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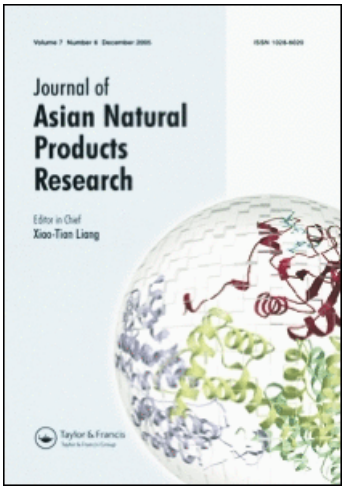

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A NEW MONOTERPENE FROM THE BARK OF *EUCOMMIA ULMOIDES*

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A new monoterpene, eucommidiol (**1**), was isolated from the bark of *Eucommia ulmoides* Oliv. (Eucommiaceae), together with a known compound 1,4a,5,7a-tetrahydro-7-hydroxymethyl-cyclopenta[c]pyran-4-carboxylic methyl ester. The structure of **1** was characterized as 6,6a-di(hydroxymethyl)-3,3a,4,6a-tetrahydro-2H-cyclopenta[b]furan-2-one on the basis of chemical and spectral evidence including 2DNMR studies.

Keywords: *Eucommia ulmoides*; Eucommiaceae; Monoterpene; Eucommidiol

INTRODUCTION

Eucommia ulmoides Oliv. is a commonly used traditional Chinese medicine and native in China. It has been used for the treatment of rheumatic arthritis, ischialgia neuralgia, Heine-Medin disease and hypertension [1]. Various lignans, iridoids and their glucosides have been isolated from this medicinal plant [2–4].

In this paper, we report the isolation and characterization of a new monoterpene, eucommidiol (**1**), from the barks of *E. ulmoides* (Fig. 1).

RESULTS AND DISCUSSION

From the *n*-butanol-soluble part of the water extract of *E. ulmoides*, compound **1** was isolated by silica gel column chromatography and preparative TLC.

Compound **1** was obtained as colorless oil. It showed a blue–black spot with 10% H_2SO_4. The molecular formula of $C_9H_{12}O_4$ for compound **1** was established from its EIMS, ^{1}H-NMR and ^{13}C-NMR spectra. EIMS showed $[M - H_2O]^+$ ion peak at *m/z* 166 and $[M - CH_2OH]^+$ ion peak at *m/z* 153. The IR spectrum of **1** showed the presence of hydroxyl groups (3409 cm^{-1}) and a lactone carbonyl group (1749 cm^{-1}). The ^{1}H-NMR(in DMSO-d_6)

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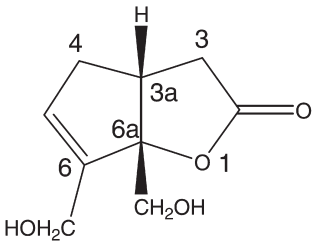

FIGURE 1 Structure of eucommidiol (**1**).

spectrum showed an olefinic proton at δ 5.83. The signals at δ 5.13 and 4.87 which disappeared in CD_3OD suggested the presence of two hydroxyl groups which were confirmed by two alcoholic acetyl signals in the ^{1}H-NMR of the peracetate derivative (**1a**) of **1**. The signals at δ 3.99(2H, brs) and 3.72, 3.43(each 1H, d, $J = 12.0$ Hz) suggested the presence of two methylenes which were attached to oxygen atoms. The other signals of five protons in the upfield region were assigned to the fragment $-CH_2CHCH_2-$ by $^1H-^1H$ COSY. The $^1H-^1H$ COSY spectrum also suggested the presence of two hydroxymethyl groups. The ^{13}C-NMR and DEPT data showed nine signals. The signal at δ 179.50(s) was due to a lactone carbonyl. The signals at δ 143.33(s) and 133.26(d) suggested the presence of a pair of olefinic carbons. In addition, the ^{13}C-NMR spectrum also displayed a sp^3 quaternary carbon (δ 102.27, s), one methine carbon (δ 39.90, d) and four methylenes (δ 65.28, t; 58.94, t; 38.66, t; 38.32, t). In the HMBC experiment of compound **1**, correlated peaks between H_{3a}(δ 2.95, m), H_3(δ 2.84 and 2.33) and C_{6a}(δ 102.27), C_2(δ 179.50) were observed, which proved the linkages to be $-CO-CH_2-$ and $-C-CH-$. Correlated peaks between 6-CH_2OH proton (δ 3.99, 2H) and carbons at δ 133.26 (C-5) and 143.33 (C-6) were observed, which proved that the 6-CH_2OH was attached to an olefinic carbon (δ 102.27). Similarly, we inferred another hydroxymethyl attached to a quaternary carbon. Besides, by the $^1H-^1H$ COSY, HMBC spectra, we inferred that the moiety of $-CH_2CHCH_2-$ was attached to the double bonds of C–C.

The relative stereostructure of **1** was characterized by NOESY experiment. In NOESY spectrum, the correlation between H-3a at δ 2.95 and 6a-CH_2OH at δ 3.43 suggested a *cis* configuration between them.

On the basis of the above evidences, compound **1** was elucidated as 6,6a-di(hydroxymethyl)-3,3a,4,6a-tetrahydro-2H-cyclopenta[b]furan-2-one.

EXPERIMENTAL SECTION

General Experimental Procedures

IR spectrum was taken on a Bruker IFS-55 infrared spectrophotometer and mass spectrum on Shimadzu MS-QP5050A spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker ARX-300(300 MHz for ^{1}H and 75 MHz for ^{13}C) in DMSO-d_6 with TMS as internal standard. Optical rotations were measured on P-E 241 MC polarimeter using methanol as the solvent. TLC and PTLC were performed on silica gel GF254 glass plates. Separation and purification were performed by column chromatography on silica gel (200–300 mesh).

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TABLE I NMR data of compound **1**

Position	*^{1}H-NMR (δ_H)*	*^{13}C-NMR (δ_C)*	*HMBC*	*^{1}H–^{1}H COSY*
2		179.50		
3	2.84 dd(18.0, 10.2)	38.66	C_2, C_{3a} C_4,C_{6a}	H-3a
	2.33 dd(18.0, 4.2)			
3a	2.95(m)	39.90	C_2,C_3,C_4,C_5,C_6, C_{6a},6a-CH_2OH	H-3,H-4
4	2.14 dt (17.1, 2.4) 2.65ddd(17.1,8.4,2.1)	38.32		H-3a,H-5 6a-CH_2OH
5	5.83(brs)	133.26	C_{3a}, C_4, C_6, 6a-CH_2OH	H-4
6		143.33		
6a		102.27		
6-C*H*$_2$OH	3.99(brs)	58.94	C_5, C_6	H-4, 6-CH_2O*H*
6-CH_2O*H*	4.87(brs)			6-C*H*$_2$OH
6a-C*H*$_2$OH	3.72 d(12.0)	65.28	C_6,C_{6a},C_{3a}	6a-CH_2O*H*
	3.43 d(12.0)			
6a-CH_2O*H*	5.13(brs)			6a-C*H*$_2$OH

Plant Material

The barks of *E. ulmoides* were bought from General Corporation of Medicinal Materials of Liaoning Province, China. A voucher specimen (2001401) was identified by Prof. Qi Shi Sun and deposited in the Department of Natural Products, Shenyang Pharmaceutical University, China.

Extraction and Isolation

The barks of *E. ulmoides* were cut into strips. Then the dried barks (3 kg) were thoroughly extracted with boiling water. The extract was concentrated to a solution of 2400 ml and was successively partitioned with chloroform, ethyl acetate and *n*-butanol. The *n*-butanol-soluble fraction (40 g) was subjected to silica gel column chromatography and eluted with $CHCl_3$–MeOH(100:5) to yield fraction A. Fraction A was further purified by Sephadex LH-20 column chromatography and PTLC with petroleum–acetone(2:3) as developing reagent to give compound **1** (80.7 mg).

Compound **1**, colorless oil (80.7 mg), showed blue–black spot with 10% H_2SO_4. $[\alpha]_D^{26}$ + 10.7 (C 1.6, methanol). IR (KBr) max 3409 (OH), 2930 and 2850 (CH), 1749 (lactone C = O) cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz) and ^{13}C-NMR(DMSO-d_6, 75 MHz) data see Table I. EI-MS *m/z* 166 $[M - H_2O]^+$, 153 $[M - CH_2OH]^+$, 135 $[M - H_2O - CH_2OH]^+$, 107.

*Acetylation of **1***: Ac_2O (0.6 ml) was added to a pyridine (0.5 ml) solution of compound **1** (14 mg). The mixture was kept at room temperature for 24 h. The solution was poured into ice water and extracted with chloroform to give **1a**, which was purified by silica gel column chromatography with petroleum–$CHCl_3$ (2:1) as eluent. ^{1}H-NMR ($CDCl_3$, 300 Hz) δ 2.08, 2.09 (3H each, s, 2X$COCH_3$), 2.27 (1H, br d, J = 17.4 Hz, H-4), 2.40 (1H, dd, J = 18.0, 4.2 Hz, H-3), 2.84 (1H, m, H-4), 2.97 (1H, dd, J = 18.0, 10.2 Hz, H-3), 3.02 (1H, m, H-3a), 4.22, 4.43 (1H each, d, J = 12.0 Hz, 6a-CH_2OAc), 4.63, 4.80 (1H each, d, J = 13.5 Hz, 6-CH_2OAc), 6.07 (1H, brs, H-5).

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References

[1] Jiangsu New Medical College (1977) Dictionary of Chinese Herbal Medicine (Shanghai People's Publishing House, Shanghai) **Vol. 1**, pp 1031–1033.
[2] Deyama, T., Nishibe, S., Kitagawa, S., Ogihara, Y., Takeda, T., Ohmoto, T., Nikaido, T. and Sankawa, U. (1988), *Chem. Pharm. Bull.* **36**(1), 435–439.
[3] Bianco, A., Iavarone, C. and Trogolo, C. (1974), *Tetrahedron* **30**, 4117–4121.
[4] Okada, N., Shirata, K., Niwano, M., Koshiro, H. and Uramoto, M. (1994), *Phytochemistry* **37**(1), 281–282.