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Synthetic Transformations of Higher Terpenoids: XIV.* Heterocyclization Reactions of 15,16,18-Ricarboxylabdadiene. New Nitrogen-Containing Diterpenoids

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Abstract—The oxidation of methyl lambertianate with Jones' reagent formed the corresponding anhydride which reacted with amines to form N-substituted terpenoid maleimides. New maleimides demonstrated high activity and stereoselectivity in the Diels–Alder reaction with cyclopentadiene. The condensation of the diterpenoid anhydride with hydrazines led to the formation of derivatives of 3,6-dioxo-1,2,3,6-tetrahydropyridazines of labdane type.

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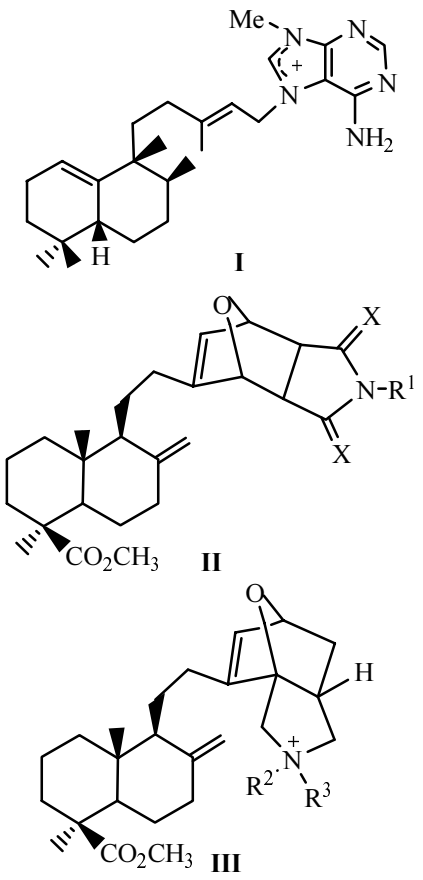
Mixed metabolites containing in their molecules covalently bonded fragments of different structural types are found in increasing numbers in natural objects. The unique structure of these so-called hybrid structures and their valuable biological activity make tham attractive models for design of molecules, promising as bioactive reagents. Among the mixed metabolites a prominent place belongs to compounds containing terpenoid moieties [2]. Apart from highly promising terpenophenols and terpenoquinones the nitrogen-containing compounds are of obvious interest. Agelasine C (**I**) in whose molecule the labdane fragment is connected to a heterocyclic ring (Scheme 1) is known as a sponge metabolite. The compound exhibits antimicrobial and malaricidal action [3]. We formerly described the synthesis of lambertian acid derivatives containing heterocyclic fragments of 10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]decene (**II**) and 10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]decene (**III**) [4, 5]. Analogs of compound **II** possss the antidepressant action [6].

We report here on an approach to new heterocyclic derivatives of labdanoids based on transformation of 15,16-epoxylabdadiene-15,16-dione (**IV**). Compound **IV** is readily obtained by oxidative transformations of methyl lambertianate (**V**).

The oxidation of furan labdanoid **V** with Jones' reagent gave rise to a mixture of the corresponding anhydride **IV**

Scheme 1.



X = H_2 or O.

* For Communication XIII see [1].

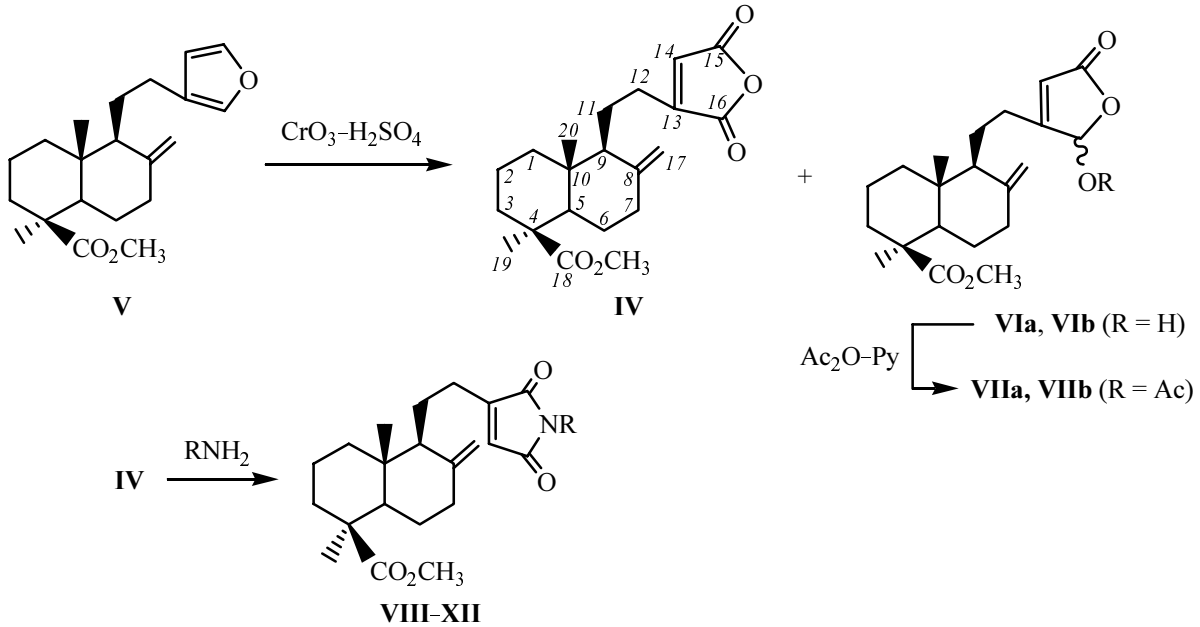
and hydroxybutenolides **VIa** and **VIb** whose ratio depended on the reaction conditions. The reaction carried out for 5 h under argon atmosphere adding 1.5 equiv furnished a mixture of anhydride **IV**, hydroxybutenolides **VIa** and **VIb**, and initial compound **V** in a ratio 1.0 : 1.0 : 1.0 : 0.7 respectively (according to the ^{1}H NMR data). At treatment with the Jones' reagent compounds **VIa** and **VIb** were quantitatively converted in labdanoid anhydride **IV**. The latter compound was obtained as the main reaction product at the use of 3.0 equiv of Jones' reagent (yield 77%). 16-Hydroxybutenolides **VIa** and **VIb** were easily isolated from the reaction mixture by column chromatography on aluminum oxide. Additional information on their structure was obtained from the NMR spectra of their 16-acetoxy derivatives **VIIa** and **VIIb**. It should be stressed that the opportunity of preparation of compounds **VIa** and **VIb** is of interest since a number of naturally occurring labdanoids with hydroxybutenolide fragment has been discovered possessing strong biological activity [7–9].

Compound **IV** by reaction with secondary amines gave new terpenyl-containing N-substituted maleimides **VIII–XII** (Scheme 2). The process was carried out by boiling a solution of anhydride **IV** and 1.2 equiv of an appropriate amine in acetic acid for 5–8 h. Yields of compounds **IX–XII** attained 48–74%. The maleimides obtained are synthetic analogs of the natural labdanoids lissoclimides produced by sea squirts (*Ascidiae*); the latter compounds possess powerful cytostatic action [10, 11].

We established that the synthesized maleimides can behave as active dienophiles in the Diels–Alder reaction (Scheme 3). The sterical course of the reaction was studied by examples of reactions of *N*-benzylmaleimide **VIII** or *N*-(1-carboxypropyl)maleimide **XI** with cyclopentadiene. The analysis of the reaction mixture of adducts showed that the reaction afforded exclusively *endo*-adducts containing a mixture of two diastereomers in a 1 : 1 ratio: **XIII** and **XIV** from compound **VIII**, and **XV** and **XVI** from dienophile **XI**. The recrystallization of the reaction mixture resulted in each case is a single individual diastereomer, **XIV** and **XV** respectively.

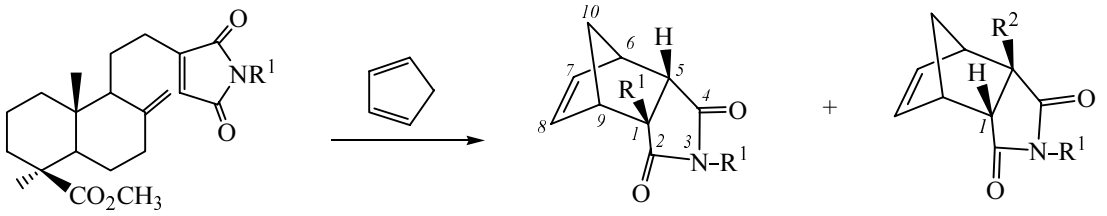
The reaction of maleic anhydride and its substituted analogs with hydrazines is an efficient procedure for pyridazinediones preparation [12–15]. The reaction of anhydride **IV** with hydrazine hydrate occurred in acetic acid at room temperature and afforded a mixture of 3,6-dioxo-1,2,3,6-tetrahydropyridazine **XVII** (yield 47%) and (*N*-amino)maleimide **XVIII** (yield 15%) separated by column chromatography (Scheme 4). The reaction of anhydride **IV** with phenylhydrazine required more stringent conditions. After boiling the reagent mixture in acetic acid were isolated as reaction products 3-hydroxy-1-phenyl-(2*H*)-pyridazin-6-one **XIX** and (*N*-anilino)maleimide **XX** in 22 and 38% yields respectively. The methylation of cyclic hydrazide **XVII** with dimethyl sulfate in an alcohol solution gave 1-methyl-3-hydroxy-(2*H*)-pyridazin-6-one **XXI** (yield 84%). Diazomethane applied as

Scheme 2.



R = Bn (**VIII**), $(CH_2)_2Ph$ (**IX**), $CH_2CH_2C_6H_4OH$-4 (**X**), $CH(CO_2H)CH_2CH_3$ (**XI**), $(CH_2)_3CO_2H$ (**XII**).

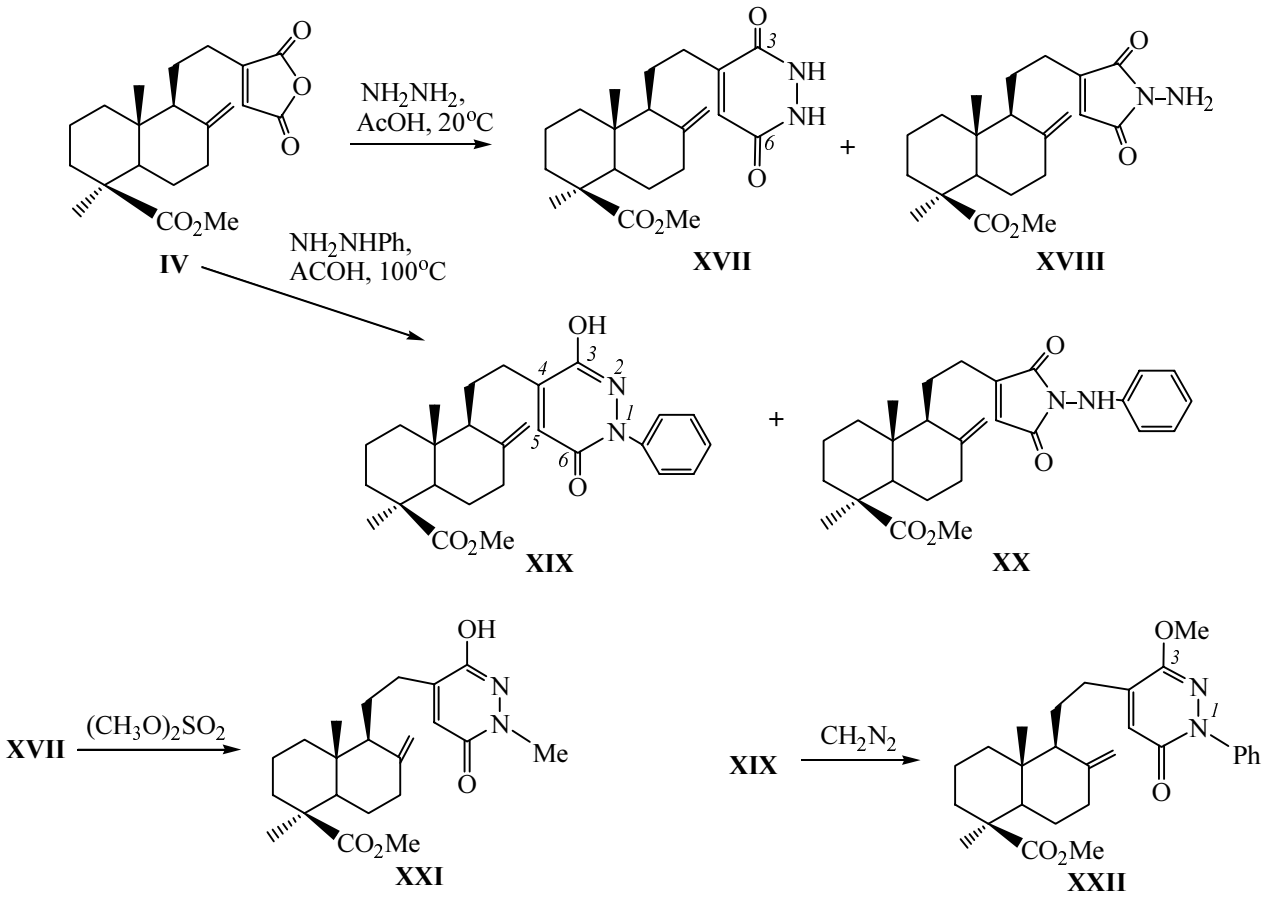
Scheme 3.



VIII, XI **XIII, XV** **XIV, XVI**

$R^1 = CH_2Ph$ (**VIII, XIII, XIV**), $CH(CO_2H)CH_2CH_3$ (**XI, XV, XVI**); R^2 = 13,14,15,16-tetranor-18-methoxycarbonyllabd-8(17)-en-12-yl.

Scheme 4.

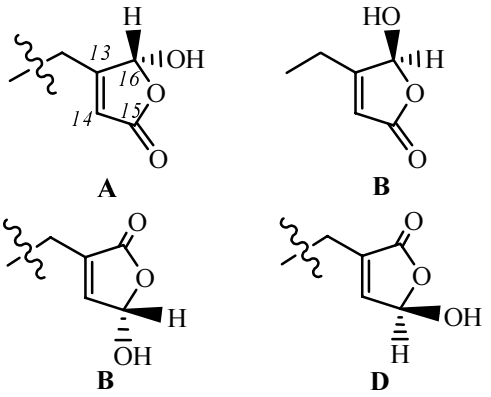


IV **XVII** **XVIII** **XIX** **XX** **XXI** **XXII**

a methylating agent led to a mixture of N-methyl-, O-methoxy-, and O-dimethoxyderivatives (according to ^{1}H NMR spectra). A structure of monolactim was ascribed to hydrazide **XIX** based on the ease of formation of a methoxy compound **XXII** in reaction with the diazomethane. A similar result was reported for the maleic acid monolactim hydrazide [16].

The structure of all compounds synthesized was established from the spectral data. In the IR spectrum of anhydride **IV** all appropriate absorption bands of carbonyl stretching vibrations are observed at 1726, 1776 (1838, overtone) cm^{-1}. The presence in the ^{1}H NMR spectrum of a triplet from the olefin proton at 6.56 ppm (H^{14}, $J_{14,12}$ 1.6 Hz) and of carbonyl signals in the ^{13}C NMR spectrum at 163.87 and 165.69 ppm confirms the existence of an anhydride ring in the structure of this compound.

The assignment to compounds **VIa** and **VIb** the structure of 16-hydroxybutenolides **A** and **B** (from the four possible structures **A**–**D)** was based on the following data.



In the ^{1}H NMR spectrum of compounds **VIa** and **VIb** are observed narrow multiplet signals at 5.78 and 5.79 ppm corresponding to H^{14} protons of each stereoisomer (the nuclei are coupled with protons H^{12}), doublets of protons H^{16} at 5.93 and 5.96 ppm coupled with the proton of the hydroxy group with constants J 7.0 and 7.1 Hz, and signals of the hydroxy group proton at 5.67 and 5.69 ppm (J 7.1 and 7.0 Hz). In the spectrum of acetates **VIIa** and **VIIb** the protons H^{16} give rise to broadebned singlets at 6.75 and 6.78 ppm. The protons H^{12} in the spectrum of compounds **VIa** and **VIb** appear as four multiplets centered at 2.10, 2.28, 2.47, and 2.59 ppm. A convincing information on the position of the hydroxy group at the atom C^{16} was obtained from the correlation spectra ^{13}C–^{13}C. The atom C^{13} is coupled with three carbon atoms: C^{16}, C^{12}, and C^{14} (J 43.9, 42.3, and 68.7 Hz respectively). The atom C^{14} is coupled with two atoms C^{13} and C^{15} (J 68.4, 65.6 Hz, respectively). The coupling constant between C^{16} and C^{13} equals 42.3 Hz. These data are consistent with those reported in [17] for 4-substituted 5-hydroxy-(5*H*)-furan-2-ones.

The characteristic feature of the ^{1}H NMR spectra of maleimides **VIII–XII**, **XVIII**, and **XX** is an upfield shift of the signal from the proton attached to C^{14} ($\Delta\delta$ 0.29–0.36 ppm) compared with its position in the spectrum of terpenoid anhydride **IV**.

The configurational assignment of terpenylnorbornenes **XIII–XVI** was established from the analysis of their ^{1}H and ^{13}C NMR spectra basing on the criteria described in the literature [18, 19]. ^{1}H NMR spectra of adduct mixtures **XIII, XIV** and **XV, XVI** contain double sets of signals from all the protons of the norbornane framework evidencing the existence of these compounds as stereoisomer mixtures. As one of the analytical criteria for revealing the *endo*- or the *exo*-configuration of isomers are utilized the chemical shifts of methine protons at atom $C^{1(5)}$: In the *endo*-isomer the $H^{5(1)}$ are *exo*-directed and appear in a weaker field, and the more upfield position of the signal is characteristic of the *exo*-isomer (*endo*-orientation of $H^{1(5)}$). This difference commonly amounts to 1.5–2.0 ppm. In our case the mentioned protons appear as doublets at 2.84 [H^5, J 4.5 Hz (**XIII**)], 2.88 [H^1, J 4.2 Hz (**XIV**)], 2.91 [H^5, J 4.3 Hz (**XV**)], 2.96 ppm [H^1, J 4.4 Hz (**XVI**)]. The other parameters sensitive to the stereochemical structure are the difference ($\Delta\delta$) in the chemical shifts of the olefin protons attached to atoms C^7 and C^8, and also of those at the nodal carbons $C^{6,9}$ ($\Delta\delta$ $H^{6,9}$). In our case the resonances of protons H^7 and H^8 are pairs of doublets of doublets at 5.89–6.04 ($\Delta\delta$ 0.15 ppm, J_{gem} 5.8 Hz), 5.82–5.97 ppm ($\Delta\delta$ 0.15 ppm, J_{gem} 5.6 Hz) (**XIII, XIV**), and 6.05–6.15 ($\Delta\delta$ 0.10 ppm, J_{gem} 5.8 Hz), 6.05–6.14 ppm ($\Delta\delta$ 0.09 ppm) (**XV, XVI**). The methine protons at atoms $C^{6,9}$ in isomers **XIII, XIV** gave rise to broadened signals at 2.83, 2.81 (H^6) and 3.28, 3.30 (H^9) ppm, and in isomers **XV, XVI**, at 2.87, 2.88 and 3.31, 3.32 ppm. Additional support to the assignment of compounds **XIII–XVI** to the *endo*-series gives the result of the NOE experiment. In the NOESY spectra the H^1 proton produces the NOE effect on the bridge protons H^{10} and on the proton from the terpene skeleton $H^{12'}$ (compound **XIV**). Irradiation of the proton H^5 produces the NOE effect on the protons of the *endo*-bridge H^{10} and on both protons on the atom $C^{17'}$ of the terpene skeleton (compound **XV**).

Hence as a result of Diels–Alder reaction of both dienophiles with the cyclopentadiene formed in each case two diastereomer adducts of *endo*-configuration. The establishment of the point where the terpenoid substituent added to the heterocyclic fragment poses a more difficult problem.

The conclusion on the structure of individual compounds **XIV** and **XV** followed from the data of the two-dimensional spectra COSY and COLOC: In the COSY ^{1}H–^{1}H spectrum of compound **XIV** the proton H^1 was coupled with the proton H^9 and not coupled with the proton H^6; in the COLOC ^{1}H–^{13}C spectrum the proton H^1 was coupled with atoms $C^{2,4,8,9,10',12'}$; in the COSY ^{1}H–^{1}H spectrum of compound **XV** the proton H^9 was coupled with the proton H^5.

The formation of hydrazinedione **XVII** in the reaction of compound **IV** with the anhydride is confirmed by the data of ^{1}H NMR spectrum containing a downfield signal at 6.56 ppm belonging to the proton at the double bond in the heterocycle. In the ^{13}C NMR spectrum the carbon atoms of the carbonyl groups in the pyridazinedione ring give rise to singlets at 161.44 and 160.55 ppm. The olefin

proton in 3-hydroxy(methoxy)-(2*H*)-pyridazin-6-ones **XIX, XXI**, and **XXII** is subjected to an upfield shift (δ 6.76–6.80 ppm). The formation of hydroxypyridazines is also confirmed by the UV spectra of the compounds where the absorption maxima are shifted to the longwave region. The readily occurring aromatization in the system of diamide **XVII** is revealed by the UV spectral data. In the course of spectrum recording from 0.1% alcoholic alkali solution the maximum of the absorption band shifted to the longwave region (λ_{max} 206 > 223, 307 > 334 nm).

The following data were taken in consideration for establishment of the mutual position of the substituents in the heterocyclic fragment of compounds **XIX**, **XXI**, and **XXII**. The close values of the chemical shifts of atoms $C^{3,4,5,6}$ in the mentioned dihydropyridazin-6-ones indicate that the diterpene moiety is linked in the same position. Enolization at the C^3 atom is proved by the data of ^{13}C NMR spectra from the analysis of the multiplicity of the carbonyl C^6 atom and of C^3 atom registered in the monoresonance mode. In the spectra of compounds **XIX**, **XXI**, and **XXII** the coupling of atom C^3 with protons H^{12} is observed, and also the splitting due to coupling with the proton H^5 (J ~10 Hz). In the spectrum of compound **XXI** registered in the mode of ^{13}C–^1H COLOC-experiment the carbon atom of the carbonyl group at C^6 was shown to be coupled with the proton of the N-methyl group.

Thus by oxidation of methyl lambertianate with Jones' reagent a selective preparation of labdane furandione was developed. Labdanoids were synthesized containing a fragment of an N-substituted maleimide, and their reactions were investigated. ThElectron impactr high activity and selectivity in the Diels–Alder reaction was demonstarated. Diterpenoids of new structural type, labdanopyridazinediones, were prepared for the first time.

EXPERIMENTAL

Mass spectra were measured on a high resolution mass spectrometer Finnigan MAT-8200 (ionizing electrons energy 70 eV, vaporizer temperature 190–250°C). IR spectra were recorded on a spectrophotometer VECTOR-22 from KBr pellets. UV absorption spectra were 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 [operating frequencies 200.13 (^1H) and 50.32 MHz (^{13}C)] and Bruker DRX-500 [operating frequencies 500.13 (^1H) and 125.76 MHz (^{13}C)] from solutions of compounds in $CDCl_3$. The assignment of signals in the NMR spectra was performed applying various types of proton-proton and carbon-proton correlation spectroscopy (COSY, COLOC), and also ^1H 2D NMR spectroscopy utilizing Overhauser effect, NOESY (for compounds **XIII**–**XVI**, and **XXV**). The specific optical rotation ($[\alpha]_{580}$) was measured on a Polamat A polarimeter or wxq-4 device (China) in ethanol and chloroform.

The reactions progress was monitored by TLC on Silufol UV-254 plates. Reaction products were isolated by column chromatography on silica gel or aluminum oxide (for hydroxybutenilides **VIa** and **VIb**), eluents chloroform–methanol 200:1, 50:1.

Jones' reagent was prepared by the known method [20].

Methyl (1*S*,4a*R*,5*S*,8a*S*)-1,4a-dimethyl-6-methylene-5-[2-(2,5-dioxo-2,5-dihydro-3-furyl)-ethyl]decahydronaphthalene-1-carboxylate [methyl 15,16-dioxo-15,16-epoxy-8(17),13-labdadien-18-oate] (IV). To a stirred solution of 1.07 g (3.2 mmol) of methyl lambertianate (**V**) in 80 ml of acetone at 0°C in an argon flow was added dropwise 2.5 ml of 3 M solution of Jones' reagent. The reaction mixture was warmed to room temperature, and the stirring was continued for 5 h. Then the reaction mixture was poured on ice, and the reaction products were extracted into ether (3×50 ml). The combined ether extracts were washed with cold water (3×50 ml), with saturated solution of NaCl (2×50 ml), and dried over Na_2SO_4. On evaporating the solvent in a vacuum we obtained 0.70 g (71%) of a chromatographically pure light-yellow oily compound **IV**. $[\alpha]_{580}$ +36.8 (*c* 11.2, $CHCl_3$). IR spectrum, cm^{-1}: 1230, 1726, 1776, 1838 (C=O); 896, 894, 1640, 3028 (C=C). ^1H NMR spectrum, δ, ppm: 0.49 s (3H, $C^{20}H_3$), 1.02 m (2H, $H^{1,3}$), 1.16 c (3H, $C^{19}H_3$), 1.28 m (1H, H^5), 1.51 m (1H, H^2), 1.59 m (2H, $H^{9,11}$), 1.79 m (5H, $H^{1,2,6,7,11}$), 1.90 m (1H, H^6), 2.14 m (1H, H^3), 2.30 m (1H, H^{12}), 2.38 m (1H, H^7), 2.62 m (1H, H^{12}), 3.58 s (3H, OCH_3), 4.50 s, 4.89 s (2H, H^{17}), 6.56 t (1H, H^{14}, J 1.6 Hz). ^{13}C NMR spectrum, δ, ppm: 12.42 q (C^{20}), 19.75 t (C^2), 21.37 t (C^6), 25.20 t, 26.04 t ($C^{11,12}$), 28.62 q (C^{19}), 37.96 t (C^3), 38.43 t (C^7), 39.08 t (C^1), 40.26 s (C^4), 44.15 s (C^{10}), 51.01 q (OCH_3), 55.56 d (C^9), 56.06 d (C^5), 106.66 t (C^{17}), 128.16 d (C^{14}), 146.97 s (C^8), 153.96 s (C^{13}), 163.87 s, 165.69 s ($C^{15,16}$), 177.40 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): 360 $[M]^+$ (16), 301 (19), 249 (36), 189 (37), 119(17), 107 (28). Found $[M]^+$ 360.19315. $C_{21}H_{28}O_5$. Calculated *M* 360.19366.

Methyl (2*S*)- and (2*R*)-(1*S*,4a*R*,5*S*,8a*S*)-5-[2-(2-hydroxy-5-oxo-2,5-dihydro-3-furyl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylates [(16*S*)- and (16*R*)-methyl 16-hydroxy-15-oxo-15,16-epoxy-8(17),13-labdadien-18-oates] (VIa and VIb). To a solution of 1.07 g (3.2 mmol) of methyl lambertianate (**V**) in 80 ml of acetone at 0°C in an argon flow while stirring was added dropwise 1.0 ml of Jones' reagent. The reaction mixture was warmed to room temperature, and the stirring was continued for 5 h. The reaction mixture was poured on ice, the reaction products were extracted into ether (3×50 ml). The combined ether extracts were washed with cold water (3×50 ml), with saturated solution of NaCl (2×50 ml), and dried over Na_2SO_4. On evaporating the solvent in a vacuum the residue was subjected to column chromatography on aluminum oxide (gradient elution with a mixture chloroform–methanol, 100:1–25:1) to isolate 0.37 g (31%) of stereoisomers of hydroxybutenolides **VIa** and **VIb** as yellow oily substance. IR spectrum, cm^{-1}: 895, 957, 978, 3030, 3100 (C=C); 1036, 1106 (C–O–C); 1215, 1647, 1718, 1762 (C=O); 3386, 3593 (OH). ^1H NMR spectrum, δ, ppm: 0.46 C (6H, $2C^{20}H_3$), 1.00 m (4H, $2H^{1,3}$), 1.13 s (6H, $2C^{19}H_3$), 1.27 m (2H, $2H^5$), 1.47 m (2H, $2H^2$), 1.59 m (4H, $2H^{9,11}$), 1.71–1.79 m (10H, $2H^{1,7,2,6,11}$), 1.94 m (2H, $2H^6$), 2.13 m (2H, $2H^3$), 2.10 m (1H, H^{12}), 2.28 m (1H, H^{12}), 2.36 m (2H, $2H^7$), 2.47 d.d.d (1H, H^{12}, *J* 17.0, 9.7, 4.2 Hz), 2.59 d.d.d (1H, H^{12}, *J* 17.0, 10.3, 4.4, 1.8 Hz), 3.57 C (6H, $2OCH_3$), 4.41 C, 4.84 C (4H, $2H^{17}$), 5.67 d, 5.69 d (2H, OH, *J* 7.0, 7.1 Hz), 5.79 m (2H, $2H^{14}$), 5.93 d, 5.96 d (2H, H^{16}, *J* 7.0, 7.1 Hz). ^{13}C NMR spectrum, δ, ppm: 12.33 q, 12.35 q (C^{20}), 19.68 t ($2C^2$), 20.68 t, 20.80 t (C^{11}), 25.96 t ($2C^6$), 26.55 t, 26.63 t (C^{12}), 28.59 q ($2C^{19}$), 37.83 t, 37.86 t (C^3), 38.35 t, 38.37 t (C^7), 38.92 t ($2C^1$), 40.10 s, 40.17 s (C^4), 44.08 s ($2C^{10}$), 51.16 q ($2OCH_3$), 55.19 d, 55.41 d (C^9), 55.90 d, 55.94 d (C^5), 98.95 d, 99.41 d (C^{16}), 106.44 t, 106.57 t (C^{17}), 116.58 d, 116.85 d (C^{14}), 147.06 s ($2C^8$), 170.55 s ($2C^{13}$), 171.93 s, 171.94 s (C^{15}), 177.82 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): 362 $[M]^+$ (16), 318 (8), 302 (12), 284 (24), 249 (15), 189 (31), 121 (100), 109 (28), 93 (20), 81 (27), 67 (13), 55 (17), 41 (16). Found $[M]^+$ 362.20840. $C_{21}H_{30}O_5$. Calculated *M* 362.20931.

Methyl (2*S*)- and (2*R*)-(1*S*,4a*R*,5*S*,8a*S*)-5-[2-(2-acetoxy-5-oxo-2,5-dihydro-3-furyl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [(16*S*)- and (16*R*)-methyl 16-acetoxy-15-oxo-15,16-epoxy-8(17),13-labdadien-18-oates] (VIIa and VIIb). To 0.25 g (0.95 mmol) of a mixture of compounds **VIa** and **VIb** was added 0.5 ml of acetic anhydride and 1 ml of pyridine. The solution was left overnight. Then the reaction mixture was poured on ice, the formed reaction product was extracted into chloroform (3×20 ml). The combined organic extracts were washed with water (4×20 ml) and dried with $MgSO_4$. The solvent was evaporated in a vacuum to obtain 0.21 g (86%) of compounds **VIIa** and **VIIb**. IR spectrum, cm^{-1}: 863, 882, 956, 997, 3084 (C=C); 1043, 1055, 1162 (C–O–C); 1211, 1227, 1648, 1717, 1767, 1780, 1810 (C=O). ^1H NMR spectrum, δ, ppm: 0.49 s (6H, $2C^{20}H_3$), 1.02 m (4H, $2H^{1,3}$), 1.15 s (6H, $2C^{19}H_3$), 1.26 m (2H, $2H^5$), 1.59 m (6H, $2H^{2,9,11}$), 1.80 m (10H, $2H^{1,7,2,6,11}$), 1.94 m (2H, $2H^6$), 2.11 s (6H, $2CH_3CO$), 2.13 m (3H, $2H^3$, 1H, H^{12}), 2.28 m (1H, H^{12}), 2.38 m (2H, $2H^7$), 2.47 m (2H, H^{12}), 3.58 C (6H, $2OCH_3$), 4.39 s, 4.42 s, 4.86 s (4H, $2H^{17}$), 5.90 br.s, 5.92 br.s (2H, $2H^{14}$), 6.75 s, 6.78 s (2H, H^{16}). ^{13}C NMR spectrum, δ, ppm: 12.26 q ($2C^{20}$), 19.63 t ($2C^2$), 19.63 q ($2CH_3CO$), 20.69 t, 20.81 t (C^6), 25.92 t ($2C^{11}$), 26.14 t, 26.23 t (C^{12}), 28.47 q ($2C^{19}$), 37.81 t ($2C^3$), 38.32 t ($2C^7$), 38.92 t ($2C^1$), 40.06 s, 40.13 s (C^4), 43.98 s ($2C^{10}$), 50.81 q ($2OCH_3$), 55.09 d, 55.29 d (C^9), 55.89 d ($2C^5$), 93.38 d, 93.89 d (C^{16}), 106.16 t, 106.25 t (C^{17}), 117.74 d ($2C^{14}$), 147.03 s, 147.12 s (C^8), 167.58 s ($2C^{13}$), 168.72 s ($2CH_3CO$), 169.60 s ($2C^{15}$), 177.814 s ($2C^{18}$). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): $[M]^+$ 404 (36), 344 (25), 312 (17), 284 (74), 249 (29), 189 (39), 121(100), 109 (32), 91 (23), 81 (32), 83 (72), 67 (18), 55 (20), 43 (15). Found $[M]^+$ 404.22417. $C_{23}H_{32}O_6$. Calculated *M* 404.21987.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-{2-[1-benzyl-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [methyl (*N*-benzyl)-15,16-dioxo-15,16-aza-8(17),13-labdadieno-18-ate] (VIII). To a solution of 0.70 g (1.9 mmol) of compound **IV** in 10 ml of acetic acid 0.23 g (2.1 mmol) of benzylamine was added. The reaction mixture was boiled for 6 h, the solvent was removed in a vacuum, and to the residue was added 10 ml of ether saturated with HCl. The separated precipitate was filtered off and dried in a vacuum to give 0.45 g (48%) of compound **VIII**, mp 104–106°C (from ether). $[\alpha]_{580}$ +4.6° (*c* 1.6, $CHCl_3$). IR spectrum, cm^{-1}: 699, 715, 725, 891, 1500, 3089 (C=C); 1694, 1700, 1718, 1769 (C=O); 1498, 1633, 3450 (C–N). ^1H NMR spectrum, δ, ppm: 0.45 s (3H, $C^{20}H_3$), 0.96 m (2H, $H^{1,3}$), 1.11 s (3H, $C^{19}H_3$), 1.22 m (1H, H^5), 1.42 m (1H, H^2), 1.56 m (2H, $H^{9,11}$), 1.72–1.83 m (5H, $H^{1,7,2,6,11}$), 1.91 d.d.d (1H, H^6, *J* 14.2, 7.3, 3.3 Hz), 2.10 m (1H, H^3, J_{gem} 13.0 Hz),

2.19 m (1H, H^{12}), 2.34 d.t (1H, H^{7}, *J* 12.8, 3.6, 2.2 Hz), 2.50 m (1H, H^{12}), 3.52 s (3H, OCH_3), 4.50 C (1H, H^{17}), 4.55 s (2H, CH_2), 4.82 s (1H, H^{17}), 6.21 s (1H, H^{14}), 7.16 m (1H, H$^{4'}$), 7.19 m (2H, H$^{3',5'}$), 7.24 m (2H, H$^{2',6'}$). ^{13}C NMR spectrum, δ, ppm: 12.11 q (C^{20}), 19.48 t (C^{2}), 21.11 t (C^{11}), 24.42 t (C^{6}), 26.74 t (C^{12}), 28.33 q (C^{19}), 37.69 t (C^{3}), 38.14 t (C^{7}), 38.69 t (C^{1}), 39.85 s (C^{4}), 40.88 t (CH_2), 43.76 s (C^{10}), 50.67 q (OCH_3), 55.14 d (C^{9}), 55.69 d (C^{5}), 106.36 t (C^{17}), 125.74 d (C^{14}), 127.22 d (C$^{3'}$), 127.86 d (C$^{2',6'}$), 128.13 d (C$^{3',5'}$), 136.13 s (C$^{1'}$), 146.79 s (C^{8}), 150.07 s (C^{13}), 170.00 s, 170.70 s (C^{15,16}), 177.94 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): [*M*]$^+$ 449 (18), 389 (18), 374 (10), 249 (12), 201(25), 189 (36), 121 (86), 91 (100), 67 (21). Found [*M*]$^+$ 449.25650. $C_{28}H_{35}NO_4$. Calculated *M* 449.25659.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-1,4a-dimethyl-6-methylene-5-{2-[2,5-dioxo-2,5-dihydro-1-phenylethyl-(1*H*)-pyrrol-3-yl]ethyl}decahydronaphthalene-1-carboxylate [methyl 15,16-dioxo-*N*-(2-phenylethyl)-15,16-aza-8(17),13-labdadien-18-oate] (IX). To a solution of 0.70 g (1.9 mmol) of compound **IV** in 10 ml of acetic acid was added 0.25 g (2.1 mmol) of 2-phenylethylamine. The reaction mixture was boiled for 6 h, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent chloroform–methanol, 200:1). We obtained 0.58 g (65%) of oily compound **IX**. $[\alpha]_{580}$ +49.1° (*c* 9.0, $CHCl_3$). IR spectrum, cm^{-1}: 700, 750, 861, 890, 1500 (C=C); 1228, 1644, 1706, 1715, 1771 (C=O); 1545, 1633, 3461 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.50 s (3H, C^{20}H$_3$), 1.02 m (2H, H^{1,3}), 1.17 s (3H, C^{19}H$_3$), 1.26 m (1H, H^{5}), 1.55 m (3H, H^{2,9,11}), 1.68–1.92 m (6H, H^{1,7,2,6,6,11}), 2.08–2.24 m (2H, H^{3,12}), 2.39 d.d.d (1H, H^{7}, *J* 12.7, 3.6, 1.8 Hz), 2.50 m (1H, H^{12}), 2.86 t (2H, CH_2, *J* 7.6 Hz), 3.60 s (3H, OCH_3), 3.70 m (2H, CH_2), 4.54 s (1H, H^{17}), 4.88 s (1H, H^{17}), 6.21 s (1H, H^{14}), 7.19 m, 7.22 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.31 q (C^{20}), 19.69 t (C^{2}), 21.53 t (C^{11}), 24.53 t (C^{6}), 25.96 t (C^{12}), 28.54 q (C^{19}), 35.86 t (CH_2), 37.93 t (C^{3}), 38.38 t (C^{7}), 38.80 t (C^{1}), 38.95 t (CH_2), 40.08 s (C^{4}), 44.03 c (C^{10}), 50.85 q (OCH_3), 55.49 d (C^{9}), 56.00 d (C^{5}), 106.52 t (C^{17}), 125.71 d (C^{14}), 126.30 d (C$^{4'}$), 128.22 d (C$^{2',6'}$), 128.54 d (C$^{3',5'}$), 137.79 s (C$^{1'}$), 146.02 s (C^{8}), 150.14 s (C^{13}), 170.42 s, 170.07 s (C^{15,16}), 177.20 s (C^{18}). Found, %: C 74.98; H 8.01; N 3.02. $C_{29}H_{37}NO_4$. Calculated, %: C 76.16; H 7.99; N 3.02.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-{2-[1-(4-hydroxyphenylethyl)-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate {methyl [*N*-(4-hydroxyphenyl)ethyl]-15,16-dioxo-15,16-aza-8(17),13-labdadien-18-oate} (X). To a solution of 0.70 g (1.9 mmol) of compound **IV** in 10 ml of acetic acid was added 0.29 g (2.1 mmol) of 4-(2-aminoethyl)phenol. The reaction mixture was boiled for 8 h, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent chloroform–methanol, 200:1). We obtained 0.64 g (yield 68%) of compound **X**. $[\alpha]_{580}$ +52.1° (*c* 8.4, $CHCl_3$). IR spectrum, cm^{-1}: 821, 862, 895, 986, 1515 (C=C); 1251, 1643, 1705, 1771 (C=O); 1643, 3450 (C–N); 3460, 3601 (C=O). UV spectrum, λ_{max}, nm (log ε): 225 (3.62), 278 (2.02). ^{1}H NMR spectrum, δ, ppm: 0.46 s (3H, C^{20}H$_3$), 1.01 m (2H, H^{1,3}), 1.15 s (3H, C^{19}H$_3$), 1.23 m (1H, H^{5}), 1.57 m (3H, H^{2,9,11}), 1.75–1.93 m (6H, H^{1,7,2,6,6,11}), 2.18 m (2H, H^{3,12}), 2.39 m (1H, H^{7}), 2.50 m (1H, H^{12}), 2.75 t (2H, CH_2, *J* 7.8 Hz), 3.58 s (3H, OCH_3), 3.65 m (2H, CH_2), 4.51 s (1H, H^{17}), 4.86 s (1H, H^{17}), 6.20 C (1H, H^{14}), 6.40 br.s (1H, OH), 6.71 d (2H, H$^{2',6'}$, *J* 8.2 Hz), 7.98 d (2H, H$^{3',5'}$, *J* 8.2 Hz). ^{13}C NMR spectrum, δ, ppm: 12.36 q (C^{20}), 19.70 t (C^{2}), 21.53 t (C^{11}), 24.58 t (C^{6}), 25.96 t (C^{12}), 28.57 q (C^{19}), 33.48 t (CH_2), 37.93 t (C^{3}), 38.39 t (C^{7}), 38.97 t (C^{1}), 39.17 t (CH_2), 40.13 s (C^{4}), 44.14 s (C^{10}), 51.02 q (OCH_3), 55.54 d (C^{9}), 56.06 d (C^{5}), 106.56 t (C^{17}), 115.24 d (C$^{3',5'}$), 125.76 d (C^{14}), 129.38 s (C$^{1'}$), 129.65 d (C$^{2',6'}$), 147.05 s (C^{8}), 150.29 s (C$^{4'}$), 154.64 s (C^{13}), 170.85 s, 171.36 s (C^{15,16}), 177.68 s (C^{18}). Found, %: C 72.89; H 7.29; N 3.01. $C_{29}H_{37}NO_5$. Calculated, %: C 72.65; H 7.72; N 2.92.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-{2-[1-(1-carboxypropyl)-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [methyl *N*-(1-carboxypropyl)-15,16-dioxo-15,16-aza-8(17),13-labdadien-18-oate] (XI). To a solution of 2.38 g (6.6 mmol) of compound **IV** in 10 ml of acetic acid was added 0.82 g (7.9 mmol) of α-aminobutyric acid. The reaction mixture was boiled for 6 h, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent chloroform–methanol, 50:1). The fraction containing the reaction product was dissolved in hexane. On cooling 1.82 g (62%) of compound **XI** was filtered off, mp 47–50°C (from hexane). IR spectrum, cm^{-1}: 755, 822, 857, 888 (C=C); 1030, 1090 (C–O–C); 1680, 1714, 1750, 1780 (C=O); 1643 (C–N); 3200 (OH). ^{1}H NMR spectrum, δ, ppm: 0.48 s (3H, C^{20}H$_3$), 0.90 t (3H, CH_3, *J* 7.0 Hz), 1.05 m (2H, H^{1,3}), 1.15 s (3H, C^{19}H$_3$), 1.28 m (1H, H^{5}), 1.48 m (1H, H^{2}), 1.58 m (2H,

H^{9,11}), 1.70–1.90 m (5H, H^{11,1,7,2,6}), 1.95 m (1H, H^{6}), 2.00–2.33 m (4H, CH_2, H^{3,12}), 2.39 m (1H, H^{7}), 2.60 m (1H, H^{12}), 3.59 s (3H, OCH_3), 4.52 s (1H, H^{17}), 4.55 m (1H, CH), 4.87 s (1H, H^{17}), 6.29 s (1H, H^{14}), 9.02 br.s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 10.70 q (CH_3), 12.36 q (C^{20}), 19.69 t (C^{2}), 21.36 t (C^{11}), 21.69 t (CH_2), 24.68 t (C^{6}), 27.15 t (C^{12}), 28.55 q (C^{19}), 37.46 t (C^{3}), 37.94 t (C^{7}), 38.99 t (C^{1}), 40.12 s (C^{4}), 44.12 s (C^{10}), 50.97 q (OCH_3), 53.24 d (CH), 55.41 d (C^{9}), 56.08 d (C^{5}), 106.57 t (C^{17}), 126.49 d (C^{14}), 147.06 s (C^{8}), 150.40 s (C^{13}), 170.09 s, 170.69 s (C^{15,16}), 174.38 s (C=O), 177.53 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): [*M*]$^+$ 445 (8), 413 (5), 385 (20), 370 (10), 249 (16), 197 (22), 189 (31), 151 (30), 121 (100), 109 (32), 95 (22), 81 (39), 67 (21), 55 (25), 45 (22), 31 (34). Found [*M*]$^+$ 445.24662. $C_{25}H_{35}NO_6$. Calculated *M* 445.24642.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-{2-[1(3-carboxypropyl)-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]-ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [methyl *N*-(3-carboxypropyl)-15,16-dioxo-15,16-aza-8(17),13-labdadien-18-oate] (XII). To a solution of 0.50 (1.4 mmol) of compound **IV** in 10 ml of acetic acid was added 0.17 g (1.7 mmol) of γ-aminobutyric acid. The reaction mixture was boiled for 10 h, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent chloroform–methanol, 50:1). We obtained 0.44 g (74%) of compound **XII**. UV spectrum, λ_{max}, nm (log ε): 223 (3.12). IR spectrum, cm^{-1}: 1644, 1711, 1780 (C=O); 861, 892, 990 (C=C); 3216, 3460 (OH). ^{1}H NMR spectrum, δ, ppm: 0.47 s (3H, C^{20}H$_3$), 1.02 m (2H, H^{1,3}), 1.15 s (3H, C^{19}H$_3$), 1.24 m (1H, H^{5}), 1.50 m (1H, H^{2}), 1.59 m (2H, H^{9,11}), 1.70–1.95 m (5H, H^{11,1,7,2,6}), 1.95 m (1H, H^{6}), 2.09 m (4H, C$\underline{H}_2$, H^{3,12}), 2.27 m (3H, C$\underline{H}_2$, H^{7}), 2.50 m (1H, H^{12}), 3.38 t (2H, NCH_2, *J* 7.0 Hz), 3.57 s (3H, OCH_3), 4.52 s (1H, H^{17}), 4.87 s (1H, H^{17}), 6.24 s (1H, H^{14}), 6.61 br.s (OH, W_S 16 Hz). ^{13}C NMR spectrum, δ, ppm: 12.36 q (C^{20}), 19.73 t (C^{2}), 21.50 t (C^{11}), 23.74 t (CH_2), 24.66 t (C^{6}), 26.01 t (C^{12}), 28.58 q (C^{19}), 31.26 t (CH_2), 36.93 t (NCH_2), 37.98 t (C^{3}), 38.44 t (C^{7}), 39.05 t (C^{1}), 40.17 s (C^{4}), 44.14 s (C^{10}), 50.90 q (OCH_3), 55.6 d (C^{9}), 56.12 d (C^{5}), 106.54 t (C^{17}), 125.83 d (C^{14}), 147.16 s (C^{8}), 150.34 s (C^{13}), 170.73 s, 171.39 s (C^{15,16}), 176.21 s (C=O), 177.39 s (C^{18}). Found, %: C 67.21; H 7.71; N 3.28. $C_{25}H_{35}NO_6$. Calculated, %: C 67.42; H 7.87; N 3.15.

3-Benzyl-(1*R*,5*S*)-1- (XIII) and (1S,5R)-5-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-3-azatricyclo[5.2.1.0^{1,5}]dec-7-ene-2,4-diones (XIV). To a solution of 0.50 g (1.03 mmol) of *N*-benzylamino-substituted maleimide **VIII** in 20 ml of benzene was added 0.14 g (2.06 mmol) of cyclopentadiene. The reaction mixture was boiled for 10 h, the solvent was removed in a vacuum, the residue was subjected to column chromatography on silica gel (eluent chloroform–methanol, 200:1). We obtained 0.48 g of a mixture of compounds **XIII** and **XIV** (overall yield 84%). The crystallization from ether furnished an individual diastereomer **XIV**, mp 87–89°C (from ether). UV spectrum, λ_{max}, nm (log ε): 257 (2.33), 252 (2.31). IR spectrum, cm^{-1}: 727, 899, 1645, 2982 (C=C); 1699, 1722, 1761 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.26 s (3H, C$^{20'}$H$_3$), 0.84 t.d (1H, H$^{1'}$, *J* 13.3, 4.6 Hz), 0.95 t.d (1H, H$^{3'}$, *J* 13.5, 4.0 Hz), 1.04–1.14 m (2H, H$^{2',11'}$), 1.12 s (3H, C$^{19'}$H$_3$), 1.19 d.d (1H, H$^{5'}$, *J* 12.1, 2.3 Hz), 1.24 m (1H, H$^{7'}$, J_{gem} 12.6 Hz), 1.38 d.d.d.d (1H, H$^{11'}$, J_{gem} 14.2, *J* 7.2, 3.9, 2.8 Hz), 1.44 d.d (1H, H$^{9'}$, *J* 6.5, 4.3 Hz), 1.63 d.t (1H, H^{10}, *J* 9.1, 1.7, 1.6 Hz), 1.65 d.t (1H, H^{10}, *J* 9.1, 1.7, 1.3 Hz), 1.69–1.82 m (6H, H$^{1',2',7',6',12',12'}$), 1.92 d.d.d (1H, H$^{6'}$, *J* 13.1, 4.5, 2.9 Hz), 2.11 d.d.d.d (1H, H$^{3'}$, *J* 13.2, 3.2, 1.4 Hz), 2.33 m (1H, H$^{7'}$, *J* 12.6, 4.0, 2.5 Hz), 2.81 m (1H, H^{6}), 2.88 d (1H, H^{1}, *J* 4.5 Hz), 3.30 m (1H, H^{9}), 3.58 s (3H, OCH_3), 4.31 s (1H, H$^{17'}$), 4.41 d, 4.51 d (2H, CH_2Ph, *J* 13.9), 4.78 s (1H, H$^{17'}$), 5.89 d.d (1H, H^{8}, *J* 5.8, 3.1 Hz), 6.04 d.d (1H, H^{7}, *J* 5.8, 3.1 Hz), 7.21 m, 7.29 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.16 q (C$^{20'}$), 19.68 t, 19.73 t (C$^{2',11'}$), 26.06 t (C$^{6'}$), 28.61 q (C$^{19'}$), 34.82 t (C$^{12'}$), 38.02 t (C$^{3'}$), 38.44 t (C$^{7'}$), 38.49 t (C$^{1'}$), 40.16 C (C$^{4'}$), 41.69 t (C$\underline{H}_2$), 44.08 c (C$^{10'}$), 45.43 d (C^{9}), 49.96 d (C^{5}), 50.29 d (C^{6}), 50.38 t (C^{10}), 51.03 q (OCH_3), 55.97 d (C$^{9'}$), 56.13 d (C$^{5'}$), 56.65 C (C^{5}), 105.94 t (C$^{17'}$), 127.56 d (Ph), 128.26 d, 128.64 d (4C-Ph), 134.04 d (C^{8}), 135.96 s (Ph), 136.26 d (C^{7}), 147.94 s (C$^{8'}$), 177.09 s (C^{4}), 177.53 s (C$^{18'}$), 180.04 s (C^{2}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): [*M*]$^+$ 515 (11), 455 (27), 235 (18), 121 (77), 91 (100).

Compound **XIII**. The data were obtained from the spectrum of the mixture of compounds **XIII** and **XIV**. ^{1}H NMR spectrum, δ, ppm: 0.28 s (3H, C$^{20'}$H$_3$), 0.83 m (1H, H$^{1'}$), 0.94 m (1H, H$^{3'}$), 1.09 m (4H, H$^{2',6',7'}$),1.13 s (3H, C$^{19'}$H$_3$), 1.18 m (1H, H$^{5'}$), 1.23 m (1H, H$^{7'}$), 1.38 m (1H, H$^{2'}$), 1.44 m (1H, H$^{9'}$), 1.63–1.75 m (5H, H$^{2',6'10,10,11'}$), 1.78–1.98 m (4H, H $^{7',11',12',12'}$), 2.10 m (1H, H$^{3'}$), 2.32 m (1H, H$^{7'}$), 2.83 m (1H, H^{9}), 2.84 d (1H, H^{5}, *J* 4.5 Hz), 3.28 m (1H, H^{6}), 3.58 s (3H, OCH_3), 4.39 s (1H, H$^{17'}$), 4.44 d, 4.48 d (2H, CH_2Ph, *J* 13.9 Hz), 4.79 s (1H, H$^{17'}$), 5.82 d.d (H, H^{7}, *J* 5.6, 3.0 Hz), 5.97 d.d (H, H^{8}, *J* 5.6, 3.0 Hz), 7.21–7.30 m (5H, Ph).

(1*R*,5*S*)-1- (XV) and (1*S*,5*R*)-5-[18-Methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-3-(1-carboxypropyl)-3-azatricyclo[5.2.1.0^{1,5}]-dec-7-ene-2,4-diones (XVI). To a solution of 0.47 g (1.06 mmol) of maleimide **XI** in 20 ml of benzene was added 0.11 g (1.58 mmol) of cyclopentadiene. The reaction mixture was boiled for 10 h, the solvent was removed in a vacuum, the reaction products were isolated by column chromatography on silica gel (eluent chloroform–methanol, 200:1). We obtained 0.51 g (87%) of a mixture of *endo*-isomers. The crystallization from ether furnished an individual stereoisomer **XV**, mp 209–211°C, $[\alpha]_D^{20}$ +24.6° (*c* 0.8, $CHCl_3$). IR spectrum, cm^{-1}: 1671, 1706, 1726, 1742, 1771 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.39 s (3H, C$^{20'}$H$_3$), 0.83 t (3H, CH$_3$, *J* 7.0 Hz), 0.98 t.d (1H, H$^{1'}$, *J* 13.4, 4.2 Hz), 1.01 t.d (1H, H$^{3'}$, *J* 13.9, 5.6 Hz), 1.14 s (3H, C$^{19'}$H$_3$), 1.21–1.27 m (3H, H$^{5',11'}$ and 1H, CH$_2$), 1.44–1.56 m (3H, H$^{2',11',9'}$), 1.69 d, 1.70 d (2H, H^{10}, J_{gem} 9.0, *J* 1.6, 1.7 Hz), 1.72–1.80 m (6H, H$^{1',7',2',12',6',12'}$), 2.06 m (1H, H$^{6'}$), 2.12 m (1H, H$^{3'}$, J_{gem} 14.3 Hz), 2.30–2.42 m (2H, H$^{7'}$ and 1H, CH$_2$), 2.88 m (1H, H^9), 2.91 d (1H, H^5, *J* 4.3 Hz), 3.32 m (1H, H^6), 3.56 s (3H, OCH$_3$), 4.44 d.d (1H, CH, *J* 10.8, 8.4 Hz), 4.46 s (1H, H$^{17'}$), 4.82 s (1H, H$^{17'}$), 6.05 d.d.d (1H, H^7, 5.8, 2.9, 0.7 Hz), 6.15 d.d.d (1H, H^8, *J* 5.8, 3.0, 0.9 Hz), 8.22 br.s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 10.80 q (CH$_3$), 12.25 q (C$^{20'}$), 19.79 t (C$^{2'}$), 20.09 t (C$^{11'}$), 21.01 t (C$^{12'}$), 26.09 t (C$^{6'}$), 28.66 q (C$^{19'}$), 35.13 t (CH$_2$), 38.12 t (C$^{3'}$), 38.61 t (C$^{7'}$), 38.11 t (C$^{1'}$), 40.28 s (C^4), 44.19 s (C$^{10'}$), 45.50 d (C^6), 50.07 d (C^5), 50.37 d (C^9), 50.47 t (C^{10}), 51.01 q (OCH$_3$), 53.60 d (CH), 56.23 d (C$^{5'}$), 56.64 d (C$^{9'}$), 57.13 C (C^1), 107.01 t (C$^{17'}$), 134.46 d (C^7), 136.74 d (C^8), 147.04 s (C$^{8'}$), 173.57 s (C=O), 176.87 s (C^2), 177.64 s (C^{18}), 179.63 s (C^4). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): $[M]^+$ 511 (4), 479 (4), 451 (41), 386 (6), 340 (4), 278 (5), 235 (11), 203 (13), 181 (14), 161 (22), 121 (100), 107 (29). Found $[M]^+$ 511.29426. $C_{30}H_{41}NO_6$. Calculated *M* 511.29337.

Compound **XVI**. The data were obtained from the spectrum of the mixture of compounds **XV** and **XVI**. ^{1}H NMR spectrum, δ, ppm: 0.32 s (3H, C$^{20'}$H$_3$), 0.84 t (3H, CH$_3$, *J* 7.0 Hz), 1.01 m (2H, H$^{1',3'}$), 1.13 s (3H, C$^{19'}$H$_3$), 1.20–1.30 m (3H, H$^{5',6'}$ and 1H, CH$_2$), 1.50 m (3H, H$^{2',9',6'}$), 1.70–2.00 m (8H, H$^{10,10,2',1',7',11',12',11'}$), 2.07–2.15 m (2H, H$^{12',3'}$), 2.32 m (2H, H$^{7'}$ and 1H - CH$_2$), 2.88 m (1H, H6), 2.96 d (1H, H^1, *J* 4.4 Hz), 3.32 m (1H, H^9), 3.57 s (3H, OCH$_3$), 4.44 d.d (1H, CH, *J* 10.6, 4.7 Hz), 4.46 s (1H, H$^{17'}$), 4.83 s (1H, H$^{17'}$), 6.08 m (1H, H^8), 6.14 m (1H, H^7). Found, %: C 70.53; H 7.84; N 2.71. $C_{30}H_{41}NO_6$. Calculated, %: C 70.58; H 7.84; N 2.74.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-[2-(3,6-dioxo-1,2,3,6-tetrahydropyridazin-4-yl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate {4-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-3,6-dioxo-1,2,3,6-tetrahydropyridazine} (XVII). To a solution of 1.20 g (3.33 mmol) of compound **IV** in 20 ml of acetic acid at 0°C was added dropwise while stirring 0.19 g (3.33 mmol) of 90% hydrazine hydrate. The reaction mixture was warmed to room temperature, stirred for 6 h, and left overnight. The solvent was removed in a vacuum, the residue was treated with 20 ml of ethanol. The formed precipitate was filtered off, washed with ethanol (3×20 ml), and dried in an oil-pump vacuum. We obtained 0.59 g (47%) of pyridazinedione **XVII**. By column chromatography from the mother liquor was additionally isolated 0.19 g (15%) of oily maleimide **XVIII** (eluent chloroform–methanol, 100:1). Compound **XVII**, mp 279–281°C (ethanol). IR spectrum, cm^{-1}: 775, 814, 894, 1500, 1605 (C=C); 1537, 1575, 1658 [C(=O)NH]; 1722 (C=O); 2845, 3085, 3423 (NH). UV spectrum, λ_{max}, nm (log ε): 206 (3.26), 307 (2.44) (EtOH); 206 (3.12), 305 (2.63) (EtOH + HCl); 223 (3.08), 334 (2.40) (EtOH + KOH). ^{1}H NMR spectrum (CD_3OD), δ, ppm: 0.46 s (3H, C$^{20'}$H$_3$), 0.89–1.00 m (2H, H$^{1',3'}$), 1.14 s (3H, C$^{19'}$H$_3$), 1.20 d.d (1H, H$^{5'}$, *J* 12.5, 3.2 Hz), 1.30–1.80 m (8H, H$^{2',11',9',11',6',7',1',2'}$), 2.11–2.23 m (3H, H$^{6',12',3'}$), 2.34 m (1H, H$^{7'}$), 2.54 m (1H, H$^{12'}$), 3.57 s (3H, OCH$_3$), 4.57 s (1H, H$^{17'}$), 4.82 s (1H, H$^{17'}$), 6.56 m (1H, H^5, *J* ~2.0 Hz). ^{13}C NMR spectrum, δ, ppm: 12.12 q (C$^{20'}$), 19.52 t (C$^{2'}$), 21.36 t (C$^{11'}$), 25.83 t (C$^{6'}$), 28.34 q (C$^{19'}$), 28.91 t (C$^{12'}$), 37.75 t (C$^{3'}$), 38.26 t (C$^{7'}$), 38.66 t (C$^{1'}$), 39.95 C (C$^{4'}$), 43.92 c (C$^{10'}$), 50.74 q (OCH$_3$), 55.42 d (C$^{9'}$), 55.87 d (C$^{5'}$), 106.23 t (C$^{17'}$), 127.72 d (C^5), 145.77 C (C^4), 147.29 s (C$^{8'}$), 160.53 s, 161.44 s (C^{3,6}), 177.62 s (C$^{18'}$). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): $[M]^+$ 374 (7), 315 (10), 299 (8), 249 (21), 207 (11), 189 (21), 139 (18), 126 (100), 121 (31), 105 (12), 81 (14). Found $[M]^+$ 374.22100. $C_{21}H_{30}N_2O_4$. Calculated *M* 374.22054.

Methyl (1*S*,4a*R*,5*S*,8am)-5-{2-[1-amino-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]-ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [methyl (*N*-amino)-15,16-dioxo-15,16-aza-8(17),13-labdadien-18-oate] (XVIII). $[\alpha]_D^{20}$ +18.6° (*c* 0.6, $CHCl_3$). IR spectrum, cm^{-1}: 892, 1602 (C=C); 1645, 1723, 1771, 1842 (C=O); 1450, 2849, 3085, 3200, 3430 (NH–NH$_2$). UV spectrum, λ_{max}, nm (log ε):

300 (2.06). ^{1}H NMR spectrum, δ, ppm: 0.50 s (3H, $C^{20}H_3$), 0.88–1.10 m (2H, $H^{1,3}$), 1.20 s (3H, $C^{19}H_3$), 1.25 m (1H, H^5), 1.53–1.90 m (7H, $H^{2,11,9,1,7,2,6}$), 1.90–2.04 m (2H, $H^{6,11}$), 2.24 m (1H, H^3), 2.27 m (1H, H^{12}), 2.38 m (1H, H^7), 2.61 m (1H, H^{12}), 3.59 s (3H, OCH_3), 4.52 s (1H, H^{17}), 4.88 s (1H, H^{17}), 6.46 m (1H, H^{14}, *J* 2.6, 2.1 Hz), 7.20 br.s (NH_2). ^{13}C NMR spectrum, δ, ppm: 12.47 q (C^{20}), 19.82 t (C^2), 21.19 t (C^{11}), 25.44 t (C^6), 26.10 t ($C^{12'}$), 28.68 q (C^{19}), 38.05 t (C^3), 38.50 t (C^7), 39.13 t (C^1), 40.30 s (C^4), 44.22 s (C^{10}), 51.01 q (OCH_3), 55.61 d (C^9), 56.15 d (C^5), 106.70 t (C^{17}), 125.71 d (C^{14}), 147.08 C (C^8), 150.64 s (C^{13}), 165.34 s, 166.50 s ($C^{15,16}$), 177.43 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): $[M]^+$ 374 (5), 360 (4), 315 (7), 299 (9), 249(21), 207 (9), 189(23), 181 (11), 126 (78), 121 (70), 109 (22), 81 (25), 28 (100). Found $[M]^+$ 374.22654. $C_{21}H_{30}N_2O_4$. Calculated *M* 374.22054.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-[2-(3-hydroxy-6-oxo-1-phenyl-1,6-dihydropyridazin-4-yl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate {4-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-3-hydroxy-6-oxo-1-phenyl-1,6-dihydropyridazine} (XIX). To a solution of 1.00 g (2.8 mmol) of compound **IV** in 15 ml of acetic acid was added 0.33 ml (3.3 mmol) of phenylhydrazine. The reaction mixture was boiled for 10 h. The solvent was removed in a vacuum, the residue was subjected to chromatography on silica gel. We isolated in succession 0.48 g (38%) of (*N*-anilinyl)maleimide **XX** (eluent chloroform–methanol, 200:1) and 0.28 g (22%) of 6-hydroxypyridazin-3-one **XIX** (eluent chloroform–methanol, 100:1). Compound **XIX**, mp 212–214°C (from ether), $[\alpha]_D^{20}$ +49.0° (*c* 0.6, EtOH). IR spectrum, cm^{-1}: 689, 761, 897, 1500, 1594 (C=C); 1519, 1562, 1645, 1670 [C(=O)NH]; 1721 (C=O); 2589, 2695, 2844, 3077, 3424 (NH, OH). UV spectrum, λ_{max}, nm (log ε): 327 (3.12). ^{1}H NMR spectrum, δ, ppm: 0.46 s (3H, $C^{20'}H_3$), 0.98 d.d.d (1H, $H^{1'}$, *J* 13.1, 12.6, 4.3 Hz), 1.03 (1H, $H^{3'}$, *J* 13.5, 13.0, 4.2 Hz), 1.16 s (3H, $C^{19'}H_3$), 1.27 d.d (1H, $H^{5'}$, *J* 12.6, 3.2 Hz), 1.45–1.54 m (2H, $H^{2',11'}$), 1.56 m (1H, $H^{9'}$), 1.60–1.83 m (4H, $H^{1',6',2',11'}$), 1.87 t.d (1H, $H^{7'}$, *J* 13.0, 4.5 Hz), 1.97 m (1H, $H^{6'}$, J_{gem} 12.5 Hz), 2.08 d.d.d (1H, $H^{12'}$, *J* 14.5, 9.4, 5.6 Hz), 2.15 m (1H, $H^{3'}$, J_{gem} 3.5 Hz), 2.39 d.d.d (1H, $H^{7'}$, *J* 13.0, 3.9, 2.6 Hz), 2.55 d.d.d.d (1H, $H^{12'}$, *J* 14.5, 10.4, 3.8, 1.2 Hz), 3.60 s (3H, OCH_3), 4.48 s (1H, $H^{17'}$), 4.83 s (1H, $H^{17'}$), 6.81 s (1H, H^5), 7.27 m (1H, *p*-H, Ph), 7.33 m (2H, *m*-H, Ph), 7.45 m (2H, *o*-H, Ph), 9.52 br.s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 12.45 q ($C^{20'}$), 19.76 t ($C^{2'}$), 22.02 t ($C^{11'}$), 26.05 t ($C^{6'}$), 28.67 q ($C^{19'}$), 29.14 t ($C^{12'}$), 37.99 t ($C^{3'}$), 38.48 t ($C^{7'}$), 38.94 t ($C^{1'}$), 40.20 s ($C^{4'}$), 44.14 s ($C^{10'}$), 51.12 q (OCH_3), 55.67 d ($C^{9'}$), 56.06 d ($C^{5'}$), 106.72 t ($C^{17'}$), 125.26 d ($C^{2'',6''}$), 127.79 d ($C^{4''}$), 128.52 d ($C^{3'',5''}$), 130.52 d (C^5), 140.38 c ($C^{1''}$), 142.50 C (C^4), 147.14 s ($C^{8'}$), 152.95 s (C^3), 159.47 s (C^6), 177.63 s ($C^{18'}$). Found, %: C 71.71; H 7.79; N 6.39. $C_{27}H_{34}N_2O_4$. Calculated, %: C 72.00; H 7.56; N 6.22.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-{2-[1-anilino-2,5-dioxo-2,5-dihydro-(1*H*)-pyrrol-3-yl]ethyl}-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate [methyl (*N*-anilino)-15,16-dioxo-15,16-aza-8(17),13-labdadien-18-oate] (XX), mp 59–62°C (from hexane), $[\alpha]_D^{20}$ +54.1° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 691, 752, 862, 887, 1498, 1604 (C=C); 1720, 1726, 1784 (C=O); 1450, 1630, 1660, 2845, 3200, 3326 (NH–N). UV spectrum, λ_{max}, nm (log ε): 228 (4.35), 279 (3.37). ^{1}H NMR spectrum, δ, ppm: 0.49 s (3H, $C^{20}H_3$), 0.97–1.07 m (2H, $H^{1,3}$), 1.16 s (3H, $C^{19}H_3$), 1.28 d.d (1H, H^5, *J* 12.6, 3.2 Hz), 1.46–1.52 m (1H, H^2, J_{gem} 14.1 Hz), 1.59–1.66 m (2H, $H^{11,9}$), 1.71–1.90 m (5H, $H^{11,1,7,2,6}$), 1.97 d.d.d.d (1H, H^6, *J* 13.0, 12.2, 10.6, 4.4 Hz), 2.15 m (1H, H^3, J_{gem} 13.0 Hz), 2.29 d.d.d.d (1H, H^{12}, *J* 15.6, 12.2, 3.9, 2.7 Hz), 2.40 d.d.d (1H, H^7, *J* 13.0, 4.2, 2.5 Hz), 2.62 m (1H, H^{12}, J_{gem} 15.6 Hz), 3.59 s (3H, OCH_3), 4.54 s (1H, H^{17}), 4.88 s (1H, H^{17}), 6.04 s (1H, NH), 6.35 d (1H, H^{14}, *J* 1.8 Hz), 6.69 m (2H, *O*-H, Ph), 6.90 m (1H, *n*-H, Ph), 7.18 m (2H, *m*-H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.38 q (C^{20}), 19.71 t (C^2), 21.18 t (C^{11}), 25.10 t (C^{12}), 25.98 t (C^6), 28.62 q (C^{19}), 37.94 t (C^3), 38.40 t (C^7), 39.05 t (C^1), 40.17 s (C^4), 44.08 c (C^{10}), 51.05 q (OCH_3), 55.37 d (C^9), 56.02 d (C^5), 106.66 t (C^{17}), 113.50 d ($C^{2',6'}$), 121.88 d ($C^{4'}$), 124.67 d (C^{14}), 129.09 d ($C^{3',5'}$), 145.61 s ($C^{1'}$), 147.01 s (C^8), 149.24 s (C^{13}), 168.54 s, 169.34 s ($C^{15,16}$), 177.45 s (C^{18}). Found, %: C 71.89; H 7.64; N 6.20. $C_{27}H_{34}N_2O_4$. Calculated, %: C 72.00; H 7.56; N 6.22.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-[2-(3-hydroxy-1-methyl-6-oxo-1,6-dihydropyridazin-4-yl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate {3-hydroxy-1-methyl-4-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl-18-oate]-3-oxo-1,6-dihydropyridazine} (XXI). In 20 ml of ethanol was dissolved 0.46 g (1.20 mmol) of compound **XVII**, and the solution was placed into a three-neck flask equipped with a mechanical mixer and a thermometer. To the solution was poured 0.45 g (3.5 mmol) of a freshly distilled dimethyl sulfate and at vigorous stirring within 15 min was added dropwise a solution of 0.34 g of potassium hydroxide in 0.34 ml of water (the temperature should be maintained below

40°C). The reaction mixture was stirred for 5 h at room temperature and then was left overnight. Then 20 ml of water was added, the reaction product was extracted with $CHCl_3$ (3×20 ml). The combined organic solutions were washed with water (3×20 ml) and dried with $MgSO_4$. The solvent was evaporated in a vacuum, and the residue was treated with 15 ml of ether. The separated precipitate was filtered off and dried in a vacuum. We obtained 0.39 g (84%) of compound **XXI**, mp 207–209°C (from ether), $[\alpha]_{580}$ +37.0° (*c* 4.8, $CHCl_3$). IR spectrum, cm^{-1}: 1253, 1512, 1550, 1643, 1663, 1717 (C=O, C=N); 902, 2598, 2845, 3078 (C=C, C–NMe); 3418 (OH). UV spectrum, λ_{max}, nm (log ε): 217 (4.04), 313 (3.42). ^{1}H NMR spectrum, δ, ppm: 0.47 s (3H, $C^{20'}H_3$), 0.96–1.03 m (2H, $H^{1',3'}$), 1.15 s (3H, $C^{19'}H_3$), 1.26 m (1H, $H^{5'}$, *J* 12.2, 2.3 Hz), 1.46 m (1H, $H^{2'}$, J_{gem} 14.0 Hz), 1.57–1.65 m (2H, $H^{11',9'}$), 1.70–1.82 m (4H, $H^{2',1',11',7'}$), 1.87 d.d.d.d (1H, $H^{6'}$, *J* 12.8, 12.2, 4.1, 2.8 Hz), 1.96 d.d.d.d (1H, $H^{6'}$, *J* 12.8, 8.8, 4.0, 2.3 Hz), 2.13 d.d.d (1H, $H^{3'}$, *J* 13.3, 5.2, 2.9 Hz), 2.25 m (1H, $H^{12'}$), 2.38 m (1H, $H^{7'}$, *J* 12.8, 4.2, 2.5 Hz), 2.67 m (1H, $H^{12'}$, J_{gem} 15.2 Hz), 3.56 s (3H, NCH_3), 3.58 s (3H, OCH_3), 4.58 s (1H, $H^{17'}$), 4.86 s (1H, $H^{17'}$), 6.80 s (1H, H^5), 6.86 br.s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 12.44 q ($C^{20'}$), 19.76 t ($C^{2'}$), 22.02 t ($C^{11'}$), 26.05 t ($C^{6'}$), 28.65 q ($C^{19'}$), 29.04 t ($C^{12'}$), 37.97 t ($C^{3'}$), 38.29 q (NCH_3), 38.49 t ($C^{7'}$), 38.97 t ($C^{1'}$), 40.19 s ($C^{4'}$), 44.13 s ($C^{10'}$), 51.07 q (OCH_3), 55.50 d ($C^{9'}$), 56.06 d ($C^{5'}$), 106.56 t ($C^{17'}$), 129.47 d (C^5), 142.21 s (C^4), 147.32 s ($C^{8'}$), 153.16 s (C^3), 159.92 s (C^6), 177.57 s ($C^{18'}$). Mass spectrum, *m/z* (I_{rel}, %) (Electron impact): $[M]^+$ 388 (3), 329 (2), 313 (2), 249 (3), 221 (2), 189 (3), 153 (14), 140 (100). Found $[M]^+$ 388.23721. $C_{22}H_{32}N_2O_4$. Calculated *M* 388.23619.

Methyl (1*S*,4a*R*,5*S*,8a*S*)-5-[2-(3-methoxy-6-oxo-1-phenyl-1,6-dihydropyridazin-4-yl)ethyl]-1,4a-dimethyl-6-methylenedecahydronaphthalene-1-carboxylate {3-methoxy-4-[18-methoxycarbonyl-13,14,15,16-tetranorlabd-8(17)-en-12-yl]-6-oxo-1-phenyl-1,6-dihydropyridazine} (XXII). ^{1}H NMR spectrum, δ, ppm: 0.49 s (3H, $C^{20'}H_3$), 0.98–1.11 m (2H, $H^{1',3'}$), 1.16 s (3H, $C^{19'}H_3$), 1.29 d.d (1H, $H^{5'}$, *J* 12.8, 3.5 Hz), 1.46–1.52 m (1H, $H^{2'}$, J_{gem} 12.9 Hz), 1.56–1.68 m (2H, $H^{9',11'}$), 1.72–1.84 m (3H, $H^{1',6',11'}$), 1.87 t.d (1H, $H^{7'}$, *J* 13.2, 3.9 Hz), 1.91 m (1H, $H^{6'}$, J_{gem} 12.8 Hz), 1.97 m (1H, $H^{2'}$, J_{gem} 12.9 Hz), 2.14 d.d.d.d (1H, $H^{3'}$, *J* 13.3, 5.2, 2.0 Hz), 2.24 d.d.d (1H, $H^{12'}$, *J* 14.3, 9.6, 5.2 Hz), 2.39 d.d.d (1H, $H^{7'}$, *J* 13.2, 7.9, 2.6, 1.8 Hz), 2.66 d.d.d.d (1H, $H^{12'}$, *J* 14.3, 10.1, 3.6, 1.6 Hz), 3.58 s (3H, OCH_3), 3.84 s (3H, OCH_3), 4.56 s (1H, $H^{17'}$), 4.88 s (1H, $H^{17'}$), 6.76 m (1H, H^5, *J* 1.8, 1.6 Hz), 7.29 m (1H, *n*-H, Ph), 7.42 m (2H, *m*-H, Ph), 7.65 m (2H, *o*-H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.41 q ($C^{20'}$), 19.79 t ($C^{2'}$), 21.83 t ($C^{11'}$), 26.03 t ($C^{6'}$), 28.53 t ($C^{12'}$), 29.63 q ($C^{19'}$), 37.94 t ($C^{3'}$), 38.47 t (C^7), 38.99 t ($C^{1'}$), 40.19 s (C^4), 44.08 s ($C^{10'}$), 51.00 q (OCH_3), 54.19 q (OCH_3), 55.53 d ($C^{9'}$), 56.03 d ($C^{5'}$), 106.44 t ($C^{17'}$), 124.65 d ($C^{2',6'''}$), 127.16 d ($C^{4''}$), 128.37 d ($C^{3'',5''}$), 129.69 d (C^5), 141.35 s ($C^{1''}$), 141.91 s (C^4), 147.35 s ($C^{8'}$), 152.53 s (C^3), 159.22 s (C^6), 177.50 s ($C^{18'}$). Found, %: C 71.58; H 7.89; N 6.21. $C_{28}H_{36}N_2O_4$. Calculated, %: C 71.68; H 7.96; N 6.19.

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