"Anhydrolycaconitine," a new diterpene alkaloid from *Aconitum septentrionale* K.

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A new alkaloid, anhydrolycaconitine ($C_{36}H_{46}N_2O_9$), was isolated from roots of *Aconitum septentrionale* K. Based on the results of ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry of the alkaloid and the product of its alkaline hydrolysis and on the data of X-ray diffraction analysis of the hydrolysis product, the structure of 1α,6β,14α,16β-tetramethoxy-7-oxo-18-succinylanthranoyloxy-17-(7→8)*abeo*-aconane was assigned to anhydrolycaconitine.

Key words: northern wolfsbane *Aconitum septentrionale* K., roots; diterpene alkaloids.

Over 30 alkaloids have been already isolated from different organs of northern wolfsbane *Aconitum septentrionale* K.[1–8]

In this work, we studied total alkaloids isolated by aqueous-acetone extraction from roots of *Aconitum septentrionale* K.

Total alkaloids were treated with acetone and then lappaconitine was separated. Compounds in the mother liquor were converted into sulfates and separated depending on the basicity by fractional alkalization followed by extraction with benzene to obtain five fractions, *viz.*, *A* (pH 3), *B* (pH 5.5), *C* (pH 7), *D* (pH 9), and *E* (pH 12).

The previously unknown crystalline alkaloid (**1**) of composition $C_{36}H_{46}N_2O_9$ was isolated from fraction *B*. According to the data of IR spectroscopy, molecule **1** contains an ester group (1720 cm^{-1}), which was confirmed by alkaline hydrolysis of the alkaloid giving rise to aminoalcohol **2**. The IR spectrum of compound **2** has intense absorption bands of the carbonyl group at 1712 cm^{-1}. A comparison of the molecular masses of the initial alkaloid (M^+ 650) and the resulting aminoalcohol (M^+ 449) and analysis of the spectral data for **1** and **2** (^1H and ^{13}C NMR, IR, and mass spectra) indicate that succinylanthranilic acid serves as the esterificating moiety in **1**. These data also suggest that aminoalcohol **2** contains four methoxy groups (signals at δ 3.21, 3.22, 3.31, and 3.49) and the *N*-ethyl group and indicate that this compound belongs to C_{19}-diterpene alkaloids.

The ^{13}C NMR spectrum of compound **2** measured in the JMODCH mode has 14 signals for the carbon atoms of the CH_3 and CH groups and 11 signals for the carbon atoms of the methylene groups and for the quaternary carbon atoms. Four signals at δ 79.3, 82.99, 83.25, and 83.62 belong to the methine C atoms bound to the OCH_3 group. The signals at δ 55.5, 56.6, 57.03, and 59.5 correspond to the C atoms of the methoxy groups. The signals for the C atoms of the methyl (δ 9.76) and methylene (δ 48.2) groups of the *N*-ethyl fragment and the signal of the carbonyl group (δ 201.7) are observed at higher field than those in the ^{13}C NMR spectra typical of C_{19}-diterpene alkaloids.

X-ray diffraction study demonstrated that aminoalcohol **2** has the anhydrolycoctonine structure, *i.e.*, its skeleton differs from those of usual C_{19}-diterpene alkaloids by the replacement of the C(7)—C(17) bridge by the C(8)—C(17) fragment. Previously,[9] a compound with the structure of **2** has been prepared from lycoctonine by pinacolic rearrangement and was described as an amorphous compound. Several more examples of the chemical synthesis of compounds with the anhydrolycoctonine-type skeleton are available in the literature.[9,10] Recently,[11] a new natural alkaloid acoseptine with the "anhydrolycoctonine" skeleton was isolated from *Aconitum septentrionale* and the anthranoylanhydrolycoctonine structure was suggested for this compound.

To exclude the possibility of formation of alkaloid **1** in the course of isolation of total alkaloids from plant material and their separation depending on the basicity, we reproduced the stage of treatment of total alkaloids with sulfuric acid in the presence of a benzene solution using methyllycaconitine and lycoctonine as model compounds. The time of treatment with sulfuric acid was increased by a factor of 20 compared to that used in the standard procedure for the isolation and separation of total alkaloids. No traces of **2** were detected by TLC. In the case of methyllycaconitine, no products other than

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the starting alkaloid were observed on the chromatogram. In this connection, it is unlikely that compound **1** can form as a result of pinacolic rearrangement.

The results of X-ray diffraction studies demonstrated that the molecular conformation changes substantially on going from the usual skeleton of C_{19}-diterpene alkaloids to the modified skeleton of "anhydro derivatives." The cycloheptanone fragment (the C(6), C(9), and C(10) atoms deviate from the plane through the remaining atoms of the ring by −0.31, −1.52, and −1.22 Å, respectively) and the cyclohexane fragment (the C(3) and C(4) atoms deviate from the plane through the remaining atoms of the ring by 0.96 and 1.27 Å, respectively) adopt a distorted boat conformation (Fig. 1). The cyclopentanone ring has an envelope conformation (the C(14) atom deviates from the plane through the remaining atoms of the ring by −0.78 Å). The remaining rings also adopt either a boat or an envelope conformation.

As a result, the conformation of the molecule becomes somewhat strained. The latter fact is confirmed by elongation of a number of $C(sp^3)$—$C(sp^3)$ bonds compared to the standard values[12] and by distortion of tetrahedral configurations of some atoms (Tables 1 and 2). Both these effects are observed primarily at the C(4), C(8), C(10), and C(11) atoms. The N(1) atom has a trigonal-pyramidal configuration (the sum of the bond angles is 338.9(6)°).

The methoxy groups at the C(1), C(6), and C(14) atoms are in axial positions (the C(11)—C(5)—C(6)—O(2), C(5)—C(11)—C(1)—O(3), and C(16)—C(13)—C(14)—O(4) torsion angles are 100.6(3)°, −115.3(2)°, and 49.0(3)°, respectively), whereas the methoxy group at the C(16) atom and the oxymethyl group at the C(4) atom are in equatorial positions (the C(12)—C(13)—C(16)—O(5) and C(11)—C(5)—C(4)—C(18) torsion angles are 153.9(2)° and 168.1(2)°, respectively). The methyl groups at the O(2), O(3), O(4), and O(5) atoms have the *−sp*, *+ac*, *−ap*, and *+ap* conformations, respectively (the C(22)—O(2)—C(6)—C(7), C(23)—O(3)—C(1)—C(2), C(24)—O(4)—C(14)—C(9), and C(25)—O(5)—C(16)—C(13) torsion angles are −121.1(3)°, 82.3(3)°, −173.9(3)°, and 177.2(3)°, respectively).

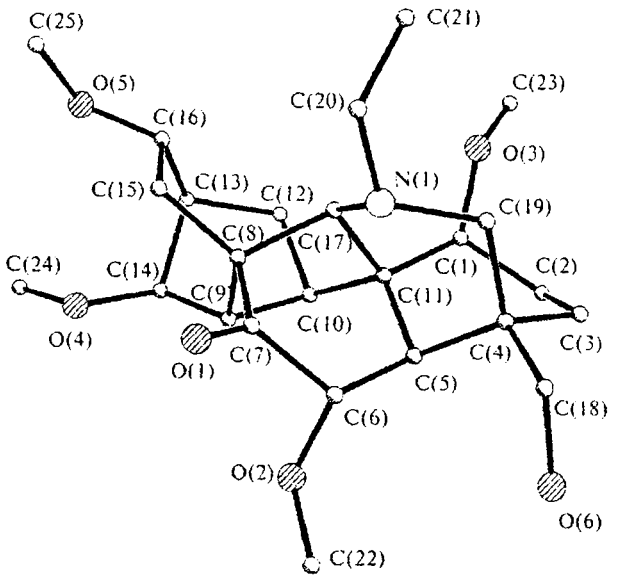


Fig. 1. Molecular structure of anhydrolycoctonine (**2**).

Table 1. Bond lengths (d) in molecule **2**

Bond	d/Å	Bond	d/Å
O(2)—C(6)	1.450(4)	C(8)—C(15)	1.525(3)
O(3)—C(1)	1.441(4)	C(8)—C(17)	1.575(4)
O(4)—C(14)	1.419(3)	C(9)—C(10)	1.530(4)
O(5)—C(16)	1.435(3)	C(9)—C(14)	1.523(4)
N(1)—C(17)	1.489(3)	C(10)—C(11)	1.532(4)
C(4)—C(3)	1.545(4)	C(10)—C(12)	1.591(4)
C(4)—C(19)	1.548(4)	C(11)—C(1)	1.566(4)
C(5)—C(4)	1.559(4)	C(11)—C(5)	1.566(3)
C(5)—C(6)	1.568(4)	C(11)—C(17)	1.532(4)
C(7)—C(6)	1.551(4)	C(12)—C(13)	1.563(4)
C(7)—C(8)	1.512(3)	C(13)—C(14)	1.534(4)
C(8)—C(9)	1.586(4)	C(16)—C(15)	1.556(4)

Table 2. Bond angles (ω) in molecule **2**

Angle	ω/deg	Angle	ω/deg
C(22)—O(2)—C(6)	112.8(2)	C(17)—C(8)—C(9)	108.4(2)
C(23)—O(3)—C(1)	112.7(2)	C(9)—C(10)—C(11)	106.6(2)
C(24)—O(4)—C(14)	111.4(2)	C(9)—C(10)—C(12)	101.3(2)
C(25)—O(5)—C(16)	114.5(2)	C(11)—C(10)—C(12)	112.6(2)
C(19)—N(1)—C(17)	114.0(2)	C(1)—C(11)—C(5)	112.8(2)
C(19)—N(1)—C(20)	111.3(2)	C(10)—C(11)—C(1)	107.0(2)
C(20)—N(1)—C(17)	113.6(2)	C(10)—C(11)—C(5)	116.3(2)
C(3)—C(4)—C(5)	109.4(2)	C(10)—C(11)—C(17)	100.8(2)
C(3)—C(4)—C(19)	110.0(2)	C(17)—C(11)—C(1)	116.8(2)
C(18)—C(4)—C(3)	107.2(2)	C(17)—C(11)—C(5)	102.9(2)
C(18)—C(4)—C(5)	115.0(2)	C(14)—C(13)—C(16)	109.4(2)
C(18)—C(4)—C(19)	106.2(2)	C(16)—C(13)—C(12)	117.2(2)
C(19)—C(4)—C(5)	108.9(2)	O(3)—C(1)—C(2)	112.1(2)
C(4)—C(5)—C(11)	105.3(2)	O(3)—C(1)—C(11)	109.9(2)
C(7)—C(6)—C(5)	117.5(2)	O(2)—C(6)—C(7)	106.0(2)
C(7)—C(8)—C(9)	104.4(2)	O(4)—C(14)—C(9)	113.4(2)
C(7)—C(8)—C(15)	118.9(2)	O(4)—C(14)—C(13)	117.3(2)
C(7)—C(8)—C(17)	100.5(2)	O(5)—C(16)—C(13)	104.6(2)
C(15)—C(8)—C(9)	110.2(2)	O(6)—C(18)—C(4)	110.9(2)
C(15)—C(8)—C(17)	113.3(2)		

Steric hindrance of molecule **2** results also from the presence of shortened intramolecular O...H contacts, which are undoubtedly attractive in character (O(2)...H(9A), 2.14 Å; O(3)...H(19A), 2.25 Å; O(4)...H(15A), 2.36 Å; the sum of the van der Waals radii[13] is 2.45 Å).

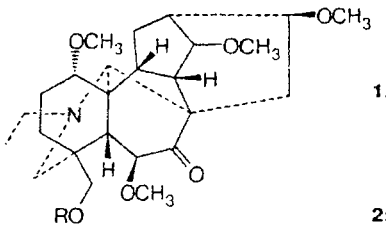
In the crystal, molecules **2** are linked in a three-dimensional framework through weak intermolecular O(6)—H...O(1′) hydrogen bonds ($-x$, $y - 0.5$, $-z - 0.5$) (H...O, 2.14 Å; O—H...O, 164.6°).

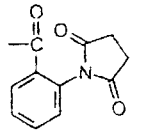
Initially, the assignment of the signals in the ^1H and ^{13}C NMR spectra was made for aminoalcohol **2**. For this purpose, the spectra were recorded in different modes. Thus, we recorded the fully proton-decoupled ^{13}C NMR spectrum, the spectrum with modulation of the C—H coupling constant, and the two-dimensional C—H-correlation spectrum. In addition, a comparative analysis of the spectral parameters of compounds **1** and **2**, methyllycaconitine (**3**),[14] and lycoctonine (**4**)[15] (Table 3) and the X-ray diffraction data were used for the assignment of the signals in the ^{13}C NMR spectrum.

In the ^{13}C NMR spectrum of alkaloid **1**, the signals for the C atoms of the major skeleton completely correspond to those observed in the case of aminoalcohol **2**. In the spectrum of alkaloid **1** recorded in the *J*-modulation mode, additional signals correspond to the succinylanthranoyl fragment.

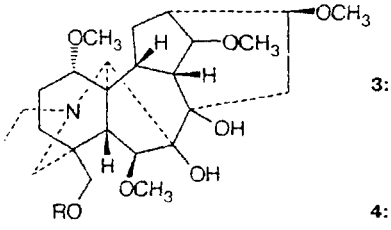
Table 3. Chemical shifts (δ) in the ^{13}C NMR spectra of anhydrolycaconitine (**1**), anhydrolycoctonine (**2**), methyllycaconitine (**3**), and lycoctonine (**4**)

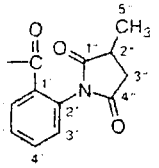
Atom	δ			
	1	**2**	**3**	**4**
C(1)	79.0	79.3	83.9	84.2
C(2)	25.9	26.0	26.0	26.1
C(3)	29.3	28.9	32.0	31.6
C(4)	38.9	40.3	37.6	38.6
C(5)	48.9	49.0	43.2	43.3
C(6)	83.7	83.6	90.8	90.6
C(7)	201.2	201.7	88.5	88.3
C(8)	58.9	59.1	77.4	77.5
C(9)	46.3	45.5	50.3	49.7
C(10)	39.5	39.5	38.0	38.0
C(11)	51.2	51.2	49.0	48.9
C(12)	31.3	31.4	28.7	28.8
C(13)	42.2	42.4	46.1	46.1
C(14)	82.8	83.0	83.9	84.0
C(15)	20.1	20.4	33.6	33.7
C(16)	83.7	83.3	82.5	82.7
C(17)	65.8	65.9	64.5	64.8
C(18)	70.5	69.5	69.5	67.6
C(19)	55.6	56.1	52.3	52.9
$\underline{CH_3}$—CH_2—N	9.8	9.8	14.0	14.1
CH_3—$\underline{CH_2}$—N	48.1	48.2	50.9	51.1
C(1)—OCH_3	56.9	57.0	55.7	55.7
C(6)—OCH_3	55.5	55.5	57.8	57.7
C(14)—OCH_3	59.5	59.5	58.1	58.0
C(16)—OCH_3	56.6	56.6	56.3	56.2
C=O	164.2		164.1	
C(1′)	126.6		127.1	
C(2′)	132.7		133.0	
C(3′)	128.6		129.4	
C(4′)	133.6		133.6	
C(5′)	131.4		131.0	
C(6′)	128.8		130.0	
C(1″)	176.8		179.8	
C(2″)	28.9		37.0	
C(3″)	28.9		35.3	
C(4″)	176.3		175.8	
C(5″)			16.4	



1: R = 

2: R = H



3: R = 

4: R = H

The assignment of the signals for the protons in the ^1H NMR spectrum of aminoalcohol **2** was made using the C—H-correlation spectrum (Fig. 2). The lowest-field singlet signal of H—C(6) (δ 3.83) does not have a coupling constant with the proton at C(5) (δ 2.1). Two doublet signals at δ 3.78 and 3.18 with the geminal constant $J_{gem} = -10.85$ Hz belong to the diastereotopic protons at C(18). An analogous situation is observed for the protons at the C(19) atom (doublets at δ 2.75 and 2.0, $J_{gem} = -11.85$ Hz). Signals for several protons at the C(1), C(9), C(14), C(16), and C(17) atoms are observed at δ 3.28—3.55. These signals overlap with singlet signals of the methoxy groups. However, the singlet signal for the proton at C(14) as well as the signal for the proton at C(17) (as a distorted triplet with approximately equal coupling constants with the protons at C(9) and C(13)) are well pronounced. In turn, the signal for the proton at C(13) is observed as a complex multiplet at δ 1.80—1.95. Since the conformational state of the molecule is hindered, all protons of the methylene groups of the cyclohexane fragments are diastereotopic and their signals form several groups of complex multiplets. The signals for the C(12)H_a, C(3)H_a, and C(15)H_a protons are observed at δ 1.2—1.5. Another multiplet at δ 1.8—2.1 consists of signals for the C(12)H_e, C(2)H_a, C(3)H_e, C(15)H_e, C(13)H, C(5)H, and C(19)H protons. The signals at δ 2.2—2.3 belong to the C(10)H and C(2)H_e groups.

Changes associated with the replacement of the substituent at the C(18) atom are manifested in the ^1H NMR spectrum of alkaloid **1**. Thus, two doublets of the diastereotopic protons are observed at lower field (δ 4.00 and 4.28) compared to those in the case of **2**, whereas the singlet signal for the proton at C(6) remains unchanged (δ 3.8). The signals for the protons at C(1), C(14), C(16), and C(17) form one overlapping multiplet. The singlets for the protons of the methoxy groups are insignificantly shifted. The signal for one of the diastereotopic protons at C(19) coincides with the signals for four methylene protons of the succinimide

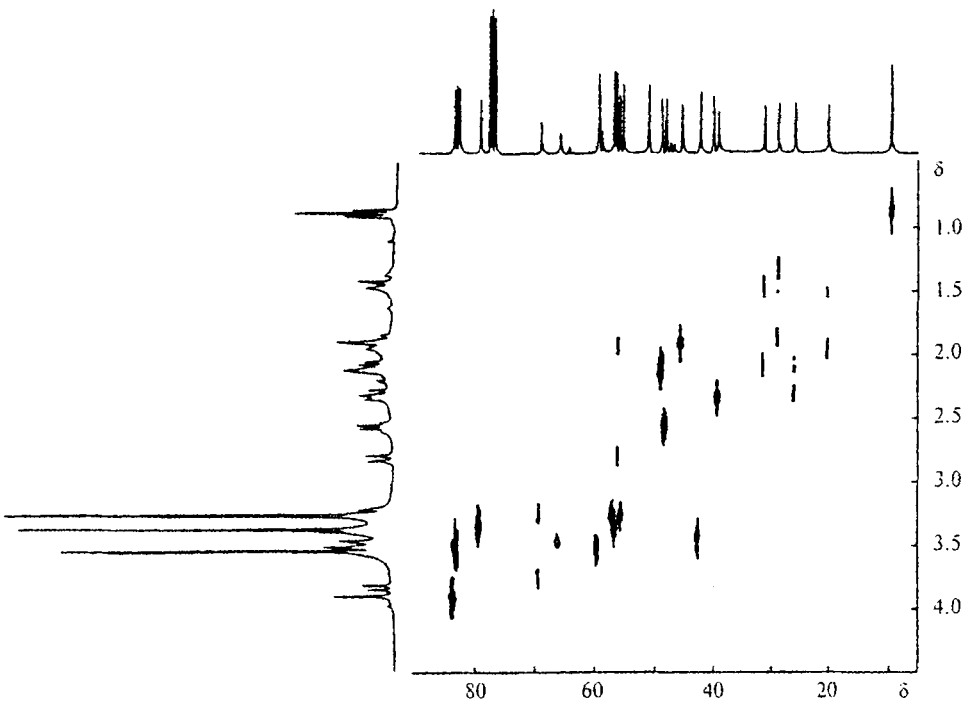


Fig. 2. Two-dimensional C—H-correlation spectrum of compound **2**.

fragment. Two doublets at δ 8.22 and 7.27 and two triplets at δ 7.69 and 7.57 correspond to signals for the protons of the *ortho*-substituted phenyl fragment. The quartet and triplet signals of the *N*-ethyl fragment retain their positions in the spectrum.

By analogy with compound **2**, the new alkaloid was called "anhydrolycaconitine."

Experimental

The IR spectra were recorded on UR-20 and Specord M-80 spectrometers. The mass spectra were measured on a Varian Mat-CH5 mass spectrometer; ionizing voltage was 70 eV. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AMX-III 300 instruments using $CDCl_3$ as the solvent and Me_4Si as the internal standard.

Extraction from *Aconitum septentrionale* K. Finely divided air-dried roots of northern wolfsbane *Aconitum septentrionale* K. (1 kg, Bashkortostan, August, 1998) were extracted (six times) with 70% aqueous acetone at room temperature. The combined extracts (12 L) were concentrated. The aqueous residue (3.5 L) was acidified to pH 3, washed with benzene (1 L), alkalized with solid sodium carbonate to pH 10, and extracted with benzene (4×1.2 L). The benzene extract was concentrated, Me_2CO was added to the total alkaloids, and lappaconitine that precipitated (5.86 g) was separated. The mother liquor was concentrated.

Anhydrolycaconitine (1). After separation of lappaconitine, total alkaloids were dissolved in 5% H_2SO_4 (100 mL) and extracted with benzene. The solution was concentrated and total alkaloids *A* (pH 3) was obtained in a yield of 2.03 g. Fractional alkalization of an acidic solution of alkaloids with a saturated solution of sodium carbonate followed by extraction with benzene afforded mixtures of alkaloids *B* (pH 5.5, 0.78 g), *C* (pH 7, 13.56 g), *D* (pH 9, 4.79 g), and *E* (with NaOH; pH 12, 0.65 g).

A mixture of alkaloids *B* was dissolved in Me_2CO, the crystalline precipitate that formed was filtered off, and alkaloid **1** was obtained in a yield of 267 mg, m.p. 215—216 °C (from acetone), $[\alpha]_{589}^{20}$ +21° (*c* 0.1, $CHCl_3$). MS, *m/z* (I_{rel} (%)): 650 $[M]^+$ (100), 635 (31), 619 (33), 591 (11), 589 (16), 202 (55), 174 (30). ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, C<u>H</u>$_3$—CH$_2$—N, *J* = 7.0 Hz); 1.40—1.60 (m, 2 H, C(12)H$_a$, C(15)H$_a$); 1.60—1.80 (m, 2 H, C(3)H$_a$, C(12)H$_e$); 1.95—2.20 (m, 5 H, C(15)H$_e$, C(2)H$_a$, C(3)H$_e$, C(2)H$_e$, C(13)H); 2.18 (s, 1 H, C(5)H); 2.28 (d, 1 H, C(19)H$_b$, *J* = 12.6 Hz); 2.31 (m, 1 H, C(10)H); 2.58 (q, 2 H, CH$_3$—C<u>H</u>$_2$—N, *J* = 7.0 Hz); 2.84—3.02 (m, 5 H, C(19)H, C(2″)H$_2$, C(3″)H$_2$); 3.27, 3.29, 3.38, and 3.42 (all s, 3 H each, 4 OMe); 3.45—3.63 (m, 4 H, C(1)H, C(14)H, C(16)H, C(17)H); 3.81 (s, 1 H, C(6)H); 4.00 and 4.28 (both d, 1 H each, C(18)H$_2$, *J* = 11.0 Hz); 7.27 and 8.22 (both d, 1 H each, C(3′)H, C(6′)H); 7.57 and 7.69 (both t, 1 H each, C(4′)H, C(5′)H).

Anhydrolycoctonine (2). A solution of alkaloid **1** (0.17 g) in 5% methanolic alkali (10 mL) was heated with stirring for 6 h. The methanolic solution was diluted with water and extracted with benzene. After evaporation of the solvent, aminoalcohol **2** was obtained in a yield of 0.11 g, m.p. 175—177 °C (from a benzene—hexane mixture), $[\alpha]_{589}^{20}$ +9° (*c* 0.24, $CHCl_3$). MS, *m/z* (I_{rel} (%)): 449 $[M]^+$ (100), 434 (29), 418 (32), 406 (13), 404 (22), 402 (11), 390 (15), 388 (24), 374 (10), 358 (11). ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, C<u>H</u>$_3$—CH$_2$—N, *J* = 7 Hz); 1.20—1.50 (m, 3 H, C(12)H$_a$, C(3)H$_a$, C(15)H$_a$); 1.80—1.95 (m, 3 H, C(12)H$_e$, C(3)H$_e$, C(13)H); 2.00 (d, 1 H, C(19)H$_b$, *J* = 11.85 Hz); 2.05—2.10 (m, 3 H, C(15)H$_e$, C(2)H$_a$, C(5)H); 2.20—2.30 (m, 2 H, C(2)H$_e$, C(10)H); 2.50 (q, 2 H, CH$_3$—C<u>H</u>$_2$—N, *J* = 7 Hz); 2.75 (d, 1 H, C(19)H$_a$, *J* = 11.85 Hz); 3.18 (d, 1 H, C(18)H$_b$, *J* = 10.85 Hz); 3.21, 3.22, 3.31, and 3.49 (all s, 3 H each, 4 OMe); 3.28 (m, 1 H, C(1)H); 3.35 (m, 1 H, C(9)H); 3.40 (s, 1 H, C(17)H); 3.43 (t, 1 H, C(14)H, *J* = 4.4 and 4.8 Hz); 3.50 (m, 1 H, C(16)H); 3.78 (d, 1 H, C(18)H$_a$, *J* = 10.85 Hz); 3.83 (s, 1 H, C(6)H).

Table 4. Crystallographic data for the structure of **2**

Parameter	Characteristic
Molecular formula	$C_{25}H_{39}NO_6$
Habit	Parallelepipeds
Color	Colorless
Molecular weight	449.57
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	4
Temperature/K	138(2)
a/Å	12.082(4)
b/Å	13.250(4)
c/Å	14.497(11)
V/Å^3	2321(2)
d_{calc}/g cm^{-3}	1.287
μ/mm^{-1}	0.091
$F(000)$	976
Number of measured reflections	3770
Diffractometer	Syntex $P2_1$/PC
$2\theta_{max}$/deg	30
Number of reflections used in the refinement	3696
Number of reflections with $F > 4\sigma(F)$	3203
R_1^{exp}	0.062
wR_2 (based on all data)	0.178
S (based on all data)	1.11

X-ray diffraction study of compound 2. Crystals of **2** suitable for X-ray diffraction study were grown by slow evaporation of its solution in ethanol. The crystallographic data for the structure of **2** are given in Table 4. The profile analysis of the X-ray diffraction data was carried out using the XDISK program.[16]

The structure was solved by direct methods using the SHELXTL PLUS 5 program package.[17] The positions of the hydrogen atoms were calculated geometrically. All hydrogen atoms were refined using the riding model with fixed values of $U_{iso} = nU_{eq}$ of the nonhydrogen atoms to which the hydrogen atoms are attached ($n = 1.5$ for the methyl group and 1.2 for the remaining hydrogen atoms). The atomic coordinates were deposited with the Cambridge Structural Database. The bond lengths and bond angles in molecule **2** are given in Tables 1 and 2, respectively.

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