

Petatrichol B: A Pentacyclic Triterpenoid with Unusual Skeleton from *Petasites tricholobus*

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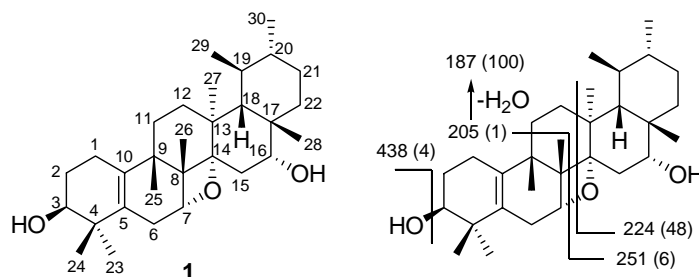
Abstract: A novel pentacyclic triterpenoid, petatrichol B, was isolated from the rhizome of *Petasites tricholobus*. Its structure was established by means of spectroscopic analysis (EIMS, HRSIMS, IR, 1D NMR and 2D NMR).

Keywords: *Petasites tricholobus*, Compositae, triterpenoid, petatrichol B.

The flower buds of *Petasites tricholobus* were usually used as that of *Tussilago farfara* in northwest China for treatment of coughs, bronchitis and asthmatic disorders. In the continuous phytochemical research of this genus, a novel pentacyclic triterpenoid, compound **1**, which represents an unusual triterpenoid carbon framework, was isolated and its structural elucidation is reported here.

Compound **1** m.p. 191 – 192 °C, $[\alpha]_D^{20} - 20$ (c 0.12, CHCl₃), was isolated as white powder. Its EIMS spectrum showed the molecular ion peak at m/z 456, combined with the ¹H and ¹³C NMR (DEPT) data, the molecular formula was deduced to be C₃₀H₄₈O₃, which was further confirmed by positive HRSIMS (m/z 439.3571 [M - H₂O + 1]⁺, calcd. for C₃₀H₄₇O₂, 439.3576). The IR spectrum showed the absorption for hydroxy (3306 cm⁻¹) and double bond (1654 cm⁻¹). Its ¹H NMR spectrum (**Table 1**) displayed signals

Figure 1 Compound **1** and its EIMS fragmentation pattern



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Table 1 ^1H (400 MHz), ^{13}C NMR (100MHz) and DEPT data of **1** (CDCl_3 , TMS, δ ppm, J_{Hz})^{a, b}

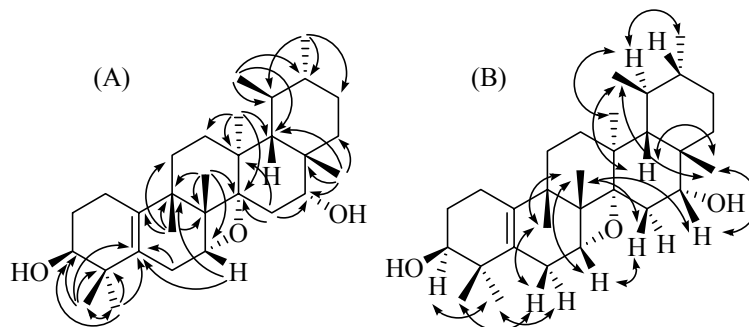
No	δ_{H}	δ_{C}	DEPT
1 α , 1 β	1.86 m, 2.05 m	23.3	CH ₂
2 α , 2 β	1.65 m, 1.72 m	27.4	CH ₂
3	3.52 dd (9.2, 2.8)	75.7	CH
4	—	39.3	C
5	—	130.7	C
6 α , 6 β	1.74 m, 2.18 m	27.2	CH ₂
7	4.51 dd (4.4, 4.0)	78.7	CH
8	—	47.6	C
9	—	39.7	C
10	—	134.0	C
11 α , 11 β	1.26 m, 1.43 m	28.8	CH ₂
12 α , 12 β	1.46 m, 1.58 m	31.7	CH ₂
13	—	40.4	C
14	—	89.8	C
15 α , 15 β	1.90 m, 2.54 dd (13.8, 3.6)	35.7	CH ₂
16	3.35 dd (13.2, 3.6)	75.5	CH
17	—	37.5	C
18	1.26 m	52.0	CH
19	1.12 m	36.0	CH
20	1.83 m	32.0	CH
21 α , 22 β	1.26 m, 1.48 m	27.8	CH ₂
22 α , 22 β	1.58 m, 1.88 m	23.5	CH ₂
23	1.05 s	25.7	CH ₃
24	0.94 s	20.8	CH ₃
25	0.98 s	24.8	CH ₃
26	1.12 s	17.7	CH ₃
27	0.83 s	20.1	CH ₃
28	1.21 s	32.7	CH ₃
29	1.06 d (6.0)	23.7	CH ₃
30	0.93 d (6.0)	22.3	CH ₃

^a assigned by ^1H - ^1H COSY and HMBC spectrum.

^b some ^1H peaks overlapped in the range of 1.1 – 2.2 ppm, hence the coupling constants could not be measured.

for eight methyls at δ_{H} 0.83, 0.94, 0.98, 1.05, 1.06, 1.12 and 1.21. The signals resonating at δ_{H} 3.35, 3.52 and 4.51 were assigned to three oxygen-bearing methines. The ^{13}C NMR spectrum (**Table 1**) of **1** showed resonances for all 30 carbons in the molecule. The DEPT spectrum showed the presences of eight methyls, eight methylenes, six methines and eight quarternary carbons. These data along with the analysis of the EIMS fragmentation (**Figure 1**) and consideration of seven degrees of unsaturation, suggested that **1** was a pentacyclic triterpenoid possessing a tetrasubstituted double bond (δ_{C} 130.7, 134.0, C), two methines connected with hydroxy (δ_{H} 3.35, 3.52 and δ_{C} 75.7, 75.5) and an epoxide group (δ_{H} 4.51 and δ_{C} 78.7 CH, 89.8 C) (**Table 1**).

The basic framework of **1** was constructed by the HMBC correlations of the eight methyl groups (**Figure 2**). The correlations of CH₃-23 (δ_{H} 1.05) and CH₃-24 (δ_{H} 0.94) with C-3 (δ_{C} 75.7) indicated that a hydroxy was located at C-3. The correlations of CH₃-28 (δ_{H} 1.21) with C-16 (δ_{C} 75.5) and H-15 (δ_{H} 1.90, 2.54) with C-16 (δ_{C} 75.5) showed that the second hydroxy was attached to C-16. The double bond between C-5 and C-10 was confirmed by the correlations of CH₃-23 (δ_{H} 1.05) and CH₃-24 (δ_{H} 0.94)

Figure 2 HMBC correlations (A) and key correlations in the NOESY spectrum (B) of **1**

with C-5 (δ_C 130.7), CH₃-25 (δ_H 0.98) with C-10 (δ_C 134.0) and H-6 (δ_H 1.74, 2.18) with C-5 (δ_C 130.7). The correlations of CH₃-26 (δ_H 1.12) with C-7 (δ_C 78.7), C-8 (δ_C 89.8), CH₃-27 (δ_H 0.83) with C-14 (δ_C 89.8), H-15 (δ_H 1.90, 2.54) with C-14 (δ_C 89.8) and H-7 (δ_H 4.51) with C-9 (δ_C 39.7) suggested that a four-membered epoxy group formed between C-7 and C-14. The relative configurations of 3 β -OH and 16 α -OH were confirmed by the coupling constants of H-3 (dd, J = 9.2, 2.8 Hz)¹ and H-16 (dd, J = 13.2, 3.6 Hz). The coupling constant of H-7 (dd, J = 4.4, 4.0 Hz) and the correlation of H-7 (δ_H 4.51) with CH₃-26 (δ_H 1.12) in NOESY spectrum showed that the epoxy group was α oriented. The other relative configurations were resolved by NOESY spectrum (**Figure 2**). The correlations of CH₃-26 with CH₃-25, H-7, H-16 and CH₃-28 with H-16, H-18, CH₃-29 suggested that 25, 26, 28, 29 methyls and H-18 situated on β orientation. The correlations between H-19 and CH₃-27, CH₃-30 indicated α orientation of 27 and 30 methyl. Therefore the structure and relative configuration of compound **1** were fully confirmed and named as petatrichol B. To the best of our knowledge, this kind of carbon framework of triterpenoid has not been reported up to now.

Acknowledgments

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