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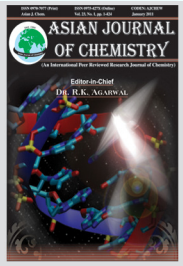

NOTE

Lignans from the Leaf of *Smallanthus sonchifolius*

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Phytochemical investigation of the leaf of *Smallanthus sonchifolius* led to the isolation and identification of a new lignan (smallanlignan A) and five known lignans. The structures were elucidated by the analysis of spectroscopic data. The antioxidant activity of smallanlignan A was evaluated and it showed antioxidant activity with an IC_{50} value of 1.65 μg/mL.

Key Words: *Smallanthus sonchifolius*, Lignan, Antioxidant activity.

Smallanthus sonchifolius is a member of asteraceae family. It is a perennial plant grown in the Andes of Perú for its crisp, sweet-tasting tubers. The texture and flavour have been described as a cross between a fresh apple and watermelon. This is the reason, it is sometimes referred to as the apple of the earth. The tuber is composed mostly of water and fructooligosaccharides[1-3]. It has recently been introduced into farmer's markets and natural food stores in Yunnan Province, P.R. China. The leaf and root of *Smallanthus sonchifolius* has also received more and more attentions because of their biological activities[3-7].

In order to investigates the components of the aerial parts and search for potential leads for drug development, phytochemical investigation on the leaf of *Smallanthus sonchifolius* was carried out. This led to the isolation of one new lignans (smallanlignan A), together with five known lignans *i.e.*, epiwulignan A (**2**)[8], epischisandrone (**3**)[8], 8'-β-hydroxyhinokinin (**4**)[9], (-)-hinokinin (**5**)[10] and (-)-zuonin A (**6**)[11]. The structure was established by means of extensive NMR spectra and the antioxidant activity of mallanlignan A was evaluated (Fig. 1).

Optical rotation was measured in Horiba SEPA-300 high sensitive polarimeter. 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. ^1H, ^{13}C NMR and 2D NMR spectra were recorded on Bruker DRX-500 instruments with TMS as internal standard. On second separate used Agilent 1100 HPLC high performance liquid chromatography equipped with Zorbax-C_{18} (9.4 nm × 250 nm, 5.0 μm) column and DAD detector. Column chromatography was performed on silica gel (200-300 mesh) or on silica gel H (10-40 μm, Qingdao Marine Chemical Inc., P.R. China).

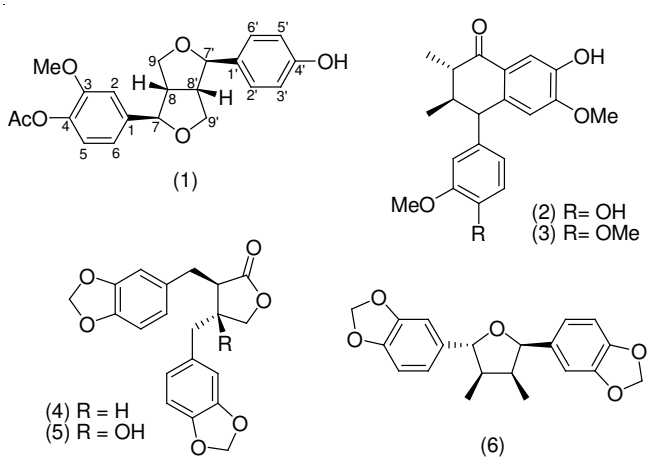

Fig. 1. Structure of lignans in *Smallanthus sonchifolius*

The leaf of *Smallanthus sonchifolius* were collected in Kunming of Yunnan Province, P.R. China, in September 2009 and was identified by Prof. S.F. WU. A voucher specimen (No. YNNI 09-18-09) was deposited in our laboratory.

Extraction and isolation: The dried sample (5.6 kg) was extracted with MeOH at room temperature (4 × 5 L) to obtain 0.92 kg of the solid extract. The MeOH extract was suspended in H_2O and extracted successively with hexane (3 × 3 L) and EtOAc (3 × 3 L) to give the hexane- (63.5 g) and EtOAc-soluble fractions (218 g), respectively. The EtOAc-soluble fraction (218 g) was chromatographed on a silica gel column eluted with a stepwise gradient of $CHCl_3$ and MeOH to yield five fractions (A-E: 35.4, 18.5, 23.6, 11.2 and 8.86 g, respec-

tively). Fraction B was further purified by HPLC with mobile phase (MeOH-H_2O 65:35) to yield **3** (36.2 mg), **4** (14.6 mg), **6** (15.4 mg). Fraction C was further purified by HPLC with mobile phase (MeOH-H_2O 60:40) to yield **1** (15.4 mg), **2** (64.5 mg), **5** (128.6 mg).

Antioxidant activity assay: Antioxidant activity was determined by the detection of the oxidative products with the 2',7'-dichlorofluorescin diacetate (DCFH) method reported previously[12].

Smallanlignan A (**1**) was obtained as a white amorphous solid, showing $[\alpha]2_D^{23.2}$ -55.02 (c 0.28, $CHCl_3$). The molecular formula of **1** was determined to be $C_{21}H_{22}O_6$ from high resolution ESIMS (positive model). IR spectrum of **1** showed an absorption at 3326 cm^{-1} for hydroxyl groups. The ^1H NMR spectrum (Table-1) of **1** showed signals of 1,3,4-trisubstituted phenyl protons at δ 7.02 (d, 1.5), 6.99 (d, 8.2) and 6.95 (dd, 8.2, 1.5) and 1,4-substituted phenyl protons at δ 7.19 (2H, d, 8.4) and 6.79 (2H, d, 8.4), a signal due to a methoxyl protons at δ 3.89 (3H, s) and an acetyl methoxyl protons at δ 1.95 (3H, s). The ^{13}C NMR spectrum revealed 21 carbon signals typical to the lignan skeleton besides a methoxyl carbon signal at δ 55.6 and acetyl carbon signal at δ 21.4 q, 169.5 s. The methoxyl group was thought to be attached at C-3 position by consideration of heteronuclear multiple bond connectivity (HMBC) correlations between the protons at δ 3.89 (3H, s) and the carbon at δ 148.2 (C-3). In addition, the planar structure of **1** was also supported by other HMBC correlations, *i.e.*, between the hydroxyl proton at δ 5.48 (1H, brs) and δ 154.6 (C-4'), 116.1 (C-3', 5') (Figs. 2 and 3).

TABLE-1
^1H AND ^{13}C NMR DATA OF SMALLANLIGNAN-A C IN $CDCl_3$

No.	δ_C (mult.)	δ_H (mult, *J*, Hz)	No.	δ_C (mult.)	δ_H (mult, *J*, Hz)
1	135.6 s		3-OMe	55.6 q	3.89 s
2	110.5 d	7.02, d, 1.5	1'	133.5 s	
3	148.2 s		2'	126.8 d	7.19, d, 8.4
4	140.4 s		3'	116.1 d	6.79, d, 8.4
5	121.8 d	6.99, d, 8.2	4'	154.6 s	
6	119.8 d	6.95, dd, 8.2, 1.5	5'	116.1 d	6.79, d, 8.4
7	86.1 d	4.72 m	6'	126.8 d	7.19, d, 8.4
8	54.6 d	3.13, m	7'	85.9 d	4.70 m
9α	71.8 t	3.85 m	8'	54.2 d	3.11, m
9β		4.26 m	9'α	71.3 t	3.83 m
4-OAc	169.5 s		9'β		4.25 m
	21.4 q	1.95 s	4'-OH		5.48 brs

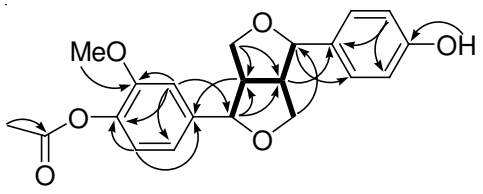

Fig. 2. Selected HMBC (®) and ^1H-^1H COSY (–) of compound **1**

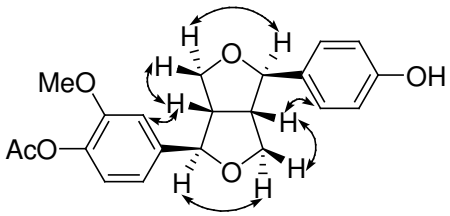

Fig. 3. Selected NOESY correlations of compound **1**

By the comparison of circular dichroism (CD) spectrum of **1** ($[\theta]_{242}$ + 268.6, $[\theta]_{280}$ -1016) with that of known compound ((-)-pinoresinol), ($[\theta]_{242}$ +228, $[\theta]_{282}$ -1038), it is indicated that the absolute stereochemistry of **1** was as same as that of(-)-pinoresinol[13]. Thus, the structure of **1** was finally concluded to be the acetyl derivative of (-)-pinoresinol: (8S,2R, 5S,6R)-2-(4-hydroxyphenyl)-6-(3-methoxy-4-acetylphenyl)-3,7-dioxabicyclo[3.3.O]octane.

The antioxidant activity of smallanlignan A was determined by the detection of the oxidative products with the 2',7'-dichlorofluorescin diacetate (DCFH) method reported previously[12]. It shows antioxidant activity with an IC_{50} value of 1.65 μg/mL. Smallanlignan A shows high antioxidant activity.

Smallanactone A: White amorphous solid; $[\alpha]_D^{223.2}$ -55.02 (c 0.28, $CHCl_3$); UV λ_{max} ($CDCl_3$) nm (log ε): 282 (1.61), 226 (5.18); CD (EtOH, c = 0.006) $[\theta]_{242}$ +268.6, $[\theta]_{280}$ -1016; IR (KBr, ν_{max}, cm^{-1}): 3418, 3326, 2874, 1757, 1602, 1587, 1526, 1476, 1342, 1268, 1118, 1027, 934, 855; ^1H and ^{13}C NMR data are shown in Table-1. HRESIMS (positive ion mode) m/z 393.1311 $[M + Na]^+$ (calcd. (%) 393.1314 for $C_{21}H_{22}O_6$).

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