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NOTE

A New Xanthone from the Stems of *Garcinia oligantha* and their Anti-tobacco Mosaic Virus Activity

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For more bioactive compounds, phytochemical investigations of the methanol extract of the stems of *Garcinia oligantha* resulted in the isolation of a new xanthone, (S)-1,8-dihydroxy-4-(1-hydroxy-3-oxobutyl)-3-methoxy-9*H*-xanthen-9-one (**1**). Structural elucidation of **1** was performed by spectral methods. Compound **1** showed anti-tobacco mosaic virus (anti-TMV) activities with inhibition rates of 15.2 %.

Keywords: Xanthone, *Garcinia oligantha*, Anti-tobacco mosaic virus activity.

Genus *Garcinia* (Guttiferae family) is known to be a rich source of polyisoprenylated benzophenones and xant-hones[1,2]. It has been widely used as a traditional Chinese medicine for treating toothache, sore mouth, and scald[3]. In our continuing efforts to finding more bioactive compounds from *Garcinia* species, we explored the chemical constituents of *G. oligantha*, a shrub 1-3 m tall, which is distributed in 200-1200 m dense forests in the district of Xishuangbanna Prefecture Yunnan province, People's Republic of China. The present studies on chemical constituents of the methanol extract of the dried stems of *G. oligantha* afforded a new xanthones, (S)-1,8-dihydroxy-4-(1-hydroxy-3-oxobutyl)-3-methoxy-9*H*-xanthen-9-one (**1**) (Fig. 1). In this paper, we describe the isolation, structure elucidation, and anti-tobacco mosaic virus (anti-TMV) activities of this compound.

Optical rotations were measured by a JASCO DIP-1000 polarimeter. Ultraviolet absorption spectra were recorded using a Perkin-Elmer Lambda L14 spectrometer. A Perkin Elmer spectrum 100 FT-IR spectrometer was used for scanning IR spectroscopy. The ^{1}D and ^{2}D NMR spectra were recorded on a Bruker AV-400 spectrometer with TMS as the internal standard. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. HRMS were obtained using a nano LC-MS/MS system, with a nano Acquity ultra-performance liquid chromatography (UPLC) module and a quadrupole time-of-flight (Q-TOF) spectrometer equipped with a nanoelectrospray ion source (Waters, Milford, MA) and connected to a lock-mass apparatus to perform a real-time calibration correction. Column chromatography was performed with silica gel (200-300 mesh, Qingdao Marine Chemical, Inc.), Sephadex LH-20 (Pharmacia), and reversed-phase C_{18} silica gel (250 mesh, Merck). Precoated TLC sheets of silica gel 60 GF_{254} were used. An Agilent 1200 series equipped with an Alltima C_{18} column (4.6 × 250 mm) was used for HPLC analysis, and semipreparative and preparative Alltima C_{18} columns or Zorbax SB-C_{18} columns (9.4 × 250 and 22 × 250 mm) were used in sample preparation. Spots were visualized by heating silica gel plates sprayed with 10 % H_2SO_4 in EtOH.

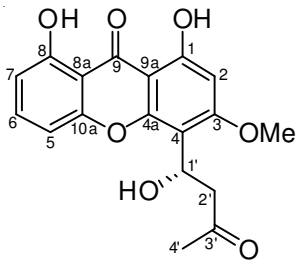

Fig. 1. Structure of compound **1**

The stems of *Garcinia oligantha* were collected in October 2012 from the district of Xishuangbanna Prefecture Yunnan Province in China. The plant was identified by Rong-Jing Zhang. A voucher specimen (YNNI 12-9-27) has been deposited at the Key Laboratory of Ethnic Medicine Resource Chemistry (Yunnan University of Nationalities), State Ethnic Affairs Commission & Ministry of Education.

Extraction and isolation: An methanol extract prepared from the stems of *Garcinia oligantha* (2.5 kg) was decolorized by MCI and chromatographed on a silica gel column eluting with hexane/acetone (1:0, 4:1, 2:1, 1:1, and 0:1) to afford five fractions A-E. Further separation of fraction B (11.5 g) on silica gel, eluted with petroleum ether-acetone (9:1-1:2), yielded fractions B1-B7. Fraction B2 (2.65 g) was subjected to silica gel column chromatography using petroleum ether-acetone followed by semipreparative HPLC (72 % MeOH-H_2O, flow rate 3 mL/min) to give 1 (8.6 mg).

(S)-1,8-Dihydroxy-4-(1-hydroxy-3-oxobutyl)-3-methoxy-9*H*-xanthen-9-one (1): Obtained as a yellow gum; $[\alpha]_D^{22.5}$ -45.6 (*c* 0.25, MeOH); UV (MeOH) λ_{max} (log ε) 210 (4.18), 244 (3.72), 302 (3.75) nm; CD (MeOH, c 0.25) $\Delta\varepsilon_{215}$ + 1.26, $\Delta\varepsilon_{235}$ -5.96, $\Delta\varepsilon_{274}$ + 0.38, $\Delta\varepsilon_{320}$ -0.98; IR (KBr ν_{max}, cm^{-1}) 3421, 3065, 2870, 2802, 1708, 1646, 1602, 1565, 1470, 1351, 1166, 1062, 878, 765; ESIMS *m/z* (positive ion mode) 367 $[M + Na]^+$; HRESIMS (positive ion mode) *m/z* 367.0790 $[M + Na]^+$ (calcd $C_{18}H_{16}NaO_7$ for 367.0794).

Compounds (**1**) was isolated as a yellow gum, and its molecular formula was determined as $C_{18}H_{16}NaO_7$ through HRESI-MS analysis (pseudomolecular ion $[M + Na]^+$ at *m/z* 367.0790). Its UV spectrum showed the maximum absorption at 302, 244, and 210 nm. Strong absorption bands accounting for hydroxy (3421 cm^{-1}), carbonyl (1708, 1646 cm^{-1}), and aromatic groups (1602, 1565, 1470 cm^{-1}) could also be observed in its IR spectrum. The ^1H- and ^{13}C NMR spectrum (Table-1) displayed signals for all 18 carbons and 16 protons, including a xanthones skeleton[4] (C-1-C-9, C-4a, C-8a-C-10a; H-2, H-5-H-7), a methoxy groups (δ_C 55.9 q, δ_H 3.82 s), a 1-hydroxy-3-oxobutyl moiety[5] [δ_C 63.7 d, 51.2 t, 205.4 s, 31.2 q; δ_H 5.18 dd (8.8, 3.2), 2.82 dd (15.4, 3.2), 2.46 dd (15.4, 8.8), 2.18 s], and two phenolic hydroxyl group (δ_H 12.24 s and 13.05 s). The HMBC correlation (Fig. 2) of the methoxy proton signal (δ_H 3.82) with C-3 (δ_C 161.2) showed this methoxy group was located at C-3. The long-range correlations of H-1' (δ_H 5.18) to C-3 (δ_C 161.2), C-4 (δ_C 110.3) and C-4a (δ_C 156.4), of H_2-2' (δ_H 2.82 and 2.46) to C-4 (δ_C 110.3) were observed in **1**. This led us to conclude that the 1-hydroxy-3-oxobutyl moiety was located on C-4. Finally, HMBC correlations between the hydroxy proton (δ_H 12.24) and C-1 (δ_C 162.5), C-2 (δ_C 97.4), and C-9a (δ_C 105.7), as well as those between the other hydroxy proton (δ_H 13.05) and C-7 (δ_H 108.2), C-8 (δ_H 162.9), and C-8a (δ_H 107.5), led to the assignment of the phenolic groups at C-1 and C-8. The typical proton signals of ring A [δ_H 6.85 d (8.3), 7.42 t (8.3), 6.65 d (8.3)] and ring B (δ_H 6.47 s) also supported that **1** should be a 1,3,4,8-tetrasubstituted xanthone[4]. To determine the absolute configuration of **1**, the circular dichroism (CD) analysis was employed. The experimental CD spectrum of **1** exhibited a positive Cotton effect at 215 nm and a negative Cotton effect near 235 nm. The Cotton effects, optical rotation, and coupling constant valves of **1** were in excellent agreement with these of known compound[5], (1'S)-7-hydroxy-3-(1'-hydroxy-3'-butanoyl) chromone-5-carboxylic acid. Therefore, compound **1** was assigned as (S)-1,8-dihydroxy-4-(1-hydroxy-3-oxobutyl)-3-methoxy-9*H*-xanthen-9-one.

Since certain chromones exhibit potential ant-TMV activities[4,6,7], compounds **1** was tested for it anti-TMV activity. The inhibitory activities of compound **1** against TMV replication were tested using the half-leaf method[6]. Ningnanmycin, a commercial biochemical pesticide against virus diseases on tomato, pepper, melons, tobacco, and many other crops with high efficiency, was used as a positive control. The result showed that compound **1** exhibited inhibition rates of 15.2 %.

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

No.	δ_C (m)	δ_H (m, J, Hz)
1	162.5 s	-
2	97.4 d	6.47 s
3	161.2 s	-
4	110.3 s	-
5	112.5 d	6.85 d (8.3)
6	135.7 d	7.42 t (8.3)
7	108.2 d	6.65 d (8.3)
8	162.9 s	-
9	183.1 s	-
4a	156.4 s	-
8a	107.5 s	-
9a	105.7 s	-
10a	159.0 s	-
1′	63.7 d	5.18 dd (8.8, 3.2)
2′	51.2 t	2.82 dd (15.4, 3.2); 2.46 dd (15.4, 8.8)
3′	205.4 s	-
4′	31.2 q	2.18 s
3-OMe	55.9 q	3.82 s
Ar-OH-1	-	12.24 s
Ar-OH-8	-	13.05 s

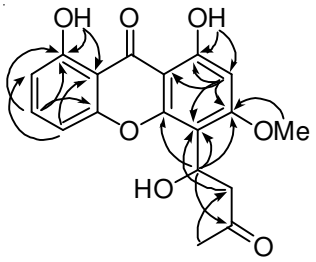

Fig. 2. Key HMBC (↷) correlations of **1**

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