ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 8, pp. 1081–1089. © Pleiades Publishing, Ltd., 2012.
Original English Text © Yu.V. Kharitonov, E.E. Shults, M.M. Shakirov, I.Yu. Bagryanskaya, G.A. Tolstikov, 2012, published in Zhurnal Organicheskoi Khimii, 2012, Vol. 48, No. 8, pp. 1085–1092.

Synthetic Transformations of Higher Terpenoids: XXIX.* Gold Catalyzed Cycloisomerization of Propargylaminomethyl Substituted and Propargyloxymethyl Substituted Furanolabdanoids

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Received February 22, 2012

Abstract—16-Propargylaminomethyl substituted and 16-propargyloxymethyl substituted furanolabdanoids were synthesized, which under the action of $AuCl_3$ in acetonitrile underwent cycloisomerization forming 7-hydroxyisoindolines or 7-hydroxydihydroisobenzofurans substituted by a terpenoid fragment.

DOI: 10.1134/S1070428012080088

Vegetable furanolabdanoids are natural compounds possessing versatile pharmacologic activity [2]. Lambertianic acid (**I**) and its methyl ester **II** produced by the Siberian pine *Pinus sibirica* R. Mayr. belong to available compounds of this type [3]. Synthetic transformations of methyl lambertianate led to the preparation of a number of natural substances [4–6] and pharmacologically promising agents [7, 8].

Aiming at the preparation of heterocyclic derivatives of the methyl lambertianate with 7-hydroxyisoisoindolinone or 7-hydroxydihydroisobenzofuran substituents we studied the method of gold-catalyzed synthesis of benzarenes fused with five- and six-membered rings [9]. The method of enyne cycloisomerization of ω-alkynylfurans catalyzed with Au(III) was successfully used in the synthesis of number of biologically active compounds, of some natural substances among them [9, 10], but the application of this method to the transformations of polyfunctional furan compounds of diterpene type was not described.

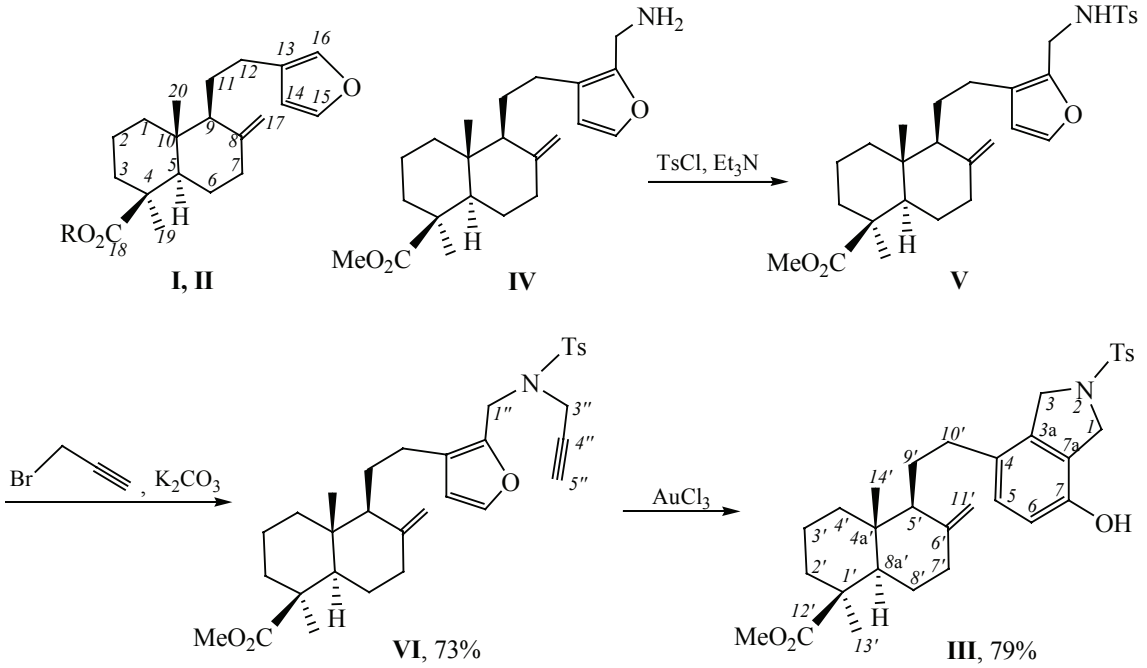
The key compound in the synthesis of 7-hydroxyisoindoline-substituted labdanoid **III** is methyl 16-(aminomethyl)lambertianate (**IV**) [8], whose reaction with *p*-toluenesulfonyl chloride in dichloromethane in the presence of triethylamine furnishes the corresponding sulfamide **V** (Scheme 1). The alkylation of compound **V** with propargyl bromide led to the formation of methyl *N*-tosyl-16-(propargylaminomethyl)lambertianate (**VI**). After the treatment of compound **VI** with $AuCl_3$ (5 mol%) in acetonitrile 7-hydroxyisoindoline substituted in the position *4* with terpenoid fragment, compound **III**, was obtained.

Methyl 16-(formyl)lambertianate (**VII**) [11] was utilized as the initial compound in the synthesis of dihydroisobenzofurans with a terpene substituent **VIII, IXa, IXb** (Scheme 2). The reduction of methyl 16-(formyl) lambertianate (**VII**) with sodium borohydride in methanol gave rise to the corresponding 16-hydroxymethyl derivative **X** whose reaction with propargyl bromide in the presence of sodium hydride in DMF provided propargyl furyl ether **XI**. The catalyzed by $AuCl_3$ cycloisomerization of compound **XI** gave cleanly 7-hydroxy-1,3-dihydroisobenzofuran **VIII** with a terpenoid fragment in the position *4*.

In the reaction of methyl 16-(formyl)lambertianate (**VII**) with propargyl bromide in the presence of activated zinc powder in the mixture THF–aqueous NH_4Cl homopropargyl alcohols **XIIa, XIIb** were obtained as mixtures of 1'(*R*)- and 1'(*S*)-diastereomers in a ratio

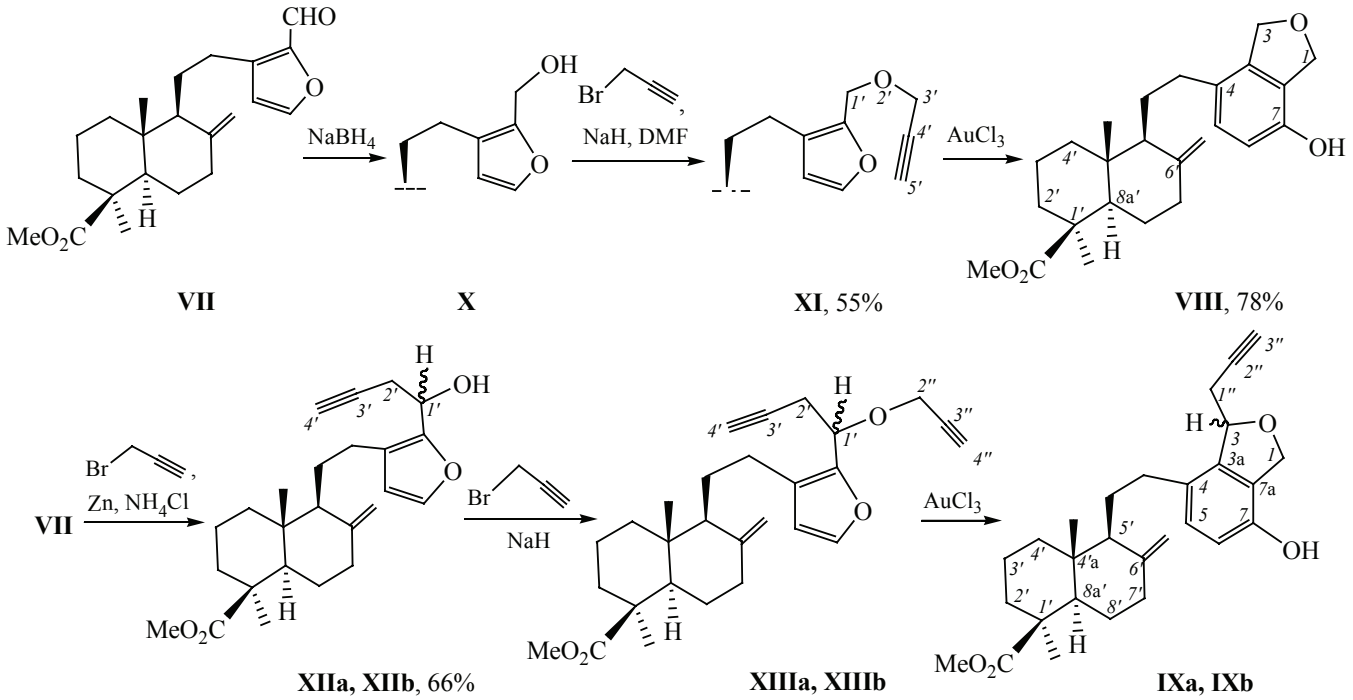
* For Communication XXVIII, see [1]

Scheme 1.



R = H (**I**), CH_3 (**II**).

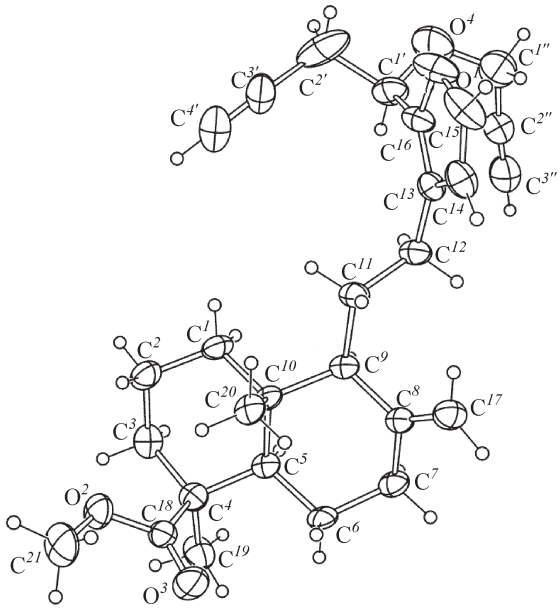
Scheme 2.



~1 : 1. Compounds **XIIa, XIIb** were also obtained from diterpene aldehyde **VII** and propargylmagnesium bromide (ratio ~1 : 1, yield 74%). In the reaction of diterpene alcohols **XIIa, XIIb** with propargyl bromide in DMF in the presence of sodium hydride we obtained the corresponding diacetylene derivatives of methyl

lambertianate **XIIIa, XIIIb** as a mixture of 1'(*R*)- and 1'(*S*)-diastereomers (oily substance); during keeping in air 1'(*R*)-diastereomer **XIIIa** slowly crystallized from the mixture. A single crystal of compound **XIIIa** was subjected to XRD analysis (see the figure). The cycloisomerization of the mixture of stereomers **XIIIa, XIIIb** catalyzed by $AuCl_3$ occurred selectively involving the acetylene bond activated with oxygen and resulted in the formation of a mixture of 3(*R*)- and 3(*S*)-7-hydroxy-3-(prop-2-yn-1-yl)-1,3-dihydroisobenzofurans **IXa, IXb** substituted in the position *4* with a terpenoid fragment.

The structure of **XIIIa** was elucidated by an X-ray crystal structure determination (see the figure). The six-membered rings in the molecule exist in the *chair* conformation, the furan ring is flat (root-mean-square deviation of atoms from the plane is 0.008 Å). The bond lengths and bond angles in molecule **XIIIa** are close to the average statistical values [12] and in the main part of the skeleton coincide in the 3σ limits with the parameters of the nearest analog, the methyl 16-cyanolambertianate [13]. The crystal packing contains no shortened compared to the sum of van der Waals radii nonvalent contacts.



Molecular structure of methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl-6-methylidene-5-(2-{2-[(*R*)-1-(prop-2-yn-1-yloxy)but-3-yn-1-yl]furan-3-yl}ethyl)decahydronaphthalene-1-carboxylate (**XIIIa**) from X-ray data.

The structure of all compounds is confirmed by the ^{1}H and ^{13}C NMR spectra. The formation of compounds **XIIa, XIIb, XIIIa, XIIIb** in the form of diastereomers mixture (owing to the introduction of the propargyl substituent) is seen from the doubling of some proton and carbon signals in the ^{1}H and ^{13}C NMR spectra. The difference in the chemical shifts of protons H$^{2'}$ of diastereomers **XIIa, XIIb** equals 0.01 ppm, of diastereomers **XIIIa, XIIIb**, 0.03–0.04 ppm.

The formation of heterocyclic systems of isoindoline **III** and of dihydroisobenzofuran **VIII, IXa, IXb** was confirmed by the ^{1}H and ^{13}C NMR data. In the ^{13}C NMR spectrum of the diastereomers **IXa, IXb** mixture a doubling of signals of some carbon atoms of the terpene skeleton and dihydroisobenzofuran was observed originating from the introduction of the propargyl substituent into the position C^3. The formation of dihydroisobenzofurans **IXa, IXb** as a mixture of diastereomers follows from the presence in their ^{1}H NMR spectra of double signals of protons H$^{1'}$ and H^3 (Δδ 0.03–0.06 ppm). A characteristic feature of the ^{1}H NMR spectra of compounds **III, VIII, IXa, IXb** is the appearance of doublet signals of protons H^6 and H^5 at 6.59–6.67 and 6.88–6.95 ppm respectively, *J* 7.8–8.0 Hz. The introduction of a hydroxy group in the position C^7 of 4-terpenyl substituted derivatives of isoindoline **III** and dihydroisobenzofuran **VIII** and **IXa, IXb** results in the nonequivalence of protons H^1 and in the appearance in the ^{1}H NMR spectra of two one-proton doublets in a weak field [e.g., δ 5.05, 5.10 ppm, *J* 10.2 Hz (**VIII**)]. Similar changes were observed in the spectra of *N*-substituted 7-hydroxyisoindolines [14].

The appearance a substituent in the position *3* of terpenoid dihydroisobenzofurans **IXa, IXb** led to the increase in the difference in the chemical shifts of the doublet signals of protons H^1 (δ 5.25, 5.09 ppm, *J* 10.2 Hz). ^{13}C NMR spectra of compounds **III, VIII, IXa, IXb** contain characteristic signals of atoms C^{3a} (136.40–139.52 ppm), C^4 (127.96–129.44 ppm), C^5 (128.54–128.77 ppm), C^6 (114.16–114.61 ppm), C^7 (147.44–147.81 ppm), C^{7a} (122.42–125.53 ppm). The position of the hydroxy group at the atom C^7 is confirmed by the data of 2D spectra of ^{1}H–^{13}C correlation. In the spectra ^{1}H–^{13}C COLOC and ^{1}H–^{13}C HMBC of compound **VIII** cross-peaks were observed between the signals of the protons H$^{10'}$ of the terpene skeleton and the signal of the atom C^5 (δ 128.61 ppm). Besides in the monoresonance spectra the signals of atoms C^1 and C^3 appear as broadened singlets (*J* 1.7–2.0 Hz) confirming the presence of substituents at the atoms C^4 and C^7 of the dihydroisobenzofuran fragment.

Thus new derivatives of lambertianic acid were obtained containing the 16-propargylaminomethyl or

16-propargyloxymethyl substituents in the position C^{16}. The new acetylene derivatives of furanolabdanoids exhibited a high activity and regioselectivity in the cycloisomerization catalyzed by gold(III) chloride. Hybride structures were synthesized combining the fragments of 7-hydroxy-1,3-dihydroisobenzofurans or 7-hydroxyisoindolines and labdane diterpenoids.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometers Bruker AV-300 [operating frequencies 300.13 (^1H), 75.47 MHz (^{13}C)] and Bruker AV-400 [operating frequencies 400.13 (^1H), 100.78 MHz (^{13}C)] from solutions of compounds in $CDCl_3$, the signals of the solvent served as internal references (δ_H 7.24, δ_C 76.9 ppm). The multiplicity of signals in the ^{13}C NMR spectra was determined by standard procedures at registering spectra in the mode of J-modulation (JMOD). The assignment of signals in NMR spectra was performed taking into account the data of [8, 13]; for compound **VIII** were taken 2D correlation proton-proton and carbon-proton spectra COSY, HXCO, COLOC, HMBC. In the description of the ^1H and ^{13}C NMR spectra the used numeration of atoms of diterpene framework was indicated in Scheme 1 in formula **I** for compounds **V, VI, X, XII, XIII** and formula **III** for compounds **VIII, IX**. The recording of mass spectra, determination of molecular masses and elemental composition of compounds was performed on a high resolution mass spectrometer DFS Thermo Scientific (ionizing electrons energy 70 eV, vaporizer temperature 230–280°C). The specific rotation was measured on a polarimeter PoLAAr 3005 at room temperature (20–23°C). IR spectra were taken on a spectrophotometer Vector-22 from mulls in mineral oil. UV spectra were recorded on a spectrophotometer HP 8453 UV Vis in ethanol. The XRD analysis of compound **XIIIa** was carried out on a diffractometer Kappa Apex II Bruker with a two-coordinate CCD detector (MoK_α-radiation, graphite monochromator, ω-φ scanning in the range up to 2θ<51°). Melting points were measured on a heating block Stuart SMF-38.

The monitoring of reaction progress and checking of homogeneity of compounds obtained was performed by TLC on Silufol UV-254 plates, eluents chloroform–ethanol, 3 : 1, petroleum ether–ethyl acetate, 10 : 1. The spots were visualized by spraying the plates with 10% water solution of H_2SO_4 followed by heating at 100°C or by UV irradiation.

Synthesis of methyl 16-aminomethyl lambertianate (**IV**) was described in [8]. Methyl 16-formyllambertianate (**VII**) and methyl 16-(hydroxymethyl)lambertianate (**X**) were obtained by procedure [11].

Methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl-6-methylidene-5-(2-{2-[(4-methylphenylsulfonamido) methyl]furan-3-yl}ethyl)decahydronaphthalene-1-carboxylate (V). To a solution of 1.00 g (2.2 mmol) of methyl 16-(aminomethyl)lambertianate (**IV**) in 20 ml of dichloromethane was added at stirring 0.77 ml (5.6 mmol) of triethylamine and 0.42 g (2.2 mmol) of tosyl chloride. The reaction mixture was stirred for 24 h at room temperature, diluted with 50 ml of chloroform, washed with water (3 × 50 ml), dried with $MgSO_4$, and evaporated. Yield 1.06 g (93%), oily substance, $[\alpha]_D$ +29.12° (*c* 0.57, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 225 (4.07). IR spectrum, cm^{-1}: 3277, 3022, 2945, 2876, 2847, 1722, 1645, 1447, 1331, 1229, 1161, 1094, 1051, 984, 891, 814, 756, 663. ^1H NMR spectrum, δ, ppm: 0.45 s (3H, $C^{20}H_3$), 0.92 d.t (1H, H^1, *J* 13.5, 4.2 Hz), 0.99 d.t (1H, H^3, *J* 13.6, 4.2 Hz), 1.15 s (3H, $C^{19}H_3$), 1.22 d.d (1H, H^5, *J* 12.1, 3.1 Hz), 1.45 m (1H, H^2), 1.47 m (1H, H^9), 1.58 m (1H, H^{11}), 1.70–1.81 m (4H, $H^{1,2,6,11}$), 1.85 m (1H, H^7), 1.96 m (1H, H^6), 2.13 m (2H, $H^{3,12}$), 2.34 m (1H, H^{12}), 2.37 m (1H, H^7), 2.41 s (3H, CH_3), 3.60 s (3H, OCH_3), 4.03 d, 4.06 d (2H, CH_2, *J* 11.6 Hz), 4.48 s, 4.85 s (2H, H^{17}), 4.72 m (1H, NH), 6.11 d (1H, H^{14}, $J_{14,15}$ 2.0 Hz), 7.16 d (1H, H^{15}, $J_{14,15}$ 2.0 Hz), 7.23 d (2H, $H^{3',5'}$, *J* 7.8 Hz), 7.67 d (2H, $H^{2',6'}$, *J* 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 12.52 q (C^{20}), 19.81 t (C^2), 21.43 q (CH_3), 22.79 t (C^{12}), 24.10 t (C^{11}), 26.15 t (C^6), 28.67 q (C^{19}), 37.95 t (CH_2), 38.04 t (C^3), 38.60 t (C^7), 38.91 t (C^1), 40.03 s (C^{10}), 44.16 s (C^4), 51.06 q (OCH_3), 54.71 d (C^9), 56.05 d (C^5), 106.52 t (C^{17}), 111.31 d (C^{14}), 122.96 s (C^{13}), 126.97 d ($C^{2',6'}$), 129.46 d ($C^{3',5'}$), 136.71 s ($C^{4'}$), 141.77 d (C^{15}), 143.18 s ($C^{1'}$), 144.40 s (C^{16}), 147.64 s (C^8), 177.64 s (C^{18}). Mass spectrum, *m/z* (I_{rel}, %): 513 (0.19), 429 (11), 358 (29), 342 (29), 283 (12), 263 (12), 249 (18), 235 (12), 194 (11), 189 (34), 184 (12), 181 (90), 171 (18), 161 (16), 155 (33), 149 (17), 133 (14), 122 (19), 121 (100), 119 (17), 110 (12), 109 (49), 107 (26), 105 (17), 95 (13), 94 (11), 93 (56), 91 (56), 85 (35), 83 (52), 81 (23), 79 (16), 55 (13). Found $[M]^+$ 513.2537. $C_{29}H_{39}NO_5S$. Calculated *M* 513.2543.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl-5-[2-(2-{[4-methyl-*N*-(prop-2-yn-1-yl)phenylsulfonamido] methyl}furan-3-yl)ethyl]-6-methylidenedecahydronaphthalene-1-carboxylate (VI). To the stirred solution

of 1.00 g (1.9 mmol) of compound **V** in 20 ml of acetone at room temperature was added in succession 0.54 g (3.9 mmol) of K_2CO_3 and 0.32 ml (2.9 mmol) of 80% solution of propargyl bromide in toluene. The reaction mixture was stirred for 24 h, diluted with 50 ml of water, the reaction product was extracted into chloroform (3 × 30 ml), the extract was washed with water (3 × 50 ml), dried with $MgSO_4$, and evaporated. The residue was chromatographed on a column packed with silica gel (eluent chloroform). Yield 0.78 g (73%), oily substance. ^{1}H NMR spectrum, δ, ppm: 0.48 s (3H, $C^{20}H_3$), 0.96 m (1H, H^1), 1.00 d.t (1H, H^3, J 13.4, 4.3 Hz), 1.15 s (3H, $C^{19}H_3$), 1.24 m (1H, H^5), 1.46 m (1H, H^2), 1.54 m (1H, H^9), 1.64 m (1H, H^{11}), 1.72–1.82 m (4H, $H^{1,2,6,11}$), 1.86 m (1H, H^7), 1.94 m (1H, H^6), 2.13 m (1H, H^3), 2.28 m (1H, H^{12}), 2.38 m (1H, H7), 2.41 s (3H, CH_3), 2.49 m (1H, H^{12}), 2.55 m (1H, $H^{5''}$), 3.58, 3.60 s (3H, OCH_3), 3.93 d, 3.95 d (2H, $H^{3''}$, J 9.3 Hz), 4.31 d, 4.36 d (2H, $H^{1''}$, J 10.1 Hz), 4.56 s, 4.87 s (2H, H^{17}), 6.19 d, 6.20 d (1H, H^{14}, J 2.0 Hz), 7.27 s (1H, H^{15}), 7.27 d (2H, $H^{3',5'}$, J 8.0 Hz), 7.71 d (2H, $H^{2',6'}$, J 8.0 Hz). ^{13}C NMR spectrum, δ, ppm: 12.52 q (C^{20}), 19.82 t (C^2), 21.43 q (CH_3), 22.56 t, 22.87 t (C^{12}), 24.34 t (C^{11}), 26.16 t (C^6), 28.67 q (C^{19}), 35.92 t ($C^{3''}$), 38.05 t (C^3), 38.63 t (C^7), 38.95 t (C^1), 40.06 c (C^{10}), 40.62 t ($C^{1''}$), 44.17 s (C^4), 51.01 q (OCH_3), 54.93 d (C^9), 56.13 d (C^5), 73.68 s ($C^{4''}$), 77.65 d ($C^{5''}$), 106.53 t (C^{17}), 111.40 d (C^{14}), 124.79 s (C^{13}), 126.90 d, 127.68 d ($C^{2',6'}$), 129.29 d ($C^{3',5'}$), 135.93 s ($C^{4'}$), 142.17 d (C^{15}), 143.38 s ($C^{1'}$), 143.62 s (C^{16}), 147.56 s (C^8), 177.60 s (C^{18}).

Methyl (1*S*,4a*R*,5*S*,8a*R*)-5-[2-(7-hydroxy-2-tosylisoindolin-4-yl)ethyl]-1,4a-dimethyl-6-methylidenedecahydronaphthalene-1-carboxylate (III). To a solution of 0.300 g (0.544 mmol) of compound **VI** in 10 ml of acetonitrile was added at room temperature 0.008 g (0.027 mmol) of $AuCl_3$, and the mixture was stirred for 24 h (TLC monitoring). The solvent was distilled off, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ether, 1 : 1). Yield 0.230 g (73%), oily substance, $[\alpha]_D$ +17.26° (*c* 0.34, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 226 (4.11), 275 (3.25). IR spectrum, cm^{-1}: 3423, 2925, 2851, 1722, 1620, 1609, 1580, 1503, 1456, 1346, 1315, 1290, 1231, 1163, 1097, 1065, 816, 757, 662. ^{1}H NMR spectrum, δ, ppm: 0.46 s (3H, $C^{14'}H_3$), 0.96 m (1H, $H^{4'}$), 1.00 m (1H, $H^{2'}$), 1.16 c (3H, $C^{13'}H_3$), 1.24 m (1H, $H^{8'}$), 1.49 m (1H, $H^{3'}$), 1.53 br.s(1H, $H^{5'}$), 1.66 m (1H, $H^{9'}$), 1.70–1.78 m (4H, $H^{3',4',8',9'}$), 1.85 m (1H, $H^{7'}$), 1.97 m (1H, $H^{8'}$), 2.14 m (2H, $H^{2',10'}$), 2.38 s (3H, CH_3), 2.40 m (1H, $H^{7'}$), 2.42 m (1H, $H^{10'}$), 3.60 s (3H, OCH_3), 4.50 d (1H, H^1, J 10.4 Hz), 4.53 d (1H, H^1, J 10.4 Hz), 4.56 m (2H, H^3), 4.58 s (1H, $H^{11'}$), 4.91 s (1H, $H^{11'}$), 5.50 br.s(1H, OH), 6.59 d (1H, H^6, J 7.6 Hz), 6.88 d (1H, H^5, J 7.6 Hz), 7.29 d (2H, $H^{3'',5''}$, J 7.8 Hz), 7.75 d (2H, $H^{2'',6''}$, J 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 12.49 q ($C^{14'}$), 19.84 t ($C^{3'}$), 21.40 q (CH_3), 24.44 t ($C^{9'}$), 26.17 t ($C^{8'}$), 30.91 t ($C^{10'}$), 28.67 q ($C^{13'}$), 38.01 t ($C^{2'}$), 38.59 t ($C^{7'}$), 38.92 t ($C^{4'}$), 40.15 s ($C^{4a'}$), 44.20 s ($C^{1'}$), 51.09 q (OCH_3), 51.79 t (C^3), 53.24 t (C^1), 55.29 d ($C^{8a'}$), 56.09 d ($C^{5'}$), 106.38 t ($C^{11'}$), 114.40 d (C^6), 122.42 s (C^{7a}), 127.47 d ($C^{2'',6''}$), 128.73 d (C^5), 129.44 s (C^4), 129.70 d ($C^{3'',5''}$), 133.56 s ($C^{4''}$), 136.40 s (C^{3a}), 143.57 s ($C^{1''}$), 147.74 s ($C^{6'}$), 147.78 s (C^7), 178.07 s ($C^{12'}$). Mass spectrum, *m/z* (I_{rel}, %): 551 (6), 399 (18), 398 (66), 397 (37), 396 (88), 338 (15), 336 (12), 302 (10), 301 (38), 273 (10), 189 (11), 160 (16), 155 (15), 149 (13), 148 (19), 147 (34), 146 (100), 133 (11), 123 (12), 121 (39), 119 (12), 109 (18), 107 (19), 105 (14), 95 (18), 93 (17), 92 (10), 91 (48), 81 (22), 79 (13), 77 (11), 69 (12), 67 (12), 57 (13), 55 (18). Found $[M]^+$ 551.2684. $C_{32}H_{41}NO_5S$. Calculated *M* 551.2700.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl-6-methylidene-5-(2-{2-[(prop-2-yn-1-yloxy)methyl]furan-3-yl}ethyl)decahydronaphthalene-1-carboxylate (XI). To a stirred solution of 1.00 g (2.8 mmol) of compound **X** in 10 ml of DMF was added at 0°C by portions 0.33 g (8.3 mmol) of 60% dispersion of sodium hydride in mineral oil, the mixture was stirred for 30 min, and 0.61 ml (5.5 mmol) of 80% solution of propargyl bromide in toluene was added. The reaction mixture was warmed to room temperature and the stirring continued for 4 h. The reaction mixture was poured on 50 g of ice, the reaction product was extracted into chloroform (3 × 50 ml). The combined extracts were washed with water (7 × 50 ml) and dried with $MgSO_4$. The solvent was distilled off, the residue was chromatographed on silica gel (eluent petroleum ether–ether, 4 : 1). Yield 0.61 g (55%), oily substance, $[\alpha]_D$ +37.29° (*c* 3.10, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 221 (3.83). IR spectrum, cm^{-1}: 741, 891, 1074, 1153, 1229, 1382, 1449, 1466, 1643, 1724, 2849, 2934, 2943, 3306. ^{1}H NMR spectrum, δ, ppm: 0.42 s (3H, $C^{20}H_3$), 0.89 d.t (1H, H^1, J 13.4, 3.2 Hz), 0.93 d.t (1H, H^3, J 13.3, 3.5 Hz), 1.08 s (3H, $C^{19}H_3$), 1.19 m (1H, H^5), 1.40 m (1H, H^2), 1.51 m (1H, H^9), 1.62 m (1H, H^{11}), 1.68–1.83 m (5H, $H^{1,2,6,7\alpha,11}$), 1.89 m (1H, H^6), 2.06 d.m (1H, H^3, J_{zem} 13.2 Hz), 2.23 m (1H, H^{12}), 2.33 m (1H, H^7), 2.48 m (1H, H^{12}), 2.50 m (1H, $H^{5'}$), 3.51 s (3H, OCH_3), 4.01 d (1H, $H^{3'}$, J 2.3 Hz), 4.02 d (1H, $H^{3'}$, J 2.3 Hz), 4.38 s (2H, $H^{1'}$), 4.52 s, 4.82 s (2H, H^{17}), 6.16 d (1H, H^{14}, J 1.5 Hz), 7.24 d (1H, H^{15}, J 1.5 Hz). ^{13}C NMR

spectrum, δ, ppm: 12.32 q (C^{20}), 19.62 t (C^{2}), 22.87 t (C^{12}), 24.38 t (C^{11}), 25.94 t (C^{6}), 28.43 q (C^{19}), 37.83 t (C^{3}), 38.37 t (C^{7}), 38.68 t (C^{1}), 39.80 s (C^{10}), 43.91 s (C^{4}), 50.74 q (OCH_3), 54.51 d (C^{9}), 55.85 d (C^{5}), 56.25 t ($C^{3'}$), 60.70 t ($C^{1'}$), 74.38 d ($C^{5'}$), 79.25 s ($C^{4'}$), 106.18 t (C^{17}), 111.17 d (C^{14}), 124.63 s (C^{13}), 141.90 d (C^{15}), 146.11 s (C^{16}), 147.47 s (C^{8}), 177.21 c (C^{18}). Mass spectrum, *m/z* (I_{rel}, %): 398 (1.58), 342 (13), 283 (13), 189 (28), 188 (12), 161 (12), 133 (14), 121 (100), 120 (15), 119 (21), 110 (15), 109 (16), 107 (27), 105 (23), 95 (29), 94 (38), 93 (22), 91 (33), 85 (16), 83 (14), 81 (36), 79 (23), 77 (18), 71 (20), 69 (16), 67 (19), 57 (34), 55 (37), 53 (14), 43 (33), 41 (39), 39 (16), 29 (14). Found $[M]^+$ 398.2455. $C_{25}H_{34}O_4$. Calculated *M* 398.2452.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-5-[2-(7-hydroxy-1,3-dihydroisobenzofuran-4-yl)ethyl]-1,4a-dimethyl-6-methylidenedecahydronaphthalene-1-carboxylate (VIII). To a solution of 0.300 g (0.753 mmol) of compound **XI** in 10 ml of acetonitrile was added at room temperature 0.011 g (0.038 mmol) of $AuCl_3$, and the stirring was continued for 24 h. The solvent was distilled off, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ether, 1 : 1). Yield 0.23 g (78%), oily substance, $[\alpha]_D$ +39.62° (*c* 1.81, $CHCl_3$). UV spectrum, λ_{max}, nm (log ε): 214 (4.72), 278 (3.10). IR spectrum, cm^{-1}: 3375, 3080, 3019, 2945, 2849, 1722, 1701, 1643, 1609, 1500, 1452, 1379, 1317, 1292, 1231, 1186, 1155, 1132, 1092, 1055, 1032, 1005, 984, 891, 816, 756, 710. ^{1}H NMR spectrum, δ, ppm: 0.47 s (3H, $C^{14'}H_3$), 0.96 d.t (1H, $H^{4'}$, *J* 13.8, 4.6 Hz), 1.01 d.t (1H, $H^{2'}$, *J* 13.4, 4.4 Hz), 1.16 s (3H, $C^{13'}H_3$), 1.26 d.d (1H, $H^{8a'}$, *J* 12.5, 3.2 Hz), 1.48 m (1H, $H^{3'}$), 1.57 br.s(1H, $H^{5'}$), 1.70 m (1H, $H^{9'}$), 1.76 m, 1.79 m, 1.81 m (4H, $H^{9',8',4',3'}$), 1.88 m (1H, $H^{7'}$), 1.98 m (1H, $H^{8'}$), 2.14 d.m (1H, $H^{2'}$, *J* 13.0 Hz), 2.22 m (1H, $H^{10'}$), 2.41 d.d.d (1H, $H^{7'}$, *J* 11.9, 4.0, 2.3 Hz), 2.60 m (1H, $H^{10'}$), 3.60 s (3H, OCH_3), 4.59 s, 4.89 s (2H, $H^{11'}$), 5.05 d (1H, H^{1}, *J* 10.2 Hz), 5.10 d (1H, H^{1}, *J* 10.2 Hz), 5.16 s (2H, H^{3}), 5.40 br.s(1H, OH), 6.61 d (1H, H^{6}, *J* 8.0 Hz), 6.90 d (1H, H^{5}, *J* 8.0 Hz). ^{13}C NMR spectrum, δ, ppm: 12.52 q ($C^{14'}$), 19.82 t ($C^{3'}$), 24.64 t ($C^{9'}$), 26.18 t ($C^{8'}$), 28.70 q ($C^{13'}$), 31.35 t ($C^{10'}$), 38.03 t ($C^{2'}$), 38.62 t ($C^{7'}$), 38.92 t ($C^{4'}$), 40.16 s ($C^{4'a}$), 44.24 s ($C^{1'}$), 51.20 q (OCH_3), 55.28 d ($C^{5'}$), 56.12 d ($C^{8a'}$), 72.19 t (C^{3}), 73.37 t (C^{1}), 106.36 t ($C^{11'}$), 114.16 d (C^{6}), 124.59 s (C^{7a}), 128.02 s (C^{4}), 128.61 d (C^{5}), 139.30 s (C^{3a}), 147.80 s ($C^{6'}$), 148.44 s (C^{7}), 178.04 s ($C^{12'}$). Mass spectrum, *m/z* (I_{rel}, %): 398 (7), 237 (12), 236 (53), 235 (25), 202 (13), 201 (19), 189 (34), 177 (10), 162 (49), 161 (17), 149 (50), 148 (100), 135 (11), 133 (10), 121 (66), 120 (15), 119 (11), 109 (12), 107 (20), 105 (12), 95 (10), 93 (14), 91 (20), 81 (21), 79 (10). Found $[M]^+$ 398.2450. $C_{25}H_{34}O_4$. Calculated *M* 398.2452.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-5-(2-{2-[(*R*)-1-hydroxybut-3-yn-1-yl]furan-3-yl}ethyl)- and 5-(2-{2-[(*S*)-1-hydroxybut-3-yn-1-yl]furan-3-yl}ethyl)-1,4a-dimethyl-6-methylidenedecahydronaphthalene-1-carboxylates (XIIa, XIIb). *a*. To a stirred solution of 0.40 g (2.8 mmol) of propargylmagnesium bromide in 20 ml of anhydrous ether at –40°C in an argon flow was added dropwise a solution of 1.00 g (2.8 mmol) of methyl 16-formyllambertianate (**VII**) in 10 ml of ether. The temperature of the reaction mixture was raised to 10°C, and the stirring was continued for 10 min. The formation of a white dispersion with large grains was observed. To the reaction mixture was cautiously added 100 ml of water solution of ammonium chloride (17 g of NH_4Cl per 100 g of H_2O), and the mixture was vigorously stirred till phase separation. The organic layer was separated, the reaction product was extracted from the water layer into ether (3 × 30 ml). Combined organic solutions were dried with $MgSO_4$. The solvent was removed to give in the residue 0.83 g (74%) of oily mixture of diastereomers **XIIa, XIIb**.

b. To a stirred dispersion of 1.00 g (2.8 mmol) of methyl 16-formyllambertianatea (**VII**), 0.91 g (5.6 mmol) of activated zinc powder, and 0.62 ml of 80% solution of propargyl bromide in toluene in 20 ml of THF at 0°C was added dropwise within 1 h 5 ml of saturated solution of ammonium chloride. The temperature of the reaction mixture was raised to ambient, and the stirring was continued for 24 h more. The organic layer was separated, the reaction product was extracted from the water layer into ethyl ether (3 × 30 ml). The combined organic solutions were washed with saturated water solution of ammonium chloride (2 × 20 ml), with brine (2 × 20 ml), and dried with $MgSO_4$. The solvent was distilled off, the residue was chromatographed on a column packed with silica gel (eluent petroleum ether–ether, 4 : 1). Yield of the mixture of diastereomers **XIIa, XIIb** 0.74 g (66%), oily substance. UV spectrum, λ_{max}, nm (log ε) 220 (3.85), 279 (3.09). IR spectrum, cm^{-1}: 3481, 3308, 3078, 2945, 2846, 2122, 1958, 1722, 1643, 1464, 1449, 1381, 1333, 1229, 1159, 1090, 1034, 986, 891, 748, 640. ^{1}H NMR spectrum, δ, ppm: 0.47 s (3H, $^*C^{20}H_3$), 0.85 m (1H, $^*H^{1}$), 0.99 d.t (1H, $^*H^{3}$, *J* 13.4, 4.0 Hz), 1.14 s, 1.23 s (3H, $C^{19}H_3$), 1.25 m (1H, $^*H^{5}$), 1.46 d.m (1H, $^*H^{2}$, J_{zem} 13.9 Hz), 1.56 m (1H, $^*H^{9}$), 1.59 m (1H, $^*H^{11}$), 1.68–1.83 m (4H, $^*H^{1,2,6,11}$),

1.83 m (1H, *H7), 1.91 m (1H, *H6), 2.01 m (2H, *H4′, 2H, *OH), 2.12 d.m (1H, *H3, J_{zem} 13.2 Hz), 2.25–2.34 m (1H, *H12), 2.40 m (1H, H7), 2.50–2.55 m (1H, *H12), 2.62 d.d (1H, H2′, *J* 6.8, 2.6 Hz), 2.67 d.d (1H, H2′, *J* 6.8, 2.6 Hz), 2.79 d.d (1H, H2′, *J* 7.0, 2.6 Hz), 2.84 d.d (1H, H2′, *J* 7.0, 2.6 Hz), 3.57 s (3H, *CH_3O), 4.58 s (1H, *H17), 4.79 m (1H, *H1′), 4.89 s (1H, *H17), 6.20 d (1H, *H14, *J* 1.8 Hz), 7.28 d (1H, *H15, *J* 1.8 Hz). ^{13}C NMR spectrum, δ, ppm: 12.53 q (C20), 19.82 t (C2), 22.94 t (C12), 24.55 t (C11), 26.03 t (C6), 26.17 t (C2′), 28.70 q (C19), 38.07 t (C3), 38.59 t (C7), 38.96 t (C1), 40.08 s (C10), 44.17 s (C4), 51.04 q (OCH_3), 54.91 d (C9), 56.16 d (C5), 64.27 d (C1′), 70.43 d (C4′), 80.41 s (C3′), 106.52 t (C17), 111.47 d (C14), 122.50 s (C13), 141.51 d (C15), 147.72 s, 147.88 s (C16), 148.70 s (C8), 177.61 s (C18). Mass spectrum, *m/z* (I_{rel}, %): 398 (3), 341 (18), 315 (29), 299 (25), 281 (23), 249 (13), 189 (37), 181 (16), 173 (13), 161 (15), 148 (25), 147 (17), 131 (28), 123 (29), 121 (100), 119 (17), 110 (36), 109 (18), 107 (25), 105 (18), 95 (14), 93 (20), 91 (21), 81 (30), 79 (16), 77 (15), 55 (14), 41 (14). Found $[M]^+$ 398.2453. $C_{25}H_{34}O_4$. Calculated *M* 398.2452.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl-6-methylidene-5-(2-{2-[(*R*)-1-(prop-2-yn-1-yloxy)- but-3-yn-1-yl]furan-3-yl}ethyl)- and methyl (1*S*,4a*R*,5*S*,8a*R*)-1,4a-dimethyl -6-methylene-5-(2-{2-[(*S*)-1-(prop-2-yn-1-yloxy)but-3-yn-1-yl]furan-3-yl}ethyl)decahydronaphthalene-1-carboxylates (XIIIa, XIIIb). To a stirred solution of 0.52 g (1.3 mmol) of compound **XIIa, XIIb** in 10 ml of DMF at 0°C was added by portions 0.31 g (13.1 mmol) of 60% dispersion of sodium hydride in mineral oil, the mixture was stirred for 30 min, then 0.58 ml (6.56 mmol) of 80% solution of propargyl bromide in toluene was added. The reaction mixture was warmed to room temperature and the stirring continued for 4 h. The reaction mixture was poured on 50 g of ice, the reaction product was extracted into chloroform (3 × 50 ml). The extract was washed with water (7 × 50 ml), dried with $MgSO_4$, and evaporated. The residue was chromatographed on silica gel (eluent petroleum ether–ether, 10 : 1). We obtained 0.32 g (57%) of oily mixture of compounds **XIIIa**, **XIIIb**. The purification was performed by column chromatography. At keeping in air from the enriched fraction of stereoisomers individual compound **XIIIa** was isolated, mp 55–58°C, which was subjected to XRD analysis.

Mixture of compounds **XIIIa, XIIIb**. UV spectrum, λ_{max}, nm (log ε): 220 (3.74). IR spectrum, cm^{-1}: 3422, 3296, 3078, 2930, 2851, 2120, 1722, 1771, 1643, 1600, 1510, 1466, 1449, 1383, 1333, 1229, 1155, 1078, 1040, 889, 770, 642. ^{1}H NMR spectrum, δ, ppm: 0.47 s (3H, *$C^{20}H_3$), 0.96 d.t (1H, *H1, *J* 12.6, 3.6 Hz), 1.01 d.t (1H, *H3, *J* 13.2, 4.6 Hz), 1.13 s (3H, $C^{19}H_3$), 1.14 s (3H, $C^{19}H_3$), 1.26 m (1H, *H5), 1.46 m (1H, *H2), 1.59 m (1H, H9), 1.61 m (1H, H9), 1.65–1.71 m (1H, *H11), 1.72–1.82 m (5H, *H11,6,1,2,7), 1.96 m (1H, *H6), 2.13 m (1H, *H3), 2.24–2.35 m (1H, *H12), 2.38 m (2H, *H4′,4″), 2.40 m (1H, *H7), 2.51–2.63 m (1H, *H12), 2.73–2.79 m (2H, *H2′), 3.57 s (3H, *CH_3O), 3.81 d (1H, H2″, *J* 16.2 Hz), 3.82 d (1H, H2″, *J* 15.9 Hz), 4.05 d.d (1H, H2″, *J* 15.9, 2.6 Hz), 4.06 d.d (1H, H2″, *J* 16.2, 2.7 Hz), 4.59 s (1H, *H17), 4.70 m (1H, *H1′), 4.89 c (1H, *H17), 6.21 d (1H, H14, $J_{14,15}$ 1.5 Hz), 6.22 d (1H, H14, $J_{14,15}$ 2.0 Hz), 7.31 d (1H, *H15). ^{13}C NMR spectrum, δ, ppm: 12.38 q, 12.44 q (C20), 19.75 t (*C2), 22.88 t, 22.99 t (C12), 23.88 t, 26.17 t (C2′), 24.51 t, 24.78 t (C11), 26.08 t (*C6), 28.60 q (*C19), 38.01 t (*C3), 38.48 t, 38.55 t (C7), 38.89 t, 39.00 t (C1), 40.01 s, 40.06 s (C4), 44.06 s (*C10), 50.90 q (*OCH_3), 54.89 d, 55.27 d (C9), 55.02 t, 55.08 t (C2″), 56.06 d, 56.09 d (C5), 63.38 d, 69.60 d (C1′), 69.70 d (*C4′), 74.40 d (*C4″), 79.29 c (*C3′), 79.85 s, 80.01 s (C3″), 106.44 t, 106.50 t (C17), 111.05 d (*C14), 125.52 s, 152.60 s (C13), 142.13 d, 142.15 d (C15), 145.31 s, 145.54 s (C16), 147.56 s (*C8), 177.39 s (*C18). Mass spectrum, *m/z* (I_{rel}, %): 436 (0.25), 341 (24), 316 (23), 315 (100), 281 (29), 255 (17), 189 (15), 181 (28), 173 (12), 161 (50), 147 (45), 132 (11), 131 (29), 121 (90), 119 (14), 109 (24), 107 (22), 105 (20), 95 (17), 93 (18), 91 (31), 85 (12), 81 (31), 79 (19), 77 (21), 71 (17), 69 (14), 67 (15), 57 (26), 55 (26), 43 (17), 41 (20), 39 (15). Found $[M]^+$ 436.2604. $C_{28}H_{36}O_4$. Calculated *M* 436.2608.

Methyl (1*S*,4a*R*,5*S*,8a*R*)-5-{2-[(*R*)- and (*S*)-7-hydroxy-3-(prop-2-yn-1-yl)-1,3-dihydroisobenzo-furan-4-yl]ethyl}-1,4a-dimethyl -6-methylidenedecahydronaphthalene-1-carboxylate (IXa, IXb). To a solution of 0.300 g (0.687 mmol) of a mixture of compounds **XIIIa, XIIIb** in 10 ml of acetonitrile was added at room temperature 0.010 g (0.034 mmol) of $AuCl_3$, and the mixture was stirred for 24 h. The solvent was distilled off, the residue was chromatographed on silica gel (eluent – petroleum ether–ether, 1 : 1). Yield 0.21 g (70%). Oily mixture of diastereomers, 1 : 1. UV spectrum, λ_{max}, nm (log ε): 224 (3.93), 282 (3.32). IR spectrum, cm^{-1}: 3381, 3308, 3308, 3080, 3017, 2945, 2874, 2849, 2122, 1722, 1643, 1607, 1501, 1464, 1450, 1381, 1367, 1335, 1292, 1248, 1231, 1211, 1155, 1092, 1053, 1030, 984, 962, 891, 819, 756, 667, 640. ^{1}H NMR spectrum, δ, ppm: 0.49 s (3H,

* Doubling of the signal.

*C$^{14'}$H$_3$), 1.01 m (2H, *H$^{2',4'}$), 1.16 s (3H, *C$^{13'}$H$_3$), 1.27 m (1H, *H$^{8a'}$), 1.49 m (1H, H$^{3'}$), 1.60 m (1H, *H$^{5'}$), 1.52 m (1H, H$^{9'}$), 1.78–1.91 m (5H, *H$^{4',3',7',8',9'}$), 1.98 m (1H, H$^{8'}$), 2.14 d.m (1H, *H$^{2'}$, *J* 13.9 Hz), 2.24 m (1H, *H$^{10'}$), 2.41 m (1H, *H$^{7'}$), 2.51 m (1H, H$^{1''}$), 2.57 m (1H, H$^{1''}$), 2.60–2.68 m (2H, *H$^{10'}$, *H$^{3''}$), 2.73 m, 2.79 m (2H, H$^{1''}$), 3.60 s (3H, *CH$_3$O), 4.60 s (1H, *H$^{11'}$), 4.91 s (1H, *H$^{11'}$), 5.09 d (1H, *H^{1}, *J* 10.2 Hz), 5.25 d.t (1H, *H^{1}, *J* 10.2, 2.0 Hz), 5.40 m, 5.44 m (1H, H^{3}), 5.95 br.s(1H, *HO), 6.67 d (1H, *H^{6}, *J* 7.9 Hz), 6.95 d (1H, *H^{5}, *J* 7.9 Hz). ^{13}C NMR spectrum, δ, ppm: 12.20 q (*C$^{14'}$), 19.49 t, 19.52 t (C$^{3'}$), 24.33 t, 24.57 t (C$^{1''}$), 25.41 t, 25.51 t (C$^{9'}$), 25.87 t (*C$^{8'}$), 28.73 q, 28.40 q (C$^{13'}$), 30.01 t, 30.09 t (C$^{10'}$), 37.72 t (*C$^{2'}$), 38.24 t, 38.29 t (C$^{7'}$), 38.63 t (*C$^{4'}$), 39.86 s, 39.91 s (C$^{4a'}$), 43.92 s (*C$^{1'}$), 50.88 q (*OCH$_3$), 55.03 d (*C$^{8a'}$), 55.81 d (*C$^{5'}$), 69.45 d, 69.50 d (C^{3}), 70.99 t, 71.10 t (C^{1}), 80.38 s (*C$^{2''}$), 82.18 d, 82.26 d (C$^{3''}$), 106.06 t, 106.11 t (C$^{11'}$), 114.59 d, 114.61 d (C^{6}), 125.08 s, 125.53 s (C^{7a}), 127.96 s (*C^{4}), 128.54 d, 128.77 d (C^{5}), 139.52 s (*C^{3a}), 147.56 s, 147.63 c (*C^{7}), 147.81 s (C$^{6'}$), 177.70 s (*C$^{12'}$). Mass spectrum, *m/z* (I_{rel}, %): 436 (4), 398 (27), 397 (100), 379 (28), 337 (14), 319 (28), 249 (13), 201 (15), 199 (26), 189 (34), 187 (24), 186 (48), 185 (27), 173 (15), 161 (42), 159 (15), 157 (14), 148 (33), 145 (12), 133 (12), 121 (89), 120 (20), 119 (16), 109 (18), 107 (29), 105 (18), 95 (17), 93 (22), 91 (32), 81 (38), 79 (17), 77 (13), 67 (14), 55 (21), 41 (18). Found $[M]^+$ 436.2605. $C_{28}H_{36}O_4$. Calculated *M* 436.2608.

X-ray crystallographic data for compound XIIIa. For the experiment a needle crystal of compound **XIIIa** was selected of the size 0.80 × 0.40 × 0.04 mm. Crystals monoclinic, *a* 11.533(2), *b* 7.169(1), *c* 15.427(3) Å, β 99.139(6)°, *V* 1259.4(4) Å^3, space group $P2_1$, *Z* 2. $C_{28}H_{36}O_4$. d_{calc} 1.151 g/cm^3, μ 0.075 mm^{-1}. The intensities of 4539 independent reflections were measured. The corrections for extinction were introduced with the help of SADABS program [15]. The structure was solved by the direct method and was refined by the full-matrix least-squares method in the anisotropic approximation (except for H atoms) using SHELX-97 software [16]. The positions of the hydrogen atoms wer calculated geometrically and refined in the *rider* model (parameters of hydrogen atoms were calculated in each refinement cycle from the coordinates of the corresponding carbon atoms). The final refinement of the structure was performed with respect to all F^2 to wR_2 0.2032, *S* 1.04, 292 parameters were refined (*R* 0.0669 for 3237 $F > 4\sigma$).

CIF file containing full information on the studied structure has been deposited into CCDC, no. 862589 and can be obtained freely by the address www.ccdc.cam.ac.uk/data_request/cif.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Foundation for Basic Research (grant no. 11-03-00242) and of the Program of the President of the Russian Federation for the support of the leading scientific schools (grant NSh-3986.2012.3).

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