Study of alkaloids of the Siberian and Altai flora
7.* Synthesis of 18-amino-18-deoxy derivatives of elatidine

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Reduction of elatidal oxime and imines based on methylamine, ethanolamine, tyramine, and *S*- and (±)-alaninols gave rise to the 18-amino-18-deoxy derivatives of elatidine.

Key words: diterpene alkaloids, elatidine, elatidal, aldimines, diamines.

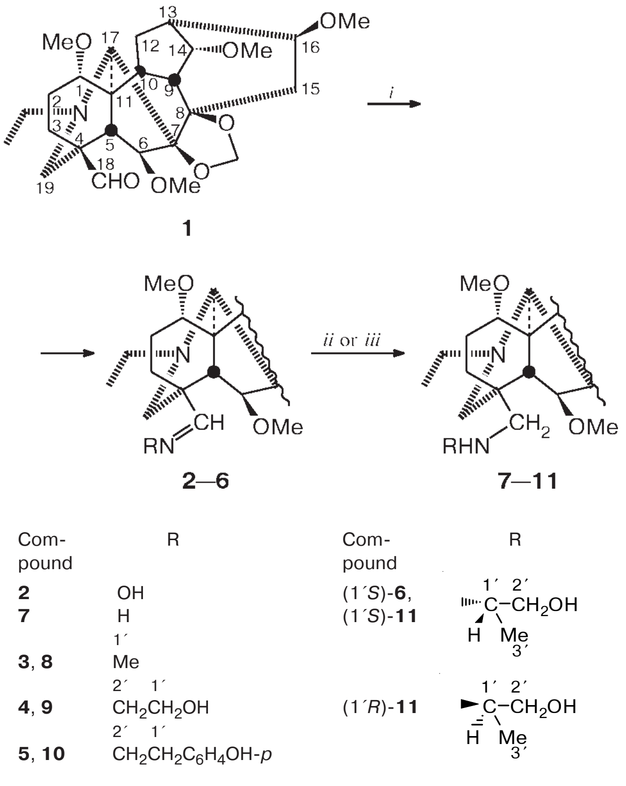
As a development of our research into the synthesis of derivatives of diterpene alkaloids promising as neurotropic and cardioactive agents, we turned to compounds containing nitrogenous functions in the side chain. Here we describe the synthesis of 18-amino-18-deoxy derivatives of elatidine on the basis of elatidal (**1**), the oxidation product of elatidine, prepared from the elatine alkaloid, which is, in turn, isolated from the bee larkspur plant (*Delphinium elatum* L.), widely distributed in the Altai.[2] As the initial compound, we used oxime **2** [2] and elatidal imines **3**—**6**. Aldimines **3**—**6** are formed in high yields upon condensation of elatidal with primary amines (Scheme 1).

According to ^{1}H NMR data, complete transformation of the initial elatidal (**1**) gives imines **3**—**6**, to which *E* configurations were ascribed. As we noted previously for similar cases,[2] the *E* configuration appears more likely due to lower steric hindrance to the formation of an imine bond.

Reduction of elatidal oxime **2** with $LiAlH_4$ and reduction of imines **3**—**6** with $NaBH_4$ gave the corresponding diamines **7**—**11** (Scheme 1).

The reduction of diastereomeric imines prepared by the reaction of elatidal with (±)-alaninol gives rise to an equimolar mixture of diamines (1´*R*)- and (1´*S*)-**11**. The ^{1}H NMR spectrum of this mixture is rather complicated as regards the assignment of signals of each component. In the ^{13}C NMR spectrum of the same mixture (Table 1), nine signals for the carbon atoms in each diastereomer differ in chemical shifts, the greatest difference being 0.25 ppm; the chemical shifts of other signals coincide.

Scheme 1



1

2—6

7—11

Compound	R	Compound	R
2	OH	(1´*S*)-**6**, (1´*S*)-**11**	$C(H)(Me)–CH_2OH$ (1´, 2´, 3´)
7	H		
3, **8**	Me (1´)	(1´*R*)-**11**	$C(H)(Me)–CH_2OH$ (1´, 2´, 3´)
4, **9**	CH_2CH_2OH (2´ 1´)		
5, **10**	$CH_2CH_2C_6H_4OH$-*p* (2´ 1´)		

Reagents, conditions, and product yields. *i*. RNH_2 (—H_2O): (a) $MeNH_2$, MeOH, H_2O, **3** (97%); (b) $H_2NCH_2CH_2OH$, MeOH, **4** (91%); (c) tyramine, MeOH, **5** (90%); (d) *S*-alaninol, $CHCl_3$, (1´*S*)-**6** (95%). *ii*. $LiAlH_4$, THF, **7** (78%). *iii*. $NaBH_4$, MeOH: (a) **8** (88%); (b) **9** (89%); (c) **10** (90%); (d) (1´*S*)-**11** (87%) or (1´*R*,*S*)-**11** (83%).

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Table 1. Chemical shifts of signals in the ^{13}C NMR spectra (10% solutions in $CDCl_3$, δ) of compounds **3—11***

Atom	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	(1´*R*)-**11**	(1´*S*)-**11**
C(1)	83.1	82.6	83.1	82.9	82.9	82.9	83.1	83.4	82.72	82.72
C(2)	25.9	25.5	26.0	25.8	26.0	26.0	26.3	26.5	25.95	25.95
C(3)	32.5	32.2	32.6	32.7	30.8	31.7	31.2	32.2	31.59	31.66
C(4)	42.1	41.8	42.2	41.9	36.9	36.5	36.6	37.1	36.33	36.33
C(5)	52.8	52.5	52.9	53.1	52.7	53.1	53.5	53.7	53.02	53.12
C(6)	89.1	88.9	89.4	89.6	89.0	88.9	89.4	89.5	89.14	89.03
C(7)	91.9	91.4	92.0	91.6	91.6	91.6	91.8	92.1	91.41	91.41
C(8)	83.2	82.8	83.4	83.2	82.8	82.7	83.1	83.3	82.66	82.66
C(9)	39.7	39.2	39.8	39.4	39.4	39.3	39.5	39.8	39.08	39.08
C(10)	48.1	47.5	48.0	47.8	48.0	47.9	48.2	48.4	47.81	47.81
C(11)	49.3	48.8	49.4	49.1	49.3	49.3	49.5	49.9	49.03	49.03
C(12)	27.8	27.2	27.8	27.5	27.3	27.3	27.6	27.9	27.14	27.14
C(13)	38.3	37.8	38.2	38.1	38.0	37.9	38.2	38.6	37.84	37.78
C(14)	81.5	81.0	81.6	81.2	81.1	81.0	81.3	81.6	80.89	80.89
C(15)	34.8	34.2	34.8	34.4	34.1	34.2	34.3	34.6	33.87	33.87
C(16)	81.3	80.7	81.4	80.9	81.1	81.0	81.3	81.6	80.89	80.89
C(17)	64.1	63.5	64.2	63.9	63.9	63.8	64.2	64.2	63.82	63.82
C(18)	169.6	169.8	169.6	168.38	48.7	59.1	54.7	55.0	54.36	54.36
C(19)	52.2	51.9	52.6	52.5	54.2	54.4	51.6	52.3	53.34	53.59
N—$\underline{\mathrm{C}}\mathrm{H_2Me}$	50.3	49.7	50.3	49.9	49.9	49.9	50.2	50.2	49.83	49.83
N—$\mathrm{CH_2\underline{C}H_3}$	13.7	13.2	13.7	13.5	13.4	13.4	13.7	13.6	13.34	13.34
OCH_2O	93.3	92.8	93.3	92.9	92.8	92.8	93.0	93.2	92.59	92.59
1-OMe	55.1	54.6	55.2	54.8	54.5	54.5	54.8	54.8	54.48	54.48
6-OMe	57.5	57.0	57.5	57.2	57.1	57.1	57.5	57.5	57.06	57.06
14-OMe	59.0	58.6	59.0	58.9	58.4	58.1	58.6	58.5	58.36	58.40
16-OMe	55.9	55.4	55.7	55.6	55.5	55.5	55.8	55.9	55.46	55.46
C(1´)	—	61.2**	63.2	63.4	—	—	60.3	57.0	54.58	54.65
C(2´)	47.6	62.7**	36.2	66.6	—	37.1	56.2	35.2	64.90	64.75
C(3´)	—	—	—	17.9	—	—	—	—	16.61	16.65
C(1″)	—	—	130.7	—	—	—	—	131.4	—	—
C(2″)	—	—	129.8	—	—	—	—	129.5	—	—
C(3″)	—	—	115.3	—	—	—	—	115.5	—	—
C(4″)	—	—	154.7	—	—	—	—	154.6	—	—
C(5″)	—	—	115.3	—	—	—	—	115.5	—	—
C(6″)	—	—	129.8	—	—	—	—	129.5	—	—

* The data correspond to the spectrum of an equimolar mixture of diastereomers (1´*R*)-**11** and (1´*S*)-**11**.

** The chemical shifts of the signals may have to be interchanged.

A distinctive feature of this spectrum is that the signals of C(19) shift downfield by 0.25 ppm and the signals of C(2´) shift upfield by 0.15 ppm in the 1´*S* isomer with respect to the corresponding signals of the 1´*R* isomer. The signals of diastereomers in the ^{13}C NMR spectrum of the mixture were assigned based on the increase in the intensity of some of them after the addition of pure diastereomer (1´*S*)-**11**. Thus, the reduction of elatidal oxime and imines based on primary amines provided the synthesis of elatidal 18-amino-18-deoxy derivatives. The differences in the chemical shifts and the relative intensities in the ^{13}C NMR spectra of the resulting diastereomeric diamines make it possible to determine the enantiomer ratios in mixtures of the initial chiral primary amines using a reaction sequence including imination of elatidal and reduction of the resulting imines.

Experimental

Freshly distilled solvents and pure grade reagents were used. Analytical and preparative TLC were carried out using glass plates with a sorbent layer containing Al_2O_3, K-35 luminophore, and Na_2CO_3 prepared as described above.[3] The spots were detected under UV radiation; in analytical TLC, they were visualized with iodine vapor.

IR spectra were recorded on a Vector 22 spectrometer, UV spectra were measured on a Specord UV-VIS spectrophotometer. The molecular weights and the elemental compositions of new compounds were determined using a high-resolution mass spectrometer (Finnigan MAT, version MS 8200, EI, 70 eV). Melting points were measured on a Koefler hot stage.

The optical rotation angles were measured on a Polamat A polarimeter (Carl Zeiss, λ = 578 nm). Specific rotation was expressed in (deg mL) (g dm)$^{-1}$, and the concentrations of solutions were expressed in g (100 mL)$^{-1}$. The ^{13}C NMR spectra of diamines (1´*R*)- and (1´*S*)-**11** were recorded at 25 °C on a Bruker AM-400 instrument (100.62 MHz). ^{1}H and ^{13}C NMR spectra of other compounds were recorded at 25 °C on a Bruker AC-200 spectrometer (200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C) with resonance stabilization relative to the deuterium signal of the solvent (CDCl$_3$). The chemical shifts (ppm) were referred to the solvent signal (δ_H 7.24 and δ_C 76.90). The signal multiplicities in the ^{13}C NMR spectra were determined by standard procedures[4a] in the J-modulation mode (JMOD) and with off-resonance proton irradiation. The ^{13}C NMR data for compounds are presented in Table 1. The ^{1}H and ^{13}C NMR signals were assigned using data for model compounds: elatidine,[3] tyramine,[5] and *p*-cresol.[4b] Since the assignment of all ^{1}H NMR signals is a complicated task, the data of characteristic signals are presented for compounds synthesized for the first time.

Commercial ethanolamine and tyramine (Aldrich) were used. Elatidal (m.p. 146.5—148 °C (Et$_2$O), $[\alpha]^{20}_{578}$ −17.2 (*c* 5, CHCl$_3$)) was prepared by a previously described procedure.[2] *S*-Alaninol was synthesized from *S*-alanine produced at the pilot plant of the Institute of Bioorganic Chemistry of the Ukrainian Republic. For *S*-alaninol prepared by a previously described procedure,[6] b.p. 84 °C (23 Torr), $[\alpha]^{20}_{578}$ +24.0 (*c* 3.0, EtOH) (Ref. 7: b.p. 84 °C (23 Torr), $[\alpha]^{25}_{D}$ +21.8 (*c* 2.94, EtOH)). Commercial (±)-alanine (Fluka) was used for the synthesis of (±)-alaninol.

Preparation of imines (3—6) (general procedure). A solution of elatidal **1** (0.239 g, 0.50 mmol) in 0.6 mL of MeOH was added to primary amine (0.50 mmol). The mixture was refluxed for 30 min and the solvent was removed *in vacuo*. Chloroform (1 mL) was added to the residue, and the traces of moisture were removed by distillation as an azeotrope. The residue was dried at 50 °C (3 Torr).

18(*E*)-Methylimino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (3) was prepared by the above-desctibed general procedure. A 29% aqueous solution of MeNH$_2$ was used. Colourless crystals, m.p. 143—144 °C, $[\alpha]^{20}_{578}$ −2.3 (*c* 6.9, MeOH). Found, *m/z*: 490.3073 [M]$^+$. $C_{27}H_{42}N_2O_6$. Calculated: M = 490.3043. ^{1}H NMR, δ: 0.99 (t, 3 H, NCH$_2$C$\underline{H}_3$, *J* = 7 Hz); 3.11, 3.19, 3.26 and 3.34 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 3.21 (d, 3 H, NMe, *J* = 1.4 Hz); 4.93 and 4.96 (both s, each 1 H, OCH$_2$O); 7.35 (q, 1 H, C(18)H, *J* = 1.4 Hz). IR (KBr), ν/cm^{-1}: 934, 956, 978, 989, 1009, 1036, 1088, 1115, 1146, 1450, 1669 (C=N), 2816, 2858, 2907, 2963.

18(*E*)-[(2-Hydroxyethyl)imino]-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (4). Thick oil, $[\alpha]^{20}_{578}$ +7.6 (*c* 2.1, MeOH). Found, *m/z*: 520.3144 [M]$^+$. $C_{28}H_{44}N_2O_7$. Calculated: M = 520.3148. ^{1}H NMR, δ: 0.83 (t, 3 H, NCH$_2$Me, *J* = 7 Hz); 2.98, 3.03, 3.10 and 3.17 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.77 and 4.80 (both s, each 1 H, OCH$_2$O); 7.27 (s, 1 H, C(18)H). IR (KBr), ν/cm^{-1}: 728, 753, 962, 1090, 1116, 1198, 1297, 1334, 1385, 1450, 1469, 1669 (C=N), 2752, 2822, 2883, 2931, 2973, and 3441 (OH).

18(*E*)-[2-(4-Hydroxyphenyl)ethyl]imino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (5). Amorphous powder, $[\alpha]^{20}_{578}$ +7.6 (*c* 2.1, MeOH). Found, *m/z*: 596.3461 [M]$^+$. $C_{34}H_{48}N_2O_7$. Calculated: M = 596.3461. ^{1}H NMR, δ: 1.00 (t, 3 H, NCH$_2$C$\underline{H}_3$, *J* = 7 Hz); 3.06, 3.22, 3.30, and 3.37 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.97 and 5.00 (both s, each 1 H, OCH$_2$O); 5.32 (broad, 1 H, OH); 6.71 (dm, 2 H, *J* = 8 Hz); 6.95 (dm, 2 H, *J* = 8 Hz) (AA´BB´ system, H(3″), H(5″), H(2″), H(6″), respectively); 7.28 (s, 1 H, C(18)H). IR (KBr), ν/cm^{-1}: 962, 991, 1014, 1042, 1090, 1133, 1169, 1199, 1216, 1264, 1378, 1447, 1516, 1614, 1664 (C=N), 2822, 2930, and 2970. UV (EtOH), λ_{max}/nm (logε): 225 (4.00), 279 (3.30).

18(*E*)-(2-Hydroxy-1*S*-methylethyl)imino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane ((1´*S*)-6). Thick oil, $[\alpha]^{20}_{578}$ — 0.3 (*c* 12.8, MeOH). Found, *m/z*: 534.3301 [M]$^+$. $C_{29}H_{46}N_2O_7$. Calculated: M = 534.3305. ^{1}H NMR, δ: 0.88—1.08 (m, 6 H, NCH$_2\underline{Me}$, C(3´)H$_3$); 3.11 (6 H), 3.19 (3 H), 3.27 (3 H) (all s, 1-, 6-, 14-, and 16-OMe); 4.89 (s, 2 H, OCH$_2$O); 7.38 (s, 1 H, C(18)H). IR, KBr), ν/cm^{-1}: 753, 962, 980, 1007, 1050, 1090, 1121, 1198, 1332, 1384, 1451, 1470, 1663 (C=N), 2821, 2883, 2931, 2966, 3456 (OH).

18-Amino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (7). A solution of elatidal oxime **2** (0.247 g, 0.50 mmol) in 1.3 mL of THF was added dropwise with stirring at 20 °C under argon to a suspension of LiAlH$_4$ (0.057 g, 1.50 mmol) in 1.3 mL of THF. The reaction mixture was stirred for 1 h, and a solution of water (0.12 g, 6.7 mmol) in 2.6 mL of THF was added. The precipitate was collected on a filter and washed with Et$_2$O (2×5 mL). The combined filtrate was dried with anhydrous K$_2$CO$_3$ and the solvent was evaporated. The residue was dried at 50 °C (3 Torr) to give diamine **7** as a thick oil, yield 0.187 g (78%). $[\alpha]^{20}_{578}$ +2.2 (*c* 13.4, CHCl$_3$). Found, *m/z*: 478.3045 [M]$^+$. $C_{26}H_{42}N_2O_6$. Calculated: M = 478.3043. ^{1}H NMR, δ: 0.88 (t, 3 H, NCH$_2\underline{Me}$, *J* = 7 Hz); 3.09, 3.17, 3.19, 3.26 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.88 (s, 2 H, OCH$_2$O). IR (KBr), ν/cm^{-1}: 728, 751, 963, 1010, 1087, 1126, 1156, 1200, 1334, 1385, 1454, 1474, 1531, 1610, 1651, 2812, 2929, 2983, 3384 (NH).

Reduction of imines 3—6 (general procedure). NaBH$_4$ (0.2 g, 5.6 mmol) was added in portions to a solution of imine (0.40 mmol) in 5.5 mL of MeOH. After 0.5 h, 7.4 mL of H$_2$O was added and the mixture was extracted with CHCl$_3$ (3×5 mL). The solvent was removed from the extract was dried at 50 °C (3 Torr).

18-Methylamino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (8). Thick oil, $[\alpha]^{20}_{578}$ +4.7 (*c* 18.3, MeOH). Found, *m/z*: 492.3203 [M]$^+$. $C_{27}H_{44}N_2O_6$. Calculated: M = 492.3199. ^{1}H NMR, δ: 0.86 (t, 3 H, NCH$_2$C$\underline{H}_3$, *J* = 7 Hz); 2.24 (s, 1 H, NMe); 3.07, 3.15, 3.18, 3.24 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.87 (s, 2 H, OCH$_2$O). IR (KBr), ν/cm^{-1}: 731, 752, 964, 1008, 1086, 1116, 1157, 1198, 1384, 1446, 1469, 2816, 2878, 2943, 2969, 3337 (NH).

18-[(2-Hydroxyethyl)amino]-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (9). Thick oil, $[\alpha]^{20}$ +5.7 (*c* 19.7, MeOH). Found, *m/z*: 522.3291 [M]$^+$. $C_{28}H_{46}N_2O_7$. Calculated: M = 522.3341. ^{1}H NMR, δ: 0.96 (t, 3 H, NCH$_2$C$\underline{H}_3$, *J* = 7 Hz); 3.17, 3.25, 3.28, 3.34 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.97, 4.98 (both s, each 1 H, OCH$_2$O). IR (KBr), ν/cm^{-1}: 731, 964, 1010, 1089, 1121, 1160, 1197, 1263, 1299, 1333, 1386, 1453, 2818, 2883, 2931, 3452 (OH, NH).

18-[2-(4-Hydroxyphenyl)ethylamino]-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane (10). Amorphous powder, $[\alpha]^{20}_{578}$ +4.7 (*c* 3.8, MeOH). Found, *m/z*: 598.3622 [M]$^+$. $C_{34}H_{50}N_2O_7$. Calculated: M = 598.3618. ^{1}H NMR, δ: 0.98 (t, 3 H, NCH$_2$C$\underline{H}_3$, *J* = 7 Hz); 3.20, 3.28, 3.30, 3.38 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 5.01 (s, 2 H, OCH$_2$O); 6.72 (dm, 2 H, *J* = 8 Hz); 6.98 (dm, 2 H, $J = 8$ Hz) (AA´BB´ system, H(3″), H(5″) and H(2″), H(6″), respectively). IR (KBr), ν/cm^{-1}: 753, 964, 1090, 1118, 1162, 1199, 1265, 1385, 1448, 1469, 1516, 1614, 2817, 2889, 2930, 3416 (NH). UV (EtOH), λ_{max}/nm (logε): 224 (4.10); 279 (3.86).

18-(2-Hydroxy-1*S*-methylethyl)amino-7,8-methylenedioxy-1α,6β,14α,16β-tetramethoxy-20-ethylaconitane ((1´*S*)-11). Thick oil, $[\alpha]^{20}_{578}$ +7.1 (*c* 8.2, $CHCl_3$). Found, *m/z*: 536.3467 $[M]^+$. $C_{29}H_{48}N_2O_7$. Calculated: M = 536.3461. ^{1}H NMR, δ: 0.85—0.89 (m, 6 H, $NCH_2\underline{Me}$, C(3´)H_3); 3.09, 3.19, 3.20, 3.25 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.87, 4.89 (both s, each 1 H, OCH_2O). IR (KBr), ν/cm^{-1}: 731, 869, 964, 1015, 1050, 1090, 1116, 1156, 1197, 1385, 1449, 1474, 2818, 2883, 2931, and 3449 (OH).

Mixture of diastereomeric diamines (1´*R*)-11 and (1´*S*)-11. Condensation of elatidal **1** with (±)-alaninol according to the general procedure for the preparation of imines **3**—**6** gave a mixture of imines as a thick oil. Treatment of this mixture according to the general procedure for reduction of imines **3**—**6** resulted in an equimolar mixture of diastereomeric diamines (1´*R*)- and (1´*S*)-**11** as a thick oil with $[\alpha]^{20}_{578}$ −3.2 (*c* 8.2, $CHCl_3$). The yield was 83% based on the initial elatidal. Found, *m/z*: 536.3467 $[M]^+$. $C_{29}H_{48}N_2O_7$. Calculated: M = 536.3461. ^{1}H NMR, δ: 0.82—0.86 (m, 12 H, the $NCH_2\underline{Me}$ and C(3´)H_3 groups of both diastereomers); 3.05 (6 H), 3.13 (6 H), 3.16 (3 H), 3.17 (3 H), 3.22 (6 H) (all s, 1-, 6-, 14-, and 16-OMe of both isomers); 4.84 and 4.86 (both s, each 2 H, OCH_2O groups of both isomers).

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