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Two new C_{19}-diterpenoid alkaloids from roots *Aconitum hemsleyanium* var. *atropurpureum*

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Abstract

A new franchetine-type C_{19}-diterpenoid alkaloid 3-hydroxyfranchetine **1** and a new aconitine-type C_{19}-diterpenoid alkaloid atropurpursine **2** have been isolated from the roots of *Aconitum hemsleyanium* var. *atropurpureum*. The structures of these new alkaloids were established on the basis of spectral data.

Keywords: *Aconitum hemsleyanium* var. *atropurpureum*; Rranunculaceae; C_{19}-diterpenoid alkaloid; 3-Hydroxyfranchetine; Atropurpursine

The genus *Aconitum* is well known as poisonous and medicinal plants, which comprises *ca*. 400 species, and more than a half of them are growing in China [1]. *Aconitum hemsleyanium* var. *atropurpureum* (Hand.–Mazz.) W.T. Wang is endemic to China, especially in classificately falling into the Ser. Volubilia Steinb. of Subgen. *Aconitum* [2]. To our knowledge, no phytochemistry of this plant has been reported yet. The investigation of *A. hemsleyanium* var. *atropurpureum* led to a new franchetine-type C_{19}-diterpenoid alkaloid 3-hydroxyfranchetine **1** and a new aconitine-type C_{19}-diterpenoid alkaloid atropurpursine **2** (Fig. 1). In this paper, we report the isolation and structural elucidation of the new alkaloids.

3-Hydroxyfranchetine (**1**), white amorphous powder, $C_{31}H_{41}NO_7$ ($[M + H]^+$ ion at *m/z* 540.2961 in HR-ESIMS) calcd. 540.2956, showed the distinct NMR features of a franchetine-type C_{19}-diterpenoid alkaloid skeleton [3], bearing an *N*-ethyl group (δ_H 1.04, t, 3H, J = 7.2 Hz), three methoxyl groups (δ_H 3.26, 3.32, and 3.36, s, each 3H), and a benzoyl group (δ_H 8.05, d, 2H, J = 7.8 Hz; 7.55, t, 1H, J = 7.8 Hz; 7.44, t, 2H, J = 7.8 Hz), as well as an *N*,*O*-mixed ketal moiety (δ_H 4.40, s, 1H; 4.42, d, 1H, J = 6.0 Hz; δ_C 91.9, d, 74.8, d). One-proton triplet signal at δ_H 5.15 could be attributed to H-14β [4], indicating the presence of an ester group at C-14. A hydroxyl group should be attributed at C-3 based on a carbon signal at 42.1 (s) assignable to C-4, since it was shifted downfield (4.8 ppm) in **1** comparing with that of **3** [3] due to the β effect of hydroxyl group at C-3 [4], as well as the HMBC correlations of H-3/C-2, C-4. Furthermore, the α-hydroxyl group at C-3 was confirmed by the NOE relationships between the H-3 (δ_H 3.88) and H-5 (δ_H 2.23), and also H-3 and H-18 (δ_H 3.37). All available evidence strongly suggested the structure of 3-hydroxyfranchetine as depicted in **1**.

Atropurpursine **2**, was obtained as white amorphous powder. The HR-ESIMS showed the proton molecular ion peak at *m/z* 646.3240 for $C_{34}H_{48}NO_{11}$ ($[M + H]^+$ cacld. 646.3227). Compound **2** exhibited characteristic NMR

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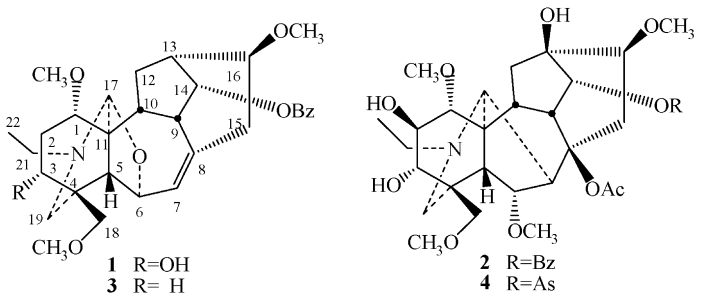

Fig. 1. Structures of new diterpenoid alkaloids **1** and **2**.

Table 1
^{1}H and ^{13}C NMR spectral data of compounds (**1**: 600 MHz for ^{1}H, 150 MHz for ^{13}C; **2**: 400 MHz for ^{1}H, 100 MHz for ^{13}C, $CDCl_3$, δ ppm, J_{Hz})

Position	**1**		**3** [3]	**2**		**4** [6]
	δ_H	δ_C	δ_C	δ_H	δ_C	δ_C
1	3.39 m	84.2 d	86.6 d	3.19 d (5.2)	83.5 d	83.5 d
2	2.24 br s (α) 2.59 br s (β)	33.0 t	24.3 t	4.05 m	65.2 d	65.4 d
3	3.88 dd (12, 4.8)	71.4 d	32.7 t	3.55 dd (8.8, 4.4)	67.8 d	67.9 d
4	–	42.1 s	37.3 s	–	43.9 s	43.9 s
5	2.23 m	46.0 d	47.9 d	2.30 d (6.8)	45.8 d	49.9 d[a]
6	4.42 d (6.0)	74.8 d	74.8 d	4.08 d (6.0)	82.5 d	82.6 d
7	5.78 d (6.0)	128.6 d	128.8 d	3.10 s	49.7 d	45.7 d[a]
8	–	137.2 s	136.8 s	–	85.1 s	85.2 s
9	3.05 br s	42.9 d	42.9 d	3.00 t (4.4)	45.5 d	46.0 d
10	2.38 m	49.1 d	49.4 d	2.19 s	40.5 d	40.7 d
11	–	50.4 s	50.5 s	–	52.7 s	52.7 s
12	1.58 br s (β) 2.09 m (α)	30.0 t	29.9 t	2.20 s (β) 2.66 s (α)	37.3 t	37.4 t
13	2.62 m	38.4 d	38.3 d	–	74.6 s	74.7 s
14	5.15 br s	78.7 d	78.7 d	4.91 d (4.8)	78.5 d	78.4 d
15	2.54 m (α) 2.91 m (β)	38.6 t	38.5 t	2.43 d (6.8) (α) 2.95 d (6.8) (β)	39.4 t	39.5 d
16	3.34 s	85.5 d	85.4 d	3.31 (hidden)	83.6 d	83.8 d
17	4.40 s	91.9 d	92.4 d	2.73 s	60.1 d	60.1 d
18	3.23 ABq (9.6) 3.37 ABq (hidden)	76.3 t	79.0 t	3.46 ABq (8.0) 3.62 ABq (8.0)	71.8 t	71.9 t
19	1.78 ABq (11.4) 2.90 ABq (11.4)	45.6 t	52.0 t	2.24 ABq (12.0) 2.63 ABq (12.0)	45.2 t	48.5 t[b]
21	2.44 m 2.60 m	48.9 t	49.0 t	2.64 m	48.4 t	45.5 t[b]
22	1.04 t (7.2)	13.1 q	13.0 q	1.14 t (7.2)	12.0 q	12.1 q
1-OCH_3	3.36 s	57.1 q	57.1 q	3.32 s	55.9 q	55.9 q
6-OCH_3	–	–	–	3.21 s	58.3 q	58.8 q
16-OCH_3	3.26 s	56.1 q	56.1 q	3.52 s	58.7 q	58.4 q
18-OCH_3	3.32 s	59.5 q	59.4 q	3.30 s	58.8 q	58.8 q
4′-OCH_3	–	–	–	–	–	55.4q
OAc(CO)	–	–	–	–	169.7 s	169.7 s
OAc(CH_3)	–	–	–	1.32 s	21.3 q	21.5 q
OAr(CO)	–	166.5 s	166.5 s	–	166.3 s	166.1 s
1′	–	130.6 s	130.5 s	–	130.1 s	122.7 s
2′,6′	8.05 d (7.8)	129.7 d	129.6 d	8.05 d (8.0)	129.7 d	131.7 d
3′,5′	7.44 t (7.8)	128.4 d	128.3 d	7.44 t (8.0)	128.5 d	113.8 d
4′	7.55 t (7.8)	132.8 d	132.7 d	7.56 t (8.0)	133.1 d	163.6 s

[a,b]Data may be exchanged.