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NEW DITERPENOID ALKALOIDS FROM THE ROOTS OF *ACONITUM SEPTENTRIONALE*: ISOLATION BY AN ION EXCHANGE METHOD

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ABSTRACT.—Eight new diterpenoid alkaloids, acoseptrine [**5**] acosepticine [**6**], 4-anthranoyllapaconidine [**7**], acoseptridinine [**8**], acoseptridine [**9**], acoseptrinine [**10**], 14-*O*-methylforesticine [**11**], and 6-demethyldelphatine [**12**], have been isolated from the roots of *Aconitum septentrionale*, along with seven known alkaloids: *N*-deacetyllappaconitine [**1**], septentrionine [**2**], sepaconitine [**4**], delvestidine [**13**], anthranoyllycoctonine [**14**], lapaconidine [**15**], and lycoctonine [**16**]. The structures of the new compounds were assigned by comparison of spectroscopic data with those of related known compounds. The structures of compounds **6** and **7** were confirmed by chemical correlation with the known compounds 6-acetylacosepticine and lapaconidine, respectively. All known compounds were identified by comparison of their spectroscopic data and tlc behavior with those of authentic samples. The use of strongly acidic resins leads to a cleavage of the *N*-acetyl group in the case of lappaconitine.

In 1967 Marion *et al.* (1) reported the isolation and characterization of seven alkaloids from the roots of *Aconitum septentrionale* Koelle (Ranunculaceae). Two alkaloids, lappaconitine and *N*-deacetyllappaconitine [**1**], were identified, but the structures of five other alkaloids were not elucidated. In previous work we have reported isolation and structure elucidation of three new alkaloids, septentrionine [**2**], septentriodine [**3**] (2), and septentriocine (3), from the roots of this plant. Usmanova *et al.* (4) have reported a new alkaloid, sepaconitine [**4**], from this plant and Sirotenko and Rashkes (5) have indicated by ms the presence of twenty-one diterpenoid alkaloids in *A. septentrionale*. Of the thirteen known alkaloids, eight are new to this plant. The structures of the remaining eight bases have not been established.

RESULTS AND DISCUSSION

In continuing our studies of the alkaloids of the genus *Aconitum* (6), utilizing newly available isolation techniques (7), we have examined the minor alkaloids of the roots of *A. septentrionale*. We report here the isolation and structure elucidation of three new C_{18}-diterpenoid alkaloids, acoseptrine [**5**], acosepticine [**6**], and 4-anthranoyllapaconidine [**7**], and five new norditerpenoid alkaloids, acoseptridinine [**8**], acoseptridine [**9**], acoseptrinine [**10**], 14-*O*-methylforesticine [**11**], and 6-demethyldelphatine [**12**]. Seven known norditerpenoid alkaloids, *N*-deacetyllappaconitine [**1**], septentrionine [**2**], sepaconitine [**4**], delvestidine [**13**], anthranoyllycoctonine [**14**], lapaconidine [**15**], and lycoctonine [**16**], were also isolated; of these compounds **13**, **14**, and **16** have not previously been reported from this plant.

The ion exchange method of isolation, used in the present work, was based on a report of the isolation (8) of pyrrolizidine alkaloids from the ragwort plant. Previously an ion exchange.resin method has been used by Fang and Huo (9) and in our laboratory

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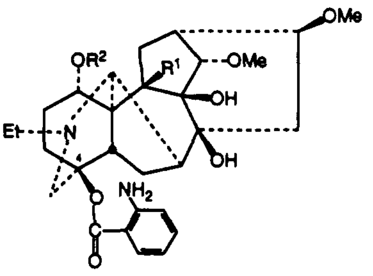
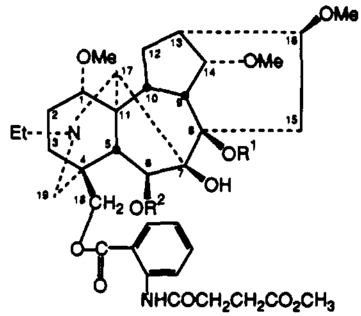
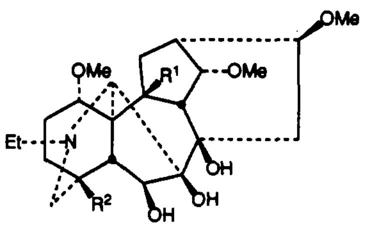


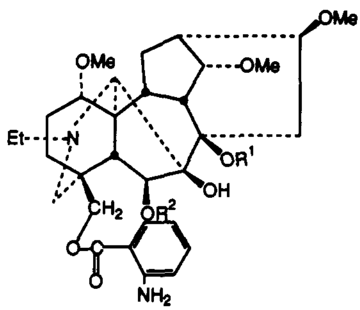
1 R^1=H, R^2=Me
4 R^1=OH, R^2=Me
7 R^1=R^2=H
15 R^1=R^2=H, C-4◀OH



2 R^1=R^2=Me
3 R^1=H, R^2=Me



5 R^1=OH, R^2=H
6 R^1=R^2=H
21 R^1=OH, R^2=Me



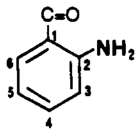
10 R^1=R^2=H
13 R^1=R^2=Me
14 R^1=H, R^2=Me

(10) to obtain total diterpenoid alkaloids. The total alkaloidal mixture obtained by this method (see Experimental) was subjected to various chromatographic techniques, viz., vacuum liquid chromatography (vlc) (11), centrifugally accelerated radial tlc (Chromatotron) (12), and preparative tlc, to obtain pure homogeneous alkaloids.

The major alkaloid present in this plant is reported to be lappaconitine (**1** with monoacetate of -NH_2 group) (1,2,5). In the present investigation we have found that the major alkaloid isolated is *N*-deacetyllappaconitine [**1**], mp 213–214° $[\alpha]$D +29.4° (c=0.395, $CHCl_3$), having spectral data and tlc behavior identical with those of an authentic sample prepared from lappaconitine (13,14). [The mp and specific rotation reported here for **1** are the correct values for a pure sample, cf. lit. (13) mp 120–121°] The following ^{13}C-nmr chemical shifts are revised (reported values in parentheses) C-5 δ 50.0 d (48.9), *N*-CH_2CH_3 49.0 t (50.0) (on the basis of DEPT experiments), C-10 48.7 (36.5), C-13 36.5 (48.7), C-1′ 56.2 (56.5), C-16′ 56.6 (56.2) [on the basis of reasons given by Pelletier and Joshi (15)].

4-Anthranoyllapaconidine [**7**] is an amorphous compound. Its molecular formula, $C_{29}H_{40}N_2O_7$, was derived from its eims *m/z* (%) 528 $[M]^+$ (0.103), 511 $[M-OH]^+$ (0.14), 120 (100), and its ^{13}C nmr spectral chemical shifts (Table 1). Its ir spectrum (Nujol) showed the presence of OH (3450), 3350), primary amine (3200), ester carbonyl (1685), and aromatic groups (1620, 1580, 1530, 1470 cm^{-1}). The ^{1}H-nmr spectrum showed the presence of an Me of an *N*-ethyl group (δ 1.15 ppm, 3H, t, J=7.4 Hz), two

TABLE 1. ^{13}C-nmr Chemical Shifts and Assignments for Compounds **5–12**.[a]

Carbon	Compound							
	5	**6**	**7**	**8**	**9**	**10**[b]	**11**	**12**
C-1	84.1 d	84.7 d	72.0 d	72.1 d	83.8 d	83.6 d	85.1 d	84.1 d
C-2	25.6 t	25.6 t	29.7 t	28.4 t	25.2 t	25.4 t	26.1 t	25.7 t
C-3	29.1 t	29.3 t	30.3 t	29.5 t	21.1 t	31.8 t	32.3 t	31.9 t
C-4	37.2 d	37.2 d	81.0 s	36.7 s	47.1 s	37.9 s	38.6 s	38.5 s
C-5	48.1 d	53.0 d	48.2 d	43.9 d	43.8 d	53.4 d	49.8 d	54.2 d
C-6	77.4 d	82.4 d	27.1 t	26.6 t	91.9 d	80.3 d	72.1 d	80.7 d
C-7	87.1 s	87.8 s	46.4 d	46.5 d	89.3 s	87.3 s	54.2 d	87.2 s
C-8	76.9 s	78.7 s	75.9 s	77.1 s	80.2 s	77.4 s	76.8 s	78.2 s
C-9	54.1 d	45.3 d	77.2 s	45.2 d	49.0 d	45.3 d	45.7 d	45.6 d
C-10	80.6 s	44.1 d	43.9 d	41.6 d	40.3 d	42.9 d	45.4 d	44.0 d
C-11	54.1 s	48.5 s	50.0 s	48.6 s	49.3 s	48.0 s	48.1 s	48.1 s
C-12	36.9 t	29.3 t	23.4 t	24.9 t	28.5 t	28.4 t	29.5 t	28.9 t
C-13	35.1 d	35.4 d	36.1 d	39.8 d	38.2 d	37.9 d	36.5 d	37.0 d
C-14	82.7 d	84.1 d	90.1 d	75.6 d	82.9 d	83.7 d	84.5 d	84.1 d
C-15	39.3 t	36.6 t	44.8 t	42.2 t	30.2 t	34.6 t	42.5 t	36.4 t
C-16	81.9 d	83.5 d	82.7 d	81.9 d	81.1 d	82.0 d	82.5 d	82.2 d
C-17	66.4 d	66.1 d	63.0 d	63.6 d	65.3 d	64.7 d	64.1 d	65.9 d
C-18	—	—	—	69.2 t	66.2 t	68.0 t	79.4 t	79.2 t
C-19	50.2 t	50.3 t	57.9 t	56.2 t	165.6 d	52.3 t	54.4 t	53.4 t
N-CH_2	51.5 t	51.6 t	48.1 t	48.3 t	—	50.9 t	49.5 t	51.7 t
CH_3	14.3 q	14.5 q	12.9 q	12.9 q	—	13.9 q	13.6 q	14.6 q
C-1′[c]	55.6 q	55.9 q	—	—	56.0 q	55.4 q	56.2 q	55.7 q
C-6′	—	—	—	—	59.9 q	—	—	—
C-8′	—	—	—	—	52.0 q	—	—	—
C-14′	57.6 q	57.7 q	57.8 q	—	57.6 q	57.4 q	57.4 q	57.8 q
C-16′	56.0 q	56.1 q	56.1 q	56.2 q	56.4 q	55.9 q	56.2 q	56.3 q
C-18′	—	—	—	—	—	—	59.6 q	59.6 q
 C=O	—	—	166.9 s	167.9 s	167.8 s	168.1 s	—	—
1	—	—	111.3 s	110.4 s	110.2 s	109.9 s	—	—
2	—	—	150.5 s	150.6 s	150.2 s	150.3 s	—	—
3	—	—	116.6 d	116.7 d	116.6 d	116.4 d	—	—
4	—	—	133.9 d	134.1 d	134.2 d	134.0 d	—	—
5	—	—	116.0 d	116.1 d	116.2 d	115.9 d	—	—
6	—	—	131.2 d	130.8 d	130.9 d	130.7 d	—	—

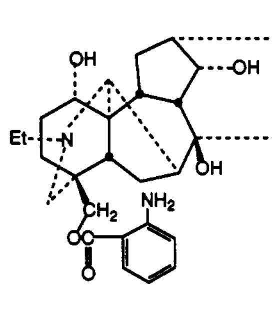
[a]Chemical shifts in ppm downfield from TMS in $CDCl_3$.
[b]Spectra recorded in $CDCl_3$ + 1 drop of MeOH.
[c]Values given for primed carbons refer to shifts for methoxyls.

aliphatic MeO groups (δ 3.31, 3.39 ppm, each 3H, s), a primary amino group of an aromatic system (δ 5.69 ppm, 2H, br s), and aromatic proton similar to those of *N*-deacetyllappaconitine [**1**], indicating the presence of an anthranoyl ester at C-4. Comparison of the ^{1}H-nmr spectra of **7** and **1** shows that **7** has one methoxyl group fewer than does **1**. The ^{13}C-nmr spectrum of **7** gave twenty-nine signals for the twenty-nine carbon atoms in the molecule. The DEPT experiments revealed the presence of seven quaternary carbons, twelve methine carbons, seven methylene carbons, and three methyl carbons. The ^{13}C-nmr signal at δ 72.0 (d) ppm indicates that the alkaloid bears an α-OH group at C-1 (13). Most of the ^{13}C-nmr chemical shifts are similar to those reported for lapaconidine (13) except for those of C-3, C-4, and the extra anthranoyl ester group. The absence of a methylene carbon around 66–81 ppm and the presence of a quaternary carbon at 81.0 ppm suggest the lack of C-18 (CH_2) in **7**. The alkaloid bears an esterified OH group at C-4 as in **1** (13). Structure **7** assigned to this compound was confirmed by its alkaline hydrolysis to lapaconidine [**15**].

Acoseptrinine [**10**], mp 220–222°; possesses the molecular formula $C_{31}H_{44}N_2O_8$, derived from the eims *m/z* 572 [M]$^+$ (2.49%) and ^{13}C nmr chemical shifts (Table 1). Its ir spectrum indicated the presence of -OH and -NH_2 groups (3530, 3460, 3350 cm^{-1}), a carbonyl group (1695 cm^{-1}), and an aromatic system (1630, 1460 cm^{-1}). The ^1H-nmr spectrum indicated the presence of an *N*-ethyl group (δ 1.05, 3H, t, *J*=7.3 Hz, *N*-CH_2CH_3), and three MeO groups (δ 3.25, 3.34 and 3.40, each 3H, s); a one-proton triplet (δ 3.65, *J*=4.3 Hz) assignable to the H-14β reveals that there is no substituent present on C-9 or C-13 in this molecule. The presence of an anthranoyl ester group is indicated by the aromatic protons at δ 6.67 (2H, t), 7.29 (1H, t), 7.82 (1H, d), and 5.72 (2H, br s, -NH2). Its ^{13}C-nmr spectrum gave thirty-one resonances for the thirty-one carbon atoms of the molecule. The DEPT spectra showed the presence of seven quaternary carbons, thirteen methine carbons, seven methylene carbons, and four methyl carbons. There are two norditerpenoid alkaloids, delectine (13) and isodelectine (16), that have the same molecular formula, $C_{31}H_{44}N_2O_8$, as **10**. A tlc and ^{13}C-nmr spectral comparison of **10** with authentic samples of delectine and isodelectine revealed differences. In compound **10** the absence of a chemical shift for a methine around δ 71–73 ppm rules out an OH group on C-1. The absence of a methine around δ 75–76 ppm and the presence of a 1H triplet at δ 3.40 ppm (*J*=4.3 Hz) for the H-14β rules out an -OH group on C-14. Hence, the -OH group present in **10** must be located on C-3, C-6, or C-10. The quaternary carbons present at δ 37.9 ppm and 48.0 ppm, assignable to C-4 and C-11, respectively, rule out an -OH group on C-3 or C-10. The -OH group in **10** must therefore be located at C-6 (δ 80.3 ppm) as in 6-*epi*-pubescenine (17) (δ 81.1 ppm).

Acoseptridine [**9**] is an amorphous compound. Its molecular formula $C_{31}H_{42}N_2O_8$ was derived from the eims *m/z* 570 [M]$^+$ and the ^{13}C-nmr spectra. The ir spectrum indicated the presence of -OH, NH_2, (3440, 3350 cm^{-1}), ester carbonyl (1700 cm^{-1}), and aromatic (1620, 1470 cm^{-1}) groups. The ^1H-nmr spectrum exhibited the presence of five aliphatic MeO groups (δ 3.17, 3.37, 3.38, 3.40, and 3.45 ppm, each 3H, s), an H-14β (δ 3.55, 1H, t, *J*=4.5 Hz), an -NH_2 group (δ 5.75, 2H, br s), aromatic protons showing the pattern of the anthranoyl ester group (δ 6.56, 2H, t, *J*=8.1 Hz; 7.30, 1H, t, *J*=8.1 Hz; and 7.85, 1H, d, *J*=8.0 Hz), and a broad 1H singlet at δ 7.64 ppm. It can be seen from the ^1H-nmr spectrum that this alkaloid does not possess any -*N*Et or -*N*Me group. Its ^{13}C-nmr spectrum gave thirty-one signals for the thirty-one carbon atoms of the molecule. The DEPT spectra showed the presence of seven quaternary carbons, fourteen methine carbons, five methylene carbons, and five methyl carbons. The ^1H- and ^{13}C-nmr spectral patterns of compound **9** show that it is a lycoctonine-type alkaloid with an anthranoyl ester on the C-18 hydroxymethylene group. The majority of the ^{13}C-nmr chemical shifts are identical with those reported for delvestidine [**13**] (15) except for carbons 3, 4, 5, 9, 10, and 19. The quaternary carbon chemical shift at δ 47.1 ppm appears 9.4 ppm downfield when compared with C-4 of delvestidine [**13**] (15), suggesting the presence of an -OH, -CO, or an olefinic carbon ortho to C-4. A methine carbon at δ 165.7 (d) ppm and a one-proton broad singlet at δ 7.64 ppm in the ^1H-nmr spectrum of **9** suggest the presence of an azomethine grouping in the molecule as in barbeline (15). That the -N=CH- is between -N and C-19 is supported by the presence of a chemical shift at δ 65.3 (d) ppm and absence of a chemical shift at δ 53.3 (t) ppm, assignable to C-17 and C-19, respectively. The ^{13}C-nmr chemical shifts of **9** have been reported in Table 1 by comparison with anthranoyllycoctonine [**14**] (13) and anhweidelphinine (18). These assignments support structure **9** for acoseptridine.

Acoseptridinine [**8**] is an amorphous alkaloid. Its molecular formula $C_{29}H_{40}N_2O_6$ was derived from its eims *m/z* 512 [M]$^+$ and ^{13}C-nmr chemical shifts. Its ir spectrum showed the presence of -OH and -NH_2 groups (3490, 3350, 3280 cm^{-1}), a carbonyl (1690 cm^{-1}), and an aromatic system (1620 cm^{-1}). The ^1H-nmr spectrum gave signals



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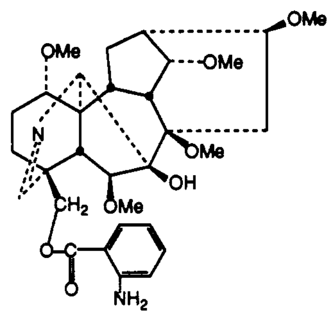
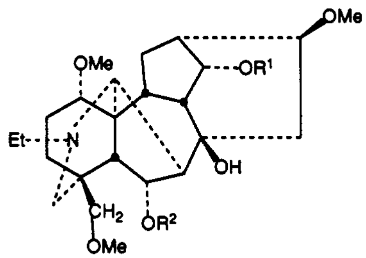


9

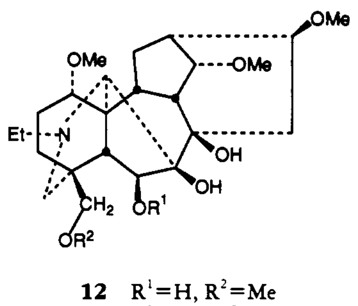


11 R^1=Me, R^2=H
17 R^1=R^2=H
18 R^1=H, R^2=Me
19 R^1=-CO-C_6H_4-OMe, R^2=H

at δ 1.12 (3H, t, J=7.2 Hz, NCH_2CH_3), 3.30 (3H, s, -OMe), 3.71 (1H, br s, H-1β), 4.14 (1H, t, J=4.5 Hz, H-14β), 5.77 (2H, br s, $-NH_2$), and aromatic proton signals indicating the presence of an anthranoyl ester. The ^{13}C-nmr spectrum showed twenty-eight signals for the twenty-nine carbon atoms of the molecule. DEPT spectra indicated the presence of six quaternary carbons, thirteen methine carbons, eight methylene carbons, and two methyl carbons. A tall signal at δ 56.2 ppm in the ^{13}C-nmr spectrum of **8** represented two carbons belonging to a methylene and a methyl and was easily assigned to C-19 and C-16′. The quaternary carbons at δ 74.1, 48.6, and 36.7 ppm have only one oxygenated carbon (δ 74.1 ppm), indicating that **8** is an aconitine-type alkaloid; these signals are assigned to C-8, C-11, and C-4, respectively. The presence of eight methylene carbons indicated an additional methylene as compared with those present in the majority of the aconitine-type alkaloids having no substitutions on C-3 and C-15 (13,15). Hence, the methylene carbon at δ 26.6 ppm is assigned to C-6. Most of the ^{13}C-nmr chemical shifts are identical with those reported for isotalatizidine (13), except for the triplet at δ 69.2 ppm and the shifts due to the anthranoyl ester. The chemical shift at δ 69.2 ppm is assigned to C-18, indicating that the anthranoyl ester belongs to the hydroxymethyl group attached to C-4. The methylene triplets at δ 42.2 and 48.3 ppm have been assigned to C-15 and $-NCH_2CH_3$, respectively, and are comparable with the values reported for isotalatizidine (13). The above data are consistent with the structure **8** assigned to acoseptridinine.

14-*O*-Methylforesticine [**11**], mp 127–129°, has a molecular formula, $C_{25}H_{41}NO_6$, derived from its eims *m/z* 451 $[M]^+$ and its ^{13}C-nmr chemical shifts (Table 1). Its ir spectrum showed absorptions at 3550 and 3450 cm^{-1} (-OH groups). The ^1H-nmr spectrum showed the presence of an Me of an *N*-Et (δ 1.04 ppm, 3H, t, *J*=7.0 Hz) and four MeO groups (δ 3.26, 3.32, 3.33, and 3.39 ppm, each 3H, s). The presence of an H-14β was indicated by a signal at δ 3.70 ppm (1H, t, *J*=4.5 Hz); an H-6β is indicated by a signal at δ 4.35 ppm (1H, d, *J*=7.0 Hz). The ^{13}C-nmr spectrum of **11** showed twenty-four lines for the twenty-five carbon atoms in molecule. The DEPT experiments exhibited the presence of three quaternary, ten methine, seven methylene, and four Me carbons. A tall signal at δ 56.2 ppm represented two carbons bearing MeO groups at C-1 and C-16, a conclusion supported by the presence of four methoxyl groups as shown in the ^1H-nmr spectrum. The presence of three quaternary carbons at δ 76.8 (oxygenated), 48.1, and 38.6 ppm indicated that the compound is an aconitine-type alkaloid. Comparison of the ^{13}C-nmr chemical shifts of **11** with those reported for foresticine [**17**] (13) shows that the majority of shifts are identical except for an additional MeO group present in **11**. Of the four MeO groups, one is present on C-1 as indicated by an ms fragment at *m/z* 420 $[M-OMe]^+$ (40%) (19), a second at C-16 (the majority of norditerpenoid alkaloids possess a 16β-OMe group), a third at C-18 as indicated by a methoxymethyl signal at δ 59.6 ppm, and the fourth either on C-6 or on C-14. An MeO group on C-6 leads to the known alkaloid chasmanine [**18**] (13). The ^{13}C-nmr chemical shifts and tlc comparison of **11** with those of chasmanine proved them to be different. The ^{13}C-nmr chemical shift pattern of **11** is similar to that reported for the known alkaloid geniconitine [**19**] (15), which has an anisoyl group on C-14.

6-Demethyldelphatine [**12**] is an amorphous alkaloid. Its molecular formula, $C_{25}H_{41}NO_7$, was derived from the eims *m/z* 467 $[M]^+$ and the ^{13}C-nmr chemical shifts (Table 1). Its ir spectrum showed absorption at 3400 cm^{-1} (OH). The ^1H-nmr spectrum indicated the presence of an *N*-Et group (δ 1.03 ppm, 3H, t, *J*=7.1 Hz), four aliphatic MeO groups (δ 3.23, 3.32, 3.33, and 3.39 ppm, each 3H, s), an H-14β (δ 3.68 ppm, 1H, t, *J*=4.5 Hz), and an H-6α (δ 4.30 ppm, 1H, s). Its ^{13}C-nmr spectrum (15.03 MHz) showed twenty-four lines for the twenty-five carbon atoms of the molecule. The tall signal at δ 84.2 ppm (15.03 MHz) resolved into two signals at δ 84.19 and 84.12 ppm in the DEPT-90 spectrum (75.47 MHz). The ^{13}C-nmr spectrum (DEPT) showed the presence of four quaternary carbons, nine methines, seven methylenes, and five methyl carbons. The pattern of the ^{13}C-nmr spectrum and the chemical shifts are almost identical with those reported for delphatine [**20**] (13) except for the absence of a fifth MeO group in **12**. Absence of a chemical shift at δ 90.6 ppm in the ^{13}C-nmr spectrum of **12**, assigned to C-6 in delphatine, indicates the lack of a 6-MeO group. Hence, the methine carbon at δ 80.7 ppm in **12** is assigned to C-6 bearing a β-OH group and the quaternary carbon at δ 82.2 ppm is assigned to C-7 (20,21).



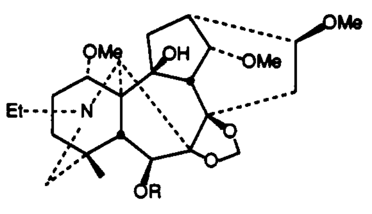
12 R^1=H, R^2=Me
16 R^1=Me, R^2=H
20 R^1=R^2=Me

Acoseptrine [**5**], mp 105–107°, has a molecular formula, $C_{23}H_{37}NO_7$, derived from its eims *m/z* 439 $[M]^+$ and the ^{13}C-nmr chemical shifts (see Table 1). Its ir spectrum (Nujol) showed absorption at 3400 cm^{-1} (OH). The ^1H-nmr spectrum showed the presence of the Me (δ 1.05 ppm) of an *N*-Et group (3H, t, J=7.2 Hz) and three MeO groups (δ 3.25, 3.33, and 3.42 ppm, each 3H, s). A signal at δ 4.20 ppm (1H, t, J=4.5 Hz) indicated the presence of H-14β; one at δ 4.32 ppm (1H, s) indicated an H-6α (13). The ^{13}C-nmr spectrum showed twenty-two lines for the twenty-three carbon atoms in the molecule. A signal at δ 54.1 ppm represented two carbon atoms. The DEPT spectra showed the presence of four quaternary carbons, nine methine carbons, six methylenes, and four Me carbons. Of the seven oxygenated carbons represented by the chemical shifts between δ 87.0 and 77.0 ppm, three are accounted for by the three methoxylated carbons; hence, the remaining four are hydroxylated carbons. Of the four hydroxylated carbons, three are quaternary carbons appearing at δ 87.0 80.6, and 77.0 ppm, and the fourth at δ 77.4 ppm is a methine carbon. The fourth quaternary carbon signal at δ 54.1 ppm is assigned to C-11, and the singlet at δ 80.6 ppm may be assigned to C-10 bearing an -OH group (13). The singlets at δ 87.0 and 77.0 ppm are assigned to C-7 and C-8, respectively, and not to C-9 and C-8, because of the absence of a chemical shift around δ 90–91 ppm assignable to C-14 bearing a methoxyl group in a molecule having a C-9 hydroxyl group (as in *N*-deacetyllappaconitine [**1**]) (13). Acoseptrine [**5**] is a lycoctonine-type alkaloid having a methine carbon at C-4 and is a new addition to the C_{18}-diterpenoid alkaloids (13,15). By comparison of the ^{13}C-nmr chemical shifts of **5** with those of 7,8-demethylenedeltamine [**21**] (15), the signal δ 77.4 ppm in **5** has been assigned to C-6 having a β-OH group. The spectroscopic data of acoseptrine are in agreement with the proposed structure **5**.

Acosepticine [**6**] is an amorphous alkaloid having the molecular formula $C_{23}H_{37}NO_6$, derived from its eims and ^{13}C-nmr chemical shifts. The ir spectrum indicated the presence of an OH group (3350 cm^{-1}). Its ^1H-nmr spectrum showed an Me of an *N*-Et group (δ 1.04 ppm, 3H, t) and three MeO groups (δ 3.24, 3.33, 3.40, each 3H, s). A triplet at δ 3.70 ppm (1H) and a singlet at δ 4.28 (1H) indicated the presence of H-14β and H-6α, respectively (13). Its ^{13}C-nmr spectrum showed twenty-two lines for the twenty-three carbon atoms of the molecule. The DEPT experiments showed the presence of three quaternary, ten methine, six methylene, and four Me carbons. Of the three quaternary carbons, two are oxygenated (δ 87.8 and 78.7 ppm) and can be assigned to C-7 and C-8. An -OH group on C-9 is ruled out because of the presence of a one-proton triplet at δ 3.70 (J=4.5 Hz) assignable to H-14β (13). The pattern of ^1H- and ^{13}C-nmr spectra indicates that compound **6** is a lycoctonine-type diterpenoid alkaloid. The basic lycoctonine-type skeleton usually has four quaternary carbons (C-4, C-7, C-8, and C-11) with no substitution on C-10 or C-13. The DEPT spectrum of **6** indicates the presence of only three quaternary carbons. The quaternary carbon at δ 48.5 ppm may be assigned to C-11, since this carbon is always quaternary in norditerpenoid alkaloids. The above assignment indicates that C-4 is a methine carbon which makes **6** a C_{18}-diterpenoid alkaloid. Comparison of the ^{13}C-nmr chemical shifts of **6** ($C_{23}H_{37}NO_6$) with those of **12** ($C_{25}H_{41}NO_7$, reported in this paper) shows that most are identical except that for C-4 which is a quaternary carbon in **12** and a methine carbon in **6**. The major differences present are for C-19 (**6**, δ 50.3 t and **12**, δ 53.4 t ppm) C-5 (**6**, δ 53.0 d and **12**, δ 54.2 d ppm), and C-3 (**6**, δ29.3 and **12**, δ 31.9 ppm) which are all neighbors of C-4. In compound **12**, C-4 (a quaternary carbon) bears a methoxymethylene group and thus contains two additional carbons as compared with those of compound **6**. Hydrolysis of 6-acetylacosepticine (22) with ethanolic KOH gave compound **6** (identical tlc behavior, ir, ^1H- and ^{13}C-nmr spectra).

Besides the above-mentioned eight new alkaloids, the known alkaloids N-deacetyllappaconitine [**1**], anthranoyllycoctonine [**14**], sepaconitine [**4**], delvestidine [**13**], septentrionine [**2**], lapaconidine [**15**], and lycoctonine [**16**] were also isolated during this investigation. The identity of these known alkaloids was established by comparing their tlc behavior, mp's, ir, ^{1}H- and ^{13}C-nmr spectra with those of authentic samples.

In order to confirm that the strongly acidic ion exchange resin hydrolyzes the amide group of lappaconitine, a separate experiment was performed. Lappaconitine was processed by the ion exchange method under conditions identical to those used for the isolation of crude base. Lappaconitine was deacetylated to give N-deacetyllappaconitine in quantitative yield, leaving the anthranoyl ester group intact. Another experiment was conducted to see if the acetate group would be cleaved during basification with the 5% aqueous NH_4OH used to liberate the crude bases. Deltaline [**22**] having an acetate group on C-6 and an acid labile methylene dioxy group (13) was subjected to the conditions of isolation. The results showed that 93% of deltaline was recovered unchanged and 7% of it was found to be hydrolyzed to deltamine [**23**]. This experiment demonstrated that the methylenedioxy group of deltaline was unaffected during this procedure. We have observed that the methylenedioxy group of deltaline can be cleaved easily by warming a solution of deltaline in 10% H_2SO_4 (23).



22 R=Ac
23 R=H

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were determined on a Thomas-Kofler hot stage equipped with a microscope and a polarizer and are corrected. Optical rotations were measured on a Perkin-Elmer model 141 polarimeter in $CHCl_3$ solutions. Ir spectra were recorded in Nujol on a Perkin-Elmer model 1420 spectrophotometer. ^{1}H-nmr spectra were determined on a Bruker AC-300 (300 MHz) spectrometer in $CDCl_3$ ^{13}C-nmr spectra were recorded on JEOL FX 60 (15.03 MHz) and Bruker AC-300 (75.47 MHz) spectrometers in $CDCl_3$; the ^{13}C-nmr chemical shift assignments for all compounds were determined from the DEPT spectra and are reported in Table 1. Eims (70 eV) were recorded on a Finnegan Quadrupole 4023 mass spectrometer. Chromatographic separations were carried out by vacuum liquid chromatography (vlc) followed by separations on a Chromatotron with rotors of 1-mm thickness coated with Al_2O_3 (EM 1104-3) or SiO_2 (EM 7749). All the known compounds isolated were identified by comparing their spectral data and tlc behavior with those of authentic samples.

PLANT MATERIAL.—The plant material was collected by one of the authors (A.J.A.) in Norway in 1979; a voucher specimen (#AJAA/790719/1) is deposited in the Herbarium of the Department of Pharmacy, University of Oslo, Norway.

ISOLATION OF ALKALOIDS.—Dried and powdered roots of *A. septentrionale* (5.1 kg) were first extracted with hexane at room temperature and then with 85% EtOH at room temperature till the last extract gave minimum residue. The EtOH extract was concentrated in vacuo to a syrupy mass. The syrupy mass was divided into four equal parts. One part (200.0 g) was again dissolved in 85% EtOH (8.0 liters) and the solution was passed over a column of cation exchange resin (700.0 g, DOWEX 50W X8, H^+, 20–50 mesh) at a flow rate of 40 drops/min. The eluate was tested frequently for the presence of alkaloids when a negative test indicated that the alkaloids were retained on the resin column. When all of the 85% EtOH solution was exhausted the column was washed with 85% EtOH (2.0 liters) until it gave no more residue. The column was then washed with distilled H_2O (1.5 liters) and finally with NH_4OH (5% aqueous solution, 700 ml) until the eluate became strongly basic. The liberated alkaloids retained on the column (as they are insoluble in H_2O), were collected by washing the column with CH_2Cl_2 to give a crude base fraction (16.5 g). The crude basic material was dissolved in CH_2Cl_2 (200 ml), and the solution was extracted with ice cold 2% H_2SO_4 solution (5×150 ml). The acidic layer was basified (under ice-cold conditions) to pH 4–5 ($NaHCO_3$) and extracted with $CHCl_3$ (3×200 ml). The $CHCl_3$ extract was washed with H_2O, dried (Na_2SO_4), and evaporated to dryness in vacuo to give the basic fraction A (8.7 g). The aqueous layer at pH 4–5 was further basified to pH 8 (Na_2CO_3) and extracted with $CHCl_3$ (3×200 ml) as above to give basic fraction B (3.7 g). The pH 14 (20% NaOH) fraction gave the basic fraction C (0.065 g).

ISOLATION OF *N*-DEACETYLLAPPACONITINE [**1**], DELVESTIDINE [**13**], ACOSEPTRIDINE [**9**], ANTHRANOYLLYCOCTONINE [**14**], ACOSEPTRIDININE [**8**], 4-ANTHRANOYLLAPACONIDINE [**7**], SEPACONITINE [**4**], ACOSEPTRININE [**10**], AND SEPTENTRIONINE [**2**].—Fraction A (8.7 g) was dissolved in CH_2Cl_2 (20 ml) and was adsorbed on Si gel (15 g, EM 7736). The dried mixture was placed on a vlc column (Si gel, 50.0 g, EM 7736), well packed, and covered with a 1-cm layer of sea sand. The column was eluted with a gradient of hexane, $CHCl_3$, and MeOH. Sixteen fractions (200 ml each), F_1–F_{16}, were collected, evaporated, and examined on tlc (Si gel or Al_2O_3) for their alkaloid content. The alkaloids were visualized by spraying the plates with Dragendorff's reagent followed by a spray of 5% $NaNO_2$ solution. Homogeneous fractions, showing similar spots, were combined for further fractionations.

Fractions F_1–F_3 (0.22 g, hexane/25 and 75% $CHCl_3$), showing very faint alkaloidal spots, gave a non-alkaloidal oil as the major component on further fractionation on an Al_2O_3 rotor.

Fractions F_4–F_6 (hexane/75% $CHCl_3$, 6.5 g) were combined, and the residue was dissolved in Me_2CO (20 ml) when crystals of *N*-deacetyllappaconitine [**1**] separated. Recrystallization gave a pure sample (3.5 g) of **1**, mp 213–214°, [α]D +29.4° (*c*=0.395), identical with an authentic sample of **1** prepared by acidic hydrolysis of lappaconitine. For ^{13}C-nmr chemical shift assignments see Table 1. The mother liquor was reserved for further fractionation as fraction D.

Fractions F_7–F_8 (0.13 g, $CHCl_3$ and $CHCl_3$/1% MeOH) were subjected to fractionation on an Al_2O_3 rotor and eluted with a gradient of hexane, Et_2O and MeOH. This fraction gave compound **1** (79.2 mg, mp 212–214°) and anthranoyllycoctonine [**14**] (20.3 mg, mp 165–166°).

Fraction F_9 (0.62 g, $CHCl_3$/2% MeOH) was subjected to fractionation on an Al_2O_3 rotor, and elution was carried out with a gradient of hexane, Et_2O, and MeOH. This separation gave **1** (240.0 mg) and **14** (130.3 mg) and a fraction (130.2 mg) showing a mixture of at least three alkaloids on tlc (Si gel, $CHCl_3$/10% MeOH). The latter fraction was once again subjected to fractionation on an Al_2O_3 rotor and eluted as above. The major compound (89.0 mg) showed two spots on tlc (Si gel) and was subjected to a preparative tlc separation on a Si gel plate (20×20 cm, 0.75 mm, $CHCl_3$ 3% MeOH). The major band isolated (49.0 mg) was identified as the new alkaloid 4-anthranoyllapaconidine [**7**]: amorphous [α]D +48.8° (*c*=0.16); eims *m/z* (%) $[M]^+$ 528 (0.03), $[M-OH]^+$ 511 (0.24), 120 (100) for $C_{29}H_{40}N_2O_7$; ir ν max 3450, 3350 (OH), 3200 (NH_2), 1685 (C=O), 1620, 1580, 1530, 1470 (aromatic) cm^{-1}; ^1H nmr δ 1.15 (3H, t, *J*=7.4 Hz, NCH_2CH_3), 3.31, 3.39 (each 3H, s, 2×OMe), 3.46 (1H, d, *J*=4.8 Hz, H-14β), 3.77 (1H, br s, H-1β), 5.69 (2H, br s, NH_2), aromatic protons at δ 6.60 (2H, t, *J*= 8.1 Hz), 7.22 (1H, d, *J*=7.9 Hz), 7.73 (1H, d, *J*=7.9 Hz); ^{13}C nmr see Table 1.

Fraction F_{10} (0.44 g, $CHCl_3$/2% MeOH), when crystallized from Me_2CO, gave a mixture of crystals. The mixture was resolved by preparative tlc on Al_2O_3. The major crystalline compound (60.2 mg) (mp 252–254°, eims *m/z* 559 $[M+1]^+$) was identified as sepaconitine [**4**]. The mother liquor was saved as fraction E.

Fraction F_{11} (0.15 g, $CHCl_3$/2% MeOH) was subjected to a fractionation on a Si gel rotor, and additional sepaconitine [**4**] (10.5 mg, mp 251–253°) was obtained.

Fractions F_{12}-F_{13} (0.18 g, $CHCl_3$/5% MeOH), upon fractionation on an Al_2O_3 rotor, gave acoseptrinine [**10**] (4.1 mg), mp 220–222°, [α]D −14.3° (*c*=0.063); eims *m/z* (%), $[M]^+$ 572 (2.49), $[M-OMe]^+$ 541 (75), [anthranilic acid]$^+$ 137 (10.6), 120 (100) for $C_{31}H_{44}N_2O_8$; ir ν max 3530, 3460, 3350 (OH,NH_2), 1695 (C=O), 1625, 1460 (aromatic) cm^{-1}; ^1H nmr δ 1.05 (3H, t, *J*=7.3 Hz, NCH_2CH_3), 3.25, 3.34, 3.40 (each 3H, s, 3×OMe), 3.65 (1H, t, *J*=4.3 Hz, H-14β), 4.41 (1H, s, H-6α), 5.72 (2H, br s, -NH_2), aromatic protons at δ 6.67 (2H, t), 7.29 (1H, t), 7.82 (1H, d); ^{13}C nmr see Table 1.

Fractions F_{14}–F_{16} (0.28 g, $CHCl_3$/20% MeOH) on fractionation on a Si gel rotor gave septentrionine [**2**] (27.2 mg, mp 123–125°).

The mother liquors D and E were combined (3.7 g) on the basis of similarities in the tlc behavior and fractionated on a vlc column. The combined residue was dissolved in CH_2Cl_2 and was adsorbed on Al_2O_3 (25 g, EM 1085). The dry mixture was placed on a vlc column (Al_2O_3, 90 g, EM 1085) and eluted with a gradient of hexane, Et_2O, and MeOH. Twelve fractions G_1–G_{12} (200 ml each) were collected and examined by tlc.

Fractions G_1–G_3 (120.1 mg, hexane and hexane/10 and 20% Et_2O) gave a nonalkaloidal fraction (oil) with an aromatic odor.

Fraction G_4 (518.0 mg, hexane/30% Et_2O) was subjected to futher fractionation on an Al_2O_3 rotor. Elution was carried out with a gradient of hexane and Et_2O; fifteen fractions (10 ml each) were collected. Fractions 4–6, upon preparative tlc (Si gel) separation, furnished delvestidine [**13**] (amorphous). Fractions 7–8 (102.3 mg, hexane/20 and 30% Et_2O), upon crystallization from hexane, gave anthranoyllycoctonine [**14**], mp 165–166°. Fractions 9–12 (42.1 mg, hexane/40–70% Et_2O) afforded *N*-deacetyllappaconitine [**1**] (mp 212–214°). Fractions 13–15 (32.5 mg, hexane/80 and 90% Et_2O and Et_2O) were subjected to preparative tlc (Si gel, hexane/90% Et_2O) to give an amorphous compound (29.7 mg), acoseptridine [**9**]: $[\alpha]_D$ +65° (c=0.1); eims *m/z* (%), $[M]^+$ 570 (8) ($C_{31}H_{42}N_2O_8$), $[M-Me]^+$ 555 (15), $[M-OMe]^+$ 539 (12), $[M-136]^+$ 434 (3), [anthranilic acid]$^+$ 137 (15), 120 (100); ir ν max 3440, 3350 (OH,NH_2), 1700 (C=O), 1620, 1470 (aromatic) cm^{-1}; ^1H nmr δ 3.17, 3.37, 3.38, 3.40, 3.45 (each 3H, s, 5×OMe), 3.55 (1H, t, J=4.5 Hz, H-14β), 3.87 (1H, br s, H-6α), 5.75 (2H, br s, $-NH_2$), 7.64 (1H, br s, $N=CH_{19}$), 6.56 (2H, t), 7.30 (1H, t), 7.85 (1H, d) (aromatic protons); ^{13}C nmr see Table 1.

Fractions G_7–G_8 (901.1 mg, hexane/60 and 70% Et_2O), when crystallized from hexane, gave anthranoyllycoctonine [**14**], mp 165–166°.

Fractions G_9–G_{12} (77.5 mg, Et_2O/5 and 10% MeOH) were subjected to preparative tlc (Si gel, $CHCl_3$/20% MeOH). The major band visualized in short uv light gave acoseptridinine [**8**] (59.8 mg) as an amorphous solid: $[\alpha]_D$ +1.5° (c=0.345); eims *m/z* (%) $[M]^+$ 512 (12) ($C_{29}H_{40}N_2O_6$), $[M-OH]^+$ 495 (75), $[M-136]^+$ 376 (5), [anthranilic acid]$^+$ 137 (13.5), 120 (100); ir ν max 3490, 3350, 3280, (OH, NH_2), 1690 (C=O), 1620, 1470 (aromatic) cm^{-1}; ^1H nmr δ 1.12 (3H, t, J=7.1 Hz), NCH_2CH_3), 3.30 (3H, s, OMe), 3.71 (1H, br s, H-1β), 4.14 (1H, t, J=4.5 Hz, H-14β), 5.77 (2H, br s, $-NH_2$), 6.64 (2H, t), 7.25 (1H, t), 7.79 (1H, d) for aromatic protons; ^{13}C nmr see Table 1.

ISOLATION OF *N*-DEACETYLLAPPACONITINE [**1**], 14-*O*-METHYLFORESTICINE [**11**], ACOSEPTRINE [**5**], 6-DEMETHYLDELPHATINE [**12**], ACOSEPTICINE [**6**], LAPACONIDINE [**15**], SEPACONITINE [**4**], AND LYCOCTONINE [**16**].—The combined basic material (B+C=4.1 g) was dissolved in CH_2Cl_2 (15 ml), and the solution was mixed with Al_2O_3 (10 g, EM 1085) and dried. The homogeneous mixture was placed on the top of a vlc column (Al_2O_3, 90 g, EM 1085). Elution was carried out with a gradient of hexane, Et_2O, and MeOH. Twelve fractions (M_1–M_{12}, 200 ml each) were collected and the alkaloids were isolated as described below.

Fraction M_3 (0.156 g, hexane/50% Et_2O) gave *N*-deacetyllappaconitine [**1**] (45.1 mg, mp 212–214°) after purification on a Si gel rotor.

Fraction M_4 (0.149 g, hexane/75% Et_2O), upon fractionation on an Al_2O_3 rotor, afforded 14-*O*-methylforesticine [**11**] (22.3 mg): mp 127–129° (Me_2CO); $[\alpha]_D$ +20.9° (c=0.134); eims *m/z* (%), $[M]^+$ 451 (0.03) for $C_{25}H_{41}NO_6$, $[M-Me]^+$ 436 (20), $[M-OMe]^+$ 420 (40); ir ν max 3550, 3450 (OH) cm^{-1}; ^1H nmr δ 1.04 (3H, t, J=7.0 Hz, NCH_2CH_3), 3.26, 3.32, 3.33, 3.39 (each 3H, s, 4×OMe), 3.70 (1H, t, J=4.5 Hz, H-14β), 4.35 (1H, d, J=7.3 Hz, H-6β), 4.80 (1H, br s, -OH); ^{13}C nmr see Table 1.

Fraction M_5 (0.255 g, Et_2O) was subjected to a fractionation on an Al_2O_3 rotor eluting with a gradient of hexane, Et_2O, and MeOH. Fractions were collected according to the bands seen in short uv light (λ 254 nm). Fraction 4, eluted with hexane/30% Et_2O, gave an additional quantity (57.1 mg) of compound **1**. Fractions 9–11, eluted with hexane/80 and 90% Et_2O and Et_2O, gave a mixture of polar alkaloids (47.3 mg). The mixture was resolved by preparative tlc (Si gel, 20×20 cm, 0.75 mm, $CHCl_3$/20% MeOH), and the major compound isolated was characterized as the new alkaloid 6-demethyldelphatine [**12**] (amorphous, 29.9 mg); $[\alpha]_D$ +19.3° (c=0.295); eims *m/z* (%) $[M]^+$ 467 (1.3) for $C_{25}H_{41}NO_7$ $[M-OMe]^+$ 436 (77.5); ir ν max 3400 cm^{-1} (OH); ^1H nmr δ 1.03 (3H, t, J=7.1 Hz, NCH_2CH_3), 3.23, 3.32, 3.33, 3.39 (each 3H, s, 4×OMe), 3.68 (1H, t, J=4.2 Hz, H-14β), 4.30 (1H, s, H-6α); ^{13}C nmr see Table 1.

Fraction M_6 (1.073 g, Et_2O and Et_2O/2% MeOH) was loaded on a Si gel rotor, and elution was carried out with a gradient of hexane, $CHCl_3$, and MeOH. Ten fractions (50 ml each) were collected, and most of the fractions consisted of a mixture of alkaloids. Fractions 8–9, eluted with $CHCl_3$/4 and 6% MeOH, were combined (50.2 mg) on the basis of their tlc similarity (at least 3 spots on Si gel plate, $CHCl_3$/10% MeOH) and subjected to preparative tlc (Si gel, $CHCl_3$/10% MeOH). Two bands were isolated. The compound extracted from the first band (less polar) was crystallized from hexane/Me_2CO to afford acoseptrine [**5**]: mp 105–107° (Me_2CO/hexane) (25.2 mg), $[\alpha]_D$ +19.6° (c=0.245); eims *m/z* (%) $[M]^+$ 439 (4.1) ($C_{23}H_{37}NO_7$), $[M-Me]^+$ 424 (5), $[M-OMe]^+$ 408 (10); ir ν max 3400 cm^{-1} (OH); ^1H nmr δ 1.05 (3H, t, J=7.2 Hz, NCH_2CH_3), 3.25, 3.33, 3.42 (each 3H, s, 3×OMe), 4.20 (1H, t, J=4.2 Hz, H-14β), 4.32 (1H, s, H-6α); ^{13}C nmr see Table 1.

The second band (polar) yielded an amorphous alkaloid (19.2 mg) characterized as acosepticine [**6**]: $[\alpha]_D$ +23.4° (c=0.385); eims *m/z* (%) $[M]^+$ 423 (0.4) for $C_{23}H_{37}NO_6$; ir ν max 3350 cm^{-1} (OH); ^1H nmr δ 1.04 (3H, t, J=7.0 Hz, NCH_2CH_3), 3.24, 3.33, 3.40 (each 3H, s, 3×OMe), 3.70 (1H, t, J=4.5 Hz, H-14β), 4.28 (1H, s, H-6α); ^{13}C nmr see Table 1.

Fractions M_7 and M_8 were combined (0.724 g, Et_2O/4 and 6% MeOH) on the basis of their tlc similarity and fractionated on a Si gel rotor; elution was carried out with a gradient of hexane, $CHCl_3$, and MeOH (50 ml each, fractions were collected). Fractions 5 and 6 (0.248 g, hexane/10 and 20% $CHCl_3$) gave a complex mixture of alkaloids. Separation of fraction 7 (50.1 mg, hexane/30% $CHCl_3$) with preparative tlc on a Si gel plate (20×20 cm, 0.75 mm, hexane/40% $CHCl_3$) furnished lapaconidine [**15**] (30.2 mg, mp 206–207°).

Fraction M_9 (0.55 g, Et_2O/8% MeOH) after purification on a Si gel rotor gave sepaconitine [**4**] (70.3 mg, mp 252–253°).

Fractions M_{10}–M_{12}(0.921 g, Et_2O/10 and 50% MeOH) were combined and fractionated on a Si gel rotor. No bands could be visualized under uv light. Forty fractions (15 ml each) were collected by gradient elution with $CHCl_3$ and MeOH. Fractions 25–30 were combined (77.5 mg) on the basis of their tlc similarity and subjected to crystallization to give the known alkaloid lycoctonine [**16**] (35.7 mg).

ALKLINE HYDROLYSIS OF COMPOUND **7**.—Compound **7** (8.0 mg) was dissolved in ethanolic KOH solution (5%, 3 ml), and the solution was allowed to stand at room temperature for two days. Usual workup gave a gummy residue (5.7 mg), which crystallized from Me_2CO, mp 203–205°. The crystalline compound was found to be identical with an authentic sample of lapaconidine [**15**] (tlc, mmp, ir, ^1H- and ^{13}C-nmr spectra).

ALKALINE HYDROLYSIS OF 6-*O*-ACETYLACOSEPTICINE.—This reaction was carried out exactly as reported by Ross and Pelletier (22). The hydrolysis product was found to be identical with acosepticine [**6**] (amorphous tlc, ^1H- and ^{13}C-nmr spectra).

ACTION OF DOWEX 50W X8 RESIN ON LAPPACONITINE.—Lappaconitine (100 mg) was dissolved in 85% EtOH (30 ml), and the solution was passed through a column of cation exchange resin (DOWEX 50W X8, 15 g). The eluate was processed by the isolation procedure described in this work. The isolated base (95.7 mg), mp 212–214°, was identified as *N*-deacetyllappaconitine [**1**] (tlc, mmp, ir, ^1H- and ^{13}C-nmr spectra).

ACTION OF DOWEX 50W X8 RESIN ON DELTALINE [**22**].—Deltaline [**22**] (300 mg) was dissolved in 85% EtOH (100 ml), and the solution was passed through a column of cation exchange resin (DOWEX 50W X8, 10 g). The alkaloid was completely retained on the column. On processing the reaction product by the procedure used in this work to isolate the crude bases, a gum (299.5 mg) was obtained. The tlc of the gum (Al_2O_3, Et_2O) indicated the presence of a polar compound (very minor) besides the major spot corresponding to the starting material **22**. The mixture was resolved on an Al_2O_3 rotor [a gradient of hexane and Et_2O was used, dark bands were seen in long (λ 365 nmr) uv light] to give deltaline [**22**] (270.3 mg, mp 185–187°) and deltamine [**23**] (19.1 mg, mp 225–227°). The two samples were identified by comparing their mmp, tlc behavior, ^1H- and ^{13}C-nmr spectra with those of authentic samples.

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