2-Acetylseptentriosine, a New Diterpenoid Alkaloid from Aconitum septentrionale

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2-ACETYLSEPTENTRIOSINE, A NEW DITERPENOID ALKALOID FROM *ACONITUM SEPTENTRIONALE*

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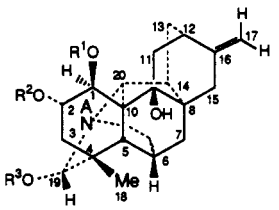
ABSTRACT.—A new diterpenoid alkaloid, 2-acetylseptentriosine [**2**] (2α-acetoxyhetisane-1β,9β,19α-triol), has been isolated from the roots of *Aconitum septentrionale*, and its structure established by correlation studies and a single crystal X-ray structure determination.

Isolation and structure determination of norditerpenoid alkaloids, 6-*O*-acetylacosepticine, *N*-acetylsepaconitine, acoseptrigine, acoseptriginine, *N*-deacetyllappaconitine, lapaconidine, lappaconine, lappaconitine, lycoctonine, 8-*O*-methyllycaconitine, puberaconitine, septentriodine, and septentrionine, from the roots of *Aconitum septentrionale* Koelle (Ranunculaceae) has been reported earlier (1–4). Further, the structure elucidation of the diterpenoid alkaloid septentriosine [**1**] was recently described by us (5). In this communication, we report the isolation and structure determination of 2-acetylseptentriosine [**2**] obtained in 0.04% yield from the roots of *A. septentrionale.*



1 $R^1=R^2=R^3=H$
2 $R^1=R^3=H$, $R^2=Ac$
3 $R^1=R^2=R^3=Ac$

RESULTS AND DISCUSSION

An alkaloid **2**, mp 182–184°; ir (Nujol) ν 3560, 3460, 3320 (broad, OH), 1730 (ester), 1650 (exocyclic methylene) cm^{-1}; ms *m/z* $[M]^+$ 387, was obtained from the alkaloidal mixture of *A. septentrionale.* These data, together with the ^1H- and ^{13}C-nmr spectral analysis, suggested that the alkaloid **2** is a monoacetate of septentriosine [**1**]. Elemental analysis indicated a molecular formula $C_{22}H_{29}NO_5$ for **2** and showed that the crystals retained a molecule of H_2O of crystallization.

The ^{13}C-nmr spectrum of **2** consisted of 21 lines for twenty-two carbon atoms, and the signal at 67.9 ppm represented two carbons. A DEPT experiment revealed that the twenty-two carbons included six non-protonated carbons (δ 169.9, 150.4, 79.6, 53.7, 42.1, 41.6), eight methines (δ 91.2, 73.0, 67.9, 67.9, 60.5, 50.7, 43.7, 36.1), six methylenes (δ 104.7, 39.2, 33.8, 32.9, 30.9, 30.7), and two Me groups (δ 22.2, 21.5). The three lowest field signals belonged to an acetate carbonyl (δ 169.9) and an exocyclic methylene group (δ 150.4 and 104.7); these are characteristic chemical shifts of the hetisane-type (6) diterpenoid alkaloids. The absence of an OMe, Me, or *N*-Et group suggested that all the carbons (except the acetate) are part of the hetisane skeleton (7). Of the five oxygens, two belong to the acetoxyl group and the remaining are hydroxyls, as no ether oxygens are present in the molecule.

Of the three OH groups, one is a

tertiary alcohol and is therefore located at C-5, C-6, C-9, C-12, C-14, or C-20 in the hetisane skeleton to form a quaternary carbon, which appears at δ 79.6. Location of the OH at C-5 or C-20 is considered unlikely, as no other alkaloid has been isolated with this pattern of substitution (8). Location of the OH group at C-6 was discounted as this carbinolamine carbon would have shifted the C-6 signal downfield to about 97–101 ppm (9,10). An OH at C-12 would have produced a downfield shift of C-16 to ca. 154–156 ppm, analogous to the β effect produced by hydroxylation at C-15. As this was not observed, an OH at C-12 was not considered. Placement of the OH at C-9 appeared most likely, since the singlet at 53.7 ppm, attributed to C-10, is in the expected range of 51–55 ppm when both C-1 and C-9 bear oxygen functions (sadosine 51.4 ppm, hypognavine 54.9 ppm) (11,12). If the hydroxyl group was located at C-14, a downfield shift of C-20 to ca. 69–70 ppm would have been observed (guan-fu base z 69.1 ppm, tangutisine 70.3 ppm) (13,14).

Of the remaining three secondary oxygen functions, an OH group or an acetoxyl group should be located at C-19, as the carbon resonance at 91.2 ppm appears in the expected range for a carbon bearing both an oxygen and a nitrogen function (5,15,16).When no OH group is present at C-1, C-2, or C-3 in ring A, the signal for C-2 appears around 19.8 ppm (8,17,18). As there is no resonance for a methylene carbon around this region, the other two oxygen functions have to be located in ring A. We therefore surmised that the new alkaloid might be a monoacetyl derivative of septentriosine [**1**] (5), in which one of the OH groups at C-1, C-2, or C-19 is acetylated.

Mild alkaline hydrolysis of **2** gave a crystalline compound identical with septentriosine [**1**]. Acetylation of **2** with Ac_2O and pyridine afforded a diacetyl derivative, 1,2,19-triacetylseptentriosine [**3**]. The tertiary OH group at C-9 was acetylated when **2** was treated with acetyl chloride for 3 days; however, the reaction mixture could not be purified to yield identifiable compounds.

On the basis of the spectral and correlation data alone, it was not possible to decide which of the hydroxyl groups (at C-1, C-2, or C-19) of **1** is acetylated. The complete structure and the relative stereochemistry of **2** were therefore solved by a single crystal X-ray analysis. The X-ray structure determination established that alkaloid **2** is 2-acetylseptentriosine (2α-acetoxyhetisane-1β,9β,19α-triol).

X-RAY CRYSTAL STRUCTURE.[1]—A crystal of **2** was fixed in a random orientation on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. Cell dimensions (Table 1) were determined by least squares refinement of the angular positions of 25 independent reflections in the 15–25° θ range during the normal alignment procedure. A total of 5637 reflections were collected over a θ range of 2–75° using ω–2θ technique with a variable scan width and scan range. Systematic absences indicated space group $P4_12_12$ (#92) or the enantiomorph $P4_32_12$ (#96). Because of the low value of the absorption coefficient, the data were not corrected for absorption. After Lorentz-polarization correction, averaging redundant data, and eliminating systematic absences, a total of 5030 reflections ($F_O > 3\sigma$) were considered observed and unique and were used in the structural analysis.

The structural analysis was performed on a VAX 6210 using the MolEN structure analysis program system (19). The structure was solved using SIR88 (20)

[1]Atomic coordinates for compound **2** have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

TABLE 1. Crystal Structure Data for **2**.

Crystal shape	colorless plates
Crystal dimensions	0.4×0.4×0.1 mm
Molecular formula	$C_{24}H_{29}NO_5 \cdot H_2O$
Molecular weight	429.52
a	10.344 (3) Å
c	45.434 (9) Å
V	4861 (2)
F(000)	1840
μ(CuKα)	6.5 cm^{-1}
λ(CuKα)	1.54184 Å
D_{calc}	1.174 g/cm^3
Z	8
θ	2–75°
Number of reflections measured	5637
Number of reflections used ($F_O > 3\sigma$)	3324
R	0.073
R_w	0.101
Space group	$P4_32_12$

with 8 symbols and using the seminvariant option. All non-hydrogen atoms, including one water of crystallization, were located in several difference Fourier maps and then refined by full-matrix least-squares, first isotropically, then anisotropically. Some hydrogen positions could be located from difference Fourier maps, and some hydrogen positions were calculated. All hydrogen atoms, with isotropic thermal parameters fixed, were refined along with positional and thermal parameters of non-hydrogen atoms via full matrix least squares to yield the final structure shown in the ORTEP drawing (Figure 1). The final unweighted R value was 0.073. Values for positional parameters and their estimated standard deviations for **2** are given in Table 2. Bond lengths and angles for the alkaloid are within a normal range and exhibit no unusual features.

A cluster of three peaks dominated the resulting difference map; these peaks were not close enough to be hydrogen atoms on the main structure. The geometry of the group and chemical intuition suggested a molecule of EtOH, although these peaks could not be refined sufficiently to distinguish O from C. All three peaks were treated as C atoms. An H_2O molecule is strongly hydrogen-bonded to

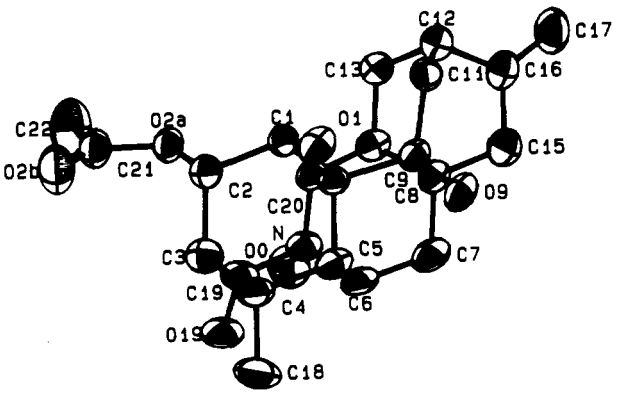


FIGURE 1. ORTEP Drawing of **2**.

TABLE 2. Positional Parameters and Their Estimated Standard Deviations for Compound **2**.

Atom	*x*	*y*	*z*	B(A2)
O-0	0.2290 (4)	0.8673 (4)	0.78706 (8)	5.9 (1)
O-1	0.9087 (3)	0.9116 (3)	0.73922 (6)	3.32 (6)
O-2a	0.6581 (3)	0.6823 (3)	0.72103 (6)	3.20 (6)
O-2b	0.6656 (4)	0.6302 (4)	0.67302 (8)	5.40 (9)
O-9	0.8370 (3)	1.0904 (3)	0.78853 (6)	3.57 (6)
O-19	0.3424 (3)	0.9502 (3)	0.72413 (8)	4.81 (8)
N	0.4752 (3)	0.9197 (4)	0.76623 (8)	3.33 (7)
C-1	0.7986 (4)	0.8323 (4)	0.74506 (9)	2.67 (7)
C-2	0.7406 (4)	0.7941 (4)	0.71586 (9)	3.10 (8)
C-3	0.6686 (5)	0.9035 (5)	0.7007 (1)	3.66 (9)
C-4	0.5783 (4)	0.9819 (4)	0.7203 (1)	3.47 (9)
C-5	0.6447 (4)	1.0286 (4)	0.7486 (1)	3.24 (8)
C-6	0.5304 (4)	1.0515 (4)	0.7691 (1)	3.48 (9)
C-7	0.5659 (5)	1.0877 (5)	0.8002 (1)	4.0 (1)
C-8	0.6580 (4)	0.9859 (4)	0.81330 (9)	3.19 (8)
C-9	0.7771 (4)	0.9683 (4)	0.79325 (9)	2.88 (8)
C-10	0.7113 (4)	0.9138 (4)	0.76444 (8)	2.54 (7)
C-11	0.8727 (4)	0.8764 (4)	0.80821 (9)	3.19 (9)
C-12	0.8083 (5)	0.8083 (5)	0.8384 (1)	3.63 (9)
C-13	0.6795 (5)	0.7457 (5)	0.8241 (1)	3.8 (1)
C-14	0.5939 (5)	0.8505 (4)	0.81002 (9)	3.43 (9)
C-15	0.6978 (6)	1.0185 (5)	0.8450 (1)	4.6 (1)
C-16	0.7784 (5)	0.9081 (5)	0.8577 (1)	3.9 (1)
C-17	0.8157 (7)	0.9005 (6)	0.8860 (1)	5.5 (1)
C-18	0.5321 (6)	1.1015 (5)	0.7026 (1)	5.0 (1)
C-19	0.4636 (4)	0.9034 (5)	0.7339 (1)	3.73 (9)
C-20	0.5869 (4)	0.8411 (4)	0.77635 (9)	2.92 (8)
C-21	0.6265 (5)	0.6096 (5)	0.6973 (1)	3.9 (1)
C-22	0.5327 (7)	0.5081 (6)	0.7057 (1)	7.0 (2)
C-31	0.188 (1)	0.2170 (9)	0.1081 (2)	13.7 (3)
C-32	0.133 (1)	0.3497 (9)	0.1120 (2)	12.9 (4)
C-33	0.118 (1)	0.135 (1)	0.1299 (2)	13.1 (4)
H_a-O	0.2346	0.8019	0.8122	12 (2)[a]
H-1	0.8081	0.7464	0.7554	1.4 (7)[a]
HO-1	0.9431	0.8675	0.7339	1.5 (7)[a]
H-2	0.8272	0.7739	0.7106	7 (2)[a]
H_b-3	0.7403	0.9683	0.6909	3.6 (9)[a]
H_a-3	0.6187	0.8865	0.6797	4 (1)[a]
H-5	0.6915	1.0895	0.7476	4 (1)[a]
H-6	0.4632	1.1077	0.7581	2.5 (8)[a]
H_a-7	0.6030	1.1989	0.8026	5 (1)[a]
H_b-7	0.4627	1.1256	0.8022	30 (4)[a]
HO-9	0.9308	1.0696	0.7714	7 (1)[a]
H_b-11	0.9430	0.9272	0.8167	3 (1)[a]
H_a-11	0.9029	0.8144	0.7875	4 (1)[a]
H-12	0.8653	0.7286	0.8545	14 (2)[a]
H_a-13	0.7123	0.6577	0.8021	12 (2)[a]
H_b-13	0.6211	0.6937	0.8485	10 (2)[a]
H-14	0.4929	0.8338	0.8202	2.9 (9)[a]
H_b-15	0.7455	1.1180	0.8432	4 (1)[a]
H_a-15	0.5812	1.0155	0.8608	10 (2)[a]
H_a-18	0.5106	1.0847	0.6855	5 (1)[a]
HO-19	0.2531	0.8709	0.7251	9 (2)[a]
H-19	0.4936	0.7881	0.7304	6 (1)[a]
H-20	0.598	0.7560	0.7696	1.6 (7)[a]
H_a-31	0.298	0.201	0.098	4.0[a]
H_b-31	0.192	0.172	0.087	4.0[a]
H_a-31	0.254	0.188	0.087	4.0[a]

[a]These atoms were refined isotropically. Isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gama)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

N [N—O_0 distance 2.770(6) Å] and to O_{19} [O_{19}—O_0 distance 2.898(6) Å] in another molecule related to the first by $-y,-x,1/2-z$ symmetry. There are no other intermolecular contact distances less than 3.5 Å.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURE.—Mp's were determined on a Thomas-Kofler hot stage equipped with a microscope and polarizer and are corrected. Ir spectra were taken on a Perkin-Elmer Model 1420 spectrophotometer. ^{1}H- and ^{13}C-nmr spectra were determined in $CDCl_3$ on Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) and Bruker AC-250 (250 MHz for ^{1}H and 62.5 MHz for ^{13}C) spectrometers. Ms was recorded on a Finnigan Quadrupole model 4023 spectrometer at an ionizing voltage of 70 eV. Optical rotations were measured on a Perkin-Elmer model 141 polarimeter. Chromatographic separations were carried out using vlc on alumina H basic, type E (EM Art. no. 1085).

PLANT MATERIAL.—The roots of *A. septentrionale* were collected on October 27 and November 4, 1990 in Sorkedalen, 10 miles north of Oslo, Norway. The plant was identified by A.J.A., and a voucher specimen (AJAA/901027/1) has been deposited in the Herbarium of the Department of Pharmacy, University of Oslo.

ISOLATION OF 2-ACETYLSEPTENTRIOSINE [**2**].—The dried and powdered roots of *A. septentrionale* (495 g) were extracted with hexane (3 liters) and then at room temperature with 80% EtOH. Evaporation of the EtOH in vacuo gave a residue (75.2 g) which was partitioned between $CHCl_3$ (1.5 liters) and 2% aqueous H_2SO_4 (2 liters). The $CDCl_3$ extract gave a neutral fraction (0.79 g). Basification of the acidic layer with NaOH (pH 12) and extraction with $CHCl_3$ (6 liters) gave a crude alkaloidal fraction (24.2 g) which was dissolved in Me_2CO (50 ml) and kept at ca. 5° for 2 h. The precipitate (13.95 g) was crystallized twice from $CHCl_3/Me_2CO$ to afford lappaconitine (7.59 g). The mother liquors after separation of lappaconitine were combined and chromatographed (vlc) on Al_2O_3. Two fractions were collected: fraction 1 (3.50 g; elution with 40%, 60%, and 70% Et_2O/hexane), and fraction 2 (2.02 g; 80% Et_2O/hexane). The mixture was recrystallized from Et_2O/hexane to afford **2** (200 mg) as colorless crystals: mp 182–184° (with swelling and darkening at 150–156°); found C 65.13, 65.08, H 7.59, 7.61; N 3.49 ($C_{22}H_{29}NO_5 \cdot H_2O$ requires C 65.18, H 7.65, N 3.46%); $[\alpha]^{15}D$ +6.4° (*c*=1, EtOH); ir (Nujol) ν 3560, 3470, 3440, 3320, 1730, 1705, 1650 cm^{-1}; ms *m/z* $[M]^+$ 387 (2.8%), $[M-OH]^+$ 370 (3), $[M-COCH_2]$345 (0.6), $[370-Ac]^+$ 327 (6), 309 (5), 105 (7), 91 (2), 56 (16), 43 (100); ^{1}H nmr δ 1.08 (3H, s, tert-CH_3- 18), 207 (3H, s, OAc), 2.76 (1H, brs, H-20), 3.60 (1H, brs, H-6), 4.18 (1H, s, H-19), 4.52 (1H, s, H-1), 4.59, 4.74 (each 1H, d, *J*=1.5 Hz, H-17), 5.00 (1H, t, *J*=1.5 Hz, H-2); ^{13}C nmr δ 67.9 (d, C-1), 73.2 (d, C-2), 39.2 (t, C-3), 42.1 (s, C-4), 50.7 (d, C-5) 60.5 (d, C-6), 30.9 (t, C-7), 42.1 (s, C-8), 79.6 (s, C-9), 53.7 (s, C-10), 33.8 (t, C-11), 36.1 (d, C-12), 32.9 (t, C-14), 43.7 (d, C-14), 30.7 (t, C-15), 150.4 (s, C-16), 104.7, (t, C-17), 21.5 (q, C-18), 91.7 (d, C-19), 67.9 (d, C-20), 169.9 (s, *C*OMe), 22.5 (q, $COCH_3$).

ALKALINE HYDROLYSIS OF 2-ACETYLSEPTENTRIOSINE.—To a solution of the alkaloid **2** (20 mg) in EtOH (5 ml) was added 5% ethanolic KOH (5 ml), and the mixture was kept at room temperature for 24 h. The EtOH was evaporated in vacuo; the residue was dissolved in $CHCl_3$ (8.5 ml) and EtOH (1.5 ml) and passed through a small column of neutral Al_2O_3 (1 g, Woelm). The filtrate on evaporation gave a residue (15 mg) which was crystallized from MeOH to give septentriosine [**1**] as colorless cubes (11 mg): mp 259–262°; ms *m/z* $[M]^+$ 345 (23%), 329 (10), $[M-OH]^+$ 328 (57), 310 (9), 218 (20), 131 (13), 117 (17), 105 (26), 91 (55), 79 (34), 77 (38), 56 (59), 53 (32), 42 (100). The hydrolyzed alkaloid was found to be identical in its tlc, mp, mixture mp, and ir spectral comparison with an authentic sample of septentriosine.

1,2,19-TRIACETYLSEPTENTRIOSINE [**3**].—The alkaloid **2** (20 mg) was added to a mixture of Ac_2O (1.5 ml) and C_5H_5N (1.5 ml) and kept at room temperature for 3 days. Usual workup furnished a residue which was crystallized from Me_2CO to give **3** as colorless crystals: mp 210.5–212.5°; ms *m/z* $[M]^+$ 471 ($C_{26}H_{33}NO_7$) (0.6%), $[M-OH]^+$ 454 (2), $[M-COCH_2]^+$ 429 (0.5), $[454-COCH_2]^+$ 412 (30), 370 (7), 43 (100); ^{1}H nmr δ 0.97 (3H, s, tert-CH_3- 18), 2.07, 2.10, 2.13 (each 3H, s, 3×OAc), 2.52 (1H, s), 3.08 (1H, s, H-20), 3.55 (1H, s, H-6), 4.58, 4.75 (each 1H, s, H-17), 5.04 (1H, q, *J*=4.7 Hz, H-2), 5.30 (1H, s, H-1), 5.55 (1H, s, H-19); ^{13}C nmr δ 69.5 (C-1), 70.9 (C-2), 39.2 (C-3), 42.4 (C-4), 52.0 (C-5), 62.7 (C-6), 30.7 (C-7), 42.4 (C-8), 79.2 (C-9), 53.3 (C-10), 33.4 (C-11), 35.9 (C-12), 32.6 (C-13), 43.8 (C-14), 30.7 (C-15), 150.1 (C-16), 104.8 (C-17), 21.6 (C-18), 92.3 (C-19), 68.9 (C-20), 170.2, 169.2, 169.0 (*C*OMe), 21.3, 21.1, 20.8 ($COCH_3$).

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