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Synthetic Transformations of Higher Terpenoids: X. Intramolecular Cyclization of *N*-Allyl- and *N*-Propargyl-16-dialkylammoniomethyl-12-furfuryl-13,14,15,16-tetranorlabdanoid Bromides

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Abstract—Quaternary ammonium salts obtained by quaternization of lambertian acid 16-dialkylaminomethyl derivatives effected by allyl halides or propargyl bromide undergo intramolecular [4+2]-cycloaddition resulting in diterpenoids of labdane type containing a heterocyclic fragment of 10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]decene or 10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]deca-6,8-diene.

Intramolecular reaction of furane compounds is a convenient method of preparation of fused heteropolycyclanes containing a fragment of 7-oxabicyclo[2.2.1]-heptene (7-oxanorbornene) [2]. The cyclization of *N*-alkenylfurylamines is widely used in the synthesis of indoline and tetrahydroquinoline derivatives [3]. Hexahydroepoxyisoindoles are produced by cyclization of the corresponding N-alkenylfurfurylamines. Inasmuch as the compounds of this structural type possess valuable biological activity [4] various alkenylfurfurylamines were brought into the reaction, and the result of the process was established to depend on the substituent attached to the nitrogen atom. The reaction occurred under mild conditions furnishing 10-oxa-3-azatricyclo-[5.2.1.$0^{1,5}$]-decene derivatives when the dienophilic part of the molecule contained an aryl substituent [5] activated by a carbonyl group [6], or when bulky substituents were present in the α-position with respect to the nitrogen atom [7].

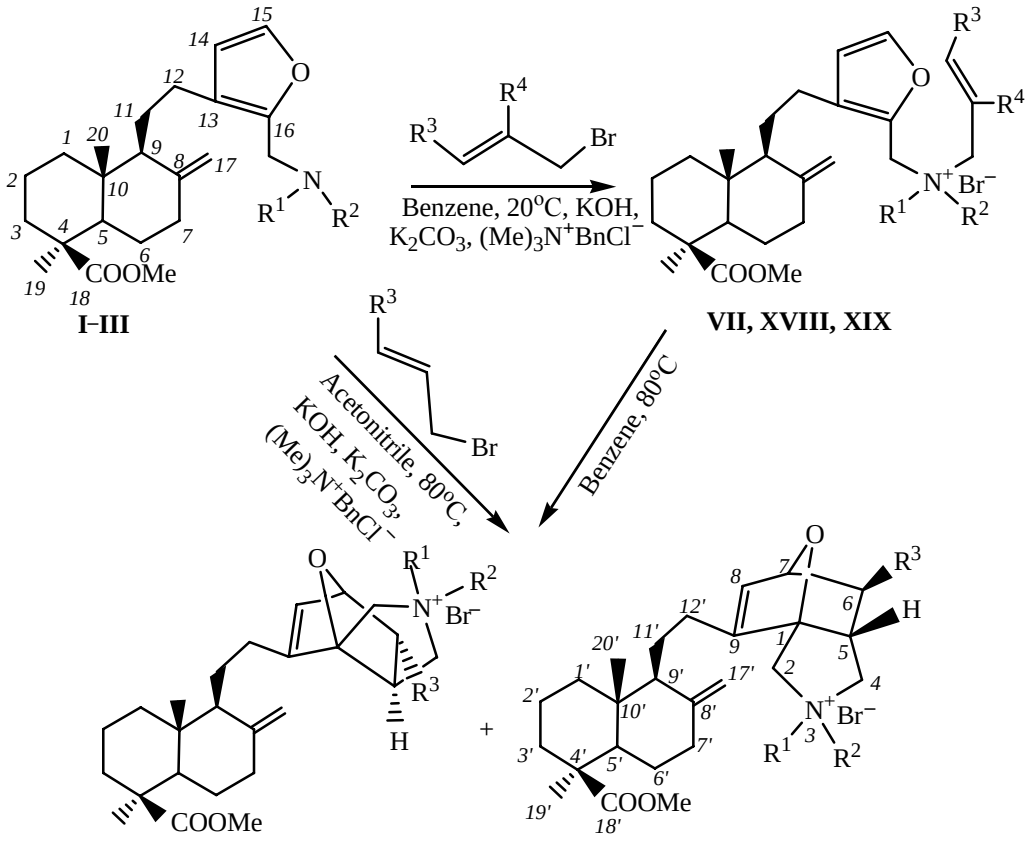
It was shown by an example of methallyl-(furfuryl)amine that amines with allyl and furfuryl groups did not undergo cyclization [8] but the corresponding hydrochlorides furnished cyclization products [8, 9]. The ready cyclization of dialkyl(allyl)furfurylammonium salts was shown to occur [8, 10] affording 2,2-dialkyl-5,7α-epoxytetrahydroisoindolinium salts..

* For communication IX see [1].

Aiming at preparation of new diterpenoids of labdane series containing a heterocyclic fragment of 10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]decene we investigated an intramolecular [4+2]-cycloaddition reaction of quaternary ammonium salts obtained by quaternization with allyl, methallyl, or propargyl bromides of lambertian acid dialkylaminomethyl derivatives.

We used as initial aminofuranes previously synthesized methyl 16-(*N*,*N*-dimethyl-aminomethyl- (**I**) and 16-morpholinomethyl)lambertianates (**II**) [11], unknown before methyl 16-(piperidinomethyl)lambertianate (**III**), and also $C^{8(17)}$-hydrogenated diterpenoids **IV–VI**. It should be noted that the hydrogenation of the 8(17)-double bond in labdanoids I–III using the catalyst Pd/$BaSO_4$ [12] proceeded stereoselectively affording the corresponding labdane diterpenoids **IV–VI** with an axially oriented methyl group linked to the atom C^8.

Salt **VII** obtained from aminoterpene (**I**) easily underwent cyclization at boiling in benzene affording a mixture of (*S*)-*exo* and (*R*)-*endo* isomers **VIII** and **IX** in a ratio 1:1 (yield 78%). The reaction can be preformed avoiding isolation the quaternary salt by generating the salts *in situ* from the corresponding aminoterpenes **I–VI**. The salts form at short boiling of compounds **I–VI** oxalates in acetonitrile in the presence of bases and a phase transfer catalyst [13]. The cyclization in all instances afforded a mixture of the corresponding (*S*)-*exo* and



$R^1 = R^2 = Me$ (**I, VII–IX, XVIII**); $R^1 + R^2 = (CH_2)_2O(CH_2)_2$ (**II, X, XI, XIV, XV**), $(CH_2)_5$ (**III, XII, XIII, XVI, XVII**); $R^3 = H$ (**VIII–XIII**), CH_3 (**XIV–XVII**); $R^1 = R^2 = R^4 = Me$, $R^3 = H$ (**XIX**).

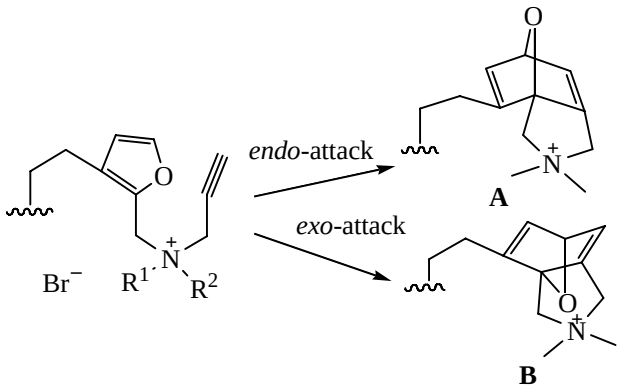
(*R*)-*endo* adducts **VIII, IX; X, XI; XII**, **XIII** in a 1:1 ratio. (5*R*)-Isomers **XI** and **XIII**, and (5*S*)-isomer **VIII** were easily isolated in an individual state by recrystallization of the adducts from ethyl acetate. The application of catalysts (zinc chloride or molybdenum hexacarbonyl) to the cyclization of salt **VII** did not affect the reaction selectivity. The substituents present in the aminomethyl fragment form the following series according to their positive effect on the reaction rate and the yield of products: $(CH_2)_5 > (CH_2)_2O(CH_2)_2 > (CH_3)_2$. Allyl bromide reacted with labdanoid **III** at heating in acetonitrile in the presence of bases and a phase transfer catalyst providing cycloaddition products **XII** and **XIII** in 1 h (yield 91%), the reaction with labdanoid **I** afforded compounds **VIII** and **IX** (yield 82%) at heating for 6 h. Labdanoids **II** and **III** reacted with crotyl bromide in acetonitrle in the presence of a base giving rise to adducts **XIV, XV** and **XVI, XVII** respectively in a fair yield. Reaction of diterpenoid **I** both with crotyl bromide and methallyl bromide under the cyclization conditions stopped at the stage of salts **XVIII** and **XIX** formation (yield 59 and 20% respectively). Further attempts to bring about intramolecular cyclization of salts **XVIII** and **XIX** were unsuccessful. It should be noted that the polarity of solvent did not appreciably affect the result of the reaction. The reaction of compound **III** with allyl bromide in acetonitrile and in aqueous acetonitrile in the presence of a base gave virtually the same result: yield of the cyclization products was 80–82%.

7-Oxanorbornadiene derivatives were obtained in reaction of aminoterpenes **I–III** with propargyl bromide. As seen on the Scheme, the cycloaddition may occur with the *endo*- or *exo*-attack of the diene by the triple bond to afford isomers **A** or **B**.

The boiling of aminolabdanoids **I–III** with propargyl bromide in acetonitrile in the presence of bases for 2 h resulted in a mixture of adducts originating from the *endo*- and *exo*-attack **XX–XXV** obtained in a fair yield. The reaction is not stereoselective and in every case afforded a mixture of stereoisomers. We failed to obtain adducts from salt **XXVI** by boiling in DMF.

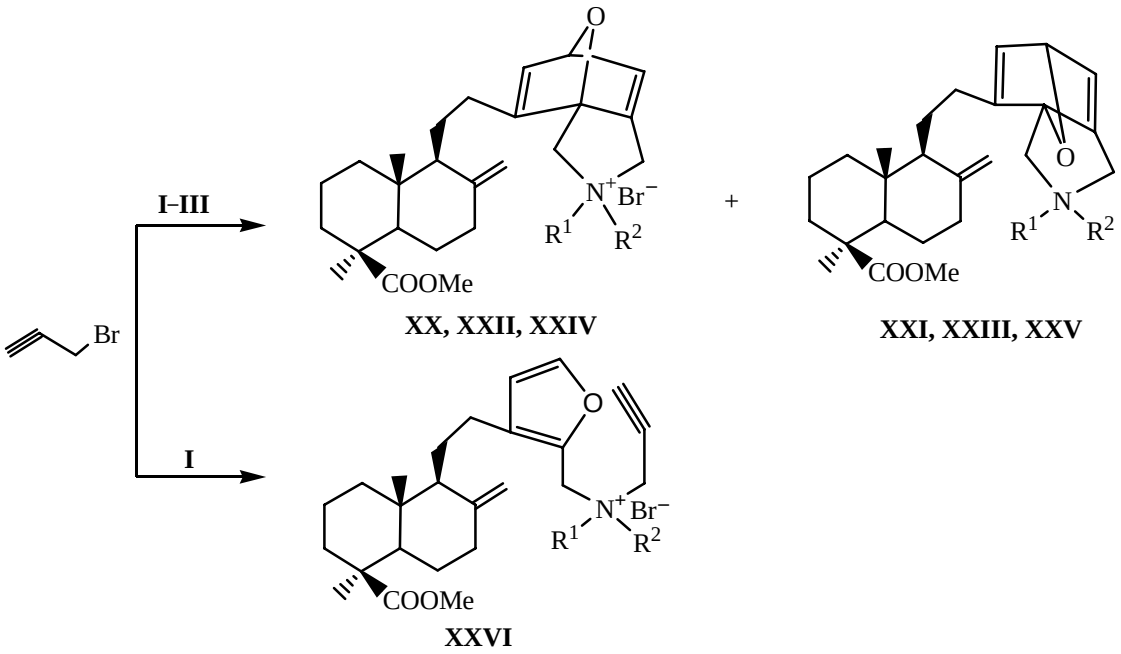
Dihydrolabdanoids **IV–VI** react with allyl bromide at heating in acetonitrile to give rise to cyclization products **XXVII–XXXII** in a 50–58% yield. The reaction of terpenoid **IV** with propargyl bromide under these conditions led to strong tarring of the reaction mixture. After 1.5 h of the reaction we isolated from the reaction mixture 30% of salt **XXXIII** and 10% of cyclization products **XXXIV** and **XXXV**. At the longer process time (3 h) the yield of the oxaadducts **XXXIV** and **XXXV** increased to 17%, salt **XXXIII** was additionally separated (yield 6%)], and a strong tarring was observed. Thus amines **IV–VI** exhibit significantly lower reactivity in reactions with allyl and propargyl bromides.

The structure of all compounds obtained was established by the analysis of spectral data. The axial position of the methyl group attached to C^{8} atom in compounds **IV–VI** is evidenced by the value of the coupling constant of protons $H^{8,9}$ [in the ^{1}H NMR spectrum of compound **IV**, δ, ppm: 1.89 (H^{8}), 1.06 (H^{9}), $J_{8,9}$ 11.3 Hz] [14]. The methyl group at the atom C^{8} gives rise to a resonance at δ, ppm, 0.81–0.92 d [J (CH_3, H^{8}) 7.2 Hz]. The characteristic feature of the spectra from $C^{8,17}$-hydrogenated derivatives of labdanoids **IV**–**VI** is the broadening of signals belonging to protons $H^{14,15,16}$, of singlets from the methyl groups at nitrogen (in compound **IV**), or the proton signals of the methyl groups in the heterocyclic fragment (in compounds **V** and **VI**) probably due to hindered rotation. In the ^{13}C NMR



spectra of compound **IV–VI** a characteristic upfield shift is observed of signals from atoms $C^{7,9}$ ($\Delta\delta \approx 4.0$ ppm), and a downfield shift of the peak from atom C^{20} ($\Delta\delta \approx 2.0$ ppm) compared to the positions of the corresponding signals in the spectra of compounds **I–III**.

The assignment of compounds **VIII, X, XII, XIV**, and **XVI** to the (*S*)-*exo*-series, and compounds **IX, XI**, **XIII, XV**, and **XVII** to the (*R*)-*endo*-seried was based on the analysis of the ^{1}H NMR spectra. The H^{5} proton in the *endo*-isomers is located downfield with respect to the corresponding signal in the spectrum of the *exo*-isomer due to the effect of the oxygen from the epoxy bridge. For instance, in the spectra of isomers **VIII** and **IX** these protons give rise to multiplets centered at 2.49 and 2.59 ppm respectively. In the spectra of *endo*-isomers **VIII** and **XVII** the difference between the chemical shifts

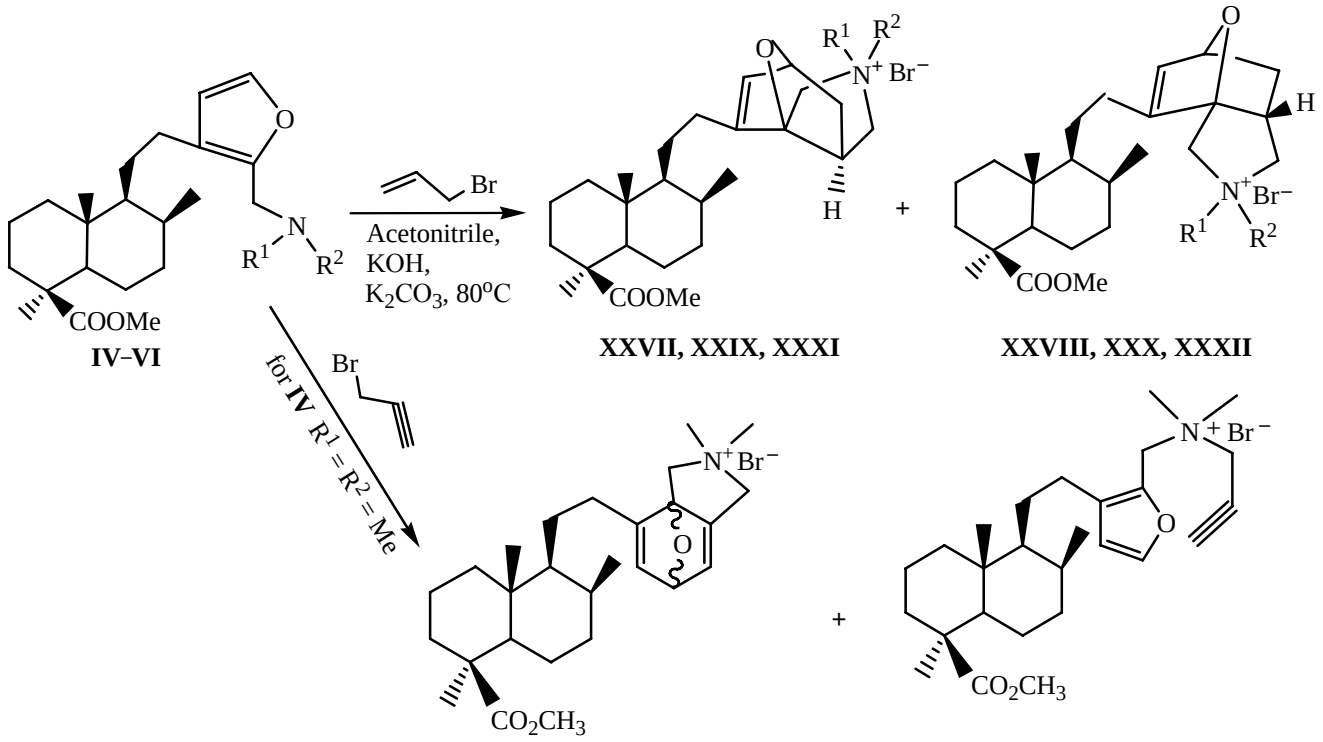


XX, XXII, XXIV

XXI, XXIII, XXV

XXVI

XX, XXI, $R^1 = R^2 = Me$; **XXII, XXIII**, $R^1 + R^2 = (CH_2)_2O(CH_2)_2$; **XXIV, XXV**, $R^1 + R^2 = (CH_2)_5$.



of the singlets from methyl groups attached to nitrogen is larger than in the spectra of *exo*-isomers [δ 3.54, 3.63 (**VIII**) and 3.52, 3.66 ppm (**IX**)]. Introduction of bulky substituents to the nitrogen results in increase in the chemical shift difference of protons of the fused piperidine ring. In the spectrum of individual (*R*)-isomer **XIII** methylene protons at C^2 atom give peaks at δ 3.78 and 4.19 ppm, whereas the corresponding signals in the spectrum of the (*S*)-isomer **XII** are located at δ 3.84 and 4.15 ppm. Introducing a methyl group into oxatricyclanes **XIV–XVII** leads to increased difference in the chemical shifts of protons at C^2 atom [δ 4.00 and 4.62 (**XIV**); 3.89 and 4.45 ppm (**XV**)]. The methyl group linked to C^6 atom gives rise to a doublet at 0.83–0.87 ppm (*J* 7.0 Hz).

In the spectra of adducts **XXVII–XXXII** the signals of protons at C^2 atom suffer downfield shift, and the difference between their chemical shifts grows. Besides in the ^{13}C NMR spectra of these compounds icreases the difference in the chemical shifts of atoms $C^{9'}$ in the terpene skeleton (δ 51.44, 51.88 ppm) and atoms $C^{8,9}$ in the heterocyclic moiety [δ 128.55, 128.92 (C^8) and 147.57, 147.74 (C^9) ppm]

The ^1H NMR spectra of 7-oxanorbornadiene derivatives **XX–XXV** also possess a number of characteristic features suggesting their assignment to a certain stereoisomer series. In the spectra of adduct with β-located oxide bridge **XX**, **XXII**, and **XXIV** the olefin protons signals are shifted downfield, and protons H^4 are displaced upfield [δ 4.58(**XXII**), 4.76 ppm (**XXIII**)]. In the spectra of oxanorbornadienes an enhanced magnetic nonequivalence of $H^{17'}$ protons is also observed, and therewith the difference in the chemical shifts (δ, ppm) increased for *exo*-isomers [for instance, in compound **XX** 4.32 s and 4.74 s ($H^{17'}$), in compound **XXI** 4.20 s and 4.70 s ($H^{17'}$)]. In the ^1H NMR spectra of adducts **XXXIV** and **XXXV** the protons of methyl group at $C^{8'}$ appear as doublets centered at 0.84 (*exo*) and 0.87 (*endo*) ppm (*J* 7.1 Hz). Similar characteristic features in the ^1H NMR spectra of oxanorbornadiene adducts were observed before [15].

Hence the intramolecular cyclization of quaternary ammonium salts obtained from the lambertian acid 16-methylamino derivatives with allyl and propargyl bromides is a general procedure for preparation of a new group of nitrogen-containing diterpenoids involving a fragment of 10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]decene (hexahydro- and tetrahydroepoxyindolinium salts of labdanoids).

EXPERIMENTAL

IR spectra were recorded on spectrometer Vector-22 from samples pelletized with KBr. UV absorption was

taken on HP 8453 UV Vis instrument from ethanol solutions (C 10^{-4} mol l^{-1}). NMR spectra were registered on spectrometers Bruker AC-200 at operating frequencies 200.13 (^{1}H) and 50.32 MHz (^{13}C) and Bruker DRX-500 [operating frequencies 500.13 (^{1}H) and 125.76 MHz (^{13}C)] from solutions in $CDCl_3$. The assignment of signals in the NMR spectra were carried out using various proton-proton and carbon-propton correlation spectra (COSY, COLOC, CORRD). Melting points were measured on the Koeffler heating block.

The reactions progress was monitored by TLC on Silufol UV-254 plates. Reaction products were isolated by column chromatography on aluminum oxide (eluents chloroform–methanol, 200:1, 50:1). The specific rotation ($[\alpha]_{580}$) was measured on polarimeter Polamat A in ethanol. Labdanoids **I–VI** were isolated as crystalline oxalates and were brought into reaction with alkenyl halides.

Crotyl bromide and propargyl bromide were prepared from the corresponding alcohols by procedure [16].

Methyl 16-piperidinomethyl-15,16-epoxy-8(17),13(16),14-labdatrien-18-oate (III). To a solution of 1.0 g (3.03 mmol) of methyl lambertianate and 1.1 g (6.04 mmol) of *N*-bis(piperidino)methane in 20 ml of anhydrous CH_2Cl_2 at 0°C was added dropwise while stirring 0.35 g (4.53 mmol) of AcCl in 5 ml of CH_2Cl_2. The stirring was continued for 1 h at 20°C, then 50 ml of water was added and ammonia solution till alkaline reaction. The organic layer was separated, the products were extracted from the water layer with CH_2Cl_2, the combined organic solutions were dried over $MgSO_4$ and evaporated. The yellow oily substance obtained was dissolved in 15 ml of *t*-BuOMe and at stirring thereto was added dropwise saturated solution 0.27 g of oxalic acid in the same solvent. The precipitate was filtered off, washed with *t*-BuOMe, and dried. We obtained 1.10 g (70%) of oxalate of tertiary amine **III**, mp. 66–69°C, $[\alpha]_{580}$ +14.3 (*c* 3.5, EtOH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.45 s (3H, $C^{20}H_3$), 0.98 m (2H, $H^{1,3}$), 1.13 s (3H, $C^{19}H_3$), 1.23 m (H, H^5), 1.51 m (5H, $H^{2,12,12,9,6}$), 1.75 m (16H, $H^{6,1,2,7,6,11,3}$, $5CH_2$), 2.10 m (H, H^{11}), 2.30 m (H, H^7), 3.56 s (3H, OCH_3), 4.15 s (2H, NCH_2), 4.49 s (H, H^{17}), 4.87 s (H, H^{17}), 6.29 d (H, H^{14}, *J* 1.8), 7.38 d (H, H^{15}, *J* 1.8). ^{13}C NMR spectrum, δ, ppm: 12.43 q (C^{20}), 19.75 t (C^2), 21.42 t (C^{12}), 22.83 t ($C^{3',4',6',7'}$), 23.00 t ($C^{5'}$), 23.67 t (C^{11}), 26.09 t (C^6), 28.54 q (C^{19}), 37.91 t (C^3), 38.45 t (C^7), 38.87 t (C^1), 40.07 s (C^4), 44.13 s (C^{10}), 50.90 q (OCH_3), 52.41 t ($C^{1'}$), 54.76 d (C^9), 55.94 d (C^5), 106.44 t (C^{17}), 111.53 d (C^{14}), 129.18 s (C^{13}), 138.38 s (C^{16}), 143.99 d (C^{15}), 147.56 s (C^8), 177.49 s (C^{18}). Found, %: C 67.21; H 8.62; N 2.57. $C_{29}H_{43}NO_7$. Calculated, %: C 67.31; H 8.32; N 2.71.

Methyl 8(*S*)-methyl-16-(*N*,*N*-dimethyl)aminomethyl-15,16-epoxy-13(16),14-labdadien-18-oate (IV). To a solution of 0.70 g (1.47 mmol) of compound **I** oxalate in 20 ml of ethanol was added 0.28 g of 10% $Pd/BaSO_4$, the reaction mixture was saturated with hydrogen and kept at room temperature for 3 days at intermittent stirring. The catalyst was filtered off, the solvent was evaporated. To the residue was added ethyl acetate, and the colorless precipitate was filtered off. We obtained 0.60 g (86%) of compound **IV**, mp 159–162°C, $[\alpha]_{580}$ +69.9 (*c* 1.3, EtOH). IR spectrum, cm^{-1}: 1154, 1229, 1717 (C=O); 2677 (NR_3). ^{1}H NMR spectrum, δ, ppm: 0.63 s (3H, $C^{20}H_3$), 0.79 m (H, H^1), 0.99 d (3H, $C^{17}H_3$, *J* 7.2 Hz), 1.00 m (H, H^3), 1.02 m (2H, $H^{5,7}$), 1.06 m (H, H^9), 1.13 s (3H, $C^{19}H_3$), 1.40 m (3H, $H^{12,12,6}$), 1.59 m (H, H^6), 1.67 m (2H, $H^{1,7}$), 1.75 m (2H, $H^{2,2}$), 1.89 m (H, H^8), 2.09 m (H, H^7), 2.18 m (H, H^{11}), 2.44 m (H, H^{11}), 2.74 s (6H, $2CH_3$, half-width 10.0), 3.59 s (3H, OCH_3), 4.22 s (2H, NCH_2, half-width 12.0), 6.31 br.s (H, H^{14}, half-width 5.0), 7.39 s (H, H^{15}, half-width 5.0). ^{13}C NMR spectrum, δ, ppm: 14.10 q (C^{20}), 14.75 q (C^{17}), 18.56 t (C^2), 18.77 t (C^{12}), 22.77 t (C^{11}), 26.20 t (C^6), 28.58 q (C^{19}), 28.86 d (C^8), 34.50 t (C^7), 37.82 t (C^3), 38.34 C (C^4), 39.55 t (C^1), 41.79 q ($C^{17}H_3$), 43.63 s (C^{10}), 50.22 t (NCH_2), 50.84 q (OCH_3), 51.93 d (C^9), 57.06 d (C^5), 111.76 d (C^{14}), 129.41 s (C^{13}), 138.37 s (C^{16}), 143.90 d (C^{15}), 177.43 s (C^{18}). Found, %: C 65.15; H 8.75; N 2.76. $C_{26}H_{41}NO_7$. Calculated, %: C 65.13; H 8.56; N 2.92.

Methyl 8(*S*)-methyl-16-morpholinomethyl-15,16-epoxy-13(16),14-labdadien-18-oate (V). The hydrogenation of labdanoid **II** by the above procedure afforded compound **V** in 87% yield, mp 138–140°C (from ethyl acetate). $[\alpha]_{580}$ +23.7 (*c* 1.7, EtOH). IR spectrum, cm^{-1}: 1190, 1228, 1725 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62 s (3H, $C^{20}H_3$), 0.79 m (H, H^1), 0.89 d (3H, H^{17}, *J* 7.2), 0.97 m (H, H^3), 1.04 m (2H, $H^{5,9}$), 1.12 s (3H, $C^{19}H_3$), 1.42 m (3H, $H^{12,6,7}$), 1.58 m (H, H^6), 1.68 m (2H, $H^{1,7}$), 1.80 m (2H, $H^{2,12}$), 1.86 m (H, H^8), 2.08 m (H, H^3), 2.16 m (H, H^{11}), 2.40 m (H, H^{11}), 3.16 br.s (4H, $2NCH_2$), 3.58 s (3H, OCH_3), 3.90 br.s (4H, $2OCH_2$), 4.21 br.s (2H, NCH_2), 6.31 d (H, H^{14}, *J* 1.8), 7.39 d (H, H^{15}, *J* 1.8). ^{13}C NMR spectrum, δ, ppm: 14.10 q (C^{20}), 14.73 q (C^{17}), 18.58 t (C^{11}), 18.81 t (C^2), 22.86 t (C^{12}), 26.20 t (C^6), 28.57 q (C^{19}), 28.96 d (C^8), 34.54 t (C^7), 37.83 t (C^3), 38.37 s (C^4), 39.59 t (C^1), 43.72 c (C^{10}), 50.30 t and 50.71 t (NCH_2), 50.88 d (C^9),

52.00 q (OCH_3), 57.09 d (C^5), 63.83 t (OCH_2), 111.86 d (C^{14}), 129.76 s (C^{13}), 137.68 s (C^{16}), 143.90 d (C^{15}), 177.73 s (C^{18}). Found, %: C 64.52; H 7.75; N 2.69. $C_{29}H_{49}NO_7$. Calculated, %: C 64.49; H 7.87; N 2.69.

Methyl 8(*S*)-methyl-16-piperidinomethyl-15,16-epoxy-13(16),14-labdadien-18-oate (VI). The hydrogenation of labdanoid **III** by the above procedure afforded compound **VI** in 82% yield, mp 140–142°C. $[\alpha]_D$ +18.7 (*c* 2.3, EtOH). IR spectrum, cm^{-1}: 1640 (C=C); 1725, 1194, 1228, (C=O). ^1H NMR spectrum, δ, ppm: 0.61 s (3H, $C^{20}H_3$), 0.79 m (H, H^1), 0.88 d (3H, H^{17}, *J* 7.2 Hz), 0.96 m (H, H^3), 1.01 m (3H, $H^{5,7,9}$), 1.11 s (3H, $C^{19}H_3$), 1.38 m (3H, $H^{12,6,12}$), 1.56 m (H, H^6), 1.66 m (8H, $H^{1,7}$, $6CH_2$), 1.79 m (2H, $H^{2,2}$), 1.86 m (H, H^8), 2.07 m (H, H^7), 2.17 m (H, H^{11}), 2.39 m (H, H^{11}), 2.59 br.s (2H, CH_2), 2.36 br.s (2H, CH_2), 3.57 s (3H, OCH_3), 4.08 br.s (2H, NCH_2), 6.30 s (H, H^{14}), 7.37 s (H, H^{15}). ^{13}C NMR spectrum, δ, ppm: 14.00 q (C^{20}), 14.66 q (C^{17}), 18.48 t (C^{12}), 18.71 t (C^2), 21.32 t, 22.61 t (CH_2), 22.95 t (C^{11}), 26.13 t (C^6), 28.47 q (C^{19}), 28.86 d (C^8), 34.46 t (C^7), 37.75 t (C^3), 38.28 s (C^4), 39.51 t (C^1), 43.62 s (C^{10}), 50.76 q (OCH_3), 51.94 d (C^9), 57.02 d (C^5), 111.76 d (C^{14}), 129.45 s (C^{13}), 137.92 s (C^{16}), 143.90 d (C^{15}), 177.59 s (C^{18}). Found, %: C 63.94; H 9.06; N 2.90. $C_{27}H_{43}NO_3$. Calculated, %: C 63.65; H 8.45; N 2.75.

N-Allyl-*N*,*N*-dimethyl-*N*-{3-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-furfuryl}ammonium bromide (VII). To a solution of 1.0 g (2.10 mmol) of compound **I** in 20 ml of benzene was added 0.47 g (8.39 mmol) of KOH, 0.29 g (2.10 mmol) of K_2CO_3, and 0.21 g (1.16 mmol) of benzyltrimethylammonium chloride, and the mixture was stirred for 1 h. Then to the reaction mixture was added 0.25 g (4.20 mmol) of allyl bromide, and the stirring at room temperature was continued for 4 h. The precipitate was filtered off and washed with chloroform (40 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$. The solvent was evaporated, ethyl acetate was added to the residue, and the formed colorless precipitate was filtered off. Thus we obtained 0.55 g (52%) of salt **VII**. By chromatography of the mother liquor we additionally isolated 0.22 g (21%) of salt **VII**, mp 151–152°C (from ethyl acetate), $[\alpha]_{580}$ +9.00 (*c* 2.9, EtOH). UV spectrum, λ_{max}, nm (log ε): 224 (4.07). IR spectrum, cm^{-1}: 845, 1614, 1645, 3023 (C=C); 1153, 1211, 1717 (C=O); 3409, 3473 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.43 s (3H, $C^{20}H_3$), 0.98 m (2H, $H^{1,3}$), 1.10 s (3H, $C^{19}H_3$), 1.24 d.d (H, H^5, *J* 12, 2), 1.43 m (H, H^2), 1.59 m (H, H^9), 1.62 m, 1.66 m (2H, $2H^{12}$), 1.69 m (H, H^1), 1.74 m (2H, $H^{7,2}$), 1.81 m, 1.91 m, (2H, $2H^6$), 2.06 d (H, H^3), 2.32 m (H, H^{11}), 2.47 m (H, H^7), 2.54 m (H, H^{11}), 3.21 C [6H, $(CH_3)_2N$], 3.53 s (3H, OCH_3), 4.35 d (2H, $2H^{1'}$, *J* 7), 4.49 s (H, H^{17}), 4.70 q (2H, $2H^{3'}$, *J* 12), 4.84 s (H, H^{17}), 5.68 d.d (H, $H^{5a'}$, *J* 10, 1), 5.83 d (H, $H^{5b'}$, *J* 16), 5.99 m (H, $H^{4'}$, *J* 7), 6.32 s (H, H^{14}), 7.43 c (H, H^{15}). ^{13}C NMR spectrum , δ, ppm: 12.37 q (C^{20}), 19.68 t (C^2), 22.99 t (C^{12}), 23.80 t (C^{11}), 26.03 t (C^6), 28.50 q (C^{19}), 37.80 t (C^3), 38.42 t (C^7), 38.76 t (C^1), 40.06 s (C^4), 44.06 s (C^{10}), 49.46 and 49.56 q [$2N(CH_3)_2$], 50.89 q (OCH_3), 54.53 d (C^9), 55.72 d (C^5), 57.63 t ($C^{1'}$), 65.75 t ($C^{3'}$), 106.37 t (C^{17}), 111.95 d (C^{14}), 124.33 d ($C^{4'}$), 130.15 s (C^{13}), 131.58 t ($C^{5'}$), 137.86 s (C^{16}), 144.85 d (C^{15}), 147.71 s (C^8), 177.48 s (C^{18}). Found, %: C 64.31; H 8.15; Br 15.21; N 2.69. $C_{27}H_{42}BrNO_3$. Calculated, %: C 63.78; H 8.27; Br 15.75; N 2.76.

5(*S*)- and 5(*R*)-3,3-Dimethyl-9-[18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-10-oxa-3-azoniatricyclo[5.2.1.$0^{1,5}$]dec-8-ene bromides (VIII, IX). *a*. To a solution of 0.5 g (1.05 mmol) of aminoterpene **I** in 20 ml of acetonitrile was added at stirring 0.24 g (4.20 mmol) of KOH, 0.15 g (1.05 mmol) of K_2CO_3, and 0.11 g (0.58 mmol) of benzyltrimethylammonium chloride, and the mixture was boiled for 30 min. Then 0.25 g (2.10 mmol) of allyl bromide was added, and the mixture was heated at reflux for 6 h more (TLC monitoring) till the initial compound was completely consumed. On cooling to room temperature the precipitate was filtered off and washed with acetonitrile (30 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$. The solvent was evaporated, the residue was subjected to chromatography on aluminum oxide. We obtained 0.42 g (82%) of a mixture of compounds **VIII** and **IX**. By recrystallization of the adducts mixture from ethyl acetate 0.15 g of individual compound **VIII** was isolated.

b. A solution of 0.50 g of compound **VII** in 7 ml of benzene was heated at reflux for 19 h (TLC monitoring). The solvent was evaporated, the residue was subjected to chromatography on aluminum oxide. We obtained 0.40 g (80%) of a mixture of compounds **VIII** and **IX**. By recrystallization of the adducts mixture from ethyl acetate individual compound **VIII** was isolated.

c. To a stirred solution of 0.5 g (0.98 mmol) of salt **VII** in 10 ml of anhydrous THF and 10 ml of CH_2Cl_2 under an argon flow was added 0.13 g (0.98 mmol) of freshly calcined $ZnCl_2$. The reaction mixture was left

standing at room temperature for 20 h with intermittent stirring. On completion of the reaction the mixture was diluted with 30 ml of water, the organic layer was separated, and the reaction products were extracted from the water layer into $CHCl_3$ (2×25 ml). The combined organic solutions were washed with water (2×20 ml), dried over $MgSO_4$, and evaporated. According to ^{1}H NMR data, the residue contained a mixture of isomers **VIII** and **IX** in a 1:1 ratio and also initial compound **VII**.

d. To a stirred solution of 0.5 g (0.98 mmol) of salt **VII** in 20 ml of anhydrous THF was added in an argon flow 0.26 g (0.098 mmol) of $Mo(CO)_6$. The reaction mixture was left standing at room temperature for 20 h with intermittent stirring. On completion of the reaction the mixture was diluted with 30 ml of water, the organic layer was separated, and the reaction products were extracted from the water layer into $CHCl_3$ (2×25 ml). The combined organic solutions were washed with water (2×20 ml), dried over $MgSO_4$, and evaporated. According to ^{1}H NMR data, the residue contained a mixture of isomers **VIII** and **IX** in a 1:1 ratio and also initial compound **VII**.

Compound VIII, mp 178–180°C, $[\alpha]_{580}$ +21 (*c* 3.1, EtOH). IR spectrum, cm^{-1}: 1616, 1644, 2915 (C=C); 1132, 1233, 1720 (C=O); 3419 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.38 s (3H, $C^{20'}H_3$), 0.96 m (2H, $H^{1',3'}$), 1.06 s (3H, $C^{19'}H_3$), 1.19 m (H, $H^{5'}$), 1.39 m (H, $H^{2'}$), 1.42 m (H, $H^{12'}$), 1.53 m (H, $H^{9'}$), 1.55 m (H, H^6), 1.65 m (H, $H^{6'}$), 1.69 m (H, $H^{1'}$), 1.71 m (H, $H^{2'}$), 1.78 m (2H, $H^{7',6}$), 1.88 m (H, $H^{6'}$), 1.95 m (H, $H^{11'}$), 2.04 m (H, $H^{3'}$), 2.15 m (H, $H^{11'}$), 2.28 m (H, $H^{7'}$), 2.49 m (H, H^5), 3.18 t (H, H^4, *J* 11), 3.49 s (3H, OCH_3), 3.54 s, 3.63 s [6H, $(CH_3)_2N$], 3.79 d, 4.20 d (2H, $2H^2$, *J* 14), 4.27 s (H, $H^{17'}$), 4.51 q (H, H^4, *J* 8), 4.72 s (H, $H^{17'}$), 4.95 d (H, H^7, *J* 2), 5.90 d (H, H^8, *J* 2). ^{13}C NMR spectrum, δ, ppm: 12.20 q ($C^{20'}$), 19.59 t ($C^{2'}$), 20.76 t ($C^{12'}$), 24.88 t ($C^{11'}$), 25.86 t ($C^{6'}$), 28.44 q ($C^{19'}$), 33.16 d (C^6), 37.79 t ($C^{3'}$), 38.28 t ($C^{7'}$), 38.85 t ($C^{1'}$), 40.02 s ($C^{4'}$), 42.68 d (C^5), 43.95 s ($C^{10'}$), 50.78 q (OCH_3), 55.13 d (C^9), 55.32 q (CH_3), 55.79 d ($C^{5'}$), 56.76 q (CH_3), 66.68 t (C^2), 71.08 t (C^4), 80.25 d (C^7), 96.08 s (C^1), 106.11 t ($C^{17'}$), 128.20 d (C^8), 147.38 s, 147.60 s ($C^{9,8'}$), 177.32 s ($C^{18'}$). Found, %: C 63.64; H 8.31; Br 13.62; N 2.83. $C_{27}H_{42}BrNO_3$. Calculated, %: C 63.78; H 8.27; Br 15.75; N 2.76.

Compound IX. Data obtained from the spectrum of the mixture of compounds **VIII** and **IX**. Characteristic signals of isomer **IX** in the ^{1}H NMR spectrum, δ, ppm: 2.59 m (H, H^5), 3.55 s (3H, OCH_3), 3.52 s, 3.66 s [6H, $(CH_3)_2N$], 4.30 s, 4.78 s (2H, $2H^{17'}$), 5.89 d (H, H^8, *J* 2 Hz).

11(*S*)- and 11(*R*)-14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-6,15-dioxa-3-azoniatricyclo[9.4.0.1^{1,12}]hexadec-13-ene bromides (X, XI). The reaction of aminoterpenoid **II** with allyl bromide in conditions of procedure *a* (boiling for 11 h) afforded a mixture of compounds **X** and **XI** in an overall yield 61%. By crystallization of the adducts mixture from ethyl acetate was isolated individual **compound (XI)**, mp 137–139°C, $[\alpha]_D$ +18.6 (*c* 1.0, EtOH). IR spectrum, cm^{-1}: 752, 1645, 2946 (C=C); 1154, 1230, 1721 (C=O); 3422 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.39 s (3H, $C^{20'}H_3$), 0.94 m (H, $H^{1'}$), 0.98 m (H, $H^{3'}$), 1.12 s (3H, $C^{19'}H_3$), 1.20 m (H, $H^{5'}$), 1.40 m (2H, $H^{2',12'}$), 1.49 m (H, $H^{12'}$), 1.57 m (2H, $H^{9',6}$), 1.64 m (H, $H^{6'}$), 1.66 m (H, $H^{1'}$), 1.69 m (H, $H^{2'}$), 1.79 m (2H, $H^{7',6}$), 1.85 m (H, $H^{6'}$), 1.87 m (H, $H^{11'}$), 2.03 m (H, $H^{3'}$), 2.15 m (H, $H^{11'}$), 2.25 m (H, $H^{7'}$), 2.88 q (H, H^5, *J* 7), 3.39 q (H, H^4, *J* 10), 3.49 s (3H, OCH_3), 3.68 m, 3.79 m (2H, $2CH_2N$), 3.94 m, 3.98 m, 4.02 m (5H, $2CH_2N$, $3CH_2O$), 4.01 d (H, H^2, *J* 14), 4.12 m (H, CH_2O), 4.31 s (H, $H^{17'}$), 4.41 d (H, H^2, *J* 14), 4.59 q (H, H^4, *J* 10), 4.71 s (H, $H^{17'}$), 4.92 d (H, H^7, *J* 3), 5.87 C (H, H^8). ^{13}C NMR spectrum, δ, ppm: 12.25 q ($C^{20'}$), 19.53 t ($C^{2'}$), 20.40 t ($C^{12'}$), 25.01 t ($C^{11'}$), 25.84 t ($C^{6'}$), 28.41 q ($C^{19'}$), 34.88 t (C^6), 37.72 t ($C^{3'}$), 38.22 t ($C^{7'}$), 38.73 t ($C^{1'}$), 39.87 C ($C^{4'}$), 41.44 d (C^5), 43.89 s ($C^{10'}$), 50.79 q (OCH_3), 54.69 d (C^9), 55.63 d ($C^{5'}$), 61.97 t, 62.05 t (CH_2), 62.48 t (C^2), 64.07 t (C^4), 80.25 d (C^7), 95.04 s (C^1), 105.99 t ($C^{17'}$), 128.33 d (C^8), 147.35 s, 147.55 s ($C^{9,8'}$), 177.38 s ($C^{18'}$). Found, %: C 62.89; H 7.73; Br 13.94; N 2.27. $C_{29}H_{44}BrNO_4$. Calculated, %: C 63.27; H 8.00; Br 14.55; N 2.54.

Compound X. Data obtained from the spectrum of the mixture of compounds **XI** and **X**. Characteristic signals of isomer **X** in the ^{1}H NMR spectrum, δ, ppm: 2.79 m (H, H^5), 4.39 s, 4.79 s (2H, $2H^{17'}$), 4.74 s (H, $H^{17'}$), 4.98 s (H, H^7), 5.89 s (H, H^8).

11(*S*)- and 11(*R*)- 14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-15-oxa-3-azoniatricyclo[9.4.0.1^{1,12}]hexadec-13-ene bromides (XII, XIII). *e*. To a solution of 0.2 g (0.39 mmol) of aminoterpene **III** in a mixture acetonitrile–water, 1:1, was added at stirring 0.09 g (1.56 mmol) of KOH and 0.05 g (0.39 mmol) of K_2CO_3. The reaction mixture was boiled for 30 min, then 0.09 g (0.78 mmol) of allyl bromide was added, and the boiling was continued for 6 h more (TLC monitoring) till the initial compound was completely consumed. On cooling to room temperature the precipitate was filtered off and washed

with acetonitrile (10 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$. The solvent was evaporated. According to ^1H NMR data, the residue contained a mixture of isomers **XII** and **XIII**.

The reaction of aminoterpenoid **III** with allyl bromide in conditions of procedure *a* (boiling for 8 h) afforded a mixture of compounds **XII** and **XIII** in an overall yield 60%. By crystallization of the adducts mixture from ethyl acetate was isolated individual **compound XIII**, mp 180–182°C. $[\alpha]_D$ +16.9 (*c* 3.1, EtOH). IR spectrum, cm^{-1}: 887, 1620, 1643, 2945 (C=C); 1154, 1229, 1722 (C=O); 3422 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.46 s (3H, $C^{20'}H_3$), 1.00 m (H, $H^{1'}$), 1.07 m (H, $H^{3'}$), 1.13 s (3H, $C^{19'}H_3$), 1.25 m (H, $H^{5'}$), 1.45 m (H, $H^{2'}$), 1.48 m (H, $H^{12'}$), 1.57 m (H, H^6), 1.62 m (H, $H^{9'}$), 1.65 m (H, $H^{6'}$), 1.75 m (6H, $H^{1'}$, $5CH_2$), 1.76 m (H, $H^{2'}$), 1.82 (H, H^6), 1.86 (H, $H^{7'}$), 1.89 m (H, CH_2), 1.92 m (H, $H^{6'}$), 1.95 m (H, $H^{11'}$), 2.11 m (H, $H^{3'}$), 2.13 m (H, CH_2), 2.27 m (H, $H^{11'}$), 2.34 m (H, $H^{7'}$), 2.81 q (H, H^5, *J* 7), 3.18 t (H, H^4, *J* 9), 3.56 s (3H, OCH_3), 3.58 m (H, CH_2), 3.78 d (H, H^2, *J* 14), 3.87 m, 3.99 m (2H, $2CH_2$), 4.19 d (H, H^2, *J* 14), 4.28 m (H, CH_2), 4.37 s (H, $H^{17'}$), 4.62 q (H, H^4, *J* 9), 4.78 s (H, $H^{17'}$), 5.01 d (H, H^7, *J* 3), 5.95 s (H, H^8). ^{13}C NMR spectrum, δ, ppm: 12.42 q ($C^{20'}$), 19.70 t ($C^{2'}$), 20.21 t ($C^{12'}$), 20.63 t, 21.77 t, 22.08 t (CH_2), 25.24 t ($C^{11'}$), 26.02 t ($C^{6'}$), 28.58 q ($C^{19'}$), 34.28 t (C^6), 37.89 t ($C^{3'}$), 38.42 t ($C^{7'}$), 38.95 t ($C^{1'}$), 40.08 s (C^4), 41.32 d (C^5), 44.07 s ($C^{10'}$), 50.95 q (OCH_3), 55.00 d ($C^{9'}$), 55.86 d ($C^{5'}$), 63.11 t (C^2), 65.06 t (C^4), 80.43 d (C^7), 95.23 s (C^1), 106.10 t ($C^{17'}$), 128.52 d (C^8), 147.60 s, 147.77 s ($C^{9,8'}$), 177.53 s ($C^{18'}$). Found, %: C 65.18; H 8.41; Br 14.90; N 2.74. $C_{30}H_{46}BrNO_3$. Calculated, %: C 65.69; H 8.39; Br 14.60; N 2.55.

Compound XII. Data obtained from the spectrum of the mixture of compounds **XIII** and **XII**. Characteristic signals of isomer **XII** in the ^1H NMR spectrum, δ, ppm: 2.69 m (H, H^5), 3.84 d, 4.15 d (2H, $2H^2$, *J* 14 Hz), 4.81 s (H, $H^{17'}$), 5.97 s (H, H^8).

11(*S*)- and 11(*R*)-14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-11-methyl-6,15-dioxa-3-azoniatricyclo[9.4.0.1^{1,12}]-hexadec-13-ene bromides (XIV, XV). The reaction of aminoterpenoid **II** with crotyl bromide in conditions of procedure *a* (boiling for 12 h) afforded a mixture of compounds **XIV** and **XV** in an overall yield 44%. By crystallization of the adducts mixture from ethyl acetate was isolated individual **compound XV**, mp 124–126°C. $[\alpha]_D$ +13.8 (*c* 1.2, EtOH). UV spectrum, λ_{max}, nm (log ε): 657 (1.12). IR spectrum, cm^{-1}: 901, 1642, 2945 (C=C); 1130, 1154, 1229, 1721 (C=O); 3429 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.46 s (3H, $C^{20'}H_3$), 0.87 d (3H, CH_3, *J* 7), 1.01 m (H, $H^{1'}$), 1.09 m (H, $H^{3'}$), 1.13 s (3H, $C^{19'}H_3$), 1.29 m (H, $H^{5'}$), 1.49 m (3H, $H^{2',12',12'}$), 1.57 m (H, $H^{9'}$), 1.67 m (H, $H^{6'}$), 1.73 m (H, $H^{1'}$), 1.75 m (H, $H^{2'}$), 1.79 m (H, $H^{7'}$), 1.86 m (H, $H^{6'}$), 1.94 m (H, $H^{11'}$), 2.10 m (H, $H^{3'}$), 2.29 m (H, $H^{11'}$), 2.34 m (2H, $H^{5,6}$), 2.52 m (H, $H^{7'}$), 3.48 q (H, H^4, *J* 10), 3.56 s (3H, OCH_3), 3.66 m, 3.85 m (2H, $2CH_2N$), 3.89 d (H, H^2, *J* 14), 4.00 m (4H, $2CH_2N$, $2CH_2O$), 4.17 m (H, CH_2O), 4.38 C (H, $H^{17'}$), 4.50 m (H, CH_2O), 4.65 d (H, H^2, *J* 14), 4.72 q (H, H^4, *J* 11), 4.78 s, 4.79 s (2H, $H^{17',7}$), 5.93 s (H, H^8). ^{13}C NMR spectrum, δ, ppm: 12.44 q ($C^{20'}$), 16.61 q (CH_3), 19.72 t ($C^{2'}$), 20.65 t ($C^{12'}$), 25.18 t ($C^{11'}$), 26.05 t ($C^{6'}$), 28.60 q ($C^{19'}$), 37.91 t ($C^{3'}$), 38.41 t ($C^{7'}$), 38.88 t ($C^{1'}$), 40.05 s (C^4), 44.09 s ($C^{10'}$), 44.54 d (C^5), 49.57 q (OCH_3), 50.96 d (C^6), 54.80 d ($C^{9'}$), 55.81 d ($C^{5'}$), 62.07 t, 62.10 t ($C^{2,4}$), 62.74 t (NCH_2), 64.05 t (OCH_2), 83.74 d (C^7), 96.19 s (C^1), 106.10 t ($C^{17'}$), 125.89 d (C^8), 147.84 s, 149.30 s ($C^{9,8'}$), 177.63 s ($C^{18'}$). Found, %: C 63.68; H 7.98; Br 13.95; N 2.25. $C_{30}H_{46}BrNO_4$. Calculated, %: C 63.83; H 8.15; Br 14.18; N 2.48.

Compound XIV. Data obtained from the spectrum of the mixture of compounds **XIV** and **XV**. Characteristic signals of isomer **XIV** in the ^1H NMR spectrum, δ, ppm: 4.00 d, 4.62 d (2H, $2H^2$, *J* 14 Hz), 4.41 s, 4.91 s (2H, $2H^{17'}$), 5.95 s (H, H^8).

11(*S*)- and 11(*R*)-14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-11-methyl-15-oxa-3-azoniatricyclo[9.4.0.1^{1,12}]-hexadec-13-ene bromides (XVI, XVII). The reaction of aminoterpenoid **III** with crotyl bromide in conditions of procedure *a* (boiling for 20 h) afforded a mixture of compounds **XVI** and **XVII** in an overall yield 61% (in 1:1 ratio). mp 47–50°C. IR spectrum, cm^{-1}: 1625, 1643, 2947 (C=C); 1132, 1229, 1721 (C=O); 3425 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.45 s (6H, $2C^{20'}H_3$), 0.83 d (6H, $2CH_3$, *J* 7), 0.98 m (2H, $2H^{1'}$), 1.05 m (2H, $2H^{3'}$), 1.12 s (6H, $2C^{19'}H_3$), 1.24 m (2H, $2H^{5'}$), 1.50 m (4H, $2H^{2',12'}$), 1.62 m (6H, $2H^{9',6',12'}$), 1.78 m (16H, $2H^{1',2',7'}$, $10CH_2$), 1.83 m (2H, $2H^{6'}$), 1.89 m (2H, $2H^{11'}$), 2.10 m (4H, $2H^{3'}$, $2CH_2$), 2.28 m (2H, $2H^{11'}$), 2.41 m (6H, $2H^{5,6,7'}$), 3.22 t (2H, $2H^4$, *J* 10), 3.54 s (6H, $2OCH_3$), 3.60 m, 3.70 m, 3.84 m, 4.07 m (8H, $8CH_2$), 3.66 d (H, H^2, *J* 14), 3.69 d, 4.12 d (H, H^2, *J* 14, XVI), 4.16 d (H, H^2, *J* 14), 4.35 s (2H, $2H^{17'}$), 4.62 t (2H, $2H^4$, *J* 10),

4.79 s (4H, 2H$^{17',7}$), 5.93 s (H, H^{8}), 5.96 s (H, H^{8}, **XVI**). ^{13}C NMR spectrum, δ, ppm: 12.33 q and 12.41 q (C$^{20'}$), 16.32 q (CH_3), 19.74 t (C$^{2'}$), 20.18 t, 21.28 t, 21.65 t, 22.07 t (CH_2), 20.84 t (C$^{12'}$), 24.99 t (C$^{11'}$), 26.01 t (C$^{6'}$), 28.56 q (C$^{19'}$), 37.93 t (C$^{3'}$), 38.44 t (C$^{7'}$), 39.01 t (C$^{1'}$), 40.10 s and 40.19 s (C$^{4'}$), 42.69 d and 42.94 d (C^{5}), 44.11 s (C$^{10'}$), 49.30 d, 49.41 d (C^{6}), 50.88 q (OCH_3), 55.00 d and 55.23 d (C$^{9'}$), 55.99 d (C$^{5'}$), 62.63 t and 62.79 t (C^{2}), 64.68 t (C^{4}), 83.83 d (C^{7}), 96.08 s (C^{1}), 106.71 t (C$^{17'}$), 126.31 d (C^{8}), 147.69 s, 147.87 s, 148.65 s (C$^{9,8'}$), 177.43 s (C$^{18'}$). Found, %: C 65.98; H 8.33; Br 13.96; N 2.34. $C_{31}H_{48}BrNO_3$. Calculated, %: C 66.19; H 8.54; Br 14.23; N 2.49.

***N*,*N*-Dimethyl-*N*-methallyl-*N*-[18-methoxycarbonyl-15,16-epoxy-8(17),13(16),14(15)-labdatrien-16-ylmethyl]ammonium bromide (XVIII).** To a solution of 0.5 g (1.05 mmol) aminoterpene **III** in 20 ml of acetonitrile was added at stirring 0.24 g (4.20 mmol) of KOH, 0.15 g (1.05 mmol) of K_2CO_3, and 0.11 g (0.58 mmol) of benzyltrimethylammonium chloride. The reaction mixture was boiled for 30 min, then 0.29 g (2.10 mmol) of crotyl bromide was added, and the boiling was carried on for 10 h (no cyclization products were detected by TLC). The reaction mixture was cooled to room temperature, the precipitate was filtered off and washed with acetonitrile (30 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography on aluminum oxide. Crystallization from ethyl acetate afforded 0.28 g (59%) of salt **XVIII**, mp 152–155°C. $[\alpha]_D$ +9.4 (*c* 3.2, EtOH). UV spectrum, λ_{max}, nm (log ε): 238 (3.96). IR spectrum, cm^{-1}: 981, 1642, 2933 (C=C); 1155, 1384, 1722 (C=O); 3428 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.43 s (3H, C^{20}H$_3$), 0.99 m (2H, H^{1,3}), 1.06 s (3H, C^{19}H$_3$), 1.21 m (H, H^{5}), 1.41 m (H, H^{2}), 1.58 m (3H, H^{9,12,12}), 1.68 m (H, H^{1}), 1.73 m (H, H^{7}), 1.78 d (4H, H^{6}, C$^{6'}$, H$_3$, *J* 7), 1.89 m (H, H^{6}), 2.07 d (H, H^{3}, *J* 13), 2.31 m (H, H^{11}), 2.49 m (H, H^{7,11}), 3.11 s [6H, $(CH_3)_2$N], 3.53 s (3H, OCH_3), 4.19 d (2H, 2H$^{1'}$, *J* 7), 4.48 s (2H, 2H^{17}), 4.60 s (2H, 2H$^{3'}$), 4.84 s (2H, 2H^{17}), 5.58 m (H, H^{5}), 6.23 m (H, H$^{4'}$), 6.32 d (H, H^{14}, *J* 1.5), 7.41 d (H, H^{15}, *J* 1.5). ^{13}C NMR spectrum, δ, ppm: 12.36 q (C^{20}), 18.21 q (CH_3), 19.67 t (C^{2}), 22.93 t (C^{12}), 23.75 t (C^{11}), 26.01 t (C^{6}), 28.49 q (C^{19}), 37.79 t (C^{3}), 38.39 t (C^{7}), 38.72 t (C^{1}), 40.03 C (C^{4}), 44.05 c (C^{10}), 49.04 q and 49.15 q [2N$(CH_3)_2$], 50.88 q (OCH_3), 54.55 d (C^{9}), 55.72 d (C^{5}), 57.10 t (C$^{1'}$), 65.63 t (C$^{3'}$), 106.29 t (C^{17}), 111.90 d (C^{14}), 117.12 d (C$^{4'}$), 131.30 s (C^{13}), 138.06 s (C^{16}), 142.56 d (C^{15}), 142.57 t (C$^{5'}$), 147.73 s (C^{8}), 177.48 s (C^{18}). Found, %: C 64.19; H 8.55; Br 15.12; N 2.53. $C_{28}H_{44}BrNO_3$. Calculated, %: C 64.24; H 8.41; Br 15.30; N 2.68.

***N*,*N*-Dimethyl-*N*-β-methallyl-*N*-[18-methoxycarbonyl-15,16-epoxy-8(17),13(16),14(15)-labdatrien-16-ylmethyl]ammonium bromide (XIX).** The reaction of labdanoid **I** with methallyl bromide under conditions used in preparation of salt **XVIII** (boiling for 51 h) afforded salt **XIX** in a 20% yield, mp 62–65°C. $[\alpha]_D$ +23.4 (*c* 3.1, EtOH). λ_{max}, nm (log ε): 202 (3.08). IR spectrum, cm^{-1}: 1643, 2945, (C=C); 1208, 1722 (C=O), 3427 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.43 s (3H, C^{20}H$_3$), 0.99 m (2H, H^{1,3}), 1.06 s (3H, C^{19}H$_3$), 1.20 m (H, H^{5}), 1.43 m (H, H^{2}), 1.57 m (3H, H^{9,12,12}), 1.72 m (4H, H^{1,7,6,2}), 1.91 m (H, H^{6}), 1.97 s (3H, CH_3), 2.07 d (H, H^{3}, *J* 13), 2.34 m (H, H^{11}), 2.49 m (2H, H^{7,11}), 3.11 s [6H, $(CH_3)_2$N], 3.54 s (3H, OCH_3), 4.22 s (2H, 2H$^{1'}$), 4.49 s (H, 2H^{17}), 4.68 s (2H, 2H$^{3'}$), 4.84 s (H, 2H^{17}), 5.49 s (2H, 2H$^{5'}$), 6.33 d (H, H^{14}, *J* 1.5), 7.43 d (H, H^{15}, *J* 1.5). ^{13}C NMR spectrum, δ, ppm: 12.49 q (C^{20}), 19.82 t (C^{2}), 23.04 t (C^{12}), 23.78 t (C^{11}), 23.89 q (CH_3), 26.15 t (C^{6}), 28.59 q (C^{19}), 37.93 t (C^{3}), 38.51 t (C^{7}), 38.81 t (C^{1}), 40.16 C (C^{4}), 44.19 c (C^{10}), 49.86 q [2N$(CH_3)_2$], 50.96 q (OCH_3), 54.72 d (C^{9}), 55.85 d (C^{5}), 58.78 t (C$^{1'}$), 69.86 t (C$^{3'}$), 106.36 t (C^{17}), 111.06 d (C^{14}), 128.20 t (C$^{4'}$), 131.84 s (C^{13}), 133.20 s (C$^{4'}$), 137.95 s (C^{16}), 142.56 d (C^{15}), 147.86 s (C^{8}), 177.58 s (C^{18}). Found, %: C 70.03; H 9.27; Cl 8.13; N 2.91. $C_{28}H_{44}ClNO_3$. Calculated, %: C 70.37; H 9.21; Cl 7.43; N 2.93.

***endo*- and *exo*-3,3-Dimethyl-9-[18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-10-oxa-3-azoniatricyclo[5.2.1.0^{1,5}]deca-5,8-diene bromides (XX, XXI)**. To a solution of 0.5 g (1.05 mmol) of compound **I** in 20 ml of acetonitrile was added at stirring 0.24 g (4.20 mmol) of KOH, 0.15 g (1.05 mmol) of K_2CO_3, and 0.11 g (0.58 mmol) of benzyltrimethylammonium chloride. The reaction mixture was boiled for 30 min, then 0.25 g (2.10 mmol) of propargyl bromide was added, and the boiling was continued for 2 h more (TLC monitoring) till complete disappearance of the initial compound. The reaction mixture was cooled to room temperature, the precipitate was filtered off and washed with acetonitrile (30 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$, the solvent was evaporated, and the residue was subjected to column chromatography to isolate 0.29 g (66%) of a mixture of compounds **XX** and **XXI** in a 1:1 ratio, mp 35–38°C. UV

spectrum, λ_{max}, nm (log ε): 256 (2.98), 263 (3.02). IR spectrum, cm^{-1}: 752, 1642, 2945 (C=C); 1155, 1722 (C=O); 3423 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.39 s (6H, $2C^{20'}H_3$), 0.92 m, 0.95 m (4H, $2H^{1',3'}$), 1.07 s (6H, $2C^{19'}H_3$), 1.20 m (2H, $2H^{5'}$), 1.44 m (6H, $2H^{2',12',12'}$), 1.56 m (2H, $2H^{9'}$), 1.64 m (2H, $2H^{6'}$), 1.67 m (2H, $2H^{1'}$), 1.70 m (2H, $2H^{2'}$), 1.77 m, 1.80 m (2H, $2H^{7'}$), 1.87 m, 1.89 m (4H, $2H^{6',6'}$), 1.94 d (2H, $2H^2$, *J* 15), 2.05 m (2H, $2H^{3'}$), 2.26 m, 2.29 m (2H, $2H^{7'}$), 2.36 m (2H, $2H^{11'}$), 2.66 m, 2.67 m (2H, $2H^4$), 3.49 s (6H, $2OCH_3$), 3.66 s, 3.67 s, 3.77 s [12H, $4(CH_3)_2N$], 3.92 d, 3.96 d (2H, $2H^2$, *J* 15), 4.20 s, 4.32 s (2H, $2H^{17'}$), 4.51 d, 4.62 d (2H, $2H^4$, *J* 15), 4.70 s, 4.74 s (2H, $2H^{17'}$), 5.13 s (2H, $2H^7$), 6.23 s (2H, $2H^8$), 6.93 s, 6.96 s (2H, $2H^6$). ^{13}C NMR spectrum, δ, ppm: 12.30 q and 12.32 q ($C^{20'}$), 19.61 t and 19.64 t ($C^{2'}$), 20.89 t and 20.92 t ($C^{12'}$), 25.20 t and 25.29 t ($C^{11'}$), 25.89 t and 25.93 t ($C^{6'}$), 28.51 q and 28.53 q ($C^{19'}$), 30.54 t and 30.60 t (C^4), 37.84 t ($C^{3'}$), 38.34 t ($C^{7'}$), 38.90 t and 39.04 t ($C^{1'}$), 40.08 s and 40.12 s ($C^{4'}$), 44.00 s ($C^{10'}$), 50.94 q (OCH_3), 54.97 d and 55.16 d ($C^{9'}$), 55.82 d and 55.88 s ($C^{5'}$), 56.73 q, 56.76 q, 56.80 q and 56.89 q [$N(CH_3)_2$], 66.19 t and 66.21 t (C^2), 81.90 d and 81.90 d (C^7), 97.33 c and 97.37 C (C^1), 106.06 t 106.53 t ($C^{17'}$), 127.76 d and 127.87 d (C^8), 131.83 d and 132.09 d (C^6), 140.42 s and 140.62 s (C^5), 145.63 s and 145.92 s ($C^{8'}$), 147.26 s and 147.80 s (C^9), 177.40 s and 177.44 s ($C^{18'}$). Found, %: C 63.96; H 8.17; Br 15.30; N 2.71. $C_{27}H_{40}BrNO_3$. Calculated, %: C 64.03; H 7.91; Br 15.81; N 2.77.

***endo*- and *exo*-14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-11-methyl-6,15-dioxa-3-azoniatricyclo[9.4.0.1^{1,12}]-hexadeca-10,13-diene bromides (XXII, XXIII)**. The reaction of oxalate **II** with propargyl bromide under conditions used in preparation of compounds **XX** and **XXI** within 2 h afforded compounds **XXII** and **XXIII** in an overall yield 18% (at a ratio 1:1), mp 96–102°C. UV spectrum, λ_{max}, nm (log ε): 238(3.32), 255 (3.14), 262 (2.11), 270 (3.07). IR spectrum, cm^{-1}: 920, 984, 2947 (C=C); 1155, 1203, 1721 (C=O); 3431 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.47 s (6H, $2C^{20'}H_3$), 1.02 m (4H, $2H^{1',3'}$), 1.14 s (6H, $2C^{19'}H_3$), 1.26 m (2H, $2H^{5'}$), 1.50 m (6H, $2H^{2',12',12'}$), 1.65 m (2H, $2H^{9'}$), 1.72 m (2H, $2H^{6'}$), 1.75 m (2H, $2H^{1'}$), 1.77 m (2H, $2H^{2'}$), 1.80 m (2H, $2H^{7'}$), 1.94 m (2H, $2H^{6'}$), 1.97 m (2H, $2H^{11'}$), 2.04 d (2H, $2H^2$, *J* 16), 2.12 m (2H, $2H^{3'}$), 2.35 m (2H, $2H^{7'}$), 2.41 m (2H, $2H^{11'}$), 2.81 m (2H, $2H^4$, *J* 14), 3.57 s (6H, $2OCH_3$), 3.88 m, 4.12 m (4H, $4CH_2N$), 4.18 m (12H, $4CH_2N$, $6CH_2O$, $2H^2$), 4.26 m (2H, $2CH_2O$), 4.29 s, 4.41 s (2H, $2H^{17'}$), 4.58 d, 4.75 d (2H, $2H^4$, *J* 14), 4.79 s, 4.81 s (2H, $2H^{17'}$), 5.21 d (2H, $2H^7$, *J* 3), 6.31 s (2H, $2H^8$), 7.41 s, 7.46 s (2H, $2H^6$). ^{13}C NMR spectrum, δ, ppm: 12.35 q and 12.38 q ($C^{20'}$), 19.69 t and 19.70 t ($C^{2'}$), 21.09 t and 21.28 t ($C^{11'}$), 25.13 t ($C^{12'}$), 25.95 t and 25.99 t ($C^{6'}$), 28.56 q and 28.59 q ($C^{19'}$), 30.99 t, 31.04 t (C^4), 37.90 t ($C^{3'}$), 38.41 t ($C^{7'}$), 38.96 t and 39.11 t ($C^{1'}$), 40.18 s and 40.22 s ($C^{4'}$), 44.07 s ($C^{10'}$), 51.00 q (OCH_3), 54.87 d and 54.91 d ($C^{9'}$), 55.85 d and 55.92 d ($C^{5'}$), 61,97 t, 62.02 t, 62.08 t (C^2, NCH_2), 63.15 t, 63.19 t, 63.34 t, 63.37 t (OCH_2), 82.00 d and 82.03 d (C^7), 96.45 s (C^1), 106.16 t and 106.46 t ($C^{17'}$), 132.12 d, 132.29 d ($C^{8,6}$), 145.57 s and 145.92 s ($C^{8'}$), 147.66 s, 148.05 s ($C^{5,9}$), 177.43 s and 147.46 s ($C^{18'}$). Found, %: C 63.16; H 7.87; Br 14.95; N 2.57. $C_{29}H_{42}BrNO_4$. Calculated, %: C 63.50; H 7.66; Br 14.60; N 2.55.

***endo*- and *exo*-14-[18'-Methoxycarbonyl-13',14',15',16'-tetranorlabda-8'(17')-en-12'-yl]-15-oxa-3-azoniatricyclo[9.4.0.1^{1,12}]hexadeca-10,13-diene bromides (XXIV, XXV)**. The reaction of oxalate **III** with propargyl bromide under conditions used in the process with oxalate **II** within 3 h afforded compounds **XXIV** and **XXV** in and overall yield 58%, mp 53–56°C (for the 1:1 mixture). IR spectrum, cm^{-1}: 1625, 1643, 2944 (C=C); 1154, 1229, 1721 (C=O); 3426 (N^+R_4). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.47 s (6H, $2C^{20'}H_3$), 1.00 m (4H, $2H^{1',3'}$), 1.24 s (6H, $2C^{19'}H_3$), 1.21 m, 1.25 m (2H, $2H^{5'}$), 1.48 m (4H, $2H^{2',12'}$), 1.61 m (2H, $2H^{9'}$), 1.72 m (2H, $2H^{6'}$), 1.75 m (2H, $2H^{1'}$), 1.77 m (2H, $2H^{2'}$), 1.80 m (2H, $2H^{7'}$), 1.86 m (12H, $2H^{6'}$, $10CH_2$), 1.96 m (2H, $2H^{11'}$), 2.01 d (2H, $2H^2$, *J* 16), 2.05 m (2H, $2CH_2$), 2.13 m (2H, $2H^{3'}$), 2.36 m (4H, $2H^{7',11'}$), 2.76 m (2H, $2H^4$, *J* 14), 3.51 m, 3.56 m, 4.35 m, 4.49 m (8H, $8CH_2$), 3.53 s (6H, $2OCH_3$), 3.75 d, 3.76 d (2H, $2H^2$, *J* 16), 4.28 d, 4.40 d (2H, $2H^4$, *J* 14), 4.31 s, 4.39 s (2H, $2H^{17'}$), 4.80 s, 4.81 s (2H, $2H^{17'}$), 5.20 d (2H, $2H^7$, *J* 3), 6.31 s (2H, $2H^8$), 7.17 s, 7.24 s (2H, $2H^6$). ^{13}C NMR spectrum, δ, ppm: 12.35 q ($C^{20'}$), 19.55 t and 19.58 t ($C^{2'}$), 19.69 t and 19.72 t ($C^{12'}$), 21.18 t, 21.47 t, 21.49 t, 21.53 t, 22.08 t (CH_2), 24.98 t and 25.08 t ($C^{11'}$), 25.96 t and 26.01 t ($C^{6'}$), 28.58 q and 28.60 q ($C^{19'}$), 30.70 t and 30.75 t (C^4), 37.90 t and 37.91 t ($C^{3'}$), 38.42 t and 38.44 t ($C^{7'}$), 39.02 t and 39.16 t ($C^{1'}$), 40.19 s and 40.25 s ($C^{4'}$), 44.08 s ($C^{10'}$), 51.03 q (OCH_3), 55.02 d and 55.06 d ($C^{9'}$), 55.94 d and 55.96 d ($C^{5'}$), 64.67 t and 64.70 t (C^2), 82.02 d and 82.03 d (C^7), 96.53 s and 96.54 s (C^1), 106.26 t and 106.31 t ($C^{17'}$), 132.27 d, 132.39 d ($C^{8,6}$), 145.53 s and 145.84 s ($C^{8'}$), 147.70 s, 147.90 s ($C^{5,9}$), 177.42 s ($C^{18'}$). Found, %: C 65.69; H 8.23; Br 13.96;

N 2.34. $C_{30}H_{44}BrNO_3$. Calculated, %: C 65.93; H 8.05; Br 14.65; N 2.56.

***N*,*N*-Dimethyl-*N*-[18-methoxycarbonyl-15,16-epoxy-8(17),13(16),14(15)-labdatrien-16-ylmethyl]-*N*-propargylammonium bromide (XXVI).** To a solution of 1.0 g (2.10 mmol) of compound **I** in 10 ml of acetonitrile was added 0.50 g (4.2 mmol) of propargyl bromide, and this mixture was boiled for 3 h. The solvent was evaporated, and the residue was subjected to chromatography on aluminum oxide to isolate 0.17 g (29%) of compound **XXVI**, mp 54–57°C. $[\alpha]_D$ +10.6 (*c* 3.0 , EtOH). UV spectrum, λ_{max}, nm (log ε): 221 (3.95). IR spectrum, cm^{-1}: 866, 1642, 2936, 3023 (C=C); 1154, 1230, 1721 (C=O); 2120 (C≡C); 3430 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.47 s (3H, $C^{20}H_3$), 1.03 m (2H, $H^{1,3}$), 1.14 s (3H, $C^{19}H_3$), 1.29 m (H, H^5), 1.48 m (H, H^2), 1.57 m (3H, $H^{9,12,12}$), 1.63 m (H, H^1), 1.72 m (2H, $H^{7,2}$), 1.79 m, 1.95 m (2H, $2H^6$), 2.09 d (H, H^3), 2.35 m (H, H^{11}), 2.59 m (2H, $H^{7,11}$), 2.89 s (1H, $H^{5'}$), 3.40 s [6H, $(CH_3)_2N$], 3.57 s (3H, OCH_3), 4.54 s (H, H^{17}), 4.89 s (H, H^{17}), 4.93 m (2H, $2H^{1'}$), 5.00 d (2H, $2H^{3'}$, *J* 2), 6.36 s (H, H^{14}, *J* 2), 7.47 d (H, H^{15}, *J* 2). Found, %: C 63.64; H 7.89; Br 14.68; N 2.83. $C_{27}H_{40}BrNO_3$. Calculated, %: C 64.03; H 7.91; Br 15.81; N 2.77.

5(*S*)- and 5(*R*)-3,3-Dimethyl-9-[8'(*S*)-methyl-18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-12'-yl]-10-oxa-3-azoniatricyclo[5.2.1.0^{1,5}]dec-8-ene bromides (XXVII, XXVIII). To a solution of 0.5 g (1.04 mmol) of compound **IV** in 20 ml of acetonitrile was added at stirring 0.23 g (4.18 mmol) of KOH, 0.14 g (1.04 mmol) of K_2CO_3, and 0.11 g (0.57 mmol) of benzyltrimethylammonium chloride. The reaction mixture was boiled for 30 min, then 0.25 g (2.08 mmol) of allyl bromide was added, and the boiling was continued for 6 h more (TLC monitoring) till complete disappearance of the initial compound. The reaction mixture was cooled to room temperature, the precipitate was filtered off and washed with acetonitrile (30 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography on aluminum oxide to isolate 0.31 g (58%) of a mixture of compounds **XXVII** and **XXVIII** in a 1:1 ratio, mp 185–187°C. IR spectrum, cm^{-1}: 968, 1619, 2954 (C=C); 1151, 1242, 1720 (C=O); 3431 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.61 s (6H, $2C^{20'}H_3$), 0.78 m (2H, $2H^{1'}$), 0.84 d (6H, $2C^{17'}H$, *J* 7.2), 0.97 m (2H, $2H^{3'}$), 1.04 m (6H, $2H^{5',9',7'}$), 1.11 s (6H, $2C^{19'}H_3$), 1.39 m (6H, $2H^{12',6',12'}$), 1.61 m (4H, $2H^{6',6}$), 1.67 m (4H, $2H^{1',7'}$), 1.72 m (4H, $2H^{2',2}$), 1.80 m (2H, $2H^6$), 1.87 m (2H, $2H^{8'}$), 2.08 m (2H, $2H^{7'}$), 2.17 m (2H, $2H^{11'}$), 2.23 m (2H, $2H^{11'}$), 2.68 m (H, H^5, **XXVII**), 2.72 m (H, H^5), 3.25 t (2H, $2H^4$, *J* 11), 3.57 s (6H, $2OCH_3$), 3.59 s and 3.79 s (12H, $4CH_3$), 3.83 d (2H, $2H^2$, *J* 14), 4.37 d (2H, $2H^2$, *J* 14), 4.59 m (2H, $2H^4$), 5.01 d (2H, $2H^7$, *J* 3), 5.96 s (2H, $2H^8$). ^{13}C NMR spectrum, δ, ppm: 13.83 q and 13.89 q ($C^{20'}$), 14.54 q and 14.63 q ($C^{17'}$), 18.35 t ($C^{2'}$), 18.58 t ($C^{12'}$), 22.59 t and 22.73 t ($C^{11'}$), 24.20 t and 24.34 t ($C^{6'}$), 28.38 q ($C^{19'}$), 28.56 d and 28.71 d ($C^{8'}$), 33.34 t (C^6), 34.31 t ($C^{7'}$), 37.61 t ($C^{3'}$), 38.14 C and 38.20 C ($C^{4'}$), 39.41 t ($C^{1'}$), 42.67 d (C^5), 43.47 s and 43.57 s ($C^{10'}$), 50.71 q (OCH_3), 51.32 d and 51.59 d ($C^{9'}$), 55.51 q (CH_3), 56.84 d and 56.87 d (C^5), 66.53 t and 66.59 t (C^2), 72.03 t and 72.11 t (C^4), 80.15 d (C^7), 96.03 s and 96.08 s (C^1), 128.38 d and 128.62 d (C^8), 147.17 s and 147.30 s (C^9), 177.60 s ($C^{18'}$). Found, %: C 63.17; H 8.38; Br 16.10; N 2.76. $C_{27}H_{44}BrNO_3$. Calculated, %: C 63.52; H 8.63; Br 15.69; N 2.74.

11(*S*)- and 11(*R*)-14-[8'(*S*)-Methyl-18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-12'-yl]-6,15-dioxa-3-azoniatricyclo[9.4.0.1^{1,12}]hexadec-13-ene bromides (XXIX, XXX). The reaction of oxalate **V** with allyl bromide under the above conditions (boiling for 10 h) afforded compounds **XXIX** and **XXX** in an overall yield 56% (at a ratio 1:1), mp 175–177°C. IR spectrum, cm^{-1}: 1126, 1193, 1384, 1722 (C=O); 1620, 2949 (C=C); 3427 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62 s (6H, $2C^{20'}H_3$), 0.82 m (2H, $2H^{1'}$), 0.85 d (6H, $2C^{17'}H$, *J* 7.2), 0.99 m (2H, $2H^{3'}$), 1.06 m (6H, $2H^{5',9',7'}$), 1.13 s (6H, $2C^{19'}H_3$), 1.40 m (6H, $2H^{12',6',12'}$), 1.63 m (4H, $2H^{6',6}$), 1.71 m (8H, $2H^{1',7',2',2'}$), 1.80 m (2H, $2H^6$), 1.90 m (2H, $2H^{8'}$), 2.06 m (2H, $2H^{7'}$), 2.13 m (2H, $2H^{11'}$), 2.29 m (2H, $2H^{11'}$), 2.93 m (2H, $2H^5$), 3.41 t (2H, $2H^4$, *J* 11), 3.59 s (6H, $2OCH_3$), 3.67 m (2H, NCH_2), 3.77 m (2H, NCH_2), 3.96 m, 4.04 m (8H, $2NCH_2$, $2OCH_2$), 4.04 d (2H, $2H^2$, *J* 14), 4.11 d (2H, $2H^2$, *J* 14), 4.25 m (2H, $2OCH_2$), 4.57 m (4H, $2H^4$, $2OCH_2$), 5.01 d (2H, $2H^7$, *J* 3), 5.95 s (2H, $2H^8$). ^{13}C NMR spectrum, δ, ppm: 14.07 q and 14.14 q ($C^{20'}$), 14.83 q ($C^{17'}$), 18.64 t ($C^{11'}$), 18.87 t ($C^{2'}$), 22.89 t and 23.09 t ($C^{12'}$), 24.24 t and 24.48 t ($C^{6'}$), 28.61 q ($C^{19'}$), 28.75 d and 28.95 d ($C^{8'}$), 34.61 t, 34.86 t ($C^{7',6}$), 37.89 t ($C^{3'}$), 38.40 s and 38.47 s ($C^{4'}$), 39.65 t ($C^{1'}$), 41.47 d (C^5), 43.74 s ($C^{10'}$), 50.88 q (OCH_3), 51.44 d and 51.88 d ($C^{9'}$), 57.15 d ($C^{5'}$), 62.27 t (CH_2), 62.60 t (C^2), 63.75 t (CH_2), 64.21 t (C^4), 80.44 d (C^7), 95.29 C and 95.36 C (C^1), 128.55 d and 128.92 d

(C^{8}), 147.57 s and 147.74 s (C^{9}), 177.83 s ($C^{18'}$). Found, %: C 63.73; H 8.33; Br 14.50; N 2.66. $C_{29}H_{46}BrNO_4$. Calculated, %: C 63.04; H 8.38; Br 14.49; N 2.66.

14-[8'(*S*)-Methyl-18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-12'-yl]-15-oxa-3-azoniatricyclo[9.4.0.1^{1,12}]hexadec-13-ene bromides (XXXI, XXXII). The reaction of oxalate **VI** with allyl bromide under the conditions used in preparation of substances **XXVII** and **XXVIII** (boiling for 5 h) afforded compounds **XXXI** and **XXXII** in an overall yield 50% (at a ratio 1:1), mp 155–158°C. IR spectrum, cm^{-1}: 1151, 1190, 1226, 1226, 1384, 1723 (C=O); 1626, 2949 (C=C); 3429 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62 s (6H, $2C^{20'}H_3$), 0.81 m (2H, $2H^{1}$), 0.86 d (6H, $2C^{17'}H$, *J* 7.2), 0.98 m (2H, $2H^{3'}$), 1.05 m (4H, $2H^{5',9',7'}$), 1.23 s (6H, $2C^{19'}H_3$), 1.40 m (6H, $2H^{12',6',12'}$), 1.63 m (4H, $2H^{6',6}$), 1.69 m (16H, $2H^{1',7'}$, $12CH_2$), 1.74 m (4H, $2H^{2',2'}$), 1.81 m (2H, $2H^{6}$), 1.87 m (2H, $2H^{8'}$), 2.06 m (2H, $2H^{7'}$), 2.13 m (2H, $2H^{11'}$), 2.29 m (2H, $2H^{11'}$), 2.82 m (H, H^{5}, **XXXI**), 2.86 m (H, H^{5}), 3.19 t (2H, $2H^{4}$, *J* 11), 3.58 s (6H, $2OCH_3$), 3.65 s, 3.83 s, 4.17 s, 4.61 s (10H, $10CH_2$), 3.81 d, 3.83 d (2H, $2H^{2}$, *J* 14), 4.33 d (2H, $2H^{2}$, *J* 14), 4.61 m (2H, $2H^{4}$), 4.99 d (2H, $2H^{7}$, *J* 3), 5.95 s (2H, $2H^{8}$). ^{13}C NMR spectrum, δ, ppm: 13.96 q and 14.04 q ($C^{20'}$), 14.67 q and 14.77 q ($C^{17'}$), 18.51 t ($C^{11'}$), 18.75 t ($C^{2'}$), 20.13 t, 21.78 t, 22.00 t (CH_2), 22.88 t and 23.06 t ($C^{12'}$), 24.51 t and 24.75 t ($C^{6'}$), 28.51 q ($C^{19'}$), 28.70 d and 28.91 d ($C^{8'}$), 34.21 t, 34.48 t ($C^{7',6}$), 37.76 t and 37.79 t ($C^{3'}$), 38.30 s and 38.38 s ($C^{4'}$), 39.57 t and 39.60 t ($C^{1'}$), 41.37 d (C^{5}), 43.64 s ($C^{10'}$), 50.79 q (OCH_3), 51.49 d and 51.89 d ($C^{9'}$), 57.00 d and 57.07 d ($C^{5'}$), 63.24 t (C^{2}), 65.10 t (C^{4}), 80.27 d and 80.30 d (C^{7}), 95.17 s and 95.21 s (C^{1}), 128.55 d and 128.84 d (C^{8}), 147.47 s and 147.59 s (C^{19}), 177.71 s ($C^{18'}$). Found, %: C 65.37; H 8.74; Br 14.39; N 2.39. $C_{30}H_{48}BrNO_3$. Calculated, %: C 65.45; H 8.73; Br 14.55; N 2.54.

***N*,*N*-Dimethyl-*N*-[8(*S*)-methyl-19-methoxycarbonyl-15,16-epoxy-13(16),14-labdadien-16-ylmethyl]-*N*-propargylammonium bromide (XXXIII).** To a solution of 0.5 g (1.04 mmol) of compound **IV** in 20 ml of acetonitrile was added at stirring 0.23 g (4.18 mmol) of KOH, 0.14 g (1.04 mmol) of K_2CO_3, and 0.11 g (0.57 mmol) of benzyltrimethylammonium chloride. The reaction mixture was boiled for 30 min, then 0.25 g (2.08 mmol) of propargyl bromide was added, and the boiling was continued for 1 h 30 min. The reaction mixture was cooled to room temperature, the precipitate was filtered off and washed with acetonitrile (30 ml). The combined organic solutions were washed with water (3×10 ml) and dried over $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography on aluminum oxide to isolate in succession 0.160 g (30%) of salt **XXXIII** (eluent chloroform–methanol, 50:1) and 0.053 g (10%) of a mixture of cycloaddition products **XXXIV** and **XXXV** (eluent chloroform–methanol, 20:1).

Compound (XXXIII), mp 44–46°C. UV spectrum, λ_{max}, nm (log ε): 663 (2.63), 270 (2.63). IR spectrum, cm^{-1}: 1626, 2949 (C=C); 1152, 1227. 1384, 1720 (C=O); 2124 (Ca"C); 3436 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.61 s (3H, $C^{20}H_3$), 0.83 m (H, H^{1}), 0.89 d (3H, H^{17}, *J* 7.2), 0.96 m (H, H^{3}), 1.01 m (2H, $H^{5,7}$), 1.07 m (H, H^{9}), 1.11 s (3H, $C^{19}H_3$), 1.40 m (3H, $H^{12,6,12}$), 1.65 m (3H, $H^{6,1,7}$), 1.79 m (2H, $H^{2,2}$), 1.96 m (H, H^{8}), 2.09 m (H, H^{7}), 2.41 m (H, H^{11}), 2.54 m (H, H^{11}), 2.90 s (H, H^{5}), 3.21 s (6H, $2CH_3$), 3.58 s (3H, OCH_3), 4.71 s (2H, $H^{1'}$), 4.88 s (2H, $H^{3'}$), 6.34 d (H, H^{14}, *J* 3), 7.44 d (H, H^{15}, *J* 3). ^{13}C NMR spectrum, δ, ppm: 14.09 q (C^{20}), 14.83 q (C^{17}), 18. 61 t (C^{11}), 18.83 t (C^{2}), 22.73 t (C^{12}), 26.25 t (C^{6}), 28.57 q (C^{19}), 28.84 d (C^{8}), 34.55 t (C^{7}), 37.83 t (C^{3}), 38.38 s (C^{4}), 39.53 t (C^{1}), 43.73 s (C^{10}), 49.69 q (CH_3), 50.85 q (OCH_3), 51.80 d (C^{9}), 53.92 t ($C^{1'}$), 57.01 d (C^{5}), 57.89 t ($C^{3'}$), 71.83 d ($C^{5'}$), 71.83 s ($C^{4'}$), 112.22 d (C^{14}), 132.38 s (C^{13}), 137.39 s (C^{16}), 143.90 d (C^{15}), 177.80 s (C^{18}). Found, %: C 63.92; H 8.49; Br 15.38; N 2.54. $C_{27}H_{42}BrNO_3$. Calculated, %: C 63.78; H 8.26; Br 15.74; N 2.76.

***endo*- and *exo*-3,3-Dimethyl-9-[8'(*S*)-methyl-18'-methoxycarbonyl-13',14',15',16'-tetranorlabda-12'-yl]-10-oxa-3-azoniatricyclo[5.2.1.0^{1,5}]deca-5,8-diene bromides (XXXIV, XXXV),** mp 52–55°C (1:1 ratio). UV spectrum, λ_{max}, nm (log ε): 241 (3.00), 274 (2.69). IR spectrum, cm^{-1}: 1151, 1384, 1722 (C=O); 1626, 2950 (C=C); 3433 (N^+R_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.63 s (6H, $2C^{20'}H_3$), 0.80 m (2H, $2H^{1'}$), 0.84 d and 0.87 d (6H, $2C^{17'}H_3$, *J* 7.2), 0.97 m (2H, $2H^{3'}$), 1.02 m (2H, $2H^{5'}$), 1.06 m (4H, $2H^{9',7'}$), 1.13 s (6H, $2C^{19'}H_3$), 1.41 m (6H, $2H^{12',6',12'}$), 1.67 m (6H, $2H^{1',7',6'}$), 1.78 m (4H, $2H^{2',2'}$), 1.84 m (2H, $2H^{8'}$), 2.03 d (2H, $2H^{2}$, *J* 15), 2.10 m (2H, $2H^{7'}$), 2.24 m (2H, $2H^{11'}$), 2.42 m (2H, $2H^{11'}$), 2.75 m 2.79 m (2H, $2H^{4}$), 3.57 s, 3.63 s [12H, $4(CH_3)_2N$], 3.59 s (6H, $2OCH_3$), 3.98 d, 4.00 d (2H, $2H^{2}$, *J* 15), 4.63 d, 4.64 d (2H, $2H^{4}$, *J* 15), 5.19 s (2H, $2H^{7}$), 6.30 s (2H, $2H^{8}$), 6.56 s (2H, $2H^{6}$). ^{13}C NMR spectrum, δ, ppm: 14.14 q ($C^{20'}$), 14.78 q ($C^{17'}$), 18.59 t ($C^{12'}$), 18.84 t ($C^{2'}$), 23.18 t and 23.27 t ($C^{11'}$), 24.67 t and 24.89 t ($C^{6'}$), 28.63 q ($C^{19'}$), 29.12 d ($C^{8'}$), 30.59 t (C^{4}), 34.51 t and 34.56 t ($C^{7'}$), 37.88 t ($C^{3'}$), 38.49 s ($C^{4'}$), 39.67 t and

39.74 t ($C^{1'}$), 43.76 s (C^{10}), 50.96 q (OCH_3), 51.79 d and 51.97 d ($C^{9'}$), 56.39 q, 56.46 q and 56.55 q (CH_3), 57.10 d and 57.14 ($C^{5'}$), 65.74 t and 65.83 t (C^{2}), 81.96 d (C^{7}), 97.63 s and 97.66 s (C^{1}), 132.29 d, 132.49 d ($C^{8,6}$), 141.31 s and 141.38 s (C^{5}), 145.86 C and 145.93 s (C^{9}), 177.83 s (C^{18}). Found, %: C 63.43; H 8.44; Br 15.48; N 2.59. $C_{27}H_{42}BrNO_3$. Calculated, %: C 63.78; H 8.26; Br 15.74; N 2.76.

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