Norditerpenoid Alkaloids from the Aerial Parts of *Aconitum cochleare* WOROSCHIN

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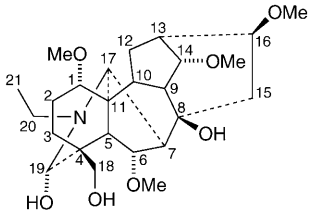
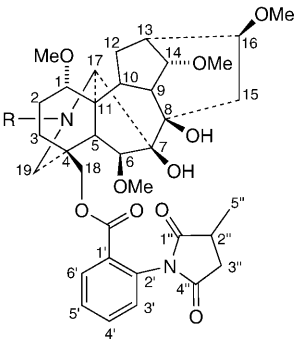
From the aerial parts of *Aconitum cochleare* WOROSCHIN, two new norditerpenoid alkaloids named aconitilearine (**1**) and *N*-deethylmethyllycaconitine (**2**) were isolated along with the eight known norditerpenoid alkaloids **3**–**10**. The structures for the new compounds were established on the basis of ^{1}H, ^{13}C, DEPT, homonuclear ^{1}H,^{1}H-COSY, NOESY, HSQC, and HMBC NMR studies.

Introduction. – *Aconitum* (Wolfslayer) species contain diterpenoid and norditerpenoid alkaloids, and they are very toxic plants. The toxicity is due especially to the norditerpenoid alkaloids [1]. In continuation of our investigations on Turkish *Aconitum* species [2–6], we now report the alkaloid contents from the aerial parts of *Aconitum cochleare* WOROSCHIN. Previously, the diterpenoid alkaloid content of the roots from the same plant has been studied [7]. The chemical investigation of the aerial parts of *A. cochleare* led to the isolation of two new norditerpenoid alkaloids, aconitilearine (**1**) and *N*-deethylmethyllycaconitine (**2**), together with eight known norditerpenoid alkaloids, lycoctonine (**3**) [8], delsoline (**4**) [9], neoline (**5**) [10], chasmanine (**6**) [11], acoseptrigine (**7**) [12], methyllycaconitine (**8**) [13], delsemine A (**9**) [14], and delsemine B (**10**) [14].

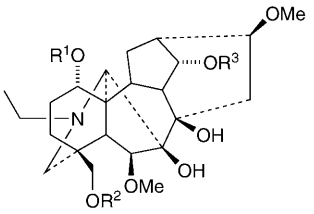
Results and Discussion. – The first novel norditerpenoid alkaloid isolated from the aerial parts of *A. cochleare* is the optically active aconitilearine (**1**). The molecular formula $C_{25}H_{41}NO_7$ (EI-MS: M^+ at m/z 467) was derived from the HR-MS (M^+ at m/z 467.59618, calc. 467.59558) and confirmed by the ^{1}H- and ^{13}C-NMR and DEPT data (*Tables 1* and *2*). The IR spectrum showed an OH absorption at 3420 cm^{-1} but no carbonyl or aromatic absorptions. A completely decoupled ^{13}C-NMR spectrum confirmed the presence of 25 C-atoms in the molecule. Diterpenoid alkaloids usually conform to two main groups, those with a C_{19} lycoctonine/aconitine-type skeleton with characteristic MeO groups and those derived from a C_{20} atisine type having an exocyclic CH_2 group [15]. The ^{1}H-NMR spectrum of aconitilearine (**1**) revealed the presence of MeO groups, so it must be a C_{19} norditerpenoid alkaloid with an *N*-ethyl group. Com-



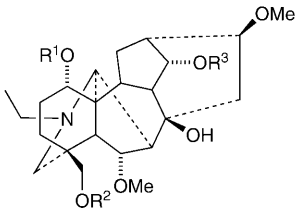
Aconitilearine (**1**)



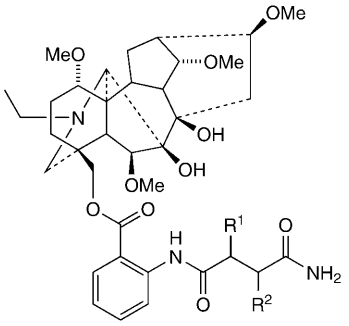
N-Deethylmethyllycaconitine (**2**)[1] R = H
Methyllycaconitine (**8**)[1] R = Et



Lycoctonine (**3**) $R^1 = R^3 = Me$, $R^2 = H$
Delsoline (**4**) $R^1 = H$, $R^2 = R^3 = Me$



Neoline (**5**) $R^1 = R^3 = H$, $R^2 = Me$
Chasmanine (**6**) $R^1 = R^2 = Me$, $R^3 = H$
Acoseptrigine (**7**) $R^1 = R^3 = Me$, $R^2 = H$



Delsemine A (**9**) $R^1 = Me$, $R^2 = H$
Delsemine B (**10**) $R^1 = H$, $R^2 = Me$

parison of all NMR data (*Tables 1* and *2*) with those of lycoctonine (**3**), neoline (**5**), and chasmanine (**6**) allowed to establish the structure of **1**.

The DEPT spectra of **1** showed three quaternary C-atoms at δ 80.4, 48.9, and 38.5, eleven signals for CH groups at δ 90.5, 84.0, 83.8, 82.6, 77.2, 64.7, 52.3, 44.6, 43.2, 43.0, and 38.0, six signals for CH_2 groups at δ 67.7, 51.2, 45.0, 33.7, 33.5, and 28.8, and five signals for Me groups at δ 57.9, 57.8, 56.3, 55.8, and 13.0. The *N*-ethyl group appeared at δ(H) 1.07 (*t*, $J = 7$ Hz, *Me*CH_2) and δ(C) 13.0. There were seven O-bearing C-atoms present as shown by the signals at δ(C) 90.5, 84.0, 83.8, 82.6, 77.2, 67.7, and 64.7, four of them carrying MeO groups; the other three, therefore, should have OH groups. There are several norditerpenoid alkaloids with the molecular mass 467 including lycoctonine (**3**) which was also isolated from this plant. Aconitilearine (**1**) showed some similarities with **3** having four MeO and three OH groups. Thereof, three MeO groups were located at C(1) (δ(C) 82.6), C(14) (84.0, *d*), and C(16) (83.8, *d*) in both alkaloids. They also both had one OH group at C(18) (δ(C) 67.7, *t*). The characteristic OH-substituted C(7) (δ(C) 88.4, *s*) of **3** could not be found in **1**. Like in neoline (**5**) and chasmanine (**6**), C(7) of **1** appeared at δ(C) 52.3 (*d*) establishing that **1** is an aconitine-type norditerpenoid alkaloid. One of the

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

Table 1. *^{1}H- and ^{13}C-NMR Data of Aconitilearine* (**1**) *and ^{13}C-NMR Data of Lycoctonine* (**3**) *for Comparison.* δ in ppm, J in Hz.

	1		**3**
	δ(H)	δ(C)	δ(C)
H_β–C(1)	3.20 (*dd*, *J* = 9, 6)	82.6 (*d*)	82.7 (*d*)
H_α–C(2)	1.70–1.73 (*m*)	28.6 (*t*)	28.8 (*t*)
H_β–C(2)	1.66–1.68 (*m*)		
H_α–C(3)	1.74–1.77 (*m*)	33.6 (*t*)	31.7 (*t*)
H_β–C(3)	2.43–2.47 (*m*)		
C(4)	–	38.5 (*s*)	38.6 (*s*)
H–C(5)	1.89–1.91 (*m*)	43.2 (*d*)	49.7 (*d*)
H–C(6)	4.10 (*dd*, *J* = 1, 6)	83.3 (*d*)	90.6 (*d*)
H–C(7)	2.25 (*d*, *J* = 1)	52.3 (*d*)	88.4 (*s*)
C(8)	–	73.4 (*s*)	77.6 (*s*)
H–C(9)	1.79–1.82 (*m*)	43.2 (*d*)	43.3 (*d*)
H–C(10)	1.61–1.65 (*m*)	44.6 (*d*)	46.1 (*d*)
C(11)	–	48.9 (*s*)	48.9 (*s*)
H_a–C(12)	2.29–2.31 (*m*)	28.8 (*t*)	26.2 (*t*)
H_b–C(12)	1.61–1.65 (*m*)		
H–C(13)	2.39–2.42 (*m*)	38.0 (*d*)	38.1 (*d*)
H–C(14)	3.57 (*t*, *J* = 5)	84.0 (*d*)	84.3 (*d*)
H_a–C(15)	1.69–1.71 (*m*)	33.8 (*t*)	33.6 (*t*)
H_b–C(15)	2.52 (*dd*, *J* = 12, 14)		
H–C(16)	3.60 (*dd*, *J* = 7, 12)	83.8 (*d*)	84.0 (*d*)
H–C(17)	2.87 (*s*)	64.7 (*d*)	64.9 (*d*)
H_a–C(18)	3.32 (*d*, *J* = 10)	67.7 (*t*)	67.7 (*t*)
H_b–C(18)	3.58 (*d*, *J* = 10)		
H–C(19)	3.85 (*s*)	90.5 (*d*)	52.7 (*t*)
H_a–C(20)	2.59–2.61 (*m*)	51.1 (*t*)	51.2 (*t*)
H_b–C(20)	2.43–2.47 (*m*)		
Me(21)	1.07 (*t*, *J* = 7)	13.0 (*q*)	14.2 (*q*)
*Me*O–C(1)	3.38 (*s*)	55.8 (*q*)	55.8 (*q*)
*Me*O–C(6)	3.36 (*s*)	57.9 (*q*)	57.8 (*q*)
*Me*O–C(14)	3.34 (*s*)	57.9 (*q*)	57.8 (*q*)
*Me*O–C(16)	3.33 (*s*)	56.3 (*q*)	56.3 (*q*)

remaining OH groups and the remaining MeO group of **1** should be located at C(8) (δ(C) 73.4, *d*) and C(6) (δ(C) 83.3, *d*), respectively, like in **5**. Most norditerpenoid alkaloids contain no substituents at C(19) giving rise to a *t* at δ(C) 52–57. No such signal was found in the spectrum of **1** but a *d* at δ(C) 90.5 suggested that the third OH group of **1** was located at C(19). Some norditerpenoid alkaloids have an epoxy bridge between C(1) and C(19) [17][18] giving rise to a *d* at δ(C) 87–91. However, the presence of a MeO group at C(1) of **1** (see above) confirmed the substitution of C(19) by an OH group. All attributions were confirmed by COSY, NOESY, and HMBC correlations (*Table 2*).

The second novel compound, *N*-deethylmethyllycaconitine (**2**), is very similar to methyllycaconitine (**8**) which was also isolated from the same plant. The only difference is the absence of the *N*-ethyl group and the presence of an NH group in the ^{1}H-NMR spectrum (δ(H) 3.26 (*s*, 1 H)). The molecular formula $C_{35}H_{46}N_2O_{10}$ (EI-MS: M^+ at *m*/*z*

Table 2. *Summary of COSY, NOESY, and HMBC Correlation Data of Aconitilearine* (**1**)

	COSY	NOESY	HMBC
H_β–C(1)	H_α–C(2), H_β–C(2)	H_α–C(2), H_β–C(2), H–C(10), H_b–C(12)	C(3), C(10), *Me*O–C(1)
H_α–C(2)	H_β–C(1), H_α–C(3), H_β–C(3)	H_β–C(1), H_β–C(3)	C(4), C(5), C(10)
H_β–C(2)	H_α–C(2)	H_β–C(1), H–C(5)	C(5), C(10)
H_α–C(3)	H_α–C(2), H_β–C(2), H_β–C(3)	–	–
H_β–C(3)	H_α–C(2), H_β–C(2), H_α–C(3)	H_α–C(2), H_b–C(18)	C(1), C(2), C(19)
H–C(5)	H–C(6)	H_β–C(2), H–C(6), H–C(9), H_a–C(18), H_b–C(19)	C(19), C(17), C(18)
H–C(6)	H–C(5)	H–C(5), H–C(7), H_a–C(18), H_b–C(18), *Me*O–C(6)	*Me*O–C(6)
H–C(7)	H–C(6), H–C(17)	H–C(6), H_b–C(15), H–C(17), H_b–C(19), *Me*O–C(6)	C(9), C(17)
H–C(9)	H–C(10), H–C(14)	H–C(5), H–C(10), H_a–C(12), H–C(14)	C(7), C(12), C(13), C(14), C(16)
H–C(10)	H–C(9), H_b–C(12)	H_β–C(1), H–C(9), H_b–C(12), H–C(14), *Me*O–C(16)	–
H_a–C(12)	H_b–C(12), H–C(13)	H_b–C(12), H–C(13), H–C(14)	–
H_b–C(12)	H–C(10), H_a–C(12)	H_β–C(1), H_a–C(12), H–C(13), H–C(16), H–C(17)	C(14), C(16)
H–C(13)	H_a–C(12), H–C(14)	H_a–C(12), H_b–C(12), H–C(14), H–C(16), *Me*O–C(16)	C(14), C(15), C(16)
H–C(14)	H–C(9), H–C(13)	H–C(9), H–C(10), H_a–C(12), H–C(13)	C(16), *Me*O–C(14)
H_a–C(15)	H_b–C(15)	H–C(16), *Me*O–C(14)	C(7), C(16)
H_b–C(15)	H_a–C(15), H–C(16)	–	C(7), C(16)
H–C(16)	H_b–C(15)	H–C(7), H_b–C(12), H–C(13), H_a–C(15), *Me*O–C(16), H–C(17)	C(12), C(14), *Me*O–C(16)
H–C(17)	H–C(5)	H–C(7), H_b–C(12), H–C(16), CH_2(20), Me(21)	C(5), C(6), C(10), C(19)
H_a–C(18)	H_b–C(18)	H–C(5), H–C(6), H_b–C(18), *Me*O–C(6)	C(3), C(19)
H_b–C(18)	H_a–C(18)	H_β–C(3), H–C(6), H_a–C(18), H–C(19)	C(3), C(5), C(19)
H–C(19)	–	H–C(6), H–C(7), H_a–C(18), H_b–C(18), CH_2(20)	C(3), C(5), C(17)
CH_2(20)	H_b–C(20), H_a–C(20), Me(21)	H–C(17), H–C(19), Me(21)	C(17), C(19), C(21)
Me(21)	H_a–C(20), H_b–C(20)	H–C(17), CH_2(20)	
*Me*O–C(1)	–	H–C(17), Me(21)	C(1)
*Me*O–C(6)	–	H_a–C(18)	C(6)
*Me*O–C(14)	–	H_a–C(15)	C(14)
*Me*O–C(16)	–	H–C(13), H–C(16), H–C(10)	C(16)

654) was derived from the HR-MS (M^+ at m/z 654.75090, calc. 654.75764) and confirmed by the ^{1}H- and ^{13}C-NMR and DEPT data (*Tables 3* and *4*). The IR spectrum showed absorptions for OH (3460 cm^{-1}) and C=O groups (1780 and 1720 cm^{-1}) and

Table 3. *^{1}H- and ^{13}C-NMR Data of* N-*Deethylmethyllycaconitine* (**2**) *and ^{13}C-NMR Data of Methyllycaconitine* (**8**) *for Comparison*[1]). δ in ppm, J in Hz. Arbitrary numbering of the pyrrolidinedione moiety.

	2		**8**
	δ(H)	δ(C)	δ(C)
H_β–C(1)	3.22 (*dd*, *J* = 9, 6)	84.2 (*d*)	83.8 (*d*)
H_α–C(2)	1.67–1.71 (*m*)	24.8 (*t*)	26.0 (*t*)
H_β–C(2)	1.67–1.71 (*m*)		
H_α–C(3)	1.79–1.83 (*m*)	33.3 (*t*)	34.0 (*t*)
H_β–C(3)	2.49–2.53 (*m*)		
C(4)	–	38.1 (*s*)	37.6 (*s*)
H–C(5)	1.96–1.98 (*m*)	43.6 (*d*)	43.5 (*d*)
H–C(6)	3.95 (br. *s*)	90.8 (*d*)	90.9 (*d*)
C(7)	–	88.0 (*s*)	88.4 (*s*)
C(8)	–	77.3 (*s*)	77.5 (*s*)
H–C(9)	1.79–1.83 (*m*)	51.2 (*d*)	50.9 (*d*)
H–C(10)	1.59–1.63 (*m*)	38.6 (*d*)	38.3 (*d*)
C(11)	–	49.0 (*s*)	49.1 (*s*)
H_a–C(12)	2.49–2.53 (*m*)	29.2 (*t*)	28.9 (*t*)
H_b–C(12)	1.59–1.63 (*m*)		
H–C(13)	2.49–2.53 (*m*)	45.0 (*d*)	46.2 (*d*)
H–C(14)	3.69 (*t*, *J* = 5)	84.8 (*d*)	83.8 (*d*)
H_a–C(15)	1.67–1.71 (*m*)	35.2 (*t*)	35.3 (*t*)
H_b–C(15)	2.59 (*dd*, *J* = 12, 14)		
H–C(16)	3.58–3.60 (*m*)	82.5 (*d*)	83.7 (*d*)
H–C(17)	2.87 (*s*)	65.0 (*d*)	64.3 (*d*)
H_a–C(18)	4.20 (*d*, *J* = 10)	69.3 (*t*)	69.5 (*t*)
H_b–C(18)	4.22 (*d*, *J* = 10)		
H_a–C(19)	1.79–1.81 (*m*)	50.9 (*t*)	52.7 (*t*)
H_b–C(19)	3.28–3.31 (*m*)		
Me*C*H_2N	–	–	50.8 (*t*)
*Me*CH_2N	–	–	13.8 (*q*)
NH	3.26 (*s*)	–	–
*Me*O–C(1)	3.38 (*s*)	55.8 (*q*)	55.5 (*q*)
*Me*O–C(6)	3.41 (*s*)	57.8 (*q*)	57.6 (*q*)
*Me*O–C(14)	3.34 (*s*)	58.1 (*q*)	58.2 (*q*)
*Me*O–C(16)	3.33 (*s*)	56.4 (*q*)	56.1 (*q*)
Ar–CO	–	164.7 (*s*)	164.1 (*s*)
C(1′)	–	128.2 (*s*)	127.9 (*s*)
C(2′)	–	133.1 (*s*)	133.3 (*s*)
H–C(3′)	7.26 (*dd*, *J* = 1.5, 8)	129.4 (*d*)	129.0 (*d*)
H–C(4′)	7.52 (*ddd*, *J* = 1.5, 8, 8)	133.7 (*d*)	133.3 (*d*)
H–C(5′)	7.68 (*ddd*, *J* = 1.5, 8, 8)	130.9 (*d*)	130.8 (*d*)
H–C(6′)	8.00 (*dd*, *J* = 1.5, 8)	130.1 (*d*)	130.0 (*d*)
C(1″)	–	178.0 (*s*)	179.1 (*s*)
H–C(2″)	2.87 (br. *s*)	38.1 (*d*)	37.0 (*d*)
H_α–C(3″)	2.87 (br. *s*)	35.2 (*t*)	35.3 (*t*)
H_β–C(3″)	2.87 (br. *s*)		
C(4″)	–	173.9 (*s*)	175.0 (*s*)
Me(5″)	1.44 (*d*, *J* = 7)	16.3 (*q*)	16.3 (*q*)

Table 4. *Summary of COSY, NOESY, and HMBC Correlation Data of* N-*Deethylmethyllycaconitine* (**2**)[1]). Arbitrary numbering of the pyrrolidinedione moiety.

	COSY	NOESY	HMBC
H_{β}–C(1)	H_{α}–C(2), H_{β}–C(2)	H_{α}–C(2), H_{β}–C(2), H–C(10), H_b–C(12)	C(3), C(10)
H_{α}–C(2)	H_{β}–C(1), H_{α}–C(3), H_{β}–C(3)	H_{β}–C(1), H_{β}–C(3)	C(4), C(5)
H_{β}–C(2)	H_{α}–C(2)	H_{β}–C(1), H–C(5)	C(5), C(10)
H_{α}–C(3)	H_{α}–C(2), H_{β}–C(2), H_{β}–C(3)	–	–
H_{β}–C(3)	H_{α}–C(2), H_{β}–C(2), H_{α}–C(3)	H_{α}–C(2), H_b–C(18)	C(1), C(2), C(19)
H–C(5)	H–C(17)	H_{β}–C(2), H_a–C(18), H_b–C(19)	C(17), C(18), C(19)
H–C(9)	H–C(10), H–C(14)	H_{β}–C(1), H–C(10), H_a–C(12), H–C(14)	C(12)
H–C(10)	H–C(9), H_b–C(12)	H_{β}–C(1), H–C(9), H_b–C(12)	C(8), C(11)
H_a–C(12)	H_b–C(12), H–C(13)	H_b–C(12), H–C(13), H–C(14)	–
H_b–C(12)	H_{β}–C(1), H–C(10), H_a–C(12)	H_{β}–C(1), H_a–C(12)	C(14)
H–C(13)	H_a–C(12), H–C(14)	H_a–C(12), H–C(14), H–C(16)	C(14), C(15), C(16)
H–C(14)	H–C(9), H–C(13)	H–C(9), H–C(13)	C(8), C(16), *Me*O–C(14)
H_a–C(15)	H_b–C(15)	H–C(16)	C(16)
H_b–C(15)	H_a–C(15), H–C(16)		C(16)
H–C(16)	H_b–C(15)	H_a–C(15), H–C(17)	C(12), C(14), C(15)
H–C(17)	H–C(5)	H–C(16)	C(5), C(6), C(10), C(19)
H_a–C(18)	H_b–C(18)	H–C(5), H_b–C(18)	C(3), C(19)
H_b–C(18)	H_a–C(18)	H_a–C(18), H_b–C(19)	C(3), C(5), C(19)
H_a–C(19)	–	H_{α}–C(3), H_b–C(18)	C(3), C(18)
H_b–C(19)		H_a–C(18), H_b–C(18)	C(3), C(5), C(17)
*Me*O–C(1)	–	–	–
*Me*O–C(6)	–	–	–
*Me*O–C(14)	–	–	–
*Me*O–C(16)	–	–	–
H–C(3′)	H–C(4′)	–	C(5′)
H–C(4′)	H–C(3′), H–C(5′)	–	C(6′)
H–C(5′)	H–C(4′), H–C(6′)	–	C(3′)
H–C(6′)	H–C(5′)	–	C(4′)
H–C(2″)	H_{α}–C(3″), H_{β}–C(3″)	–	–
H_{α}–C(3″)	H–C(2″), H_{β}–C(3″)	–	–
H_{β}–C(3″)	H–C(2″), H_{α}–C(3″)	–	–
Me(5″)	–	–	–

for an aromatic moiety (1490 cm^{-1}). Treatment of **8** with potassium permanganate in aqueous acetone gave *N*-deethylmethyllycaconitine (**2**) [19], which was previously obtained from methyllycaconitine (**8**) by the same method [20]. The isolation of *N*-deethylmethyllycaconitine (**2**) as a natural product is reported here for the first time.

Experimental Part

General. Vacuum liquid chromatography (VLC). *Merck* Al_2O_3 (*EM 1085*) and SiO_2 *60 G* (*7735*). Chromatographic separations: *Chromatotron*, on rotors coated with a 1-mm thick layer of *Merck* Al_2O_3 *60 GF-254* (*1092*) or SiO_2 *60 PF-254* (*7749*). TLC: toluene/AcOEt/Et_2NH 7:2:1 and $CHCl_3$/MeOH/NH_4OH 8:2:0.3. Optical rotations: *Perkin-Elmer 241* polarimeter. NMR Spectra: *Bruker 500-MHz* spectrometer. MS: *Finnigan MAT-90* spectrometer.

Plant Material. The aerial parts (2 kg) of *Aconitum cochleare* WOROSCHIN were collected and identified by one of us (*H. O.*) in Van, Güzeldere Pass, Turkey, at an elevation of 2800 m, in June 2000. A voucher specimen (No. Ozcelik 9352) has been deposited in the Herbarium of the Faculty of Science and Literature, Suleyman Demirel University, Isparta, Turkey.

Extraction and Isolation. The crude alkaloid extract (6.3 g) obtained from 2 kg of aerial parts was first separated by VLC (basic SiO_2, petroleum ether/$CHCl_3$/MeOH). *Fr. 18* (with $CHCl_3$/MeOH 96:4; 750 mg) was chromatographed on a SiO_2 rotor (petroleum ether/$CHCl_3$/MeOH: *N*-deethylmethyllycaconitine (**2**; 8 mg; $[\alpha]_D^{25} = +35.0$ ($c = 0.25$, $CHCl_3$), methyllycaconitine (**8**, 16 mg), acoseptrigine (**7**; 3 mg). *Fr. 20* (with $CHCl_3$/MeOH 92:8; 390 mg) was chromatographed on a Al_2O_3 rotor (petroleum ether/$CHCl_3$/MeOH): delsemine A/B (**9**/**10**; 20 mg), chasmanine (**6**; 6 mg), lycoctonine (**3**; 7 mg), and neoline (**5**; 8 mg). *Fr. 21* (with $CHCl_3$/MeOH 90:10; 750 mg) was chromatographed on a SiO_2 rotor (petroleum ether/$CHCl_3$/MeOH): delsoline (**4**; 5 mg). *Fr. 22–23* (with $CHCl_3$/MeOH 80:20 to 70:30; 300 mg) were chromatographed on a SiO_2 rotor (petroleum ether/$CHCl_3$/MeOH): aconitilearine (**1**; 14 mg; $[\alpha]_D = +55.0$ ($c = 0.11$, $CHCl_3$)).

Aconitilearine (= *(1α,6α,14α,16β)-20-Ethyl-4-(hydroxymethyl)-1,6,14,16-tetramethoxyaconitan-8,19-diol*; **1**), *N*-deethylmethyllycaconitine (= *(1α,6β,14α,16β)-1,6,14,16-Tetramethoxy-4-{[[2-(3-methyl-2,5-dioxopyrrolidin-1-yl)benzoyl]oxy}methyl}aconitane-7,8-diol*; **2**), delsemine A (**9**) and B (**10**), and chasmanine (**6**) were obtained in pure state directly from chromatotron fractions. Methyllycaconitine (**8**), acoseptrigine (**7**), delsoline (**5**) were purified by prep. TLC (toluene/AcOEt/Et_2NH 7:2:1), and lycoctonine (**3**) and neoline (**4**) by prep. TLC ($CHCl_3$/MeOH/NH_4OH 8:2:0.3). All the known compounds were identified by comparison of their ^1H- and ^{13}C-NMR data and co-TLC behavior with those of authentic samples.

N-*Deethylmethyllycaconitine* (**2**) *from Methyllycaconitine* (**8**). To a soln. of **8** (10 mg) in a mixture of Me_2CO (7.5 ml) and H_2O (0.5 ml), $KMnO_4$ (30 mg) dissolved in Me_2CO (13 ml) and H_2O (7 ml) was added, and the mixture was stirred at r.t. for 10 min. Excess $KMnO_4$ was destroyed with NH_4OH, and the mixture was extracted with $CHCl_3$. After evaporation, the residue was separated by TLC (silica gel, toluene/AcOEt/Et_2NH 7:2:1): two compounds. The polar band was isolated and identified as **2**.

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