Pergamon

Tetrahedron Letters 41 (2000) 1955–1958

TETRAHEDRON LETTERS

A novel semi-quinone chalcone sharing a pyrrole ring *C*-glycoside from *Carthamus tinctorius*

Hong-Bin Yin and Zhi-Sheng He *

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 200031, China

Received 18 November 1999; accepted 11 January 2000

Abstract

Cartormin, a novel semi-quinone chalcone sharing a pyrrole ring *C*-glycoside, was isolated from *Carthamus tinctorius* L. and its structure was established from various spectral data and a single-crystal X-ray analysis.

Keywords: Carthamus tinctorius L.; compositae; semi-quinone chalcone; hydrogen bond; cartormin; *C*-glycoside.

Carthamus tinctorius L. (compositae) is a widely used traditional Chinese plant medicine having the function of promoting blood circulation by removing blood stasis. During the course of our investigation, cartormin (**1**, see Fig. 1), a novel semi-quinone chalcone sharing a pyrrole ring *C*-glycoside, was isolated from *Carthamus tinctorius* L. This paper describes the structure elucidation and provides the complete assignments of ^{1}H NMR and ^{13}C NMR data of **1** (see Table 1).

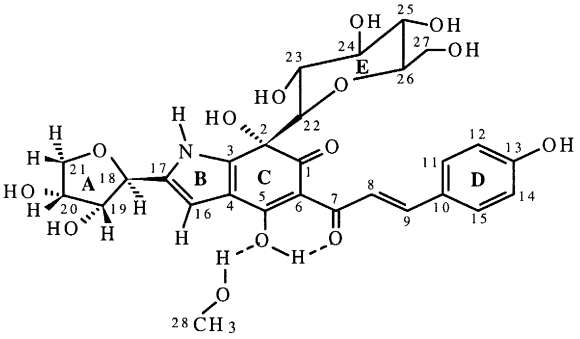


Fig. 1. Structure of **1**

Cartormin (**1**), yellow crystals from methanol, was obtained by repeated column chromatography on silica gel, macroporous resin and sephadex LH-20 from its polar fraction. Yield: 0.001%. Mp

* Corresponding author. Fax: +00 86 21 64370269; e-mail: zshe@mail.shcnc.ac.cn (Z.-S. He)

0040-4039/00/$ - see front matter
PII: S0040-4039(00)00100-3

Table 1
NMR data for **1** (400 MHz, in DMSO-d_6)[a]

Position	^{1}H (J in Hz)	^{13}C[b]	HMBC
1		196.2 (s)	OH-2
2		78.3 (s)	OH-2
3		142.2 (s)	OH-2, H-16
4		114.8 (s)	H-16, -NH-
5		185.7 (s)	
6		109.3 (s)	
7		180.4 (s)	H-8, H-9
8	7.36 d (15.8)	118.8 (d)	
9	7.65 d (15.8)	141.3 (d)	H-11, H-15
10		126.3 (s)	H-8, H-9, H-12, H-14
11	7.56 d (8.4)	130.6 (d)	H-8, H-9, H-15
12	6.84 d (8.4)	116.0 (d)	H-14
13		160.0 (s)	H-11, H-12, H-14, H-15
14	6.84 d (8.4)	116.0 (d)	H-12
15	7.56 d (8.4)	130.6 (d)	H-8, H-9, H-11
16	6.37 s	103.4 (d)	H-18, -NH-
17		135.0 (s)	H-16, -NH-
18	4.53 d (7.6)	76.6 (d)	H-21
19	4.06 m	76.0 (d)	H-18, H-21, OH-19
20	4.11 m	70.5 (d)	H-21
21	3.62 m	72.9 (t)	
	4.13 m		
22	3.29 d (9.5)	84.2 (d)	OH-2, H-23, OH-23
23	3.43 (overlap)	69.1 (d)	H-22, H-24
24	3.12 m	78.5 (d)	H-23, H-25
25	3.11 m	69.3 (d)	H-24
26	2.86 m	79.5 (d)	H-22
27	3.50 (overlap)	60.7 (t)	OH-27
28	4.11 m	48.7 (q)	

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

>230°C (decomp.). ESIMS: *m/z* 1151 $[2M+H]^+$ (MF: $C_{27}H_{29}NO_{13}$), 598 $[M+Na]^+$, 576 $[M+H]^+$, 414 $[(M+H)-Glc]^+$. Anal. $C_{27}H_{29}NO_{13}\cdot CH_3OH$; calcd: C, 55.34; H, 5.48; N, 2.31. Found: C, 55.31; H, 5.26; N, 2.58. $[\alpha]_D^{27}$ −153.4 (*c* 0.0123, py). The IR spectrum revealed the presence of a keto-enol system (1600–1640cm^{-1}) and hydroxyl groups which were due to sugar moieties [3400, 1070 (br) cm^{-1}], the ν_{C-N} absorption was found at 1269 cm^{-1}. Acetylation of **1** with acetic anhydride in pyridine afforded an octa-*O*-acetate (**1A**, see Fig. 2). The ^{1}H NMR spectrum (400 Hz, $CDCl_3$) of **1A** showed the presence of eight acetyl signals at δ_H: 1.82, 1.96, 2.01, 2.02, 2.06, 2.14, 2.18, 2.29, one hydroxyl signal at δ_H: 18.81 (1H, s, OH-5) and the -NH- signal of the pyrrole ring at δ_H: 10.67 (1H, s, -NH-). The ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **1** contained the following signals: an aromatic proton and a -NH- group of the pyrrole ring at δ_H: 6.37 (1H, s, H-16) and δ_H: 11.67 (1H, s, -NH-), respectively; four aromatic protons at δ_H: 7.56 (2H, d, *J*=8.4 Hz, H-11, H-15), 6.84 (2H, d, *J*=8.4 Hz, H-12, H-14), two *trans*-olefinic protons at δ_H: 7.36 (1H, d, *J*=15.8 Hz, H-8), 7.65 (1H, d, *J*=15.8 Hz, H-9) and a phenolic hydroxyl proton at δ_H: 10.08 (1H, s, OH-13); one β-*C*-erythrosyl anomeric proton resonated at δ_H: 4.53 (1H, d, *J*=7.6 Hz, H-18) and four sugar protons of the erythrosyl moiety were present at δ_H: 4.06 (1H, m, H-19), 4.11 (1H, m, H-20), 3.62 (1H, m, H-21), 4.13 (1H, m, H-21′); one β-*C*-glucosyl anomeric proton resonated at δ_H: 3.29 (1H, d, *J*=9.5 Hz, H-22) and six sugar protons of the glucosyl moiety were found at δ_H: 3.43 (1H, overlap, H-23), 3.12 (1H, m, H-24), 3.11 (1H, m, H-25), 2.86 (1H, m, H-26), 3.50 (2H, overlap, H-27, H-27′). In the HMBC spectrum of **1**, the presence of the cross peaks between C-16 (δ_C: 103.4) and H-18

indicated that rings A and B were connected via the C_{17}–C_{18} bond and the presence of the cross peaks between C-22 (δ_C: 84.2) and OH-2 indicated that rings C and E were connected via the C_2–C_{22} bond; at the same time, the presence of the cross peaks between C-1 (δ_C: 196.2) and OH-2, C-3 (δ_C: 142.2) and H-16, C-3 and OH-2, C-4 (δ_C: 114.8) and H-16, C-4 and -NH- proved that ring B shared the two unsaturated quaternary carbons C-3 and C-4 with ring C; the presence of the *p*-hydroxyl cinnamoyl unit was found by observing the cross peaks between C-7 (δ_C: 180.4) and H-9, C-11 (δ_C: 130.6) and H-9. The unusual downfield chemical shift of OH-5 (δ_H: 17.87, 1H, s) suggested that the two quaternary carbons C-5 (δ_C: 185.7) and C-6 (δ_C: 109.3) should be connected in the enol form with the carbonyl carbon C-7 (δ_C: 180.4) forming an internal hydrogen bond just like the keto-enol systems in tinctormine[1] isolated from the same plant and munchiwarin[2] isolated from *Crotalaria trifoliastrum*. A surprising feature of the spectrum of **1** was the detection of a methyl signal at δ_H: 3.17 and a hydroxyl signal at δ_H: 4.11 in the ^1H NMR spectrum and a methyl signal at δ_C: 48.7 in the ^{13}C NMR spectrum revealing the presence of one molecule of methanol in the crystal of **1**. The relative stereorelationship of **1** was confirmed by observing the cross peaks between OH-28 and H-16, OH-28 and OH-5, -NH- and OH-2, -NH- and H-18, H-16 and H-18 in the NOESY spectrum of **1**.

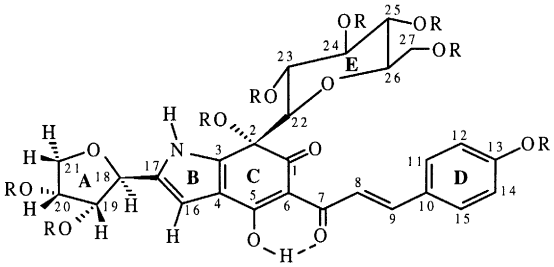


Fig. 2. Structure of **1A**: R=$COCH_3$

The structure of **1** was proved unequivocally by an X-ray crystallographic analysis.[3] A view of the solid-state conformation is provided in Fig. 3. Fig. 3 shows the internal hydrogen bonds: OH-5···O=C-7, the O···O distance is 2.40 Å; OH-28···O-C-5, the O···O distance is 2.75 Å. These two hydrogen bonds contributed simultaneously to the very downfield chemical shift of OH-5 (δ_H: 17.87, s).

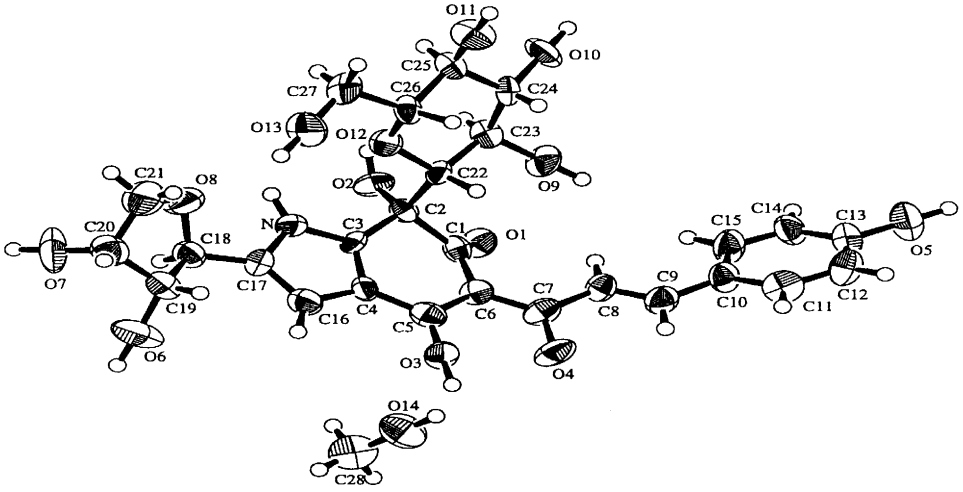


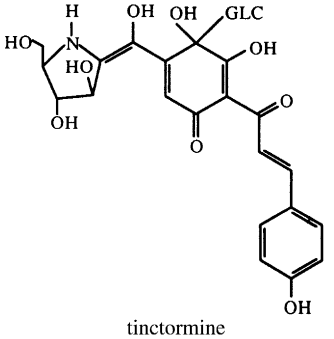
Fig. 3. Perspective view of a molecule of **1**

Acknowledgements

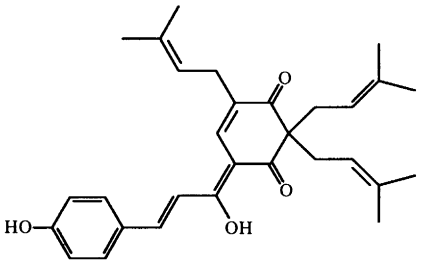
The authors wish to thank Sun-Jie (Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences) for the X-ray measurement.

References

1. Meselhy, R. M. *Chem. Pharm. Bull.* **1993**, *41*, 1796–1802.
2. Shu-Wei Yang. *J. Nat. Prod.* **1998**, *61*, 1274–1276.



tinctormine



munchuwarin

3. *Crystal data*. Empirical formula: $C_{28}H_{33}NO_{14}$; formula weight: M=607.57; crystal color, habit: yellow, prismatic; crystal dimensions: 0.20×0.20×0.30 mm; crystal system: orthorhombic; lattice type: primitive; no. of reflections used for unit cell determination (2θ range): 20 (13.7–21.4°); Omega scan peak width at half-height: 0.23°; lattice parameters: *a*=11.979(3) Å, *b*=29.256(3) Å, *c*=7.761(2) Å, *V*=2720.1(10) Å^3; space group: $P2_12_12_1$ (#19); Z value: 4; D*calc*: 1.483 g/cm^3; F_{000}: 1280.00; μ(MoKα): 1.20cm^{-1}. A total of 3574 reflections were measured on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation using the ω-2θ scan technique to a maximum 2θ value of 55.0° at a temperature of 20±1°C. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.