Asian Journal of Chemistry; Vol. 26, No. 14 (2014), 4515-4516

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16469

NOTE

A New Chromone from Stems of *Cassia fistula* and Its Anti-Tobacco Mosaic Virus Activities

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Received: 5 October 2013; *Accepted*: 25 March 2014; *Published online*: 5 July 2014; AJC-15509

A new chromone, 5-hydroxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one (**1**) was isolated from the stems of *Cassia fistula*. Its structure was elucidated by spectroscopic methods, including extensive 1D- and 2D-NMR techniques. Compound **1** was evaluated for its anti-tobacco mosaic virus (anti-TMV) activity. The results showed that **1** exhibit potential anti-TMV activity with inhibition rate of 16.8 %.

Keywords: *Cassia fistula*, Chromone, Anti-tobacco mosaic virus activity.

Cassia fistula L., (Leguminosae) is an ornamental tree with beautiful yellow flowers[1]. In China, it has been used as traditional Chinese medicine by people of Dai nationality (who lived in Xishuangbanna, Yunnan province) for treatment of diarrhea, gastritis, ringworm and fungal skin infections[2,3]. Previous phytochemical studies of *C. fistula* have shown the presence of anthraquinones[4,5], steroids[6], chromones[7,8] and flavonoids[9]. Motivated by a search for new bioactive metabolites from this plant, our group has investigated the chemical constituents of the bark and stem of *C. fistula*, which led to the isolation and characterization of a new chromone (Fig. 1). This paper deals with the isolation, structural characterization and anti-tobacco mosaic virus (anti-TMV) activities of this compound.

UV spectra were obtained on a Shimadzu UV-2401A spectrophotometer. A Tenor 27 spectrophotometer was used for scanning IR spectroscopy with KBr pellets. 1D and 2D NMR spectra were recorded on a DRX-500 NMR spectrometer with TMS as internal standard. Unless otherwise specified, chemical shifts (d) are expressed in ppm with reference to the solvent signals. HRESIMS was performed on a VG Autospec-3000 spectrometer. Semipreparative HPLC was performed on a Shimadzu LC-8A preparative liquid chromatograph with Zorbax PrepHT GF (21.2 mm × 25 cm) or Venusil MP C18 (20 mm × 25 cm) columns. Column chromatography was performed using silica gel (200-300 mesh, Qing-dao Marine Chemical, Inc., Qingdao, People's Republic of China), Lichroprep RP-18 gel (40-63 μm, Merck, Darmstadt, Germany) and MCI gel (75-150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan). The fractions were monitored by TLC and spots were visualized by heating silica gel plates sprayed with 5 % H_2SO_4 in EtOH.

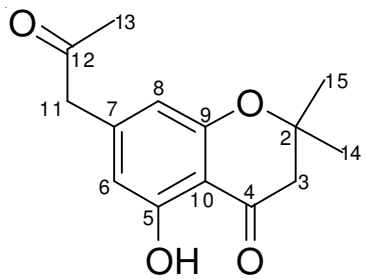

Fig. 1. Structure of compound **1**

The stems of *C. siamea* were collected in Honghe prefecture of Yunnan Province, People's Republic of China, in September 2012. The identification of plant material was verified by Prof. Ning Yuan. A voucher specimen (Ynni-12-09-64) has been deposited in our Laboratory.

Extraction and isolation: The air-dried and powdered *C. siamea* (2.8 kg) were extracted four times with 70 % aqueous acetone (4 × 3 L) at room temperature and filtered. The filtrate was evaporated under reduced pressure and the crude extract (71.8 g) was decolorized by MCI. The 90 % methanol part (31.2 g) was chromatographed on a silica gel column eluting with a chloroform-acetone gradient system (20:1, 9:1, 8:2, 7:3, 6:4, 5:5), to give six fractions A-F. The further separation of fraction B (9:1, 6.42 g) by silica gel column chromatography, eluted with petroleum ether-acetone (9:1-1:2), yielded mixtures

B1-B6. Fraction B3 (7:3, 0.97 g) was subjected to silica gel column chromatography using petroleum ether-acetone and semi-preparative HPLC (60 % MeOH-H_2O, flow rate 12 mL/min) to give **1**.

5-Hydroxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one (1): Obtained as pale yellow oil; UV (MeOH), λ_{max} (log e) 210 (4.35), 260 (3.82), 352 (3.18) nm; IR (KBr, ν_{max}, cm^{-1}) 3435, 2920, 2873, 1718, 1662, 1608, 1553, 1435, 1357, 1145, 924, 835; ^1H NMR and ^{13}C NMR data ($CDCl_3$, 500 and 125 MHz), in Table-1; Negative ESIMS *m/z* 247 $[M-H]^-$; negative HRESIMS *m/z* 247.2673 $[M-H]^-$ (calcd. for $C_{14}H_{16}O_4$, 247.2665).

TABLE-1
^{1} H AND ^{13}C NMR DATA OF COMPOUND **1**

No.	δ_C (m)	δ_H (m, *J*, Hz)
2	80.2 s	
3	47.6 t	2.64 s
4	192.4 s	
5	161.8 s	
6	115.0 d	6.72 (d) 1.8
7	143.5 s	
8	110.0 d	6.64 (d) 1.8
9	155.8 s	
10	113.4 s	
11	49.2 t	4.15 s
12	206.5 s	
13	30.6 q	2.36 s
14,15	25.8 q	1.54 s
Ar-OH		10.82 s

Compound **1** was obtained as pale yellow oil. It gives a parent ion by HR-ESIMS at *m/z* 247.2673 $[M - H]^-$ (Calcd. for 247.2665) corresponding to a molecular formula of $C_{14}H_{16}O_4$, requiring seven degrees of unsaturation. The ^1H and ^{13}C NMR spectrum of 1 along with analysis of the DEPT spectra (Table-1) displayed 14 carbon and 16 proton signals, respectively, corresponding to a chromone nucleus[10] [δ_C 80.2 s, 47.6 t, 192.4 s, 161.8 s, 115.0 d, 143.5 s, 110.0 d, 155.8 s, 113.4 s, 25.8 q (2C); δ_H 2.64 s, 6.72 (d) *J* = 1.8, 6.64 (d) *J* = 1.8 and 1.54 s], an 2-oxopropyl group (-$CH_2C(O)CH_3$) 11, 12, 13 (δ_C 49.2 t, 206.5 s, 30.6 q; δ_H 4.15 s, 2.36 s) and a phenolic hydroxy group (δ_H 10.82 s). Strong absorption bands accounting for hydroxy (3435 cm^{-1}), carbonyl group (1718, 1662 cm^{-1}) and aromatic groups (1608, 1553, 1435 cm^{-1}) could also be observed in its IR spectrum. The UV spectrum of **1** showed absorption maxima at 253, 260 and 210 nm, which confirmed the existence of the aromatic functions. The HMBC correlations (Fig. 2) of H-11 (δH 4.15) with C-6 (δ_C 115), C-7 (δ_C 143.5) and C-8 (δ_C 110), of H-6 (δ_H 6.72) and H-8 (δ_H 6.64) with C-11 (δ_C 49.2), indicated that the 2-oxopropyl group should be located at C-7 on the chromone ring. The phenolic hydroxy group located at C-5 was supported by the HMBC correlation of the hydroxy proton (δ_H 10.82) with C-5 (δ_C 161.8), C-6 (δ_C 115) and C-10 (δ_C 113.4). Thus, the structure of **1** was established as 5-hydroxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one.

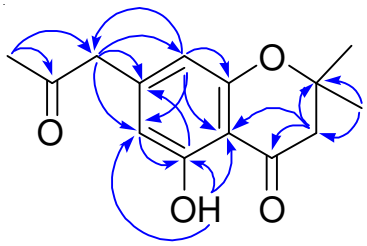

Fig. 2. Key HMBC correlations (↷) of **1**

Since certain of the chromone derivatives exhibit potential anti-TMV activities[11,12] compound **1** was tested for its anti-TMV activity. The inhibitory activities of **1** against TMV replication were tested using the half-leaf method[12]. Ningnanmycin, a commercial product for plant disease in China, was used as a positive control. The result showed that compound **1** exhibited inhibition rates of 16.8 %.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (No. 21302164), the excellent Scientific and Technological Team of Yunnan High School (2010CI08), the Yunnan University of Nationalities Green Chemistry and Functional Materials Research for Provincial Innovation Team (2011HC008) and Open Research Fund Program of Key Laboratory of Ethnic Medicine Resource Chemistry (Yunnan University of Nationalities) (2010XY08).

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