

NORDITERPENOID ALKALOIDS FROM THE AERIAL PARTS OF *ACONITUM BALFOURII* STAPF

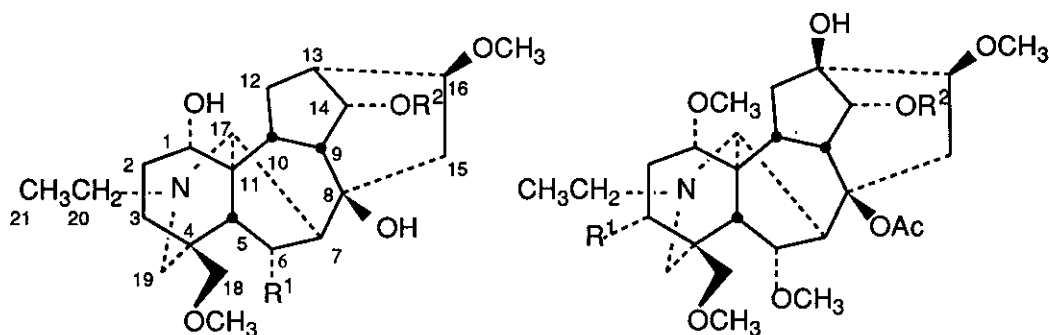
Khadga S. Khetwal¹, Haridutt K. Desai, Balawant S. Joshi, and S. William Pelletier*

Institute for Natural Products Research and Department of Chemistry,
The University of Georgia, Athens, Georgia 30602-2556, U.S.A.

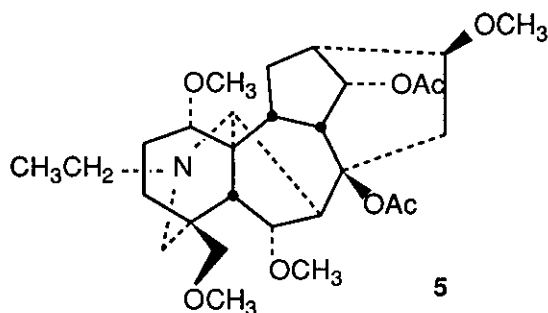
Abstract - From the aerial parts of *Aconitum balfourii* Stapf nine norditerpenoid alkaloids: condelphine (1), bullatine C (2), neoline (3), isotalatizidine (4), 1-*O*-methyldelphisine (5), pseudoaconitine (6), yunaconitine (7), bikhaconitine (8), and indaconitine (9), were isolated. The identity of these alkaloids was determined by comparison of mp, tlc and ir spectra with those of authentic samples and the carbon-13 nmr spectra of 2, 5, 6, 7 and 8 with the published chemical shifts. Detailed nmr spectral studies (¹H, ¹³C, ¹H homonuclear COSY, HETCOR, and selective INEPT) carried out on 1, 3, 4 and 9 have provided accurate chemical shift assignments for these alkaloids.

Our earlier investigations of the roots of *Aconitum balfourii* Stapf resulted in the isolation of eleven norditerpenoid alkaloids: balfourine, bikhaconitine, chasmanine, 8-deacetylyunaconitine, indaconitine, ludaconitine, 8-*O*-methylveratroylpseudoaconine, neoline, pseudoaconine, pseudoaconitine, and veratroylbikhaconine.¹ In continuation of these studies, we have isolated from the aerial parts of *A. balfourii*, nine norditerpenoid alkaloids: condelphine (1), bullatine C (2), neoline (3), isotalatizidine (4), 1-*O*-methyldelphisine (5), pseudoaconitine (6), yunaconitine (7), bikhaconitine (8), and indaconitine (9). The alkaloids (3), (6), (8) and (9) were also isolated from the roots of this plant. The structures of these alkaloids were established by comparison of the physical constants, tlc, and ir spectra with authentic samples and also detailed nmr spectral studies of the alkaloids (1), (3), (4), and (9). Carbon-13 nmr spectra of the remaining alkaloids were compared with the published chemical shifts. The alkaloids (1-9) isolated from this plant have been reported to be naturally occurring in earlier literature.^{2,3a} Compound (5) was previously prepared by the methylation of delphisine with trimethylxonium tetrafluoroborate and proton sponge.⁴

¹ On leave from the University of Kumaon, Nainital, India.



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|----------------------------|-------------------------------------|
| 1. $R^1 = H; R^2 = Ac$ | 6. $R^1 = OH; R^2 = Vr$ (Veratroyl) |
| 2. $R^1 = OCH_3; R^2 = Ac$ | 7. $R^1 = OH; R^2 = As$ (Anisoyl) |
| 3. $R^1 = OCH_3; R^2 = H$ | 8. $R^1 = H; R^2 = Vr$ |
| 4. $R^1 = R^2 = H$ | 9. $R^1 = OH; R^2 = Bz$ |



The alkaloids (1-4) were previously isolated from the following *Aconitum* and *Delphinium* species: (a) condelphine (1) has been isolated from eight species: *A. anthoroideum*,^{3a} *A. delphinifolium*,^{3b} *A. japonicum*,^{3a} *A. sanyoyense*,^{3b} *D. bicolor*,^{3b} *D. confusum*,^{3a} *D. denudatum*,^{3a} and *D. nuttalianum*.^{3b} (b) Bullatine C (2) has been reported from nine species: *A. bullatifolium*,^{3a} *A. flavum*,⁵ *A. jinyangense*,^{3a} *A. kusnezoffii*,⁵ *A. nagarum*,^{3a} *A. pendulum*,⁵ *A. yezoense*,^{3a} *D. pictum*,^{3b} and *D. staphisagria*.^{3b} (c) Neoline (bullatine B) (3) has been isolated from twenty four different species: *A. balfourii*,¹ *A. bullatifolium*,^{3a} *A. carmichaeli*,^{3b} *A. flavum*,^{3b} *A. fukutomei*,⁶ *A. ibukiense*,^{3b} *A. jalunense*,⁷ *A. japonicum*,^{3a} *A. karakolicum*,^{3b} *A. kusnezoffii*,⁵ *A. liangshanium*,⁸ *A. mitakense*,^{3a} *A. nagarum* var. *lasiandram*,^{3b} *A. napellus*,^{3b} *A. nevadense*,^{3b} *A. pendulum*,⁵ *A. sachaliense* var. *compactum*,⁹ *A. sczukini*,^{3a} *A. soongaricum*,^{3a} *A. stoerckianum*,^{3a} *A. subcuneatum*,^{3b} *A. taipeicum*,¹⁰ *A. yezoense*,^{3a} and *D. staphisagria*.^{3b} (d) Isotalatizidine (4) has been reported from seventeen species: *A. austroyunnanense*,^{3b} *A. carmichaeli*,^{3a} *A. columbianum*,^{3b} *A. confusum*,^{3b} *A. delphinifolium*,^{3b} *A. fukutomei*,⁶ *A. japonicum*,^{3a} *A. nevadense*,^{3b} *A. sanyoense*,^{3b} *A. subcuneatum*,^{3b} *A. tallasicum*,^{3a} *A. tranzschelii*,^{3a} *A. vilmorrianum*,¹¹ *A. yezoense*,¹² *D. bicolor*,^{3a} *D. denudatum*,^{3a} and *D. nuttalianum*.¹³ The alkaloids (6-9) have been isolated only from the *Aconitum* species: (e) pseudaconitine (6) has been reported from seven species: *A. balfourii*,¹ *A. deinorrhizum*,^{3a} *A. fal-*

coneri,^{3a} *A. ferox*,^{3a} *A. geniculatum* var. *unguiculatum*,^{3a} *A. hemsleyanum* var. *circinatum*,^{3a} and *A. spicatum*.^{3a} (f) Yunaconitine (7) has been isolated from sixteen species: *A. austroyunnanense*,^{3b} *A. crassicaule*,^{3b} *A. delavyi*,^{3a} *A. dolichorhynchum*,¹⁴ *A. episcopale*,¹⁵ *A. forrestii*,^{3b} *A. geniculatum* var. *unguiculatum*,^{3b} *A. hemsleyanum* var. *circinatum*,^{3a} *A. legendrei*,¹⁶ *A. longtounense*,^{3b} *A. pseudogeniculatum*,^{3b} *A. stapfianum*,^{3b} *A. sungpanense*,^{3b} *A. taipeicum*,¹⁰ *A. transsectum*,¹⁵ and *A. vilmorrianum*,^{3a} (g) Bikhaconitine (8) has been isolated from only four species: *A. balfourii*,¹ *A. ferox*,^{3a} *A. spicatum*,^{3a} and *A. violaceum*.^{3a} (h) Indaconitine (9) occurs in seven species: *A. balfourii*,¹ *A. chasmanthum*,^{3a} *A. falconeri*,^{3a} *A. ferox*,^{3a} *A. franchetti*,^{3a} *A. vilmorrianum* var. *patentipilum*,¹⁷ and *A. violaceum*.^{3a}

In spite of the frequent reports of the isolation of these alkaloids, accurate ¹³C and detailed ¹H nmr assignments for many of these alkaloids have not been carried out. In order to establish the proton and carbon-13 nmr chemical shifts, we have carried out a detailed nmr study of condelphine (1; Tables 1 and 2), neoline (3; Tables 3 and 4), isotalatizidine (4; Tables 5 and 6) and indaconitine (9; Tables 7 and 8). We accomplished this by DEPT, ¹H-¹H COSY, HETCOR and selective INEPT spectral data. This work resulted in the revision of the published values¹⁸ of the chemical shift assignments for C-3, C-7, C-9, C-10, C-12 and C-13 in condelphine (1). In the case of neoline (3), the assignments for C-2, C-3, C-10 and C-13 have been changed from the literature values.¹⁸ The ¹³C assignments of bullatine C (2, 14-acetylneoline) are nearly the same as those of neoline and agree with those reported,¹⁹ and the values given for C-10, and C-13 differ from those quoted for delstaphisagnine (identical with 2).²⁰ The chemical shifts of C-3, C-10, C-12 and C-13 in isotalatizidine differ from those given in the literature.^{18,21} The H-20 methylene protons (a,b) in condelphine (1), neoline (3) and isotalatizidine (4) exhibit nonequivalence²² due to their attachment to the nitrogen atom which is hydrogen bonded to the C-1 hydroxyl group in the boat conformation.¹⁸ A number of previous assignments for indaconitine (9) e.g. C-1, C-2, C-5, C-6, C-7, C-9, C-10, C-12, C-16 C-19 and C-20 need to be revised from the published values.²³ In a recent detailed ¹H and ¹³C nmr investigation of bikhaconitine and pseudaconitine,²⁴ the previously assigned values^{1,25} for C-1, C-6, C-14, C-16 and C-18 for bikhaconitine and C-1, C-2, C-6, C-12, C-16, C-19 and C-20 for pseudaconitine have been revised.

Table 1. ^1H and ^{13}C Chemical shifts and assignments of condelfine (1) (in CDCl_3)

Carbon	δ (ppm) (DEPT)	Proton	δ (ppm)	Multiplicity	Correlation (COSY)	
1	72.0	d	1β	3.72	br s	H-2
2	29.6	t	$2_{\alpha,\beta}$	1.61	m	H-3
3*	26.5	t	3_{α}	1.62	m	H-2
			3β	1.88	m	H-2
4	37.1	s	-	-	-	-
5	41.3	d	5	1.84	s	H-17
6	24.9	t	6	1.75	-	-
7*	44.6	d	7	2.26	-	-
8	74.7	s	-	-	-	-
9*	45.4	d	9β	2.08	s	-
10*	43.1	d	10	1.90	-	-
11	48.8	s	-	-	-	-
12*	29.0	t	12_{α}	1.70	-	-
			12_{β}	2.10	-	-
13*	36.5	d	13	2.60	-	-
14	77.0	d	14	4.84	t, $J=6.0$ Hz	-
15	42.5	t	15_{α}	1.94	d, $J=13.2$ Hz	H-15 $_{\alpha}$ to
			15_{β}	2.31	d, $J=13.2$ Hz	H-15 $_{\beta}$
16	82.0	d	$16'$	3.27	m	H-15'
17	63.6	d	17	2.72	s	H-5
18	78.9	t	18β	2.98	d, $J_{\text{gem}}=10.5$ Hz	-
			18_{α}	3.14	d, $J_{\text{gem}}=10.5$ Hz	-
19	56.5	t	19_{α}	2.05	m	-
			19_{β}	2.30	m	-
20	48.4	t	20_a	2.44	dq, $J_{a,b}=12.8$ Hz	-
				$J_a, C_{H_3} = 7.1$ Hz	-	-
		20_b	2.51	dq $J_{b,a}=12.8$ Hz	H-21	$J_b, C_{H_3} = 7.1$ Hz
21	13.0	q	21	1.10	t, $J=7.1$ Hz	H-20
16'	56.0	q	$16'$	3.26	s	-
18'	59.4	q	$18'$	3.35	s	-
CO (22)	170.4	s	-	-	-	-
CH ₃	21.3	q	23	2.04	s	-

* These assignments are revised.

Table 2. Nmr data from selective INEPT experiments on condelfine (1).

Selectively pulsed proton	δ	Strong	Responding carbons*
			Medium
H-21	1.10	48.4 (C-20)	
H-23, H-19, H-9	2.04	170.4 (C-22)	74.7 (C-8), 48.8 (C-11), 48.4 (C-20), 44.6 (C-7) 63.6 (C-17)
$16'-(\text{OCH}_3)$	3.26	82.0 (C-16)	
$18'-(\text{OCH}_3)$	3.35	78.9 (C-18)	
H-3	1.62	41.3 (C-5)	
H-13, H-17	2.60	82.0 (C-16), 44.6 (C-7)	77.0 (C-14), 43.1 (C-10)
H-17	2.72	41.3 (C-5)	74.7 (C-8), 56.5 (C-19), 48.8 (C-11), 43.1 (C-10)
H-18a	2.98	41.3 (C-5)	24.9 (C-6) 59.4 (OCH ₃ -18'), 37.1 (C-4), 26.5 (C-3)
H-18b	3.14	26.5 (C-3)	59.4 (OCH ₃ -18'), 56.5 (C-19), 41.3 (C-5), 37.1 (C-4)
H-1	3.72	43.1 (C-10), 26.5 (C-3)	48.8 (C-11)
H-14	4.84	82.0 (C-16), 74.7 (C-8)	

* Strong = 60 - 100%; Medium = 20 - 59%.

Table 3. ¹H and ¹³C Chemical shifts and assignments of neoline (3) (in CDCl₃)

Carbon	δ(ppm) (DEPT)	Proton	δ(ppm)	Multiplicity	Correlation (COSY)
1	72.2 d	1 _β	3.65	s	H-2
2*	29.9 t	2 _{α,β}	1.61	m	H-1
3*	29.3 t	3 _α	1.58	m	
		3 _β	1.70	m	
4	38.1 s	-	-	-	
5	44.8 d	5	2.16	d, J=6.5 Hz	H-6, H-17
6	83.1 d	6	4.16	d, J=6.5 Hz	H-5, H-7
7	52.1 d	7	2.00	s	H-6
8	74.2 s	-	-	-	
9	48.2 d	9 _β	2.17	s	H-10, H-14
10*	44.1 d	10	1.90	m	H-9
11	49.4 s	-	-	-	
12	29.3 t	12 _α	1.85	m	
		12 _β	1.92	m	
13*	40.3 d	13	2.30	m	H-14
14	75.9 d	14	4.20	t, J=4.9 Hz	H-9, H-13
15	42.8 t	15 _α	2.05	m	H-15 _α to
		15 _β	2.50	m	H-15 _β , H-16
16	81.8 d	16	3.33	m	H-15 _α , H-15 _β
17	63.7 d	17	2.66	s	H-5
18	80.2 t	18 _β	3.25	d, J _{gem} =9.0 Hz	
		18 _α	3.63	d, J _{gem} =9.0 Hz	
19	57.0 t	19 _α	2.30	d, J= 11.0 Hz	H-19 _α to
		19 _β	2.69	d, J= 11.0 Hz	H-19 _β
20	48.2 t	20 _a	2.46	dq, J _{a,b} =13.5Hz J _{a,CH₃} = 7.1 Hz	
		20 _b	2.56	dq, J _{b,a} = 13.5 Hz J _{b,CH₃} = 7.1 Hz	
21	13.0 q	21	1.19	t, J=7.1Hz	H-20
6'	57.9 q	6'	3.33	s	
16'	56.3 q	16'	3.33	s	
18'	59.2 q	18'	3.32	s	
OH	-	14 (OH)	2.93	br s	
OH	-	1 (OH)	3.65	s	

* These assignments are revised.

Table 4. Nmr data from selective INEPT experiments on neoline (3).

Selectively pulsed proton	δ	Responding carbons*	
		Strong	Medium
H-5, H-9	2.16	38.1 (C-4), 63.7 (C-17) 74.2 (C-8)	75.9 (C-14), 49.4 (C-11), 40.3 (C-13)
H-13, H-15, H-19 _α	2.35	74.2 (C-8), 52.1 (C-7)	63.7 (C-17), 38.1 (C-4), 44.8 (C-5)
H-17	2.66	83.1 (C-6), 44.8 (C-5)	49.4 (C-11)
H-17, H-19 _β	2.69	83.1 (C-6), 44.8 (C-5)	74.2 (C-8), 57.0 (C-19), 49.4 (C-11), 38.1 (C-4)
H-18 _β	3.25	44.8 (C-5)	59.2 (OCH ₃ -18'), 38.1 (C-4)
H-18 _α , H-1	3.64	57.0 (C-19), 49.4 (C-11), 44.1 (C-10), 38.1 (C-4)	
H-14, H-6	4.20	81.8 (C-16), 74.2 (C-8), 57.9 (C-6')	38.1 (C-4)

* Strong = 60 - 100%; Medium = 20 - 59%.

Table 5. ^1H and ^{13}C Chemical shifts and assignments of isotalatizidine 4 (in CDCl_3)

Carbon	δ (ppm) (DEPT)	Proton	δ (ppm)	Multiplicity	Correlation (COSY)
1	72.1 d	1 β	3.69	br s	H-2
2	29.6 t	2 α,β	1.60	m	H-1
3*	26.6 t	3 α	1.61	m	H-2, H-3 α to
		3 β	1.85	m	H-3 β
4	37.1 s	-	-		
5	41.5 d	5	1.80	m	H-17
6	24.8 t	6 α	1.60	m	
		6 β	1.90	m	
7	45.0 d	7	2.02	d, J=4.8 Hz	
8	74.2 s	-	-		
9	46.5 d	9 β	2.18	m	H-10
10*	43.8 d	10	1.80	m	H-9
11	48.5 s	-	-		
12*	28.5 t	12 α	1.55	m	H-12 α to
		12 β	2.05	m	H-12 β
13*	39.9 d	13	2.30	m	H-15
14	75.6 d	14	4.17	t, J=5.0 Hz	
15	42.3 t	15 α	2.02	m	H-9, H-13,
		15 β	2.38	m	H-15 α to H-15 β
16	81.9 d	16	3.38	m	H-15 α , H-
				15 β	
17	63.9 d	17	2.74	s	H-5
18	78.9 t	18 β	3.01	d, J _{gem} =8.8 Hz	
		18 α	3.14	d, J _{gem} =8.8 Hz	
19	56.5 t	19 α	2.05	m	
		19 β	2.35	m	
20	48.4 t	20 _a	2.40	dq, J _{a,b} =12.3 Hz J _{a,C_H3} = 7.1 Hz	H-21
		20 _b	2.51	dq, J _{a,b} = 12.3 Hz J _{b,C_H3} = 7.1 Hz	
21	13.0 q	21	1.10	t, J=7.1 Hz	H-20
16'	56.3 q	16'	3.30	s	
18'	59.3 q	18'	3.29	s	

* These assignments are revised.

Table 6. Nmr data from selective INEPT experiments on isotalatizidine (4).

Selectively pulsed proton	δ	Responding carbons*	
		Strong	Medium
H-9	2.18	74.2 (C-8), 39.9 (C-13)	75.6 (C-14)
H-13, H-15, H-19	2.31	74.2 (C-8), 41.5 (C-5), 37.1 (C-4)	81.9 (C-16), 63.9 (C-17), 45.0 (C-7), 39.9 (C-13)
H-17	2.74	41.5 (C-5), 24.8 (C-6)	74.2 (C-8), 56.5 (C-19)
H-18 _b	3.01	41.5 (C-5), 37.1 (C-4), 26.6 (C-3)	59.3 (C-18'), 56.5 (C-19)
H-18 _a	3.12	37.1 (C-4), 26.6 (C-3)	59.3 (C-18'), 56.5 (C-19), 41.5 (C-5)
OCH ₃ -16, OCH ₃ -18	3.28	81.9 (C-16)	78.9 (C-18)
H-1	3.69	48.5 (C-11), 43.8 (C-10), 26.6 (C-3)	
H-14	4.17	74.2 (C-8)	81.9 (C-16)

* Strong = 60 - 100%; Medium = 20 - 59%.

Table 7. ^1H and ^{13}C Chemical shifts and assignments of indaconitine (9) (in CDCl_3)

Carbon	δ (ppm) (DEPT)	Proton	δ (ppm)	Multiplicity	Correlation (COSY)
1*	82.2 d	1 β	3.10	m	H-2 α , H-2 β
2*	33.5 t	2 α	2.03	m	H-1, H-3
		2 β	2.35	m	H-1, H-3
3	71.6 d	3 β	3.76	d,d J=4.6, 9.0 Hz	H-2 α , H-2 β
4	43.1 s	-	-		
5*	40.8 d	5	2.09	s	H-6
6*	83.1 t	6	4.02	d, J=6.5	H-5, H-7
7*	48.6 d	7	3.01		H-6
8	85.5 s	-	-		
9*	44.6 d	9 β	2.90		H-14, H-10
10*	47.3 d	10	2.09		H-10
11	50.2 s	-	-		
12*	35.1 t	12 α	2.08		H-12 α to
		12 β	2.60		H-12 β
13	74.7 s	13	-		
14	78.7 d	14	4.90	d, J=5.1 Hz	H-9
15	39.5 t	15 α	2.40		H-15 α to
		15 β	3.05		H-15 β
16*	83.4 d	16	3.40	dd, J=8.8,5.5Hz	H-15 α , H-15 β
17	61.7 d	17	2.90	s	
18	77.0 t	18 β	3.53	d, J _{gem} =8.9 Hz	
		18 α	3.64	d, J _{gem} =8.9 Hz	
19*	47.4 t	19 α	2.34	m	H-19 α to H-19 β
		19 β	2.90	m	
20*	48.8 t	20	2.50		H-21
21	13.3 q	21	1.10	t, J=7.2 Hz	H-20
1'	55.9 q	1'	3.26	s	
6'	57.8 q	6'	3.16	s	
16'	58.7 q	16'	3.54	s	
18'	59.1 q	18'	3.30	s	
CO (22)	169.8 s	-	-		
CH ₃	21.5 q	23	1.29	s	
14'	166.2 s	14'	-		
1''	130.0 s	1''	-		
2'',6''	129.6 d)	2'', 6''	8.06	d, J=7.0 Hz	
3'',5''	128.5 d	3'',5''	7.45	dd, J=7.5, 7.0 Hz	
4''	133.1 d	4''	7.57	dd, J=7.5, 2.0 Hz	

* These assignments are revised. Double primed numbers are for the aromatic group in (9)

Table 8. Nmr data from selective INEPT experiments on indaconitine (9).

Selectively pulsed proton	δ	Responding carbons*	
		Strong	Medium
H-21	1.10		48.8 (C-20)
H-23	1.29	169.8 (C-22)	
H-5, H-10, H-12	2.09	48.6 (C-7)	43.1 (C-4)
H-7, H-15	3.01	85.5 (C-8), 50.2 (C-11)	74.7 (C-13)
6'-(OCH ₃)	3.16	83.1 (C-6)	
1'-(OCH ₃)	3.26	82.2 (C-1)	
18'-(OCH ₃)	3.30	77.0 (C-18)	
H-16	3.40	74.7 (C-13)	
H-18 β , 16'-(OCH ₃)	3.53	83.4 (C-16)	
H-18 α	3.64	43.1 (C-4)	

Table 8 (continued)

Selectively pulsed proton	δ	Responding carbons*	
		Strong	Medium
OH-13	3.89	74.7 (C-13)	35.1 (C-12)
H-6	4.02	57.8 (OCH ₃ -6')	
H-14	4.90	74.7 (C-13)	35.1 (C-12)
H-3", H-5"	7.45	128.5 (C-3", C-6")	130.0 (C-1")
H-4"	7.57	129.6 (C-2", C-6")	
H-2", H-6"	8.06	129.6 (C-2", C-6")	166.2 (C-14')

* Strong = 60 - 100%; Medium = 20 - 59%.

EXPERIMENTAL

General: – Mps are corrected and were determined on a Kofler hot stage equipped with a microscope and a polarizer. Ir spectra were determined on a Perkin Elmer model 1420 spectrophotometer. ¹H (300.13 MHz) and ¹³C (75.47 MHz) and selective INEPT nmr spectra were recorded on a Bruker AC-300 spectrometer. The ¹³C chemical shift multiplicities were determined from DEPT spectra. Chromatographic separations on a Chromatotron ²⁶ were carried out on rotors coated with a 1 mm thick layer of Al₂O₃ 60 PF-254, 365 (EM 1104) or SiO₂ 60H (EM 7749); vlc²⁷ was carried out with Merck Al₂O₃ (EM 1085) and SiO₂ 60H (EM 7736).

Plant material: – The plant was collected at an altitude of 17,500 ft from Kumaon Himalayan glaciers in August 1991 and identified in the Department of Botany, Kumaon University, Nainital where the voucher specimen is deposited.

Extraction: –The shade dried and powdered aerial parts of *A. balfourii* (1720 g) were extracted at room temperature with 70% EtOH (30 l) for 10 days. The extracts were evaporated *in vacuo* to give a dark colored residue (182 g). This residue was shaken with hexane (3 x 500 ml) and the hexane extract evaporated to give (41.5 g) of residue. The defatted extract was suspended in CHCl₃ (500 ml) and extracted several times with 2% H₂SO₄. The CHCl₃ layer gave a neutral fraction (11.5 g). Basification of the acidic extract (Na₂CO₃; pH 5) and extraction with CHCl₃ (8x500 ml) gave a crude alkaloidal fraction (5.75 g; A).

The alkaloidal fraction (A) was purified by vacuum liquid chromatography (vlc) over SiO₂ with gradient elution in increasing polarity with hexane, CHCl₃ and MeOH (200 ml fractions were collected). Fractions were pooled on the basis of their tlc behavior as: **a** (1-6, 0.65 g hexane and hexane:CHCl₃ 20:80), **b** (7, 0.23 g CHCl₃), **c** (8, 0.6 g CHCl₃:1% MeOH), and **d** (9, 2.1 g CHCl₃:5% MeOH).

Isolation of condelfine (1), bullatine C (2), and indaconitine (9): – The vlc fraction **b** was separated on an Al₂O₃ rotor with gradient elution with hexane:ether (90:5) to afford bullatine C (**2**; 0.066 g), C₂₆H₄₁NO₇, as colorless crystals, mp 198-200°C. Elution with hexane : ether (90:10) gave colorless crystals of condelfine (**1**; 0.047 g), C₂₅H₃₉NO₆, mp 157-158°C. For ¹H and ¹³C nmr

assignments see Tables 1 and 2. Further elution with hexane:ether (20:80) gave a fraction (0.014 g) which on crystallization from ether gave indaconitine (**9**; 0.008 g), $C_{34}H_{47}NO_{10}$, mp 202-203°C. For 1H and ^{13}C nmr assignments see Tables 7 and 8.

Isolation of pseudoaconitine (6), yunaconitine (7), bikhaconitine (8), neoline (3), isotalatizidine (4) and 1-O-methyldehphisine (5): – Part of the vlc fraction (**d**; 1.3 g) was purified on an Al_2O_3 rotor and eluted with hexane, ether (10:90) to afford pseudoaconitine (**6**; 0.35 g), $C_{35}H_{51}NO_{12}$, mp 205-207°C. Further elution with ether and ptlc on Al_2O_3 gave neoline (**3**; 0.024 g), $C_{24}H_{39}NO_6$, mp 159-160°C. For 1H and ^{13}C nmr assignments, see Tables 3 and 4. Elution with ether afforded isotalatizidine (**4**; 0.041 g), $C_{23}H_{37}NO_5$, mp 115-116°C. Another part of **d** (0.5 g) was separated on an Al_2O_3 rotor and eluted with hexane:ether (90:10 to 60:40, 50 ml fractions) to give 1-O-methyldehphisine, $C_{29}H_{45}NO_8$, isolated as colorless crystals (**5**; 0.0035 g), mp 137-138°C. Elution with hexane:ether (20:80) and ptlc on Al_2O_3 afforded yunaconitine, $C_{35}H_{49}NO_{11}$, (**7**; 0.008 g), mp 140-142°C. The vlc fraction **e** (0.6 g) was purified twice on an Al_2O_3 rotor and eluted with hexane:ether (30:70 to 10:90, 50 ml fractions) and further purified and crystallized to give bikhaconitine, $C_{36}H_{51}NO_{11}$, (**8**; 0.0057 g) isolated as colorless plates, mp 104-106°C.

ACKNOWLEDGMENT

We are grateful to the U. S. National Science Foundation (INT-8905629) and Department of Science and Technology, New Delhi, India for financial support.

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Received, 30th November, 1993