Unexpected transformation of methyl 3,6-anhydro-2,7-dideoxy-7-iodo-4,5-*O*-isopropylidene-D-*allo*-heptonate in the dehydroiodination reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene

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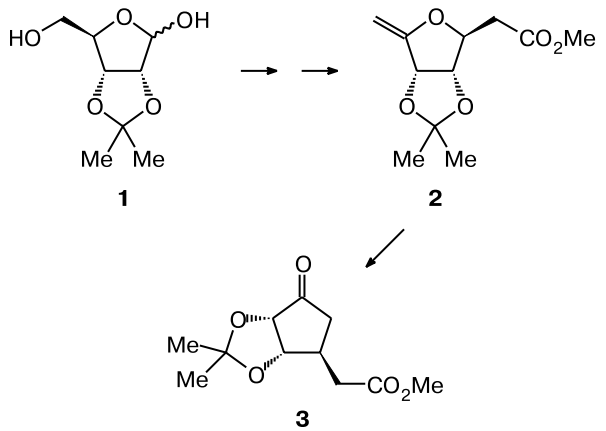
The reaction of methyl 3,6-anhydro-2,7-dideoxy-7-iodo-4,5-*O*-isopropylidene-D-*allo*-heptonate with 1,8-diazabicyclo[5.4.0]undec-7-ene affords methyl 3,6-anhydro-2,7-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-6-enonate, which undergoes the previously unknown rearrangement into a 2,2-dimethyl-1,3-dioxole derivative.

Key words: 2,3-*O*-isopropylidene-D-ribose, olefination, dehydroiodination, rearrangement.

Monosaccharides are widely used in the synthesis of optically active carbocycles.[1,2] Among these compounds, D-ribose and, particularly its *O*-isopropylidene derivative **1**, have attracted considerable attention. The latter compound is involved in atom-economic transformations into chiral cyclopentanes and cyclopentenes.[3—8] The present study is a continuation of our investigation[9] and was aimed at performing a new version of a carbocyclization **1** → **3** involving recyclization of enol ether **2** under the action of strong deprotonating agents as the key step (Scheme 1).

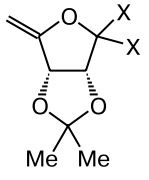
Scheme 1



The key compound **2** was synthesized as follows. The reaction of isopropylidene derivative **1** with methoxycarbonylmethylenetriphenylphosphorane under standard conditions (refluxing benzene, 2 h) gave a mixture of diastereomers **4** and **4′** (6 : 1, GLC) in 90% yield. The main isomer, *viz.*, alcohol **4**,[10] was isolated by chromatography and was transformed into iodide **5**. Dehydroiodination of the latter by refluxing in benzene with 1 equiv. of DBU occurred rapidly and was accompanied by the simultaneous transformation of the resulting enol ether **2** into a more polar compound. In the presence of 2.5 equiv. of DBU, iodide **5** was completely transformed into a new product after 2 h. This product was identified as dioxole **6** (Scheme 2) based on spectroscopic data (^{1}H and ^{13}C NMR). We failed to isolate compound **2** in individual form and its spectroscopic characteristics were obtained from the spectra of a mixture of compounds **2** and **5**.

The stepwise sequence of transformations proposed for the rearrangement **2** → **6** involves the DBU-induced retro-Michael ring opening of **2** and tautomerization of the intermediate enol to form α,β-unsaturated ester **7** (Scheme 3). Under rather drastic conditions, a stepwise (double) migration of the double bond in the latter compound to the thermodynamically more favorable γ,δ position occurs under the action of DBU. The 4,5-double bond in dioxole **6** is stabilized by the *vic*-dialkoxy substituents and conjugation with the keto group.

To our knowledge, the rearrangement **2** → **6** is unprecedented. It should be noted that enol ethers/esters **8** (see Refs 11 and 12) related to compound **2** are rather stable and are not prone to such skeletal rearrangements.



8

X = H, OMe; X + X = O

For this rearrangement to occur, an ester or other electron-withdrawing group, *i.e.*, the enolate-assisted principle, must be present in compounds of the type **2**. In the ab-

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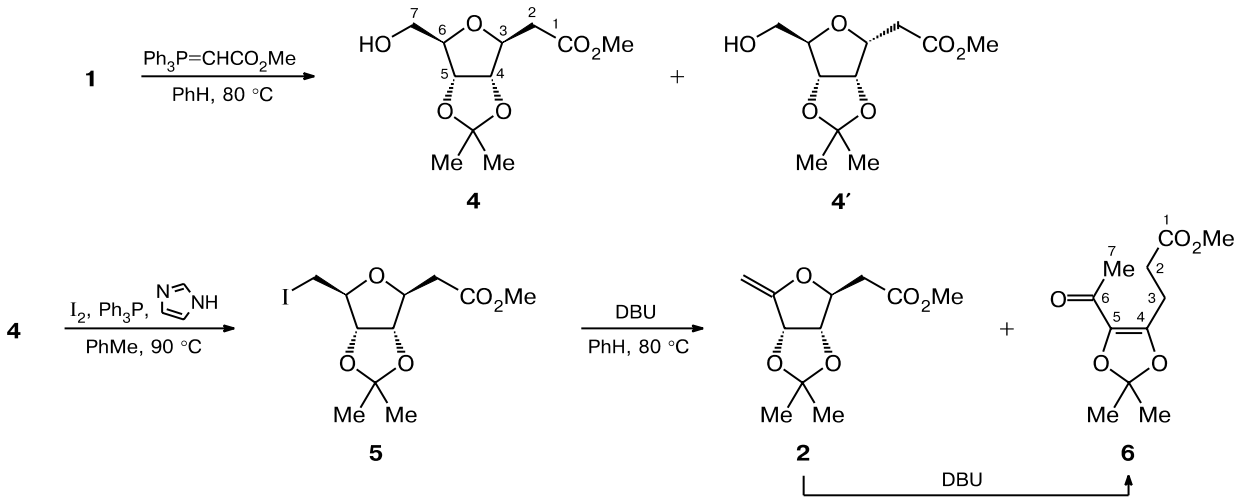
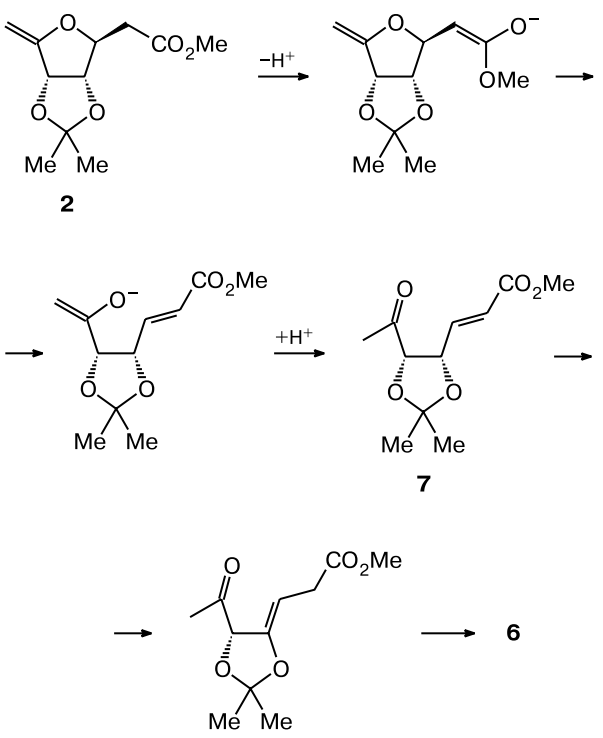
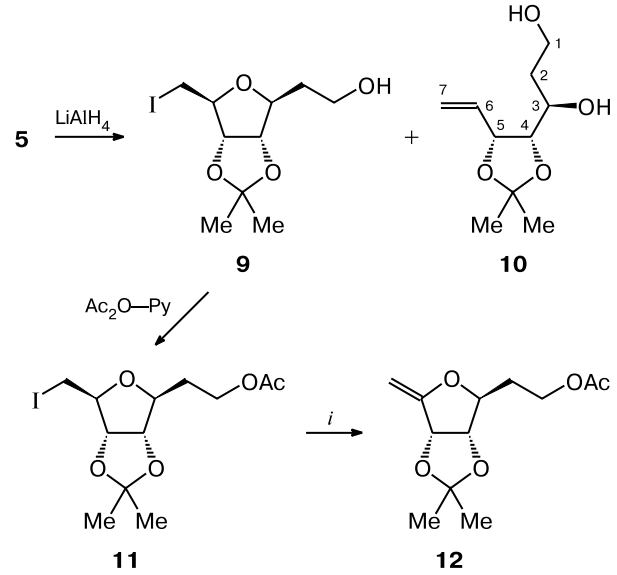
Scheme 2



Scheme 3



Scheme 4



i. 1.5 equiv. DBU.

sence of such groups, dioxole (type **6**) is apparently not formed. This was exemplified in dehydroiodination of acetate **11**. The reaction afforded the expected enol ether **12** (Scheme 4).

In conclusion, we call attention of synthetic chemists to the fact that when working with saccharide derivatives analogous to compounds **2** and **5** their possible dechiralization according to the above-described scheme should be kept in mind.

Experimental

The IR spectra were recorded on UR-20 and Specord M-80 instruments (in films). The NMR spectra were measured on a Bruker AM-300 spectrometer (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) in $CDCl_3$ (or CD_2Cl_2) using signals of the residual protons of the solvent (δ 7.27 or 5.31) and the signals of the solvent (δ 77.00 or 53.86) as the internal standard for ^{1}H and ^{13}C NMR spectroscopy, respectively. The course of the reactions was monitored by TLC (Silufol); spots were visualized with a 10% anisaldehyde solution in ethanol with addition of sulfuric acid.[13] The GLC analysis was performed on a Shimadzu instrument equipped with a quartz column (35 mm × 5 m) with

OV-101. The optical rotation was measured on a Perkin—Elmer 241 MC polarimeter.

Synthesis of esters 4 and 4´. To a solution of compound **1** (0.1 g, 0.53 mmol) in anhydrous benzene (5 mL), $Ph_3P{=}CHCO_2Me$ (0.26 g, 0.78 mmol) was added portionwise. The mixture was refluxed with stirring for 2 h and then concentrated. The residue was purified by silica gel column chromatography, and esters **4** and **4´** were isolated as oily liquids in yields of 0.1 g (76.7%) and 0.016 g (12.3%), respectively.

Methyl 3,6-anhydro-2-deoxy-4,5-*O*-isopropylidene-D-*allo*-heptonate (4), R_f 0.49 ($CHCl_3$—MeOH, 97 : 3, three runs), $[\alpha]^{20}_D$ −5.2 (*c* 1.0, $CHCl_3$). Found (%): C, 53.88; H, 7.52. $C_{11}H_{18}O_6$. Calculated (%): C, 53.65; H, 7.37. IR, ν/cm^{-1}: 1745 (C=O), 3420 (OH). ^{1}H NMR ($CDCl_3$), δ: 1.34 and 1.53 (both s, 3 H each, 2 Me); 2.62 (dd, 1 H, H_A(2), $J_{2A,3}$ = 6.7 Hz, $J_{2A,2B}$ = 16.0 Hz); 2.86 (dd, 1 H, H_B(2), $J_{2B,3}$ = 4.9 Hz, $J_{2A,2B}$ = 16.0 Hz); 3.62 (dd, 1 H, H_A(7), $J_{7A,6}$ = 3.9 Hz, $J_{7A,7B}$ = 11.7 Hz); 3.71 (s, 3 H, OMe); 3.82 (dd, 1 H, H_B(7), $J_{7B,6}$ = 3.9 Hz, $J_{7A,7B}$ = 11.7 Hz); 4.08 (q, 1 H, H(6), J = 3.9 Hz); 4.42 (ddd, 1 H, H(3), $J_{3,2B} = J_{3,4}$ = 4.9 Hz, $J_{3,2A}$ = 6.7 Hz); 4.53 (dd, 1 H, H(4), $J_{4,3}$ = 4.9 Hz, $J_{4,5}$ = 6.7 Hz); 4.74 (dd, 1 H, H(5), $J_{5,6}$ = 3.9 Hz, $J_{5,4}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.48 (Me), 27.43 (Me), 37.60 (C(2)), 51.95 (OMe), 62.67 (C(7)), 80.71 (C(3)), 81.60 (C(6)), 83.96 (C(4)), 84.77 (C(5)), 114.40 ($Me_2\underline{C}$), 171.30 (C(1)).

Methyl 3,6-anhydro-2-deoxy-4,5-*O*-isopropylidene-D-*altro*-heptonate (4´), R_f 0.33 ($CHCl_3$—MeOH, 97 : 3, three runs), $[\alpha]^{20}_D$ +3.3 (*c* 1.0, $CHCl_3$). IR, ν/cm^{-1}: 1730 (C=O), 3470 (OH). ^{1}H NMR (CD_2Cl_2), δ: 1.35 and 1.50 (both s, 3 H each, 2 Me); 2.20 (br.s, 1 H, OH); 2.67 (dd, 1 H, H_A(2), $J_{2A,3}$ = 9.5 Hz, $J_{2A,2B}$ = 13.5 Hz); 2.73 (dd, 1 H, H_B(2), $J_{2B,3}$ = 3.5 Hz, $J_{2A,2B}$ = 13.5 Hz); 3.61 (d, 2 H, H(7), $J_{7,6}$ = 6.9 Hz); 3.70 (s, 3 H, OMe); 4.05 (t, 1 H, H(6), $J_{6,7}$ = 6.9 Hz); 4.35 (ddd, 1 H, H(3), $J_{3,2B}$ = 3.5 Hz, $J_{3,5}$ = 4.1 Hz, $J_{3,2A}$ = 9.5 Hz); 4.60 (d, 1 H, H(5), $J_{5,4}$ = 6.1 Hz); 4.75 (dd, 1 H, H(4), $J_{4,3}$ = 4.1 Hz, $J_{4,5}$ = 6.1 Hz). ^{13}C NMR (CD_2Cl_2), δ: 25.06 (Me), 26.33 (Me), 34.67 (C(2)), 51.95 (OMe), 62.12 (C(7)), 77.28 (C(3)), 81.76 (C(6)), 82.94 (C(4)), 84.62 (C(5)), 112.89 ($Me_2\underline{C}$), 171.95 (C(1)).

Methyl 3,6-anhydro-2,7-dideoxy-7-iodo-4,5-*O*-isopropylidene-D-*allo*-heptonate (5). Finely crystalline iodine (3.50 g, 13.80 mmol) was added portionwise to a solution of alcohol **4** (1.70 g, 6.90 mmol), Ph_3P (3.90 g, 14.9 mmol), and imidazole (1.40 g, 20.90 mmol) in anhydrous toluene (30 mL) at 95 °C. The reaction mixture was stirred for 1 h, diluted with an equal volume of ethyl acetate, washed with a saturated aqueous $Na_2S_2O_3$ solution and water, and dried with Na_2SO_4. The solvent was evaporated and the residue was chromatographed on silica gel column (light petroleum). Iodide **5** was obtained in a yield of 1.95 g (79.4%) as a colorless oil, R_f 0.36 (light petroleum—ethyl acetate, 7 : 3), $[\alpha]^{20}_D$ −11.9 (*c* 1.0, $CHCl_3$). Found (%): C, 37.28; H, 4.62; I, 35.40. $C_{11}H_{17}IO_5$. Calculated (%): C, 37.10; H, 4.81; I, 35.69. IR, ν/cm^{-1}: 1050 (C—O), 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.35 and 1.55 (both s, 3 H each, 2 Me); 2.62 (dd, 1 H, H_A(2), $J_{2A,3}$ = 6.9 Hz, $J_{2A,2B}$ = 15.9 Hz); 2.72 (dd, 1 H, H_B(2), $J_{2B,3}$ = 5.6 Hz, $J_{2A,2B}$ = 15.9 Hz); 3.28 (dd, 1 H, H_A(7), $J_{7A,6}$ = 4.4 Hz, $J_{7A,7B}$ = 10.4 Hz); 3.25 (dd, 1 H, H_B(7), $J_{7B,6}$ = 5.3 Hz, $J_{7A,7B}$ = 10.4 Hz); 3.71 (s, 3 H, OMe); 3.91 (dd, 1 H, H(6), $J_{6,5} = J_{6,7A}$ = 4.4 Hz, $J_{6,7B}$ = 5.3 Hz); 4.30 (ddd, 1 H, H(3), $J_{3,4}$ = 4.0 Hz, $J_{3,2B}$ = 5.6 Hz, $J_{3,2A}$ = 6.8 Hz); 4.50 (dd, 1 H, H(4), $J_{4,3}$ = 4.0 Hz, $J_{4,5}$ = 6.7 Hz); 4.71 (dd, 1 H, H(5), $J_{5,6}$ = 4.4 Hz, $J_{5,4}$ = 6.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.11 (C(7)), 25.52 (Me), 27.34 (Me), 38.12 (C(2)), 51.84 (OMe), 80.91 (C(3)), 82.84 (C(4)), 84.14 (C(5)), 85.20 (C(6)), 114.76 ($Me_2\underline{C}$), 170.65 (C(1)).

Reaction of iodide 5 with DBU. ***A.*** 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.110 g, 0.70 mmol) was added to a solution of iodide **5** (0.2 g, 0.56 mmol) in anhydrous benzene (5 mL), and the mixture was stirred at 80 °C for 2 h. Chromatography afforded a mixture (0.15 g) of iodide **5** and enol ether **2** in a ratio of 2 : 1 (^{1}H NMR).

B. Under analogous conditions, compound **6** was prepared in a yield of 0.09 g (70.5%) from iodide **5** (0.2 g, 0.56 mmol) and DBU (0.21 g, 1.38 mmol) in anhydrous benzene (5 mL).

Methyl 3,6-anhydro-2,7-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-6-enonate (2), R_f 0.36 (light petroleum—ethyl acetate, 7 : 3). ^{1}H NMR ($CDCl_3$), δ: 1.37 and 1.47 (both s, 3 H each, 2 Me); 2.59 (dd, 1 H, H_A(2), $J_{2A,3}$ = 6.0 Hz, $J_{2A,2B}$ = 11.8 Hz); 2.62 (dd, 1 H, H_B(2), $J_{2B,3}$ = 6.2 Hz, $J_{2B,2A}$ = 11.8 Hz); 3.70 (s, 3 H, OMe); 4.26 (br.s, 1 H, H_A(7)); 4.47 (m, 1 H, H(4)); 4.48 (br.s, 1 H, H_B(7)); 4.62 (ddd, 1 H, H(3), $J_{3,4}$ = 2.0 Hz, $J_{3,2A} = J_{3,2B}$ = 6.0 Hz); 5.08 (d, 1 H, H(5), $J_{5,4}$ = 6.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.63 (Me), 27.07 (Me), 37.90 (C(2)), 51.99 (OMe), 79.90 (C(3)), 82.47 (C(5)), 82.98 (C(4)), 86.46 (C(7)), 161.47 (C(6)), 113.54 ($Me_2\underline{C}$), 170.33 (C(1)).

Methyl 3-(5-acetyl-2,2-dimethyl-1,3-dioxol-4-yl)propionate (6). A colorless oily compound, R_f 0.33 (benzene—ethyl acetate, 95 : 5, three runs). Found (%): C, 57.65; H, 7.28. $C_{11}H_{16}O_5$. Calculated (%): C, 57.88; H, 7.07. IR, ν/cm^{-1}: 1050 (C—O), 1710, 1745 (C=O). ^{1}H NMR ($CDCl_3$), δ: 1.55 (s, 6 H, Me_2C); 2.23 (s, 3 H, MeC=O); 2.58 (t, 2 H, H(2), $J_{2,3}$ = 7.5 Hz); 2.95 (t, 2 H, H(3), $J_{3,2}$ = 7.5 Hz); 3.70 (s, 3 H, OMe). ^{13}C NMR ($CDCl_3$), δ: 21.49 (C(3)), 25.45 ($\underline{Me}$C=O), 27.46 ($\underline{Me}_2$C), 30.88 (C(2)), 51.60 (OMe), 115.22 ($Me_2\underline{C}$), 134.90 (C(5)), 148.08 (C(4)), 173.50 (C(1)), 189.92 (C=O).

Reaction of iodide 5 with $LiAlH_4$. Lithium aluminum hydride (0.08 g, 2.1 mmol) was added portionwise with stirring to a solution of iodide **5** (0.5 g, 1.4 mmol) in anhydrous THF (10 mL) under argon at −15 °C. The reaction mixture was stirred for 0.5 h, water (5 mL) was added, and the reaction mixture was concentrated *in vacuo*. The residue was extracted with ethyl acetate, and the extract was washed with brine and dried with Na_2SO_4. The solvent was evaporated. Silica gel column chromatography of the residue (light petroleum—ethyl acetate, 97 : 3 → 8 : 2) afforded alcohol **9** in a yield of 0.36 g (77.9%) and olefin **10** in a yield of 0.05 g (17.7%).

3,6-Anhydro-2,7-dideoxy-7-iodo-4,5-*O*-isopropylidene-D-*allo*-heptitol (9). A colorless oily compound, R_f 0.36 ($CHCl_3$—MeOH, 95 : 5), $[\alpha]^{20}_D$ −11 (*c* 1.0, $CHCl_3$). Found (%): C, 36.41; H, 5.44; I, 38.40. $C_{10}H_{17}IO_4$. Calculated (%): C, 36.60; H, 5.22; I, 38.67. IR, ν/cm^{-1}: 1050 (C—O), 3420 (OH). ^{1}H NMR (CD_2Cl_2), δ: 1.28 and 1.50 (both s, 3 H each, 2 Me); 1.75 (m, 2 H, H(2)); 2.21 (br.s, 1 H, OH); 3.30 (d, 2 H, H(7), $J_{7,6}$ = 5.2 Hz); 3.71 (t, 2 H, H(1), $J_{1,2}$ = 5.8 Hz); 3.85 (td, 1 H, H(3), $J_{3,4}$ = 2.7 Hz, $J_{3,2A} = J_{3,2B}$ = 5.2 Hz); 4.02 (tdd, 1 H, H(6), $J_{6,4}$ = 1.5 Hz, $J_{6,5}$ = 3.0 Hz, $J_{6,7A} = J_{6,7B}$ = 5.2 Hz); 4.43 (dd, 1 H, H(5), $J_{5,6}$ = 3.0 Hz, $J_{5,4}$ = 6.0 Hz); 4.45 (ddd, 1 H, H(4), $J_{4,6}$ = 1.5 Hz, $J_{4,3}$ = 2.7 Hz, $J_{4,5}$ = 6.0 Hz). ^{13}C NMR (CD_2Cl_2), δ: 7.66 (C(7)), 25.63, 27.49 (Me), 36.35 (C(2)), 60.31 (C(1)), 83.11 (C(4)), 83.89 (C(3)), 85.28 (C(6)), 85.36 (C(5)), 115.21 ($Me_2\underline{C}$).

(1*R*)-1-[(4*S*,5*R*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl]propane-1,3-diol (10). A colorless oily compound, R_f 0.14 ($CHCl_3$—MeOH, 95 : 5), $[\alpha]^{20}_D$ +1.9 (*c* 1.0, $CHCl_3$).

Found (%): C, 59.23; H, 8.77. $C_{10}H_{18}O_4$. Calculated (%): C, 59.39; H, 8.97. IR, ν/cm^{-1}: 1050 (C—O), 3410 (OH). ^{1}H NMR (CD_2Cl_2), δ: 1.32 and 1.40 (both s, 3 H each, 2 Me); 1.63—1.78 (m, 1 H, H_A(2)); 1.85—1.97 (m, 1 H, H_B(2)); 2.65 (br.s, 1 H, OH); 3.72—3.90 (m, 3 H, H(1), OH); 4.02 (dd, 1 H, H(4), $J_{4,3}$ = 6.3 Hz, $J_{4,5}$ = 7.4 Hz); 4.64 (t, 1 H, H(5), $J_{5,4}$ = $J_{5,6}$ = 7.4 Hz); 5.29 (dt, 1 H, H_A(7), $J_{7A,7B}$ = 1.5 Hz, $J_{7A,6}$ = 10.2 Hz); 5.42 (dt, 1 H, H_B(7), $J_{7B,7A}$ = 1.5 Hz, $J_{7B,6}$ = 17.2 Hz); 6.00 (ddd, 1 H, H(6), $J_{6,5}$ = 7.4 Hz, $J_{6,7A}$ = 10.2 Hz, $J_{6,7B}$ = 17.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 25.46 (Me), 27.86 (Me), 35.83 (C(2)), 61.35 (C(1)), 70.2 (C(3)), 79.13 (C(5)), 80.74 (C(4)), 108.99 ($Me_2\underline{C}$), 118.11 (C(7)), 135.11 (C(6)).

1-*O*-Acetyl-3,6-anhydro-2,7-dideoxy-7-iodo-4,5-*O*-isopropylidene-D-*allo*-heptitol (11). Acetic anhydride (0.17 g, 1.7 mmol) was added to a solution of alcohol **9** (0.28 g, 0.85 mmol) in dry Py (3 mL) at room temperature. The reaction mixture was stirred for 17 h. Then a saturated NaCl solution (7 mL) was added. The reaction product was extracted with ethyl acetate, and the extract was dried with Na_2SO_4. The solvent was evaporated. After silica gel column chromatography of the residue (light petroleum—ethyl acetate, 7 : 3), $[\alpha]^{20}_D$ −19.9 (*c* 0.73, $CHCl_3$). Found (%): C, 38.77; H, 5.40; I, 34.43. $C_{12}H_{19}IO_5$. Calculated (%): C, 38.93; H, 5.17; I, 34.28. IR, ν/cm^{-1}: 1050, 1085 (C—O), 1740 (C=O). ^{1}H NMR (CD_2Cl_2), δ: 1.32 and 1.49 (both s, 3 H each, 2 Me); 1.85—2.05 (m, 2 H, H(2)); 2.01 (s, 3 H, MeC=O); 3.29 (m, 2 H, H(7)); 3.86 (dt, 1 H, H(3), $J_{3,4}$ = 3.4 Hz, $J_{3,2A}$ = $J_{3,2B}$ = 5.4 Hz); 4.00 (ddd, 1 H, H(6), $J_{6,5}$ = 4.1 Hz, $J_{6,7A}$ = 5.6 Hz, $J_{6,7B}$ = 9.6 Hz); 4.15 (t, 1 H, H_A(1), $J_{1A,2A}$ = $J_{1A,2B}$ = 6.3 Hz); 4.16 (t, 1 H, H_B(1), $J_{1B,2A}$ = $J_{1B,2B}$ = 6.3 Hz); 4.42 (dd, 1 H, H(4), $J_{4,3}$ = 3.0 Hz, $J_{4,5}$ = 6.8 Hz); 4.44 (dd, 1 H, H(5), $J_{5,6}$ = 4.1 Hz, $J_{5,4}$ = 6.8 Hz). ^{13}C NMR (CD_2Cl_2), δ: 7.67 (C(7)), 21.01 ($\underline{Me}$C=O), 25.51 (Me), 27.36 (Me), 32.96 (C(2)), 60.12 (C(1)), 81.95 (C(4)), 82.96 (C(3)), 85.16 (C(6)), 85.37 (C(5)), 114.89 ($Me_2\underline{C}$), 170.92 (C=O).

1-*O*-Acetyl-3,6-anhydro-2,7-dideoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-6-enitol (12). 1,8-Diazabicyclo[5.4.0]undec-7-ene (0.06 g, 0.4 mmol) was added to a solution of iodide **11** (0.1 g, 0.27 mmol) in anhydrous benzene (3 mL). The reaction mixture was stirred for 1 h, and the solvent was evaporated. After silica gel column chromatography of the residue (light petroleum—ethyl acetate, 95 : 5), enol ether **12** was obtained in a yield of 0.042 g (65%) as an oily yellow compound, R_f 0.35 (light petroleum—ethyl acetate, 7 : 3), $[\alpha]^{20}_D$ +35.5 (*c* 0.6, $CHCl_3$). Found (%): C, 59.37; H, 7.58. $C_{12}H_{18}O_5$. Calculated (%): C, 59.49; H, 7.49. IR, ν/cm^{-1}: 1050, 1090 (C—O), 1740 (C=O). ^{1}H NMR (CD_2Cl_2), δ: 1.32 and 1.45 (both s, 3 H each, 2 Me); 1.72 (ddt, 1 H, H_A(2), $J_{2A,1A}$ = $J_{2A,1B}$ = 5.7 Hz, $J_{2A,3}$ = 9.0 Hz, $J_{2A,2B}$ = 14.3 Hz); 1.86 (ddd, 1 H, H_B(2), $J_{2B,3}$ = 4.8 Hz, $J_{2B,1B}$ = 6.7 Hz, $J_{2B,1A}$ = 7.5 Hz, $J_{2B,2A}$ = 14.3 Hz); 2.01 (br.s, 1 H, $\underline{Me}$C=O); 4.12 (dd, 1 H, H_A(1), $J_{1A,2A}$ = 5.7 Hz, $J_{1A,2B}$ = 7.5 Hz); 4.14 (dd, 1 H, H_B(1), $J_{1B,2A}$ = 5.7 Hz, $J_{1B,2B}$ = 6.7 Hz); 4.20—4.25 (m, 1 H, H_A(7)); 4.37 (ddd, 1 H, H(3), $J_{3,4}$ = 2.0 Hz, $J_{3,2B}$ = 4.8 Hz, $J_{3,2A}$ = 9.0 Hz); 4.41—4.43 (m, 1 H, H_B(7)); 4.47 (dd, 1 H, H(4), $J_{4,3}$ = 2.0 Hz, $J_{4,5}$ = 6.0 Hz); 4.89 (dt, 1 H, H(5), $J_{5,7A}$ = $J_{5,7B}$ = 1.0 Hz, $J_{5,4}$ = 6.0 Hz). ^{13}C (CD_2Cl_2), δ: 21.01 ($\underline{Me}$C=O), 25.75 (Me), 27.14 (Me), 32.96 (C(2)), 53.07 (C(1)), 61.78 (C(6)), 79.88 (C(4)), 83.14 (C(3)), 86.35 (C(5)), 113.56 ($Me_2\underline{C}$), 161.79 (C(7)), 171.01 (C=O).

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