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A NEW FLAVANONE GLUCOSIDE FROM THE FLOWERS OF *Carthamus tinctorius* AND ASSIGNMENT OF ABSOLUTE CONFIGURATION

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A new flavanone glucoside was isolated from the flowers of Carthamus tinctorius*. The structural elucidation was performed mainly by mean of FAB-MS, NMR, and acid hydrolysis; the absolute configuration was also determined by circular dichroism spectroscopy.*

Keywords: *Carthamus tinctorius*, Compositae, flavanone glucoside.

Carthamus is one of the most important genera in the Compositae family. The dried flower of *Carthamus tinctorius* (safflower) has long been used traditionally in China and southeast Asia. It showed therapeutic potential for treating coronary heart disease, stroke, gynecological disease, angina, and hypertension [1–7]. Many studies concerning the chemical constituents of *Carthamus tinctorius* have been carried out, which have led to the isolation of a series of secondary metabolites, including flavonoids, alkaloids, lignans, and fatty acids. These constituents were found to be responsible for the overall curative effects of safflower [8–18]. In this article, we present the isolation and structure elucidation of a new flavanone glucoside based on extensive spectroscopic and chemical studies.

Compound **1** was obtained as white needles, $[\alpha]_D^{30}$ –20.2° in MeOH; its IR spectrum (KBr) showed absorption bands for hydroxyl (3390 cm^{-1}), conjugated carbonyl (1645 cm^{-1}) groups, and aromatic rings (1616 and 1520 cm^{-1}). HR-FAB-MS showed an *m/z* 473.1062 $(M + Na)^+$ corresponding to the molecular formula $C_{21}H_{22}O_{11}$.

The ^1H NMR spectrum of compound **1** exhibited doublets at δ 5.80 and 5.89 (each 1H, d, J =2.10 Hz) due to meta coupling of two protons of the A-ring. The specific dihydropyrone core of a flavanone aglycone was confirmed by the ^1H NMR spectrum, in which the signals due to the H-2, H-3a, and H-3b protons were observed as an ABX type at δ 5.44 (dd, J_{XA} = 12.36, J_{XB} = 3.42 Hz), 2.71 (dd, J_{AB} = 17.16, J_{BX} = 3.42 Hz, *cis*), and 3.21 (dd, J_{AB} = 17.16, J_{AX} = 12.36 Hz, *trans*), respectively. The ^1H NMR data also showed signals attributed to an anomeric proton at δ 4.69 (1H, d, J = 7.56 Hz, H-1″), together with five glycosyl protons in the range δ 3.8–3.4. The ^{13}C NMR and DEPT spectra of **1** displayed 21 carbon signals consisting of six carbons of the glycosyl moiety. All of the above data revealed that **1** is a flavanone monoglycoside with a *β* sugar unit; acid hydrolysis of compound **1** also indicates that the monosaccharide moiety was a D-glucose.

The signals in the ^1H and ^{13}C NMR spectra were unambiguously assigned by HMQC, HMBC, H–H COSY, and NOESY experiments (Fig. 1). Long-range correlation from the anomeric proton δ 4.69 (d, J = 7.56 Hz) to C-4′ (δ 145.4) in the HMBC spectrum and the correlation between δ 7.12 (d, J = 8.22 Hz, H-5′) and 4.69 (d, J = 7.56 Hz, H-1″) in the NOESY spectrum unequivocally established that the sugar linkage to the aglycone in **1** was at C-4′.

Additionally, the absolute configuration at C-2 was found to be *S* as it showed a negative Cotton effect at 290 nm ($\Delta\varepsilon = -11.2$, $c = 11.10 \times 10^{-5}$ M) and positive Cotton effect ($\Delta\varepsilon = +8.2$, $c = 11.10 \times 10^{-5}$ M) at 334 nm in the CD spectrum. Accordingly, the structure of **1** was determined as (2*S*)-5,7,3′-trihydroxyflavanone-4′-*O*-*β*-D-glucopyranoside [19].

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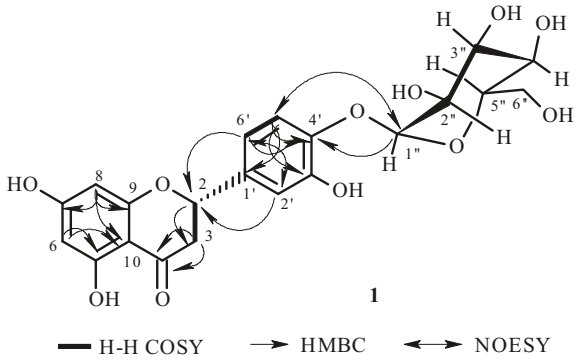

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Fig. 1. Structure of compound **1**.

EXPERIMENTAL

General. NMR spectra were recorded on a Varian Inova AS 600 system; CD spectra were measured on a Jasco J-720 W spectrometer; FAB-MS spectra were recorded with a JEOL JMS-SX 102A mass spectrometer. Diaion HP-20 (Mitsubishi Chemical Corporation) and Chromatorex ODS DM1020T (100–200 mesh, Fuji Silysia Chemical Ltd.) were used for column chromatography. Preparative HPLC: Shimadzu LC-10AD with refractive index detector; preparative column: YMC-Pack ODS-A (250 × 20 mm i.d., S-5 μm, 12 nm); sugar identification HPLC: optical rotation detector (Shodex OR-2), Kaseisorb LC NH_2-60-5, 250 × 4.6 mm.

Plant Material. The flowers of *Carthamus tinctorius* were collected from Xinjiang, China in 2011. A voucher specimen of this plant was deposited at the College of Agronomy, Sichuan Agricultural University.

Extraction and Isolation. The flowers of *Carthamus tinctorius* (2 kg) were extracted three times with MeOH under reflux for 3 h. Evaporation of the solvent under reduced pressure provided the MeOH extract (40.1 g). The MeOH extract was passed through a Diaion HP-20 column chromatograph and sequentially eluted twice with H_2O and MeOH to give an H_2O-eluted fraction (15.5 g) and an MeOH-eluted fraction (24.5 g). The MeOH-eluted fraction (24.5 g) was chromatographed on ODS columns using a gradient of MeOH–H_2O (20: 80→40: 60→60: 40→80: 20)→MeOH to give 10 fractions (1–10). Fraction 4 (2.0 g) was repeatedly chromatographed on RP-C_{18} [MeOH–H_2O (45:55)] to give **1** (6.0 mg).

Compound 1. White needles. ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.71 (1H, dd, J = 3.42, 17.16, H-3a), 3.21 (1H, dd, J = 12.36, 17.16, H-3b), 3.40 (2H, m, H-4″, 5″), 3.46 (2H, m, H-2″, 3″), 3.71 (2H, dd, J = 3.42, 11.7, H-6″), 4.69 (1H, d, J = 7.56, H-1″), 5.44 (1H, dd, J = 3.42, 12.36, H-2), 5.80 (1H, d, J = 2.10, H-6), 5.89 (1H, d, J = 2.10, H-8), 6.85 (1H, dd, J = 2.04, 8.22, H-6′), 6.95 (1H, d, J = 2.04, H-2′), 7.12 (1H, d, J = 8.22, H-5′). ^{13}C NMR (150 MHz, DMSO-d_6, δ, ppm): 78.1 (C-2), 42.0 (C-3), 196.1 (C-4), 163.4 (C-5), 95.8 (C-6), 166.6 (C-7), 95.0 (C-8), 162.7 (C-9), 101.8 (C-10), 133.2 (C-1′), 114.4 (C-2′), 146.7 (C-3′), 145.4 (C-4′), 116.6 (C-5′), 117.7 (C-6′), 102.2 (C-1″), 73.3 (C-2″), 75.8 (C-3″), 69.8 (C-4″), 77.2 (C-5″), 60.7 (C-6″).

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