLC, MCI, and Sephadex LH-20.

Compound **1** was a pale yellow powder. The ^{13}C NMR showed the characteristic signals of flavonoid at δ 181.9 (C=O), 164.1 (C-2), and 103.8 (C-3). The signals of H at δ 6.50 (1H, d, J = 2.05 Hz, H-6) and 6.81 (1H, d, J = 2.05 Hz, H-8) were meta-coupled with each other, and the signals of C-6 (δ 99.5) and C-8 (δ 94.8) moved to higher field, confirming that the ring A was substituted by O at C-5 and C-7.

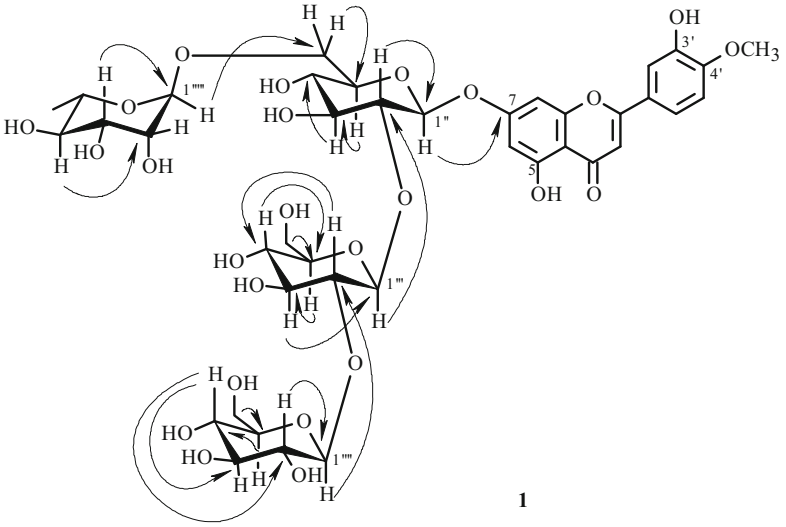

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Fig. 1. Key HMBC correlations (H to C) of compound **1**.

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TABLE 1. NMR of Aglycone Moiety (δ, ppm, J/Hz)

C atom	δ_C	δ_H	C atom	δ_C	δ_H
2	164.1	–	10	105.3	–
3	103.8	6.80 (1H, s)	1′	122.9	–
4	181.9	–	2′	113.1	7.43 (1H, d, J = 2.3)
5	161.1	–	3′	146.7	–
6	99.5	6.50 (1H, d, J = 2.05)	4′	151.3	–
7	162.6	–	5′	112.2	7.13 (1H, d, J = 8.5)
8	94.8	6.81 (1H, d, J = 2.05)	6′	118.9	7.56 (1H, dd, J = 2.3, 8.5)
9	156.8	–	OCH_3	55.7	3.87 (3H, s)

TABLE 2. NMR of Sugar Moiety (δ, ppm, J/Hz)

C atom	δ_C	δ_H	C atom	δ_C	δ_H
1″	98.1	5.23 (1H, d, J = 7.5)	1⁗	104.1	4.52 (1H, d, J = 8.0)
2″	82.9	3.45–3.51 (1H, m)	2⁗	74.6	3.03–3.07 (1H, m)
3″	76.4	3.15–3.21 (1H, m)	3⁗	75.3	3.63–3.69 (1H, m)
4″	69.7	3.06–3.10 (1H, m)	4⁗	68.6	3.20–3.26 (1H, m)
5″	76.1	3.18–3.22 (1H, m)	5⁗	75.3	3.60 (1H, ddd)
6″	65.8	3.86 ($1H_a$, m), 3.46 ($1H_b$, m)	6⁗	60.2	3.40–3.46 (2H, m)
1‴	102.3	4.59 (1H, d, J = 7.5)	1⁗⁗	100.4	4.55 (1H, d, J = 1.0)
2‴	83.1	3.15–3.21 (1H, m)	2⁗⁗	70.3	3.65–3.63 (1H, m)
3‴	76.0	3.44–3.48 (1H, m)	3⁗⁗	70.7	3.44–3.48 (1H, m)
4‴	69.1	3.17–3.22 (1H, m)	4⁗⁗	72.0	3.12–3.16 (1H, m)
5‴	77.3	3.16–3.20 (1H, m)	5⁗⁗	68.3	3.38–3.44 (1H, m)
6‴	60.9	3.50 ($1H_a$, m), 3.75 ($1H_b$, m)	6⁗⁗(CH_3)	17.7	1.07 (3H, d, J = 2.25)

The coupling correlations of H at δ 7.56 (1H, dd, J = 2.3, 8.5 Hz, H-6′), 7.13 (1H, d, J = 8.5 Hz, H-5′), and 7.43 (1H, d, J = 2.3 Hz, H-2′) showed that the ring B was substituted at C-4′ (δ 151.3) and C-3′ (δ 146.7). In the HMBC spectrum, the correlation (Fig. 1) between the signal of H of methoxyl group (δ 3.87, 3H, s) and the signal of C-4′ (δ 151.3) indicated that the ring B was substituted at C-4′ by the methoxyl group, and at C-3′ by the hydroxyl group. So the aglycone moiety was confirmed to be diosmetin [7–9].

The molecular ion peaks of ESI-MS-MS at 769 $[M - H - Glu]^-$, 607 $[M - H - Glu - Glu]^-$, and 299 [aglycone – H]$^-$ showed that the structure contained three hexoses (*m/z* 162) and one methyl pentose (*m/z* 146). Signals of anomeric C and H of the tetrasaccharide were found at: δ 98.1(C-1″), 102.3 (C-1‴), 104.1 (C-1⁗), 100.4 (C-1⁗⁗) and δ 5.23 (d, J = 7.5 Hz, H-1″), 4.59 (d, J = 4.5 Hz, H-1‴), 4.52 (d, J = 8.0 Hz, H-1⁗), and 4.55 (d, J = 1.0 Hz, H-1⁗⁗).

The characteristic signals at δ 17.7 (CH_3), 100.4, 70.3, 70.7, 72.0, and 68.3 indicated that the methyl pentose was α-L-rhamnopyranose. The other three hexoses were determined as β-D-glucopyranose by the ^1H and ^{13}C NMR spectra. The three methylenes observed in DEPT were suggested to be C-6″ (δ 65.8), C-6‴ (δ 60.9), and C-6⁗ (δ 60.2).

Moreover, the sugar sequence was determined by these correlations (Fig. 1): between the signals of C-7 (δ 162.6) and H-1″ (δ 5.23), C-2″ (δ 82.9) and H-1‴ (δ 4.59), C-2‴ (δ 83.1) and H-1⁗ (δ 4.52), and C-6″ (δ 65.8) and H-1⁗⁗ (δ 4.55). Upon substitution [10, 11], the signals of C-2″, C-2‴, and C-6″ shifted from δ 75.0, 75.0, 62.0 to δ 82.9, 83.1, 65.8, respectively, further confirming the sugar sequence. From the date above, compound **1** was identified as diosmetin 7-*O*-β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl(1→2)-[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside.

EXPERIMENTAL

General. Column chromatography (CC): silica gel (200 – 300 mesh) and TLC plates were from Qingdao Marine Chemical Plant, Qingdao, P. R. China; Sephadex LH-20 was purchased from GE Healthcare Bio-Sciences AB; MCI gel was from Mitsubishi Chemical Corporation, Tokyo, Japan.

^1H, ^{13}C, and 2D NMR spectra: Bruker-AV-500 spectrometer; δ in ppm rel. to Me_4Si, J in Hz. MS: Agilent-1100-JC/MSD-Trap (ESI-MS-MS) spectrometer; in *m/z*.

Plant Material. *P. nigellastrum* aerial parts were collected from Minqin of Gansu Province, P. R. China. A voucher specimen was identified by Prof. Xue-Hua Song (China Pharmaceutical University) and has been deposited at the Herbarium of China Pharmaceutical University, Nanjing, P. R. China (reference No. 200701208).

Extraction and Isolation. The dried aerial part was extracted with 95% ethanol. The concentrated extract (1 kg) was passed through a silica gel column, eluted with petroleum, ethyl acetate, ethyl acetate–methanol, and methanol. The EtOAc–MeOH (1:1) part was applied to an MCI column eluted with H_2O, 20% EtOH, 50% EtOH, and 95% EtOH. The 20% EtOH eluate afforded compound **1** (22 mg) via a combination of TLC (EtOAc–MeOH, 1:1) and Sephadex LH-20 (MeOH–H_2O, 1:1).

Compound 1. ESI-MS-MS *m/z* 931 $[M - H]^-$, 769 $[M - H - Glu]^-$, 607 $[M - H - Glu - Glu]^-$, 299 [aglycone – H]$^-$, $C_{40}H_{52}O_{25}$. ^1H NMR and ^{13}C NMR (500 and 125 MHz, DMSO-d_6, δ): see Table 1 and 2.

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