NOTE

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

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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 flowers¹. 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}, steroids⁶, chromones^{7,8} and flavonoids⁹. 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 (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 $\times$ 25 cm) or Venusil MP C18 (20 mm $\times$ 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 μ m, Merck, Darmstadt, Germany) and MCI gel (75-150 μ m, Mitsubishi Chemical Corporation, Tokyo, Japan). The fractions were monitored by TLC and spots were visualized by heating silica gel plates sprayed with 5 % H₂SO₄ in EtOH.

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 $\times$ 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

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

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-H₂O, 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 ϵ) 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 ¹³C NMR data (CDCl₃, 500 and 125 MHz), in Table-1; Negative ESIMS m/z 247 [M-H]⁻; negative HRESIMS m/z 247.2673 [M-H]⁻ (calcd. for C₁₄H₁₆O₄, 247.2665).

TABLE-1
¹H AND ¹³C 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 C₁₄H₁₆O₄, requiring seven degrees of unsaturation. The ¹H and ¹³C 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 nucleus¹⁰ [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 (-CH₂C(O)CH₃) 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 (δ_{H} 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),

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

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.

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 method¹². 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 %.

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REFERENCES

- V. Duraipandiyan and S. Ignacimuthu, *J. Ethnopharmacol.*, **112**, 590 (2007).
- S. Rajan, D.S. Baburaj, M. Sethuraman and S. Parimala, *Ethnobotany*, **6**, 19 (2001).
- J. Ma, L.X. Zhang and Y.H. Guan, *Chin. J. Ethnomed. Ethnopharm.*, **5**, 178 (2004).
- K.A. Abo, A.A. Adeyemi and A.O. Sobowale, *Afr. J. Med. Med. Sci.*, **30**, 9 (2001).
- S. Aurapa and G. Wandee, *Int. J. Biomed. Pharm. Sci.*, **3**, 42 (2009).
- P. Sartorelli, S.P. Andrade, M.S. Melhem, F.O. Prado and A.G. Tempone, *Phytother. Res.*, **21**, 644 (2007).
- Y.H. Kuo, P.H. Lee and Y.S. Wein, *J. Nat. Prod.*, **65**, 1165 (2002).
- S.L. Jothy, Z. Zakaria, Y. Chen, Y.L. Lau, L.Y. Latha, L.N. Shin and S. Sasidharan, *Molecules*, **16**, 7583 (2011).
- W. Zhao, X.Y. Zeng, T. Zhang, L. Wang, G.Y. Yang, Y.K. Chen, Q.F. Hu and M.M. Miao, *Phytochem. Lett.*, **6**, 179 (2013).
- Q. Hu, M. Miao, W. Zhao, T. Zhang, L. Wan, G. Yang, Y. Chen and D. Mou, *Heterocycles*, **85**, 2485 (2012).
- Q.F. Hu, B. Zhou, X.M. Gao, L.Y. Yang, L.D. Shu, Y.Q. Shen, G.P. Li, C.T. Che and G.Y. Yang, *J. Nat. Prod.*, **75**, 1909 (2012).
- Q.F. Hu, B. Zhou, J.M. Huang, X.M. Gao, L.D. Shu, G.Y. Yang and C.T. Che, *J. Nat. Prod.*, **76**, 292 (2013).