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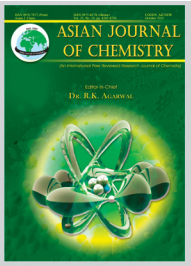

NOTE

A New Monoterpene from the Fruits of *Ziziphus jujuba* Mill and Its Antioxidant Activity

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A new monoterpene 4-acetyl-3-hydroxy-6-isopropyl-pyran-2-one (m.f. $C_{10}H_{12}O_4$) was isolated from the fruits of *Ziziphus jujuba* Mill. The structure was elucidated on the basis of extensive NMR and MS means. The antioxidant activity of the new monoterpene was evaluated and it showed antioxidant activity with an IC_{50} value of 3.53 μg/mL.

Key Words: Monoterpene, Fruit, *Ziziphus jujuba* Mill, Antioxidant activity.

Ziziphus jujuba Mill belongs to the genus *Ziziphus* (Rhamnaceae), originated in China and call as "Da Zao" where they have been cultivated for more than 4,000 years[1-3]. The fruit of *Ziziphus jujuba* Mill is highly nutritional value and good tasting. In addition to fruit utilization, it has also been used as a traditional Chinese medicine for a long time, which shows various beneficial activities including antioxidant, antihepatitis, anxiolytic, antitumor and the like[4-6]. The extract of Da Zao has also been used as cigarette additives[7,8].

Previous phytochemical research on *Ziziphus jujuba* has revealed that flavones[9,10], triterpene acid[11,12], alkaloid[13,14] as well as polysaccharides[15] are major principles isolated from this plant. With the aim of continuing efforts to evaluate the quality of cigarette additives and to identify bioactive natural products from the plants, a chemical investigation on the fruits of *Ziziphus jujuba* Mill indigenous to the Hanzhong Prefecture of Shangxi Province of China was carried out. A new monoterpene 4-acetyl-3-hydroxy-6-isopropyl-pyran-2-one (m.f. $C_{10}H_{12}O_4$) was separated from this plant. In addition, the antioxidant activity of the new monoterpene was evaluated.

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 and ^2D NMR spectra were recorded on Bruker DRX-500 instruments 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). On second separate used Agilent 1100 HPLC equipped with ZORBAX-C_{18} (21.2 nm × 250 nm, 5 μm) column and DAD detector.

The fruit of *Ziziphus jujuba* Mill was collected in Hanzhong Prefecture, Shangxi Province, P. R. China, in February 2009 and was identified by Prof. N Yuan. A voucher specimen (No. YNNi 09-2-02) was deposited in our laboratory.

Extraction and isolation: The air-dried and powdered fruit of *Ziziphus jujuba* Mill. (1.5 kg) were extracted with 70 % aqueous ethanol (3.0 L × 3, 24 h each) at room temperature and the extract was concentrated under vacuum condition. The dried extract (118 g) was applied to silica-gel (200-300 mesh) column chromatography eluting with a $CHCl_3$-Me_2CO gradient system (9:1, 8:2, 7:3, 6:4, 5:5, 2:1) to give six fractions A-F. The separation of fraction A ($CHCl_3$-Me_2CO 9:1, 8.26 g) by silica-gel column chromatography eluted with $CHCl_3$-Me_2OH (9:1-1:2) yielded mixtures A1-A5. Fraction A1 (1.2 g) was subjected to preparative HPLC (68 % MeOH-H_2O, flow rate 12 mL/min) to give the new monoterpene (18.2 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[16].

The new monoterpene was obtained as colourless needle. It has the molecular formula $C_{10}H_{12}O_4$ from HRESIMS (m/z: 219.0638 $[M+Na]^+$, calcd 219.0633). IR absorptions at 3438, 1708 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^{13}C NMR spectrum of the new

compounds (Table-1) along with analysis of the DEPT spectra displayed 10 carbon signals corresponding to three methyl (δ_C 22.8, 22.8, 31.8), one methine (δ_C 28.2), two double bond (δ_C 181.0, 99.7, 103.2, 172.1) and two carbonyl carbons (δ_C 162.5, 206.8). Due to the scarcity of proton-proton spin system, the assembly of backbone was completely performed *via* HMBC interactions. The observation of HMBC correlations of H-8 with C-7 and C-4; H-5 with C-3, C-4, C-6, C-7 and C-9; H-9 with C-5 and C-6; H-10 with C-6; H-11 with C-6 indicated the partial structure of C-3 to C-11. Taking the chemical shifts of C-2, C-3, C-6 and the degrees of unsaturation into account, the remaining moiety should be a lactone functional group and C-2 linked with C-6 *via* oxygen atom. Thus, the structure of the new compound was assigned as 4-acetyl-3-hydroxy-6-isopropyl-pyran-2-one (Fig. 1).

TABLE-1
^{1}H NMR AND ^{13}C NMR DATA OF COMPOUND (**1**) IN CD_3OD

No.	δ_C (mult.)	δ_H (mult. *J*, Hz)	No.	δ_C (mult.)	δ_H (mult. *J*, Hz)
2	162.5 s		7	206.8 s	
3	181.0 s		8	31.8 q	2.64 s
4	99.7 s		9	28.2 d	2.57 m
5	103.2 d	5.94 s	10	22.8 q	0.92, d, *J* = 7.1
6	172.1 s		11	22.8 q	0.92, d, *J* = 7.1

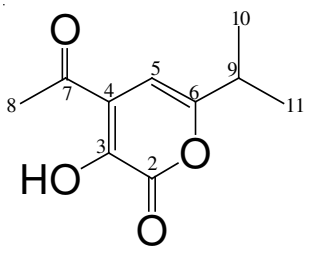

Fig. 1. Structure of the new monoterpene

The antioxidant activity of the new compound was determined by the detection of the oxidative products with the 2',7'-dichlorofluorescin diacetate (DCFH) method reported previously[16]. It shows antioxidant activity with an IC_{50} value of 3.53 μg/mL. The new compound shows high antioxidant activity.

4-Acetyl-3-hydroxy-6-isopropyl-pyran-2-one: $C_{10}H_{12}O_4$, colourless needle; UV ($CHCl_3$), λ_{max} (log ε) 310 (3.96), 288 (3.54), 214 (3.47); IR (KBr, ν_{max}, cm^{-1}): 3438, 3025, 2947, 2896, 1708, 1622, 1548, 1357, 1026, 926, 837, 762; ^{13}C NMR and ^{1}H NMR data (CD_3OD, 500 MHz) (Table-1); positive ESIMS m/z 219 $[M+Na]^+$; HRESIMS m/z 219.0638 $[M+Na]^+$ (calcd. for $C_{10}H_{12}O_4$, 219.0633).

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