Five New C_{19}-Diterpenoid Alkaloids from *Aconitum hemsleyanum*

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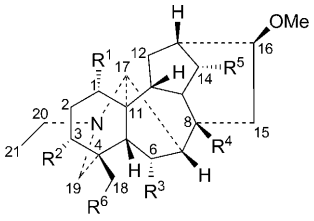
Five new C_{19}-diterpenoid alkaloids, named hemsleyaconitines A – E (**1** – **5**, resp.), were isolated from *Aconitum hemsleyanum* PRITZ. By UV, IR, MS, 1D- and 2D-NMR analyses, their structures were elucidated as 18-dehydroxygeniculatine D (**1**), 6-hydroxy-14-*O*-veratroylneoline (**2**), 14-*O*-acetyl-8-ethoxysachaconitine (**3**), 18-veratroylkaracoline (**4**) and 8-*O*-ethylaustroconitine B (**5**).

Introduction. – *Aconitum hemsleyanum* PRITZ. (Ranunculaceae), a perennial herb distributed in Sichuan and Yunnan Provinces of China, has long been used as a folk medicine to treat rheumatism and pains [1]. Previous studies on this plant revealed that aconitine-type C_{19}-norditerpenoid alkaloids were the main constituents [2 – 4]. During our search for bioactive chemicals from natural sources, *A. hemsleyanum* was phytochemically investigated to afford five new C_{19}-norditerpenoid alkaloids, as well as four known ones, sachaconitine [5], karakoline [6], acoforestinine [7], and isotalatizidine [8], identified by comparing the spectral data with those reported. All of the compounds **1** – **5** (*Fig. 1*), as well as sachaconitine, karakoline, and acoforestinine, showed positive reactions to *Dragendorff*'s reagent. Here, we report the isolation and structure elucidation of the five new alkaloids.



	R^1	R^2	R^3	R^4	R^5	R^6
1	MeO	H	H	OH	VrO	H
2	OH	H	OH	OH	VrO	MeO
3	MeO	H	H	EtO	AcO	H
4	OH	H	H	OH	OH	VrO
5	MeO	OH	MeO	EtO	AnO	MeO

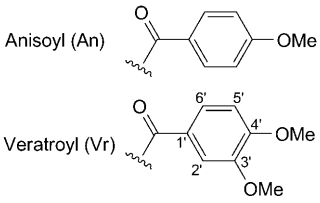


Fig. 1. *The structures of compounds* **1** – **5**

Results and Discussion. – Hemsleyaconitine A (**1**) was obtained as white prisms. Its molecular formula was determined to be $C_{32}H_{45}NO_7$ based on EI-MS (M^+, m/z 555) and HR-ESI-MS (m/z 556.3287 ([M + H]$^+$; calc. 556.3274)) analyses, indicating eleven degrees of unsaturation. The IR spectrum showed the absorption for OH (3453 cm^{-1}), conjugated ester CO (1713 cm^{-1}), and aromatic ring (1602, 1516, 1463 cm^{-1}) functions.

The ^{1}H-NMR spectra of compound **1** displayed signals of one *N*-ethyl (δ(H) 2.47–2.51 (*m*), 2.48–2.54 (*m*), 1.07 (*t*, J = 7.0)), two MeO groups (δ(H) 3.20 (*s*), 3.29(*s*)), and one veratroyl group (δ(H) 7.64 (*dd*, J = 8.3, 1.7), 7.57 (*d*, J = 1.7), 6.89 (*d*, J = 8.4), 3.92 (*s*), 3.93 (*s*)). Its ^{13}C-NMR (DEPT) spectrum revealed the presence of 32 C-atoms including six Me, seven CH_2, and twelve CH groups, as well as seven quaternary C-atoms. These spectral data suggested that compound **1** might be an aconitine-type C_{19}-diterpenoid alkaloid [9][10]. Comparing the ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*) of compound **1** with those of geniculatine D [11] showed high similarity except that the signal due to C(18) was shifted upfield from δ(C) 69.0 (CH_2) in geniculatine D to δ(C) 26.4 (Me) in compound **1**, which suggested that there should be a Me(18) group located at C(4). The long-range correlations between Me(18) (δ(H) 0.78 (*s*)) and C(3), C(4), C(5), and C(19) in the HMBC spectrum further confirmed the structure (*Fig. 2*).

Compound **1** had the same relative configuration as geniculatine D, not only being supported by their almost identical ^{1}H- and ^{13}C-NMR data (*Tables 1* and *2*), but also verified by a ROESY spectrum (*Fig. 3*). As shown in *Fig. 2*, the correlations between H–C(10) (assumed to be in β-orientation with reference to the aconitine type C_{19}-diterpenoid alkaloids [2–4]), and H–C(1), H–C(9), H–C(13), and MeO–C(16) were observed, indicating the β-orientations of H–C(1), H–C(9), H–C(13), and MeO–C(16). Thus, the structure of compound **1** was determined as 18-dehydroxy-geniculatine D, named hemsleyaconitine A (**1**).

Hemsleyaconitine B (**2**) was obtained as colorless prisms and had a molecular formula of $C_{32}H_{45}NO_9$ based on EI-MS (M^+, m/z 587) and HR-ESI-MS (588.3173, [M + H]$^+$; calc. 588.3172) analyses. Careful interpretation of the NMR spectra suggested that compound **2** was also an aconitine type C_{19}-diterpenoid alkaloid. The ^{1}H- and ^{13}C-NMR data (*Tables 1* and *2*) of compound **2** were almost identical to those of 14-*O*-veratroylneoline [12] except that the C-atom signal assignable to C(6) in compound **2** was shifted upfield at δ(C) 72.0 from δ(C) 83.2 in 14-*O*-veratroylneoline, implying that there was only one OH group located at C(6). This was further confirmed by the cross-peaks between H–C(6) (δ(H) 4.67 (*d*, J = 6.2)), and C(4), C(5), C(7), and C(8) in the HMBC spectrum. Consequently, hemsleyaconitine B (**2**) was elucidated as 6-hydroxy-14-*O*-veratroylneoline.

Hemsleyaconitine C (**3**) was assigned the molecular formula $C_{27}H_{43}NO_5$ by analyses of EI-MS (M^+, m/z 461) and HR-ESI-MS (462.3226 [M + H]$^+$; calc. 462.3219). The 1D-NMR spectra (*Tables 1* and *2*) resembled those of 8-ethoxysachaconitine [13] with the exception of an additional AcO signal appearing at δ(C) 171.4 (*s*), 21.4 (*q*). The AcO group was determined to be linked at C(14) by HMBCs between δ(H) 4.71 (*t*, J = 4.8, H–C(14)) and δ(C) 171.4 (C=O of the AcO group)). The ROESY correlations of H–C(14) with H–C(10) and H–C(13), together with the ^{1}H,^{1}H-coupling constant similar to that of 8-ethoxysachaconitine, established the α-orientation of the AcO

Table 1. *^{13}C-NMR Data of Compounds* **1**–**5**. At 125 MHz in $CDCl_3$; δ in ppm.

Position	**1**	**2**	**3**	**4**	**5**
C(1)	86.0 (*d*)	72.0 (*d*)	86.0 (*d*)	72.1 (*d*)	83.5 (*d*)
C(2)	26.7 (*t*)	29.2 (*t*)	27.0 (*t*)	26.7 (*t*)	33.0 (*t*)
C(3)	37.8 (*t*)	29.7 (*t*)	36.3 (*t*)	29.6 (*t*)	72.0 (*d*)
C(4)	34.5 (*s*)	37.8 (*s*)	34.3 (*s*)	36.9 (*s*)	42.9 (*s*)
C(5)	45.3 (*d*)	45.8 (*d*)	50.5 (*d*)	41.8 (*d*)	48.6 (*d*)
C(6)	25.4 (*t*)	72.9 (*d*)	24.5 (*t*)	25.1 (*t*)	82.7 (*d*)
C(7)	50.8 (*d*)	55.8 (*d*)	40.8 (*d*)	45.1 (*d*)	45.4 (*d*)
C(8)	74.0 (*s*)	75.6 (*s*)	77.6 (*s*)	74.1 (*s*)	78.3 (*s*)
C(9)	46.6 (*d*)	45.8 (*d*)	45.1 (*d*)	46.6 (*d*)	45.1 (*d*)
C(10)	45.3 (*d*)	43.7 (*d*)	43.2 (*d*)	44.0 (*d*)	45.1 (*d*)
C(11)	49.0 (*s*)	50.1 (*s*)	50.5 (*s*)	48.7 (*s*)	50.9 (*s*)
C(12)	28.6 (*t*)	29.3 (*t*)	29.1 (*t*)	28.4 (*t*)	28.7 (*t*)
C(13)	36.6 (*d*)	37.8 (*d*)	38.1 (*d*)	39.9 (*d*)	38.4 (*d*)
C(14)	76.6 (*d*)	76.6 (*d*)	75.8 (*d*)	75.7 (*d*)	75.9 (*d*)
C(15)	41.0 (*t*)	42.0 (*t*)	37.8 (*t*)	42.3 (*t*)	36.5 (*t*)
C(16)	81.8 (*d*)	82.1 (*d*)	83.4 (*d*)	81.8 (*d*)	83.2 (*d*)
C(17)	61.9 (*d*)	63.3 (*d*)	61.3 (*d*)	63.8 (*d*)	60.8 (*d*)
C(18)	26.4 (*q*)	80.4 (*t*)	26.5 (*q*)	70.0 (*t*)	76.8 (*t*)
C(19)	56.7 (*t*)	56.9 (*t*)	56.7 (*t*)	56.3 (*t*)	48.5 (*t*)
Me*C*H_2N	49.3 (*t*)	48.2 (*t*)	49.2 (*t*)	48.4 (*t*)	47.7 (*t*)
MeCH_2N	13.6 (*q*)	13.0 (*q*)	13.5 (*q*)	13.0 (*q*)	13.3 (*q*)
*Me*O–C(1)	56.3 (*q*)	–	56.2 (*q*)	–	55.7 (*q*)
*Me*O–C(6)	–	–	–	–	58.6 (*q*)
*Me*O–C(16)	56.0 (*q*)	56.2 (*q*)	56.2 (*q*)	56.3 (*q*)	56.3 (*q*)
*Me*O–C(18)	–	59.1 (*q*)	–	–	59.1 (*q*)
Me*C*H_2–C(8)	–	–	55.5 (*t*)	–	55.9 (*t*)
MeCH_2–C(8)	–	–	16.3 (*q*)	–	15.5 (*q*)
Acyl group	VrO–C(14)[a])	VrO–C(14)	AcO–C(14)	VrO–C(18)	AnO–C(14)[b])
C=O	166.3 (*s*)	165.9 (*s*)	171.4 (*s*)	166.3 (*s*)	166.2 (*s*)
C(1′)	123.0 (*s*)	122.6 (*s*)	21.4 (*q*)	122.6 (*s*)	123.3 (*s*)
C(2′)	112.0 (*d*)	112.1 (*d*)	–	112.0 (*d*)	131.7 (*d*)
C(3′)	148.5 (*s*)	148.5 (*s*)	–	148.7 (*s*)	113.4 (*d*)
C(4′)	152.8 (*s*)	152.9 (*s*)	–	153.1 (*s*)	163.1 (*s*)
C(5′)	110.3 (*d*)	110.2 (*d*)	–	110.3 (*d*)	113.4 (*d*)
C(6′)	123.5 (*d*)	123.5 (*d*)	–	123.4 (*d*)	131.7 (*d*)
*Me*O–C(3′)	55.9 (*q*)	55.9 (*q*)	–	56.0 (*q*)	–
*Me*O–C(4′)	56.0 (*q*)	56.0 (*q*)	–	56.0 (*q*)	55.3 (*q*)

[a]) Vr = Veratroyl. [b]) An = Anisoyl.

group. Therefore, hemsleyaconitine C (**3**) was identified as 14-*O*-acetyl-8-ethoxysachaconitine.

The molecular formula of hemsleyaconitine D (**4**) was deduced as $C_{31}H_{43}NO_8$ from EI-MS (M^+, *m*/*z* 557) and HR-ESI-MS (558.3076 $[M+H]^+$; calc. 558.3066) experiments. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) of compound **4** were almost identical to those of columbianine [14] except for the presence of an additional veratroyl group (δ(H) 7.62 (*dd*, *J* = 8.4, 1.9, H–C(6′)), 7.51 (*d*, *J* = 1.9, H–C(2′)), 6.88

Table 2. *^{1}H-NMR Data of Compounds* **1**–**5**. At 500 MHz in $CDCl_3$; δ in ppm, J in Hz.

Position	**1**	**2**	**3**	**4**	**5**
1	3.15 (*dd*, *J* = 10.5, 6.6)	3.70 (br. *s*)	3.07 (*dd*, *J* = 10.4, 6.7)	3.75 (br. *s*)	3.15 (*dd*, *J* = 10.4, 6.2)
2a	1.96–2.00 (*m*)	1.83 (*dd*, *J* = 14.0, 9.7)	1.93–1.98 (*m*)	1.76 (*dd*, *J* = 14.0, 4.3)	1.81–1.86 (*m*)
2b	2.32–2.37 (*m*)	2.21–2.28 (*m*)	2.22–2.29 (*m*)	1.90–1.95 (*m*)	2.30–2.35 (*m*)
3a	1.20–1.25 (*m*)	1.48–1.53 (*m*)	1.92–1.97 (*m*)	1.59–1.64 (*m*)	3.81 (*dd*, *J* = 12.3, 7.6)
3b	1.23–1.27 (*m*)	1.59–1.66 (*m*)	2.11 (*dd*, *J* = 14.2, 9.0)	1.64–1.68 (*m*)	–
5	1.45 (*d*, *J* = 7.1)	1.96 (*d*, *J* = 5.7)	1.34 (*d*, *J* = 7.3)	1.63–1.66 (overlapped)	2.39 (*d*, *J* = 7.2)
6a	1.51 (*dd*, *J* = 14.9, 8.1)	4.67 (*d*, *J* = 6.2)	1.28–1.36 (*m*)	1.61–1.66 (*m*)	4.13 (*d*, *J* = 6.3)
6b	1.88–1.94 (*m*)	–	1.92–1.98 (*m*)	1.92–1.98 (*m*)	–
7	2.10 (br. *d*, *J* = 7.8)	1.90 (br. *s*)	2.34–2.37 (overlapped)	1.88–1.93 (overlapped)	2.47–2.49 (overlapped)
9	1.89–1.92 (overlapped)	2.35–2.39 (overlapped)	2.34–2.38 (overlapped)	2.20–2.23 (overlapped)	1.93–1.95 (overlapped)
10	2.43–2.49 (*m*)	2.06–2.10 (*m*)	1.83–1.89 (*m*)	2.07–2.11 (*m*)	2.10–2.15 (*m*)
12a	1.95–1.99 (*m*)	1.57–1.64 (*m*)	1.92–1.99 (*m*)	1.59–1.65 (*m*)	1.92–1.95 (*m*)
12b	2.25 (*dd*, *J* = 15.0, 5.9)	2.11–2.17 (*m*)	1.83–1.89 (*m*)	2.00–2.05 (*m*)	2.14–2.19 (*m*)
13	2.63 (*dd*, *J* = 6.7, 5.4)	2.59 (*dd*, *J* = 6.2, 5.8)	2.34–2.39 (overlapped)	2.31 (*dd*, *J* = 7.5, 5.4)	2.45–2.51 (overlapped)
14	5.14 (*t*, *J* = 4.7)	5.09 (*t*, *J* = 4.3)	4.71 (*t*, *J* = 4.8)	4.21 (*t*, *J* = 4.9)	4.96 (*t*, *J* = 4.8)
15a	2.02–2.07 (*m*)	2.06–2.12 (*m*)	1.17–1.23 (*m*)	2.05–2.11 (*m*)	2.10–2.15 (*m*)
15b	2.47–2.52 (*m*)	2.27–2.31 (*m*)	1.57 (*d*, *J* = 11.3)	2.38 (*dd*, *J* = 12.9, 9.2)	2.13–2.19 (*m*)
16	3.27–3.30 (overlapped)	3.27–3.37 (overlapped)	3.21–3.24 (overlapped)	3.36 (*dd*, *J* = 9.1, 5.1)	3.31–3.34 (overlapped)
17	2.99 (br. *s*)	2.68 (br. *s*)	2.73 (br. *s*)	2.81 (br. *s*)	2.66 (br. *s*)
18a	0.78 (*s*)	3.30–3.35 (*m*)	0.73 (*s*)	3.95 (*d*, *J* = 10.8)	3.41 (*d*, *J* = 8.7)
18b	–	3.64 (*d*, *J* = 8.4)	–	4.11 (*d*, *J* = 10.8)	3.57 (*d*, *J* = 8.6)
19a	2.00–2.04 (overlapped)	2.31–2.35 (overlapped)	1.93–1.97 (*m*)	2.20–2.23 (*m*)	3.31–3.35 (overlapped)
19b	2.41–2.46 (*m*)	2.74 (*d*, *J* = 10.6)	2.38–3.46 (*m*)	2.44 (*d*, *J* = 11.0)	3.45 (*d*, *J* = 11.1)
Me*C*H_2N	2.47–2.51 (*m*), 2.48–2.54 (*m*)	2.51 (*dd*, *J* = 12.8, 7.1), 2.53 (*dd*, *J* = 12.9, 7.1)	2.30–2.36 (*m*), 2.41–2.45 (*m*)	2.48 (*dd*, *J* = 12.6, 7.2), 2.57 (*dd*, *J* = 12.4, 7.2)	2.39–2.45 (*m*), 2.46–2.50 (*m*)
MeCH_2N	1.07 (*t*, *J* = 7.0)	1.14 (*t*, *J* = 7.0)	1.03 (*t*, *J* = 7.1)	1.13 (*t*, *J* = 7.2)	1.07 (*t*, *J* = 7.1)
MeO–C(1)	3.20 (*s*)	–	3.24 (*s*)	–	3.24 (*s*)
MeO–C(6)	–	–	–	–	3.30 (*s*)
MeO–C(16)	3.29 (*s*)	3.27 (*s*)	3.30 (*s*)	3.33 (*s*)	3.33 (*s*)
MeO–C(18)	–	3.31 (*s*)	–	–	3.29 (*s*)
Me*C*H_2–C(8)	–	–	3.29–2.36 (*m*)	–	2.85–2.88 (*m*)
MeCH_2–C(8)	–	–	1.07 (*t*, *J* = 6.9)	–	0.80 (*t*, *J* = 6.9)

Table 2 (cont.)

Position	**1**	**2**	**3**	**4**	**5**
Acyl group	VrO–C(14)[a])	VrO–C(14)	AcO–C(14)	VrO–C(18)	AnO–C(14)[b])
1′	–	–	2.00 (*s*)	–	–
2′	7.57 (*d*, *J* = 1.7)	7.59 (*s*)	–	7.51 (*d*, *J* = 1.9)	8.02 (*d*, *J* = 8.7)
3′	–	–	–	–	6.89 (*d*, *J* = 8.8)
5′	6.89 (*d*, *J* = 8.4)	6.87 (*d*, *J* = 8.4)	–	6.88 (*d*, *J* = 8.5)	8.02 (*d*, *J* = 8.7)
6′	7.64 (*dd*, *J* = 8.3, 1.7)	7.65 (*d*, *J* = 8.3)	–	7.62 (*dd*, *J* = 8.4, 1.9)	6.89 (*d*, *J* = 8.8)
MeO–C(3′)	3.92 (*s*)	3.91 (*s*)	–	3.91 (*s*)	–
MeO–C(4′)	3.93 (*s*)	3.92 (*s*)	–	3.92 (*s*)	3.84 (*s*)

[a]) Vr = Veratroyl. [b]) An = Anisoyl.

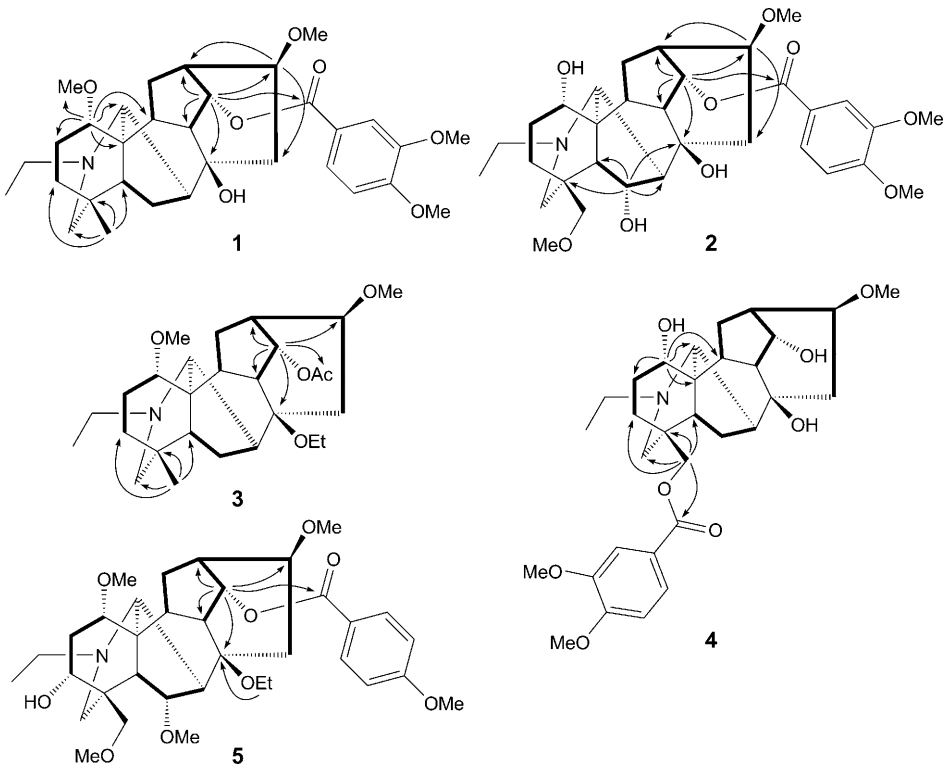


Fig. 2. *Selected* $^1H,^1H$*-COSY* (—) *and HMBC* (H→C) *correlations of compounds* **1**–**5**

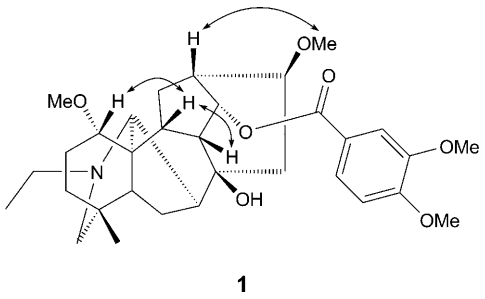


Fig. 3. *Selected ROESY correlations of compound* **1**

(*d*, *J* = 8.5, H–C(5′)), 3.91 (*s*, MeO–C(3′)), 3.92 (*s*, MeO–C(4′)) in compound **4**. The veratroyl group at C(18) was evidenced by the HMBC correlations from H_a–C(18) and H_b–C(18) to C=O of the veratroyl group. Accordingly, hemsleyaconitine D (**4**) was established as 18-veratroylkaracoline (*Fig. 1*).

Hemsleyaconitine E (**5**) had the molecular formula $C_{35}H_{51}NO_9$, in agreement with the EI-MS (M^+, *m*/*z* 629) and HR-ESI-MS (positive-ion mode; 630.3649 ($[M+H]^+$;

calc. 630.3642)) analyses. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) differed from those of austroconitine B [15] in the substitution pattern of C(8), where an EtO group (δ(H) 2.85–2.88 (*m*, 2 H), 0.80 (*t*, *J* = 6.9, 3 H)) was discernible, instead of a OH group in austroconitine B. This contention was also confirmed by the HMBC between δ(H) 2.85–2.88 (EtO) and C(8). Hence, hemsleyaconitine E (**5**) was determined as 8-*O*-ethylaustroconitine B.

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh, *Qingdao Marine Chemical Ltd.*, Qingdao, P. R. China); Al_2O_3 (*Shanghai Wusi Chemical Reagents Company, Ltd.*); *Sephadex LH-20* (*Pharmacia Fine Chemical Co. Ltd.*, Germany). M.p.: *XRC-1* micro-melting-point apparatus, uncorrected. Optical rotations: *Horiba SEPA-300* polarimeter. UV Spectra: *Shimadzu UV-2401A* spectrophotometer. IR Spectra: *Bio-Rad FTS-135* spectrometer. 1D- and 2D-NMR spectra: *Bruker AM-400* and *DRX-500* spectrometers; chemical shifts δ in ppm with reference to the solvent signals. MS: *VG Autospec-3000* spectrometer at 70 eV; in *m*/*z*. HR-ESI-MS: *API Qstar-Pulsar-1* spectrometer.

Plant Material. The roots of *Aconitum hemsleyanum* PRITZ. were collected in Wuding County, Yunnan Province, P. R. China, in October, 2006, and authenticated by Prof. Dr. *Li-Gong Lei* from Kunming Institute of Botany. A voucher specimen (No. KIB 2006-10-01) has been deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The roots of *A. hemsleyanum* (54 kg) were powdered and extracted three times with 95% EtOH for 2 h under reflux. After removing the solvent, the crude extract was dissolved in 15 l of 2% HCl soln. and filtered. The acidic soln. was basified to pH 9.0 with NH_3 (25%) and then extracted with $CHCl_3$ to obtain crude alkaloid extract (460 g) after removal of $CHCl_3$ *in vacuo*. The extract was chromatographed over a SiO_2 column (4.6 kg, 200–300 mesh) and eluted with gradient petroleum ether (PE)/acetone/Et_2NH (10:1:1 → 5:1:1) to provide six fractions, *Frs. 1–6*. *Fr. 2* (14.6 g) was successively chromatographed on a SiO_2 column (PE/acetone/Et_2NH, 15:1:1), an Al_2O_3 column (PE/acetone, 6:1), and *Sephadex LH-20* ($CHCl_3$/MeOH, 1:1) to yield **1** (12 mg), **3** (20 mg), and sachaconitine [5] (67 mg). *Fr. 3* (30.3 g) was subjected to a SiO_2 column and eluted with PE/acetone/Et_2NH 15:3:1, followed by Al_2O_3 CC (PE/acetone 5:1) to yield **4** (18 mg), karakoline [6] (2.5 g), and isotalatizidine [8] (1.8 g). *Fr. 4* (42.0 g) was subjected to an Al_2O_3 column with the eluent of PE/acetone 4:1 to yield **2** (15 mg), **5** (25 mg), and acoforestinine [7] (800 mg).

Hemsleyaconitine A (*= 18-Dehydroxygeniculatine D = (1α,14α,16β)-20-Ethyl-8-hydroxy-1,16-dimethoxy-4-methylaconitan-14-yl 3,4-Dimethoxybenzoate*; **1**). White prisms. M.p. 91–92°. $[\alpha]_D^{25.1} = +21.38$ (*c* = 0.11, $CHCl_3$). UV (MeOH): 219 (2.26). IR (KBr): 3453, 2963, 2928, 1713, 1602, 1516, 1463, 1270, 1222, 1094, 1025, 765. NMR: *Tables 1* and *2*. EI-MS: 555 (1, M^+), 524 (100, $[M - MeO]^+$), 262 (33), 165 (100). HR-ESI-MS (pos.): 556.3287 ($[M + H]^+$; $C_{32}H_{46}NO_7^+$; calc. 556.3274).

Hemsleyaconitine B (*= 6-Hydroxy-14-O-veratroylneoline = (1α,6α,14α,16β)-20-Ethyl-1,6,8-trihydroxy-16-methoxy-4-(methoxymethyl)aconitan-14-yl 3,4-Dimethoxybenzoate*; **2**). Colorless prisms. M.p. 104–105°. $[\alpha]_D^{24.9} = +9.16$ (*c* = 0.13, $CHCl_3$). UV (MeOH): 219 (2.37). IR (KBr): 3423, 2965, 2933, 1713, 1602, 1516, 1464, 1271, 1223, 1109, 1041, 764. NMR: *Tables 1* and *2*. EI-MS: 587 (4, M^+), 570 (39, $[M - OH]^+$), 285 (10), 165 (100). HR-ESI-MS (pos.): 588.3173 ($[M + H]^+$, $C_{32}H_{46}NO_9^+$; calc. 588.3172).

Hemsleyaconitine C (*= 14-O-Acetyl-8-ethoxysachaconitine = (1α,14α,16β)-8-Ethoxy-20-ethyl-1,16-dimethoxy-4-methylaconitan-14-yl Acetate*; **3**). Colorless crystals. M.p. 133–134°. $[\alpha]_D^{25.8} = -31.98$ (*c* = 0.17, $CHCl_3$). UV (MeOH): 223 (1.45). IR (KBr): 3449, 2969, 2924, 2891, 1739, 1640, 1461, 1443, 1365, 1248, 1117, 1094. NMR: *Tables 1* and *2*. EI-MS: 461 (4, M^+), 430 (47, $[M - MeO]^+$), 402 (80), 131 (100), 91 (85), 71 (98). HR-ESI-MS (pos.): 462.3226 ($[M + H]^+$, $C_{27}H_{44}NO_5^+$; calc. 462.3219).

Hemsleyaconitine D (*=18-Veratroylkaracoline=[(1α,14α,16β)-20-Ethyl-1,8,14-trihydroxy-16-methoxyaconitan-4-yl]methyl 3,4-Dimethoxybenzoate*; **4**). White prisms. M.p. 102–103°. $[\alpha]_D^{24.3} = +13.16$ ($c = 0.30$, $CHCl_3$). UV (MeOH): 219 (2.33). IR (KBr): 3426, 2936, 2837, 1711, 1601, 1516, 1463, 1418, 1291, 1271, 1222, 1176, 1101, 1023, 763. NMR: *Tables 1* and *2*. EI-MS: 557 (12, M^+), 540 (63, $[M-OH]^+$, 319 (29), 165 (100). HR-ESI-MS (pos.): 558.3076 ($[M+H]^+$, $C_{31}H_{44}NO_8^+$; calc. 558.3066).

Hemsleyaconitine E (*=8-O-Ethylaustroconitine B=(1α,3α,6α,14α,16β)-8-Ethoxy-20-ethyl-3-hydroxy-1,6,16-trimethoxy-4-(methoxymethyl)aconitan-14-yl 4-Methoxybenzoate*; **5**). White prisms. M.p. 93–94°. $[\alpha]_D^{24.2} = +13.89$ ($c = 0.19$, $CHCl_3$). UV (MeOH): 257 (2.13). IR (KBr): 3457, 2970, 2930, 2890, 1713, 1607, 1512, 1460, 1293, 1278, 1169, 1119, 1098, 771. NMR: *Tables 1* and *2*. EI-MS: 629 (2, M^+), 598 (100, $[M-MeO]^+$), 135 (59). HR-ESI-MS (pos.): 630.3649 ($[M+H]^+$, $C_{35}H_{52}NO_9^+$; calc. 630.3642).

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