Asian Journal of Chemistry; Vol. 27, No. 9 (2015), 3511-3512

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18369

NOTE

A New Chromone from the Stem of Flue-Cured Tobacco and Its Anti-tobacco Mosaic Virus Activity

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Received: 24 June 2014; *Accepted*: 22 August 2014; *Published online*: 26 May 2015; AJC-17285

A new chromone, 6-acetyl-7-methoxy-2,3-dimethyl-4*H*-chromen-4-one (**1**), was isolated from the stems of flue-cured tobacco (a variety of *Nicotiana tabacum* L). Its structure was elucidated by spectroscopic methods, including extensive ^{1}D and ^{2}D NMR techniques. Compound **1** was also tested for its anti-tobacco mosaic virus (anti-TMV) activity and it shows potential anti-tobacco mosaic virus activity with inhibition rates of 25.4 %.

Keywords: Chromone, Flue-cured tobacco, Anti-tobacco mosaic virus activity.

Nicotiana tabacum L. is the most commonly grown of all plants in the *Nicotiana* genus and its leaves are commercially grown in many countries to be processed into tobacco[1,2]. In addition to being used in cigarette industry, *N. tabacum* is also used as insecticide, anesthetic, diaphoretic, sedative and emetic agents in Chinese folklore medicine because of it containing many useful chemical compounds[1,3-5]. In previous work, a number of bioactive compounds, such as terpenoids[6,7], alkaloids[8,9], lignans[10,11], flavonoid[12], phenylpropanoids[13], and the homologous, were isolated from this plant. The roots and stems of flue-cured tobacco are big amount of by-product in tobacco planting and are normally used as organic fertilizer. The multipurpose utilization of the roots and stems of flue-cured tobacco is an interesting topical and receives more and more attentions[14,15]. In this study, we report the isolation of a new chromone, 6-acetyl-7-methoxy-2,3-dimethyl-4*H*-chromen-4-one (**1**). Its structure was evaluated by spectroscopic methods, including HRMS and ^{1}D and ^{2}D NMR. In addition, the anti-tobacco mosaic virus (anti-TMV) activity of compound **1** was also evaluated.

General methods: UV spectra were obtained using a Shimadzu UV-2401A spectrophotometer. IR spectra were obtained in KBr disc on a Bio-Rad Wininfmred spectrophotometer. ESI-MS were measured on a VG Auto Spec-3000 MS spectrometer. ^{1}H, ^{13}C and ^{2}D NMR spectra were recorded on Bruker DRX-500 instrument with TMS as internal standard. Column chromatography was performed on silica gel (200-300 mesh), or on silica gel H (10-40 μm), Qingdao Marine Chemical Inc., China). Preparative HPLC was used an Agilent 1100 HPLC equipped with ZORBAX-C_{18} (21.2 mm × 250 mm, 7 μm) column and DAD detector.

The stems of flue-cured tobacco were collected in Puer Prefecture, Yunnan Province, People's Republic of China, in September 2012.

Extraction and isolation: The air-dried and powdered tobacco stems (2.5 kg) were extracted four times with 90 % methanol (4 × 5 L) at room temperature and filtered to yield a filtrate. The crude extract (44.5 g) was applied to silica gel (200-300 mesh) column chromatography, eluting with a chloroform-acetone system (20:1, 9:1, 8:2, 7:3, 6:4, 5:5), to give six fractions A-F. The further purification of fraction C (8:2, 11.2 g) by silica gel column chromatography, eluted with petroleum ether-acetone (9:1, 8:2, 7:3, 6:4, 5:5), yielded mixtures C-1-C-5. Fraction C-2 (8:2, 1.47 g) was subjected to preparative HPLC (60 % MeOH-H_2O, flow rate 12 mL/min) to yield compound **1** (14.8 mg).

6-Acetyl-7-methoxy-2,3-dimethyl-4*H*-chromen-4-one A (1): $C_{14}H_{14}O_4$, pale yellow gum; UV (MeOH) λ_{max} (log ε) 224 (4.06), 272 (3.78) nm; IR (KBr, ν_{max}, cm^{-1}) 3052, 2951, 2871, 1658, 1627, 1594, 1415, 11284, 1042, 880, 764; ^{1}H and ^{13}C NMR data (500 and 125 MHz), see Table-1; ESIMS *m/z* 269; HRESIMS *m/z* 269.0796 $[M + Na]^+$ (calcd $C_{14}H_{14}NaO_4$ for 269.0790).

A 90 % methanol extract prepared from the stems of flue-cured tobacco was subjected repeatedly to column chromatography on Silic gel, Sephadex LH-20, RP-18 and Preparative

TABLE-1
^{1}H AND ^{13}C NMR DATA OF COMPOUND **1** (δ IN ppm, IN C_5D_5N, 500 AND 125 MHz)

Position	δ_C (m)	δ_H (m, *J*, Hz)	Position	δ_C (m)	δ_H (m, *J*, Hz)
2	146.2 s	-	9	166.4 s	-
3	134.5 s	-	10	117.5 s	-
4	182.4 s	-	11	205.2 s	-
5	128.3 d	8.22 s	12	28.5 q	2.67 s
6	116.4 s	-	13	20.0 q	2.28 s
7	168.4 s	-	14	16.5 q	2.02 s
8	102.4 d	6.64 s	7-OMe	56.4 q	3.82 s

HPLC to afford compound **1**. The structure of **1** was shown in Fig. 1 and its ^{1}H and ^{13}C NMR data were listed in Table-1.

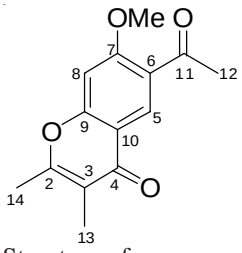

Fig. 1. Structure of compound **1**

Compound **1** had the molecular formula $C_{14}H_{14}O_4$ based on the exact mass [high resolution MS (HRMS)] at *m/z* 269.0796 $[M + Na]^+$. It showed aromatic (3052, 1627 and 1594 cm^{-1}) and conjugated carbonyl (1655 cm^{-1}) IR absorption bands[16]. The UV spectrum indicated a benzoyl group (224 and 272 nm). The ^{1}H NMR spectrum revealed the presence of an acetyl group [δ_H 2.67 (s)] attached to a phenyl residue, two singlets of a methyl group (δ_H 2.02 and 2.28) connected to the α- and β-positions of the chromone moiety and one methoxy proton present at 3.82. Two phenyl proton singlets resonated at δ_H 6.64 and 8.22 and a carbon (δ_C 102.4) corresponding to the former phenyl proton was proposed to be situated between two oxygenated phenyl carbons (δ_H 168.4 and 166.4)[17]. The phenyl carbon appearing at low field (δ_C 128.3) corresponded to the latter phenyl proton (δ_H 8.22) and was considered to be located between two carbonyl groups (δ_C 205.2 and 182.4). Two ^{13}C NMR signals at δ_C 205.2 and 182.4 were assigned as acetyl and chromone carbonyl groups, respectively. Based on the ^{1}H-^{1}H COSY and HSQC spectral data, the NMR signals were assigned. Its structure was confirmed by HMBC (Fig. 2). Therefore, the structure of **1** was assigned as 6-acetyl-7-methoxy-2,3-dimethyl-4*H*-chromen-4-one.

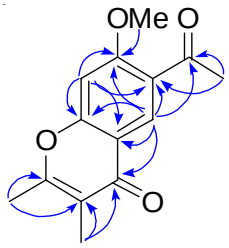

Fig. 2. Key HMBC ( ) correltaion of compound **1**

Since certain of the chromones exhibit potential anti-TMV activities, compounds **1** was tested for it anti-tobacco mosaic virus activity[18-20]. The anti-TMV activities were tested using the half-leaf method[21,22]. Ningnanmycin (2 % water solution), a commercial product for plant disease in China, was used as a positive control. The results showed that compound **1** exhibited inhibition rate of 25.4 %.

ACKNOWLEDGEMENTS

This project was supported financially by the National Natural Science Foundation of China (No.31360081), the Basic Research Foundation of Yunnan Province (2013FB097) and the Basic Research Foundation of Yunnan Tobacco Industry Co. Ltd. (2012JC01).

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