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NOTE

A New Antiviral Phenolic Compounds from *Arundina gramnifolia*

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A new phenolic compound, gramniphenol I (**1**), was isolated from the whole plant of *Arundina gramnifolia*. Its structure was determined by means of HRESIMS, extensive 1D and 2D NMR spectroscopic studies and chemical evidence. Compound **1** was also tested for its antitobacco mosaic virus (anti-TMV) activity and it exhibited notable antitobacco mosaic virus activity with inhibition rate of 16.8 %.

Keywords: *Arundina gramnifolia*, Phenolic compound, Antitobacco mosaic virus activity.

Arundina gramnifolia (D. Don) Hochr. (bamboo orchid) belongs to the orchid family (Orchidaceae). The plant is used in Chinese folkloric medicine as a detoxifying and diuretic agent, as well as for the treatment of arthritis and inflammation[1]. Previous phytochemical studies on *A. gramnifolia* has revealed the presence of stilbenoids[2-4], sterols[5,6], triterpenes[7,8] and other phenolic compounds[9-11]. Continuing the efforts to discover bioactive metabolites from local plants, we now investigated the chemical constituents of the whole plant of *A. gramnifolia* growing in the Xishuangbanna Prefecture, leading to the isolation of a new phenolic compound (**1**). Its structure was determined by means of spectroscopic methods including 1D and 2D NMR techniques. Compound **1** was also tested for its antitobacco mosaic virus (anti-TMV) activity.

General procedures: UV spectra were obtained on a Shimadzu UV-2401A spectrophotometer; and CD spectra were measured on a JASCO J-810 spectropolarimeter. Tenor 27 spectrophotometer was used for scanning IR spectra (KBr pellets). 1D and 2D NMR spectra were recorded on a DRX-500 spectrometer with TMS as internal standard. Chemical shifts (δ) were expressed in ppm with reference to TMS. HRESIMS was performed on an API QSTAR spectrometer or a VG Autospec-3000 spectrometer. Preparative HPLC was performed on a Shimadzu LC-8A liquid chromatography equipped with ZORBAX PrepHT GF (21.2 mm × 25 cm, 7 μm) column or Venusil MP C_{18} (20 mm × 25 cm, 5 μm) column. Column chromatography was performed using Si gel (200-300 mesh, Qing-dao Marine Chemical, Inc., Qingdao, China), Lichroprep RP-18 gel (40-63 μm, Merck, Darmstadt, Germany), Sephadex LH-20 (Sigma-Aldrich, Inc, USA), or MCI gel (75-150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan). Column fractions were monitored by TLC and the spots were visualized by heating the plates after spraying with 5 % H_2SO_4 in EtOH.

The whole plant of *Arundina gramnifolia* (D. Don) Hochr. was collected in the Xishuangbanna prefecture of Yunnan Province in in September 2012. The identification of the plant material was verified by Prof. Wu SG (Xishuangbanna Botanical Garden). A voucher specimen (YMU-2012-9-18) has been deposited in our laboratory.

Extraction and isolation: The air-dried and powdered whole plant of *A. gramnifolia* (2.0 kg) was extracted three times with 70 % aqueous acetone (3 × 3.5 L) at room temperature and filtered to yield a filtrate. The filtrate was concentrated and partitioned between H_2O and EtOAc. The EtOAc fraction was dried under reduced pressure and then submitted. The extract was applied to silica gel (150-200 mesh) column chromatography, eluting with $CHCl_3$-MeOH gradients (20:1, 9:1, 8:2, 7:3, 6:4, 5:5) to afford fractions A-F. Further separation of fraction B (21.2 g) by silica gel (300-400 mesh), eluted with $CHCl_3$-$CO(CH_3)_2$ (9:1-1:2), yielded fractions B1-B7. Fraction B3 (2.62 g), upon further separation on silica gel using petroleum ether-$CH_3COOC_2H_5$ and semi-preparative HPLC (46 % MeOH-H_2O, flow rate 12 mL/min), afforded compound **1** (15.4 mg).

Gramniphenol I (1): $C_{17}H_{16}O_5$, yellow gum; UV (CH_3OH) λ_{max} (log ε) 210 (3.92), 275 (3.26), 314 (3.52) nm; IR (KBr,

ν_{max}, cm^{-1}): 3448, 1620, 1497, 1469, 1385, 1145, 878, 820; ^{13}C NMR and ^{1}H NMR data (DMSO-d_6, 500 and 125 MHz) (Table-1); positive ESIMS *m/z* 323 $[M+Na]^+$; negative HRESIMS *m/z* 323.0888 $[M+Na]^+$ (calcd for $C_{17}H_{16}O_5$, 323.0895).

TABLE-1
^{1}H NMR AND ^{13}C NMR DATA OF COMPOUND **1** (δ ppm, IN DMSO-d_6)

No.	δ_C	δ_H (*J* in Hz)	No.	δ_C	δ_H (*J* in Hz)
2	148.2 s		1'	110.3 s	
3	113.5 s		2'	156.9 s	
4	119.8 d	7.42 d (8.2)	3'	103.4 d	6.40 d (1.8)
5	108.2 d	6.79 dd (1.8, 8.2)	4'	158.6 s	
6	158.9 s	6.91 s	5'	105.8 d	6.31 dd (1.8, 8.2)
7	98.2 d	7.08 d (1.8)	6'	128.9 d	7.15 dd (8.2)
8	155.1 s		6-OMe	55.8 q	3.82 s
9	122.6 s		2'-OMe	56.2 q	3.79 s
10	58.4 t	4.68 s	Ar-OH		10.02 s

Powdered whole plants of *A. gramnifolia* were extracted with 70 % aqueous acetone. The filtrate was concentrated and partitioned between H_2O and EtOAc. The EtOAc fraction was dried under reduced pressure and then submitted to silica gel, MCI, RP-18 gel column chromatography (CC) and semi-preparative HPLC to yield compound **1**. The structure of compound **1** was shown in Fig. 1 and the ^{1}H NMR and ^{13}C NMR spectroscopic data of compound **1** are listed in Table-1.

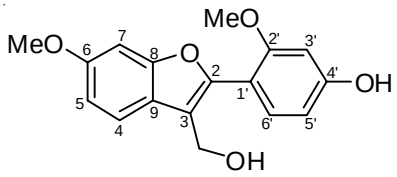

Fig. 1. Structure of compound **1**

Gramniphenol I (**1**) was obtained as yellow gum. It possessed the molecular formula $C_{17}H_{16}O_5$, as revealed by its HR-ESI-MS spectrum (*m/z* 323.0888, $[M+Na]^+$, calcd 323.0895). The IR absorptions at 3448 (OH) and 1620 (aromatic) cm^{-1} and UV absorptions at 314 and 275 nm were characteristics for 3-methylene benzofurans. On the basis of ^{1}H NMR and ^{13}C NMR spectral analysis (Table-1), compound **1** had a 14-carbon skeleton with one oxidated methylene group (δ_H 4.68/δ_C 58.4), two methoxy group (δ_H 3.82/δ_C 55.8 and δ_H 3.79/δ_C 56.2) and one phenolic hydroxy group (δ_H 10.02). Six olefinic methane carbons (δ_C 98.2, 103.4, 105.8, 108.2, 119.8 and 128.9) and eight quaternary carbons [five oxygenated sp^2 carbons (δ_H 148.2, 158.9, 155.1, 156.9, 158.6)] were observed according to HSQC and DEPT spectra. In the ^{1}H NMR spectrum, two AMX systems (δ_H 7.08, d, *J* = 1.8 Hz; 7.42, d, *J* = 8.2 Hz; 6.79, dd, *J* = 8.2, 1.8 Hz and δ_H 6.40, d, *J* = 1.8 Hz; 7.15, d, *J* = 8.2 Hz; 6.31, dd, *J* = 8.2, 1.8 Hz) were observed. In the HMBC spectrum (Fig. 2), the -CH_2OH protons at δ_H 4.68 were correlated with C-2 (148.2), C-3 (113.5) and C-9 (122.6), indicating that the -CH_2OH was connected to C-3. The correlations of the -OCH_3 protons at δ_H 3.82 and 3.79 with C-6 (158.9) and C-22 (156.9) showed that the -OCH_3 groups should be attached to C-6 and C-22, respectively. The -OH proton (δ_H 10.02) showed HMBC correlations with C-32 (103.4), C-42 (158.6) and C-52 (105.8), indicating that it was attached to C-42. Consequently, compound **1** was identified as shown.

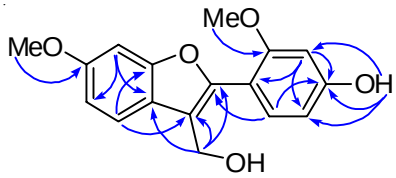

Fig. 2. Key HMBC ( ) correlations of compound **1**

Since certain of the phenolic compounds exhibit potential antitobacco mosaic virus activity.[12-14] Compound **1** was tested for its antitobacco mosaic virus activities. The inhibitory activities of compound **1** against tobacco mosaic virus replication were tested using the half-leaf method.[15] Ningnanmycin, a commercial product for plant disease in China, was used as a positive control. The results showed that compound **1** exhibited antitobacco mosaic virus activity with inhibition rate of 16.8 %.

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