

## Supporting Information

### Intramolecular 1,5- versus 1,6-Hydrogen Abstraction Reaction Promoted by Alkoxy Radicals in Carbohydrate Models

Cosme G. Francisco, Raimundo Freire, Antonio J. Herrera,  
Inés Pérez-Martín and Ernesto Suárez\*

Instituto de Productos Naturales y Agrobiología del C.S.I.C. Carretera de La Esperanza 3,  
38206 La Laguna, Tenerife, Spain

**General Methods.** Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotations were measured at the sodium line at ambient temperature in  $\text{CHCl}_3$  solutions. IR spectra were measured as thin films on NaCl plate. NMR spectra were determined at 500 MHz for  $^1\text{H}$  and 125.7 MHz for  $^{13}\text{C}$  in  $\text{CDCl}_3$  unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF<sub>254</sub> were used on a Chromatotron for centrifugally-assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in  $\text{H}_2\text{SO}_4$ –EtOH (4:1) and further heating until development of color.

**3,4,5-Tri-*O*-acetyl-2,6-anhydro-1,7-dideoxy-L-glycero-D-galacto-octitol (1).** A solution of 3,4,5-tri-*O*-acetyl-2,6-anhydro-1,7,8,9-tetradideoxy-L-glycero-D-galacto-non-8-enitol<sup>1</sup> (434 mg, 1.38 mmol) in dry  $\text{CH}_2\text{Cl}_2$ /MeOH (50 mL, 1:1) was cooled to  $-78\text{ }^\circ\text{C}$  and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess of ozone, and the mixture was heated to  $0\text{ }^\circ\text{C}$ . Afterward,  $\text{NaBH}_4$  (313 mg, 8.29 mmol) was added slowly and the solution stirred for 30 min at room temperature. The reaction mixture was then poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ ,

dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Column chromatography (hexanes–EtOAc, 25:75) of the residue afforded the title alcohol (375 mg, 1.18 mmol, 85%) as a colorless oil:  $[\alpha]_D -7.3$  (*c*, 0.48); IR 3478, 2942, 1748, 1732, 1434, 1372, 1246, 1059 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.11 (3H, d, *J* = 6.3 Hz), 1.64 (1H, m), 1.93 (1H, m), 1.96 (3H, s), 2.01 (3H, s), 2.10 (3H, s), 3.69 (2H, m), 3.98 (1H, ddd, *J* = 1.9, 6.5, 6.5 Hz), 4.34 (1H, ddd, *J* = 3.3, 5.5, 5.5 Hz), 5.13 (1H, dd, *J* = 3.3, 9.9 Hz), 5.22 (1H, dd, *J* = 1.5, 5.4 Hz), 5.24 (1H, dd, *J* = 5.4, 9.9 Hz); <sup>13</sup>C NMR 15.8 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 27.8 (CH<sub>2</sub>), 59.8 (CH<sub>2</sub>), 66 (CH), 68 (CH), 68.5 (CH), 70.4 (CH), 70.6 (CH), 169.9 (C), 170.1 (C), 170.5 (C); MS (EI) *m/z* (rel intensity) 319 (M<sup>+</sup> + H, 1), 301 (<1), 273 (10); HRMS calcd for C<sub>14</sub>H<sub>23</sub>O<sub>8</sub>, 319.1392786, found 319.135857. Anal. Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>8</sub>: C, 52.82; H, 6.97. Found: C, 52.72; H, 7.25.

**3,4,5-Tri-*O*-acetyl-2,8-anhydro-1,7-dideoxy-β-*L*-gulo-oct-2-ulopyranose (3).** A solution of compound **1** (33 mg, 0.104 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) containing (diacetoxyiodo)benzene (DIB) (50 mg, 0.156 mmol) and iodine (26.4 mg, 0.104 mmol) was irradiated with two 80 W tungsten-filament lamps at room temperature under nitrogen for 1 h. The reaction mixture was then poured into water and extracted with EtOAc. The organic layer was washed with 10% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, dried and concentrated in vacuo. Chromatotron chromatography of the residue (hexanes–EtOAc, 70:30) afforded the anhydrosugar **3** (15 mg, 0.05 mmol, 47%) as a colorless oil:  $[\alpha]_D -18.1$  (*c* = 0.16); IR 2978, 1732, 1715, 1372, 1234, 1064 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.25 (3H, s), 1.90 (1H, m), 1.98 (3H, s), 2.04 (3H, s), 2.11 (1H, m), 2.14 (3H, s), 3.76 (1H, dd, *J* = 7.1, 10.7 Hz), 3.87 (1H, ddd, *J* = 4.7, 11.3, 11.3 Hz), 4.51 (1H, ddd, *J* = 3.2, 5.9, 9.6 Hz), 5.22 (1H, d, *J* = 4.1 Hz), 5.24 (1H, dd, *J* = 5.9, 10.5 Hz), 5.68 (1H, dd, *J* = 4.0, 10.5 Hz); <sup>13</sup>C NMR (50.3 MHz) 20.7 (3 × CH<sub>3</sub>), 22.2 (CH<sub>3</sub>), 23.6 (CH<sub>2</sub>), 55.9 (CH<sub>2</sub>), 65.9 (CH), 67.1 (CH), 67.8 (CH), 71.4 (CH), 98.3 (C), 169.7 (C), 169.9 (C), 170.1 (C); MS (EI) *m/z* (rel intensity) 316 (M<sup>+</sup>, 1), 257 (17), 214 (5), 196 (16); HRMS calcd for C<sub>14</sub>H<sub>20</sub>O<sub>8</sub> 316.1158048, found 316.117523. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>8</sub>: C, 53.16; H, 6.37. Found: C, 53.06; H, 6.70.

**2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-D-galacto-non-8-enitol.**

A solution of 3,4,5-tri-*O*-acetyl-2,6-anhydro-1,7,8,9-tetradecoxy-L-glycero-D-galacto-non-8-enitol<sup>1</sup> (3.6 g, 11.45 mmol) in MeOH (25 mL) containing KOH (0.75 g, 0.013 mmol) was stirred at room temperature for 1 h. The reaction mixture was then neutralized with Dowex 50X8 acid resin, filtered and concentrated in vacuo to give an oil which was used in the following reaction without purification. To a suspension of NaH (1.65 g, 68.72 mmol) in dry DMF (50 mL) was added the crude triol previously obtained in DMF (50 mL) and the mixture stirred at 0 °C under nitrogen until the hydrogen evolution had ceased. Then an excess of methyl iodide (4.3 mL, 69.9 mmol) was added dropwise and stirring continued at room temperature for 2 h. Excess reagent was destroyed by slow addition of MeOH and the solution poured into water and extracted with EtOAc. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 70:30) of the residue afforded the title compound (1.81 g, 7.87 mmol, 68.6%) as a colorless oil:  $[\alpha]_D -86.7$  (*c*, 0.82); IR 2978, 2933, 2826, 1643, 1360, 1193, 1104 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.27 (3H, d, *J* = 6.6 Hz), 2.30 (1H, m), 2.37 (1H, m), 3.44 (3H, s), 3.48 (3H, s), 3.49 (3H, s), 3.51 (3H, m), 3.92 (1H, dq, *J* = 6.5, 3.3 Hz), 4.03 (1H, ddd, *J* = 9.1, 5.3, 3.8 Hz), 5.05 (1H, d, *J* = 10.2 Hz), 5.10 (1H, dd, *J* = 17.0, 1.5 Hz), 5.81 (1H, ddd, *J* = 17.0, 10.2, 6.8 Hz); <sup>13</sup>C NMR 15.0 (CH<sub>3</sub>), 31.9 (CH<sub>2</sub>), 58.3 (CH<sub>3</sub>), 58.5 (CH<sub>3</sub>), 59.5 (CH<sub>3</sub>), 68.2 (CH), 70.0 (CH), 77.5 (CH), 77.6 (CH), 78.4 (CH), 116.6 (CH<sub>2</sub>), 135.2 (CH); MS (EI) *m/z* (rel intensity) 230 (*M*<sup>+</sup>, 21), 189 (29); HRMS calcd for C<sub>12</sub>H<sub>22</sub>O<sub>4</sub> 230.1517976, found 230.151928. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O<sub>4</sub>: C, 62.58; H, 9.63. Found: C, 62.49; H, 9.65.

**2,6-Anhydro-1,7-dideoxy-3,4,5-tri-*O*-methyl-L-glycero-D-galacto-octitol (2).** A solution of 2,6-anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-D-galacto-non-8-enitol (1.4 g, 6.079 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub>/MeOH (50 mL, 1:1) was ozonized as described for compound **1** and the ozonide reduced with NaBH<sub>4</sub> (1.36 g). Column chromatography (CHCl<sub>3</sub>–MeOH, 95:5) afforded compound **2** (1.025 g, 4.38 mmol, 72%) as a colorless oil:  $[\alpha]_D -65.5$  (*c* =

0.6); IR 3444, 2936, 2829, 1732, 1651, 1463, 1362, 1362, 1194, 1102  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.28 (3H, d,  $J = 6.6$  Hz), 1.73 (1H, m), 1.94 (1H, m), 3.46 (3H, s), 3.49 (3H, s), 3.51 (3H, s), 3.52 (3H, m), 3.77 (2H, m), 3.95 (1H, d q,  $J = 2.8, 6.6$  Hz), 4.21 (1H, ddd,  $J = 3.6, 9.9, 9.9$  Hz);  $^{13}\text{C}$  NMR 15.4 ( $\text{CH}_3$ ), 29.5 ( $\text{CH}_2$ ), 58.3 ( $\text{CH}_3$ ), 58.9 ( $\text{CH}_3$ ), 59.9 ( $\text{CH}_3$ ), 61.5 ( $\text{CH}_2$ ), 68.5 (CH), 70.8 (CH), 77.7 (CH), 77.9 (CH), 78.9 (CH); MS (EI)  $m/z$  (rel intensity) 235 ( $\text{M}^+ + \text{H}$ , <1), 217 (<1), 202 (<1), 170 (1); HRMS calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_5$  234.1467117, found 234.146118. Anal. Calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_5$ : C, 56.39; H, 9.46. Found: C, 56.20; H, 9.70.

**2,8-Anhydro-1,7-dideoxy-3,4,5-tri-*O*-methyl- $\beta$ -L-gulo-oct-2-ulopyranose (4).** To a solution of compound **2** (131 mg, 0.559 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL), were added DIB (270 mg, 0.839 mmol) and iodine (142 mg, 0.559 mmol) and the mixture was irradiated for 1.5 h as described for compound **3**. Chromatotron chromatography (hexanes–EtOAc, 70:30) afforded the anhydrosugar **4** (75 mg, 0.32 mmol, 57%) as a colorless oil:  $[\alpha]_{\text{D}} -30.5$  ( $c = 0.59$ ); IR 2936, 2826, 1462, 1377, 1223, 1102, 1074  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.33 (3H, s), 1.76 (1H, m), 2.06 (1H, m), 3.37 (1H, d,  $J = 2.8$  Hz), 3.4 (3H, s), 3.5 (3H, s), 3.56 (3H, s), 3.60 (1H, dd,  $J = 3.3, 9.9$  Hz), 3.62 (1H, d,  $J = 6.1$  Hz), 3.79 (1H, dd,  $J = 3.3, 9.9$  Hz), 3.84 (1H, ddd,  $J = 4.3, 9.9, 9.9$  Hz), 4.37 (1H, ddd,  $J = 3.8, 6.1, 10.0$  Hz);  $^{13}\text{C}$  NMR 22.6 ( $\text{CH}_3$ ), 23.3 ( $\text{CH}_2$ ), 55.9 ( $\text{CH}_2$ ), 58.1 ( $\text{CH}_3$ ), 58.4 ( $\text{CH}_3$ ), 61.6 ( $\text{CH}_3$ ), 66.3 (CH), 77 (CH), 79 (CH), 80.2 (CH), 99.5 (C); MS (EI)  $m/z$  (rel intensity) 231 ( $\text{M}^+$ , <1), 203 (4), 187 (4); HRMS calcd for  $\text{C}_{11}\text{H}_{19}\text{O}_5$  231.1232379, found 231.129158. Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$ : C, 56.88; H, 8.68. Found: C, 56.54; H, 9.02.

**2,6-Anhydro-7,8,9-trideoxy-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-non-8-enitol.** To a solution of 1-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-mannopyranose<sup>2</sup> (104 mg, 0.374 mmol) in dry MeCN (1.5 mL) were added allyltrimethylsilane (0.176 mL, 1.122 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.114 mL, 0.935 mmol) at 0 °C. After 30 min at room temperature, the reaction mixture was poured into ice–water and extracted with EtOAc. The organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. Column chromatography (hexanes–EtOAc,

1:1) of the residue afforded the title compound (82 mg, 0.31 mmol, 83%) as a colorless oil:  $[\alpha]_D +15.6$  ( $c = 0.52$ );  $^1\text{H}$  NMR 2.33 (1H, m), 2.41 (1H, m), 3.37 (3H, s), 3.40 (3H, s), 3.41 (1H, m), 3.43 (1H, m), 3.47 (3H, s), 3.47 (3H, s), 3.57 (1H, m), 3.58 (2H, d,  $J = 4.7$  Hz), 3.63 (1H, m), 4.02 (1H, ddd,  $J = 1.9, 7.2, 7.2$  Hz), 5.07 (1H, d,  $J = 9.9$  Hz), 5.10 (1H, d,  $J = 17.1$  Hz), 5.80 (1H, dddd,  $J = 7.3, 7.3, 10.0, 17.1$  Hz);  $^{13}\text{C}$  NMR 34.1 ( $\text{CH}_2$ ), 57.4 ( $\text{CH}_3$ ), 57.6 ( $\text{CH}_3$ ), 58.9 ( $\text{CH}_3$ ), 59.6 ( $\text{CH}_3$ ), 71.5 ( $\text{CH}_2$ ), 71.8 (CH), 72.6 (CH), 76.4 (CH), 77.1 (CH), 79.3 (CH), 117.1 ( $\text{CH}_2$ ), 134.1 (CH); MS (EI)  $m/z$  (rel intensity) 219 ( $\text{M}^+ - \text{C}_3\text{H}_5$ , 35), 187 (63), 183 (15); HRMS calcd for  $\text{C}_{10}\text{H}_{19}\text{O}_5$  219.1232379, found 219.121777. Anal. Calcd for  $\text{C}_{13}\text{H}_{24}\text{O}_5$ : C, 59.98; H, 9.29. Found: C, 59.84; H, 9.14.

**2,6-Anhydro-7-deoxy-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-octitol (5).** A solution of 2,6-anhydro-7,8,9-trideoxy-1,3,4,5-tetra-*O*-methyl-D-glycero-D-manno-non-8-enitol (500 mg, 1.921 mmol) in dry  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (100 mL, 1:1) was ozonized as described for compound **1** and the ozonide reduced with  $\text{NaBH}_4$  (435 mg, 11.526 mmol). Column chromatography (EtOAc) afforded compound **5** (398 mg, 1.51 mmol, 79%) as a colorless oil:  $[\alpha]_D +19.2$  ( $c = 0.24$ ); IR 3471, 2930, 1738, 1454, 1093  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.63 (1H, m), 1.84 (1H, m), 3.29 (3H, s), 3.30 (1H, m), 3.32 (1H, m), 3.35 (3H, s), 3.39 (3H, s), 3.40 (3H, s), 3.45 (1H, m), 3.48 (1H, dd,  $J = 7.2, 10.0$  Hz), 3.56 (1H, dd,  $J = 8.1, 10.0$  Hz), 3.66 (1H, m), 3.68 (2H, t,  $J = 5.7$  Hz), 4.06 (1H, ddd,  $J = 4.7, 9.5, 9.5$  Hz);  $^{13}\text{C}$  NMR 31.7 ( $\text{CH}_2$ ), 57.5 ( $\text{CH}_3$ ), 58.2 ( $\text{CH}_3$ ), 58.9 ( $\text{CH}_3$ ), 59.4 ( $\text{CH}_3$ ), 60.5 ( $\text{CH}_2$ ), 71.2 (CH), 71.4 ( $\text{CH}_2$ ), 72.3 (CH), 76.6 (CH), 78.4 (CH), 78.9 (CH); MS (EI)  $m/z$  (rel intensity) 264 ( $\text{M}^+$ , <1), 232 (1), 219 (4), 200 (1), 187 (35); HRMS calcd for  $\text{C}_{12}\text{H}_{24}\text{O}_6$  264.157275, found 264.152969. Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{O}_6$ : C, 54.53; H, 9.15. Found: C, 54.58; H, 9.18.

**Methyl 3,7-Anhydro-2-deoxy-5,6,8-tri-*O*-methyl- $\alpha$ -D-manno-oct-4-ulofuranoside (6).** A solution of compound **5** (249 mg, 0.942 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (45 mL) containing DIB (389 mg, 1.2 mmol) and iodine (393 mg, 1.225 mmol) was irradiated for 75 min as described for compound **3**. Chromatotron chromatography (hexanes–EtOAc, 1:1) afforded the

anhydrosugar **6** (174 mg, 0.66 mmol, 70%) as a colorless oil:  $[\alpha]_D +13.3$  ( $c = 0.42$ ); IR 2933, 2828, 1740, 1456, 1194, 1106  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.87 (1H, m), 2.27 (1H, m), 3.17 (1H, dd,  $J = 2.6, 6.9$  Hz), 3.19 (3H, s), 3.30 (3H, s), 3.36 (3H, s), 3.42 (1H, dd,  $J = 3.3, 10.4$  Hz), 3.45 (3H, s), 3.52 (1H, dd,  $J = 7.2, 10.4$  Hz), 3.54 (1H, d,  $J = 2.6$  Hz), 3.65 (1H, ddd,  $J = 3.4, 6.9, 6.9$  Hz), 3.75 (1H, ddd,  $J = 6.4, 8.8, 8.8$  Hz), 4.05 (1H, ddd,  $J = 5.8, 8.7, 8.7$  Hz), 4.16 (1H, br d,  $J = 5.6$  Hz);  $^{13}\text{C}$  NMR 31.3 ( $\text{CH}_2$ ), 48.4 ( $\text{CH}_3$ ), 57.8 ( $\text{CH}_3$ ), 58.1 ( $\text{CH}_3$ ), 59.1 ( $\text{CH}_3$ ), 66.4 ( $\text{CH}_2$ ), 72.1 ( $\text{CH}_2$ ), 72.3 (CH), 76.5 (CH), 76.9 (CH), 77.2 (CH), 105.1 (C); MS (EI)  $m/z$  (rel intensity) 262 ( $\text{M}^+$ , 17), 231 (1), 217 (23); HRMS calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_6$  262.1416258, found 262.137962. Anal. Calcd for  $\text{C}_{12}\text{H}_{22}\text{O}_6$ : C, 54.95; H, 8.45. Found: C, 55.27; H, 8.10.

**1,3,4,5-Tetra-*O*-acetyl-2,6-anhydro-7-deoxy-D-glycero-D-manno-octitol (7).** A solution of 1,3,4,5-tetra-*O*-acetyl-2,6-anhydro-7,8,9-trideoxy-D-glycero-D-manno-non-8-enitol<sup>3</sup> (240 mg, 8.685 mmol) in dry  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (15 mL, 1:1) was ozonized as described for compound **1** and the ozonide reduced with  $\text{NaBH}_4$  (73 mg, 1.93 mmol). Column chromatography (hexanes-EtOAc, 25:75) afforded compound **7** (212 mg, 0.56 mmol, 87%) as a colorless oil:  $[\alpha]_D -3.1$  ( $c = 0.64$ ); IR 3542, 2960, 2888, 1756, 1651, 1434, 1372, 1242, 1049  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.75 (1H, m), 1.92 (1H, m), 1.98 (3H, s), 2.01 (3H, s), 3.66 (2H, m), 3.90 (1H, ddd,  $J = 2.8, 7.5, 7.5$  Hz), 4.00 (1H, dd,  $J = 2.8, 12.2$  Hz), 4.13 (1H, ddd,  $J = 3.8, 10.3, 10.3$  Hz), 4.41 (1H, dd,  $J = 7.5, 12.2$  Hz), 5.06 (1H, dd,  $J = 7.5, 7.5$  Hz), 5.09 (1H, dd,  $J = 3.8, 3.8$  Hz), 5.18 (1H, dd,  $J = 3.8, 7.5$  Hz);  $^{13}\text{C}$  NMR 21.0 ( $2 \times \text{CH}_3$ ), 21.1 ( $\text{CH}_3$ ), 21.2 ( $\text{CH}_3$ ), 32.0 ( $\text{CH}_2$ ), 59.6 ( $\text{CH}_2$ ), 62.4 ( $\text{CH}_2$ ), 67.7 (CH), 68.8 (CH), 70.7 (CH), 71.7 (CH), 72.3 (CH), 170.2 (C), 170.5 ( $2 \times \text{C}$ ), 171.2 (C); MS (EI)  $m/z$  (rel intensity) 377 ( $\text{M}^+ - \text{H}$ , <1), 359 (<1), 345 (<1), 317 (1), 214 (73); HRMS calcd for  $\text{C}_{16}\text{H}_{25}\text{O}_{10}$  377.144756, found 377.145386. Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_{10}$ : C, 51.06; H, 6.43. Found: C, 50.70; H, 6.75.

**1,3,4,5-Tetra-*O*-acetyl-2,8-anhydro-7-deoxy- $\beta$ -D-altro-oct-2-ulopyranose (8).** A solution of compound **7** (75 mg, 0.2 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) containing DIB (103 mg, 0.32 mmol) and iodine (51 mg, 0.2 mmol) was irradiated for 2 h as described for compound **3**.

Chromatotron chromatography (hexanes–EtOAc, 8:2→7:3) afforded the anhydrosugar **8** (36 mg, 0.096 mmol, 48%) as a colorless oil:  $[\alpha]_D -36.9$  ( $c = 0.36$ ); IR 2966, 1747, 1434, 1372, 1225, 1056  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.97 (1H, m), 1.99 (3H, s), 2.07 (3H, s), 2.08 (1H, m), 2.11 (3H, s), 2.16 (3H, s), 3.92 (1H, ddd,  $J = 2.7, 10.8, 10.8$  Hz), 3.93 (1H, d,  $J = 12.0$  Hz), 3.98 (1H, ddd,  $J = 4.7, 11.2, 11.2$  Hz), 4.17 (1H, d,  $J = 12.0$  Hz), 4.36 (1H, ddd,  $J = 2.0, 3.7, 11.1$  Hz), 5.25 (1H, dd,  $J = 2.1, 3.9$  Hz), 5.38 (1H, d,  $J = 10.3$  Hz), 5.66 (1H, dd,  $J = 3.9, 10.3$  Hz);  $^{13}\text{C}$  NMR 20.6 ( $2 \times \text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ), 20.9 ( $\text{CH}_3$ ), 26.1 ( $\text{CH}_2$ ), 57.7 ( $\text{CH}_2$ ), 63.4 ( $\text{CH}_2$ ), 67.2 ( $\text{CH}$ ), 67.8 ( $\text{CH}$ ), 69.6 ( $\text{CH}$ ), 71.9 ( $\text{CH}$ ), 97.7 (C), 169.8 (C), 170.1 (C), 170.3 (C), 170.5 (C); MS (EI)  $m/z$  (rel intensity) 375 ( $\text{M}^+ + \text{H}$ , 1), 331 (2), 315 (14); HRMS calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_{10}$  375.1291068, found 375.12664. Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_{10}$ : C, 51.33; H, 5.92. Found: C, 51.48; H, 6.11.

**2,6-Anhydro-1,7,8,9-tetradecoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-non-8-enitol.** A solution of 3,4,5-tri-*O*-acetyl-2,6-anhydro-1,7,8,9-tetradecoxy-L-glycero-L-manno-non-8-enitol<sup>4</sup> (11.5 g, 36.58 mmol) in MeOH (200 mL) containing KOH (6 g, 150 mmol) was stirred at room temperature for 1 h. The reaction mixture was then neutralized with Dowex 50X8 acid resin, filtered and concentrated in vacuo to give an oil (8.5 g) which was used in the following reaction without purification. To a suspension of NaH (5.26 g, 219.5 mmol) in dry DMF (350 mL) was added the crude triol previously obtained in DMF (150 mL) and the mixture stirred at 0 °C under nitrogen until all hydrogen evolution had ceased. Then an excess of methyl iodide (15.9 mL, 256.1 mmol) was added dropwise and stirring continued at room temperature for 3 h. Excess reagent was destroyed by slow addition of MeOH and the solution poured into water and extracted with EtOAc. The organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. Column chromatography (hexanes–EtOAc, 85:15) of the residue afforded the title compound (5.5 g, 23.88 mmol, 65.5%) as a colorless oil:  $[\alpha]_D -8.2$  ( $c, 0.73$ ); IR 3077, 2977, 2933, 2825, 1644, 1455, 1382, 1196, 1102  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.28 (3H, d,  $J = 6.3$  Hz), 2.27 (1H, m), 2.42 (1H, m), 3.16 (1H, dd,  $J = 7.7, 7.7$  Hz), 3.43 (1H, m), 3.43

(3H, s), 3.45 (1H, m), 3.47 (3H, s), 3.52 (3H, s), 3.56 (1H, m), 4.02 (1H, dq,  $J = 6.5, 3.3$  Hz), 5.09 (1H, dd,  $J = 17.0, 1.5$  Hz), 5.12 (1H, d,  $J = 10.0$  Hz), 5.79 (1H, ddd,  $J = 17.0, 10.2, 6.8$  Hz);  $^{13}\text{C}$  NMR 17.8 (CH<sub>3</sub>), 34.1 (CH<sub>2</sub>), 57.6 (2 × CH<sub>3</sub>), 60.2 (CH<sub>3</sub>), 69.1 (CH), 71.9 (CH), 77.7 (CH), 80 (CH), 81.8 (CH), 117.1 (CH<sub>2</sub>), 134.2 (CH); MS (EI)  $m/z$  (rel intensity) 189 (44), 157 (139); HRMS calcd for C<sub>9</sub>H<sub>17</sub>O<sub>4</sub> 189.1126746, found 189.115547. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O<sub>4</sub>: C, 62.58; H, 9.63. Found: C, 62.61; H, 9.64.

**2,6-Anhydro-1,7-dideoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-octitol (9).** A solution of 2,6-anhydro-1,7,8,9-tetradeoxy-3,4,5-tri-*O*-methyl-L-glycero-L-manno-non-8-enitol (2 g, 8.685 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub>/MeOH (200 mL, 1:1) was ozonized as described for compound **3** and the ozonide reduced with NaBH<sub>4</sub> (1.97 g, 52.11 mmol). Column chromatography (hexanes-EtOAc, 25:75) afforded compound **9** (1.95 g, 8.32 mmol, 96%) as a colorless oil:  $[\alpha]_{\text{D}} -17.1$  ( $c = 0.34$ ); IR 3453, 2935, 2828, 1725, 1642, 1452, 1383, 1197, 1099 cm<sup>-1</sup>;  $^1\text{H}$  NMR 1.28 (3H, d,  $J = 6.5$  Hz), 1.67 (1H, m), 1.89 (1H, m), 3.17 (1H, dd,  $J = 8.1, 8.1$  Hz), 3.36 (1H, dd,  $J = 2.8, 3.7$  Hz), 3.41 (3H, s), 3.45 (3H, s), 3.46 (3H, s), 3.47 (1H, m), 3.64 (1H, dq,  $J = 6.5, 8.1$  Hz), 3.73 (2H, t,  $J = 6.0$  Hz), 4.11 (1H, ddd,  $J = 3.7, 8.2, 8.2$  Hz);  $^{13}\text{C}$  NMR 17.5 (CH<sub>3</sub>), 31.7 (CH<sub>2</sub>), 57.6 (CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 59.7 (CH<sub>3</sub>), 60.6 (CH<sub>2</sub>), 69.3 (CH), 70.7 (CH), 78.6 (CH), 79 (CH), 81.1 (CH); MS (EI)  $m/z$  (rel intensity) 234 (M<sup>+</sup>, 1), 202 (2), 189 (1); HRMS calcd for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub> 234.1467117, found 234.148731. Anal. Calcd for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub>: C, 56.39; H, 9.46. Found: C, 56.34; H, 9.45.

**Methyl 3,7-Anhydro-2,8-dideoxy-5,6-di-*O*-methyl- $\alpha$ -L-manno-oct-4-ulofuranoside (10) and 2,8-Anhydro-1,7-dideoxy-3,4,5-tri-*O*-methyl- $\beta$ -L-altro-oct-2-ulopyranose.** A solution of compound **9** (63 mg, 0.269 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (6 mL) containing DIB (133 mg, 0.41 mmol) and iodine (68 mg, 0.269 mmol) was irradiated for 4.5 h as described for compound **3**. Chromatotron chromatography (hexanes-EtOAc, 3:2→1:1) afforded the oct-2-ulopyranose (7 mg, 0.03 mmol, 11%), and anhydrosugar **10** (28 mg, 0.12 mmol, 44.5%). 2,8-Anhydro-1,7-dideoxy-3,4,5-tri-*O*-methyl- $\beta$ -L-altro-oct-2-ulopyranose:  $[\alpha]_{\text{D}} 97.8$  ( $c = 0.45$ ); IR 2940, 2885,



2831, 1469, 1378, 1119, 1064  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.37 (3H, s), 1.58 (1H, dddd,  $J = 13.7, 10.3, 6.8, 3.5$  Hz), 2.04 (1H, dddd,  $J = 13.5, 10.8, 4.8, 2.7$  Hz), 3.25 (1H, d,  $J = 9.2$  Hz), 3.43 (1H, dd,  $J = 3.8, 2.1$  Hz), 3.48 (3H, s), 3.51 (3H, s), 3.58 (3H, s), 3.74 (1H, dd,  $J = 11.2, 6.7, 2.7$  Hz), 3.87 (1H, dd,  $J = 9.2, 3.8$  Hz), 3.90 (1H, ddd,  $J = 11.0, 11.0, 4.7$  Hz), 4.36 (1H, ddd,  $J = 10.8, 3.6, 1.9$  Hz);  $^{13}\text{C}$  NMR 23.0 ( $\text{CH}_3$ ), 25.7 ( $\text{CH}_2$ ), 56.5 ( $\text{CH}_2$ ), 57.9 ( $\text{CH}_3$ ), 58.1 ( $\text{CH}_3$ ), 61.4 ( $\text{CH}_3$ ), 66.9 (CH), 78.7 (CH), 80.1 (CH), 82.7 (CH), 99.2 (C); MS (EI)  $m/z$  (rel intensity) 232 ( $\text{M}^+$ , <1), 217 (<1), 201 (2); HRMS calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$  232.1310625, found 232.133419. Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$ : C, 56.88; H, 8.68. Found: C, 56.87; H, 8.58.

Compound **10**: colorless oil;  $[\alpha]_{\text{D}} -8.4$  ( $c = 0.55$ ); IR 2934, 2827, 1446, 1103, 1050  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.29 (3H, d,  $J = 6.7$  Hz), 1.89 (1H, m), 2.35 (1H, m), 3.07 (1H, dd,  $J = 2.4, 6.2$  Hz), 3.26 (3H, s), 3.45 (3H, m), 3.52 (3H, s), 3.61 (1H, d,  $J = 2.4$  Hz), 3.66 (1H, dq,  $J = 6.2, 6.7$  Hz), 3.82 (1H, ddd,  $J = 6.4, 8.8, 8.8$  Hz), 4.11 (1H, ddd,  $J = 5.5, 8.8, 8.8$  Hz), 4.21 (1H, dd,  $J = 1.7, 6.9$  Hz);  $^{13}\text{C}$  NMR 18.6 ( $\text{CH}_3$ ), 31.4 ( $\text{CH}_2$ ), 48.5 ( $\text{CH}_3$ ), 57.9 ( $\text{CH}_3$ ), 58.1 ( $\text{CH}_3$ ), 66.4 ( $\text{CH}_2$ ), 68.7 (CH), 76.7 ( $2 \times \text{CH}$ ); MS (EI)  $m/z$  (rel intensity) 232 ( $\text{M}^+$ , 16), 217 (1), 201 (4), 185 (2), 169 (2); HRMS calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$  232.1310625, found 232.128292. Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_5$ : C, 56.88; H, 8.68. Found: C, 57.08; H, 8.32.

**3,4,5-Tri-*O*-acetyl-2,6-anhydro-1,7-dideoxy-L-glycero-L-manno-octitol (11)**. A solution of 3,4,5-tri-*O*-acetyl-2,6-anhydro-1,7,8,9-tetradecoxy-L-glycero-L-manno-non-8-enitol<sup>4</sup> (500 mg, 1.591 mmol) in dry  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (30 mL, 1:1) was ozonized as described for compound **1** and the ozonide reduced with  $\text{NaBH}_4$  (361 mg, 9.546 mmol). Column chromatography (hexanes-EtOAc, 1:1) afforded compound **11** (361 mg, 1.13 mmol, 71%) as a colorless oil:  $[\alpha]_{\text{D}} 0.6$  ( $c = 0.36$ ); IR 3479, 2940, 2889, 1746, 1372, 1228, 1048  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.21 (3H, d,  $J = 6.3$  Hz), 1.77 (1H, m), 1.98 (3H, s), 2.00 (3H, m), 2.04 (3H, s), 2.08 (3H, s), 2.37 (1H, br d), 3.69–3.80 (3H, m), 4.08 (1H, ddd,  $J = 3.2, 3.2, 10.0$  Hz), 4.99 (1H, dd,  $J = 8.5, 8.5$  Hz), 5.14–5.17 (2H, m);  $^{13}\text{C}$  NMR 17.4 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ), 20.8 ( $\text{CH}_3$ ), 31.1 ( $\text{CH}_2$ ), 59.4 ( $\text{CH}_2$ ), 68.4 (CH), 69 (CH), 70.9 (CH), 71.4 (CH), 72.6 (CH), 169.8 (C), 170 (C), 170.2

(C); MS (EI)  $m/z$  (rel intensity) 319 ( $M^+ + H$ , 1), 273 (2), 258 (1), 198 (32), 183 (48); HRMS calcd for  $C_{14}H_{23}O_8$  319.1392786, found 319.147026. Anal. Calcd for  $C_{14}H_{22}O_8$ : C, 52.82; H, 6.97. Found: C, 52.56; H, 7.27.

**3,4,5-Tri-*O*-acetyl-2,8-anhydro-1,7-dideoxy- $\beta$ -L-*altro*-oct-2-ulopyranose (12).** A solution of compound **11** (52 mg, 0.163 mmol) in dry  $CH_2Cl_2$  (6 mL) containing DIB (67 mg, 0.212 mmol) and iodine (41 mg, 0.163 mmol) was irradiated for 9 h as described for compound **3**. Chromatotron chromatography (hexanes–EtOAc, 70:30) afforded the anhydrosugar **12** (30 mg, 0.095 mmol, 58%) as a colorless oil:  $[\alpha]_D +65$  ( $c = 0.36$ ); IR 2972, 2747, 1372, 1226, 1059  $cm^{-1}$ ;  $^1H$  NMR 1.31 (3H, s), 1.87 (1H, m), 1.98 (3H, s), 2.09 (3H, s), 2.11 (1H, m), 2.14 (3H, s), 3.83–3.94 (2H, m), 4.25 (1H, ddd,  $J = 2.2, 2.2, 10.8$  Hz), 5.21 (1H, d,  $J = 9.9$  Hz), 5.23 (1H, dd,  $J = 1.9, 3.9$  Hz), 5.63 (1H, dd,  $J = 3.9, 9.9$  Hz);  $^{13}C$  NMR 20.6 ( $CH_3$ ), 20.8 ( $CH_3$ ), 20.9 ( $CH_3$ ), 22.9 ( $CH_3$ ), 26 ( $CH_2$ ), 56.8 ( $CH_2$ ), 67.4 (CH), 69.4 (CH), 71.7 (CH), 72.2 (CH), 98.7 (C), 170.1 (C), 170.2 (C), 170.5 (C); MS (EI)  $m/z$  (rel intensity) 316 ( $M^+$ , 7), 273 (1), 257 (10), 197 (7), 155 (25); HRMS calcd for  $C_{14}H_{20}O_8$  316.1158048, found 316.118927. Anal. Calcd for  $C_{14}H_{20}O_8$ : C, 53.16; H, 6.37. Found: C, 53.23; H, 6.10.

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