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A NEW FLAVANONE GLUCOSIDE FROM *Abrus precatorius*

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*A new flavanone glycoside, (2S)5,7,4′-trihydroxyflavanone-8-*C*-β-*D*-(6″-*O*-acetyl)glucopyranoside (**1**), together with six known flavonoids, isohemiphloin (**2**), vitexin (**3**), cirsimaritin (**4**), hispidulin (**5**), apigenin (**6**), and eupatorin (**7**), was isolated from the leaves and stems of* Abrus precatorius. *Their structures were elucidated on the basis of physical and spectral analysis. Rotamers exist for compounds **1**, **2**, and **3**. Compounds **1**–**3**, **6**, and **7** were isolated from this plant for the first time.*

Keywords: *Abrus precatorius*, flavonoid, flavanone glycoside, rotamers.

Abrus precatorius L. belongs to the family Leguminosae. Its seeds, Xiang-si-zi, have been used as an insecticide and for the treatment of some skin diseases since ancient times in China [1]. Several groups of secondary compounds have been isolated from the species, including alkaloids, steroids, triterpenoids, and isoflavano-quinones [2–10]. In our research, the aqueous EtOH extract of the aerial parts was separated by repeated chromatography to give seven flavonoids. Their structures were elucidated as: (2*S*)5,7,4′-trihydroxyflavanone-8-*C*-*β*-D-(6″-*O*-acetyl)glucopyranoside (**1**), isohemiphloin (**2**) [11], vitexin (**3**) [12], cirsimaritin (**4**) [13], hispidulin (**5**) [14], apigenin (**6**) [15], and eupatorin (**7**) [16]. Compounds **1**–**3**, **6**, and **7** were isolated from this plant for the first time. In this paper, we report the isolation and structural elucidation of the new compound **1**.

Compound **1** has the molecular formula $C_{23}H_{24}O_{11}$ based on its ESI-MS data (*m/z* 475.2 $[M - H]^-$), this being supported by its ^{1}H NMR and ^{13}C NMR data. The presence of the flavanone skeleton was determined by the UV (λ_{max} 290, 334 nm) [17], ^{1}H NMR [δ 5.32 (1H, m, H-2); 3.16 (1H, m, H-3$_{trans}$); 2.79 (1H, dd, J = 2.5, 17.0, H-3$_{cis}$), Py-d_5], and ^{13}C NMR (δ 43.2 for C-3, 196.5 for C-4) spectra [18]. The ^{1}H NMR spectrum indicated the presence of an A-ring singlet (δ 6.26) as well as the characteristic seven-spin system of the protons of a *β*-D-glucopyranoside moiety C-C coupled at C-1″ to the aglycone (J = 10 Hz) [19]. Individual sugar protons were identified by means of COSY and HSQC experiments. The substitution pattern of the B-ring was elucidated from the ^{1}H NMR spectrum, showing a distinct AA′BB′-type signals [δ 7.48 (2H, d, J = 8.0 Hz, H-2′, 6′), δ 7.18 (2H, d, J = 8.0 Hz, H-3′, 5′)].

These signals appeared similar to the ^{1}H and ^{13}C NMR spectroscopic data of isohemiphloin (**2**) isolated from the roots of *Bowdichia virgilioides* [11]. The obvious difference between them was that there was one methyl signal at δ 20.7 and one carbonyl signal at δ 172.9 in the ^{13}C NMR spectrum of **1**. These data along with the appearance of one methyl proton signal at δ 2.02 in the ^{1}H NMR spectrum indicated that there was one acetyl in compound **1**. This was proved by the HMQC, HMBC, and COSY spectra. HMBC correlations between δ 2.02 (3H, s, $COCH_3$), δ 5.10 (1H, dd, J = 4.5, 11 Hz, H_a-6″), δ 4.75 (1H, dd, J = 4.5, 11 Hz, H_b-6″) and δ 172.9 indicated that acetyl was linked to the C-6″ of glucose. Furthermore, HMBC correlations of δ 5.73 (1H, d, J = 10 Hz, H-1″) with δ 167.6 (C-7), 107.1 (C-8), and 164.5 (C-9) indicated that the glucose moiety was attached to C-8 (Fig. 1). Configurational assignment at C-2 of compound **1** was determined using CD data with positive Cotton effect at $[\theta]_{334}$ and negative Cotton effect at $[\theta]_{290}$ [20]. Compound **1** was, therefore, determined to be (2*S*)5,7,4′-trihydroxyflavanone-8-*C*-*β*-D-(6″-*O*-acetyl)glucopyranoside.

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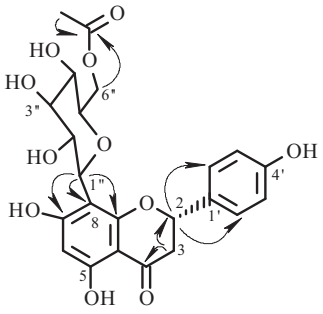

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Fig. 1. The structure and key HMBC correlations of **1**.

In the ^{1}H and ^{13}C NMR spectra, double signals were observed in the A ring and the glucose in **1**, **2**, and **3**. A similar effect in the NMR spectra of some flavonoid-6-*C*-*β*-D-glucosides has been reported by Chao [1] and Gong [21]. The unusual spectral behavior was considered to be due to the presence of two isomeric forms, in which the interconversion is slow at low temperature but rapid at high temperature.

EXPERIMENTAL

General. 1 D and 2 D NMR spectra were recorded on a Bruker-AV-500 spectrometer with TMS as internal standard. ESI-MS data were measured with a LCQDECA XP HPLC/MSn mass spectrometer, and UV spectrum was obtained on a Beckman DU-640 UV spectrophotometer. For column chromatography (CC), silica gel (200–300 mesh) and GF_{254} for TLC were obtained from the Qingdao Marine Chemical Factory, Qingdao, China.

Plant Material. The leaves and stems of *Abrus precatorius* were collected in October 2010 in the mangrove wetlands of Hainan Island, China. The identification of the plant was performed by one of the authors (S. Zhang). A voucher sample (No. 20101001) is maintained in the Herbarium of the South China Sea Institute of Oceanology.

Extraction and Isolation. The air-dried leaves and stems of *Abrus precatorius* (8 kg) were extracted with EtOH (95%) three times (7 days each time) at room temperature. The combined alcohol extracts were concentrated *in vacuo*. The residue was suspended in H_2O and extracted with petroleum ether, EtOAc, and *n*-BuOH successively. The EtOAc and *n*-BuOH layers were concentrated to afford 53.7 g and 108 g of residues, respectively. The EtOAc extract was subjected to CC (SiO_2, petroleum ether–EtOAc, and $CHCl_3$–MeOH, TLC monitoring) to afford four compounds, **4**–**7**. The *n*-BuOH extract (108 g) was subjected to CC on Amberlite XAD using MeOH/H_2O (20, 40, 60, and 95%). The 40% extract part (7.23 g) was fractionated on a silica gel column with $CHCl_3$–MeOH–H_2O 9:1:0.1 to give 10 fractions, A-J. Fraction C (1.42 g) was fractionated in CC using the solvent system $CHCl_3$–MeOH (25:1–10:1) under gradient conditions. These fractions were combined based on TLC as C1–C10. C10 was purified by Sephadex LH-20 ($CHCl_3$–MeOH 1:1) and recrystallized (MeOH) to give **1** (5 mg). Fraction F was purified by Sephadex LH-20 ($CHCl_3$–MeOH 1:1) to yield **2** (5 mg) and **3** (10 mg).

Compound 1. Pale yellow powder. ^{1}H NMR spectrum (500 MHz, Py-d_5, δ, ppm, J/Hz): 7.48 (2H, d, J = 8.0, H-2′, 6′), 7.18 (2H, d, J = 8.0, H-3′, 5′), 6.26 (1H, s, H-6), 5.73 (1H, d, J = 10, H-1″), 5.32 (1H, m, H-2), 5.10 (1H, dd, J = 4.5, 11, H_a-6″), 4.75 (1H, dd, J = 4.5, 11, H_b-6″), 4.41 (1H, m, H-3″), 4.29 (2H, m, H-4″, 5″), 3.16 (1H, m, H-3$_{trans}$), 2.79 (1H, dd, J = 2.5, 17 H-3$_{cis}$), 2.02 (3H, s, COC$\underline{H}_3$). ^{13}C NMR spectrum (125 MHz, Py-d_5, δ, ppm): 79.5 (C-2), 43.2 (C-3), 196.5 (C-4), 162.9 (C-5), 95.5 (C-6), 167.6 (C-7), 107.1 (C-8), 164.5 (C-9), 102.7 (C-10), 129.6 (C-1′), 128.8 (C-2′, 6′), 159.5 (C-4′), 116.4 (C-3′, 5′), 172.9 (C=O), 20.7 (CO$\underline{C}H_3$), 75.2 (C-1″), 72.2 (C-2″), 80.8 (C-3″), 72.1 (C-4″), 79.7 (C-5″), 65.6 (C-6″).

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