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A new cycloartane nortriterpenoid from *Quercus variabilis* Blume

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Abstract

The leaves and stems of *Quercus variabilis* Blume afforded a new cycloartane nortriterpenoid, 3α-acetyloxy-4α, 14α-dimethyl-9β, 19-cycloergost-24-oic acid (**1**), along with five known compounds (**2**–**6**). The structure of **1** was elucidated by 1D and 2D NMR and mass spectroscopy.

Keywords: *Quercus variabilis* Blume; Cycloartane nortriterpenoid

Quercus variabilis Blume is widely distributed in the north and east of China. As a Chinese folk medicine, its twig is used to treat esophagus cancer. Early studies on the plant have reported the isolation and identification of some triterpenoids [1,2]. We now report the isolation and identification of a new cycloartane nortriterpenoid, 3α-acetyloxy-4α, 14α-dimethyl-9β, 19-cycloergost-24-oic acid (**1**), along with five known compounds, 3-epicycloeucalenol (**2**) [3], 3-epicycloeucalenyl-24-one (**3**) [1], 3-epicycloeucalenyl acetate (**4**) [1], 4β, 14α-dimethyl-5α-ergosta-9β, 19-cyclo-24 (31)-en-3β-hydroxy-4α-carboxylic acid (**5**) [4], and cycloeucalenone (**6**) [5] from the chloroform extract of the air-dried leaves and stems of the plant (Fig. 1).

The leaves and stems of *Q. variabilis* Blume were collected in Dalian, Liaoning province, China and identified by Dr. Jiu-Zhi Yuan. A voucher specimen (no. 20060901) was deposited in the Herbarium of Shenyang Pharmaceutical University. The air-dried material (10 kg) was extracted with 95% EtOH. The ethanol extract (990 g) was suspended in water and partitioned with petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH, successively. The $CHCl_3$ extract (180 g) was separated by repeated silica gel column chromatography and sephadex LH-20 to give compounds **1**–**6**.

Compound **1** was obtained as colorless needles (methanol), mp 78–80 °C, $[\alpha]_D^{26}$ +2.6 (*c* 1.0, $CHCl_3$). It showed a quasimolecular ion peak at *m/z* 467.3133 $[M+Na]^+$ (calcd. 467.3137) in HR–ESI–MS corresponding to the molecular formula $C_{28}H_{44}O_4$. The IR spectrum of **1** showed the presence of carbonyl group (1731 cm^{-1}), carboxyl group (3441 cm^{-1}, 1710 cm^{-1}) and cyclopropyl group (3040 cm^{-1}, 973 cm^{-1}). Its EI–MS spectrum showed molecular ion peak at *m/z* 444 accompanied with diagnostic fragment ion peaks at *m/z* 384 $[M-CH_3COOH]^+$, 276 $[M-C_{10}H_{16}O_2$ (ring A)$]^+$, 343 $[M-C_5H_9O_2$ (side-chain)$]^+$, and 175 $[M-C_{10}H_{16}O_2$ (ring A) $-$ $C_5H_9O_2$ (side-chain)$]^+$. The ^1H NMR spectral data of **1** showed the characteristic cyclopropane methylene signals [δ 0.37 and 0.13 (d, each 1H, J = 3.9 Hz)], along with two tertiary methyls [δ 0.92 and 0.98 (s, each 3H)], two secondary methyls [δ 0.84 and 0.90 (d, each 3H,

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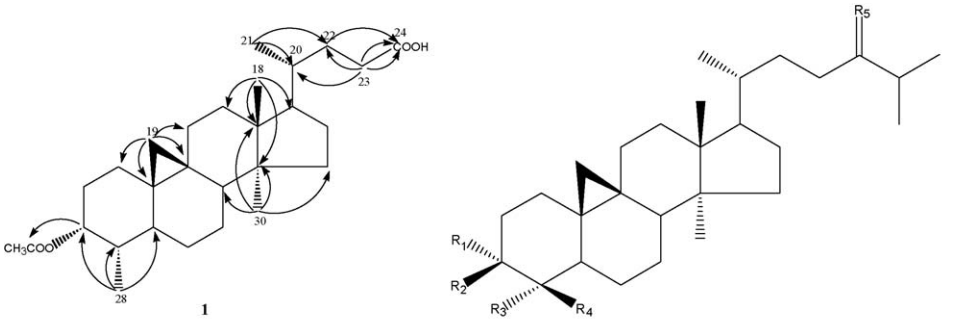

2 $R_1 = OH, R_2 = R_4 = H, R_3 = CH_3, R_5 = CH_2$, **3** $R_1 = OH, R_2 = R_4 = H, R_3 = CH_3, R_5 = O$

4 $R_1 = OAc, R_2 = R_4 = H, R_3 = CH_3, R_5 = CH_2$, **5** $R_1 = H, R_2 = OH, R_3 = COOH, R_4 = CH_3, R_5 = CH_2$

6 $R_1 = R_2 = O, R_3 = CH_3, R_4 = H, R_5 = CH_2$

Fig. 1. Structures of compounds **1**–**6** and main HMBC (H → C) correlations of **1**. **2** $R_1 = OH$, $R_2 = R_4 = H$, $R_3 = CH_3$, $R_5 = CH_2$; **3** $R_1 = OH$, $R_2 = R_4 = H$, $R_3 = CH_3$, $R_5 = O$; **4** $R_1 = OAc$, $R_2 = R_4 = H$, $R_3 = CH_3$, $R_5 = CH_2$; **5** $R_1 = H$, $R_2 = OH$, $R_3 = COOH$, $R_4 = CH_3$, $R_5 = CH_2$; **6** $R_1 = R_2 = O$, $R_3 = CH_3$, $R_4 = H$, $R_5 = CH_2$.

$J = 6.6$ Hz)], an acetyl methyl [δ 2.09 (s, 3H)], and an oxymethine proton [δ 5.00 (br s, 1H)]. These were identical to those of the other cycloartane-type triterpenoids isolated from *Q. variabilis* Blume [1,3–5]. The ^{13}C NMR spectrum of **1**, however, displayed only 28 carbon signals, and thus **1** was assigned as a norcycloartane-type triterpenoid. The ^{13}C NMR spectrum of **1** revealed a methylene carbon of cyclopropane ring at δ 26.4 (C-19), an oxygenated methine carbon at δ 75.1 (C-3), and two carbonyl carbons (δ 171.1 and 180.1) due to an acetyl carbonyl group and a free carboxylic acid group. The ^{13}C NMR spectral data of **1** were similar to those of 3-epicycloeucalenyl acetate (**4**) [1] except for the side-chain. On the basis of the HMBC spectrum and the long-range correlations observed in the HMBC spectrum (Fig. 1), the position of the carboxylic acid group was determined as C-23. The positions of the acetyl group and 4-CH_3 were determined as C-3α and C-4α by comparing the chemical shifts and the coupling constants of H-3 (δ 5.00, br s) and H-4 (δ 1.50, m) with those of 3-epicycloeucalenyl acetate (**4**). The ^1H and ^{13}C NMR data were assigned from the DEPT, HMQC, and HMBC spectra (Table 1). Therefore, the structure of **1** was established as 3α-acetyloxy-4α, 14α-dimethyl-9β, 19-cycloergost-24-oic acid.

Table 1
^1H (600 MHz) and ^{13}C (150 MHz) NMR data of compound **1** (in $CDCl_3$, δ ppm, J Hz).

No.	δ_c	δ_H	No.	δ_c	δ_H
1	27.4 (t)	1.73 (m, 1H), 1.06 (m, 1H)	17	52.0 (d)	1.60 (m, 1H)
2	30.2 (t)	1.90 (m, 1H), 1.62 (m, 1H)	18	17.9 (q)	0.98 (s, 3H)
3	75.1 (d)	5.00 (br s, 1H)	19	26.4 (t)	0.37 (d, 1H, J = 3.9)
					0.13 (d, 1H, J = 3.9)
4	39.8 (d)	1.50 (m, 1H)	20	35.6 (d)	1.48 (m, 1H)
5	39.0 (d)	1.70 (m, 1H)	21	17.9 (q)	0.90 (d, 3H, J = 6.6)
6	24.5 (t)	1.60 (m, 1H), 0.52 (ddd, 1H, J = 14.9, 12.4, 2.5)	22	31.1 (t)	1.88 (m, 1H), 1.30 (m, 1H)
7	24.8 (t)	1.36 (m, 1H), 1.08 (m, 1H)	23	31.0 (t)	2.41 (ddd, 1H, J = 15.6, 9.9, 4.8)
					2.30 (ddd, 1H, J = 15.6, 9.7, 6.7)
8	47.1 (d)	1.60 (m, 1H)	24	180.1 (s)	
9	23.2 (s)		25		
10	29.9 (s)		26		
11	26.7 (t)	1.96 (m, 1H), 1.19 (m, 1H)	27		
12	32.8 (t)	1.60 (m, 2H)	28	15.0 (q)	0.84 (d, 3H, J = 6.6)
13	45.3 (s)		29		
14	48.9 (s)		30	19.1 (q)	0.92 (s, 3H)
15	35.3 (t)	1.31 (m, 2H)	$O\underline{C}OCH_3$	171.1 (s)	
16	27.9 (t)	1.93 (m, 1H)	$OCO\underline{C}H_3$	21.3 (q)	2.09 (s, 3H)
		1.31 (m, 1H)			

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