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Reactions of Stereocontrolled Intramolecular Carbocyclization of Levoglucosenone Adduct with Isoprene

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Abstract—An intramolecular carbocyclization was found of levoglucosenone adduct with isoprene providing a fused cyclobutane. The intramolecular oxacyclization of the adduct was performed under the treatment with I_2, H_3PO_4, $SOCl_2$, and Pd/C leading to 1,4-epoxide. Methods were developed of radical and anionic (by Ferrier method) transformation of the adduct into chiral *trans*- and *cis*-decalins.

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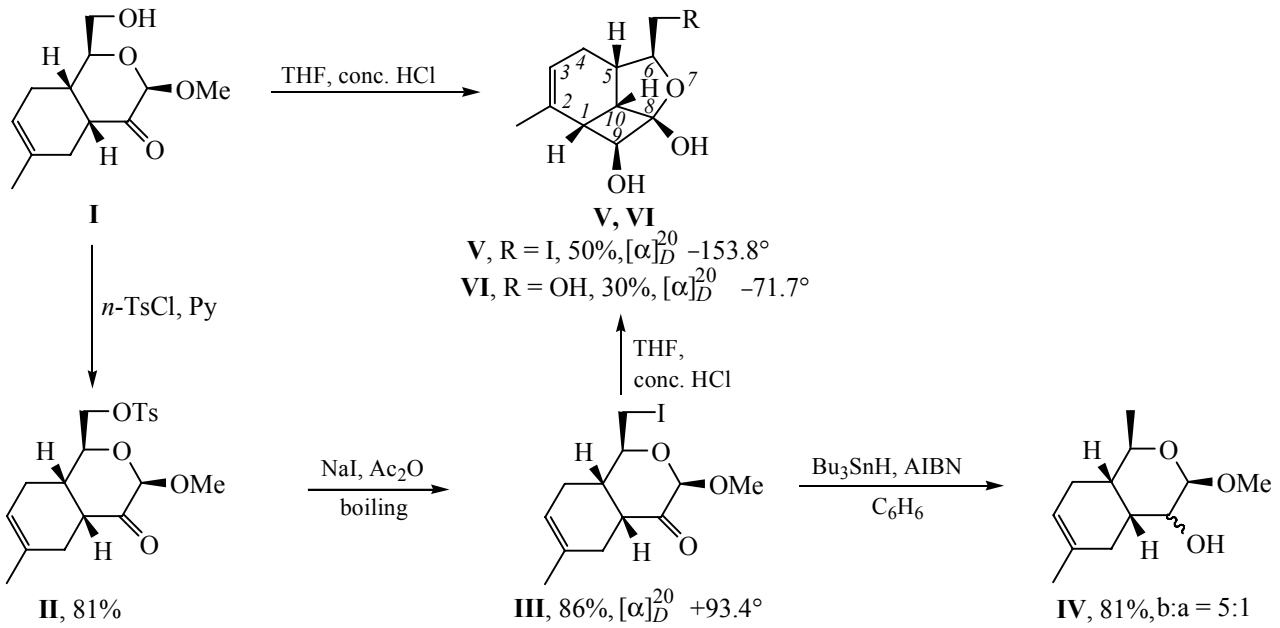
The levoglucosenone is known as a highly reactive dienophile forming in the diene synthesis functionalized chiral cyclohexanes that have found employment in the synthesis of natural compounds [1]. The procedures of transformation of the carbohydrate fragment into a carbocycle in these adducts is another important stage in solving the problem of the extension of the synthetic opportunities of levoglucosenone.

We investigated the possibilities of the radical and anionic rearrangements of the carbohydrate fragment in the adducts of the levoglucosenone with isoprene into the carbocyclic derivatives. The first step in the study of the radical transformations of the adduct was an attempt to create a C^{11}-centered radical and to establish the ways to its stabilization. The rearrangement of the primary radical might finish with the involvement of the double

Scheme 1.



bond; the possibility of its interaction with the α-keto-aldehyde fragment also could not be completely excluded in the case of the opening of the pyran ring of the molecule in the course of the reaction.

In order to obtain the key radical intermediate methylacetal **I** [2] was tosylated, and the nucleophilic substitution by the treatment with NaI afforded iodide **III**.

The treatment of iodide **III** with Bu_3SnH in the presence of 1,1'-azobisisobutyronitrile (AIBN) [3] in order to generate the radical center and to initiate the intramolecular cyclization resulted in reductive deiodination and in the transformation of the carbonyl group into a carbinol one giving α,β-epimeric alcohols **IV** (Scheme 1). Apparently the conditions for the cleavage of the methoxy group were not attained in the course of the process, and it impeded the opening of the pyran ring preceding to the closure of the carbocycle.

The attempt on the hydrolysis of the methoxy group in iodide **III** by treating its solution in THF with concn. HCl resulted in the carbocyclization with the formation of a fused cyclobutane **V**. The similar treatment of methoxy derivative **I** also led to the formation of cyclobutane **VI** but in a worse yield.

The structure of compounds **V** and **VI** was established from ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of compound **V** a doublet of doublets of H^1 is registered at 2.63 ppm ($J_{1,10}$ 5.7, $J_{1,9}$ 5.2 Hz) indicating the β-*syn*-location of protons H^1 and H^{10}. The similar value of coupling constant of protons H^{10} and H^5, 5.0 Hz, also shows their *cis*-orientation. At this *syn*-position of the rings the only possible orientation of the hemiketal hydroxy group can be the β-orientation. In the ^{13}C NMR spectra the C^8 atom was detected at 111.51 ppm, atoms C^1, C^9, and C^{10} of the cyclobutane ring, at 45.66, 84.94, and 46.55 respectively.

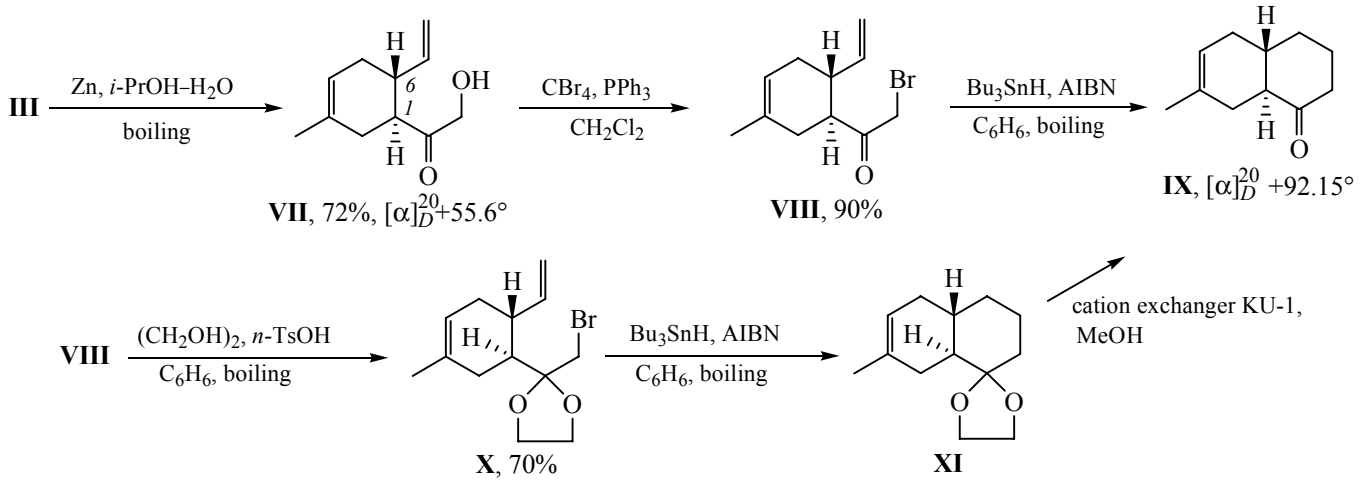
The alternative and more probable way of obtaining fused carbocycle would be the transformation of the carbohydrate part of the molecule into 6-halohexene fragment for the radical cyclization of this type compounds is known [3].

The required transformation was sufficiently effectively performed by boiling the solution of iodoketone **III** in a mixture 2-propanol–water in the presence of zinc. At the opening the pyranose ring the configuration at the asymmetric center C^1 turned to the opposite with the formation of ketoalcohol **VII**. The *S*-configuration of the C^1 atom is indicated by a large coupling constant ($J_{1,6}$ 9.7 Hz) showing the *trans*-location of protons H^1, H^6.

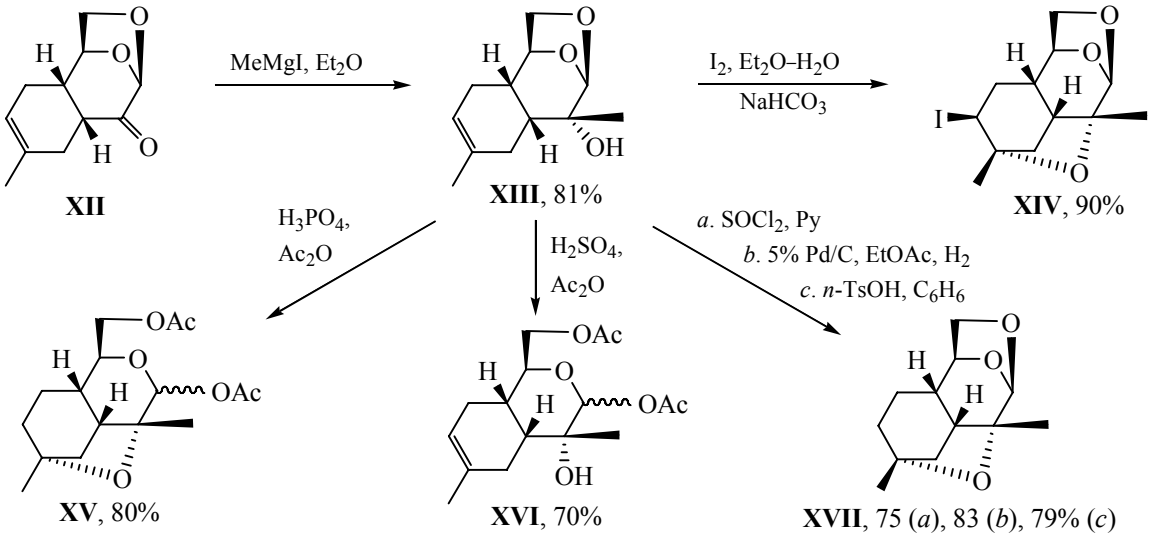
The subsequent replacement of the hydroxy group by bromine was performed using CBr_4–PPh_3. The treatment of the bromo derivative **VIII** with Bu_3SnH in boiling benzene resulted in its complete conversion, but bicyclodecanone **IX** was isolated from the reaction mixture in 35% yield.

In all likelihood the free keto group initiated competing side products leading to the decrease in the yield of the target compound. Therefore the keto group was protected by transformation into dioxolane **X**, and the radical reaction involving Bu_3SnH was repeated (Scheme 2). Already in 2 h compound **XI** was formed whose hydrolysis by treatment with cation-exchanger KU-1 in methanol resulted in bicyclodecanone **IX** in 92% yield

Scheme 2.



Scheme 3.



(with respect to the two last stages). The obtained *trans*-junked bicyclodeca-none **IX** is a chiral matrix for applying to the synthesis of natural compounds [4, 5].

In order to study the possibility of the anionic rearrangement of the carbohydrate fragment in the levoglucosenone adduct with isoprene by the type of aldol intramolecular cyclization the most reasonable way seemed the preliminary opening of the 1,6-anhydro bridge and the generation of the aldehyde function. The blocking of the keto function necessary in this case with a sufficiently stable protective group may be a problem for this bicyclic system with a *cis*-junction. Therefore it was convenient to carry out these transformations through a protected hydroxy derivative, and considering that we had found before an ability to the intramolecular oxacyclization in a bicyclic system with a *cis*-junction of (+)-δ-cadinol [6, 7], we attempted to make analogous 2-hydroxy-5-methyl-5-ene system for its subsequent cyclization into a tetrahydrofuran ring. The treatment of compound **XII** with methylmagnesium iodide furnished tertiary alcohol **XIII** whose further iodocyclization [8] cleanly provided a fused tetrahydrofuran ring in compound **XIV** (Scheme 3).

The treatment of tertiary alcohol **XIII** with phosphoric acid in Ac_2O also resulted in 1,4-oxacyclization but with the simultaneous opening of the 1,6-anhydro bridge and the formation of anomeric diacetates **XV**. The use in this reaction of sulfuric acid instead of phosphoric led only to the opening of the 1,6-anhydro bridge and the formation of the anomers of compound **XVI**, and the treatment of compound **XIII** with $SOCl_2$ or hydrogenation on Pd/C also resulted in the fused tetrahydrofuran ring in compound **XVII**.

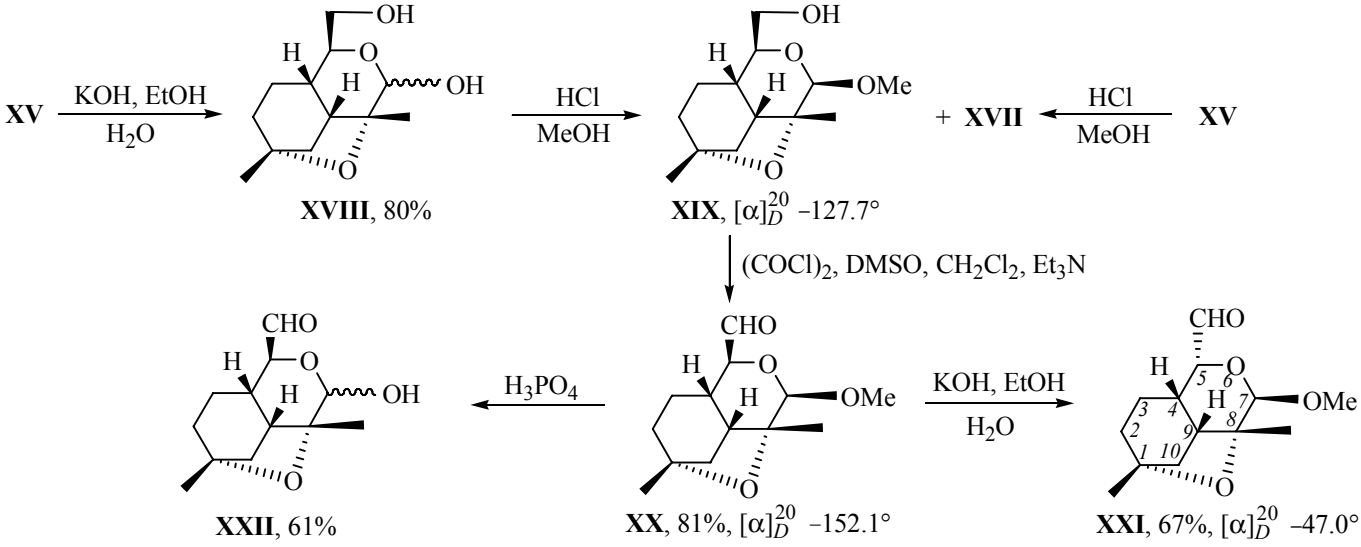
The obtained tetrahydrofuran derivative **XV** is a convenient object for the study of the opportunities of the aldol condensation with the prospect of transfer of the chiral centers into a carbobicyclodecane framework. The direct acidolysis of diacetates **XV** or the alkaline hydrolysis of the anomers of compound **XVIII** followed by treating with HCl–MeOH solution led to the formation of a mixture of methylacetal **XIX** and a side product, 1,6-anhydro derivative **XVII**.

The oxidation of the primary hydroxy group in compound **XIX** by Swern method gave aldehyde **XX**. The attempt to carry out the theoretically possible aldol cyclization by treating aldehyde **XX** with KOH in aqueous ethanol resulted in a single compound **XXI** that was more polar (according to TLC) that initial aldehyde **XX** (ΔR_f 0.05).

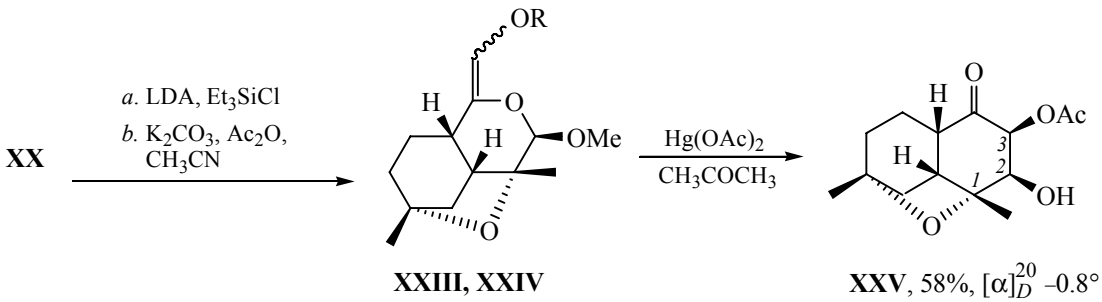
Likely the aldol condensation or the completion of ketol rearrangement was prevented by the methoxy group that was not eliminated in the course of the reaction. The hydrolysis of methylacetal **XX** occurring only at the action of 85% H_3PO_4, with the subsequent treatment of hemiacetal **XXII** with lithium diisopropylamide (LDA) led to the formation of a number of intractable products.

The alternative route consisted of two stages: The stabilization ot the enol form of aldehyde **XX** as ethers followed by their aldolization by Ferrier procedure [9, 10]. Aldehyde **XX** was treated with LDA–Et_3SiCl to obtain the desired enol ethers **XXIII** in 30% yield. A simpler

Scheme 4.



Scheme 5.



procedure was preparation of enol acetates **XXIV** under the action of Ac_2O in the presence of K_2CO_3 [11].

Ferrier procedure [9, 10] with the use of $Hg(OAc)_2$ completed the stereospecific carbocyclization of the carbohydrate fragment into tricyclic compound **XXV** (Scheme 5) with a *cis*-junction in the bicyclodecane system in 58% yield (in the two last stages). In keeping with the spectral findings the stereochemical result of the transformation was analogous to that described in [12], namely, the acetate group is oriented equatorially, and the hydroxy group axially. The coupling constant between H^2 and H^3 equals 4.0 Hz, corresponding to the coupling constant of the *cis*-located protons. Compound **XXV** is a convenient chiral precursor for the synthesis of functionalized sesquiterpenoids of the murolan type [4, 5]. One representative of these compounds, (+)-δ-cardinol, was successfully applied to the synthesis of eleuthesides [13].

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 at operating frequencies 300 (^1H) and 75.47 (^{13}C) MHz, solvent $CDCl_3$ The use of other solvents is indicated in each special case. Melting points were measured on a Koeffler heating block S 30A/G (Germany). The analytical TLC was performed on plates Sorbfil PTCKh-AF-A produced by "Sorbpolymer" (Krasnodar). The elemental analysis was carried out on a CHNS(O)-analyzer Euro-2000. IR spectra were recorded on spectrophotometers UR-20 and Specord M-80 (from films or mulls in mineral oil). Mass spectra were taken on an GC-MS instrument Shimadzu 2010EV. The optical rotation was measured on a polarimeter Perkin Elmer-341.

(1*S*,6*R*,8*R*,10*S*)-4-Methyl-8-methoxy-7-oxo-10-oxabicyclo[4.4.0]dec-2-en-10-ylmethyl *p*-toluenesulfonate (II). To a solution of 6.0 g (26.55 mmol) of

alcohol **I** in 45 ml of pyridine cooled to 0°C was added 6.30 g (31.8 mmol) of *p*-TsCl, and the mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with water, the reaction product was extracted into ethyl acetate (3×100 ml). The combined organic solutions were washed with 5% solution of HCl, a saturated solution of NaCl, with water, dried with $MgSO_4$, and concentrated. Yield 8.16 g (81%). Oily substance, R_f 0.6 (petroleum ether–EtOAc, 5:1), $[\alpha]_D^{20}$ +94.9° (*c* 1.0, $CHCl_3$). ^{1}H NMR spectrum (CCl_4 + C_6D_6), δ, ppm: 1.47 s (3H, CH_3), 1.50–2.21 m (5H, CH,CH_2), 2.28 s (3H, $PhCH_3$), 2.40 d.d.d (1H, H^6, *J* 11.3, 9.5, 6.4 Hz), 3.32 s (3H, OCH_3), 3.89 m (1H, H^{10}), 3.90 m (1H, H$^{1'}$), 4.02 m (1H, H$^{1'}$), 4.24 s (1H, H^8), 5.22 m (1H, H^3), 7.12 m (2H, Ph), 7.60 d (2H, Ph). ^{13}C NMR spectrum (CCl_4 + C_6D_6), δ, ppm: 16.52 ($PhCH_3$), 18.26 (C^2), 18.41 (CH_3), 29.42 (C^5), 35.77 (C^1), 38.65 (C^6), 50.02 (OCH_3), 63.70 (C$^{1'}$), 65.94 (C^{10}), 95.35 (C^8), 114.94 (C^3), 122.97 (Ph), 124.58 (Ph), 125.79 (C^4), 128.63 (Ph), 139.14 (Ph), 195.28 (C^7). Found, %: C 60.07; H 6.34. $C_{19}H_{24}O_6S$. Calculated, %: C 59.98; H 6.36; S 8.43.

(1*S*,6*R*,8*R*,10*S*)-10-Iodomethyl-4-methyl-8-methoxy-9-oxabicyclo[4.4.0]dec-2-en-7-one (III). To a solution of 8.0 g (21.1 mmol) of tosylate **II** in 35 ml of acetic anhydride was added 9.45 g (63.22 mmol) of sodium iodide, and the mixture was heated to boiling and boiled for 5 min. On cooling to 0°C the reaction mixture was neutralized with a saturated solution of $NaHCO_3$. The reaction product was extracted into ethyl acetate (3 × 100), the organic solutions were combined, washed with $Na_2S_2O_3$, a saturated solution of NaCl, with water, and dried with $MgSO_4$. Yield 6.01 g (86%). Oily substance, R_f 0.6 (petroleum ether–EtOAc, 10:1), $[\alpha]_D^{20}$ +93.4° (*c* 1.0, $CHCl_3$). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm: 1.62 s (3H, CH_3), 1.88 m (2H, CH_2), 1.91–2.48 m (5H, CH,CH_2), 2.70 d.d.d (1H, H^6, *J* 11.6, 9.7, 6.6 Hz), 3.22 d (1H, H$^{1'}$, *J* 9.9 Hz), 3.26 d (1H, H$^{1'}$, *J* 9.9 Hz), 3.5 s (3H, OCH_3), 3.78 m (1H, H^{10}), 4.57 s (1H, H^8), 5.42 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 7.46 (C$^{1'}$), 23.47 (CH_3), 23.62 (C^2), 32.92 (C^5), 43.49 (C^1), 45.19 (C^6), 55.79 (OCH_3), 72.09 (C^{10}), 101.14 (C^8), 119.92 (C^3), 131.62 (C^4), 203.05 (C^7). Mass spectrum: *m/z* 337 $[M + H]^+$. Found, %: C 42.57; H 5.09. $C_{12}H_{17}IO_3$. Calculated, %: C 42.87; H 5.10.

(1*S*,6*R*,7*SR*,8*R*,10*R*)-2,8-Dimethyl-4-methoxy-3-oxabicyclo[4.4.0]dec-8-en-5-ol (IV). The cyclization was carried out by adding 10 ml of benzene solution of 0.18 g (0.72 mmol) of Bu_3SnH and 0.05 equiv of AIBN within 3 h to a boiling solution of 0.20 g (0.6 mmol) of iodide **III** in 10 ml of anhydrous benzene. Afterward the same amount of Bu_3SnH was added to the reaction mixture, and the boiling was continued till the disappearance of the initial compound. Then the mixture was cooled and treated with 10% solution of NaOH (10 ml). The reaction products were extracted into ethyl acetate (3× 30 ml), the organic solutions were combined, washed with a saturated solution of NaCl, with water, and dried with $MgSO_4$. The solvent was distilled off, and the residue was subjected to chromatography on SiO_2. Yield 0.10 g (81%) of a mixture of 7β- and 7α-epimers, 5:1. Oily substance, R_f 0.4 (petroleum ether–EtOAc, 5:1). ^{1}H NMR spectrum, δ, ppm: 0.90 d [0.95 d]* (3H, CH_3, *J* 6.8 Hz), 1.15–1.45 m [1.15–1.45 m] (4H, CH_2), 1.50 s [1.52 s] (3H, =CCH_3), 1.70 m [1.75 m] (1H, CH), 2.23 m [2.10 m] (1H, CH), 3.04 d.d [3.20 m] (1H, H^7, *J* 10.2, 3.6 Hz), 3.28 s [3.21 s] (3H, OCH_3), 3.30 m [3.30 m] (1H, H^{10}), [4.32 d (1H, H^8, *J* 1.5 Hz)], 4.41 d (1H, H^8, *J* 3.6 Hz), 5.28 d [5.12 d] (1H, H^3, *J* 3.6 Hz). ^{13}C NMR spectrum, δ, ppm: 18.90 [19.10] (CH_3), 24.10 [24.10] (CH_3), 29.30 [28.12] (C^2), 32.71 [34.64] (C^5), 38.07 [36.98] (C^1), 42.29 [41.72] (C^6), 55.10 [54.82] (OCH_3), 69.12 [68.56] (C^7), 73.4 [69.6] (C^{10}), 99.8 [101.5] (C^8), 121.26 [121.64] (C^3), 131.75 [133.62] (C^4). Found, %: C 67.94; H 9.63. $C_{12}H_{20}O_3$. Calculated, %: C 67.89; H 9.50.

(1*S*,5*S*,6*S*,8*S*,9*S*,10*S*)-6-Iodomethyl-2-methyl-7-oxatricyclo[6.1.1.0^{5,10}]dec-2-ene-8,9-diol (V). To a solution of 1.0 g (2.98 mmol) of iodide **III** in 15 ml of THF was added 3 ml of water and 5 ml of concn. HCl. After the disappearance of the initial compound (TLC monitoring) the reaction mixture was neutralized with a saturated solution of $NaHCO_3$, the reaction product was extracted into ethyl acetate (3×50 ml), the extract was dried with $MgSO_4$. On evaporation of the solvent the residue was subjected to chromatography. Yield 0.47 g (50%). Oily substance, R_f 0.5 (petroleum ether–EtOAc, 1:1), $[\alpha]_D^{20}$ –153.8° (*c* 1.0, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.50 d (1H, H^4, *J* 11.9 Hz), 1.72 s (3H, CH_3), 1.72 m (1H, H^4), 2.41 m (1H, H^5), 2.63 d.d (1H, H^1, *J* 5.7, 5.2 Hz), 3.15 d.d (1H, H^{10}, *J* 5.2, 5.0 Hz), 3.32 d.d (1H, H$^{1'}$, *J* 9.6, 3.9 Hz), 3.38 d.d (1H, H$^{1'}$, *J* 9.6, 5.6 Hz), 4.0 d.d (1H, H^6, *J* 9.6, 5.6 Hz), 4.09 d (1H, H^9, *J* 5.7 Hz), 5.30 br.s (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 6.64 (C$^{1'}$), 24.75 (CH_3), 26.17 (C^4), 44.91 (C^5), 45.66 (C^1), 46.55 (C^{10}), 84.31 (C^6), 84.94 (C^9), 111.51 (C^8), 120.70 (C^3), 141.50 (C^2). Mass spectrum: *m/z* 322 $[M]^+$. Found,

%: C 41.21; H 4.66. $C_{11}H_{15}IO_3$. Calculated, %: C 41.01; H 4.69.

(1*S*,5*S*,6*S*,8*S*,9*S*,10*S*)-6-Hydroxymethyl-2-methyl-7-oxatricyclo[6.1.1.0^{5,10}]dec-2-ene-8,9-diol (VI) was similarly obtained from 1.0 g (4.42 mmol) of alcohol **I**. Yield 0.28 g (30%). Oily substance, R_f 0.3 (petroleum ether–EtOAc, 1:1), $[\alpha]_D^{20}$ –71.7° (*c* 2.1, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.50 d (1H, H^4, *J* 11.8 Hz), 1.70 s (3H, CH_3), 1.70 m (1H, H^4), 2.42 d (1H, H^5, *J* 4.2 Hz), 2.65 d.d (1H, H^{10}, *J* 5.5, 4.2 Hz), 2.78 d.d (1H, H^1, *J* 5.5, 5.2 Hz), 3.0 br.s (1H, OH), 3.30 br.s (1H, OH), 3.68 d.d (1H, H$^{1'}$, *J* 11.5, 3.5 Hz), 3.78 d.d (1H, H$^{1'}$, *J* 11.5, 6.9 Hz), 3.86 d.d (1H, H^6, *J* 6.9, 3.5 Hz), 4.11 d (1H, H^9, *J* 5.2 Hz), 5.29 br.s (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 24.80 (CH_3), 26.05 (C^4), 44.17 (C^1), 45.08 (C^5), 47.19 (C^{10}), 64.23 (C$^{1'}$), 83.64 (C^6), 85.46 (C^9), 111.52 (C^8), 120.75 (C^3), 140.95 (C^2). Found, %: C 62.23; H 7.73. $C_{11}H_{16}O_4$. Calculated, %: C 62.25; H 7.60.

1-[(1*S*,6*R*)-6-Vinyl-3-methylcyclohex-3-enyl]-2-hydroxy-1-ethanone (VII). A mixture of 1.00 g (2.98 mmol) of iodide **III**, 2.0 g of zinc, 2.5 ml of water, and 11 ml of 2-propanol was boiled for 5 h. The reaction mixture was filtered, evaporated, and subjected to chromatography. Yield 0.39 g (72%). Oily substance, R_f 0.5 (petroleum ether–EtOAc, 4:1), $[\alpha]_D^{20}$ +55.6° (*c* 1.7, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.70 s (3H, =CCH_3), 1.83–2.32 m (4H, CH, CH_2), 2.50 d.d.d (1H, H^1, *J* 9.7, 9.7, 5.3 Hz), 2.56 d (1H, CH, *J* 7.3 Hz), 3.14 br.s (1H, OH), 4.18 m (2H, H$^{2'}$), 5.0 d (1H, H$^{2''}$, *J* 10.2 Hz), 5.03 d (1H, H$^{2''}$, *J* 17.5 Hz), 5.40 m (1H, H^4), 5.61 d.d.d (1H, H$^{1''}$, *J* 17.5, 10.2, 7.3 Hz). ^{13}C NMR spectrum, δ, ppm: 23.02 (=CCH_3), 27.84 (C^5), 35.43 (C^2), 40.64 (C^6), 47.60 (C^1), 66.54 (CH_2OH), 115.96 (C$^{2''}$), 118.40 (C^4), 132.83 (C^3), 139.56 (C$^{1''}$), 212.75 (C$^{1'}$). Mass spectrum: *m/z* 181 [*M* + H]$^+$. Found, %: C 73.31; H 9.03. $C_{11}H_{16}O_2$. Calculated, %: C 73.30; H 8.95.

1-[(1*S*,6*R*)-6-Vinyl-3-methylcyclohex-3-enyl]-2-bromo-1-ethanone (VIII). To a solution of 0.30 g (1.66 mmol) of ketoalcohol **VII** and 0.72 g (2.15 mmol) of CBr_4 in 15 ml of CH_2Cl_2 at 0°C while stirring was added 0.65 g (2.49 mmol) of PPh_3. The reaction mixture was kept for 15 min. On evaporation of the solvent the residue was subjected to chromatography. Yield 0.36 g (90%). Oily substance, R_f 0.5 (petroleum ether–EtOAc, 10:1). ^{1}H NMR spectrum, δ, ppm: 1.65 s (3H, =CCH_3), 1.95 m (2H, CH_2), 2.20 m (2H, CH_2), 2.57 d.d (1H, CH, *J* 10.2, 8.5 Hz), 2.88 d.d.d (1H, CH, *J* 10.2, 10.2, 6.0 Hz), 3.92 d (1H, H$^{2'}$, *J* 12.9 Hz), 3.95 d (1H, H$^{2'}$, *J* 12.9 Hz), 5.02 d (1H, H$^{2''}$, *J* 17.2 Hz), 5.07 d (1H, H$^{2''}$, *J* 10.2 Hz), 5.39 m (1H, H^4), 5.67 d.d.d (1H, H$^{1''}$, *J* 17.1, 10.2, 8.5 Hz). ^{13}C NMR spectrum, δ, ppm: 23.17 (=CCH_3), 28.53 (C^2), 35.55 (C^5), 35.61 (C$^{2'}$), 41.39 (C^6), 44.93 (C^1), 116.22 (C$^{2''}$), 118.63 (C^4), 133.18 (C^3), 139.77 (C$^{1''}$), 204.49 (C$^{1'}$). Found, %: C 54.57; H 6.239. $C_{11}H_{15}BrO$. Calculated, %: C 54.34; H 6.22.

(1*S*,6*S*)-4-Methylbicyclo[4.4.0]dec-2-en-7-one (IX). (a) The cyclization was performed as described for compound **IV**. From 0.25 g (1.03 mmol) of compound **VIII** we obtained 0.062 g (37%) of bicyclodecanone **IX**.

(b) The cyclization of dioxolane bromide **X** was carried out by the procedure used in obtaining compound **VIII.** The mixture obtained was dissolved in aqueous methanol, and cation-exchanger KU-1 was added. On completion of the reaction the reaction mixture was filtered, evaporated, and subjected to chromatography. From 0.12 g (0.42 mmol) of dioxolane **X** 0.06 g (92%) of bicyclodecanone **IX** was obtained. Oily substance, R_f 0.4 (petroleum ether–EtOAc, 5:1), $[\alpha]_D^{20}$ +92.15° (*c* 1.1, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 1.45 m (1H, CH_2), 1.63 s (3H, =CCH_3), 1.70 m (2H, CH_2), 1.80–1.88 m (2H, CH_2), 1.95–2.18 m (5H, CH, CH_2), 2.38 m (1H, CH_2), 2.40 m (1H, CH), 5.40 m (1H, H^3). ^{13}C NMR spectrum, δ, ppm: 23.21 (=CCH_3), 24.67 (C^9), 26.11 (C^5), 32.66 (C^2), 38.36 (C^{10}), 40.49 (C^1), 42.02 (C^8), 50.26 (C^6), 119.94 (C^3), 132.34 (C^4), 212.29 (C^7). Mass spectrum: *m/z* 165 [*M* + H]$^+$. Found, %: C 80.40; H 10.03. $C_{11}H_{16}O$. Calculated, %: C 80.44; H 9.82.

(1*S*,6*R*)-6-Vinyl-1-[2-bromo-1-(2,2-ethylenedioxy)]-3-methylcyclohex-3-ene (X). A solution of 0.15 g (0.62 mmol) of ketone **VIII** in 10 ml of anhydrous benzene containing a 5-fold excess of ethylene glycol was boiled at reflux with a Dean-Stark trap in the presence of a catalytic quantity of *p*-TsOH till the complete disappearance of the initial compound (TLC monitoring). On completion of the reaction the reaction mixture was evaporated, and the residue was subjected to chromatography. Yield 0.12 g (70%). Oily substance, R_f 0.6 (petroleum ether–EtOAc, 5:1). ^{1}H NMR spectrum, δ, ppm: 1.68 s (3H, =CCH_3), 1.95–2.38 m (5H, CH_2, CH), 2.84 m (1H, H^1), 3.49 d (1H, H$^{2'}$, *J* 12.3 Hz), 3.52 d (1H, H$^{2'}$, *J* 12.3 Hz), 4.0 m (4H, CH_2), 4.90 m (1H, H$^{2''}$), 5.02 m (1H, H$^{2''}$), 5.36 m (1H, H^4), 5.80 m (1H, H$^{1''}$).

(1*S*,2*S*,7*R*,8*R*,9*R*)-5,8-Dimethyl-10,12-dioxatricyclo[7.2.1.0^{2,7}]dodec-4-en-8-ol (XIII). To 80 ml

of 1.0 M MeMgI solution in ethyl ether cooled to 0°C under an argon atmospher ewas slowly added at stirring 10.0 g (51.6 mmol) of compound **XII** in 50 ml of THF. After 5 min (TLC monitoring) a saturated solution was added to the reaction mixture, and the mixture was warmed to room temperature. The reaction products were extracted into ethyl acetate (3×100 ml), the organic solutions were combined, washed with a saturated solution of NaCl, and dried with $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography on SiO_2. Yield 8.66 g (80%). Oily substance, $[\alpha]_D^{20}$ –73.41° (*c* 1.0, $CHCl_3$), R_f 0.52 (petroleum ether–EtOAc, 5:1). IR spectrum, ν, cm^{-1}: 3480, 3260, 2920, 1650, 1120, 1080, 1000, 960, 920. ^1H NMR spectrum, δ, ppm: 1.12 s (3H, CH_3), 1.70 s (3H, CH_3), 1.85 d.d (1H, H^6, *J* 12.3, 6.6 Hz), 1.88 m (1H, CH), 2.03 m (1H, CH_2), 2.22 m (2H, CH, CH_2), 2.49 (1H, CH_2), 3.85 d.d (1H, H^{11}, *J* 7.1, 4.9 Hz), 3.90 d (1H, H^{11}, *J* 7.10 Hz), 4.35 d (1H, H^1, *J* 4.9 Hz), 5.02 s (1H, H^9), 5.48 br.s (1H, H^4). ^{13}C NMR spectrum, δ, ppm: 22.74 (CH_3), 23.38 (C^3), 23.71 (CH_3), 30.84 (C^2), 31.05 (C^6), 35.25 (C^7), 67.35 (C^{11}), 73.34 (C^8), 76.89 (C^1), 106.55 (C^9), 120.43 (C^5), 132.33 (C^4). Found, %: C 68.40; H 8.72. $C_{12}H_{18}O_3$. Calculated, %: C 68.54; H 8.63.

(1*R*,2*R*,3*R*,5*S*,6*S*,8*S*,9*S*)-2,5-Dimethyl-6-iodo-11,12,13-trioxatetracyclo[7.2.1.1^{2,5}0^{3,8}]tridecene (XIV). In 15 ml of ether and 3 ml of water was dissolved 0.54 g (2.58 mmol) of alcohol **XIII**, 0.52 g (5.1 mmol) of $NaHCO_3$ and 1.3 g (5.1 mmol) of I_2 was added at 0°C. The reaction mixture was warmed to room temperature and stirred for 1 h, then it was diluted with a saturated NaCl solution, the reaction product was extracted into ethyl acetate (3×20 ml), the organic solutions were combined, washed with $Na_2S_2O_3$ solution, with water, and dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography. Yield 0.78 g (90%), R_f 0.55 (petroleum ether–EtOAc, 5:1). ^1H NMR spectrum, δ, ppm: 1.10 s (3H, CH_3), 1.33 s (3H, CH_3), 1.70–2.0 m (3H, H^4, H^7, H^8), 2.30 d.d.d (1H, H^3, *J* 10.8, 7.3, 1.8 Hz), 2.42 d.d (1H, H^4, *J* 14.0, 10.8 Hz), 2.82 d.d (1H, H^7, *J* 14.8, 9.9 Hz), 3.73 d.d (1H, H^{10}, *J* 6.9, 4.5 Hz), 3.79 d (1H, H^{10}, *J* 6.9 Hz), 4.21 d.d.d (1H, H^6, *J* 9.9, 7.4, 2.3 Hz), 4.27 d.d (1H, H^9, *J* 4.5, 3.1 Hz), 4.86 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 17.36 (CH_3), 27.03 (CH_3), 35.50 (C^6), 36.65 (C^7), 40.33 (C^8), 46.00 (C^3), 49.33 (C^4), 69.46 (C^{10}), 74.26 (C^9), 77.43 (C^2), 86.24 (C^5), 104.32 (C^1). Found, %: C 42.64; H 5.14. $C_{12}H_{17}IO_3$. Calculated, %: C 42.87; H 5.10.

(1*R*,4*S*,5*S*,7*RS*,8*R*,9*R*)-5-Acetoxymethyl-1,8-dimethyl-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-7-yl acetate (XV). (a) To a solution of 6.0 g (28.56 mmol) of alcohol **XIII** in 50 ml of Ac_2O cooled to 0°C was added dropwise at stirring 6 ml of H_3PO_4 (86%). The mixture was stirred for 5 min at 0°C. Then the reaction mixture was poured into water with ice containing 135 g of $NaHCO_3$, and the mixture was stirred till the end of gas liberation. The reaction product was extracted into ethyl acetate (3×200 ml), the organic solutions were combined, washed with $NaHCO_3$ solution, with a saturated NaCl solution, with water, and dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography. Yield 7.2 g (80%). Oily substance, R_f 0.5 (petroleum ether–EtOAc, 3:1). ^1H NMR spectrum, δ, ppm: 1.11 s (3H, CH_3), 1.14 s (3H, CH_3), 1.46 m (1H, CH_2), 1.62–1.95 m (7H, CH, CH_2), 2.06 s (3H, CH_3), 2.08 C (3H, CH_3), 3.82 d.d (1H, H^5, *J* 7.4, 7.3 Hz), 4.22 d.d (1H, H^{12}, *J* 11.3, 7.4 Hz), 4.28 d.d (1H, $H^{1'}$, *J* 11.3, 7.3 Hz), 5.62 s (1H, H^7). ^{13}C NMR spectrum, δ, ppm: 20.33 (C^3), 20.79 (CH_3), 21.37 ($COCH_3$), 22.90 (CH_3), 24.32 ($COCH_3$), 26.72 (C^4), 31.37 (C^9), 31.48 (C^2), 38.33 (C^{10}), 65.01 ($C^{1'}$), 70.22 (C^1), 71.30 (C^8), 76.66 (C^5), 95.13 (C^7), 169.46 ($COCH_3$), 170.76 ($COCH_3$). Found, %: C 61.53; H 7.70. $C_{16}H_{24}O_6$. Calculated, %: C 61.52; H 7.74.

(1*S*,6*R*,7*R*,8*RS*,10*S*)-10-Acetoxymethyl-7-hydroxy-4,7-dimethyl-9-oxabicyclo[4.4.0]dec-2-en-8-yl acetate (XVI). To a solution of 5.0 g (23.8 mmol) of alcohol **XIII** in 30 ml of Ac_2O cooled to 0°C was added dropwise at stirring a solution of 2 ml of H_2SO_4 in 5 ml of Ac_2O. The mixture was stirred for 20 min at 0°C. Then the reaction mixture was poured into water with ice and neutralized with a saturated solution of $NaHCO_3$. The reaction products were extracted into ethyl acetate (3×150 ml), the organic solutions were combined, washed with a saturated $NaHCO_3$ solution, with a saturated NaCl solution, with water, and dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography. Yield of a mixture of 8β- and 8α-epimers, 2:1, 5.2 g (70%). Oily substance, R_f 0.51 (petroleum ether–EtOAc, 5:1). ^1H NMR spectrum, δ, ppm: 1.32 s [1.36 s] (3H, CH_3), 1.62 s [1.65 s] (3H, CH_3), 1.70–1.98 m (4H, CH, CH_2), 2.0 s [2.05 s] (6H, CH_3), 2.05–2.28 m (8H, CH, CH_2), 3.78 m (2H, CH), 4.06–4.24 m (4H, H^{12}), 4.96 C [4.88 C] (1H, H^8), 5.36 m (2H, H^3). ^{13}C NMR spectrum, δ, ppm: 14.17 [14.15] (CH_3), 20.91 (CH_3CO), 21.06 (CH_3CO), 21.99 [22.46] (C^2), 23.44 [23.40] (CH_3), 30.69 [31.26] (C^5), 33.20 [33.12]

(C^1), 41.26 [40.33] (C^6), 60.47 [80.57] (C^7), 72.33 [66.73] (C^{10}), 72.42 [71.15] (C^{12}), 95.38 [97.57] (C^8), 119.35 [120.16] (C^3), 130.36 [130.25] (C^4), 171.20 ($COCH_3$), 171.22 ($COCH_3$), 171.23 ($COCH_3$), 171.24 ($COCH_3$). Found, %: C 61.29; H 7.33. $C_{16}H_{24}O_6$. Calculated, %: C 61.52; H 7.74.

(1*R*,2*R*,3*R*,5*R*,8*S*,9*S*)-2,5-Dimethyl-11,12,13-trioxatetracyclo[7.2.1.1^{2,5}0^{3,8}]tridecene (XVII). (a) To a solution of 0.50 g (2.38 mmol) of alcohol **XIII** in 15 ml of ethyl acetate was added 0.05 g of Pd/C (5%). The reaction mixture was stirred in an atmosphere of H_2 (TLC monitoring). After 36 h the reaction mixture was filtered, evaporated, and the residue was subjected to chromatography. Yield 0.42 g (83%).

(b) A solution of 0.50 g (2.38 mmol) of alcohol **XIII**, 3 ml of pyridine, and 0.50 ml of thionyl chloride was maintained at 0°C for 1h. The reaction mixture was diluted with water, the reaction product was extracted into ethyl acetate (3 × 20 ml), the organic solutions were combined, washed with a saturated $NaHCO_3$ solution, with water, and dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography on SiO_2. Yield 0.38 g (75%).

(c) A solution of 0.25 g (1.19 mmol) of alcohol **XIII** in 10 ml of benzene was boiled in the presence of a catalytic quantity of *p*-TsOH till the initial compound disappeared (TLC monitoring). On the completion of the reaction the reaction mixture was evaporated, and the residue was subjected to chromatography. Yield 0.20 g (79%). Oily substance, $[\alpha]_D^{20}$ –81.3° (*c* 1.18, $CHCl_3$), R_f 0.5 (petroleum ether–EtOAc, 5:1). ^{1}H NMR spectrum, δ, ppm: 1.12 s (3H, CH_3), 1.17 s (3H, CH_3), 1.10–1.22 m (2H, CH_2), 1.34–2.02 m (6H, CH, CH_2), 3.68 d.d (1H, H^{10}, *J* 7.1, 4.7 Hz), 3.78 d (1H, H^{10}, *J* 7.1 Hz), 4.20 d.d (1H, H^9, *J* 4.7, 3.7 Hz), 4.85 s (1H, H^1). ^{13}C NMR spectrum, δ, ppm: 19.43 (C^7), 21.31 (CH_3), 26.45 (CH_3), 27.01 (C^8), 32.17 (C^6), 35.35 (C^3), 35.46 (C^4), 65.75 (C^{10}), 68.99 (C^5), 73.91 (C^2), 76.17 (C^9), 104.43 (C^1). Mass spectrum: *m/z* 211 $[M + H]^+$. Found, %: C 68.67; H 8.43. $C_{12}H_{18}O_3$. Calculated, %: C 68.55; H 8.63.

(1*R*,4*S*,5*S*,7*RS*,8*R*,9*R*)-5-Hydroxymethyl-1,8-dimethyl-6,11-dioxatricyclo[6.2.1.0^{4,9}]undecan-7-ol (XVIII). To a solution of 2.00 g (6.4 mmol) of epimeric acetates **XV** in 20 ml of ethanol was added 20 ml of a solution of 4.0 g of KOH in a mixture of 20 ml of water and 40 ml of ethanol. After 1 h (TLC monitoring) the mixture was neutralized with 10% solution of HCl till pH 7. The reaction products were extracted into ethyl acetate (3×20 ml), the combined organic solutions were washed with a saturated solution of NaCl and dried with $MgSO_4$, the solvent was evaporated, and the residue was subjected to chromatography. Yield 1.17 g (80%), β:α = 3:2, oily substance, R_f 0.55 (methanol–EtOAc, 1:9). ^{1}H NMR spectrum, δ, ppm: 1.11 s [1.14 s] (3H, CH_3), 1.19 s [1.18 s] (3H, CH_3), 1.20–2.00 m (9H, CH, CH_2), 3.59 d.d (1H, H^5, *J* 8.2, 4.2 Hz) [3.49 d.d (1H, H^5, *J* 10.2, 4.0 Hz)], 3.73 d.d (1H, H^{12}, *J* 9.0, 4.2 Hz) [3.90 d.d (1H, H^{12}, *J* 10.2, 4.0 Hz)], 4.0 d.d (1H, H^{12}, *J* 9.0, 8.2 Hz), 4.72 s [5.22 s] (1H, H^7). ^{13}C NMR spectrum, δ, ppm: 20.47 [20.47] (C^3), 23.62 [21.69] (CH_3), 24.36 [26.66] (CH_3), 29.40 [26.79] (C^4), 31.63 [31.94] (C^2), 32.35 [31.28] (C^9), 39.27 [38.36] (C^{10}), 65.45 [61.12] ($C^{1'}$), 70.28 [70.96] (C^1), 72.81 [72.38] (C^8), 80.38 [79.86] (C^5), 96.49 [93.36] (C^7). Found, %: C 63.23; H 8.69. $C_{12}H_{20}O_4$. Calculated, %: C 63.14; H 8.83.

(1*R*,2*R*,3*R*,5*R*,8*S*,9*S*)-2,5-Dimethyl-11,12,13-trioxatetracyclo[7.2.1.1^{2,5}0^{3,8}]tridecane (XVII) and (1*R*,4*S*,5*S*,8*R*,9*R*)-1,8-dimethyl-7-methoxy-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-5-ylmethanol (IX). (a) To a solution of 4.9 g (15.68 mmol) of epimeric acetates **XV** in 17.5 ml of methanol was added at 0°C 17.5 ml of 20% solution of HCl in methanol. Then the cooling was removed, and the solution was stirred for 3 h. The acid was neutralized with a saturated solution of $NaHCO_3$ till pH 7. The reaction products were extracted into ethyl acetate (3×30 ml), the combined organic solutions were dried with $MgSO_4$. The reaction mixture was evaporated on a rotary evaporator, and the residue was subjected to chromatography. Yield 2.17 g (57%) of methoxyalcohol **XIX** and 1.33 g (30%) of compound **XVII**.

(b) Methanolysis of epimeric alcohols **XVIII** was carried out by the procedure for the preparation of acetates **XV**. From 1.17 g (5.08 mmol) of epimeric alcohols **XVIII** we obtained 0.66 g (54%) of methoxyalcohol **XIX** and 0.32 g (30%) of compound **XVII**.

Compound XIX. Oily substance, $[\alpha]_D^{20}$ –127.7° (*c* 1.2, $CHCl_3$), R_f 0.4 (petroleum ether–EtOAc, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.24 s (3H, CH_3), 1.27 s (3H, CH_3), 1.47–1.64 m (2H, CH, CH_2), 1.72–1.83 m (2H, CH, CH_2), 1.97 d.d (1H, CH_2, *J* 12.4, 11.8 Hz) 2.05–2.18 m (3H, CH, CH_2), 3.56 s (3H, CH_3), 3.72 t (1H, H^5, *J* 5.2, 5.1 Hz), 3.80 d (1H, H^{12}, *J* 5.1 Hz), 3.88 d (1H, H^{12}, *J* 5.2 Hz), 4.27 s (1H, H^7). ^{13}C NMR spectrum, δ, ppm: 20.32 (C^3), 23.36 (CH_3), 24.48 (CH_3), 26.75 (C^4), 31.51 (C^2), 31.81 (C^9), 39.17 (C^{10}), 56.29 (OCH_3), 64.71 ($C^{1'}$), 70.10 (C^1), 72.14 (C^8), 80.46 (C^5), 104.11 (C^7).

Found, %: C 64.32; H 9.02. $C_{13}H_{22}O_4$. Calculated, %: C 64.44; H 9.15.

(1*R*,4*S*,5*S*,7*R*,8*R*,9*R*)-1,8-Dimethyl-7-methoxy-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-5-carbaldehyde (XX). A solution of 5.19 ml (70.65 mmol) of DMSO in 9.0 ml of CH_2Cl_2 was slowly added to a solution of 3.21 ml (35.31 mmol) of oxalyl chloride in 60 ml of CH_2Cl_2 cooled to –60°C. The mixture obtained was for 15 min stirred at –60°C, then was added dropwise a solution of 3.0 g (11.76 mmol) of alcohol **XIX** in 15 ml of CH_2Cl_2. The reaction mixture was kept for 30 min at –20°C, then it was cooled again to –60°C, and it was treated with 10.5 ml (70.65 mmol) of Et_3N. Afterwards the reaction mixture was stirred for 1 h at room temperature, diluted with water, the reaction product was extracted with ethyl acetate (3×30 ml), the organic solutions were combined, washed with 5% solution of HCl, with a saturated NaCl solution, with water, dried with $MgSO_4$, and concentrated. Yield 2.28 g (81%). Oily substance, $[\alpha]_D^{20}$ –152.1° (*c* 1.8, $CHCl_3$), R_f 0.65 (petroleum ether–EtOAc, 3:1). ^{1}H NMR spectrum, δ, ppm: 1.08 s (3H, CH_3), 1.12 s (3H, CH_3), 1.47 m (2H, CH_2), 1.60 d (1H, H^{10}, *J* 2.9 Hz), 1.65 d (1H, H^{10}, *J* 11.3 Hz), 1.68 d.d.d.d (1H, H^4, *J* 10.6, 2.9, 1.9, 1.5 Hz), 1.84 d (1H, H^2, *J* 12.8 Hz), 1.92 d.d.d (1H, H^3, *J* 12.2, 10.6, 4.4 Hz), 2.42 d.d.d (1H, H^9, *J* 11.3, 2.9, 2.9 Hz), 3.48 s (3H, OCH_3), 3.78 d (1H, H^5, *J* 1.9 Hz), 4.20 s (1H, H^7), 9.72 s (1H, CHO). ^{13}C NMR spectrum, δ, ppm: 20.17 (C^3), 23.17 (CH_3), 24.87 (C^4), 26.81 (CH_3), 29.90 (C^9), 31.54 (C^2), 36.82 (C^{10}), 57.08 (OCH_3), 70.06 (C^1), 72.11 (C^8), 83.22 (C^5), 104.71 (C^7), 202.82 (CHO). Mass spectrum: *m/z* 241 [*M* + H]$^+$. Found, %: C 65.10; H 8.31. $C_{13}H_{20}O_4$. Calculated, %: C 64.98; H 8.39.

(1*R*,4*S*,5*R*,7*R*,8*R*,9*R*)-1,8-Dimethyl-7-methoxy-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-5-carbaldehyde (XXI) was obtained by the method used in the preparation of compound **XVIII** from 0.40 g of aldehyde **XX**. Yield 0.27 g (67%). Oily substance, $[\alpha]_D^{20}$ –47.0° (*c* 1.28, $CHCl_3$), R_f 0.35 (petroleum ether–EtOAc, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.08 s (3H, CH_3), 1.18 s (3H, CH_3), 1.45 m (1H, H^2), 1.47 m (1H, H^3), 1.53 m (1H, H^2), 1.60 d.d (1H, H^{10}, *J* 9.6, 5.4 Hz), 1.67 d.d (1H, H^{10}, *J* 9.6, 9.4 Hz), 1.78 d.d.d (1H, H^4, *J* 4.5, 2.6, 2.0 Hz), 2.05 d.d (1H, H^3, *J* 11.2, 4.5 Hz), 2.31 d.d.d (1H, H^9, *J* 9.4, 5.4, 2.6 Hz), 3.38 s (3H, OCH_3), 4.23 d (1H, H^5, *J* 2.0 Hz), 4.30 s (1H, H^7), 9.67 s (1H, CHO). ^{13}C NMR spectrum, δ, ppm: 20.49 (C^3), 22.90 (CH_3), 26.72 (CH_3), 29.28 (C^4), 31.53 (C^2), 32.55 (C^9), 33.45 (C^{10}), 55.68 (OCH_3), 70.02 (C^1), 72.26 (C^8), 77.05 (C^5), 104.06 (C^7), 202.36 (CHO). Found, %: C 65.07; H 8.45. $C_{13}H_{20}O_4$. Calculated, %: C 64.98; H 8.39.

(1*R*,4*S*,5*S*,7*RS*,8*R*,9*R*)-7-Hydroxy-1,8-dimethyl-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-5-carbaldehyde (XXII). A solution of 0.30 g (1.25 mmol) of aldehyde **XX** in 3 ml of 86% phosphoric acid was kept at room temperature for 3 h, The reaction mixture was diluted with water, the reaction products were extracted into ethyl acetate (3×10 ml), the organic solutions were combined, washed with a saturated $NaHCO_3$ solution, with water, dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography on SiO_2. Yield of a mixture of 7β- and 7α-epimers, 1:1, 0.17 g (61%). Oily substance, R_f 0.5 (petroleum ether–EtOAc, 1:1). ^{1}H NMR spectrum, δ, ppm: 1.09 s (3H, CH_3), 1.16 s (3H, CH_3), 1.32–2.0 m (8H, CH, CH_2), [3.80 d (1H, H^5, *J* 1.8 Hz)], 3.94 d (1H, H^5, *J* 3.1 Hz), 5.21 s [5.02 s] (1H, H^7), 9.88 s (1H, CHO, *J* 3.1 Hz). ^{13}C NMR spectrum, δ, ppm: 19.55 [20.30] (C^3), 21.41 [24.31] (CH_3), 27.58 [26.60] (CH_3), 30.03 [29.37] (C^4), 31.99 [31.65] (C^9), 32.17 [32.17] (C^2), 69.89 [70.27] (C^1), 73.10 [72.64] (C^1), 82.77 [82.70] (C^5), 95.07 [105.59] (C^7), 202.77 [203.08] (CHO).

(1*R*,4*S*,7*R*,8*R*,9*R*)-1,8-Dimethyl-7-methoxy-5-(*E*,*Z*-triethylsilyloxy)methylene-6,11-dioxatricyclo[6.2.1.0^{4,9}]undecene (XXIII). Under an argon atmosphere 0.18 ml (1.25 mmol) of anhydrous diisopropylamine was dissolved in 5 ml of THF, the solution was cooled to 0°C, and 0.78 ml (0.8 M solution) of BuLi was added. After 20 min to a solution of LDA was slowly added 0.15 g (0.625 mmol) of aldehyde **XX**, the mixture obtained was kept for 20 min and then treated with 0.21 ml (1.25 mmol) of Et_3SiCl. The reaction mixture was diluted with water, the reaction products were extracted into ethyl acetate (3×20 ml). The organic solutions were combined, washed with a saturated $NaHCO_3$ solution, with water, dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography on SiO_2. Yield 0.07 g (30%), *E*:*Z* = 1:3, oily substance, R_f 0.6 (petroleum ether–EtOAc, 5:1). ^{1}H NMR spectrum, δ, ppm: 0.55–0.70 m (6H, CH_2), 0.82–1.0 m (9H, CH_3), 1.16 s [1.18 s] (3H, CH_3), 1.23 s [1.24 s] (3H, CH_3), 1.25–1.90 m [1.25–1.90 m] (7H, H^4, CH_2), 2.05 m (1H, H^9), 3.37 s [3.36 s] (3H, OCH_3), 4.21 s [4.32 s] (1H, H^7), 5.22 s (1H, =CH), 6.18 s (1H, =CH). ^{13}C NMR spectrum, δ, ppm: 4.37 [4.37] ($SiCH_2$), 6.72 [6.72] (CH_3), 20.53 [20.32] (C^3), 23.82 [23.58] (C^8), 26.95 [23.17] (C^4), 28.62 [28.86] (CH_3), 30.65 [32.78] (C^9), 31.85 [31.69] (C^2), 37.82 [38.9] (C^{10}), 70.13 [70.04] (C^1), 72.35 [73.01] (C^8), 104.19 [104.49] (C^7), 125.27 [125.27] (C^5), 143.06 [143.06] (=CH).

(1*R*,4*S*,7*R*,8*R*,9*R*)-1,8-Dimethyl-7-methoxy-6,11-dioxatricyclo[6.2.1.0^{4,9}]undec-5*E*,*Z*-ylidenemethyl acetate (XXIV) and (1*R*,5*S*,7*R*,8*R*,10*R*)-2-hydroxy-1,8-dimethyl-4-oxo-11-oxatricyclo-[6.2.1.0^{5,10}]undec-3-yl acetate (XXV). To a solution of 0.30 g (1.25 mmol) of aldehyde **XX** in 10 ml of anhydrous acetonitrile was added 1.0 g of K_2CO_3 and 1.3 ml (12.5 mmol) of Ac_2O. The reaction mixture was boiled till the initial compound disappeared (TLC monitoring). Then the reaction mixture was neutralized with a saturated solution of $NaHCO_3$, the reaction products were extracted into ethyl acetate (3×20 ml). The organic solutions were combined, washed with a saturated NaCl solution, with water, dried with $MgSO_4$.

A mixture of *Z*,*E*-isomers, 1:1, **XXIV**. Oily substance, R_f 0.5 (petroleum ether–EtOAc, 2:1). ^{1}H NMR spectrum, δ, ppm: 1.18 s [1.17 s] (3H, CH_3), [1.19 s (3H, CH_3)], [1.20 s (3H, CH_3)], 1.45–1.85 m [1.45–1.85 m] (7H, H^4, CH_2), 2.10 s [2.08 s] (3H, CH_3), 2.25 m (1H, H^9), 2.32 m (1H, H^9), 3.40 s [3.45 s] (3H, OCH_3), 4.38 s [4.28 s] (1H, H^7), 6.65 s [7.02 s] (1H, =CH).

On distilling off the solvent the residue was dissolved in a mixture of 10 ml of acetone and 4 ml of water, 0.70 g of $Hg(OAc)_2$ was added, the reaction mixture was stirred till the initial compound disappeared (TLC monitoring) and it was boiled for 4 h. On the completion of the reaction the solution was diluted with a saturated NaCl solution, the reaction products were extracted into ethyl acetate (3×20 ml). The organic solutions were combined, washed with a saturated NaCl solution, with water, dried with $MgSO_4$. The solvent was evaporated, and the residue was subjected to chromatography. Yield 0.19 g (56%) of ketone **XXV**. mp 108–109°C, $[\alpha]_D^{20}$ –0.8° (*c* 0.78, $CHCl_3$), R_f 0.4 (petroleum ether–EtOAc, 1 : 1). ^{1}H NMR spectrum, δ, ppm: 1.11–1.21 m (2H, CH_2), 1.17 s (3H, H^8), 1.39 s (3H, H^1), 1.55 m (1H, CH_2), 1.82 m (2H, CH_2), 2.0 m (1H, CH), 2.05 m (1H, CH_2), 2.18 s (3H, CH_3), 2.75 d.d.d (1H, H^5, *J* 7.4, 6.4, 3.6 Hz), 4.01 d (1H, H^2, *J* 4.0 Hz), 5.97 d (1H, H^3, *J* 4.0 Hz). ^{13}C NMR spectrum, δ, ppm: 19.90 (C^6), 20.54 (CH_3), 23.99 (CH_3), 26.65 (CH_3), 31.13 (C^{10}), 31.63 (C^7), 33.81 (C^9), 46.96 (C^5), 70.01 (C^1), 74.43 (C^2), 76.57 (C^8), 78.26 (C^3), 169.37 ($COCH_3$), 205.30 (C^4). Found, %: C 62.42; H 7.57. $C_{14}H_{20}O_5$. Calculated, %: C 62.67; H 7.51.

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