Five New Aromatic Glycosides from *Carthamus tinctorius*

by **Yu-Zhi Zhou**, **Huan Chen**, **Li Qiao**, **Xuan Lu**, **Hui-Ming Hua**, and **Yue-Hu Pei***

School of Traditional Chinese Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, P. R. China

(phone and fax: +86-24-23986485; e-mail: peiyueh@vip.163.com)

Five new aromatic glycosides, **1**–**5**, named as carthamosides B_4–B_8, together with three known compounds, 4′-(hydroxyphenacyl)-β-D-glucopyranoside (**6**), benzyl-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**7**), and 4-(methoxybenzyl)-*O*-β-D-glucopyranoside (**8**), have been isolated from the air-dried flower of *Carthamus tinctorius*. Their structures were identified on the basis of chemical and spectroscopic methods.

Introduction. – The dried flower of safflower, *Carthamus tinctorius* L. (Asteraceae) is a traditional Chinese medicine widely used in China, having the function of promoting blood circulation by removing blood stasis [1]. The chemical constituents of this plant have been examined, and the isolation of flavonoids [2][3], polyacetylenes [4], serotonin derivatives [5], steroids [6], lignans [7][8], alkane diols [9][10], and a chalcone derivative [11] have been reported. During the course of our phytochemical investigation, five new aromatic glycosides, together with three known aromatic glycosides (*Fig. 1*), were isolated from *C. tinctorius*. Here, we describe the isolation and structure characterization of these compounds.[1])

Results and Discussion. – Carthamoside B_4 (**1**) was obtained as a yellow oil with a negative optical rotation value ($[\alpha]_D^{25} = -16.8$ in MeOH). Its molecular formula of $C_{22}H_{34}O_{13}$ was determined by HR-FAB-MS (*m*/*z* 507.2080 ($[M+H]^+$, calc. 507.2077)). The structure of **1** was established as (1*R*)-2-hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl 6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranoside by analysis of ^{1}H- and ^{13}C-NMR, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*).

The ^{1}H-NMR spectrum of **1** showed three aromatic H-atoms forming an *ABX* system at δ(H) 6.63 (br. *d*, *J* = 7.8, 1 H), 6.65 (*d*, *J* = 7.8, 1 H) and 6.87 (br. *s*, 1 H), a MeO signal at δ(H) 3.74, nonequivalent CH_2 H-atoms at δ(H) 2.66 (*dd*, *J* = 13.8, 6.0, 1 H) and 2.72 (*dd*, *J* = 13.8, 6.0, 1 H), an oxymethine H-atom signal at δ(H) 3.67–3.71 (*m*, 1 H), nonequivalent CH_2O H-atoms at δ(H) 3.31 (*dd*, *J* = 11.3, 5.0, 1 H) and 3.39 (*dd*, *J* = 11.3, 5.0, 1 H), respectively. Acid hydrolysis indicated the presence of D-glucose and L-rhamnose, which was confirmed by two anomeric H-atoms at δ(H) 4.20 (*d*, *J* = 7.8, H–C(1″), 1 H) and 4.57 (br. *s*, H–C(1‴), 1 H). The ^{13}C-NMR showed the presence of six aromatic C-atom signals at δ(C) 147.3, 144.7, 129.4, 121.7, 115.2, and 113.8, respectively, a MeO signal at δ(C) 55.6, an oxymethine C-atom signal at δ(C)

[1]) Arbitrary numbering. For systematic names, see *Exper. Part*.

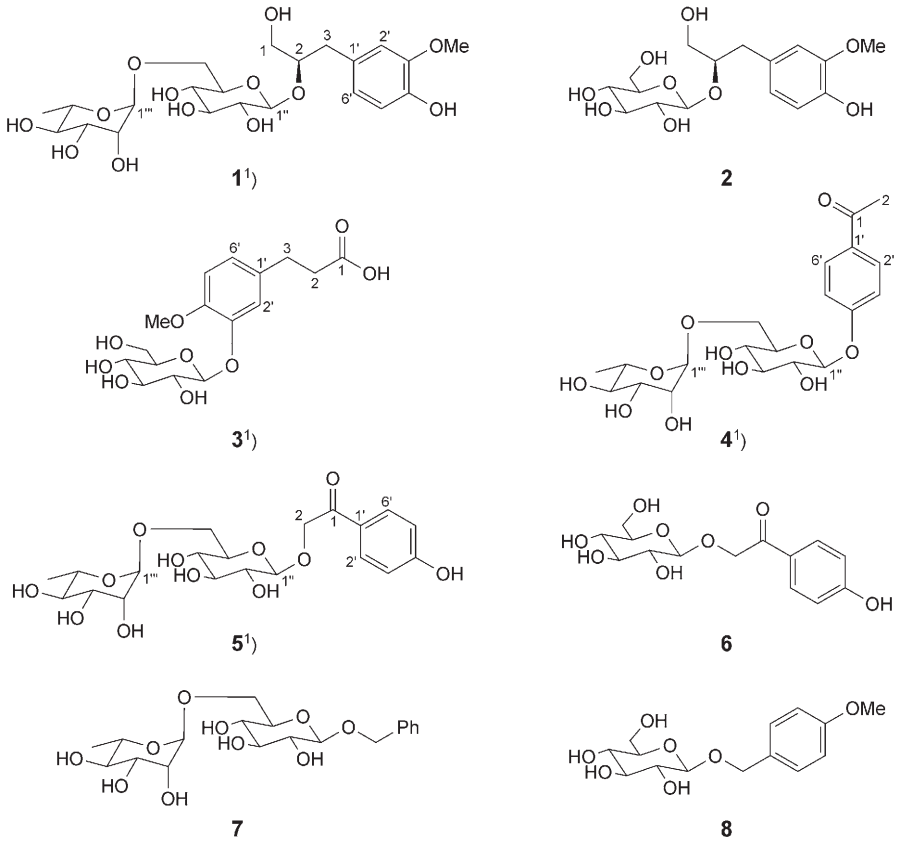

Fig. 1. *Structures of compounds* **1**–**8**

81.9, a CH_2O signal at δ(C) 63.2, and a signal for CH_2 at δ(C) 36.9. Two anomeric C-atoms at δ(C) 102.5 and 101.0, one CH_2 group at δ(C) 67.4, and one Me group at δ(C) 18.0, suggested that **1** possessed a glucopyranosyl and a rhamnopyranosyl unit.

The complete assignment of the H- and C-atom signals and the positions of the linkage of the sugar moieties in **1** were determined by HSQC, HMBC, and NOESY experiments. The cross peak in the NOESY experiment between H–C(2′) and the MeO H-atoms confirmed the pattern of substitution in the aromatic ring. In addition, in the HMBC spectrum of **1**, the long-range correlations between H–C(1″) and C(2), and between H–C(2) and C(1″) were observed, which indicated that the sugar moieties were linked to C(2) of the aglycone (see *Fig. 2*). The cross peaks between H–C(6″) and C(1‴) and between H–C(1‴) and C(6″) indicated the (1‴ → 6″) linkage of the disaccharide moiety.

Acid hydrolysis of **1** gave 3-(4-hydroxy-3-methoxyphenyl)propane-1,2-diol as the aglycone, which showed a positive optical rotation value ($[\alpha]_D^{25} = +22.6$ in MeOH). The configuration at C(2) of the aglycone was attributed by comparison of the optical rotation with that reported in the literature [12][13]. Consequently, the structure of **1**

Table 1. *^{1}H-NMR Spectral Data of Compounds* **1**–**5**[1]). In (D_6)DMSO at 600 MHz, δ in ppm, J in Hz.

Position	**1**	**2**	**3**	**4**	**5**
1	3.31 (*dd*, *J* = 11.3, 5.0), 3.39 (*dd*, *J* = 11.3, 5.0)	3.30 (*dd*, *J* = 11.3, 5.0), 3.38 (*dd*, *J* = 11.3, 5.0)			
2	3.67–3.71 (*m*)	3.73–3.76 (*m*)	2.47 (*td*, *J* = 7.8, 2.5)	2.54 (*s*)	4.78 (*d*, *J* = 15.9), 4.92 (*d*, *J* = 15.9)
3	2.66 (*dd*, *J* = 13.8, 6.0), 2.72 (*dd*, *J* = 13.8, 6.0)	2.67 (*dd*, *J* = 13.8, 6.0), 2.70 (*dd*, *J* = 13.8, 6.0)	2.72 (br. *t*, *J* = 7.8)		
2′	6.87 (br. *s*)	6.87 (br. *s*)	6.95 (br. *s*)	7.93 (*d*, *J* = 8.7)	7.93 (*d*, *J* = 8.4)
3′				7.10 (*d*, *J* = 8.7)	6.85 (*d*, *J* = 8.4)
5′	6.65 (*d*, *J* = 7.8)	6.64 (*d*, *J* = 7.8)	6.85 (*d*, *J* = 8.2)	7.10 (*d*, *J* = 8.7)	6.85 (*d*, *J* = 8.4)
6′	6.63 (br. *d*, *J* = 7.8)	6.62 (br. *d*, *J* = 7.8)	6.75 (br. *d*, *J* = 8.2)	7.93 (*d*, *J* = 8.7)	7.93 (*d*, *J* = 8.4)
MeO–C(3′)	3.74 (*s*)	3.74 (*s*)			
MeO–C(4′)			3.71 (*s*)		
COOH			12.01 (*s*)		
1″	4.20 (*d*, *J* = 7.8)	4.20 (*d*, *J* = 7.8)	4.86 (*d*, *J* = 7.2)	4.98 (*d*, *J* = 6.6)	4.30 (*d*, *J* = 7.8)
2″	2.98 (*dd*, *J* = 8.5, 3.8)	2.97 (*t*, *J* = 8.3)	3.15 (*t*, *J* = 8.8)	3.15 (*t*, *J* = 8.4)	3.02 (*t*, *J* = 7.8)
3″	3.12 (*t*, *J* = 8.8)	3.12 (*t*, *J* = 8.8)	3.24–3.27 (*m*)	3.27 (*t*, *J* = 8.8)	3.16 (*t*, *J* = 9.0)
4″	2.99 (*dd*, *J* = 9.0, 5.5)	3.02 (*t*, *J* = 8.8)	3.20–3.23 (*m*)	3.18 (*t*, *J* = 9.3)	3.05 (*t*, *J* = 8.7)
5″	3.26 (*dd*, *J* = 9.2, 7.2)	3.08 (*dd*, *J* = 9.7, 6.0)	3.23–3.25 (*m*)	3.43 (*dd*, *J* = 9.6, 6.6)	3.29 (*dd*, *J* = 9.0, 6.9)
6″	3.38 (*dd*, *J* = 10.8, 7.2), 3.80 (br. *d*, *J* = 10.2)	3.41 (*dd*, *J* = 11.4, 6.0), 3.65 (br. *d*, *J* = 11.4)	3.45 (*dd*, *J* = 11.0, 6.0), 3.63 (br. *d*, *J* = 11.0)	3.54 (*dd*, *J* = 10.8, 6.6), 3.80 (br. *d*, *J* = 10.8)	3.46 (*dd*, *J* = 10.8, 7.2), 3.81 (br. *d*, *J* = 10.8)
1‴	4.57 (br. *s*)			4.54 (br. *s*)	4.60 (br. *s*)
2‴	3.62–3.64 (*m*)			3.59–3.61 (*m*)	3.62–3.64 (*m*)
3‴	3.39–3.41 (*m*)			3.43–3.45 (*m*)	3.40–3.43 (*m*)
4‴	3.17 (*t*, *J* = 9.4)			3.29 (*t*, *J* = 9.4)	3.17 (*t*, *J* = 9.3)
5‴	3.41–3.43 (*m*)			3.45–3.47 (*m*)	3.41–3.43 (*m*)
6‴	1.12 (*d*, *J* = 6.2)			1.10 (*d*, *J* = 6.3)	1.12 (*d*, *J* = 6.3)

Table 2. *^{13}C-NMR Spectral Data of Compounds* **1**–**5**. In (D_6)DMSO at 150 MHz, δ in ppm.

Position	**1**	**2**	**3**	**4**	**5**
1	63.2	63.1	174.0	196.6	193.9
2	81.9	81.2	35.5	26.6	70.5
3	36.9	36.7	30.0		
1′	129.4	129.4	133.4	131.0	126.3
2′	113.8	113.9	115.6	130.4	130.7
3′	147.3	147.3	146.4	116.0	115.4
4′	144.7	144.7	147.3	161.1	162.5
5′	115.2	115.2	112.6	116.0	115.4
6′	121.7	121.8	121.3	130.4	130.7
*Me*O–C(3)	55.6	55.6			
*Me*O–C(4)			55.8		
1″	102.5	102.2	100.0	100.8	102.7
2″	73.5	73.7	73.3	73.2	73.4
3″	76.5	76.9	77.0	76.6	76.6
4″	70.4	70.3	69.8	70.0	70.1
5″	75.3	76.8	77.0	75.8	75.7
6″	67.4	61.3	60.7	66.7	67.2
1‴	101.0			99.9	101.0
2‴	70.4			70.6	70.8
3‴	70.7			70.8	70.6
4‴	72.1			72.1	72.1
5‴	68.4			68.5	68.5
6‴	18.0			17.9	18.0

was established to be (1*R*)-2-hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl 6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranoside.

Carthamoside B_5 (**2**) was obtained as yellow oil, with a negative optical rotation value ($[\alpha]_D^{25} = -8.2$ in MeOH). Its molecular formula of $C_{16}H_{24}O_9$ was determined by HR-FAB-MS (*m*/*z* 361.1498 ($[M + H]^+$; calc. 361.1499)). The structure of **2** was established as (1*R*)-2-hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl β-D-glucopyranoside by analysis of ^{1}H- and ^{13}C-NMR, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*).

The ^{1}H-NMR spectrum of **2** showed three aromatic H-atoms forming an *ABX* system at δ(H) 6.62 (br. *d*, *J* = 7.8, 1 H), 6.64 (*d*, *J* = 7.8, 1 H), and 6.87 (br. *s*, 1 H), a MeO signal at δ(H) 3.74, nonequivalent CH_2 H-atoms at δ(H) 2.67 (*dd*, *J* = 13.8, 6.0, 1 H) and 2.70 (*dd*, *J* = 13.8, 6.0, 1 H), an oxymethine H-atom signal at δ(H) 3.73–3.76 (*m*, 1 H), nonequivalent CH_2O H-atoms at δ(H) 3.30 (*dd*, *J* = 11.3, 5.0, 1 H), and 3.38 (*dd*, *J* = 11.3, 5.0, 1 H), respectively. Acid hydrolysis indicated the existence of the D-glucose, which was confirmed by the anomeric H-atom at δ(H) 4.20 (*d*, *J* = 7.8, H–C(1″), 1 H) and the corresponding C-atom at δ(C) 102.2. The ^{13}C-NMR showed the presence of six aromatic C-atom signals at δ(C) 147.3, 144.7, 129.4, 121.8, 115.2, and 113.9, respectively, a MeO C-atom signal at δ(C) 55.6, an oxymethine C-atom signal at δ(C) 81.2, a CH_2O signal at δ(C) 63.1, and a CH_2 C-atom signal at δ(C) 36.7.

The complete assignment of the H- and C-atom signals and the position of the linkage of the sugar moiety in **2** were determined by the HSQC and HMBC experiments (*Fig. 2*).

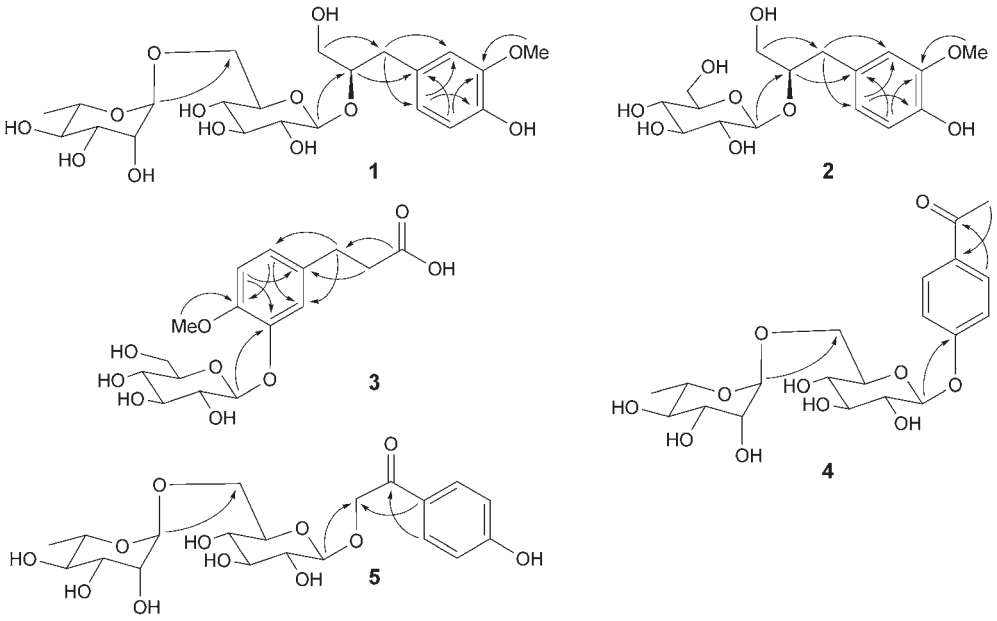

Fig. 2. *Key HMBC correlations of compounds* **1**–**5**

The determination of the configuration at C(2) of **2** was the same as that of **1**. Consequently, the structure of **2** was established to be (1*R*)-2-hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl β-D-glucopyranoside.

Carthamoside B_6 (**3**) was obtained as a white powder with a negative optical rotation value ($[\alpha]_D^{25} = -40.0$ in MeOH). Its molecular formula of $C_{16}H_{22}O_9$ was determined by HR-FAB-MS (*m*/*z* 359.1346 ($[M+H]^+$, calc. 359.1342)). The structure of **3** was established as 3-(β-D-glucopyranosyloxy)-4-methoxybenzenepropanoic acid by analysis of ^{1}H- and ^{13}C-NMR, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*).

The ^{1}H-NMR spectrum of **3** showed three aromatic H-atoms forming an *ABX* system at δ(H) 6.75 (br. *d*, $J = 8.2$, 1 H), 6.85 (*d*, $J = 8.2$, 1 H), and 6.95 (br. *s*, 1 H), a MeO signal at δ(H) 3.71, two CH_2 signals at δ(H) 2.47 (*td*, $J = 7.8$, 2.5, 2 H) and 2.72 (br. *t*, $J = 7.8$, 2 H), respectively, a H-atom of a carboxylic acid at δ(H) 12.01 (*s*, 1 H). Acid hydrolysis indicated the existence of D-glucose, which was confirmed by the anomeric H-atom at δ(H) 4.86 (*d*, $J = 7.2$, H–C(1″)) and the corresponding C-atom at δ(C) 100.0. The ^{13}C-NMR showed the presence of a CO signal at δ(C) 174.0, six aromatic C-atom signals at δ(C) 147.3, 146.4, 133.4, 121.3, 115.6, and 112.6, respectively, two CH_2 signals at δ(C) 30.0 and 35.5, and a MeO signal at δ(C) 55.8.

The complete assignment of the H- and C-atom signals and the position of the linkage of the sugar moiety in **3** were determined by the HSQC and HMBC experiments (see *Fig. 2*). The HMBC spectrum of **3** showed long-range correlations between H–C(2′) and C(1′), C(6′), C(3′), and C(4′), between H–C(5′) and C(1′) and C(3′), between H–C(6′) and C(2′) and C(4′), between the MeO H-atoms and C(4′), which indicated that the MeO group was linked to C(4′). In addition, the cross peaks

between H−C(1″) and C(3′) indicated that the glucose unit was linked to C(3′). Consequently, the structure of **3** was established to be 3-[3-(β-D-glucopyranosyloxy)-4-methoxybenzene]propanoic acid.

Carthamoside B_7 (**4**) was obtained as a white powder with a negative optical rotation value ($[\alpha]_D^{25} = -63.5$ in MeOH). Its molecular formula of $C_{20}H_{28}O_{11}$ was determined by HR-FAB-MS (*m/z* 445.1712 ($[M+H]^+$, calc. 445.1710)). The structure of **4** was established as 1-(4-{[6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranosyl]-oxy}phenyl)ethanone by analysis of ^{1}H- and ^{13}C-NMR, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*).

The ^{1}H-NMR spectrum of **4** showed signals assignable to a Me group at δ(H) 2.54 (*s*, 3 H), a *p*-substituted benzene ring (δ(H) 7.10 (*d*, *J* = 8.7, 2 H) and 7.93 (*d*, *J* = 8.7, 2 H)). Acid hydrolysis indicated the presence of D-glucose and L-rhamnose, which was confirmed by two anomeric H-atoms at δ(H) 4.98 (*d*, *J* = 6.6, H−C(1″)) and 4.54 (br. *s*, H−C(1‴)). The ^{13}C-NMR showed the presence of a CO group at δ(C) 196.6, six aromatic C-atom signals at δ(C) 161.1, 131.0, 130.4, 130.4, 116.0, and 116.0, respectively, and a MeO signal at δ(C) 26.6. Two anomeric C-atoms at δ(C) 100.8 and 99.9, one CH_2O signal at δ(C) 66.7, and one MeO group at δ(C) 17.9 further suggested that **4** possessed a glucopyranosyl and a rhamnopyranosyl unit.

The complete assignment of the H- and C-atom signals and the position of the bond of the sugar moieties in **4** were determined by HSQC and HMBC experiments (see *Fig. 2*). The HMBC spectrum of **4** showed long-range correlations between H−C(2′) and H−C(6′) and CO, which indicated that the CO group was linked to C(1′); between the Me group and C(1′), which indicated that the Me group was linked to the CO group; between H−C(1″) and C(4′), which indicated that the sugar moieties were linked to C(4′) of the aglycone. The cross peaks in the HMBC experiment between H−C(6″) and C(1‴), and between H−C(1‴) and C(6″) indicated the (1‴ → 6″) linkage of the disaccharide moiety. Consequently, the structure of **4** was established to be 1-(4-{[6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranosyl]oxy}phenyl)ethanone.

Carthamoside B_8 (**5**) was obtained as a white powder with a negative optical rotation value ($[\alpha]_D^{25} = -35.8$ in MeOH). Its molecular formula of $C_{20}H_{28}O_{12}$ was determined by HR-FAB-MS (*m/z* 461.1665 ($[M+H]^+$, calc. 461.1659)). The structure of **5** was established as 2-{[6-*O*-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranosyl]-oxy}-1-(4-hydroxyphenyl)ethanone by analysis of ^{1}H- and ^{13}C-NMR, HSQC, and HMBC (*Tables 1* and *2*, and *Fig. 2*).

The ^{1}H-NMR spectrum of **5** showed signals assignable to nonequivalent CH_2O H-atoms at δ(H) 4.78 (*d*, *J* = 15.9, 1 H) and 4.92 (*d*, *J* = 15.9, 1 H); a *p*-substituted benzene ring (δ(H) 6.85 (*d*, *J* = 8.4, 2 H) and 7.93 (*d*, *J* = 8.4, 2 H)). Acid hydrolysis indicated the presence of D-glucose and L-rhamnose, which was confirmed by two anomeric H-atoms at δ(H) 4.30 (*d*, *J* = 7.8, H−C(1″)) and δ(H) 4.60 (br. *s*, H−C(1‴)). The ^{13}C-NMR showed the presence of a CO group at δ(C) 193.9, six aromatic C-atom signals at δ(C) 162.5, 130.7, 130.7, 126.3, 115.4, and 115.4, respectively, and a CH_2O signal at δ(C) 70.5. Two anomeric C-atoms at δ(C) 102.7 and 101.0, one CH_2O C-atom at δ(C) 67.2, and one Me group at δ(C) 18.0 suggested that **5** possessed a glucopyranosyl and a rhamnopyranosyl unit.

The complete assignment of the H- and C-atom signals and the position of the linkage of the sugar moieties in **5** were determined by the HSQC and HMBC

experiments (see *Fig. 2*). The HMBC spectrum of **5** showed long-range correlations between H–C(2′) and H–C(6′) and CO, which indicated that the CO group was linked to C(1′); between the CH_2O H-atoms and C(1′), which indicated that the CH_2O group was linked to the CO group; between H–C(1″) and C(2), which indicated that the sugar moieties were linked to C(2) of the aglycone. The cross peaks in the HMBC experiment between H–C(6″) and C(1‴) and between H–C(1‴) and C(6″) indicated the (1‴ → 6″) linkage of the disaccharide moiety. Consequently, the structure of **5** was established as 2-{[6-*O*-(6-deoxy-*α*-L-mannopyranosyl)-*β*-D-glucopyranosyl]oxy}-1-(4-hydroxyphenyl)ethanone.

The three known compounds 2-(hexopyranosyloxy)-1-(4-hydroxyphenyl)ethanone (**6**), phenylmethyl 6-*O*-(6-deoxy-*α*-L-mannopyranosyl)-*β*-D-glucopyranoside (**7**) and (4-methoxyphenyl)methyl *β*-D-glucopyranoside (**8**) were identified by comparison of their spectral data (^{1}H-NMR and ^{13}C-NMR) with those reported in the literature [14–16]. Compounds **6**–**8** were found for the first time in this plant.

The authors thank *Yi Sha* and *Wen Li* for the measurement of NMR spectra.

Experimental Part

General. L-Cysteine methyl ester hydrochloride (*Tokyo Chemical Industry Co. Ltd.*). Column chromatography (CC): Silica gel (SiO_2, 200–300 mesh; *Qingdao Marine Chemical Group, Co.*); *Sephadex LH-20* (*Pharmacia*); *D 101* resin (*Cangzhou Baoen Chemical Group, Co.*). GC Analysis: *Shimadzu GC-2010* gas chromatograph equipped with an H_2 flame ionization detector (Column: *DB-5*, 30 m × 0.25 mm, 0.25 μm; detection FID; carrier gas He; injection temp. 250°, detection temp. 280°, column temp.: 160° → 5°/min → 280°). Reversed-phase HPLC (*Shimadzu LC-8A vp*, *C18*, particle size 5 μm, column: 10 × 250 mm, flow rate: 4 ml/min, detection wavelength: 210 nm). Optical rotations: *Perkin-Elmer 241 MC* polarimeter. UV Spectra: *Hitachi 200-10* spectrophotometer; λ in nm (log ε); the spectra were measured in MeOH. IR Spectra: *Bruker IFS-55* IR spectrophotometer. NMR Spectra: *Bruker AV-600* spectrometer and *Bruker ARX-300* spectrometer, Me_4Si as internal standard, δ in ppm, J in Hz. HR-FAB-MS: *MicrossMass Autospec-UltimaETOF* mass spectrometer (matrix: *m*-nitrobenzyl alcohol).

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

Extraction and Isolation. Dried petals (5 kg) of *C. tinctorius* were extracted three times with 95% EtOH (50 l) under reflux, every time for 2 h, and the combined soln. was concentrated *in vacuo* to a syrup (1200 g), which was suspended in H_2O (5 l). The suspension was extracted successively with equal volumes of petroleum ether (PE), AcOEt, and BuOH. The BuOH fraction (200 g) was further chromatographed over a *D101* macroporous resin column eluted with H_2O, 30%, 70%, and 95% EtOH gradually. The fraction eluted with 30% EtOH (60 g) was subjected to SiO_2 CC (eluted with $CHCl_3$/MeOH, 100:1 → 1:1, *v*/*v*) to obtain nine fractions (*I*–*IX*). *Fr. V* was purified by *Sephadex LH-20* CC (eluted with MeOH), and further separated by SiO_2 CC (eluted with $CHCl_3$/MeOH, 100:7 → 100:20, *v*/*v*) to give six fractions (A_1–A_6). **8** (50 mg) was obtained from *Fr.* A_1 (MeOH/H_2O (43:57, *v*/*v*), t_R 15.1 min); **3** (26 mg) was obtained from *Fr.* A_2 (MeCN/H_2O (8:92, *v*/*v*), t_R 46.6 min); **2** (30 mg) and **6** (18 mg) were obtained from *Fr.* A_3 (MeOH/H_2O (20:80, *v*/*v*), t_R 25.1 and 17.5 min, resp.); **7** (20 mg) was obtained from *Fr.* A_4 (MeOH/H_2O (28:72, *v*/*v*), t_R 35.9 min); **1** (28 mg) and **4** (12 mg) were obtained from *Fr.* A_5 (MeCN/H_2O (8:92, *v*/*v*), t_R 6.5 and 4.8 min, resp.); **5** (10 mg) was obtained from *Fr.* A_6 (MeOH/H_2O (25:75, *v*/*v*), t_R 11.4 min), resp., by preparative HPLC.

Carthamoside B_4 (=*(1*R*)-2-Hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl 6*-O-*(6-Deoxy-α-*L*mannopyranosyl)-β-*D*-glucopyranoside*; **1**). Yellow oil. $[\alpha]_D^{25} = -16.8$ ($c = 0.018$, MeOH). UV: 281 (3.51), 227 (3.86), 206 (4.14). IR (KBr): 3391, 2924, 1652, 1558, 1517, 1455, 1130, 1052. ^{1}H-NMR (600 MHz, (D_6)DMSO): *Table 1*. ^{13}C-NMR (150 MHz, (D_6)DMSO): *Table 2*. HR-FAB-MS: 507.2080 ($[M+H]^+$, $C_{22}H_{35}O_{13}^+$; calc. 507.2077).

Carthamoside B_5 (=*(1*R*)-2-Hydroxy-1-[(4-hydroxy-3-methoxyphenyl)methyl]ethyl β-*D*-Glucopyranoside*; **2**). Yellow oil. $[\alpha]_D^{25} = -8.2$ ($c = 0.022$, MeOH). UV: 281 (3.35), 226 (3.80), 205 (4.09). IR (KBr): 3395, 2925, 1650, 1560, 1517, 1454, 1130, 1050. ^{1}H-NMR (600 MHz, (D_6)DMSO): *Table 1*. ^{13}C-NMR (150 MHz, (D_6)DMSO): *Table 2*. HR-FAB-MS: 361.1498 ($[M+H]^+$; $C_{16}H_{25}O_9^+$; calc. 361.1499).

Carthamoside B_6 (=*3-(β-*D*-Glucopyranosyloxy)-4-methoxybenzenepropanoic Acid*; **3**). White powder. $[\alpha]_D^{25} = -40.0$ ($c = 0.0025$, MeOH). UV: 280 (3.30), 227 (3.95), 206 (4.15). IR (KBr): 3400, 2920, 1705, 1600, 1508, 1042. ^{1}H-NMR (600 MHz, (D_6)DMSO): *Table 1*. ^{13}C-NMR (150 MHz, (D_6)DMSO): *Table 2*. HR-FAB-MS: 359.1346 ($[M+H]^+$, $C_{16}H_{23}O_9^+$; calc. 359.1342).

Carthamoside B_7 (=*1-(4-{[6-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranosyl]oxy}phenyl)-ethanone*; **4**). White powder. $[\alpha]_D^{25} = -63.5$ ($c = 0.0047$, MeOH). UV: 263 (3.69). IR (KBr): 3410, 2924, 1685, 1600, 1517, 1445, 1047. ^{1}H-NMR (600 MHz, (D_6)DMSO): *Table 1*. ^{13}C-NMR (150 MHz, (D_6)DMSO): *Table 2*. HR-FAB-MS: 445.1712 ($[M+H]^+$, $C_{20}H_{29}O_{11}^+$; calc. 445.1710).

Carthamoside B_8 (=*2-{[6-*O*-(6-Deoxy-α-*L*-mannopyranosyl)-β-*D*-glucopyranosyl]oxy}-1-(4-hydroxyphenyl)ethanone*; **5**). White powder. $[\alpha]_D^{25} = -35.8$ ($c = 0.0056$, MeOH). UV: 280 (3.89), 216 (3.76). IR (KBr): 3414, 2925, 1680, 1603, 1517, 1441, 1135, 1048. ^{1}H-NMR (600 MHz, (D_6)DMSO): *Table 1*. ^{13}C-NMR (150 MHz, (D_6)DMSO): *Table 2*. HR-FAB-MS: 461.1665 ($[M+H]^+$, $C_{20}H_{29}O_{12}^+$; calc. 461.1659).

Acid Hydrolysis of **1**–**5**. **1** (15 mg) was refluxed in 1N aq. HCl (15 ml) for 24 h. The reaction mixture was diluted with H_2O (15 ml) and extracted with AcOEt. The AcOEt part was concentrated under reduced pressure to obtain the aglycone (5.1 mg). The aq. part was neutralized with a sat. soln. of Na_2CO_3 and filtered. The filtrate was concentrated under reduced pressure, and examined for sugar identification on TLC with an authentic sample of sugar using the solvent system $CHCl_3$/MeOH/H_2O (65 : 35 : 10, *v*/*v*/*v*) and H_2SO_4/EtOH (5 : 95, *v*/*v*) soln. as spray reagent. R_f values of D-glucose and L-rhamnose were 0.25 and 0.42, resp. The methods of acid hydrolysis of **2**–**5**, sugar detection and the determination of configuration at C(2) of **2** were the same with that of **1**.

Determination of the Absolute Configurations of the Sugars in **1**–**5**. The sugars were obtained by acid hydrolysis as described above. The solid residues (1 mg) from the aq. phase were dissolved in pyridine (100 µl) and reacted with L-cysteine methyl ester hydrochloride (1.5 mg) at 60° for 1 h. An equal volume of Ac_2O was added, and heating was continued at 90° for another 1 h. After evaporation of pyridine and surplus Ac_2O by air-blowing, the residue was dissolved in acetone, and the soln. was subjected to GC. The configurations were determined by comparison of their t_R with acetylated thiazolidine derivatives synthesized from standard sugars (t_R(D-glucose) 25.55 min, t_R(L-rhamnose) 22.03 min) [17].

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Received December 4, 2007