Oxidative and hydrolytic cleavage of cyclopropane and spirocyclobutane derivatives of 6,8-dioxabicyclo[3.2.1]octane, the products of transformation of levoglucosenone

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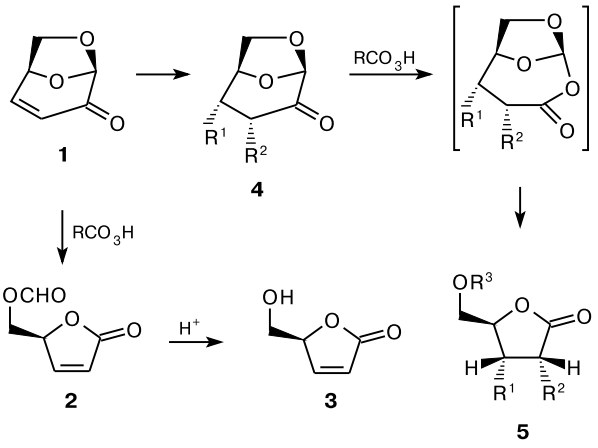
A new method for the synthesis of (1*R*,4*S*,5*S*)-4-hydroxymethyl-3-oxabicyclo[3.1.0]hexan-2-one, the cyclopropane analog of (*S*)-5-hydroxypent-2-en-4-olide, has been suggested based on oxidation of (1*S*,2*S*,4*R*,6*R*)-7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonan-5-one. Oxidation of cyclobutanones, spirojoined with the fragments of 6,8-dioxabicyclo[3.2.1]oct-2-ene, 6,8-dioxabicyclo[3.2.1]octane (at position 4), or 7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonane (at position 5), upon the action of *m*-chloroperoxybenzoic acid or the $KMnO_4$—H_2SO_4—H_2O system leads to the corresponding spirojoined butanolides in 73—85% yields. The same cyclobutanones easily undergo the four-membered ring opening upon the action of dilute H_2SO_4 at 50—90 °C to form 6,8-dioxabicyclo[3.2.1]octane-4- or 7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonane-5-propionic acid.

Key words: 7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonan-5-one, 3-oxabicyclo[3.1.0]hexan-2-ones, spiro{6,8-dioxabicyclo[3.2.1]octane-4,2′-cyclobutanones}, spiro compounds, γ-lactones, oxidation, hydration, cyclobutanones, levoglucosenone.

The structure of levoglucosenone (**1**) and its derivatives contains dioxolane and pyranone fragments, which can undergo hydrolytic and oxidative cleavage.[1] The study of oxidation of compound **1** with peroxy acids showed[2] that the first compound to isolate is (*S*)-5-formyloxypent-2-en-4-olide (**2**), whose acidic cleavage gives valuable product, (*S*)-5-hydroxypent-2-en-4-olide (**3**) containing one chiral center in the molecule (Scheme 1). Pentenolide **3** is used in the production of some medicines (burseran and isostegan), antibiotic lasalocide A, pheromones, surrogate of whisky and brandy odor.[3—5] Similarly, the Baeyer—Villiger oxidation of dihydrolevoglucosenone **4** ($R^1 = R^2 = H$) and its hydroxy derivative **4** ($R^1 = OH$, $R^2 = H$) led to (*S*)-5-hydroxypentan-4-olides **5** ($R^1 = H$, OH; $R^2 = R^3 = H$),[2,6] whereas oxidation of tricyclic ketones obtained by the Diels—Alder reaction of levoglucosenone (**1**) and 1,3-butadiene or isoprene led to fused formyloxypent-2-en-4-olides **5** ($R^1 + R^2 = CH_2CH{=}CHCH_2$, $CH_2CMe{=}CHCH_2$; $R^3 = CHO$) in high yields.[7,8] The authors of the works[1,2] consider that the formation of formates is due to the acid-catalyzed rearrangement of the intermediate bicyclic ortho esters (see Scheme 1).

Recently,[9] oxidation of dioxatricyclo[4.2.1.$0^{2,4}$]nonan-5-ones (**6**)[10] with hydrogen peroxide in acetic acid afforded 5-hydroxypentan-4-olides with the fused cyclopropane fragment in the molecule, 6-substituted (1*S*,4*S*,5*S*,6*S*)-4-hydroxymethyl-3-oxabicyclo[3.1.0]hexan-2-ones **7** (Scheme 2).

Scheme 1



Thus, the ring openings in the levoglucosenone molecule (**1**) and its derivatives can serve as a good strategy for the synthesis of substituted γ-lactones with certain configuration of chiral centers in the molecule.

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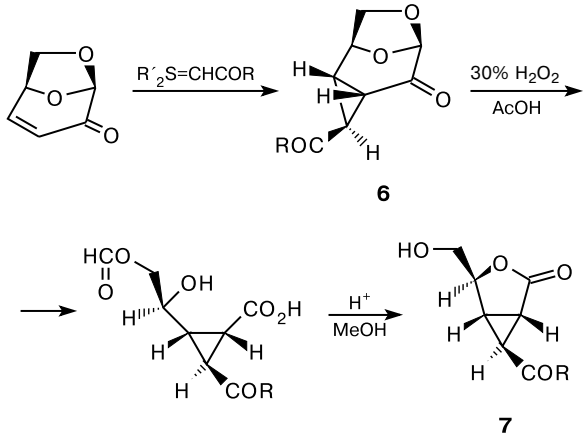
Scheme 2



R = aryl, hetaryl, 1-adamantyl, OEt

Results and Discussion

In the present work, we studied oxidation and hydrolysis of some new levoglucosenone derivatives, in particular, cyclopropane derivative **8**, as well as 6,8-dioxabicyclo-[3.2.1]octanes spirojoined with cyclobutanone fragment (see below). Tricyclic ketone **8** can be easily obtained by catalytic cyclopropanation of (1*S*,4*S*,5*R*)-6,8-dioxabicyclo[3.2.1]oct-2-en-4-ol (**9**) with diazomethane in the presence of Pd-catalyst and subsequent oxidation of obtained dioxatricyclononanol **10** upon the action of freshly prepared MnO_2 or the $RuCl_3$—$NaIO_4$ system.[11]

Under mild conditions (25 °C, 4 days), the Baeyer—Villiger oxidation of ketone **8** with *m*-chloroperoxybenzoic acid (MCPBA) gives up to 70% yield of bicyclic formate **11** (Scheme 3). Hydrolysis of formate **11** upon the action of dilute H_2SO_4 gives (1*R*,4*S*,5*S*)-4-hydroxymethyl-3-oxabicyclo[3.1.0]hexan-2-one (**12**) in quantitative yield. The same compound was also obtained by the direct oxidation of ketone **8** upon the action of activated manganese dioxide in 5% aq. H_2SO_4.

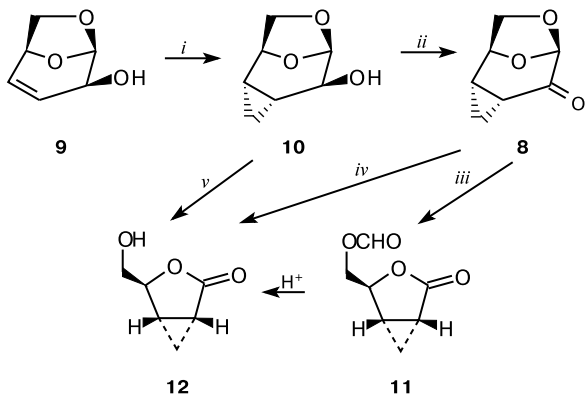
We also showed that bicyclic lactone **12** can be obtained in up to 76% yield in one experimental step starting from tricyclic hydroxy acetal **10**. The reaction was carried out at 20 °C for 1 h, using $KMnO_4$ in 5% aq. sulfuric acid as an oxidant at the ratio oxidant : substrate = 2 : 1 (an increased amount of $KMnO_4$ causes further oxidation of product **12** to *cis*-cyclopropane-1,2-dicarboxylic acid).

Bicyclic lactone **12** is of interest as a chiral block for the synthesis of various biologically active compounds, in particular, for the preparation of cyclopropane-containing amino acids and cyclopropane carbocyclic nucleosides.[12,13]

Earlier, chiral lactone **12** has been obtained in six steps in ~33% total yield from the optically active D-glyceraldehyde acetonide.[12] It should be noted that lactone **12** obtained by this method is not apparently an individual compound, since its melting point is by 10 °C below than that of the sample obtained by us (see Experimental), and the ^{13}C NMR spectrum published in the work[12] contained an additional signal at δ 29.6.

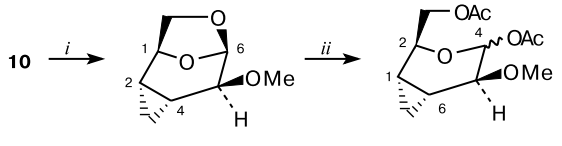
In the absence of oxidant, acidic hydrolysis of tricyclic hydroxy acetal **10** (5% H_2SO_4, 40 °C) proceeds nonselectively and gives a mixture of difficult to identify alcohols. To increase the selectivity of the process, we converted alcohol **10** to ether **13** by methylation with diazomethane in the presence of HBF_4. Acetolysis of the dioxolane fragment in compound **13** in the presence of *p*-toluenesulfonic acid gives stereoisomeric 4-acetoxy-3-oxabicyclo-[4.1.0]heptanes **14** in high yield (Scheme 4) with preservation of configuration of substituents at C(2) and C(5).

Scheme 3



Reagents and conditions: *i*. CH_2N_2, $Pd(acac)_2$, 10 °C; *ii*. MnO_2 or $RuCl_3$—$NaIO_4$, CH_2Cl_2, 20 °C; *iii*. MCPBA, 20 °C; *iv*. MnO_2, 5% H_2SO_4, 20 °C, 48 h; *v*. $KMnO_4$ (2 equiv.), 5% H_2SO_4, 20 °C, 1 h.

Scheme 4

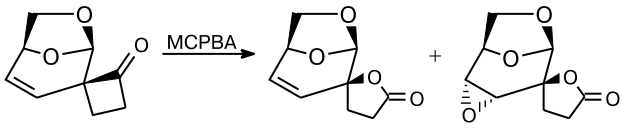


Reagents and conditions: *i*. CH_2N_2, HBF_4, Et_2O, CH_2Cl_2, 20 °C; *ii*. $TsOH \cdot H_2O$, Ac_2O, 20 °C, 24 h.

Further, we studied a possibility of oxidation and hydrolysis of 6,8-dioxabicyclo[3.2.1]octanes spirojoined with the cyclobutanone fragment. The starting cyclobutanones **15**—**17** (see Schemes 5—7) were obtained by the reaction of levoglucosenone (**1**), dihydrolevoglucosenone **4** ($R^1 = R^2 = H$), or tricyclononanone **8** with the *in situ* generated diazocyclopropane and subsequent isomerization of oxaspiropentanes formed to cyclobutanones.[14,15]

The Baeyer—Villiger oxidation[16] of unsaturated ketone (1*S*,4*S*,5*R*)-**15** with 30% molar excess of MCPBA in dichloromethane (25 °C, 5 h) provides the virtually full conversion of the starting ketone **15**, which under these conditions is stereoselectively transformed to the spirojoined lactone (1*S*,4*S*,5*R*)-**18** and partially to epoxide **19** (Scheme 5). The use of a three-fold excess of MCPBA results in the increase of the amount of epoxide **19**, however, epoxidation proceeds much slower than lactonization, and even after 5 days the yield of compound **19** did not exceed 70%.

Scheme 5

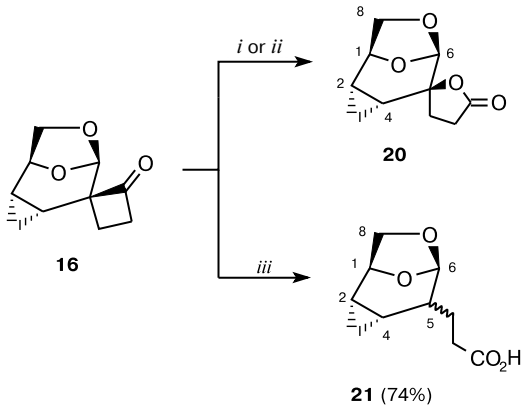


Molar ratio	Yield (%)	
15 : MCPBA	**18**	**19**
1 : 1.3	82	8
1 : 3.0	23	70

The structure of lactones **18** and **19** was established based on the ^{1}H and ^{13}C NMR spectra of their mixtures obtained in two different experiments (attempted separation of the lactones by crystallization from benzene or chromatography on SiO_2 failed and virtually produced no change in their ratio). In the ^{1}H NMR spectrum of the spirojoined lactone **18**, the chemical shifts and spin-spin coupling constant for the protons of the dioxabicyclo[3.2.1]octene fragment are similar to the corresponding signals of the starting compound **15**. In the spectrum of oxirane **19**, the signals for the protons at C(2) and C(4) are found as doublet of doublets with $^3J_{2,4}$ = 4.0, $^3J_{1,2}$ = 1.3, and $^4J_{4,6}$ = 2.5 Hz, that by analogy with the oxiranes of close structure[17] evidences the *anti*-configuration of the oxirane ring with respect to the anhydro bridge. For comparison, in the structures of 3,7,9-trioxatricyclo[4.2.1.0^{2,4}]nonanes containing a *syn*-oxirane ring, the spin-spin coupling constant $^3J_{1,2}$ is about 4.6 Hz.[18]

Treatment of (1*S*,2*S*,4*R*,5*S*,6*R*)-spiro(7,9-dioxatricyclononane-5,2′-cyclobutanone) (**16**) with 1.5-fold molar excess of MCPBA leads to the spirojoined lactone **20** with high stereoselectivity (90% yield) (Scheme 6). The same lactone **20** can be also obtained in 72% yield by oxidation of cyclobutanone **16** with equimolar amount of $KMnO_4$ in acidic medium and in this case, the reaction comes to completion within several minutes. It cannot be excluded that in this case the process is somewhat less selective, that follows from the presence of considerable number of signals for impurities in the ^{1}H and ^{13}C NMR spectra of the reaction mixture, however, chromatography on SiO_2 yielded compound **20** in the individual state.

Scheme 6



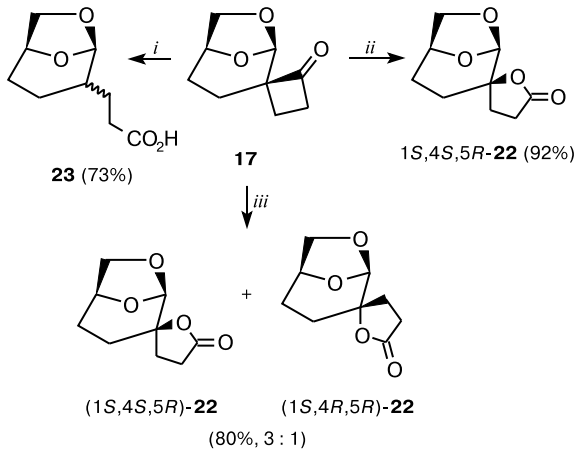
Reagents and conditions: *i*. MCPBA, CH_2Cl_2, 20 °C, 10 h; *ii*. $KMnO_4$, 5% H_2SO_4, 20 °C, 6—7 min; *iii*. 10% H_2SO_4, 50 °C, 10 min.

If the oxidant is absent, hydrolysis of compound **16** upon the action of 10% aq. H_2SO_4 leads to the isomeric 3-(7,9-dioxatricyclo[4.2.1.0^{2,4}]non-5-yl)propionic acids **21** in the ratio 4.2 : 1. According to the ^{1}H and ^{13}C NMR spectra, both isomers have the same-type set of signals, and the character of the high-field signals (δ 0.4—1.1) and the low-field signals (δ 3.7—5.1) unambiguously evidence that the cyclopropane and dioxolane fragments in the molecule remain. The splitting of the signals for the methine protons at C(6) shows that the vicinal spin-spin coupling constant $J_{5,6}$ in the major isomer is about 1.0 Hz, whereas in the minor — 3.0 Hz. Taking into account that in the bicyclo[3.2.1]octane framework, the spin-spin coupling constant $J_{1,2\text{-}exo}$ or $J_{4\text{-}exo,5}$ is larger than $J_{1,2\text{-}endo}$ or $J_{4\text{-}endo,5}$, it can be suggested that the major isomer corresponds to the *anti*-orientation of the alkyl substituent with respect to the anhydro bridge.

Similar transformations are also observed in the case of (1*S*,4*S*,5*R*)-spiro(6,8-dioxabicyclooctane-4,2′-cyclobutanone) (**17**). The action of MCPBA, as it was expected, leads to the spirojoined lactone 1*S*,4*S*,5*R*-**22** with high stereoselectivity (Scheme 7). However, oxidation of cyclobutanone **17** upon the action of the $KMnO_4$—H_2SO_4 system or acid hydrolysis at 90 °C proceed nonstereoselectively and in both cases give mixtures of two stereoisomeric lactones **22** or substituted propionic acids **23** in the ratio ~3 : 1, which are difficult to separate by chromatography on SiO_2.

A plausible mechanism of the transformations described under conditions of acid hydrolysis or oxidation upon the action of $KMnO_4$ is given in Scheme 8. In the first step, the oxygen atom of the dioxolane ring is protonated, with the oxonium cation **A** formed being in the equilibrium with carbocation **B**. Further, the four-membered ring is opened to form unsaturated acylium cation **C**, which, depending on the reaction conditions, either

Scheme 7



Reagents and conditions: *i*. 15% H_2SO_4, 90 °C, 10 min; *ii*. MCPBA, CH_2Cl_2, 20 °C, 10 h; *iii*. $KMnO_4$, 5% H_2SO_4, 40 °C, 6—7 min.

adds a proton under conditions of acid hydrolysis (**D**), or is hydroxylated upon the action of potassium permanganate (**E**). The formation of isomeric acids **23** or spirojoined lactones **22** can be explained by addition of a proton or a permanganate ion from different sides of the plane of the double bond in the intermediate **C**. In the transformations under consideration, the initial protonation and the dioxolane ring opening are the factors promoting further convertion of the cyclobutanone fragment, which on its own is fairly stable under these conditions.

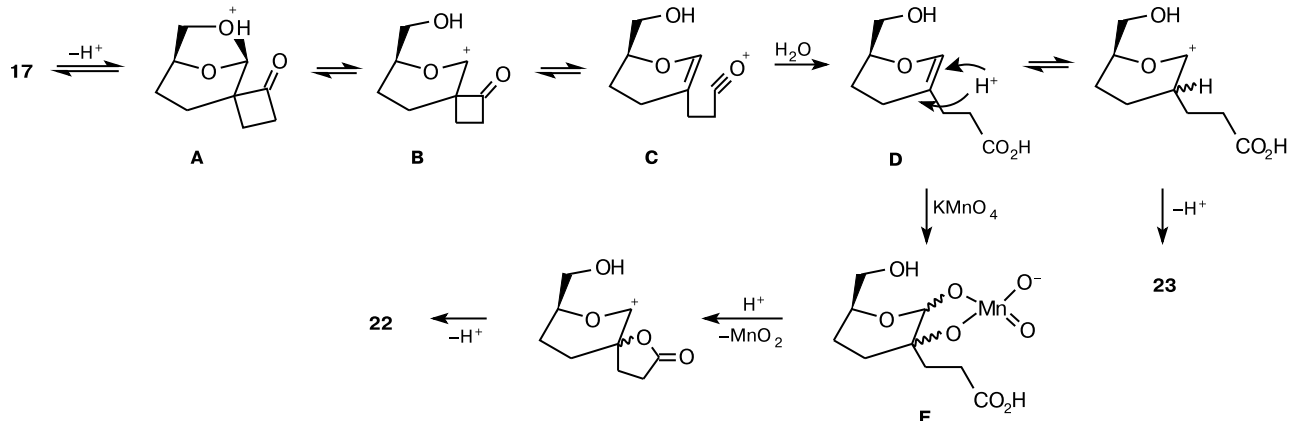
Unlike compound **17**, oxidation of cyclobutanone **16** with potassium permanganate in acidic medium, as it was previously mentioned, mainly gives lactone (1*S*,2*S*,4*R*,5*S*,6*R*)-**20**. Apparently, in the first steps leading to the intermediate similar to cation **C**, the mechanism is as suggested above, however, the hydroxylation upon the action of permanganate ion leads to the formation of considerable amount of the isomer of vicinal diol, in which the hydroxy groups after elimination of MnO_2 are in *trans*-position to the fused cyclopropane fragment hindering one of the sides of the plane of the double bond in the six-membered ring. On protonation, this factor is not apparently already so important, that results in the formation of two stereoisomeric acids **21**.

It should be noted that asymmetric center at C(1) in all the transformations considered was preserved. Taking into account the high stereoselectivity of the oxidation processes of the cyclopropane analog of levoglucosenone **8** and spirojoined cyclobutanones **15—17**, the compounds obtained can be of interest as synthetic blocks with the preset configuration of chiral centers in the molecule.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE II 300 (300 and 75.5 MHz, respectively) and Bruker DRX-500 spectrometers (500 and 125.3 MHz, respectively) in $CDCl_3$ or DMSO-d_6 containing 0.05% of Me_4Si as an internal standard; the COSY, NOESY, HSQC, and HMBC experiments were performed on a Bruker DRX-500 spectrometer. Mass spectra were recorded on a Finnigan MAT INCOS-50 (EI, 70 eV, direct inlet) and Finnigan LCQ instruments (ESI). Optical rotation was measured on a Perkin—Elmer 341 MC polarimeter at 20 °C (λ 589 nm, in a 2.5-cm cuvette). Thin-layer chromatography was performed on Silicagel 60 plates (Merck) with visualization in iodine vapors. Preparative separation was performed by column or thin-layer chromatography (silica gel 60, 0.040—0.063 mm, Merck) with the ratio substance : sorbent ~1 : 100. (1*S*,2*S*,4*R*,6*R*)-7,9-Dioxatricyclo[4.2.1.$0^{2,4}$]nonan-5-one (**8**),[11] (1*S*,2*S*,4*R*,5*S*,6*R*)-7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonan-5-ol (**10**),[11] (1*S*,4*S*,5*R*)-spiro{6,8-dioxabicyclo[3.2.1]oct-2-en-4,2′-cyclobutanone} (**15**),[14] (1*S*,2*S*,4*R*,5*S*,6*R*)-spiro{7,9-dioxatricyclo[4.2.1.$0^{2,4}$]-nonane-5,2′-cyclobutanone} (**16**),[15] and (1*S*,4*S*,5*R*)-spiro{6,8-dioxabicyclo[3.2.1]octane-4,2′-cyclobutanone} (**17**)[15] were synthesized according to the described procedures. Active manganese dioxide was obtained by addition of a solution of manga-

Scheme 8



nese sulfate and NaOH to a hot solution of potassium permanganate.[19] *m*-Chloroperoxybenzoic acid (MCPBA) and $HBF_4 \cdot OEt_2$ were purchased from Aldrich. Solvents of chemically pure grade (>99.5%) were used without additional purification.

(1*R*,4*S*,5*S*)-2-Formyloxymethyl-3-oxabicyclo[3.1.0]hexan-4-one (11). *m*-Chloroperoxybenzoic acid (173 mg, 1 mmol) was added to a solution of ketone **8** (99 mg, 0.7 mmol) in CH_2Cl_2 (4 mL) with stirring, after 4 days the reaction mixture was neutralized with aqueous $NaHCO_3$. The organic layer was separated, the aqueous layer was extracted with dichloromethane (2×4 mL), dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. Preparative TLC on SiO_2 (benzene—AcOEt, 5 : 1) yielded compound **11** (76 mg, 70%) as colorless oil, R_f 0.4. MS, *m/z* (I_{rel} (%)): 156 $[M]^+$ (40), 139 $[M - OH]^+$ (31), 110 (28), 97 (100), 69 (17). ^{1}H NMR ($CDCl_3$), δ: 0.93 (ddd, 1 H, *syn*-H(6), ^2J = 5.1 Hz, ^3J = 3.9 Hz and 4.0 Hz); 1.31 (ddd, 1 H, *anti*-H(6), ^2J = 5.1 Hz, ^3J = 8.3 Hz); 2.15 (m, 2 H, H(1) and H(5)); 4.36 (ddd, 2 H, CH_2O, ^3J = 4.3 Hz, ^4J = 1.0 Hz); 4.58 (br.t, 1 H, H(2), ^3J = 4.3 Hz); 8.11 (q, 1 H, CHO, J = 1.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.7 (C(6)), 17.4 (C(5)), 19.6 (C(1)), 64.6 (CH_2O), 77.3 (C(2)), 160.3 (CHO), 175.1 (C=O).

(1*R*,4*S*,5*S*)-4-Hydroxymethyl-3-oxabicyclo[3.1.0]hexan-2-one (12). ***A.*** Concentrated hydrochloric acid (0.1 mL) was added to a solution of formate **11** (63 mg, 0.45 mmol) in the CH_2Cl_2—MeOH (1 : 1) solvent mixture (3 mL) and the mixture was stirred for 5 h at 40 °C, followed by addition of some anhydrous $MgSO_4$. The solvents were evaporated *in vacuo* to obtain lactone **12** (56 mg, 96%) as colorless crystals with m.p. 64—65 °C (*cf.* Ref. 12: m.p. 54—55.5 °C), $[\alpha]_D^{20}$ +119 (*c* 0.05; CH_2Cl_2). Found (%): C, 56.18; H, 6.50. $C_6H_8O_3$. Calculated (%): C, 56.25; H, 6.29. MS, *m/z* (I_{rel} (%)): 128 $[M]^+$ (1), 110 $[M - H_2O]^+$ (2.5), 97 (77), 69 (16), 53 (29), 41 (100). ^{1}H NMR ($CDCl_3$), δ: 0.89 (ddd, 1 H, *syn*-H(6), ^2J = 4.9 Hz, ^3J = 3.5 Hz and 4.2 Hz); 1.27 (ddd, 1 H, *anti*-H(6), ^2J = 4.9 Hz, ^3J = 8.0 Hz, ^3J = 8.5 Hz); 2.11 (dddd, 1 H, H(5), $^3J_{5,6}$ = 8.5 Hz and 3.5 Hz, $^3J_{1,5}$ = 5.7 Hz, $^3J_{4,5}$ = 1.0 Hz); 2.18 (ddd, 1 H, H(1), $^3J_{5,6}$ = 8.0 Hz and 4.2 Hz, $^3J_{1,5}$ = 5.7 Hz); 3.21 (br.s, 1 H, OH); 3.74 and 3.85 (both dd, 1 H each, CH_2, ^2J = 12.3 Hz, ^3J = 4.5 Hz and 3.6 Hz); 4.42 (dd, 1 H, H(4), ^3J = 3.6 Hz and 4.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.7 (C(6)), 17.9 and 19.7 (C(1) and C(5)), 64.6 (CH_2O), 81.4 (C(4)), 176.7 (C=O).

B. Ketone **8** (0.20 g, 1.4 mmol) was added to a suspension of freshly prepared manganese dioxide (4.5 g) in 5% aq. H_2SO_4 (25 mL) with vigorous stirring and the mixture was stirred for 48 h at 20 °C. The major part of manganese dioxide was separated by decantation, to decompose the rest of MnO_2, anhydrous Na_2SO_3 was added in portions to the suspension and the solution obtained was extracted with ethyl acetate (3×20 mL). The organic extracts were dried with anhydrous $MgSO_4$, passed through a short layer of SiO_2, the solvents were evaporated to obtain a substance (0.16 g, 85%) as colorless oil, whose ^{1}H and ^{13}C NMR spectra were identical to those of lactone **12** obtained by method ***A*** (the purity was ~96%).

C. (1*S*,2*S*,4*R*,6*R*)-7,9-Dioxatricyclo[4.2.1.0^{2,4}]nonan-5-ol (**10**) (0.10 g, 0.7 mmol) was added in one portion to a solution of $KMnO_4$ (0.22 g, 1.4 mmol) in 5% aq. H_2SO_4 (25 mL) with stirring and the reaction mixture was stirred for 1 h at 20 °C. A precipitate of manganese dioxide formed was dissolved by in portion addition of anhydrous Na_2SO_3 until the solution became colorless. The reaction mixture was extracted with AcOEt (3×15 mL) and the organic extracts were dried with anhydrous $MgSO_4$. After the solvents were evaporated, the product was purified by column chromatography on SiO_2 (benzene—AcOEt, 1 : 3) to obtain lactone **12** (68 mg, 76%) as colorless crystals; whose physico-chemical parameters were analogous to those of the sample obtained in method ***A***.

(1*S*,2*S*,4*R*,5*S*,6*R*)-5-Methoxy-7,9-dioxatricyclo[4.2.1.0^{2,4}]-nonane (13). The compound $HBF_4 \cdot OEt_2$ (80 mg, 0.5 mmol) was added to a solution of tricyclic alcohol **10** (5.69 g, 40 mmol) in CH_2Cl_2 (60 mL), followed by a dropwise addition of an ethereal solution of diazomethane (0.56 *M*, 100 mL, 56 mmol) to the reaction mixture with stirring at 15 °C over 1 h and the mixture was stirred for additional 1 h. After the solvent was evaporated, the residue was distilled *in vacuo* to obtain methoxy derivative **13** (5.75 g, 92%) as colorless oil, b.p. 51—53 °C (0.05 Torr), $[\alpha]_D^{20}$ −83.9 (*c* 0.47; $CHCl_3$). Found (%): C, 61.34; H, 7.97. $C_8H_{12}O_3$. Calculated (%): C, 61.52; H, 7.74. MS, *m/z* (I_{rel} (%)): 125 (3), 113 (22), 110 (95), 95 (33), 79 (44), 67 (96), 45 (93), 41 (100). ^{1}H NMR ($CDCl_3$), δ: 0.48 (ddd, 1 H, *syn*-H(3), ^2J = 4.9 Hz, ^3J = 5.0 Hz and 5.2 Hz); 0.69 (ddd, 1 H, *anti*-H(3), ^2J = 4.9 Hz, ^3J = 8.0 Hz, ^3J = 9.1 Hz); 0.91 and 1.02 (both m, 1 H each, (H(2) and H(4)); 3.33 (br. d, 1 H, H(5), ^3J = 3.1 Hz); 3.47 (s, 3 H, OMe); 3.85 (dd, 1 H, *exo*-H(8), ^2J = 6.8 Hz, ^3J = 4.1 Hz); 4.10 (d, 1 H, *endo*-H(8), ^2J = 6.8 Hz); 4.61 (br. d, 1 H, H(1), ^3J = 4.1 Hz); 5.29 (br. dd, 1 H, H(6), ^3J = 3.1 Hz, ^4J = 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 6.9 (C(3)), 9.9 (C(4)), 14.6 (C(2)), 56.8 (OMe), 70.9 (C(8)), 71.2 (C(1)), 77.0 (C(5)), 98.1 (C(6)).

(1*S*,2*S*,4*S*,5*S*,6*R*)- and (1*S*,2*S*,4*R*,5*S*,6*R*)-2-Acetoxymethyl-4-acetoxy-5-methoxy-3-oxabicyclo[4.1.0]heptanes (14). *p*-Toluenesulfonic acid monohydrate (0.76 mg, 0.4 mmol) was added to a solution of 5-methoxy-7,9-dioxatricyclo[4.2.1.0^{2,4}]-nonane (**13**) (0.63 g, 4 mmol) in acetic anhydride (12 mL) with stirring. After 24 h, the brownish claret-colored reaction mixture was concentrated without heating *in high vacuo* and the residue was subjected to column chromatography on SiO_2 (benzene—AcOEt, 1 : 1) to obtain acetates **14** (0.98 g, ~90%) as colorless oil containing (^{1}H NMR data) a mixture of (1*S*,2*S*,4*S*,5*S*,6*R*)- and (1*S*,2*S*,4*R*,5*S*,6*R*)-isomers in the ratio ~5 : 1. (1*S*,2*S*,4*S*,5*S*,6*R*)-Isomer: ^{1}H NMR ($CDCl_3$) δ: 0.62 (ddd, 1 H, *syn*-H(7), ^2J = 4.9 Hz, ^3J = 5.0 Hz and 5.1 Hz); 0.90 (ddd, 1 H, *anti*-H(7), ^2J = 4.9 Hz, ^3J = 8.4 Hz, ^3J = 8.7 Hz); 1.09 and 1.20 (both m, 1 H each, H(1) and H(6)); 2.07 and 2.10 (both s, 3 H each, 2 COMe); 3.29 (dd, 1 H, H(5), ^3J = 2.3 Hz and 3.6 Hz); 3.48 (s, 3 H, OMe); 3.93 (ddd, 1 H, H(2), ^3J = 6.8 Hz, 4.4 Hz, and 4.0 Hz); 4.29 (dd, 1 H, H_a(8), ^2J = 11.5 Hz, ^3J = 6.8 Hz); 4.32 (dd, 1 H, H_b(8), ^2J = 11.5 Hz, ^3J = 4.4 Hz); 5.92 (br. d, 1 H, H(4), ^3J = 3.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.2 (C(7)); 10.7 and 11.4 (C(1) and C(6)); 20.5 and 20.7 (COMe); 56.9 (OMe); 65.8 (CH_2O); 70.4 (C(2)); 74.7 (C(5)); 91.5 (C(4)); 168.9 and 170.5 (COO). (1*S*,2*S*,4*R*,5*S*,6*R*)-Isomer: ^{1}H NMR ($CDCl_3$), δ: 0.37 (ddd, 1 H, *syn*-H(7), ^2J = 5.0 Hz, ^3J = 5.0 Hz and 5.1 Hz); 1.04 (m, 1 H, H_b(7)); 1.17 and 1.27 (both m, 1 H each, H(1) and H(6)); 2.09 and 2.12 (both s, 3 H each, 2 COMe); 3.18 (dd, 1 H, H(5), ^3J = 2.5 Hz and 4.6 Hz); 3.49 (s, 3 H, OMe); 3.76 (m, 1 H, H(2)); 4.24 (m, 2 H, CH_2O); 6.01 (br. d, 1 H, H(4), ^3J = 2.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.5 (C(7)), 10.8 and 11.6 (C(1) and C(6)), 18.7 and 24.5 (COMe), 57.1 (OMe), 64.0 (CH_2O), 66.9 (C(2)), 76.2 (C(5)), 83.4 (C(4)), 169.5 and 172.5 (COO).

Reaction of ketone 15 with *m*-chloroperoxybenzoic acid. *A.* *m*-Chloroperoxybenzoic acid (0.61 g, 3.9 mmol) was added to a solution of ketone **15** (0.50 g, 3 mmol) in CH_2Cl_2 (15 mL) with stirring and the mixture was stirred for 5 h at 25 °C. The reaction

mixture was treated with saturated aq. $NaHCO_3$ until the gas evolution ceased, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×15 mL), and the combined organic extracts were dried with anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was recrystallized from benzene to obtain colorless crystals (0.50 g, ~90%) containing compounds **18** and **19** (^{1}H and ^{13}C NMR data) in the molar ratio ~10 : 1. **(1*R*,4*S*,5*R*)-2´-Oxospiro{6,8-dioxabicyclo[3.2.1]oct-2-ene-4,5´-oxolane} (18).** ^{1}H NMR ($CDCl_3$), δ: 2.10 (ddd, 1 H, H_a(4´), ^2J = 13.5 Hz, ^3J = 9.0 Hz and 9.5 Hz); 2.41 (ddd, 1 H, H_b(4´), ^2J = 13.5 Hz, ^3J = 6.6 Hz and 7.8 Hz); 2.59 (m, 2 H, H_2C(3´)); 3.82 (dd, 1 H, *exo*-H(7), ^2J = 6.8 Hz, ^3J = 4.1 Hz); 3.94 (d, 1 H, *endo*-H(7), ^2J = 6.8 Hz); 4.73 (dd, 1 H, H(1), ^3J = 4.1 Hz and 4.2 Hz); 5.33 (d, 1 H, H(5), $J_{3,5}$ = 2.4 Hz); 5.64 (dd, 1 H, H(3), ^3J = 10.1 Hz, $J_{3,5}$ = 2.4 Hz); 6.21 (dd, 1 H, H(2), ^3J = 10.1 Hz, ^3J = 4.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.1 (C(4´)), 30.6 (C(3´)), 70.5 (C(7)), 71.5 (C(1)), 84.8 (C(4)), 102.0 (C(5)), 128.1 (C(3)), 131.6 (C(2)), 175.9 (C=O).

B. Colorless crystals (0.36 g, 93%) containing (^{1}H and ^{13}C NMR data) compounds **18** and **19** in the molar ratio ~1 : 3 were obtained similarly from ketone **15** (0.33 g, 2 mmol) and MCPBA (1.03 g, 6 mmol) after stirring for 5 days and recrystallization from benzene. **(1*R*,2*S*,4*S*,5*S*,6*R*)-2´-Oxospiro{3,7,9-trioxatricyclo[4.2.1^{2,4}]nonane-5,5´-oxolane} (19).** ^{1}H NMR ($CDCl_3$), δ: 2.21 (m, 1 H, CH_2CH_2); 2.63 (m, 3 H, CH_2CH_2); 3.15 (dd, 1 H, H(4), ^3J = 3.9 Hz, $J_{4,6}$ = 2.5 Hz); 3.28 (dd, 1 H, H(2), ^3J = 3.9 Hz and 1.5 Hz); 3.92 (dd, 1 H, *exo*-H(8), ^2J = 7.7 Hz, ^3J = 4.2 Hz); 4.18 (d, 1 H, *endo*-H(8), ^2J = 7.7 Hz); 4.78 (br. dd, 1 H, H(1), ^3J = 4.2 Hz and 1.5 Hz); 5.03 (d, 1 H, H(6), $J_{4,6}$ = 2.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 26.5 and 27.2 (C(3´) and C(4´)), 50.4 (C(2)), 52.0 (C(4)), 67.8 (C(8)), 70.2 (C(1)), 79.7 (C(5)), 100.9 (C(6)), 180.2 (C=O).

(1*S*,2*S*,4*R*,5*S*,6*R*)-2´-Oxospiro{7,9-dioxatricyclo[4.2.1.0^{2,4}]-nonane-5,5´-oxolane} (20). ***A.*** A mixture of (1*S*,2*S*,4*R*,5*S*,6*R*)-spiro{7,9-dioxatricyclo[4.2.1.0^{2,4}]nonane-5,2´-cyclobutanone} (**16**) (108 mg, 0.6 mmol) and MCPBA (155 mg, 0.9 mmol) in CH_2Cl_2 (10 mL) was stirred for 10 h and then neutralized with saturated aq. $NaHCO_3$ until the gas evolution ceased. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts were dried with anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to obtain lactone **20** (106 mg, 90%) as colorless crystals, m.p. 93—94 °C. Found (%): C, 61.04; H, 6.31. $C_{10}H_{12}O_4$. Calculated (%): C, 61.22; H, 6.17. MS, *m/z* (I_{rel} (%)): 150 $[M - HCO_2H]^+$ (100), 137 (7), 122 (15), 95 (70), 81 (65), 67 (50), 55 (85). ^{1}H NMR ($CDCl_3$), δ: 0.74 (m, 1 H, *anti*-H(3)); 1.08 (m, 3 H, H(2), *syn*-H(3), H(4)); 2.10 (ddd, 1 H, H_a(4´), ^2J = 13.5 Hz, ^3J = 9.8 Hz, ^3J = 4.5 Hz); 2.34 (ddd, 1 H, H_b(4´), ^2J = 13.5 Hz, ^3J = 10.1 Hz, ^3J = 8.5 Hz); 2.54 (ddd, 1 H, H_a(3´), ^2J = 17.6 Hz, ^3J = 8.5 Hz, ^3J = 4.5 Hz); 2.67 (ddd, 1 H, H_b(3´), ^2J = 17.6 Hz, ^3J = 10.1 Hz, ^3J = 9.8 Hz); 3.79 (dd, 1 H, *exo*-H(8), ^2J = 6.8 Hz, ^3J = 4.6 Hz); 3.92 (d, 1 H, *endo*-H(8), ^2J = 6.8 Hz); 4.69 (br. d, 1 H, H(1), ^3J = 4.1 Hz); 4.97 (s, 1 H, H(6)). ^{13}C NMR ($CDCl_3$), δ: 6.5 (C(3)), 13.8 (C(2)), 15.1 (C(4)), 28.1 (C(4´)), 31.3 (C(3´)), 69.6 (C(8)), 70.4 (C(1)), 83.2 (C(5)), 102.3 (C(6)), 176.4 (C=O).

B. Cyclobutanone **16** (90 mg, 0.5 mmol) was added to a solution of $KMnO_4$ (60 mg, 0.38 mmol) in 5% aq. H_2SO_4 (8 mL) and the reaction mixture was stirred for 6—7 min at 20 °C until the solution turned colorless. A precipitate of manganese dioxide formed was dissolved by addition in portions of anhydrous Na_2SO_3, the mixture was extracted with AcOEt (3×15 mL), the extracts were dried with anhydrous $MgSO_4$. After the solvent was evaporated, the target product was isolated by preparative TLC on SiO_2 (benzene—AcOEt, 1 : 1, R_f 0.65) to obtain lactone **20** (70 mg, 72%), identical to that obtained earlier.

(1*S*,2*S*,4*R*,5*R*,6*R*)- and (1*S*,2*S*,4*R*,5*S*,6*R*)-3-(7,9-Dioxatricyclo[4.2.1.0^{2,4}]nonan-5-yl)propionic acids (21). Cyclobutanone **16** (54 mg, 0.3 mmol) was added to a 10% aq. H_2SO_4 (4 mL) at 50 °C, the mixture was stirred for 10 min, cooled to room temperature, and extracted with EtOAc (3×10 mL). The organic extracts were dried with anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to obtain a mixture of two stereoisomeric acids (1*S*,2*S*,4*R*,5*R*,6*R*)-**21** and (1*S*,2*S*,4*R*,5*S*,6*R*)-**21** (44 mg, 74%) (colorless oil) in the ratio ~4.2 : 1 (^{1}H and ^{13}C NMR data). Found (%): C, 60.34; H, 7.27. $C_{10}H_{14}O_4$. Calculated (%): C, 60.59; H, 7.12. MS, *m/z* (I_{rel} (%)): 198 $[M]^+$ (2), 180 $[M - H_2O]^+$ (10), 152 (15), 92 (82), 83 (95), 79 (63), 55 (25). (1*S*,2*S*,4*R*,5*R*,6*R*)-Isomer. ^{1}H NMR ($CDCl_3$), δ: 0.46 (ddd, 1 H, *anti*-H(3), ^2J = 4.8 Hz, ^3J = 8.2 Hz and 8.9 Hz); 0.56 (ddd, 1 H, *syn*-H(3), ^2J = 4.8 Hz, ^3J = 5.0 Hz and 5.4 Hz); 0.91 (m, 1 H, H(4)); 1.01 (m, 1 H, H(2)); 1.56—1.70 (m, 2 H, CH_2(β)); 1.92 (ddd, 1 H, H(5), $J_{4,5}$ = 5.4 Hz, ^3J = 8.0 Hz and 11.1 Hz); 2.42 (ddd, H_a, CH_2(α), ^2J = 16.3 Hz, ^3J = 7.4 Hz and 8.8 Hz); 2.53 (ddd, H_b, CH_2(α), ^2J = 16.3 Hz, ^3J = 6.0 Hz and 8.8 Hz); 3.76 (dd, 1 H, *exo*-H(8), ^2J = 6.7 Hz, ^3J = 4.4 Hz); 3.96 (d, 1 H, *endo*-H(8), ^2J = 6.7 Hz); 4.54 (br. d, 1 H, H(1), ^3J = 4.4 Hz); 5.00 (br.s, 1 H, H(6)); 9.2—10.5 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 4.1 (C(3)); 8.1 (C(2)); 14.7 (C(4)); 25.9 ((CH_2(β)); 31.7 (CH_2(α)); 37.5 (C(5)); 69.4 (C(8)); 71.0 (C(1)); 103.6 (C(6)); 179.4 (COOH). (1*S*,2*S*,4*R*,5*S*,6*R*)-Isomer. ^{1}H NMR ($CDCl_3$), δ: 0.52 (ddd, *syn*-H(3), ^2J = 4.6 Hz, ^3J = 5.0 Hz and 5.1 Hz); (ddd, *anti*-H(3), ^2J = 4.6 Hz, ^3J = 8.4 Hz and 8.7 Hz); 3.78 (br. dd, *exo*-H(8), ^2J = 6.5 Hz, ^3J = 4.2 Hz); 3.93 (br. d, *endo*-H(8), ^2J = 6.5 Hz); 4.57 (br. d, H(1), ^3J = 4.2 Hz); 5.15 (m, H(6)), the rest of the signals overlap with signals for the major isomer. ^{13}C NMR ($CDCl_3$), δ: 9.2 (C(3)), 9.4 (C(2)), 15.0 (C(4)), 26.8 (CH_2(β)), 31.3 (CH_2(α)), 39.9 (C(5)), 70.4 (C(8)), 70.5 (C(1)), 101.6 (C(6)), 179.2 (COOH).

(1*S*,4*S*,5*R*)-2´-Oxospiro{6,8-dioxabicyclo[3.2.1]octane-4,5´-oxolane} (22). ***A.*** A mixture of (1*S*,4*S*,5*R*)-spiro{6,8-dioxabicyclo[3.2.1]octane-4,2´-cyclobutanone} (**17**) (84 mg, 0.5 mmol) and MCPBA (125 mg, 0.7 mmol) in CH_2Cl_2 (8 mL) was stirred for 10 h and neutralized with saturated aq. $NaHCO_3$ until the gas evolution ceased. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts were dried with anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to obtain lactone (1*S*,4*S*,5*R*)-**22** (85 mg, 92%) as colorless crystals, m.p. 134—135 °C. Found (%): C, 58.58; H, 6.74. $C_9H_{12}O_4$. Calculated (%): C, 58.69; H, 6.57. ^{1}H NMR ($CDCl_3$), δ: 1.53 (m, 1 H, *endo*-H(2)); 1.80—1.98 (m, 3 H, H_2C(3), H_aC(4´)); 2.12—2.29 (m, 2 H, *exo*-H(2), H_bC(4´)); 2.56 (m, 2 H, H_2C(3´)); 3.82 (ddd, *exo*-H(7), ^2J = = 7.0 Hz, ^3J = 4.9 Hz, J = 1.6 Hz); 3.89 (br. d, 1 H, *endo*-H(7), ^2J = 7.6 Hz); 4.59 (m, 1 H, H(1)); 5.12 (br.s, 1 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 25.9 (C(2)); 27.8 (C(3´)); 28.2 (C(3)); 30.0 (C(4´)); 67.2 (C(7)); 72.6 (C(1)); 82.6 (C(4)); 101.7 (C(5)); 176.0 (C=O).

B. Cyclobutanone **17** (101 mg, 0.6 mmol) was added to a solution of $KMnO_4$ (67 mg, 0.42 mmol) in 5% aq. H_2SO_4 (5 mL) and the reaction mixture was heated for 6—7 min at 40 °C. A precipitate of manganese dioxide was dissolved by addition in portions of anhydrous Na_2SO_3, the mixture was extracted with

AcOEt (3×15 mL), the extracts were dried with anhydrous $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was recrystallized from the hexane—benzene (2.5 : 1) solvent mixture to obtain stereoisomeric lactones (1*S*,4*S*,5*R*)-**22** and (1*S*,4*R*,5*R*)-**22** (the ratio ~3 : 1) (88 mg, 80%) as colorless crystals. The ^1H and ^{13}C NMR spectra of the major isomer agrees with those for (1*S*,4*S*,5*R*)-isomer obtained by method ***A***. (1*S*,4*R*,5*R*)-Isomer. ^1H NMR ($CDCl_3$), δ: 1.69 (m, *endo*-H(2)); 3.86 (ddd, *exo*-H(7), ^2J = 7.1 Hz, ^3J = 5.0 Hz, J = 1.6 Hz); 3.96 (br.d, *endo*-H(7), ^2J = 7.1 Hz); 4.53 (m, H(1)); 5.14 (br.s, H(5)), the rest of the signals overlap with signals for the major isomer. ^{13}C NMR ($CDCl_3$), δ: 26.9 and 27.1 (C(2) and C(3′)); 27.9 and 28.3 (C(3) and C(4′)); 68.0 (C(7)); 72.8 (C(1)); 84.5 (C(4)); 103.4 (C(5)); 175.9 (C=O).

(1*S*,4*R*,5*R*)- and (1*S*,4*S*,5*R*)-3-(6,8-Dioxabicyclo[3.2.1]oct-4-yl)propionic acids (23). A solution of spiro{6,8-dioxabicyclo-[3.2.1]octane-4,2′-cyclobutanone} (**17**) (50 mg, 0.3 mmol) in 15% aq. H_2SO_4 (5 mL) was heated for 10 min at 90 °C. The solution was cooled to room temperature, extracted with EtOAc (3×10 mL), dried with anhydrous $MgSO_4$, and the solvent was evaporated *in vacuo* to obtain a mixture of two stereoisomeric acids (1*S*,4*R*,5*R*)-**23** and (1*S*,4*S*,5*R*)-**23** (41 mg, 73%) (yellowish oil) in the ratio ~3 : 1 (^1H and ^{13}C NMR data). Found (%): C, 57.87; H, 7.71. $C_9H_{14}O_4$. Calculated (%): C, 58.05; H, 7.58. (1*S*,4*R*,5*R*)-Isomer. ^1H NMR ($CDCl_3$), δ: 1.32—1.56 (m, 3 H, *endo*-H(2), *endo*-H(3), H_a, $CH_2(\beta)$); 1.62—1.78 (m, 3 H, *exo*-H(2), *exo*-H(3), H_b, $CH_2(\beta)$); 1.87 (m, 1 H, H(4)); 2.36 (m, 2 H, $(CH_2(\alpha))$; 3.77 (ddd, *exo*-H(7), ^2J = 7.1 Hz, ^3J = 4.9 Hz, J = 1.6 Hz); 3.84 (dd, 1 H, *endo*-H(7), ^2J = 7.1 Hz, J = 1.1 Hz); 4.51 (m, 1 H, H(1)); 5.29 (br.s, 1 H, H(5)); 9.20 (br.s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 22.3 ($CH_2(\beta)$); 27.0 and 28.5 (C(2) and C(3)); 31.0 ($CH_2(\alpha)$); 40.1 (C(4)); 68.3 (C(7)); 73.4 (C(1)); 103.9 (C(5)); 179.2 (COOH). (1*S*,4*S*,5*R*)-Isomer. ^1H NMR ($CDCl_3$), δ: 1.95—2.01 (m, *exo*-H(2), *exo*-H(3)); 3.74 (m, *exo*-H(7)); 3.92 (dd, 1 H, *endo*-H(7), ^2J = 7.1 Hz, J = 1.0 Hz); 4.48 (m, 1 H, H(1)); 5.33 (m, 1 H, H(5)), the rest of the signals overlap with the signals for the major isomer. ^{13}C NMR ($CDCl_3$), δ: 19.5 ($CH_2(\beta)$); 24.8 and 25.5 (C(2) and C(3)); 32.3 ($CH_2(\alpha)$); 38.7 (C(4)); 67.4 (C(7)); 73.9 (C(1)); 104.1 (C(5)); 179.2 (COOH).

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