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Yu-Zhi Zhou[a]; Huan Chen[a]; Li Qiao[a]; Nan Xu[b]; Jia-Qing Cao[a]; Yue-Hu Pei[a]
[a] School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang, China [b] School of Pharmacy, Liaoning University of Traditional Chinese Medicine, Shenyang, China

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Two new compounds from *Carthamus tinctorius*

Yu-Zhi Zhou[a], Huan Chen[a], Li Qiao[a], Nan Xu[b], Jia-Qing Cao[a] and Yue-Hu Pei[a]*

[a]*School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, China;* [b]*School of Pharmacy, Liaoning University of Traditional Chinese Medicine, Shenyang 110016, China*

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From the dried petals of *Carthamus tinctorius*, a new flavonoid, (2*R*)-4′,5-dihydroxyl-6,7-di-*O*-β-D-glucopyranosyl flavanone (**1**) and a new aromatic glucoside, methyl-3-(4-*O*-β-D-glucopyranosylphenyl) propionate (**4**) were isolated along with four known compounds (2*S*)-4′,5-dihydroxyl-6,7-di-*O*-β-D-glucopyranosyl flavanone (**2**), 6-hydroxykaempferol-3,6-di-*O*-β-D-glucopyranoside (**3**), 4-*O*-β-D-glucosyl-*trans*-*p*-coumaric acid (**5**), and 4-*O*-β-D-glucosyl-*cis*-*p*-coumaric acid (**6**). Their structures were identified on the basis of chemical and spectroscopic methods.

Keywords: *Carthamus tinctorius*; flavonoids; aromatic glucosides; chemical and spectroscopic methods

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1. Introduction

The dried flower of safflower, *Carthamus tinctorius* L. is a traditional Chinese medicine widely used in china, having the function of promoting blood circulation by removing blood stasis.[1] The chemical constituents from this plant have been examined, and the isolation of flavonoids,[2,3] polyacetylenes,[4] serotonin derivatives,[5] steroids,[6] lignans,[7,8] alkane diol,[9,10] and colouring matter[11] have been reported. During the course of our phytochemical investigation, a new flavonoid and a new aromatic glucoside, together with four known compounds (Figure 1), were isolated from *C. tinctorius*. This paper describes the isolation and structural characterization of these compounds.

2. Results and discussion

Compound **1** was obtained as a yellow gummy material. The molecular formula was determined to be $C_{27}H_{32}O_{16}$ by the HR-FABMS (m/z 613.1769 $[M + H]^+$). The IR spectrum of **1** suggested the presence of conjugated carboxyl (1650 cm^{-1}) and hydroxyl groups, which were due to sugar moieties (3363 and 1075 cm^{-1}). The ^1H NMR spectrum of **1** showed the presence of the flavanone structure with a *p*-hydroxylphenyl group at δ 7.33 (2H, d, $J = 8.4$ Hz, H-2′ and H-6′) and 6.80 (2H, d, $J = 8.4$ Hz, H-3′ and H-5′). The down-field chemical shift of OH-5 (δ 11.95) suggested that it should have formed an internal hydrogen bond with the carbonyl carbon C-4 (δ 197.7). Furthermore, the characteristic signals of flavanone were revealed at δ 5.48 (1H, dd, $J = 13.1$, 2.4 Hz) for H-2α, at δ 2.70 (1H, dd, $J = 17.2$, 2.4 Hz) for H-3α, and at 3.30 (1H, dd, $J = 17.2$, 13.1 Hz) for H-3β. Particularly, in the UV spectrum, the absorption band II at 280 nm and band I at 340 nm were observed, which were strong evidence for flavanones. Two anomeric protons at δ 4.71 (1H, d, $J = 6.9$ Hz, H-1″) and δ 4.92 (1H, d, $J = 6.9$ Hz, H-1‴) demonstrated the

*Corresponding author. Email: peiyueh@vip.163.com

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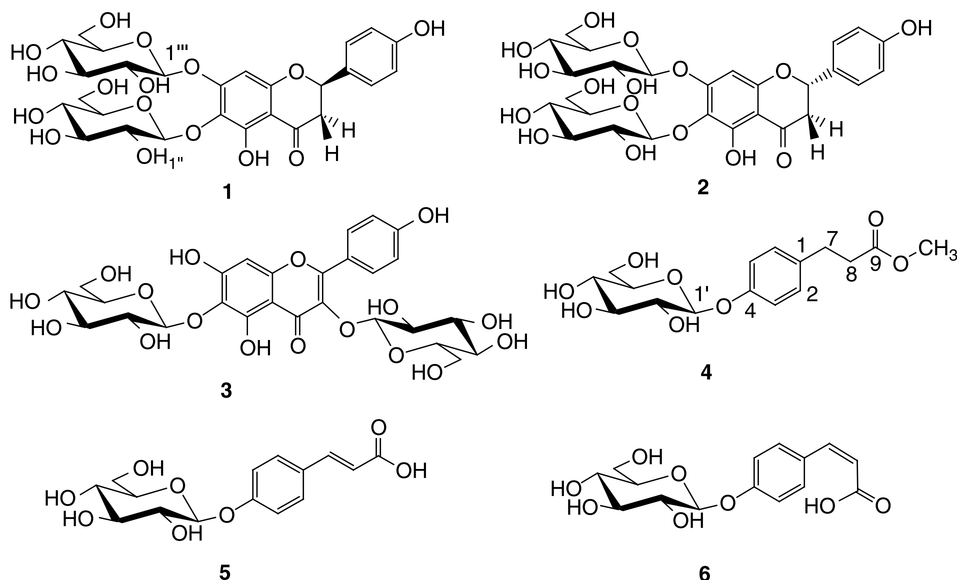

Figure 1. The structure of compounds **1**–**6**.

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presence of sugar moieties. Acid hydrolysis indicated the existence of glucose. The coupling constant ($J = 6.9$ Hz) of the anomeric protons indicated that the two glucosyl moieties exhibited a β-configuration. The above facts suggested that **1** should be a glucoside of flavanone. In the HMBC experiment of **1** (Figure 2), the correlations of H-1″ and C-6 as well as H-1‴ and C-7 confirmed that two glucosyl moieties were attached at C-6 and C-7, respectively. The absolute configuration at C-2 was determined as *R* by observing the CD spectrum, which displayed a negative Cotton effect at 345 nm and a positive Cotton effect at 290 nm.[12] On the basis of the above evidence, the structure of **1** was elucidate to be (2*R*)-4′,5-dihydroxyl-6,7-di-*O*-β-D-glucopyranosyl flavanone.

Compound **2** was isolated as a white amorphous powder. The ^{1}H NMR and ^{13}C

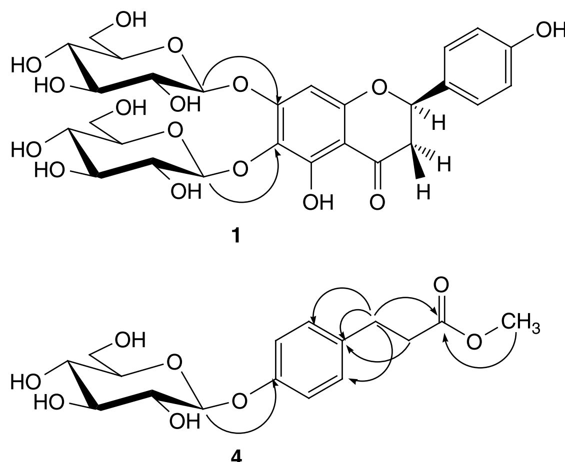

Figure 2. The key HMBC correlations of compounds **1** and **4**.

NMR data were very similar to those of **1**. But the absolute configuration at C-2 was determined as *S* by observing the CD spectrum, which displayed a positive Cotton effect at 345 nm and a negative Cotton effect at 290 nm. Furthermore, by comparison of their spectral data (^{1}H NMR and ^{13}C NMR) with those reported in the literature,[12] the structure of **2** was elucidated to be (2*S*)-4′,5-dihydroxyl-6,7-di-*O*-β-D-glucopyranosyl flavanone.

Compound **4** was isolated as a white amorphous powder. The molecular formula was determined to be $C_{16}H_{22}O_8$ by HR-FABMS (*m/z* 343.1393 [M + H]$^+$). The IR spectrum of **4** showed absorption bands at 3426, 1732, 1560, and 1458 cm^{-1}, suggesting the presence of hydroxyl group, ester carbonyl group, and aromatic rings. The ^{1}H NMR spectrum of **4** showed signals assignable to a *p*-substituted benzene ring at δ 6.93 (2H, d, $J = 8.4$ Hz) and 7.13 (2H, d, $J = 8.4$ Hz), two methylenes at δ 2.59 (2H, t, $J = 7.8$ Hz, H-8), 2.79 (2H, t, $J = 7.8$ Hz, H-7), indicating the existence of a —CH_2-—CH_2— unit, and a methoxyl at δ 3.57 (3H, s). Acid hydrolysis indicated the existence of glucose, which was confirmed from the anomeric proton at δ 4.80 (1H, d, $J = 7.5$ Hz, H-1′) and the corresponding carbon signal for the anomeric carbon at δ 100.6 (C-1′). The coupling constant ($J = 7.5$ Hz) of the glucose anomeric proton indicated that the anomeric configuration was β-oriented. In the HMBC spectrum (Figure 2), the correlations of H-1′, H-6, and H-2 with C-4 suggested that the glucosyl was linked to C-4. The correlations of H-7 with C-1, C-2, and C-6, and H-8 with C-1 indicated that the —CH_2—CH_2— unit was linked to C-1. The correlations of H-7 and H-8 with the carbonyl carbon indicated that the carbonyl carbon (C-9) was attached to C-8 (δ 35.3). The correlation of methoxyl protons with the carbonyl carbon suggested that the CH_3O— was attached to C-9. On the basis of the above evidence, the structure of **4** was elucidated to be methyl-3-(4-*O*-β-D-glucopyranosylphenyl) propionate.

6-Hydroxykaempferol-3,6-di-*O*-β-D-glucopyranoside (**3**), 4-*O*-β-D-glucosyl-*trans*-*p*-coumaric acid (**5**), and 4-*O*-β-D-glucosyl-*cis*-*p*-coumaric acid (**6**) were identified by comparison of their spectral data (^{1}H NMR and ^{13}C NMR) with those reported in the literature.[13–15]

3. Experimental

3.1 General experimental procedures

Optical rotations were obtained on a Perkin–Elmer 241MC polarimeter. IR spectra were taken on a Bruker IFS-55 infrared spectrophotometer. UV spectra were obtained on a Shimadzu UV-260 spectrophotometer. The NMR data were recorded on Bruker AV-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) in DMSO-d_6 with TMS as the internal standard. The HR-FABMS data were obtained using the Micross Mass Autospec-UltimaE TOF mass spectrophotometer. Chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Factory, Qingdao, China), Sephadex LH-20 (Pharmacia), reversed-phase HPLC (Shimadzu LC-10A vp).

3.2 Plant material

Dried petals of *C. tinctorius*, cultivated in the Xinjiang Province of China, were bought from the Corporation of Traditional Chinese Medicine of Shenyang, China, in June 2005. A voucher specimen was identified by Professor Qi-shi Sun and has been deposited at the School of Traditional Chinese Medicine of Shenyang Pharmaceutical University, China (No. 6025).

3.3 Extraction and isolation

Dried petals (5 kg) of *C. tinctorius* were extracted three times with hot 95% EtOH, every time for 2 h, and the combined solution was concentrated *in vacuo* to a syrup (1200 g), followed by suspension in water. The suspension was extracted with petroleum ether, ethyl acetate, and *n*-butanol successively.

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Table 1. ^{13}C NMR spectral data of compounds **1,** **2** and **4** in DMSO-d_6 (150 MHz).

Position	1	2	4
1			133.8
2	78.9	78.9	129.2
3	42.4	42.4	116.2
4	197.7	197.7	160.0
5	154.6	154.8	116.2
6	127.1	127.0	129.2
7	158.1	158.2	29.5
8	94.9	94.9	35.2
9	158.5	158.6	172.8
9-OCH_3			51.4
10	103.5	103.5	
1′	128.6	128.8	100.6
2′	128.6	128.6	73.3
3′	115.3	115.3	77.1
4′	157.9	157.9	69.8
5′	115.3	115.3	76.7
6′	128.6	128.6	60.8
1″	103.8	103.9	
2″	73.4	73.4	
3″	76.4	76.4	
4″	69.7	69.7	
5″	77.2	77.3	
6″	60.7	60.7	
1‴	100.7	100.7	
2‴	74.2	74.2	
3‴	76.4	76.4	
4‴	69.8	69.9	
5‴	77.2	77.3	
6‴	60.9	60.9	

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The *n*-butanol fraction (200 g) was further chromatographed over a D101 macroporous resin column eluted with H_2O, 30, 70, and 95% EtOH gradually. The fraction (60 g) eluted with 30% EtOH was subjected to silica gel column chromatography (eluted with $CHCl_3$ and MeOH in increasing polarity) to obtain nine fractions (I–IX). Fraction IV was purified using Sephadex LH-20 column chromatography and preparative HPLC to obtain compounds **1** (10 mg), **2** (25 mg), **3** (50 mg), **4** (12 mg), **5** (29 mg), and **6** (18 mg).

3.3.1 (2R)-4′,5-Dihydroxyl-6,7-di-O-β-D-glucopyranosyl flavanone (1)

Yellow gummy material, $[\alpha]_D^{25}$ − 21.6 (MeOH). IR (KBr) ν_{max} (cm^{-1}) 1650, 3363, 1075; UV (nm) 280, 340; ^{1}H NMR (DMSO-d_6) δ: 7.33 (2H, d, $J = 8.4$ Hz, H-2′ and H-6′), 6.80 (2H, d, $J = 8.4$ Hz, H-3′ and H-5′). 6.37 (1H, s, H-8), 11.95 (OH-5), 5.48 (1H, dd, $J = 13.1$, 2.4 Hz, H-2α), 2.70 (1H, dd, $J = 17.2$, 2.4 Hz, H-3α), 3.30 (1H, dd, $J = 17.2$, 13.1 Hz, H-3β). 4.71 (1H, d, $J = 6.9$ Hz, H-1″), 4.92 (1H, d, $J = 6.9$ Hz, H-1‴); ^{13}C NMR spectral data, see Table 1; HR-FABMS *m/z*: 613.1780 $[M + H]^+$ (calcd for $C_{27}H_{33}O_{16}$, 613.1769).

3.3.2 Methyl-3-(4-O-β-D-glucopyranosylphenyl) propionate (4)

White amorphous powder, $[\alpha]_D^{25}$ − 25.8 (MeOH). IR (KBr) ν_{max} (cm^{-1}) 1585, 1490; ^{1}H NMR (DMSO-d_6) δ: 7.13 (2H, d, $J = 8.4$ Hz, H-2 and H-6), 6.93 (2H, d, $J = 8.4$ Hz, H-3 and H-5), 2.59 (2H, t, $J = 7.8$ Hz, H-8), 2.79 (2H, t, $J = 7.8$ Hz, H-7), 3.57 (3H, s, 9-OCH_3), 4.80 (1H, d, $J = 7.5$ Hz, H-1′); ^{13}C NMR spectral data, see Table 1; HR-FABMS *m/z*: 343.1405 $[M + H]^+$ (calcd for $C_{16}H_{23}O_8$, 343.1393).

3.4 Acid hydrolysis of 1 and 4

Compound **1** (5 mg) was refluxed with 2 N HCl in aqueous MeOH (5 ml) for 8 h. The reaction mixture was diluted with water (10 ml) and extracted with EtOAc. The aqueous part was neutralized with a saturated solution of Na_2CO_3 and filtered. The filtrate was concentrated under reduced pressure and examined for sugar identification on PC with an authentic sample of glucose. The methods of acid hydrolysis of **4** were the same as that of **1**.

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