Cartorimine, a New Cycloheptenone Oxide Derivative from *Carthamus tinctorius*

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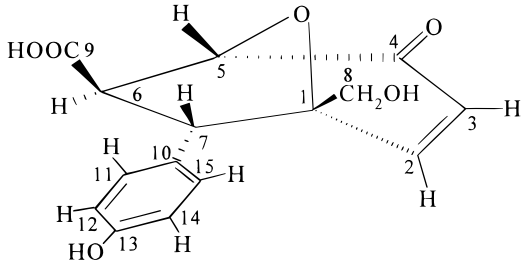
Cartorimine (**1**), a new cycloheptenone oxide derivative, was isolated from *Carthamus tinctorius*, and its structure was established from spectral data interpretation and single-crystal X-ray analysis.

Carthamus tinctorius L. (Compositae) is a widely used traditional Chinese medicine having the function of promoting blood circulation.[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 diols,[9,10] and coloring matter[11] have been reported. We now describe the isolation and structure elucidation of cartorimine (**1**), a new cycloheptenone oxide derivative obtained from the flower petals of *C. tinctorius*.



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Compound **1** was obtained as colorless prisms, mp 206−207 °C. HREIMS established a molecular formula of $C_{15}H_{14}O_6$, and its IR spectrum revealed the presence of alcoholic hydroxyl (3396 cm^{-1}), phenolic hydroxyl (3255 cm^{-1}), carboxyl (3100−2500, 1686 br, cm^{-1}), α,*β*-unsaturated ketone (1686 br, 1616 cm^{-1}, S-trans), and phenyl (1600, 1520 cm^{-1}) groups. The ^1H NMR spectrum (Table 1) of **1** showed the presence of the four aromatic protons of a *p*-hydroxyphenyl unit, two *cis*-olefinic protons, three methine groups, and two hydroxymethyl protons, respectively. The "long-range" coupling observed between H-3 and H-5 indicated that the bonds between them are W-shaped. The ^{13}C NMR spectrum (Table 1) of **1** exhibited 15 signals whose chemical shift values and multiplicity confirmed the presence of a carboxyl group, an α,*β*-unsaturated ketone, a *p*-hydroxyphenyl, and three oxygen-bearing carbons. The skeleton of **1** was deduced by observing the long-range correlations in the HMBC spectrum (Table 1), namely, C-1 to H-2, H-3, H-5 and H-7; C-2 to H-7; C-3 to H-5; C-4 to H-2, H-5, and H-6; C-5 to H-3 and H-6; C-6 to H-5 and H-7; C-7 to H-6. The presence of the cross-peaks between C-7 and H-11 indicated that the *p*-hydroxyphenyl was located at C-7; the presence of the cross-peaks between C-1 and H-8 and between C-9 and H-6 indicated that the hydroxymethyl and carboxyl groups were located at C-1 and C-6, respectively. The relative stereochemistry of **1** was determined by the NOESY NMR spectrum (Figure 1): the presence of the cross-peaks between H-8 and H-7 indicated that the hydroxymethyl and H-7 were cis to one another, and the presence of the cross-peaks between H-6 and H-11 indicated that H-6 and H-7 were in a trans orientation. The structure of **1** was proved unequivocally by single-crystal X-ray diffraction analysis. A view of the solid-state conformation is provided in Figure 2. Figure 2 shows that the bonds between H-3 and H-5 are W-shaped, which is the reason that the "long-range" coupling between them was observed in the ^1H NMR spectrum of **1**.

Table 1. NMR Data for **1** (400 Hz, in CD_3OD)[a]

position	^1H (*J* in Hz)	^{13}C[b]	HMBC
1		88.6 s	H-2, H-3, H-5, H-7, H-8
2	7.00 d (10.0)	155.5 d	H-7, H-8
3	6.40 dd (10.0, 1.5)	129.0 d	H-5
4		197.3 s	H-2, H-5, H-6
5	4.95 dd (1.5, 1.5)	85.3 d	H-3, H-6
6	3.42 dd (7.5, 1.5)	53.7 d	H-5, H-7
7	4.04 d (7.5)	53.6 d	H-6, H-8, H-11, H-15
8	4.01 d (12.5)	64.0 t	H-2, H-7
	3.90 d (12.5)		
9		176.0 s	H-5, H-6, H-7
10		127.9 s	H-6, H-7, H-12, H-14
11	7.27 dd (8.6, 2.0)	131.2 d	H-7, H-15
12	6.92 dd (8.6, 2.0)	116.7 d	H-14
13		158.5 s	H-11, H-12, H-14, H-15
14	6.92 dd (8.6, 2.0)	116.7 d	H-12
15	7.27 dd (8.6, 2.0)	131.2 d	H-7, H-11

[a] Assignments were made by $^1H-^1H$ COSY, HMQC, and HMBC data. [b] Multiplicity was established from DEPT data.

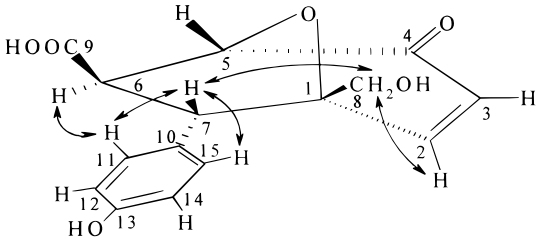

Figure 1. NOESY correlations of **1**.

Experimental Section

General Experimental Procedures. The melting point was determined on a Buchi 510 melting point apparatus. The $[\alpha]_D$ value was obtained on a DIP-181 digital polarimeter. The UV spectrum was recorded on a Cary 300 Bio spectrophotometer. The IR spectrum was recorded on a Nicolet 750 instrument. The NMR spectra were recorded on a Bruker AM-400 spectrometer with TMS as internal standard and CD_3OD as solvent. The HREIMS spectrum was obtained on a MAT-95

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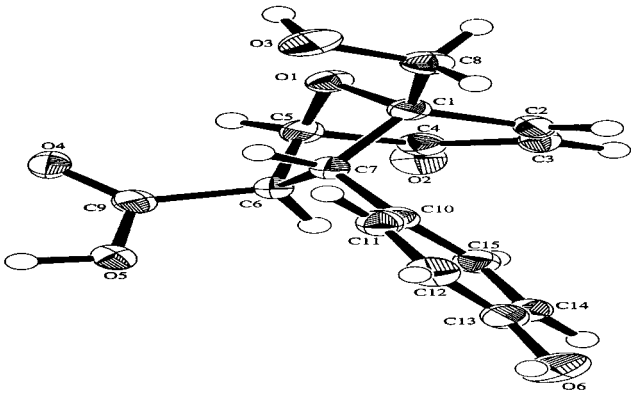

Figure 2. Perspective view of a molecule of **1**.

double-focusing spectrometer. Si gel 60 (Merck, 230−400 mesh) was used for column chromatography.

Plant Material. The flower petals of *C. tinctorius* were collected in Sichuan, People's Republic of China, and authenticated by Lan Xu at our institute. A voucher specimen (no. 77) has been deposited at Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Isolation and Purification. The air-dried flower petals (10 kg) were extracted with EtOH and partitioned with EtOAc followed by *n*-BuOH. The EtOAc fraction (95 g) was chromatographed over Si gel using $CHCl_3$ and $CHCl_3$−acetone mixtures of increasing polarity. Elution by $CHCl_3$-acetone (5:1) afforded fractions 11−12 containing compound **1**, which was purified by column chromatography over Si gel with $CHCl_3$−MeOH (25:1) as eluting solvent.

Cartorimine (**1**): 6 mg; colorless prisms from MeOH, mp 206−207 °C; $[\alpha]^{25}_D$ −2.6° (*c* 0.005, MeOH); UV (MeOH) λ_{max} (log ϵ) 225.5 (4.04) nm; IR (KBr) ν_{max} 3396, 3255, 3100−2500, 1686, 1616, 1600, 1520 cm^{-1}; ^1H and ^{13}C NMR, see Table 1; EIMS *m*/*z* 290 (17), 147 (17), 127 (100), 91 (7); HREIMS *m*/*z* 290.0789 (calcd for $C_{15}H_{14}O_6$, 290.0790).

Crystal data for 1: $C_{15}H_{14}O_6$, M = 290.27, colorless prismatic, 0.20 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/n$(#14), $T = 20 \pm 1$ °C, a = 11.585(2) Å, b = 9.033(1) Å, c = 13.235(2) Å, β = 111.134(9)°, V = 12291.9(3) $Å^3$, Z = 4, D = 1.492 g/cm^3, F_{000} = 608.00, μ(MoKα) = 1.16 cm^{-1}.

Data Collection and Structure Refinement. Intensities of 3301 reflections were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a 12-kW rotating anode generator using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 55.0° at a temperature of 20 ± 1 °C. Of these, 3153 were unique (R_{int} = 0.012). The structure was solved by direct methods[12] and expanded using Fourier techniques.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.25 and −0.18 $e^-/Å^3$, respectively. All calculations were performed using the teXsan[14] crystallographic software package of Molecular Structure Corporation.

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Supporting Information Available: X-ray crystallographic data for compound **1.** This material is available free of charge via the Internet at http://pubs.acs.org.

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