ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 4, pp. 536–541. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © E.D. Khairitdinova, E.M. Tsyrlina, L.V. Spirikhin, A.A. Balandina, Sh.K. Latypov, M.S. Yunusov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 4, pp. 541–546.

Norditerpenoid Alkaloids from *Aconitum septentrionale K.*

E. D. Khairitdinova[a], E. M. Tsyrlina[a], L. V. Spirikhin[a], A. A. Balandina[b], Sh. K. Latypov[b], and M. S. Yunusov[a]

[a] *Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia*
e-mail: msyunusov@anrb.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*

Received September 5, 2006

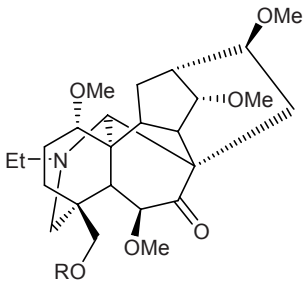
Abstract—Two new alkaloids, Septonine ($C_{35}H_{44}N_2O_9$) and Septontrionine ($C_{25}H_{39}NO_6$) were isolated from the roots of *Aconitum septentrionale K*. According to the ^{1}H and ^{13}C NMR, IR, and mass spectra, Septonin and Septontrionin were assigned the structures of 20-ethyl-7-hydroxy-1α,14α,16β-trimethoxy-6-oxo-17(7→8)abeo-aconitan-4-ylmethyl 2-(2,5-dioxopyrrolidin-1-yl)benzoate and 20-ethyl-7-hydroxy-1α,14α,16β-trimethoxy-4-methoxymethyl-17(7→8)abeoaconitan-6-one, respectively.

DOI: 10.1134/S107042800804012X

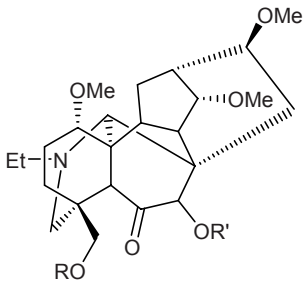
We previously reported on the isolation of a new alkaloid, anhydrolycaconitine (**I**) from weakly basic extract of the roots of *Aconitum septentrionale K.* [1]. While studying the alkaloid composition of roots of that plant, after separation of anhydrolycaconitine (**I**) from the fraction with pH 5.5, the mother liquor was subjected to column chromatography on silica gel and aluminum oxide to isolate two new alkaloids, Septonine (**II**) and Septontrionine (**III**). The molecular weight of **II** determined by high-resolution mass spectrometry was 636.305, which corresponds to the elemental composition $C_{35}H_{44}N_2O_9$. The base peak was that from the $[M - 29]^+$ ion. The IR spectrum of **II** indicated the presence in its molecule of OH (3200–3600 cm^{-1}) and C=O groups (1714 cm^{-1}). Analysis of the ^{1}H (δ 7.28–8.10 ppm, H_{arom}) and ^{13}C NMR spectra [δ_C 164.1, 176.6, 176.6 (C=O); 127.2–133.6 ppm (C_{arom})], as well as the presence in the mass spectrum of a fragment ion peak with *m*/*z* 202, led us to conclude that Septonine (**II**) contains a 2-(2,5-dioxopyrrolidin-1-yl)benzoic acid fragment. By alkaline hydrolysis of alkaloid **II** we obtained amino alcohol **IV** (Septonitine). The molecular weight of **IV** was estimated at 435.262 ($C_{24}H_{37}NO_6$) on the basis of its high-resolution mass spectrum. Compound **IV** displayed in the IR spectrum absorption bands at 3200–3600 (OH) and 1714 cm^{-1}, indicating that the carbonyl group is located in the six-membered ring. According to the ^{1}H NMR data, molecule **IV** contains three methoxy groups (δ, ppm: 3.32 s, 3.34 s, and 3.38 s) and *N*-ethyl group (δ 1.16 ppm, t, C**H**$_3$CH$_2$). The 14-H proton resonates in the ^{1}H NMR spectrum as a triplet at 3.42 ppm, indicating that one methoxy group is attached to C^{14} [2]. The presence of three methoxy groups and three CH protons neighboring to the methoxy groups is also confirmed by the ^{13}C NMR spectrum where three doublets at δ_C 83.6, 82.8, and 82.6 ppm and three quartets at δ_C 57.1, 57.3, and 57.4 ppm were observed. The chemical shifts of these carbon nuclei are well consistent with the localization of the other two methoxy groups on C^1 and C^{16}.

Comparison of the IR, ^{1}H and ^{13}C NMR, and mass spectra of alcohol **IV** and the second newly isolated alkaloid, Septontrionine (**III**), indicated their structural similarity. As follows from the IR spectrum of **III**, its molecule also contains a carbonyl group (1702 cm^{-1}) in the six-membered ring and a hydroxy group (3400 cm^{-1}). Alkaloid **III** displayed in the ^{13}C NMR spectrum 11 singlets and triplets and 14 doublets and quartets. In the ^{13}C NMR spectrum recorded using QUATD technique, three singlets at δ_C 37.1 (C^4), 49.7 (C^{11}), and 54.8 ppm (C^8) were observed in the region of quaternary carbon atoms not linked to oxygen; these data allowed us to presume anhydro structure [1].

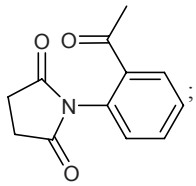
According to the high-resolution mass spectrum, the molecular weight of **III** is equal to 449.277, which



I, **VII**, **VIII**



II–VI

I, **II**, R =  ; **III**, **V**, **VI**, **VIII**, R = Me;

IV, **VII**, R = H; **II–IV**, R′ = H; **V**, R′ = MeCO; **VI**, R′ = Me.

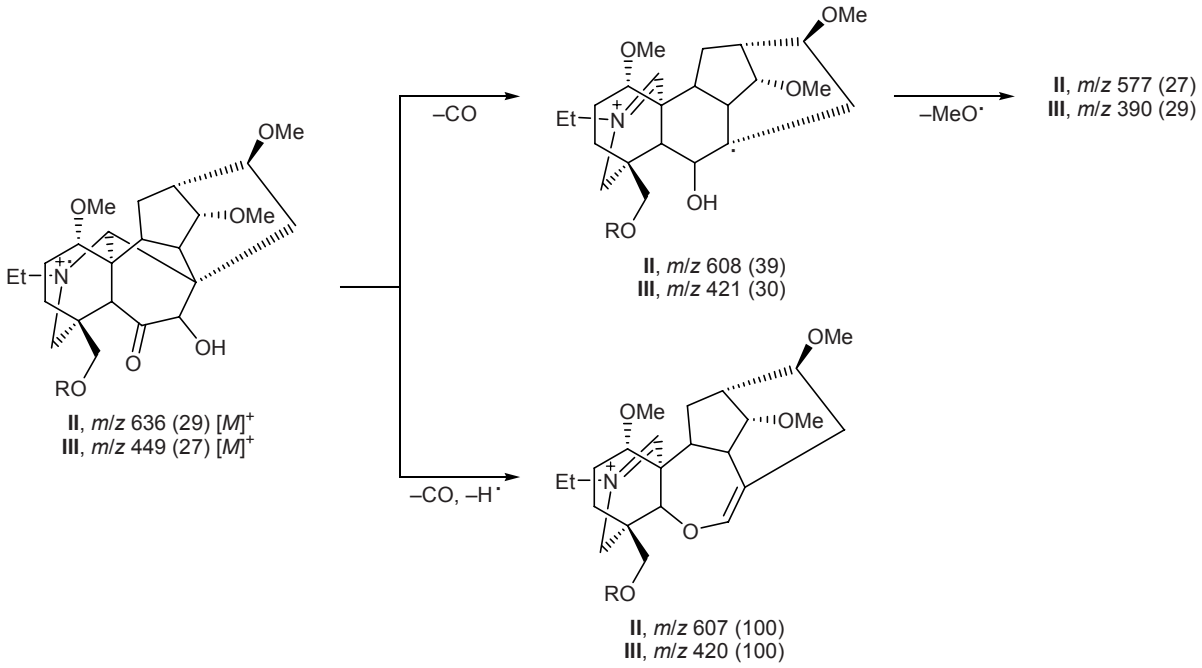
corresponds to the formula $C_{25}H_{39}NO_6$. Comparison of the high-resolution mass spectra of alkaloid **III** and compound **IV** indicated that their molecules differ by CH_2 group. The ^{1}H NMR spectrum of **III** contained signals from *N*-ethyl group (δ 1.14 ppm, t, C**H**$_3$CH$_2$) and four methoxy groups (singlets at δ 3.27, 3.29, 3.30, and 3.36 ppm), and the ^{13}C NMR data showed that additional methoxy group is attached to a methylene carbon atom. In the spectrum of **IV**, the C–OH signal appears at δ_C 69.5 ppm, whereas the corresponding signal of **III** is displaced downfield to δ_C 79.4 ppm; therefore, the additional methoxy group in **III** was assumed to be linked to that carbon atom.

The presence of downfield singlets at δ 4.24 and 4.26 ppm in the ^{1}H NMR spectra of **III** and **IV**, respectively, suggests that their molecules contain a CHOH moiety in the vicinity of a substituent exerting a deshielding effect. This is also confirmed by the ^{1}H NMR data for acetoxy derivative **V** (obtained by treatment of **III** with acetyl chloride) and methoxy derivative **VI**: the corresponding proton signal appears at δ 5.42 (CHOAc) and 3.78 ppm (CHOMe). The carbonyl carbon signal at δ_C 212.8 ppm in the ^{13}C NMR spectrum of **III** shifts upfield to δ_C 205.3 ppm for acetoxy derivative **V** and 210.6 ppm for methoxy derivative **VI**; therefore, we presumed that the hydroxy group is located in the α-position with respect to the carbonyl group. Comparison of the ^{1}H and ^{13}C NMR spectra of compounds **VI** and **VIII** (the latter was synthesized by methylation of alkaloid **VII**) revealed some differences despite structural similarity.

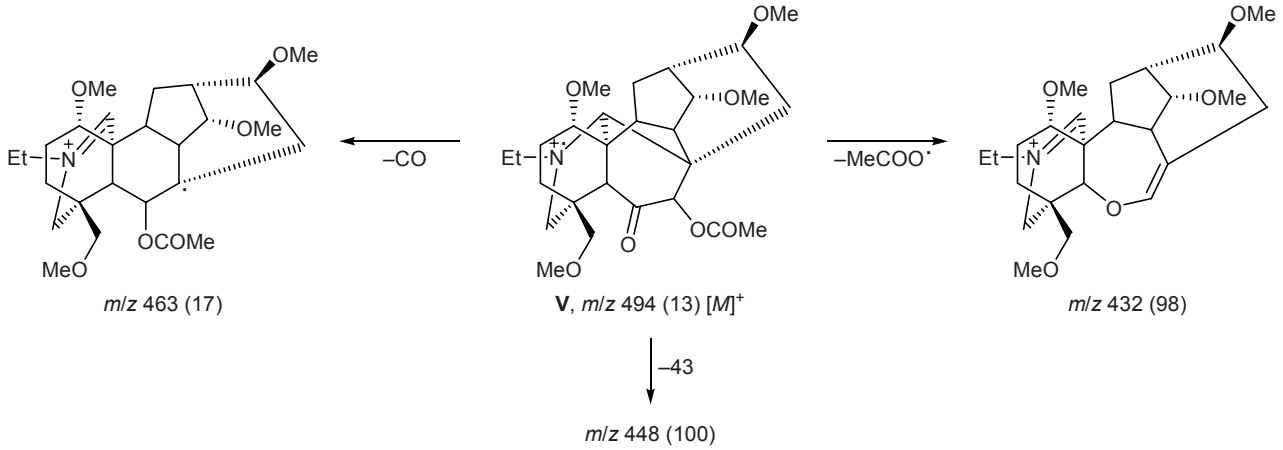
It should also be noted that the fragmentation pattern of alkaloids **II–IV** under electron impact does not conform to those usually observed for lycoctonine alkaloids [3] and anhydrolycaconitine (**I**). The base peak (I_{rel} 100%) in the mass spectrum of **I** is that of the molecular ion, while the intensities of the $[M - 31]^+$ and $[M - 15]^+$ ion peaks are 33 and 31%, respectively; the fragmentation patterns of alkaloids **II–IV** under electron impact were different (Schemes 1, 2).

Taking into account the above stated, Septonine (**II**), Septontrionine (**III**), and amino alcohol **IV** were

Scheme 1.



Scheme 2.



assigned anhydrolycoctonine-like structures with the hydroxy group attached to C^7 and the C^6=O carbonyl group. These structures are well consistent with possible fragmentation paths of alkaloids **II** and **III** and 7-*O*-acetylseptontrionine (**V**) shown in Schemes 1 and 2 (relative intensities, %, are given in parentheses).

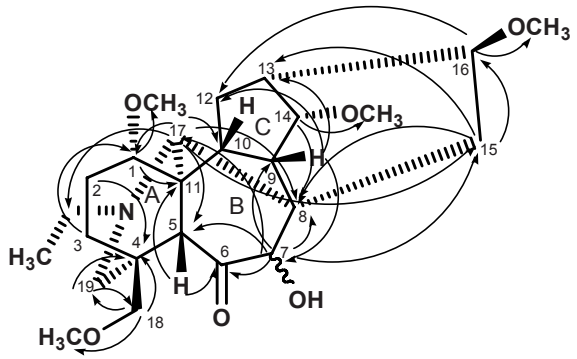


Fig. 1. Principal ^1H–^{13}C correlations in the HMBC spectrum of compound **III**.

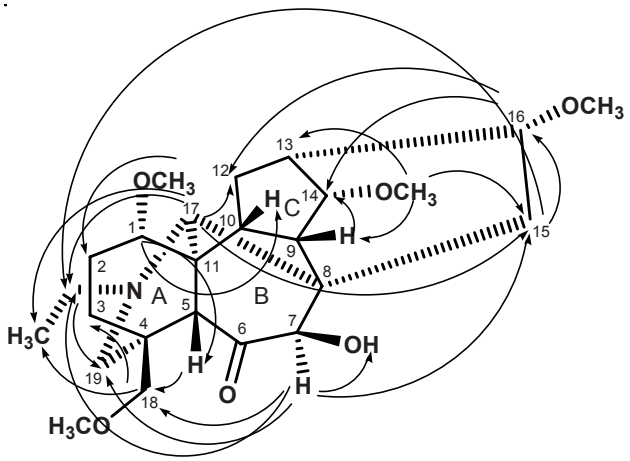


Fig. 2. Principal nuclear Overhauser effects in molecule **III**.

In order to finally prove the assumed structures and completely assign signals in the ^1H and ^{13}C NMR spectra of the isolated alkaloids, we performed a series of one- and two-dimensional NMR experiments for compound **III** (DEPT, 2D COSY, 2D HSQC, 2D HMBC) [4–7]. The 2D COSY spectrum* of **III** revealed several spin systems. Molecule **III** contains several methylene groups in which the protons are magnetically nonequivalent, and they resonate in the same region as CH protons. Therefore, it was difficult to unambiguously identify these protons by analysis of only 2D COSY spectrum. Using DEPT pulse sequence and 2D HSQC technique we succeeded in assigning signals from all directly coupled carbon and hydrogen nuclei.

As reference signal we used resonance of the carbonyl carbon atom, which is fairly characteristic: the carbonyl carbon signal is located in the downfield region of the ^{13}C NMR spectrum, at δ_C 212.7 ppm. Unlike compound **VII** which showed in the 2D HMBC spectrum (optimized for long-range ^1H–^{13}C couplings) cross peaks between the C=O carbon nucleus, on the one hand, and four CH protons and protons of one methylene group, on the other, the 2D HMBC spectrum of **III** contained cross peaks between the C=O carbon nucleus and protons of two CH groups. This provides one more evidence in favor of the assumed position of the carbonyl group (C^6=O); in this case, couplings with 5-H and 7-H are observed.

The 5-H and 7-H signals were assigned on the basis of the 2D COSY spectrum which displayed four cross peaks from one of these protons with a chemical shift of δ 2.41 ppm. However, this signal was overlapped by

* The spectra are available from the authors upon request by e-mail.

resonances of other protons. The second proton in the above couple resonated at δ 4.23 ppm, and it showed coupling with only one proton (δ 3.41 ppm) which was not coupled with any carbon nucleus (according to the 2D HSQC data). Therefore, the latter proton belongs to the hydroxy group, the signal at δ 4.23 ppm arises from 7-H, and 5-H resonates at δ 2.41 ppm. The corresponding carbon signals (C^5 and C^7) were assigned using 2D HSQC technique.

In the 2D HMBC spectrum of **III** we also observed cross peaks between 7-H, on the one hand, and three CH carbon atoms (C^5, C^9, and C^{17}; accurate assignment was not made), one methylene carbon atom ($C^{15}H_2$), and one quaternary carbon atom (C^8), on the other (Fig. 1). Then, referencing to the CH_2 resonance, some vicinal protons can be identified on the basis of the 2D COSY spectrum. It contained the following cross peaks: 15-H/16-H, 16-H/13-H, 13-H/14-H, 14-H/9-H, 9-H/10-H, and 10-H/12-H. In addition, the 2D COSY spectrum allowed us to distinguish a five-spin system consisting of one CH and two CH_2 groups (according to the DEPT and 2D HSQC spectra); we thus identified C^1H, C^2H_2, and C^3H_2 groups. Protons in the *N*-ethyl group can also be identified using the 2D COSY spectrum. The remaining CH_2 groups are $C^{18}H_2$ and $C^{19}H_2$. The signal at δ 3.60 ppm belongs to 17-H.

The other proton-containing carbon atoms were unambiguously identified from the 2D HSQC spectrum. The 2D HMBC spectrum contained cross peaks between the C^{11} quaternary carbon atom (δ_C 49.67 ppm) and the following protons: 1-H, C^2H_2, 5-H, $C^{12}H_2$, and 17-H; the C^4 quaternary carbon nucleus (δ_C 37.07 ppm) displayed couplings with C^2H_2, C^3H_2, 5-H, $C^{18}H_2$, and $C^{19}H_2$. The methoxy carbon atoms were identified by the presence of cross peaks with 1-H, 14-H, 16-H, and 18-H in the 2D HMBC spectrum, and signals of the corresponding methoxy protons were assigned using the 2D HSQC data. Furthermore, the 2D HMBC spectrum showed correlations between the C**H**$_2$CH$_3$ protons and C^{17} and C^{19} (Fig. 1). The latter cross peak allowed us to distinguish $C^{18}H_2$ and $C^{19}H_2$ resonances.

The relative configuration of the C^7 chiral center (α-OH or β-OH) was determined using 2D NOESY experiment. The principal nuclear Overhauser effects in molecule **III** are shown in Fig. 2. Coupling between the 7-H proton and one proton in each of the $C^{15}H_2$, $C^{19}H_2$, and C**H**$_2$CH$_3$ groups indicated their spatial proximity, i.e., the 7-H proton is oriented at the same side of the B ring as the above groups. Otherwise, NOEs between 7-H and 9-H and 10-H would be observed; in fact, no such couplings were detected. Thus, hydroxy group on C^7 was assigned β-orientation on the basis of the 2D HMBC and 2D NOESY data.

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 spectrometers from samples dispersed in mineral oil. The mass spectra (electron impact, 70 eV) were obtained on Varian MAT-CH5 and MKh-1310 instruments using peak superposition technique. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer; two-dimensional NMR experiments (DEPT, 2D COSY, 2D HSQC, 2D HMBC, and 2D NOESY) were performed on a Bruker Avance-600 spectrometer (600 MHz for ^1H and 150.926 MHz for ^{13}C).

A mixture of alkaloids {isolated from the mother liquor obtained after separation of anhydrolycaconitine (**I**) from the fraction with pH 6 [1]}, 0.51 g, was subjected to column chromatography on silica gel (40–100 μm) using petroleum ether–methyl *tert*-butyl ether–methanol (6:4:1) as eluent to isolate 0.106 g of a fraction enriched with Septontrionine (**III**) and 0.208 g of a fraction consisting of anhydrolycaconitine (**I**) and Septonine (**II**). Crystallization of the latter fraction from acetone gave compound **I** whose properties coincided with those reported in [1] and of an authentic sample.

Anhydrolycaconitine (I). IR spectrum, ν, cm^{-1}: 1720 (C=O), 3200–3600 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 1.4–1.6 m (2H, 12-H$_{ax}$, 15-H$_{ax}$); 1.6–1.8 m (2H, 3-H$_{ax}$, 12-H$_{eq}$); 1.95–2.20 m (5H, 15-H$_{eq}$, 2-H$_{ax}$, 3-H$_{eq}$, 2-H$_{eq}$, 13-H); 2.18 s (1H, 5-H); 2.28 d (1H, 19-H$_B$, J = 12.6 Hz); 2.31 m (1H, 10-H); 2.58 q (2H, CH$_3$C**H**$_2$N, J = 7.0 Hz); 2.84–3.02 m (5H, 19-H$_A$, 2″-H, 3″-H); 3.27 s, 3.29 s, 3.38 s, and 3.42 s (3H each, OCH$_3$); 3.45–3.63 m (4H, 1-H, 14-H, 16-H, 17-H); 3.81 s (1H, 6-H$_{ax}$); 4.00 d and 4.28 d (1H each, 18-H, J = 11.0 Hz); 7.27 d.d and 8.22 d.d (1H each, 3′-H, 6′-H, ^3J = 7.6, ^4J = 1.6 Hz); 7.57 t.d and 7.69 t.d (1H each, 4′-H, 5′-H, ^3J = 7.6, ^4J = 1.6 Hz). Mass spectrum, m/z (I_{rel}, %): 650 $[M]^+$ (100), 635 $[M - 15]^+$ (31), 619 $[M - 31]^+$ (33), 591 (11), 589 (16), 202 (55), 174 (30). Found: m/z 650.319 $[M]^+$. $C_{36}H_{46}N_2O_9$. Calculated: M 650.317.

Alkaloid mixture from the mother liquor, 0.150 g, was repeatedly subjected to chromatography on silica gel using chloroform–methanol (99:1) as eluent to isolate 0.0506 g of anhydrolycaconitine (**I**) and 0.0406 g

of a fraction containing compound **II**. The latter was purified by column chromatography on silica gel using methylene chloride–methanol (99:1) as eluent to isolate 0.0174 g of pure compound **II**.

Septonine (II). IR spectrum, ν, cm^{-1}: 1714 (C=O), 3200–3550 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 3.29 s, 3.33 s, and 3.38 s (3H each, OCH_3); 3.41 t (1H, 14β-H, J = 3.3 Hz); 4.27 s (1H, 7-H); 7.28 d.d and 8.10 d.d (1H each, 3′-H, 6′-H, ^3J = 7.8, ^4J = 1.5 Hz); 7.55 t.d and 7.69 t.d (1H each, 4′-H, 5′-H, ^3J = 7.6, ^4J = 1.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 82.7 (C^1), 24.7 (C^2), 34.3 (C^3), 36.0 (C^4), 58.5 (C^5), 212.4 (C^6), 80.8 (C^7), 54.7 (C^8), 45.3 (C^9), 46.3 (C^{10}), 49.6 (C^{11}), 31.4 (C^{12}), 39.4 (C^{13}), 82.6 (C^{14}), 28.0 (C^{15}), 83.5 (C^{16}), 63.0 (C^{17}), 70.3 (C^{18}), 53.8 (C^{19}), 14.2 (**C**H$_3$CH$_2$N), 50.1 (CH$_3$**C**H$_2$N), 57.2 (1-OCH_3), 57.3 (14-OCH_3), 56.8 (16-OCH_3), 164.1 (OC=O), 127.2 ($C^{1'}$), 132.6 ($C^{2'}$), 129.4 ($C^{3'}$), 133.6 ($C^{4'}$), 131.4 ($C^{5'}$), 129.8 ($C^{6'}$), 176.6 ($C^{1''}$), 28.8 ($C^{2''}$), 28.8 ($C^{3''}$), 176.6 ($C^{4''}$). Mass spectrum, m/z (I_{rel}, %): 636 (28.8) $[M]^+$, 608 $[M - 28]^+$ (39.4), 607 $[M - 29]^+$ (100), 577 (27.3), 202 (25.8). Found: m/z 636.305 $[M]^+$. $C_{35}H_{44}N_2O_9$. Calculated: M 636.304.

Repeated chromatography of the fraction containing Septontrionine (**III**), 0.106 g, on a column charged with Al_2O_3 (hexane–ethyl acetate–methanol, 60:40:1) gave 0.089 g of pure compound **III**.

Septontrionine (III). IR spectrum, ν, cm^{-1}: 1702 (C=O), 3400 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 1.48 t (1H, 3-H$_A$); 1.78 d (1H, 3-H$_B$); 1.85–2.04 m (5H, 2-H, 9-H, 10-H, 12-H$_A$); 2.12 m (2H, 15-H); 2.22 t (1H, 13-H); 2.41 m (3H, 5-H, 12-H$_B$, 19-H$_A$); 2.74 d (1H, 19-H$_B$); 2.84 d and 2.91 d (1H each, 18-H); 2.88 d.q and 3.13 d.q (1H each, CH$_3$C**H**$_2$N); 3.03 d.d (1H, 1-H); 3.27 s, 3.29 s, 3.30 s, and 3.36 s (3H, OCH_3); 3.36 t (1H, 14β-H, J = 3.0 Hz); 3.41 s (1H, OH); 3.60 s (1H, 17-H); 3.65 t (1H, 16-H, J = 3.0 Hz); 4.23 s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 83.0 (C^1), 24.8 (C^2), 34.4 (C^3), 37.1 (C^4), 58.5 (C^5), 212.7 (C^6), 80.7 (C^7), 54.8 (C^8), 45.2 (C^9), 46.4 (C^{10}), 49.7 (C^{11}), 31.5 (C^{12}), 39.3 (C^{13}), 82.8 (C^{14}), 28.0 (C^{15}), 83.6 (C^{16}), 63.2 (C^{17}), 79.4 (C^{18}), 54.4 (C^{19}), 14.2 (**C**H$_3$CH$_2$N), 50.1 (CH$_3$**C**H$_2$N), 57.1 (1-OCH_3), 57.2 (14-OCH_3), 56.6 (16-OCH_3), 59.1 (18-OCH_3). Mass spectrum, m/z (I_{rel}, %): 449 (27) $[M]^+$, 421 $[M - 28]^+$ (30), 420 $[M - 29]^+$ (100), 390 $[M - 59]^+$ (29), 376 (53). Found: m/z 449.277 $[M]^+$. $C_{25}H_{39}NO_6$. Calculated: M 449.277.

Septonitine (IV). A mixture of 0.0152 g of alkaloid **II** and 10 ml of 5% methanolic alkali was heated for 6 h under stirring. The solution was diluted with water and extracted with benzene, and the extract was evaporated to obtain 0.0096 g (92%) of compound **IV**. IR spectrum, ν, cm^{-1}: 1714 (C=O), 3200–3600 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 3.32 s, 3.34 s, and 3.38 s (3H each, OCH_3); 3.42 t (1H, 14β-H, J = 3.4 Hz); 4.26 s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 82.8 (C^1), 24.9 (C^2) , 34.5 (C^3), 38.4 (C^4), 57.4 (C^5), 214.5 (C^6), 80.8 (C^7), 54.1 (C^8), 45.9 (C^9), 46.6 (C^{10}) 49.4 (C^{11}), 31.4 (C^{12}), 39.4 (C^{13}), 82.6 (C^{14}), 28.1 (C^{15}), 83.6 (C^{16}), 63.3 (C^{17}), 69.5 (C^{18}), 54.5 (C^{19}), 14.2 (**C**H$_3$CH$_2$N), 50.2 (CH$_3$**C**H$_2$N), 57.1 (1-OCH_3), 57.3 (14-OCH_3), 56.7 (16-OCH_3). Mass spectrum, m/z (I_{rel}, %): 435 (59.6) $[M]^+$, 407 $[M - 28]^+$ (26.6), 406 $[M - 29]^+$ (100), 404 $[M - 31]^+$ (86.2), 376 $[M - 59]^+$ (60.6). Found: m/z 435.262 $[M]^+$. $C_{24}H_{37}NO_6$. Calculated: M 435.262.

7-*O*-Acetylseptontrionine (V). A mixture of 0.039 g of compound **III** and 1 ml of acetyl chloride was left to stand for 12 h at room temperature. The solution was treated with solid sodium carbonate to pH 10 and extracted with chloroform, and the extract was evaporated. Yield 0.039 g (91%). IR spectrum, ν, cm^{-1}: 1720 (C=O, ketone), 1750 (CO, ester). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.17 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 2.19 s (3H, CH_3CO); 3.21 s, 3.29 s, 3.38 s, and 3.38 s (3H each, OCH_3); 3.65 t (1H, 14β-H, J = 4.4, 4.8 Hz); 5.42 s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 83.0 (C^1), 24.8 (C^2) , 34.3 (C^3), 37.1 (C^4), 59.1 (C^5), 205.3 (C^6), 82.1 (C^7), 53.0 (C^8), 44.7 (C^9), 46.6 (C^{10}), 49.3 (C^{11}), 31.3 (C^{12}), 40.0 (C^{13}), 83.0 (C^{14}), 28.2 (C^{15}), 83.6 (C^{16}), 63.7 (C^{17}), 79.3 (C^{18}), 54.1 (C^{19}), 14.2 (**C**H$_3$CH$_2$N), 50.2 (CH$_3$**C**H$_2$N), 57.2 (1-OCH_3), 57.3 (14-OCH_3), 57.1 (16-OCH_3), 59.6 (18-OCH_3), 170.6 (OC=O), 20.8 (**C**H$_3$CO). Mass spectrum, m/z (I_{rel}, %): 491 $[M]^+$ (13), 463 $[M - 28]^+$ (17), 449 $[M - 42]^+$ (28), 448 $[M - 43]^+$ (100), 432 $[M - 59]^+$ (98). Found: m/z 491.283 $[M]^+$. $C_{27}H_{41}NO_7$. Calculated: M 491.288.

7-*O*-Methylseptontrionine (VI). A mixture of 0.016 g of compound **III**, 3 ml of dioxane, 0.020 g of 50% sodium hydride, and 1 ml of methyl iodide was heated for 2 h under stirring. When the reaction was complete (TLC), the mixture was evaporated, the residue was dissolved in 10 ml of chloroform, and the solution was extracted with 5% sulfuric acid (5×2 ml). The extracts were combined, adjusted to pH 10 by adding solid sodium carbonate, and extracted with chloroform, and the extract was evaporated. Yield 0.014 g (85%). IR spectrum: ν 1712 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (3H,

C**H**$_3$CH$_2$N, J = 7.0 Hz); 3.29 s, 3.30 s, 3.33 s, 3.38 s, and 3.60 s (3H each, OCH$_3$); 3.61 t (1H, 14β-H, J = 3.4 Hz); 3.78 s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 83.3 (C^1), 24.9 (C^2) , 34.4 (C^3), 36.9 (C^4), 59.2 (C^5), 210.6 (C^6), 90.8 (C^7), 54.6 (C^8), 45.2 (C^9), 46.8 (C^{10}), 49.3 (C^{11}), 28.5 (C^{12}), 39.8 (C^{13}), 83.1 (C^{14}), 28.5 (C^{15}), 84.1 (C^{16}), 63.6 (C^{17}), 80.0 (C^{18}), 54.6 (C^{19}), 14.4 (**C**H$_3$CH$_2$N), 50.5 (CH$_3$**C**H$_2$N), 57.2 (1-OCH$_3$), 57.3 (14-OCH$_3$), 56.9 (16-OCH$_3$), 60.6 (18-OCH$_3$), 60.9 (7-OCH$_3$). Mass spectrum, m/z (I_{rel}, %): 463 (27) $[M]^+$, 435 $[M - 28]^+$ (48), 434 $[M - 29]^+$ (100). Found: m/z 463.298 $[M]^+$. $C_{26}H_{41}NO_6$. Calculated: M 463.298.

Anhydrolycoctonine (VII). A mixture of 0.170 g of anhydrolycaconitine (**I**) and 10 ml of 5% methanolic alkali was heated for 6 h under stirring. The solution was diluted with water and extracted with benzene, and the extract was evaporated. Yield 0.108 g (92%), mp 175–177°C (from benzene–hexane). IR spectrum, ν, cm^{-1}: 1712 (C=O), 3200–3600 (OH). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 0.87 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz), 1.2–1.5 m (3H, 2-H$_{ax}$, 3-H$_{ax}$, 12-H$_{ax}$); 1.8–1.95 m (3H, 2-H$_{eq}$, 3-H$_{eq}$, 5-H); 1.91 d (1H, 19-H$_B$, J = 11.85 Hz); 2.05–2.1 m (3H, 10-H, 12-H$_{eq}$, 15-H$_{eq}$); 2.2–2.3 m (2H, 13-H, 15-H$_{ax}$); 2.55 q (2H, CH$_3$C**H**$_2$N, J = 7.0 Hz); 2.79 d (1H, 19-H$_A$, J = 11.85 Hz); 3.21 d (1H, 18-H$_B$, J = 10.85 Hz); 3.25 s, 3.26 s, 3.36 s, and 3.53 s (3H each, OCH$_3$); 3.34 m (1H, 1-H); 3.38 m (1H, 9-H); 3.45 s (1H, 17-H); 3.49 t (1H, 14β-H, J = 4.4, 4.8 Hz); 3.53 m (1H, 16-H); 3.81 d (1H, 18-H$_A$, J = 10.85 Hz); 3.88 s (1H, 6α-H). Mass spectrum, 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).

18-*O*-Methylanhydrolycoctonine (VIII) was synthesized according to the procedure described above for compound **VI** from 0.04 g of anhydrolycoctonine (**VII**). Yield 0.033 g (80%). IR spectrum: ν 1716 cm^{-1} (C=O). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 0.88 t (3H, C**H**$_3$CH$_2$N, J = 7.0 Hz); 3.26 s, 3.27 s, 3.35 s, 3.38 s, and 3.53 s (3H each, OCH$_3$); 3.43 t (1H, 14β-H, J = 4.4, 4.8 Hz); 3.79 s (1H, 6α-H). ^{13}C NMR spectrum, δ_C, ppm: 79.5 (C^1), 20.4 (C^2) , 29.4 (C^3), 39.5 (C^4), 45.6 (C^5), 84.1 (C^6), 202.3 (C^7), 58.9 (C^8), 42.3 (C^9), 49.1 (C^{10}), 51.2 (C^{11}), 31.5 (C^{12}), 39.7 (C^{13}), 83.4 (C^{14}), 26.1 (C^{15}), 83.1 (C^{16}), 65.9 (C^{17}), 79.5 (C^{18}), 56.2 (C^{19}), 9.8 (**C**H$_3$CH$_2$N), 48.3 (CH$_3$**C**H$_2$N), 55.5 (1-OCH$_3$), 57.0 (14-OCH$_3$), 56.7 (16-OCH$_3$), 58.9 (18-OCH$_3$), 59.7 (6-OCH$_3$). Mass spectrum, m/z (I_{rel}, %): 463 $[M]^+$ (100), 448 $[M - 15]^+$ (29), 432 $[M - 31]^+$ (32).

This study was performed under financial support by the President of the Russian Federation (program for state support of leading scientific schools, project no. NSh-139.2003.3) and by the Russian Foundation for Basic Research (project no. 05-03-32558a)

REFERENCES

1. Yunusov, M.S., Tsyrlina, E.M., Khairitdinova, E.D., Spirikhin, L.V., Kovalevskii, A.Yu., and Antipin, M.Yu., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2000, p. 1640.
2. Hanuman, J.B. and Katz, A., *J. Nat. Prod*., 1994, vol. 57, p. 1473.
3. Yunusov, M.S., Rashkes, Ya.V., Salimov, B.T., Ametova, E.F., and Fridlyanskii, G.V., *Khim. Prirodn. Soedin*., 1985, p. 525.
4. Derome, A.E., *Modern NMR Techniques for Chemistry Research*, Oxford: Pergamon, 1988, p. 280; Atta-ur-Rahman, *One and Two Dimensional NMR Spectroscopy*, Amsterdam: Elsevier, 1989, p. 579.
5. De Dios, A., *Prog. Nucl. Magn. Reson. Spectrosc*., 1996, vol. 29, p. 229; Barone, G., Gomez-Paloma, L., Duca, D., Silvestri, A., Riccio, R., and Bifulco, G., *Chem. Eur. J*., 2002, vol. 8, p. 3233; Alkorta, I. and Elguero, J., *Magn. Reson. Chem*., 2004, vol. 42, p. 955.
6. Balandina, A., Mamedov, V., Franck, X., Figadere, B., and Latypov, Sh., *Tetrahedron Lett*., 2004, vol. 45, p. 4003; Latypov, Sh., Fakhfakh, M.A., Jullian, J.-Ch., Franck, X., Hocquemiller, R., and Figadere, B., *Bull. Chem. Soc. Jpn*., 2005, vol. 78, p. 1296; Balandina, A.A., Kalinin, A.A., Mamedov, V.A., Figadere, B., and Latypov, Sh., *Magn. Reson. Chem*., 2005, vol. 43, p. 816.
7. Breitmaier, E. and Voelter, W., *Carbon-13 NMR Spectroscopy: High Resolution Methods and Applications in Organic Chemistry and Biochemistry*, Weinheim: VCH, 1987, p. 518.