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NOTE

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

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A new chromone 8-methoxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one (**1**) was isolated from the stems of *Cassia fistula*. Its structures 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 compound **1** exhibit potential anti-TMV activity with inhibition rates of 23.5 %.

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 (**1**). This paper deals with the isolation, structural characterization and their anti-tobacco mosaic virus (anti-TMV) activities of this new 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 (δ) 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 C_{18} (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.

The stems of *C. siamea* were collected in Dehong prefecture ofYunnan Province, People's Republic of China, in September 2012. The identification of plant material was verified by Prof. Ning Yuan. A voucher specimen (Ynni-12-09-66) has been deposited in our Laboratory.

Extraction and isolation: The air-dried and powdered *C. siamea* (1.8 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 (55.8 g) was decolorized by MCI. The 90 % methanol part (22.5 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 B2 (8:2, 0.82 g) was subjected to silica gel column chromatography using petroleum ether-acetone and semi-preparative HPLC (65 % MeOH-H_2O, flow rate 12 mL/min) to give compound **1** (8.5 mg).

Anti-TMV Assays: The anti TMV activities were tested using the half-leaf method[10,11] and ningnanmycin, a commercial product for plant disease in China, was used as a positive control.

8-Methoxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one (1): Obtained as pale yellow oil; UV (MeOH) max (log ε) 210 (4.27), 260 (3.82), 355 (3.11) nm; IR (KBr, ν_{max}, cm^{-1}) 3432, 2927, 2874, 1722, 1668, 1608, 1553, 1437, 1352, 1164, 920, 872; ^1H NMR and ^{13}C NMR data ($CDCl_3$, 500 and 125 MHz) in Table-1; positive ESIMS *m/z* 285 $[M + Na]^+$; positive HRESIMS *m/z* 285.1100 $[M + Na]^+$ (Calcd. for $C_{15}H_{18}NaO_4$, 285.1103).

TABLE-1
^1H AND ^{13}C NMR DATA OF COMPOUND **1** (δ in ppm, in $CDCl_3$)

No.	δ_C (m)	δ_H (m, J, Hz)	No.	δ_C (m)	δ_H (m, J, Hz)
2	79.3 s		9	148.1 s	
3	48.6 t	2.68 s	10	118.0 s	
4	192.2 s		11	49.3 t	4.16 s
5	122.6 d	7.46 (d) 8.6	12	206.8 s	
6	120.8 d	6.87 (d) 8.6	13	30.4 q	2.33 s
7	131.4 s		14,15	25.7 q	1.62 s
8	151.7 s		5-OMe	60.8 q	3.81 s

The stems of *C. siamea* were extracted with 70% aqueous acetone. The extract was subjected repeatedly to column chromatography on silica gel, RP-18 and semi-preparative RP-HPLC separation to afford compound **1**. Its structure was shown in Fig. 1. The ^1H NMR and ^{13}C NMR data of compound **1** were listed in Table-1.

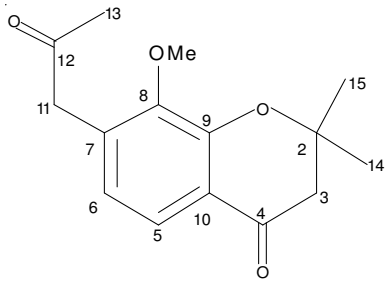

Fig. 1. Structure of compound **1**

Compound **1** was obtained as pale yellow oil. It gives a parent ion by HRESIMS at *m/z* 285.1100 $[M + Na]^+$ (Calcd. for 285.1103) corresponding to a molecular formula $C_{15}H_{18}O_4$, requiring seven degrees of unsaturation. The ^1H and ^{13}C NMR spectrum of compound **1** along with analysis of the DEPT spectra (Table-1) displayed 15 carbon signals and 18 proton signals, respectively, corresponding to an chromone nucleus[10] [δ_C 79.3 s, 48.6 t, 192.2 s, 122.6 d, 120.8 d, 131.4 s, 151.7 s, 148.1 s, 118.0 s, 25.7 q (2C); δ_H 2.68 s, 7.46 (d) *J* = 8.6, 6.87 (d) *J* = 8.6, 1.62 s], an 2-oxopropyl group ($-CH_2C(O)CH_3$)[10,11] (δ_C 49.3 t, 206.8 s, 30.4 q; δ_H 4.16 s, 2.33 s) and a methoxy group (δ_C 60.8, δ_H 3.81 s). Strong absorption bands accounting for hydroxy (3432 cm^{-1}), carbonyl group (1722 and 1668 cm^{-1}) and aromatic groups (1608, 1553 and 1437 cm^{-1}) could also be observed in its IR spectrum. The UV spectrum of compound **1** showed absorption maxima at 260 and 210 nm, which confirmed the existence of the aromatic functions. The HMBC correlations (Fig. 2) of H-11 (δ_H 4.16) with C-6 (δ_C 120.8), C-7 (δ_C 131.4) and C-8 (δ_C 151.7); of H-6 (δ_H 6.87) with C-11 (δ_C 49.3) indicated that the 2-oxopropyl group should be located at C-7 on the chromone ring. The methoxy group

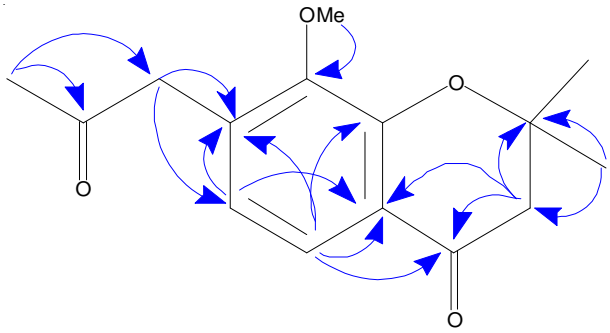

Fig. 2. Key HMBC correlation ( ) of compound **1**

located at C-8 was supported by the HMBC correlation of the methoxy proton (δ_H 3.81) with C-8 (δ_C 151.7). In addition, the ^1H-^1H COSY of H-5/H-6 and a HMBC correlation between H-5 (δ_H 7.46) and C-4 (δ_C 192.2) also supported the substituent groups at C-7 and C-8 for chromone. Thus, the structure of compound **1** was established as 8-methoxy-2,2-dimethyl-7-(2-oxopropyl)-2,3-dihydrochromen-4-one.

Since certain of the chromone derivatives exhibit potential anti-TMV activities[11]. Compound **1** was tested for its anti-TMV activity. The inhibitory activity of compound **1** against TMV replication were tested using the half-leaf method[11,12]. Ningnanmycin, a commercial product for plant disease in China, was used as a positive control. The results showed that compound **1** showed potential anti-TMV activity with inhibition rate of 23.5 %.

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