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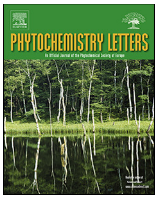

Two new stilbenoids from the whole herb of *Sphaerophysa salsula*

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ABSTRACT

Two new compounds, gnetuhainins Fa (**1**) and cassigarols Ea (**2**), were isolated from the whole herb of *Sphaerophysa salsula* along with eight known compounds (**3-10**). The compounds (**4**) were isolated for the first time from this species. Their structures were elucidated by ESI-MS, UV, IR, 1D NMR and 2D NMR data.

1. Introduction

Sphaerophysa salsula (S. salsula), also known as Yang Liao Pao, Ma Liao Pao, and Hong Ku Dou, belongs to the Leguminosae family and is the only existing species in the *Sphaerophysa* genus. It is a perennial herb widely distributed in Middle-Asia and China and used as a folk medicine for the treatment of hypertension in China (Ma et al., 2002b). Modern pharmacological studies have demonstrated that *S. salsula* has antiviral (Burali et al., 1987), anti-hepatitis (Nasri et al., 2017), anti-tumor (Zhang et al., 2017), anti-HIV-1 (Martinez-Perez et al., 2014), anti-hypertension and antimicrobial (Yu et al., 2010) activities. Previous phytochemical investigations, focused on the ethyl acetate and n-butanol fractions of rhizomes, seeds and whole herb of *S. salsula*, have shown that its main chemical constituents are isoflavanes (Ma et al., 2002a), flavonoids (Jiao et al., 2017), stilbenes (Ma et al., 2002b), sterols (Li et al., 2005), lignans (Ma et al., 2003) and triterpenes (Ma et al., 2004). However, there are no related reports on the chemical constituents of the petroleum ether fractions from *S. salsula*. Therefore, to complement previous studies, we carried out this research. This work will provide a basis for subsequent studies on the activities and chemical compositions of *S. salsula*. In the present study, we report the isolation and structure elucidation of two new stilbenoid derivatives, along with eight known compounds from *S. salsula* (Fig. 1).

2. Results and discussion

Compound **1** was obtained as a pale-brown powder. The ESI-MS data indicated a quasimolecular ion peaks at *m/z* 539.1726 $[M-H]^-$, indicating a molecular weight of 540. Its molecular formula was determined to be $C_{32}H_{28}O_8$, with 19° of unsaturation, according to ESI-MS, ^1H and ^{13}C NMR spectroscopic data. The ^1H NMR spectrum of compound **1** showed the presence of an ABX system for ring B [δ_H 7.08 (1H, d, J = 2.1 Hz, H-2′), 6.91 (1H, dd, J = 8.3, 2.1 Hz, H-6′) and 6.72 (1H, d, J = 8.3 Hz, H-5′)], two sets of AB_2 system signals at [δ_H 6.57 (2H, d, J = 2.3 Hz, H-2, H-6), 6.51 (1H, t, J = 2.3 Hz, H-4)] and [δ_H 6.77 (2H, d, J = 2.2 Hz, H-2‴, H-6‴), 6.36 (1H, t, J = 2.2 Hz, H-4‴] for the rings A and C, two inter-coupling proton signals at [δ_H 7.04 (1H, d, J = 1.2 Hz, H-2″), 7.00 (1H, d, J = 1.2 Hz, H-6″)], and two doublets for *trans*-olefinic protons at [δ_H 7.30 (1H, d, J = 16.3 Hz, H-α'), 6.94 (1H, d, J = 16.3 Hz, H-β')]. Comparing the ^1H NMR data of compound **1** with Gnetuhainin F revealed that compounds **1** and Gnetuhainin F possessed the same skeleton (Wang et al., 2000). All protonated carbons were confirmed by analysis of the HSQC spectrum. Additionally, the ^1H NMR spectrum of compound **1** showed the presence of four methoxy groups [δ_H 3.75 (6H, s, $3-OCH_3$, $5-OCH_3$), and 3.75 (6H, s, $3'''-OCH_3$, $5'''-OCH_3$)]. The ^{13}C NMR spectrum of compound **1** also indicated the presence of four methoxy groups [δ_C 55.27 (s, $3'''-OCH_3$, $5'''-OCH_3$), 55.21 (s, $3-OCH_3$, $5-OCH_3$)]. The HMBC spectrum of compound **1** (Fig. 2), the correlations between $3-OCH_3$/C-3, $5-OCH_3$/C-5, H-2/C-α, C-4, C-6, H-4/C-2, C-6, H-6/C-2, C-α, C-4, C-5 showed that the bonding position of two methoxy groups were C-3 and C-5 of the A ring; the correlations between $3'''-OCH_3$/C-3‴, $5'''-OCH_3$/C-5‴, H-4‴ /C-2‴, C-6‴ and H-2‴ /C-3‴, C-4‴, C-6‴ showed that the bonding position of additional two methoxy groups were C-3‴ and C-5‴ of the C ring. According to the correlations between H-2′/C-β, C-4′, C-6′, H-5′/C-1′, C-3′, H-6′/C-2′, C-4′ of the B ring, and the correlations between H-2″ /C-α', C-4″, C-6″, H-6″ /C-α′, C-2″, C-4″ of the D ring, the bonding positions of the three hydroxyl groups were determined. Based on the

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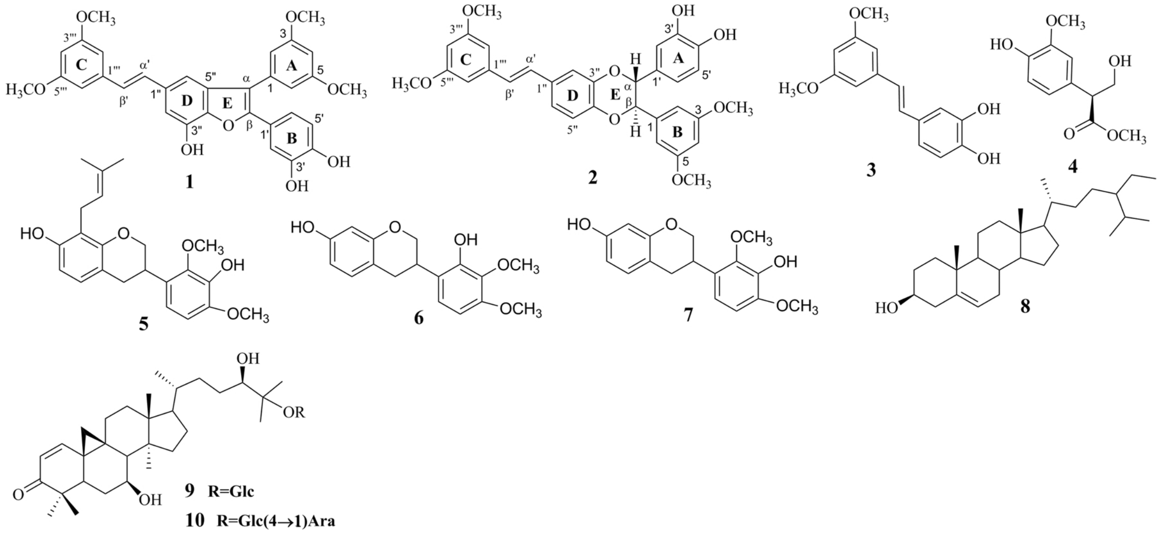

Fig. 1. The structure of ten compounds.

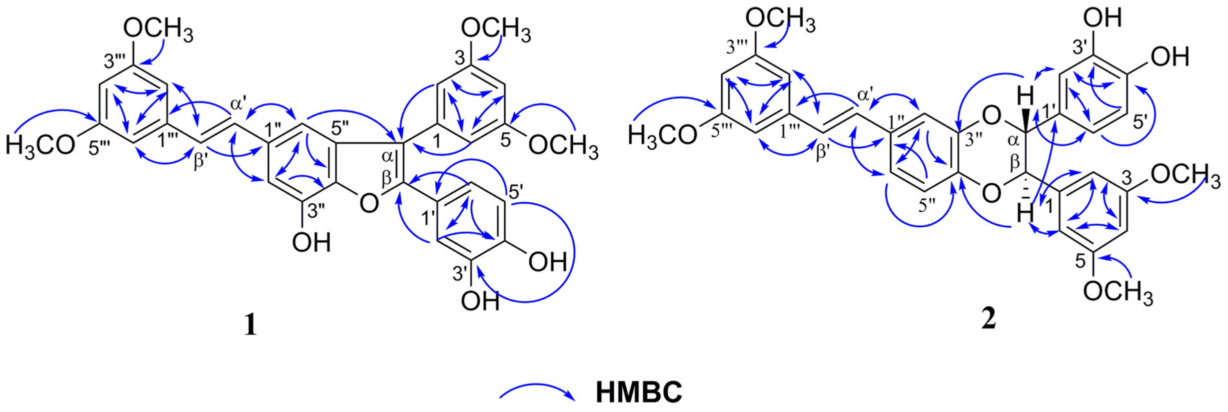

Fig. 2. The HMBC correlations of compounds **1** and **2**.

above analysis, the structure of compound **1** was determined, and named as gnetuhainins Fa. The NMR data are shown in Table 1.

Compound **2** was obtained as an amorphous brown powder. The ESI-MS data indicated a quasimolecular ion peaks at *m/z* 541.1876 $[M-H]^-$, indicating a molecular weight of 542. Its molecular formula was determined to be $C_{32}H_{30}O_8$, with 18 degrees of unsaturation, according to ESI-MS, ^1H and ^{13}C NMR spectroscopic data. The ^1H NMR spectrum of compound **2** showed the presence of two ABX system signals for the A ring [δ_H 6.68 (1H, d, $J = 1.5$ Hz, H-2′), 6.61 (1H, d, $J = 8.1$ Hz, H-5′), 6.53 (1H, dd, $J = 8.1$, 1.5 Hz, H-6′)] and the D ring [7.23 (1H, d, $J = 1.8$ Hz, H-2″), 6.99 (1H, d, $J = 8.4$ Hz, H-5″), 7.14 (1H, dd, $J = 8.4$, 1.8 Hz, H-6″)], two sets of AB_2 system signals for the B ring [δ_H 6.41 (2H, d, $J = 2.1$ Hz, H-2, H-6), 6.37 (1H, t, $J = 2.1$ Hz, H-4)] and the C ring [δ_H 6.74 (2H, d, $J = 2.1$ Hz, H-2‴, H-6‴), 6.39 (1H, t, $J = 2.1$ Hz, H-4‴)], and two doublets for the *trans*-olefinic protons at [δ_H 7.19 (1H, d, $J = 16.4$ Hz, H-α'), 7.06 (1H, d, $J = 16.4$ Hz, H-β')], and 5.05 (1H, d, $J = 8.4$ Hz, H-α), 5.07 (1H, d, $J = 8.4$ Hz, H-β). Comparing the NMR data of compound **2** with cassigarols E suggests that compounds **2** and cassigarols E have the same skeleton (Baba et al., 1994; Xiang et al., 2006). The sixteen protonated carbons of skeleton were confirmed by analysis of the HSQC spectrum. Additionally, the ^1H NMR and ^{13}C NMR spectrum of compound **2** showed the presence of four methoxy groups [δ_H 3.77 (6H, s, 3‴$-OCH_3$, 5‴$-OCH_3$), 3.66 (6H, s, $3-OCH_3$, $5-OCH_3$)] and [δ_C 55.66 (s, 3‴$-OCH_3$, 5‴$-OCH_3$), 55.61 (s, $3-OCH_3$, $5-OCH_3$)]. The bonding position of the four methoxy groups were confirmed by the HMBC spectrum of compound **2** (Fig. 2). Based on the correlations between $3-OCH_3$/C-3, $5-OCH_3$/C-5, H-2/C-β, C-4, C-6, H-4/C-2, C-6, H-6/C-2, C-β, C-4 and H-β/C-2, C-6, C-1′,C-4″, the bonding positions of the two methoxy groups of the B ring were confirmed. Similarly, the correlations between 3‴$-OCH_3$/C-3‴, 5‴$-OCH_3$/C-5‴, H-4‴/C-2‴, C-6‴ and H-2‴/C-β', C-4‴, C-6‴ showed the bonding position of additional two methoxy groups of the C ring. Furthermore, the correlations between H-2′/C-α, C-4′, C-6′, H-5′/C-1′, C-3′, H-6′/C-α, C-2′, C-4′ of A ring and H-α/C-2′, C-6′ indicated the bonding positions of the two hydroxyl groups. Based on the above analysis, the structure of compound **2** was determined and named as cassigarols Ea. The NMR data are shown in Table 1.

The other eight known compounds were identified as *Trans*-4-[2-(3, 5-dimethoxyphenyl)ethenyl]-2-hydroxylphenol (**3**) (Venkateswarlu et al., 2003), ficusol (**4**) (Li et al., 2012), sphaerosin s_1 (**5**) (Ma, 2003), 2′, 7-dihydroxyl–3′, 4′-dimethoxyisoflavane (**6**) (Zhang et al., 2012), 3′, 7-dihydroxyl–2′, 4′-dimethoxy- isoflavane (**7**) (Lu and Xu, 2007), β-sitosterol (**8**) (Qiao, 2012), sphaerophysone C (**9**) (Ma, 2003) and sphaerophysone D (**10**) (Ma, 2003).

3. Experimental section

3.1. General experimental procedures

Ultraviolet (UV) spectra were acquired using a Shimadzu UV2401PC instrument (Shimadzu, Japan). IR spectra were recorded by a BrukerTensor 27 FTIR spectrometer (Bruker, Germany). Optical rotations were obtained by a JASCO P-1020 digital polarimeter (Jasco, Japan). High resolution mass spectrometry was measured using a