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A New Triterpenoid from *Doellingeria scaber*

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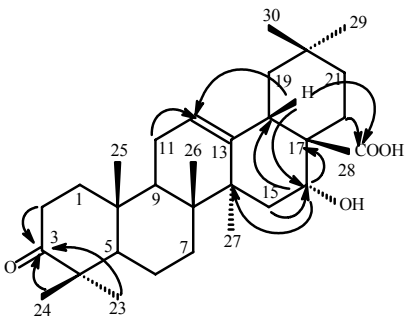
Abstract: A new oleanane-type triterpene was isolated from the roots of *Doellingeria scaber*. Its structure was identified as 3-oxo-16α-hydroxy-olean-12-en-28-oic acid based on 1D and 2D NMR spectroscopy and X-ray analysis.

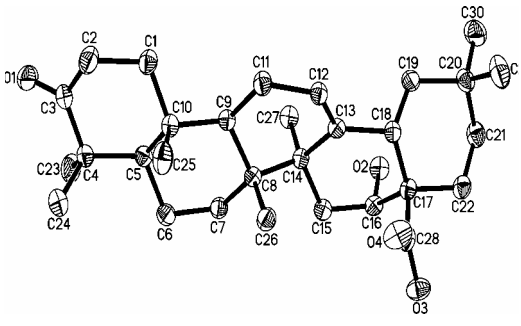
Keywords: *Doellingeria scaber*, Compositae, oleanane-type triterpenoid, 3-oxo-16α-hydroxy-olean-12-en-28-oic acid.

Doellingeria scaber Thunb. (Compositae), a traditional Chinese herb, is widely distributed in China. Its root has been used for treatment of traumatic injury and snake bite[1]. As a part of our ongoing program on finding biologically active components from Chinese herbs[2] we found a new oleanane-type triterpene, 3-oxo-16α-hydroxy-olean-12-en-28-oic acid **1**, from the roots of *D. scaber*. We report herein the structural elucidation of this new compound by spectroscopic means including 1D and 2D NMR experiments. The structure of **1** was finally confirmed by X-ray single crystal analysis[3] (**Figure 1**).

Figure 1



Key HMBC correlations of **1** (H→C).



X-ray structure (ORTEP drawing) of **1**.

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Table 1 ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data of **1** (DMSO-d_6, TMS, δ ppm, J_{Hz})

position	δ_C	δ_H	HMBC
1	38.4	1.79 (m, H-1α) , 1.39 (m, H-1β)	H-2α, H-2β, H-9α, H-25
2	33.6	2.49 (ddd, 16, 10.4, 7.1, H-2β) 2.32 (ddd, 16, 7.1, 3.7, H-2α)	H-1β
3	216.2		H-1β, H-2α, H-2β, H-23, H-24
4	46.5		H-5α, H-23, H-24
5	54.3	1.30 (m, H-5α)	H-1β, H-6β, H-9α, H-23, H-24, H-25
6	19.2	1.42 (m, 2H-6)	H-5α
7	32.0	1.48 (m, 2H-7)	H-6β, H-9α, H-26
8	38.9		H-9α, H_2-11, H-26, H-27
9	45.2	1.66 (m, H-9α)	H_2-11, H-12, H-25, H-26
10	36.2		H-6β, H-9α, H-25
11	22.9	1.85 (m, 2H-11)	H-9α, H-12
12	121.1	5.21 (t, 3.4, H-12)	H_2-11, H-18β
13	143.9		H_2-11, H-18β, H-27
14	41.1		H-12, H-16β, H-18β, H-26, H-27
15	34.9	1.68 (dd, 12.5, 3.3, H-15α) 1.27 (dd, 12.5, 3.3, H-15β)	H-27
16	72.6	4.32 (t, 3.3, H-16β)	H-15α, H-15β, H-18β, H-22α
17	47.3		H-16β, H-18β, H-22α, H-22β
18	40.2	2.88 (dd, 14.3, 4.2, H-18β)	H-12, H-16β, H-19α, H-22β
19	46.3	2.21 (t, 13.5, H-19α) 1.02 (dd, 13.5, 4.8, H-19β)	H-18β, H-21β, H-29, H-30
20	30.4		H-19α, H-21β, H-29, H-30
21	35.1	1.90 (m, H-21α), 1.07 (m, H-21β)	H-29, H-30
22	31.3	1.80 (m, H-22β), 1.58 (m, H-22α)	H-21α
23	26.3	0.99 (s)	H-5α, H-24
24	21.0	0.94 (s)	H-5α, H-23
25	14.8	0.96 (s)	H-5α, H-9α
26	16.6	0.73 (s)	H-9α
27	26.3	1.32 (s)	
28	178.1		H-18β, H-22α
29	32.8	0.82 (s)	H-19α, H-21α, H-30
30	24.1	0.89 (s)	H-19α, H-21α, H-21β, H-29

Compound **1** was obtained as colorless crystals, mp 257-259 °C, $[\alpha]_D^{20}$ +57.8 (*c* 0.76, DMSO). The EI-MS spectrum gave the molecular ion peak at *m/z* (%) 470 (45) and principal fragment ion peaks at 452 (76), 264 (33), 219 (25), 205 (37) and 201 (100), respectively. The ^{13}C and DEPT NMR spectra of **1** exhibited 30 carbon signals (7×CH_3, 9×CH_2, 5×CH and 9×C). The molecular formula of **1** was deduced to be $C_{30}H_{46}O_4$ by HR-ESI-MS that gave the molecular ion peak at 488.3739 (calcd. for $C_{30}H_{46}O_4$ + NH_4 488.3734). The IR spectrum showed the presence of hydroxyl (3524 cm^{-1}), carbonyl (1719 cm^{-1}) and double bond (1678 cm^{-1}) functionalities. The ^{1}H NMR spectrum

showed the presence of seven tertiary methyl groups at δ 0.73, 0.82, 0.89, 0.94, 0.96, 0.99 and 1.32 (each 3H, s), respectively. The ^{13}C NMR spectrum showed the presence of one carboxyl group (δ 178.1), two olefinic carbons (δ 121.1 and 143.9) and one carbonyl group (δ 216.2). These facts suggested that compound **1** was an oleanolic acid-type triterpenoid with a carbonyl group. Comparison of the ^{13}C NMR data of **1** with those of 3-oxo-olean-12-en-28-oic acid[4] suggested that the carbonyl group was located at C-3 position on A-ring, which was supported by the fragment ion peak at *m/z* 205 in the EI-MS spectrum resulting from the retro-Diels-Alder cleavage of the C-ring, and also confirmed by the correlations of C-3 with H-1, H-2α, H-2β, H-23 and H-24 in the HMBC spectrum (**Figure 1a**). Comparison of the ^{1}H and ^{13}C NMR data of **1** with those of scaberoside A_1 methyl ester[5] suggested that the hydroxyl group was connected at C-16 (δ 72.6), which was supported by the fragment ion peak at *m/z* 264 in the EI-MS spectrum resulting from the retro-Diels-Alder cleavage of the C-ring, and confirmed by the HMBC correlations of C-16 with H-15α, H-15β, H-18β and H-22α, and of H-16 with C-14, C-17, C-18. The signal at δ 4.32 (t, 1H, J=3.3 Hz) in ^{1}H NMR spectrum suggested that H-16 was equatorial (β-oriented), which was supported by the presence of NOE effects between H-16 with H-15α, H-15β and the absence of NOE effects between H-16 with H-27 in the NOESY spectrum. Therefore, compound **1** was assigned as 3-oxo-16α-hydroxy-olean-12-en-28-oic acid. The ^{1}H and ^{13}C NMR assignments together with the HMBC correlations are listed in **Table 1**. The structure of **1** was confirmed by X-ray single crystal analysis as shown in **Figure 1b**. The 16-epimer of **1** has been reported previously[6], but the ^{1}H NMR spectrum (100 MHz) was not well resolved and the ^{13}C NMR data seem questionable.

Acknowledgments

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