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Diterpenoid Alkaloids from *Aconitum racemulosum* Franch var. *pengzhouense*

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Abstract: A new diterpenoid alkaloid, racemulodine (**1**), was isolated from the whole plants of *Aconitum racemulosum* Franch var. *pengzhounense*.

Keywords: *Aconitum racemulosum* Franch var. *Pengzhounense*, Ranunculaceae, racemulodine.

From the whole plants of *Aconitum racemulosum* Franch var. *pengzhounense*, we have isolated a new diterpenoid alkaloid racemulodine **1**, together with atisinum hydrochloride, isotalatizidine, nevadenine, virescenine, 14-acetylvirescenine and anthranoyllycoctonine[1]. In this paper, we report the structural elucidation of the new diterpenoid alkaloid racemulodine **1**.

Racemulodine **1**[2] was isolated as colorless needles, and its molecular formula, $C_{21}H_{27}NO_4$, inferred from its MS and ^{13}C NMR spectra. The IR and NMR spectra of **1** revealed that it belongs to the hetidine-type diterpenoid alkaloids, showing characteristic signals at δ_H 2.45 (3H, s), δ_C 41.6 q for the *N*-methyl group; δ_H 1.16 (3H, s), δ_C 22.5 q for an angular methyl group; 1692 and 1721 cm^{-1}, δ_C 208.6 s, 208.6 s for two ketone groups, and 3030, 1606 and 820 cm^{-1}, δ_H 5.50 (1H, s), δ_C 130.9 d, 140.3 s for a trisubstituted vinyl group, from HMQC (**Table 1**), as well as a typical signal at δ_C 140.3 s for the C-16[3]. The 1H signal at δ 3.92 (hept, J=14.0, 2.0 Hz) and the 1H signal at δ 3.35 (d, J=5.6 Hz), which correlated with the carbon signals at δ 66.7 d and 76.9 d, respectively, in the HMQC spectrum, indicated that it had two secondary hydroxyl groups. The location and stereochemistry of the 2α- and 3α-hydroxyl groups were proved by showing the correlated peeks between the H-2β (δ_H 3.92) and H-3β (δ_H 3.35) in the ^1H-^1H COSY spectrum, and three-bond connections among the H-2 and C-10, the H-3 and C-5, C-18 as well as C-19, respectively, in the HMBC spectrum (**Figure 1**). The above mentioned assignments were also supported by displaying the presence of an NOE relatinonships between H-18 (δ 1.16, 3H, s) and H-5β/H-3β in the NOESY (**Figure 2**). The CD spectrum of **2** gave a negative Cotton effect ($[\theta]_{296}=3.0\times10^3$) [4, 5], in addition to three-bond connectivity of the H-20 (δ 3.06, d, *J*=3.2 Hz, HMQC δ_C 66.8 d) with C-13

(δ_C 208.6 s) in the HMBC spectrum, strongly suggesting that one ketone group in **2** was located at C-13. The ^{13}C NMR data of **1** and hetidine **2** (**Table 1**) [6] are very similar, except for C-8, C-9, C-13, C-14, C-15 and C-16, indicating that their differences were derived only from those on rings C and D. Thus, the structure of racemulodine was elucidated as **1**.

Figure 1 Major HMBC (H to C) correlations of **1**

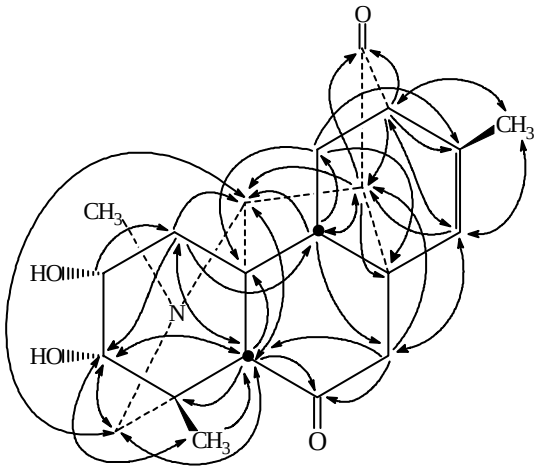
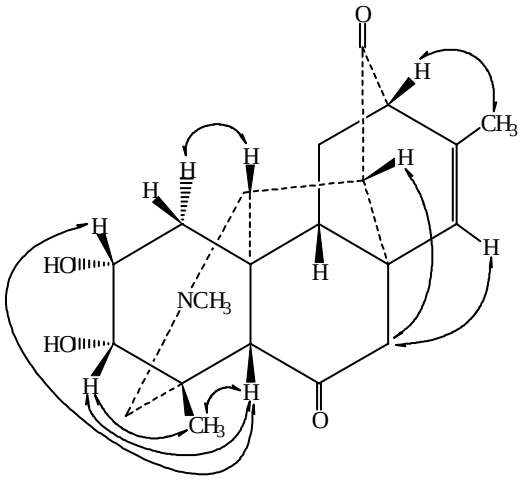
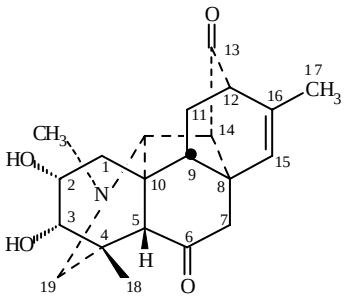
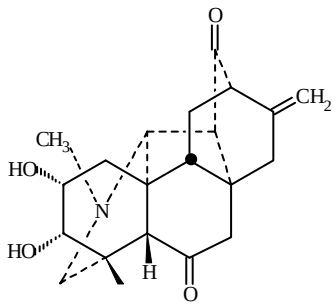


Figure 2 Key NOESY correlations of **1**





1



2

Table 1 NMR data of compound **1** (^{1}H: 400 MHz, ^{13}C: 100 MHz; $CDCl_3$) and **2** [6]

	1		**2**
Carton	δ_C	δ_H	δ_C
1	41.1 t	1.82 dd (14.2, 4.4) (β) 2.14 dd (14.2, 2.0) (α)	39.0[a] (38.9)[b]
2	66.7 d	3.92 hept (W1/2=2.0)	66.7 (67.2)
3	76.9 d	3.35 d (5.6)	76.9 (77.6)
4	41.8 s	—	41.8 (41.9)
5	58.1 d	1.85 s	58.2 (57.9)
6	208.6 s	—	208.4 (208.9)
7	51.8 t	2.79 br.s	52.1 (52.3)
8	44.4 s	—	41.2 (40.7)
9	47.6 d	1.76 dt (10.4, 2.0)	46.3 (46.1)
10	45.0 s	—	44.6 (44.4)
11	23.3 t	1.55 ddd (14.0, 10.4, 2.0) (β) 1.99 ddd (14.0, 3.0, 1.6) (α)	23.4 (23.5)
12	53.2 d	2.98 m (W1/2=5.7)	53.4 (53.7)
13	208.6 s	—	210.2 (208.9)
14	51.8 d	2.30 d (2.8)	56.5 (56.6)
15	130.9 d	5.50 s	36.1 (36.0)
16	140.3 s	—	142.3 (143.8)
17	19.4 q	1.86 d (2.0)	110.3 (109.1)
18	22.5 q	1.16 s	22.7 (23.4)
19	51.6 t	1.88, 2.64 ABq 12.4	51.7 (51.9)
20	66.8 d	3.06 d (3.2)	67.2 (67.5)
NCH_3	41.6 q	2.45 s	41.6 (41.5)

a: $CDCl_3$+CD_5N; b: C_6D_6+ $CDCl_3$.

References and notes

1. C. S. Peng, J. Z. Wang, X. X. Jian, F. P. Wang, *Natural Products R & D*, in press.
2. **Racemulodine** (**1**). a colorless needle, mp. 181-183℃ (cyclohexane-acetone), $[\alpha]_D^{17}$ -24.9 (c 0.2, EtOH). IR (KBr) cm^{-1}: 3400, 3030, 1721, 1691, 1606, 824. FABMS: *m/z* (%) 584 (100, M+1), 546 (44), 344 (18), 330 (25), 105 (54), 91 (8), 77 (19). ^{1}H- and ^{13}C- NMR: **Table 1**.
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