Chemistry of Natural Compounds, Bioorganic, and Biomolecular Chemistry

Study of alkaloids from the flora of the Siberian and Altai regions
5.* Synthesis of new elatidine derivatives

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Elatidam, elatidamic acid, and elatidal were obtained for the first time by oxidation of the diterpene alkaloid elatidine with $KMnO_4$ or CrO_3 and characterized. The reactions of elatidal with hydroxylamine, aniline, allylamine, and methyl glycinate afford the corresponding imines. Elatidal *N*-phenyl- and *N*-allylimines were reduced with $NaBH_4$ to give the corresponding diamines.

Key words: diterpene alkaloids, oxidation, elatidine, elatidam, elatidamic acid, elatidal, imines.

It is known that diterpene alkaloids from the plants of the *Delphinium* and *Aconitum* genera exhibit a variety of biological activity. Nevertheless, their pharmacological potential is still to be unveiled. Diterpene alkaloids can be chemically transformed to carry out an effective search for medicinally valuable compounds. The present work deals with the study of some transformations of elatidine **1** prepared from the available alkaloid elatine by hydrolysis.[2—5] The chemistry of elatidine, with the exception of the formation of its acetate[3] and lycoctonine, a product of the methylenedioxy group elimination,[4] is poorly investigated.

The goal of the present work is to examine the reactivity of elatidine in reactions with such oxidants as $KMnO_4$ and CrO_3 and obtain new nitrogen-containing derivatives based on its oxidation products.

We found that elatidine reacts with the above oxidants like lycoctonine[6] (Scheme 1). The major oxidation products of compound **1** were named with trivial names, as in the case of compounds obtained from lycoctonine. Thus, the oxidation of elatidine with $KMnO_4$ in acetone gave lactam **2** in 59% yield, which was named by us elatidam. Elatidam is further oxidized to form elatidamic acid **3** as a minor product.

The oxidation of elatidine with CrO_3 in acetic acid yields elatidal **4**. The latter reacts with hydroxylamine to give oxime **5**, while its reactions with aniline, allylamine, or methyl glycinate afford Schiff bases, namely, phenylimine **6**, allylimine **7**, or carbomethoxymethylimine **8**, respectively. Imines **6** and **7** are smoothly

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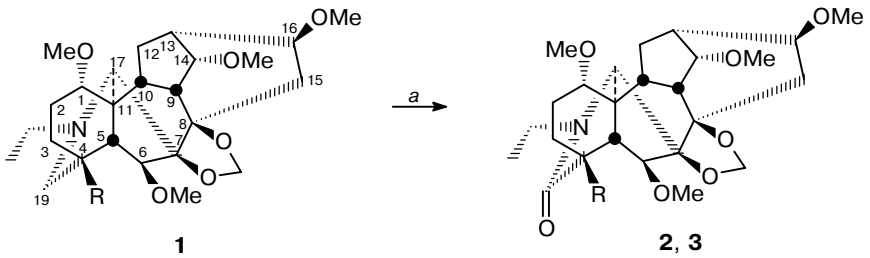
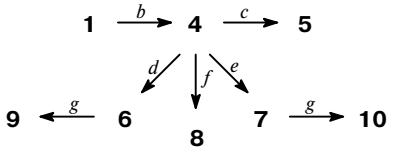
Scheme 1





Compound	R	Compound	R
1	CH_2OH	**6**	CH=N–Ph
2	CH_2OH	**7**	$CH=N–CH_2CH=CH_2$
3	COOH	**8**	$CH=N–CH_2CO_2Me$
4	CHO	**9**	CH_2NHPh
5	CH=N–OH	**10**	$CH_2NHCH_2CH=CH_2$

Reagents and conditions: *a*) $KMnO_4$, Me_2CO, the yield of **2** was 59%; *b*) CrO_3, AcOH, the yield of **4** was 39%; *c*) hydroxylamine, the yield of **5** was 76%; *d*) aniline, the yield of **6** was 87—90%; *e*) allylamine, the yield of **7** was 87—90%; *f*) methyl glycinate, the yield of **8** was 89—90%; *g*) $NaBH_4$, the yields of **9** and **10** were 87—90%.
Note. Compounds **4**—**10** are derivatives of structure **1**.

reduced with $NaBH_4$ to give the corresponding diamines **9** and **10**. ^1H NMR data indicate that elatidal **4** is fully converted to oxime **5** or to imines **6**—**8**. Note that products **5**—**8** form a single geometrical isomer with the undetermined arrangement of a substituent at the N atom of the C=N group. The *anti*-arrangement of the substituent relative to the C(4)—C(18) bond appears to be more probable than the *syn*-arrangement, because the formation of the imide bond is sterically hindered in the latter case.

Experimental

Freshly distilled solvents and high-purity reagents were used in the work. Analytical TLC was carried out on glass plates. The sorbent was neutral Al_2O_3 (0.04 g cm^{-2}, 5/40 μm, Chemapol) containing 1 wt % of the K-35 luminophore and 2% Na_2CO_3. The plates were prepared as described in Ref. 7. A Pr^iOH—Et_2O mixture (1 : 24, by volume) was used as an eluent. Spots were detected in UV light and visualized by iodine vapors.

IR spectra were recorded on a Vector 22 spectrometer. UV spectra were recorded on a Specord UV-VIS spectrophotometer. Molecular mass determination and elemental analysis of the new compounds was performed using a Finnigan MAT high-resolution mass spectrometer (MS 8200, EI, 70 eV). Melting points were determined on a Kofler hot stage.

Angles of optical rotation were measured on a Carl Zeiss Polamat polarimeter. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AC-200 instrument (200.13 and 50.32 MHz, respectively) with resonance stabilization of a signal for the deuterium atom of the solvent ($CDCl_3$). The ^1H and ^{13}C chemical shifts (ppm) are referred to $CHCl_3$ as the internal standard (δ 7.24 and 76.90, respectively). The multiplicity of ^{13}C signals was determined according to the standard procedures[8] in the *J*-modulation regime (JMOD) and the off-resonance proton irradiation. The ^{13}C NMR spectroscopic data for compounds **2**—**10** are presented in Table 1. The relevant data[1] for elatidine were used to assign signals in the ^1H and ^{13}C NMR spectra. Since all signals for the newly obtained compounds are difficult to assign, only characteristic signals in the ^1H NMR spectra are given. Elatidine (m.p. 172—174 °C (Me_2CO))[3] was prepared from elatine by alkaline hydrolysis according to the known procedure.[4]

Elatidam (20-ethyl-4-hydroxymethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitan-19-one) (2) and elatidamic acid (20-ethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxy-19-oxoaconitane-4-carboxylic acid) (3). Powdered $KMnO_4$ (1.94 g, 12.3 mmol) was added in portions (~0.1 g) with stirring to a solution of elatidine **1** (1.66 g, 3.46 mmol) in 17 mL of acetone for 10 min. After the exothermic reaction was completed, acetone (12 mL) was added, and the reaction mixture was refluxed for 1 h. On cooling, the precipitate was filtered off, and the filtrate was removed *in vacuo*. The residue was dried at 3 Torr and powdered, and the products were exhaustively extracted with boiling ether (30 mL) in a Soxhlet apparatus. The extract was cooled to give crystalline compound **2** (1.00 g, 59%), m.p. 183—185 °C, $[\alpha]^{20}_{578}$ +4.5 (*c* 4.4, $CHCl_3$). Found, *m/z*: 493.2669 $[M]^+$; for $C_{26}H_{39}NO_8$ calcd.: M = 493.2676. ^1H NMR, δ: 1.07 (t, 3 H, $NCH_2\underline{Me}$, J = 7 Hz); 3.19, 3.28, 3.29, and 3.36 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 5.00 and 5.02 (both s, each 1 H, OCH_2O). IR (KBr), ν/cm^{-1}: 935, 949, 1001, 1043, 1059, 1083, 1101, 1120, 1144, 1195, 1215, 1371, 1389, 1437, 1466, 1625 (C=O, amide), 2824, 2875, 2935, 2954, 2975, 3440 (OH). Organic material was extracted from the dry precipitate of manganese compounds with boiling water (3×10 mL). On cooling, the alkaline extract (pH ~8) was acidified with conc. HCl (0.4 mL) to pH ~4. The products were extracted from the resulting solution with $CHCl_3$ (3×10 mL), and the extract was dried over $MgSO_4$, filtered off, and concentrated. The residue was dried at 3 Torr and dissolved in 0.8 mL of MeOH, and water (2.4 mL) was added. The precipitate that formed was filtered off to give crystalline acid **3** (0.057 g, 3%), m.p. 220—225 °C (decomp. with gas evolution), $[\alpha]^{20}_{578}$ +78.5 (*c* 2.7, $CHCl_3$). Found, *m/z*: 507.2481 $[M]^+$; for $C_{26}H_{37}NO_9$ calcd.: M = 507.2468. ^1H NMR,

Table 1. Chemical shifts and assignment of the signals in the ^{13}C NMR spectra of compounds **2**—**10**

Atom	$CDCl_3$, δ								
	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C(1)	82.7	82.6	83.0	83.1	82.7	83.3	83.1	83.0	83.2
C(2)	25.9	25.6	25.1	26.1	25.5	26.0	25.8	26.1	26.4
C(3)	29.1	33.2	29.0	33.3	32.1	32.7	32.3	32.0	32.1
C(4)	47.7	55.7	49.0*	40.0	42.4	42.4	42.7	37.0	36.8
C(5)	53.2	51.2	50.3	53.2	52.5	53.3	52.9	53.4	53.5
C(6)	90.1	92.9	89.4	89.3	89.1	89.5	89.3	89.2	89.3
C(7)	89.9	90.2	91.8	91.7	91.4	92.0	91.8	91.7	91.9
C(8)	81.9	82.4	83.2	83.3	82.9	83.4	83.3	82.9	83.0
C(9)	39.3	39.3	39.7	39.7	39.3	39.9	39.7	39.5	39.6
C(10)	48.0	47.6	48.0	48.0	47.6	48.2	48.0	48.1	48.3
C(11)	48.4	48.2	49.1*	49.5	48.8	49.5	49.2	49.5	49.6
C(12)	27.6	27.6	27.7	27.7	27.4	27.9	27.7	27.4	27.6
C(13)	37.6	37.7	38.1	38.3	37.7	38.5	38.2	38.2	38.3
C(14)	80.7	81.1	81.4	81.5	81.1	81.6	81.4	81.2	81.4
C(15)	33.7	34.2	34.6	34.7	34.3	34.8	34.6	34.3	34.4
C(16)	79.1	78.3	80.7	81.2	80.7	81.4	81.1	81.0	81.4
C(17)	62.5	63.4	63.9	64.0	63.6	64.2	64.0	63.9	64.1
C(18)	66.4	172.1*	203.1	155.3	168.5	169.4	173.3	54.3	54.7
C(19)	173.6	172.2*	50.1	52.1	51.8	52.5	52.1	50.8	53.1
N—$\underline{C}H_2Me$	42.1	43.5	49.6	50.3	49.8	50.3	50.1	50.1	50.2
N—$CH_2\underline{Me}$	12.0	11.7	13.5	13.6	13.3	13.8	13.6	13.5	13.7
OCH_2O	93.5	93.9	93.3	93.4	92.9	93.4	93.2	93.0	93.1
1-OMe	54.5	54.9	55.1	55.2	54.6	55.1	55.0	54.7	54.8
6-OMe	57.6	57.6	57.4	57.6	57.0	57.6	57.4	57.3	57.5
14-OMe	58.8	60.0	59.2	59.3	59.0	59.3	59.0	58.6	58.5
16-OMe	56.0	56.0	55.8	55.9	55.4	56.0	55.8	55.7	55.8
C(1′)	—	—	—	—	151.4	63.6	—	148.3	56.2
C(2′)	—	—	—	—	119.7	135.6	—	112.5	136.8
C(3′)	—	—	—	—	128.5	115.9	—	128.8	115.6
C(4′)	—	—	—	—	114.3	—	—	117.1	—
C(5′)	—	—	—	—	128.5	—	—	128.8	—
C(6′)	—	—	—	—	119.7	—	—	112.5	—
$CO_2\underline{Me}$	—	—	—	—	—	—	51.6	—	—
$\underline{C}H_2CO_2$	—	—	—	—	—	—	61.6	—	—
$\underline{C}O_2Me$	—	—	—	—	—	—	169.8	—	—

* These chemical shifts are possibly confused.

δ: 1.17 (t, 3 H, $NCH_2\underline{Me}$, J = 7 Hz); 3.24, 3.32, 3.33, and 3.40 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 5.05 and 5.06 (both s, each 1 H, OCH_2O) and 13.5 (br.s, 1 H, OH). IR (KBr), ν/cm^{-1}: 945, 975, 1041, 1088, 1137, 1198, 1355, 1390, 1437, 1467, 1615 (C=O, amide), 1735 (C=O, carboxyl), 2823, 2886, 2941, 2979, 3441 (OH).

Elatidal (20-ethyl-4-formyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitane) (4). Chromium trioxide (1.26 g, 12.6 mmol) was added to a stirred solution of elatidine **1** (3.56 g, 7.42 mmol) in 10 mL of glacial AcOH. The reaction mixture was heated under reflux to 70 °C and stirred for 3 h. On cooling, 10% Na_2CO_3 was gently added to a basic reaction of the aqueous phase of the mixture. The products were extracted with ether (4×20 mL). The extract was filtered off, concentrated to 5 mL, and chromatographed in diethyl ether on Al_2O_3 (100 g, 50—250 μm, activity grade II, Russia) in a column 2.4 cm in diameter. Fractions (each 10 mL in volume) were collected and analyzed by TLC with Pr^iOH—Et_2O (1 : 24, by volume) as an eluent. The fractions containing a compound with R_f 0.74 (TLC data) were combined and concentrated to give elatidal **4** (1.33 g). The fractions with R_f 0.37 were treated in a similar way to recover the starting compound **1** (0.14 g, 0.29 mmol). The yield of elatidal **4** was 39% (converted to the consumed elatidine **1**). Elatidal **4**, m.p. 146.5—148 °C (Et_2O), $[\alpha]^{20}_{578}$ −17.2 (*c* 5, $CHCl_3$). Found, *m/z*: 477.2713 $[M]^+$; for $C_{26}H_{39}NO_7$ calcd.: M = 477.2726. ^1H NMR, δ: 0.97 (t, 3 H, $NCH_2\underline{Me}$, J = 7 Hz); 3.12, 3.17, 3.24, and 3.32 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.91 and 4.94 (both s, each 1 H, OCH_2O); 9.34 (s, 1 H, CHO). IR (KBr), ν/cm^{-1}: 961, 1090, 1121, 1383, 1453, 1470, 1721 (C=O), 2713, 2751, 2819, 2871, 2931, 2968.

Elatidal oxime (20-ethyl-4-hydroxyiminomethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitane) (5). Water (0.2 mL) was added to a mixture of hydroxylammonium chloride (0.038 g, 0.55 mmol) and anhydrous K_2CO_3 (0.038 g, 0.28 mmol). After CO_2 ceased to evolve, a solution of elatidal **4** (0.058 g, 0.121 mmol) in 0.6 mL of MeOH was added. The reaction mixture was refluxed for 15 min. The solvent was removed *in vacuo*, and the products were extracted from the residue with $CHCl_3$. The extract was concentrated to give oxime **5** (0.045 g, 76%) as a viscous oil, $[\alpha]^{20}_{578}$ −4.5 (*c* 3.1, $CHCl_3$). Found, *m/z*: 492.2834 $[M]^+$; for $C_{26}H_{40}N_2O_7$ calcd.: M = 492.2835. ^1H NMR, δ: 1.00 (t, 3 H, $NCH_2\underline{Me}$, J = 7 Hz); 3.20, 3.21, 3.28, and 3.36 (all s, each 3 H, 1-, 6-, 14-, and

16-OMe); 4.95 and 4.99 (both s, each 1 H, OCH_2O); 7.17 (s, 1 H, NOH). IR (KBr), ν/cm^{-1}: 942, 1090, 1121, 1198, 1298, 1386, 1451, 2820, 2883, 2932, 2964, 3396 (NOH).

Elatidal *N*-phenylimine (20-ethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxy-4-pnenyliminomethylaconitane) (6). A solution of elatidal **4** (0.239 g, 0.50 mmol) in 0.6 mL of $CHCl_3$ was added to aniline (0.047 g, 0.50 mmol). The reaction mixture was left at 20 °C for 2.5 h, and additional $CHCl_3$ (1 mL) was added. The water that formed was removed as an azeotrope by distillation. The residue was triturated with pentane and dried *in vacuo* to give phenylimine **6** (0.249 g, 90%) as an amorphous powder, $[\alpha]^{20}_{578}$ +16.8 (*c* 3.7, $CHCl_3$). Found, *m/z*: 552.3197 $[M]^+$; for $C_{32}H_{44}N_2O_6$ calcd.: M = 552.3199. ^{1}H NMR, δ: 1.03 (t, 3 H, $NCH_2\underline{Me}$, *J* = 7 Hz); 3.13, 3.19, 3.26, and 3.53 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.98 (s, 2 H, OCH_2O); 6.5—6.7 (m, 3 H) and 6.9—7.0 (m, 2 H, Ph); 7.50 (s, 1 H, N=C$\underline{H}$). IR (KBr), ν/cm^{-1}: 772, 961, 1036, 1089, 1121, 1209, 1452, 1503, 1593, 1644 (C=N), 2817, 2883, 2930, 2968. UV (EtOH), λ_{max}/nm (log ε): 218 (3.83, sh), 282 (3.22).

Elatidal *N*-allylimine (4-allyliminomethyl-20-ethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitane) (7). Allylamine (0.098 g, 1.72 mmol) was added to a solution of elatidal **4** (0.139 g, 0.291 mmol) in 1.3 mL of ether. The resulting solution was left at 20 °C for 1 h and then concentrated. The solid residue was dried at 100 °C (3 Torr) and recrystallized from diethyl ether to give compound **7** (0.136 g, 87%), m.p. 124—125 °C, $[\alpha]^{20}_{578}$ −13.9 (*c* 3.7, $CHCl_3$). Found, *m/z*: 516.3211 $[M]^+$; for $C_{29}H_{44}N_2O_6$ calcd.: M = 516.3199. ^{1}H NMR, δ: 1.04 (t, 3 H, $NCH_2\underline{Me}$, *J* = 7 Hz); 3.15, 3.23, 3.30, and 3.38 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.00 (dt, 2 H, C$\underline{H}_2$-1′, *J* = 5.5 and 1.5 Hz); 4.98 and 5.01 (both s, each 1 H, OCH_2O); 5.00—5.16 (m, 2 H, C$\underline{H}_2$-3′); 5.95 (ddt, 1 H, C$\underline{H}_2$-2′, *J* = 17, 10, and 5.5 Hz) and 7.43 (s, 1 H, C$\underline{H}$-18). IR (CCl_4), ν/cm^{-1}: 962, 990, 1034, 1081, 1128, 1197, 1288, 1312, 1386, 1447, 1468, 1667 (CH=N), 2820, 2878, 2922, 2976.

Elatidal *N*-methoxycarbonylmethylimine (20-ethyl-4-methoxycarbonylmethyliminomethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitane) (8). A solution of elatidal **4** (0.038 g, 0.08 mmol) in methyl glycinate (0.115 g, 1.29 mmol) was left at 20 °C for 16 h, and then $CHCl_3$ (1 mL) and a solvent was added. Solvent, the water that formed and the excess of methyl glycinate were removed *in vacuo*. The solid residue was dried at 50 °C (3 Torr) and recrystallized from diethyl ether to give imine **8** (0.039 g, 89%), m.p. 124—125 °C, $[\alpha]^{20}_{578}$ −13.9 (*c* 3.3, $CHCl_3$). Found, *m/z*: 548.3087 $[M]^+$; for $C_{29}H_{44}N_2O_8$ calcd.: M = 548.3097. ^{1}H NMR, δ: 0.98 (t, 3 H, $NCH_2\underline{Me}$, *J* = 7 Hz); 3.12, 3.17, 3.24, and 3.32 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 3.63 (s, 3 H, CO_2Me); 4.09 (s, 2 H, CH_2CO); 4.93 and 4.95 (both s, each 1 H, OCH_2O); 7.39 (s, 1 H, C$\underline{H}$-18). IR (KBr), ν/cm^{-1}: 954, 1073, 1094, 1127, 1202, 1386, 1448, 1466, 1668 (C=N), 1744 (C=O), 2749, 2829, 2874, 2916, 2970.

20-Ethyl-7,8-methylenebisoxy-4-phenylaminomethyl-1α,6β,14α,16β-tetramethoxyaconitane (9). Sodium borohydride (0.211 g, 5.58 mmol) was added portionwise with stirring to a solution of *N*-phenylelatidinimine **6** (0.211 g, 0.382 mmol) in 5.0 mL of anhydrous MeOH. One-half hour after, water (7.4 mL) was added, and the products were extracted from the mixture with $CHCl_3$ (3×5 mL). The extract was filtered and concentrated, and the residue was dried *in vacuo* to give diamine **9** (0.184 g, 87%) as an amorphous powder, $[\alpha]^{20}_{578}$ +5.7 (*c* 5.3, $CHCl_3$). Found, *m/z*: 554.3362 $[M]^+$; for $C_{32}H_{46}N_2O_6$ calcd.: M = 554.3356. ^{1}H NMR, δ: 1.04 (t, 3 H, $NCH_2\underline{Me}$, *J* = 7 Hz); 3.22 (s, 3 H), 3.31 and 3.40 (both s, 6 H, 3 H, 1-, 6-, 14-, and 16-OMe); 5.03 (s, 2 H, OCH_2O); 6.5—6.7 (m, 3 H, Ph) and 7.1—7.2 (m, 2 H, Ph). IR (KBr), ν/cm^{-1}: 749, 963, 1088, 1121, 1197, 1257, 1322, 1386, 1447, 1467, 1504, 1603, 2818, 2879, 2897, 2931, 2964, 3389 (NH). UV (EtOH), λ_{max}/nm (log ε): 246 (3.88), 303 (3.04).

4-Allylaminomethyl-20-ethyl-7,8-methylenebisoxy-1α,6β,14α,16β-tetramethoxyaconitane (10) was obtained in 90% yield by reducing imine **7** (0.063 g) with $NaBH_4$ as described above. Diamine **10** is a viscous oil, $[\alpha]^{20}_{578}$ −5.3 (*c* 4.9, $CHCl_3$). Found, *m/z*: 518.3344 $[M]^+$; for $C_{29}H_{46}N_2O_6$ calcd.: M = 554.3356. ^{1}H NMR, δ: 0.97 (t, 3 H, $NCH_2\underline{Me}$, *J* = 7 Hz); 3.18, 3.26, 3.28, and 3.35 (all s, each 3 H, 1-, 6-, 14-, and 16-OMe); 4.98 and 4.99 (both s, 2 H, OCH_2O); 5.00—5.15 (m, 2 H, C$\underline{H}_2$-3′), 5.82 (ddt, 1 H, C$\underline{H}_2$-2′, *J* = 17, 10, and 5.5 Hz). IR (CCl_4), ν/cm^{-1}: 909, 962, 1090, 1127, 1154, 1196, 1385, 1453, 2818, 2879, 2922, 2973, 3400 (NH).

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