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Chain Extension of Aldonolactones by Samarium Iodide Mediated Dreiding–Schmidt Reactions and Samarium Assisted Imamoto Reactions

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Abstract: Unprecedented SmI_2 mediated Dreiding–Schmidt reactions were used for chain extension reactions of aldonolactones with alkyl 2-bromomethyl acrylates or 2-bromomethyl-acrylonitrile, respectively. The reaction of aldonolactones with diiodomethane in the presence of samarium powder resulted in the formation of polyhydroxyalkyl substituted cyclopropanols.

INTRODUCTION

The main stream of carbohydrate chemistry is devoted either to the use of sugars for chiral pool [2] syntheses of enantiomerically pure natural products [3] or analogues thereof, or to the selective preparation of oligosaccharides of biological interest,[4] or to the use of carbohydrates as chiral auxiliaries.[5] The efficient construction of α- or β-configurated *O*-, *C*-, or *N*-glycosides is the central problem for all of these three fields and thus a variety of methods are now available for carbon-carbon bond formation at the anomeric center.[6]

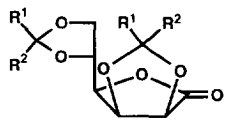
Ulosonic acids are important carbohydrates as constituents of cellular and bacterial membranes and they are implicated in many biological functions.[7] As a part of our studies on the synthetic utility of aldonolactones for the efficient construction of ulosonic acids we became interested in the synthesis of carbohydrate derived α-methylene-γ-butyrolactones and their corresponding synthetic precursors, *i.e.* 4-hydroxy-2-methylidene-butanoates, as potential candidates for drug/tumor targeting studies.

Numerous natural products containing α-methylene-γ-butyrolactone moieties have been discovered during the past decade.[8] Many of them show quite promising antibacterial, phytotoxic or antineoplastic activities and thus quite a number of different approaches have been devised for their synthesis, among them cyclization reactions of 4-hydroxy-2-methylidene-alkan(or -en)-oates, [9, 10] carbonylations [11] as well as methylenations of suitable precursors,[12] Baeyer-Villiger oxidations [13] of 2-methylidene-cyclobutanones and metal-assisted reactions of carbonyl compounds.[14]

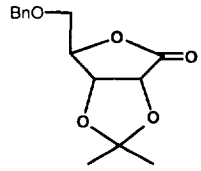
Despite first promising reports on the successful action of carbohydrate derived α-methylene-γ-butyrolactones as successful inhibitors of sulfhydryl enzymes[15] their number remained small over the years up to now due to the fact that a majority of the synthetic approaches on the whole are restricted in their application[16] and only a few seldom can be used for synthetic transformations of carbohydrate derived compounds. This finding is either due to functional group incompatibility of the methods or to tedious synthetic schemes for the preparation of the respecatble starting materials.

RESULTS AND DISCUSSION

Suitable precursors of α-methylene-γ-butyrolactones spiro-anellated to the anomeric center of carbohydrates have previously been accessed either by the fluoride anion catalyzed reaction of alkyl 2-(trimethylsilylmethyl)-acrylates with aldonolactones or by zinc mediated *Dreiding-Schmidt* reactions[17] starting from alkyl 2-bromomethyl acrylates.[18] As a part of our studies on the synthetic utility of samarium diiodide for chemoselective transformations,[19] we report on an easy access to chain elongated compounds *via* an unprecedented SmI_2-mediated *Dreiding-Schmidt* reactions of aldonolactones and of carbohydrate derived cyclopropanols by a Sm assisted *Imamoto* reaction.[20]



1 $R^1 = R^2 =$ Me
7 $R^1, R^2 = -(CH_2)_5$



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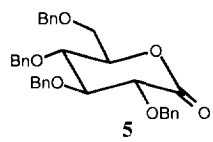

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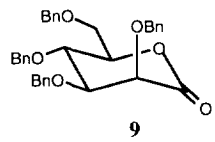

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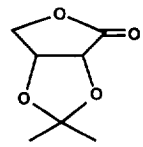

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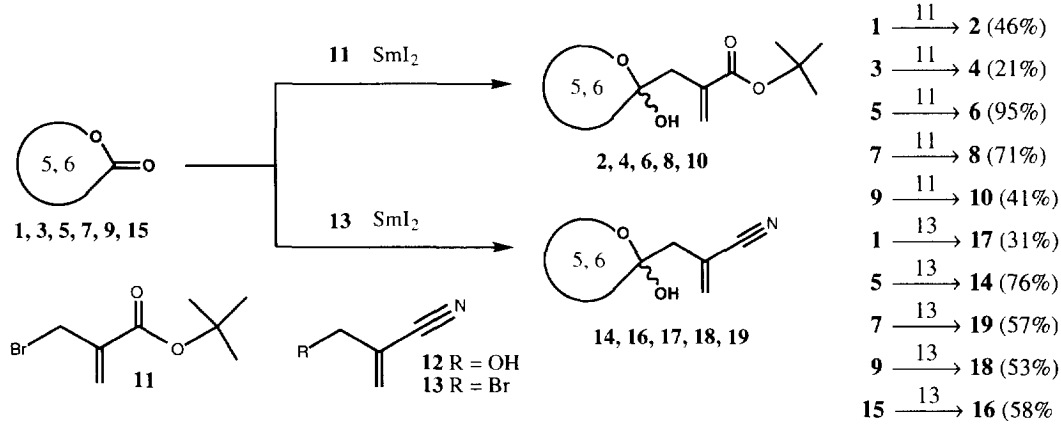


Thus, reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**5**)[21] with *tert*-butyl 2-bromomethyl-acrylate (**11**) in the presence of SmI_2 gave 95% of the chain elongation product **6**. In an analogous manner from the D-*manno*-configurated furanoid hexonolactone [21, 22] **7** the product **8** was obtained. Somewhat lower yields were obtained for 2,3;5,6-di-*O*-isopropylidene-D-mannono-1,4-lactone (**1**),[22] the D-ribono-1,4-lactone derivative **3**,[23] and the pyranoid D-mannono-lactone **9**.[24]

The chain elongated products **2**, **4**, **6**, **8** and **10** are characterized in their respective ^1H NMR spectra by a typical AB pattern for $H_{A,B}$-C(3) between δ H_A-C(3) = 2.39–2.81 and δ H_B-C(3) = 2.88–2.94 with $^3J_{A,B}$ = 14.0–14.2 Hz; the signals for the olefinic protons are found between δ = 5.52–5.78 and δ = 6.14–6.22 ppm, respectively. In the ^{13}C NMR spectra the olefinic carbon C(2) is found at δ ≈ 137 ppm whereas the signal for C(2') was detected at δ ≈ 128–129 ppm.

In analogy to the SmI_2 mediated *Reformatsky* reaction[25] it seems most likely that the reaction proceeds *via* a first single electron transfer to the 2-bromomethyl-acrylate to afford the corresponding radical that is then reduced to an organosamarium species after a second electron transfer. A kinetically controlled attack of

the organosamarium species onto the sterically hindered *re*-face of the lactone carbonyl group results in the intermediary formation of β-configurated products [26] that undergo subsequent anomerization leading to the thermodynamically more stable α-anomers.[27, 28]

This method offers the advantage of working under very mild conditions both avoiding high/low temperatures, long reaction times and the use of difficult to handle reagents.

As previously shown nitriles[29] can be well employed in chain elongation/branching reactions instead of the corresponding esters although one must expect somewhat lower yields [30] as exemplified for the reaction of **5** with **13** resulting in the formation of **14**; similarly, the furanoid erythrono-lactone derivative [31] **15** gave only 58% of **16**. These products **14, 16–18** are characterized in their respective ^{1}H NMR spectra by an AB system for $H_{A,B}$-C(3) showing $^2J_{A,B} \approx 14$ Hz. In the IR spectra the signals at ν = 2224-2235 cm^{-1} are typically for the nitrile moieties.

It is known [25] that the SmI_2 mediated reaction of *tert*-butyl 2-bromopropionate with aldonolactones affords the corresponding chain extended lactols containing a propionate side chain with fair to good stereochemical control (de = 50-80%). Interestingly enough, the SmI_2 mediated reactions of 2-bromo-γ-butyrolactone (**20**) with each of the aldonolactones proceeded with high stereoselectivity and only one of the possible four stereomers (including the anomers) was found. As exemplified for the reaction of **5** with the samarium enolate of **20** the formation of **21** as a single stereomer can be explained by an attack of the *si*-face of the samarium enolate onto the *re*-face of the lactone carbonyl group allowing an approach with only miror steric interactions. Following this pathway starting with a *si-re* attack leading *via* a six-membered chair-like transition state followed by a samario[3.3]sigmatropic rearrangement to a β-configurated primary product which undergoes rapid anomerization affording finally **21**.

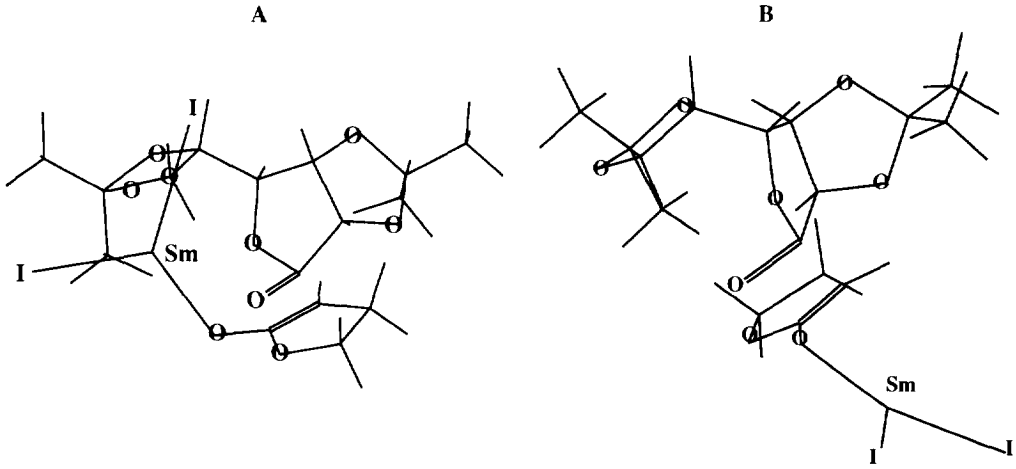
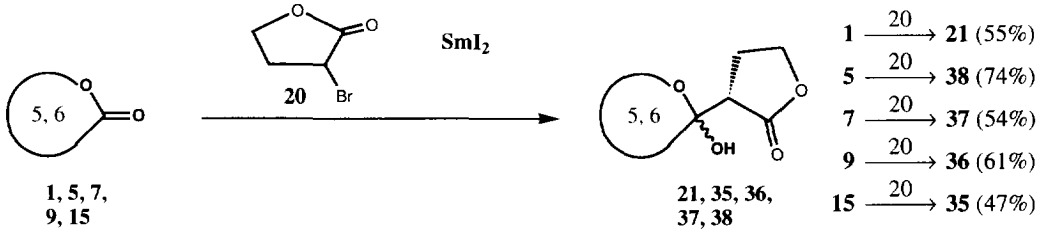


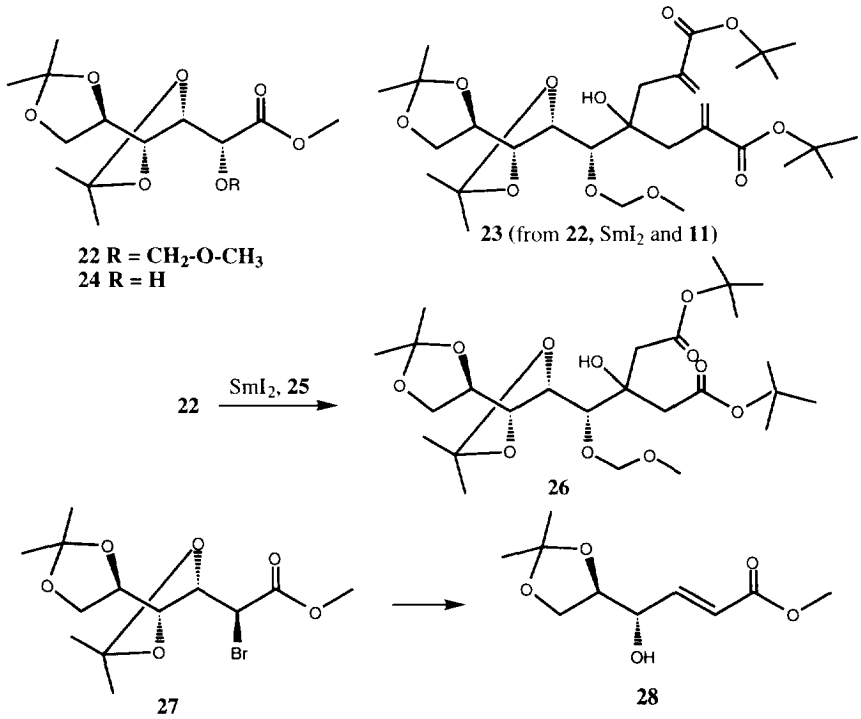
Fig. 1: Simulation [software CAChe 3.8; individual conformations optimized by AM1 calculations (after having performed a systematic conformational search by application of a MM2 force field)] of the approach of the organosamarium species from **20** (neglecting THF molecules as possible ligands to the samarium core) onto the *re*-face of the lactone carbonyl group of **1**. **A**: disfavoured *re-re* approach; B: favoured *si-re* approach.

No selfcondensation of the organometallic species [32] was observed in these reactions, as well as always a 1:1 reaction between lactone and the bromoesters took place.[33] The same strict 1:1 stoichiometry has previously been encountered for the samarium *Reformatsky* reaction [25] with simple 2-bromo-esters.



The reaction of the methyl gluconate derivate[34, 35] **22** with **11**, however, gave 15% of the bis-addition product **23**[36] but no product of a mono-addition reaction was found. The same observation was made for the reaction of **22** with *tert*-butyl bromo acetate (**25**); from this reaction **26** was obtained in 20% yield.

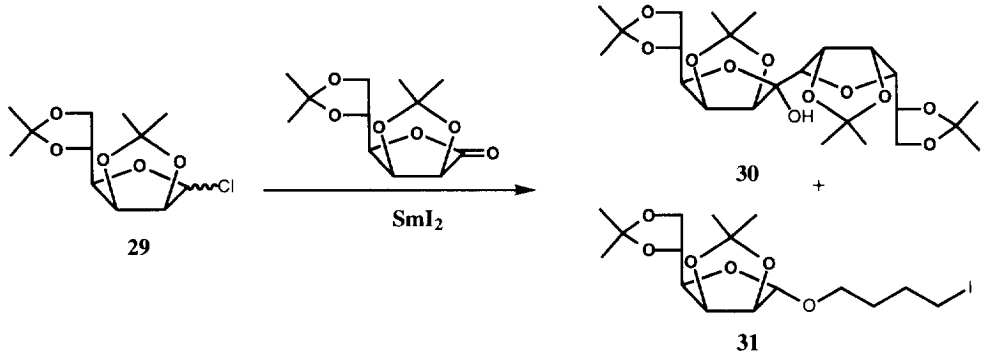
Compound **26** is characterized in its ^{1}H NMR spectrum by the presence of two signals for the *tert*-butyl group (at δ = 1.44 and 1.45 ppm) as well as 2 AB systems for $H_{A,B}$-C(2) and $H_{A,B}$-C(2'). The signal for HO-C(3) is found in the ^{1}H NMR spectrum at δ = 4.84 ppm and in the corresponding IR spectrum at ν = 3435 cm^{-1}. Similarly, for **23** the AB systems for $H_{A,B}$-C(3) and $H_{A,B}$-C(3') are found at d = 2.56, 2.59, 2.72 and 2.81 ppm, respectively.



The reaction of the methyl 2-bromo-2-deoxy-D-mannonate derivative [37] **27** with the lactone **1** in the presence of SmI_2, however, did not result in any reaction between these two carbohydrate reactants at all but instead, a *Boord*-type alkoxy-halo-elimination reaction took place leading finally to **28**. From mechanistic considerations an (*E*) configuration for the double bond in **28** is expected. Inspection of the ^{1}H NMR spectra

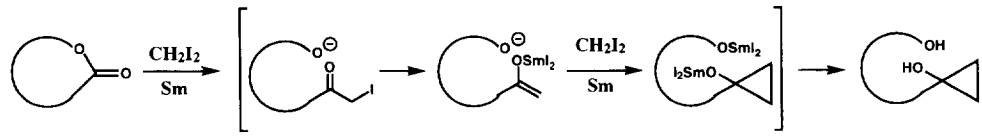
revealed the presence of a coupling constant $^3J_{H\text{-}C(2),H\text{-}C(3)}$ = 15.7 Hz as well as a chemical shift $\delta_{H\text{-}C(3)}$ = 6.93 ppm; both data are quite confirmative for the expected (*E*) configuration of the double bond.

A dimerization reaction, however, took place upon the SmI_2 mediated reaction between the manno-furanosyl chloride[38] **29** with the lactone **1** in the presence of $FeCl_3$ or more preferentially of hexamethyl phosphoric triamide and 21.5% of the dimer **30** could be isolated from the reaction mixture. As a byproduct from the cleavage of the solvent THF the 4-iodo-butyl glycoside **31** was obtained in 8% yield.

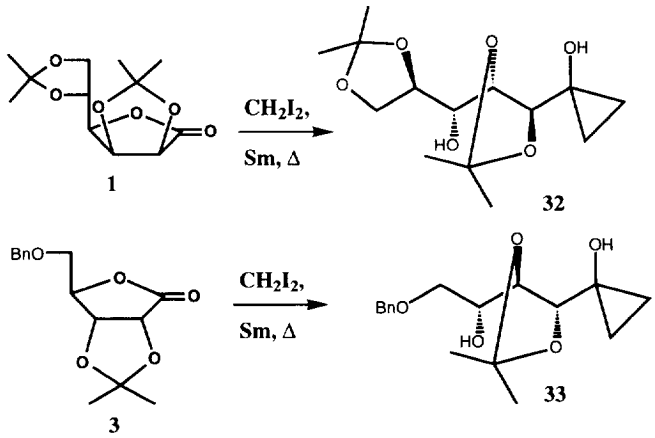


29 31

Finally, the reaction of aldonolactones with diiodomethane in the presence of samarium powder (*Imamoto* reaction)[20] was investigated. We considered from the results [20] previously obtained for simple esters that cyclopropanols might be synthesized from aldonolactones *via* a *tandem* one-carbon homologation.



Indeed, from the reaction of **1** the carbohydrate derived cyclopropanol **32** was obtained in 24% isolated yield; **3**, however, gave only a 19% yield of **33**.



1 32

3 33

Compounds **32** and **33** are characterized in their respective ^1H NMR spectra by the high field shifts for the protons of the cyclopropyl moiety (δ = 0.56–0.69 / 0.91–1.02 and 0.34–0.58 / 0.63–0.96 ppm, respectively).

EXPERIMENTAL

Melting points are uncorrected (*Reichert* hot stage microscope), optical rotations were obtained using a Perkin-Elmer 243B polarimeter (1 cm micro-cell), NMR spectra (internal Me_4Si) were recorded using either a Bruker AM250 or a Varian XL300 instrument (δ given in ppm, J in Hz, internal Me_4Si, C' and H' correspond to the atoms of the heterocycle or its synthetic precursor), IR spectra (film or KBr pellet) on a Perkin-Elmer 298 instrument or on a Perkin-Elmer 1605 FT-IR, MS spectra were taken either on a MAT311A or a Varian-112S instrument; for elemental analysis a Foss-Heraeus Vario EL instrument was used. TLC was performed on silica gel (Merck 5554, detection by dipping in a solution containing 10% sulfuric acid (400 *ml*), ammonium molybdate (20 g) and cerium$^{(IV)}$ sulfate (20 mg) followed by heating to 150°C. The tetrahydrofuran used throughout for all reactions was freshly distilled from sodium/benzophenone; all reactions were performed under dry argon.

General procedure for the reaction of aldonolactones with *tert*-butyl 2-bromomethylacrylate (11), 2-bromomethyl-acrylonitrile (13) or 2-bromo-γ-butyro-lactone (20) in the presence of SmI_2. – To a solution of SmI_2 (Aldrich Co, used as received, 0.1 M in THF, 20-60 *ml*, 2-6 mmol) the lactone (0.5 bis 1.5 mmol) was added at 20 °C; the mixture was well stirred until complete dissolution of the lactone was observed and then a solution of the bromo-alkanoate (in 10 *ml* THF) was slowly added via a syringe. When the color of the reaction mixture had changed from deep-blue to yellow, ethyl acetate (100 *ml*) was added and the reaction mixture was poured into a cold aqueous solution of $NaHCO_3$ (25-50 *ml*), the organic layer was separated, the aqueous phase was extracted twice with ethyl acetate (20 *ml* each) and the combined organic phases were washed in succession with aqueous solutions of $Na_2S_2O_3$ (10%, 25-50 *ml*), water (20 *ml*) and brine (20 *ml*). After drying ($MgSO_4$) the solvents were evaporated under diminished pressure and the residue was subjected to column chromatography (silica gel).

***tert*-Butyl 2,3-dideoxy-5,6;8,9-di-O-isopropylidene-2-methylidene-α-D-*manno*-4,7-furanoso-non-4-ulosonate (2).** – From **1** (0.26 g, 1.0 mmol), **11** (0.33 g, 1.5 mmol) and SmI_2 (4 mmol) **2** (0.19 g, 46 %) was obtained after chromatography (silica gel, hexane/ethyl acetate 10:1); mp 68-70 °C, $[\alpha]_D^{25}$ = + 9.5° (*c* =1.1, $CHCl_3$), R_F 0.38 (hexane/ethyl acetate 3:1), [Lit.:[39] mp 62 - 64 °C, $[\alpha]_D^{25}$ = + 7.5° (*c* = 1.6, $CHCl_3$)]; IR (KBr): ν 3440*m*, 2985*m*, 2950*m*, 2893*w*, 1711*s*, 1653*w*,1380*m*, 1368*s*, 1307*m*, 1269*m*, 1064*s*, 1041*s*, 859*m*, 851*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32, 1.37, 1.43, 1.49 (each *s*, 3 H, CH_3 (isopropylidene)), 1.50 (*s*, 9 H, CH_3 (*tert*-butyl)), 2.73 (*d*, *J* = 14.2, 1 H, H_A-C(3)), 2.91 (*d*, *J* = 14.2, 1 H, H_B-C(3)); 3.97 (*dd*, *J* = 4.7, 8.6, 2 H, H_A-C(9)), 4.03-4.08 (*m*, 2 H, H_B-C(9) and H-C(7)), 4.31-4.36 (*m*, 1 H, H-C(8)), 4.43 (*d*, *J* = 5.8, 1 H, H-C(5)), 4.72 (*s*, 1 H, OH), 4.83 (*dd*, *J* = 4.0, 5.8, 1 H, H-C(6)), 5.76 (*s*, 1 H, H_A-C(2')), 6.19 (*d*, *J* = 1.4, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 24.70, 25.42, 56.05, 26.88 (each *q*, CH_3 (isopropylidene)), 28.00 (*q*, CH_3(*tert*-butyl)), 36.57 (*t*, C(3)), 66.91 (*t*, C(9)), 73.32, 78.76, 80.36, 85.10 (each *d*, C(5, 6, 7, 8)), 81.78 (*s*, C_q(*tert*-butyl)), 105.12 (*s*, C(4)), 109.06, 112.63 (each *s*, C_q (isopropylidene)), 128.99 (*t*, C(2')), 136.45 (*s*, C(2)), 168.87 (*s*, C(1)); CI-MS (isobutane): 383 ([M-H_2O+1]; Anal. calcd. for $C_{20}H_{32}O_8$ (400.47): C, 59.99; H, 8.05; found: C, 60.20; H, 7.91.

***tert*-Butyl 8-O-benzyl-2,3-dideoxy-5,6-*O*-isopropylidene-2-methylidene-β-D-*ribo*-4,7-furanoso-oct-4-ulosonate (4).** – From **3** (0.28 g, 1.0 mmol), **11** (0.33 g, 1.5 mmol) and SmI_2 (4 mmol) **4** (0.90 g, 21 %) was obtained after chromatography (hexane/ethyl acetate 20:1) as a colorless oil; $[\alpha]_D^{25}$ = - 12.8° (*c* = 0.5, $CHCl_3$), R_F 0.60 (hexane/ethyl acetate 3:1); IR (film): ν 3398*bm*, 2979*m*, 2937*m*, 2869*m*, 1778*w*, 1712*s*, 1686*s*, 1629*m*, 1454*m*, 1392*m*, 1370*s*, 1353*m*, 1320*m*, 1271*m*, 1253*m*, 1211*s*, 1154*s*, 1074*s*, 1029*s*, 874*m*, 851*m*,

823*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32, 1.48 (each *s*, 3 H, CH_3 (isopropylidene)), 1.49 (*s*, 9 H, CH_3 (*tert*-butyl)), 2.81(*d*, *J* = 14.2, 1 H, H_A-C(3)), 2.93 (*d*, *J* = 14.2, 1 H, H_B-C(3)), 3.56-3.61 (*m*, 2 H, H-C(8)), 4.21-4.28 (*m*, 1 H, H-C(7)), 4.43 (*d*, *J* = 5.9, 1 H, H-C(5)), 4.53, 4.59 (each *d*, *J* = 12.0, 1 H, AB-system CH_2 (benzyl)), 4.77 (*dd*, *J* = 1.5, 5.9, 1 H, H-C(6)), 5.78 (*d*, *J* = 0.9, 1 H, H_A-C(2')), 6.18 (*d*, *J* = 1.9, 1 H, H_B-C(2')), 7.27-7.37 (*m*, 5 H, $CH_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.40, 26.70 (each *q*, CH_3 (isopropylidene)), 27.97 (*q*, CH_3(*tert*-butyl)), 36.70 (*t*, C(3)), 71.42 (*t*, C(8)), 73.38 (*t*, CH_2 (benzyl)), 81.08 (*s*, C_q(*tert*-butyl)), 82.72, 84.35, 85.99 (each *d*, C(5, 6, 7)), 106.98 (*s*, C(4)), 112.35 (*s*, C_q (isopropylidene)), 127.66-128.49 (each *d*, $CH_{arom.}$), 127.75 (*t*, C(2')), 136.82 (*s*, C(2)), 137.32 (*s*, $C_{q\ arom.}$), 168.15 (*s*, C(1)); MS (ei, 80 eV, 84 °C): 405(0.3), 345(6.8), 305(1.7), 288(2.6), 279(4.0), 243(5.0), 225(3.6), 215(1.8), 185(8.4), 158(3.2), 131(10.0), 127(6.0), 113(11.2), 92(13.5), 91(100.0); Anal. calcd. for $C_{23}H_{32}O_7$ (420.50): C, 65.70; H, 7.67; found: C, 65.73; H, 7.43.

***tert*-Butyl 5,6,7,9-tetra-*O*-benzyl-2,3-dideoxy-2-methylidene-α-D-*gluco*-4,8-pyranoso-non-4-ulosonate (6).** – From **5** (0.27 g, 0.5 mmol), **11** (0.16 g, 0.75 mmol) and SmI_2 (2 mmol) **6** (0.65 g, 95 %) was obatined after chromatography (hexane/ethyl acetate 10:1) as a colorless oil; $[\alpha]_D^{25}$ = + 7.0° (*c* = 1.2, $CHCl_3$), R_F 0.30 (hexane/ethyl acetate 3:1); IR (film): ν 3364*bm*, 3063*m*, 3030*m*, 2977*m*, 2929*m*, 2866*m*, 1709*s*, 1682*s*, 1627*m*, 1497*m*, 1454*s*, 1393*m*, 1367*s*, 1150*s*, 1094*s*, 1028*s*, 736*s*, 697*s*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.45 (*s*, 9 H, CH_3 (*tert*-butyl)), 2.39 (*d*, *J* = 14.0, 1 H, H_A-C(3)), 2.88 (*d*, *J* = 14.0, 1 H, H_B-C(3)), 3.35 (*d*, *J* = 9.2, 1 H), 3.56-3.76 (*m*, 3H), 3.93-3.98 (*m*, 1 H), 4.08 (*t*, *J* = 9.2, 1 H), 4.49, 4.56 (each *d*, *J* = 12.5, 1 H, AB-system CH_2 (benzyl)), 4.61 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 4.69 (*d*, *J* = 11.3, 1 H, part of AB system CH_2 (benzyl)), 4.84 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 4.90 (*s*, 2 H, CH_2 (benzyl)), 4.96 (*d*, *J* = 11.3, 1 H, part of AB system CH_2 (benzyl)), 5.06 (*s*, 1 H, OH), 5.59 (*s*, 1 H, H_A-C(2')), 6.14 (*d*, *J* = 1.7, 1 H, H_B-C(2')); 7.19-7.33 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (63 MHz, $CDCl_3$): δ 27.98 (*q*, CH_3 (*tert*-butyl)), 41.30 (*t*, C(3)), 68.86 (*t*, C(9)), 71.45, 78.65, 83.38, 83.84 (each *d*, C(5, 6, 7, 8)), 73.28, 74.79, 75.14, 75.59 (each *t*, CH_2 (benzyl)), 81.69 (*s*, CH_3(*tert*-butyl)), 96.86 (s, C(4)), 127.45-128.42 (each *d*, $CH_{arom.}$), 128.60 (*t*, C(2')), 136.56 (*s*, C(2)), 138.27-138.82 (each *s*, $C_{q\ arom.}$), 168.54(*s*, C(1)); MS (ei, 80 eV, 230 °C): 515(0.5), 463(0.1), 422(0.3), 365(0.2), 295(0.2), 275(0.5), 253(1.8), 240(0.2), 181(4.3), 107(9.2), 91(100.0); HRMS calcd. for $C_{42}H_{48}O_8$: 680.335; found: 680.336; Anal. calcd. for $C_{42}H_{48}O_8$ (680.84): C, 74.09; H, 7.11; found: C, 73.70; H, 7.12.

***tert*-Butyl 5,6;7,8-di-*O*-cyclohexylidene-2,3-dideoxy-2-methylidene-α-D-*manno*-4,7-furanoso-non-4-ulosonate (8).** – From **7** (0.31 g, 1.0 mmol), **11** (0.33 g, 1.5 mmol) and SmI_2 (4 mmol) **8** (0.34 g, 71 %) was obtained after chromatography (hexane/ethyl acetate 10:1) as a colorless oil; $[\alpha]_D^{25}$ = + 11.7° (*c* = 1.2, $CHCl_3$), R_F 0.51 (hexane/ethyl acetate 3:1); IR (film): ν 3417*bm*, 2939*s*, 2860*s*, 1713*s*, 1698*s*, 1694*s*, 1478*m*, 1450*m*, 1393*m*, 1367*s*, 1350*m*, 1334*m*, 1251*m*, 1102*s*, 1038*s*, 948*s*, 848*m*, 820*m*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27-1.70 (*m*, 20 H, CH_2 (cyclohexyl)), 1.50 (*s*, 9 H, CH_3 (*tert*-butyl)), 2.76 (*d*, *J* = 14.2, 1 H, H_A-C(3)), 2.92 (*d*, *J* = 14.2, 1 H, H_B-C(3)), 3.96 (*dd*, *J* = 5.7, 8.4, 1 H, H_A-C(9)), 4.03 (*dd*, *J* = 6.2, 8.4, 1 H, H_B-C(9)), 4.10 (*dd*, *J* =3.8, 6.8, 1 H, H-C(7)), 4.35 (*t*, *J* = 6.2, 1 H, H-C(8)), 4.41 (*d*, *J* =5.8, 1 H, H-C(5)), 4.59 (*s*, 1H, OH), 4.80 (*dd*, *J* = 3.8, 5.8, 1 H, H-C(6)), 5.78 (*s*, 1 H, H_A-C(2')), 6.20 (*d*, *J* = 1.8, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, CDCl3): δ 23.86, 23.97, 24.07, 24.19, 25.21 (each *t*, CH_2(cyclohexyl)), 28.04 (*q*, CH_3 (*tert*-butyl)), 34.41, 35.03, 35.92, 36.34, 36.65 (each *t*, CH_2 (cyclohexyl) and C(3)), 66.32 (*t*, C(9)), 73.06, 79.04, 80.09, 84.71 (each *d*, C(5, 6, 7, 8)), 81.74 (*s*, C_q (*tert*-butyl)), 105.30 (*s*, C(4)), 109.39, 113.36 (each *s*, C_q(cyclohexyl)), 128.90 (*t*, C(2')), 136.62 (*s*, C(2)), 168.83 (*s*, C(1)); MS (ei, 80 eV, 125 °C): 481(4.8), 480(23.1), 437(4.6), 407(4.2), 339(4.6), 291(12.8), 283(8.6), 211(7.4), 196(27.0), 193(10.0), 153(16.6), 141(52.0), 113(20.1), 99(56.5), 81(70.4), 69(34.7), 57(100.0); HRMS calcd. for $C_{26}H_{40}O_8$: 480.272; found: 480.271; Anal. calcd. for $C_{26}H_{40}O_8$ (480.60): C, 64.98; H, 8.39; found: C, 64.54; H, 8.57.

***tert*-Butyl 5,6,7,9-tetra-*O*-benzyl-2,3-dideoxy-2-methylidene-α-D-*manno*-4,8-pyranoso-non-4-ulosonate (10).** – From **9** (0.27 g, 0.5 mmol), **11** (0.17 g, 0.75 mmol) and SmI_2 (2 mmol) **10** (0.14 g, 41 %) was obatined after chromatography (hexane/ethyl acetate 10:1) as a solid; unchanged **9** (0.12 g, 45 %) was recovered; mp 86-87 °C, $[\alpha]_D^{25}$ = -10.2° (*c* = 1.3, $CHCl_3$), R_F 0.65 (hexane/ethyl acetate 3:1); IR (KBr): ν 3327*s*, 3086*w*, 3060*w*, 3028*m*, 2978*m*, 2904*m*, 2877*m*, 2855*s*, 1688*s*, 1626*m*, 1497*m*, 1476*m*, 1455*s*, 1436*s*, 1399*s*, 1367*s*, 1353*s*, 1322*s*, 1248*m*, 1215*m*, 1086*s*, 1014*s*, 976*s*, 944*s*, 916*m*, 901*m*, 864*m*, 844*m*, 819*m*, 744*s*, 699*s*; ^1H NMR (250 MHz, $CDCl_3$): δ 1.48 (*s*, 9 H, CH_3 (*tert*-butyl), 2.68 (*d*, *J* = 14.0, 1 H, H_A-C(3)); 2.91 (*d*, *J* = 14.0, 1 H, H_B-C(3)), 3.66-3.80 (*m*, 3 H), 4.00-4.07 (*m*, 2 H), 4.19-4.22 (*m*, 1 H), 4.51 (*d*, *J* = 11.8, 1 H, part of AB system CH_2 (benzyl)), 4.58 (*d*, *J* = 11.0, 1 H, part of AB system CH_2 (benzyl)), 4.60 (*d*, *J* = 11.8, 1 H, part of AB system CH_2 (benzyl)), 4.67 (*d*, *J* = 12.2, 1 H, part of AB system CH_2 (benzyl)), 4.78 (*s*, 2 H, CH_2 (benzyl)), 4.86 (*d*, *J* = 11.0, 1 H, part of AB system CH_2 (benzyl)), 5.15 (*d*, *J* = 11.8, 1 H, part of AB system CH_2 (benzyl)), 5.24 (*s*, 1 H, OH), 5.52 (*s*, 1 H, H_A-C(2')); 6.14 (*d*, *J* = 1.6, 1 H, H_B-C(2')), 7.21-7.38 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.02 (*q*, CH_3 (*tert*-butyl)), 39.65 (*t*, C(3)), 69.60 (*t*, C(9)), 72.76, 73.36, 74.03, 74.91 (each *t*, CH_2 (benzyl)), 73.00, 75.33, 77.49, 82.08 (each *d*, C(5, 6, 7, 8)), 82.13 (*s*, C_q (*tert*-butyl)), 97.77 (*s*, C(4)), 127.26-128.45 (each *d*, $CH_{arom.}$), 129.27 (*t*, C(2')), 136.60 (*s*, C(2)), 138.80, 138.86, 139.01 (each *s*, $C_{q\ arom.}$), 169.38 (s, C(1)); MS (ei, 80 eV, 179 °C): 606(0.3), 605(0.1), 516(0.2), 515(0.4), 386(0.3), 380(0.2), 375(0.1), 319(0.1), 317(0.1), 303(0.7), 301(0.2), 290(0.45), 182(1.5), 181(7.5), 133(1.1), 92(9.14), 91(100.0); Anal. calcd. for $C_{42}H_{48}O_8$ (680.84): C, 74.09; H, 7.11; found: C, 73.78; H, 7.00.

***tert*-Butyl 2,3-dideoxy-5,6-*O*-isopropylidene-2-methylidene-β-D-*threo*-4,7-furanoso-hept-4-ulosonate (12).** – From **15** (0.16 g,1 mmol), **11** (0.33 g,1.5 mmol) and SmI_2 (4 mmol) **12** (0.20 g, 66 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a colorless solid; mp 38-40 °C, $[\alpha]_D^{25}$ = - 43.2° (*c* = 1.7, $CHCl_3$), R_F 0.44 (hexane/ethyl acetate 3:1); IR (KBr): ν 3378*m*, 2982*m*, 2943*m*, 2884*w*, 1678*s*, 1626*s*, 1460*m*, 1421*m*, 1399*m*, 1382*s*, 1371*s*, 1356*s*, 1319*s*, 1274*m*, 1244*m*, 1160*s*, 1024*s*, 969*s*, 882*s*, 860*s*, 842*m*, 820*m*; ^1H NMR (300 MHz, $CDCl_3$): δ 1.32, 1.49 (each *s*, 3 H, CH_3 (isopropylidene)), 1.50 (*s*, 9 H, CH_3 (*tert*-butyl)), 2.77 (*d*, *J* = 14.0, 1 H, H_A-C(3)), 2.94 (*d*, *J* = 14.0, 1 H, H_B-C(3)), 3.87 (*d*, *J* = 10.2, 1 H, H_A-C(7)), 4.00 (*dd*, *J* = 3.9, 10.2, 1 H, H_B-C(7)), 4.38 (*d*, *J* = 5.8, 1 H, H-C(5)), 4.86 (*dd*, *J* = 3.9, 5.8, 1 H, H-C(6)), 4.99 (s, 1 H, OH), 5.78 (s, 1H, H_A-C(2')), 6.22 (*d*, *J* = 1.8, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 25.21, 26.51 (each *q*, CH_3 (isopropylidene)), 28.01 (*q*, CH_3 (*tert*-butyl)), 36.90 (*t*, C(3)), 70.99 (*t*, C(7)), 80.80 (*d*, C(6)), 81.96 (*s*, C_q (*tert*-butyl)), 84.79 (d, C(5)), 105.72 (*s*, C(4)), 112.41 (*s*, C_q (isopropylidene)), 129.22 (*t*, C(2')), 136.65 (*s*, C(2)), 169.12 (*s*, C(1)); MS (ei, 80 eV, 45 °C): 286(0.4), 285(2.7), 244(1.6), 229(2.0), 227(8.5), 186(20.1), 185(30.1), 169(16.1), 159(21.7), 151(11.1), 131(32.5), 114(33.4), 113(51.4), 99(4.8), 86(8.8), 85(42.2), 74(20.2), 71(15.4), 59(96.7), 57(100.0); Anal. calcd. for $C_{15}H_{24}O_6$ (300.35): C, 59.98; H, 8.05; found: C, 60.08; H, 7.86.

2-Bromomethyl-acrylonitrile (13). – To a solution of diethyl cyanomethyl-phosphonate (20.0 g, 0.11 mol) in an aqueous solution of formaldehyde (35%, 38 *ml*, 0.44 mol) an aqueous solution of K_2CO_3 (saturated, 24 *ml*, 0.2 mol) was added (the temperature of the reaction mixture increased to 35–40°C) and then stirring was continued at 25°C for 1 h. An aqueous solution of NH_4Cl (saturated, 40 *ml*) was added. After extraction with diethyl ether (3 x 50 *ml*) the combined organic layers were dried ($MgSO_4$) and the solvent was removed under diminished pressure. Distillation of the residue afforded 2-hydroxymethyl-acrylonitrile (**12**) (4.90 g, 54 %) as a colorless liquid; [bp 104 -105 °C (20 mm); IR (film): ν 3433*s*, 2936*m*, 2882*m*, 2228*s*, 1918*w*, 1628*w*, 1457*m*, 1410*m*, 1221*m*, 1152*m*, 1071*s*, 1044*s*, 952*s*; ^1H NMR (250 MHz, $CDCl_3$): δ 2.16 (*s*, 1 H, OH), 4.30 (*t*, *J* = 1.6, 2 H, H-C(3)), 6.09 (*dd*, *J* = 12.1, 1.6, 2 H, H_A-C(2')), 6.06 (*dd*, *J* = 12.1, 1.6, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 62.40 (*t*, C(3)), 122.96 (*s*, C(1)), 130.53 (*s*, C(2)), 134.63 (*t*, C(4))]. To

a solution of **12** (4.0 g, 48 mmol) in dry diethyl ether (50 *ml*) at -10 °C PBr_3 (distilled prior to use, 6.5 g, 24 mmol) was slowly added (temperature increased to approx. 20°C) and stirring was continued for 3 h at room temperature. After cooling to -10°C water (27 *ml*) was slowly added and the reaction mixture was extracted with hexane (3 x 25 *ml*). The combined organic layers were washed with brine (2 x 10 *ml*), dried ($MgSO_4$) and the solvent was removed under diminished pressure. Distillation of the residue gave **13** (1.96 g, 28 %)[40,41] as a colorless liquid; bp 80-85 °C (20 mm); IR (film): ν 3114*w*, 3034*w*, 2991*w*, 2229*w*, 1909*w*, 1437*m*, 1399*m*, 1219*s*, 953*s*, 891*w*, 761*m*, 734*w*, 673*s*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.01 (*bs*, 2 H, H-C(3)), 6.03, 6.06 (AB system, J = 8.4, 2 H, H-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 29.36 (*t*, C(3)), 120.46 (*s*, C(1) and C(2)), 133.32 (*t*, C(2')); MS (ei, 80 eV, 30 °C): 148(10.0), 147(18.5), 146(11.0), 145(19.1), 132(1.2), 121(2.5), 119(3.2), 95(16.4), 93(18.0), 91(3.3), 79(2.9), 66(100.0).

5,6;7,9-Tetra-*O*-benzyl-2,3-dideoxy-2-methylidene-α-D-*gluco*-4,8-pyranoso-4-nonulonitrile (14). – From **5** (0.27 g, 0.5 mmol), **13** (0.11 g, 0.75 g) and SmI_2 (2 mmol) **14** (0.23 g, 76 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a colorless oil; $[\alpha]_D^{25}$ = + 22.2° (*c* = 0.9, $CHCl_3$), R_F 0.39 (hexane/ethyl acetate 3:1); IR (film): ν 3426*m*, 3088*w*, 3063*m*, 3030*m*, 2923*s*, 2867*s*, 2224*w*, 1497*s*, 1454*s*, 1401*m*, 1362*s*, 1209*m*, 1144*s*, 1088*s*, 1070*s*, 1028*s*, 1003*m*, 946*m*, 737*s*, 698*s*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (*d*, J = 13.9, 1 H, H_A-C(3), 2.55 (*d*, J = 13.9, 1 H, H_B-C(3)), 3.44 (*d*, J = 9.1, 1 H, H-C(5)), 3.66 (*dd*, J = 3.0, 4.9, 1 H, H_A-C(9)), 3.72 (*dd*, J = 3.0, 10.0, 1 H, H_B-C(9)), 3.78 (*dd*, J = 3.8, 11.0, 1 H, H-C(7)), 3.98 (*m*, 2 H, H-C(6) and H-C(8)), 4.57 (*d*, J = 12.4, 1 H, part of AB system CH_2 (benzyl)), 4.63 (*d*, J = 12.4, 1 H, part of AB system CH_2 (benzyl)), 4.69 (*d*, J = 11.3, 1 H, part of AB system CH_2 (benzyl)), 4.82 (*d*, J = 11.0, 1 H, part of AB system CH_2 (benzyl)), 4.84 (*d*, J = 11.0, 1 H, part of AB system CH_2 (benzyl)), 4.95 (*d*, J = 11.0, 1 H, part of AB system CH_2 (benzyl)), 4.97 (*d*, J = 11.3, 1 H, part of AB system CH_2 (benzyl)), 5.71 (*s*, 1 H, H_A-C(2')), 5.98 (*s*, 1 H, H_B-C(2')), 7.17-7.41 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.68 (*t*, C(3)), 66.53 (*t*, C(9)), 73.52, 74.85, 75.11, 75.45 (each *t*, CH_2 (benzyl)), 71.98, 78.01, 80.70, 83.58 (each *d*, C(5, 6, 7, 8)), 96.92(*s*, C(4)), 116.95 (s, C(2)), 118.98 (*s*, C(1)), 127.32-128.37 (each *t*, $CH_{arom.}$), 135.13 (*t*, C(2')), 137.30, 137.86, 138.14, 138.17 (each *s*, $C_{q\ arom.}$); MS (ei, 80 eV, 179 °C): 605(0.1), 514(0.8), 497(0.2), 425(0.2), 408(0.5), 347(0.9), 253(3.0), 182(1.0), 181(5.6), 108(4.7), 92(9.8), 91(100.0); HRMS calcd. for $C_{38}H_{40}NO_6$: 66.285; found: 66.284.

2,3-Dideoxy-5,6-*O*-isopropylidene-2-methylidene-α-D-*threo*-4,7-furanoso-4-heptulonitrile (16). – From **15** (0.24 g, 1.5 mmol), **13** (0.33 g, 2.3 mmol) and SmI_2 (6 mmol) **16** (0.19 g, 58 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a solid; mp 46-48 °C, $[\alpha]_D^{25}$ = - 42.9° (*c* = 1.6, $CHCl_3$), R_F 0.22 (hexane/ethyl acetate 3:1), R_F 0.73 (hexane/ethyl acetate 1:1); IR (KBr): ν 3418*m*, 2979*m*, 2935*m*, 2870*w*, 2235*m*, 1456*m*, 1402*m*, 1373*s*, 1359*m*, 1323*s*, 1274*s*, 1195*s*, 1095*s*, 1037*s*, 999*s*, 964*s*, 938*m*, 904*m*, 882*s*, 860*s*, 823*s*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32, 1.49 (each *s*, CH_3 (isopropylidene)), 2.53 (*s*, 1 H, OH), 2.73 (*d*, J = 14.5, 1 H, H_A-C(3)), 2.83 (*d*, J = 14.5, 1 H, H_B-C(3)), 3.96-4.07 (*m*, 2 H, H-C(7)), 4.46 (*d*, J = 5.9, 1 H, H-C(5)), 4.83-4.90 (*m*, 1 H, H-C(6)), 5.98 (*d*, J = 0.9, 1 H, H_A-C(2')), 6.08 (*s*, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 24.90, 26.30 (each *q*, CH_3 (isopropylidene)), 39.86 (*t*, C(3)), 71.62, 80.58, 84.46 (each *d*, C(5, 6, 7)), 105.88 (*s*, C(4)), 112.79 (*s*, C_q (isopropylidene)), 117.38 (*s*, C(2)), 119.28 (*s*, C(1)), 135.52 (*t*, C(2')); MS (ei, 80 eV, 40 °C): 211(1.6), 210(14.6), 167(4.8), 159(3.8), 150(12.0), 114(6.7), 112(12.4), 99(6.8), 94(9.6), 85(18.6), 73(5.5), 71(8.4), 66(12.8), 59(100.0); HRMS calcd. for $C_{11}H_{16}NO_4$: 226.108; found: 226.107; Anal. calcd. for $C_{11}H_{15}NO_4$ (225.24): C, 58.66; H, 6.71; N, 6.22; found: C, 58.42; H, 6.64; N, 6.11.

2,3-Dideoxy-5,6;7,8-di-*O*-isopropylidene-2-methylidene-α-D-*manno*-4,7-furanoso-3-nonulonitrile (17). – From **1** (0.26 g, 1 mmol), **13** (0.22 g, 1.5 mmol) and SmI_2 (6.0 mmol) **17** (0.10 g, 31 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a white solid; unchanged **1** (0.08 g, 31 %) was recovered;

mp 120-122 °C, $[\alpha]_D^{25}$ = -8.8° (*c* = 0.8, $CHCl_3$), R_F 0.20 (hexane/ethyl acetate 3:1); IR (KBr): ν 3355*s*, 2989*m*, 2956*m*, 2946*m*, 2893*w*, 2226*w*, 1421*m*, 1405*m*, 1376*s*, 1323*m*, 1266*m*, 1204*s*, 1163*s*, 1112*m*, 1060*s*, 1011*m*, 973*m*, 863*s*, 848*s*; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.33, 1.38, 1.45, 1.49 (each *s*, 3 H, CH_3 (isopropylidene), 2.17 (*s*, 1 H, OH), 2.74 (*s*, 2 H, H-C(3)), 4.03 (*dd*, *J* = 4.2, 8.7, 1 H, H_A-C(9)), 4.08-4.13 (*m*, 2 H, H_B-C(9) and H-C(7)), 4.36-4.43 (*m*, 1 H, H-C(8)), 4.51 (*d*, *J* = 5.9, 1 H, H-C(5)), 4.86 (*dd*, *J* = 3.8, 5.9, 1 H, H-C(6)), 5.94 (*s*, 1 H, H_A-C(2')), 6.07 (*s*, 1 H, H_B-C(2')); ^{13}C NMR (63 MHz, $CDCl_3$): δ 24.45, 25.18, 25.89, 26.92 (each *q*, CH_3 (isopropylidene)), 39.98 (*t*, C(3)), 66.65 (*t*, C(9)), 73.08, 79.65, 80.19, 84.92 (each *d*, C(5, 6, 7, 8)), 105.07 (*s*, C(4)), 109.30, 113.08 (each *s*, C_q (isopropylidene)), 117.41(*s*, C(2)), 119.06 (*s*, C(1)), 135.46 (*t*, C(2')); MS (ei, 80 eV, 94 °C): 325(0.1), 311(12.6), 310(76.0), 267(2.2), 252(14.3), 192(6.3), 164(3.9), 150(6.0), 141(11.2), 101(100.0); HRMS calcd. for $C_{16}H_{24}NO_6$: 326.160; found: 326.161; Anal. calcd. for $C_{16}H_{23}NO_6$ (325.36): C, 59.06; H, 7.12; N, 4.30; found:C, 58.64; H, 7.11; N, 4.04.

5,6,7,9-Tetra-*O*-benzyl-2,3-dideoxy-2-methylidene-α-D-*manno*-4,8-pyranoso-4-nonulonitrile (18). From **9** (0.27 g, 0.5 mmol), **13** (0.11 g, 0.75 mmol) and SmI_2 (2 mmol) **18** (0.32 g, 53 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a colorless oil; $[\alpha]_D^{25}$ = + 13.9° (*c* = 0.5, $CHCl_3$), R_F 0.24 (hexane/ethyl acetate 3:1); IR (film): ν 3444*bm*, 3088*w*, 3063*m*, 3030*m*, 2900*m*, 2866*m*, 2227*w*, 1497*m*, 1454*s*, 1397*m*, 1367*m*, 1310*m*, 1281*m*, 1208*m*, 1183*m*, 1088*s*, 1028*s*, 947*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (*d*, *J* = 14.0, 1 H, H_A-C(3), 2.66 (*s*, 1 H, OH), 2.78 (*d*, *J* = 14.0, 1 H, H_B-C(3)), 3.69-3.73 (*m*, 2 H), 3.77-3.82 (*m*, 1 H), 3.91-4.01 (*m*, 2 H), 4.17 (*dd*, *J* = 2.6, 9.1, 1 H), 4.45 (*d*, *J* = 12.2, 1 H, part of AB system CH_2 (benzyl)), 4.57 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 4.59 (*d*, *J* = 11.6, 1 H, part of AB system CH_2 (benzyl)), 4.65 (*d*, *J* = 12.2, 1 H, part of AB system CH_2 (benzyl)), 4.78 (*s*, 2 H, CH_2 (benzyl)), 4.86 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 5.12 (*d*, *J* = 11.6, 1 H, part of AB system CH_2 (benzyl)), 5.71 (*s*, 1 H, H_A-C(2')), 6.00 (*s*, 1 H, H_B-C(2')), 7.17-7.39 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (63 MHz, $CDCl_3$): δ 42.65 (*t*, C(3)), 69.61 (*t*, C(9)), 72.98, 73.64, 74.39, 75.12(each *t*, CH_2 (benzyl)); 73.42, 74.85, 77.03, 81.71 (each *d*, C(5, 6, 7, 8)), 98.12 (*s*, C(4)), 117.54 (*s*, C(2)), 119.08 (*s*, C(1)), 127.48, 128.52 (each *d*, $CH_{arom.}$), 135.65(*t*, C(2')); 138.34, 138.59 (each *s*, $C_{q\ arom.}$); MS (ei, 80 eV, 240 °C): 604(0.1), 513(0.1), 496(0.1), 446(0.6), 346(0.5), 338(0.7), 181(6.5), 107(27.2), 91(100.0); HRMS calcd. for $C_{38}H_{40}NO_6$: 606.286; found: 606.287; Anal. calcd. for $C_{38}H_{39}NO_6$ (605.73): C, 75.35, H, 6.49, N, 2.31 found: C, 74.80, H, 6.44, N, 2.12.

5,6;8,9-Di-*O*-cyclohexylidene-2,3-dideoxy-2-methylidene-α-D-*manno*-4,7-furanoso-3-nonulonitrile (19). – From **7** (0.34 g, 1 mmol), **13** (0.22 g, 1.5 mmol) and SmI_2 (4 mmol) **19** (0.23 g, 57 %) was obtained after chromatography (hexane/ethyl acetate 10:1) as a colorless oil; $[\alpha]_D^{25}$ = + 3.2° (*c* = 1.0, $CHCl_3$), R_F 0.41 (hexane/ethyl acetate 3:1); IR (film): ν 3411*bm*, 2936*s*, 2861*m*, 2225*w*, 1738*m*, 1619*w*, 1450*m*, 1369*m*, 1282*m*, 1164*s*, 1145*m*, 1095*s*, 1044*s*, 948*m*, 909*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (*t*, *J* = 7.2, 1 H, CH_3 (ethyl acetate)), 1.24-1.67 (*m*, 20 H, CH_2 (cyclohexyl)), 2.05 (*s*, 1 H, CH_3-CO (ethyl acetate)), 2.47 (*s*, 1 H, OH), 2.70 (*d*, *J* =14.4, 1 H, H_A-C(3)), 2.80 (*d*, *J* = 14.4, 1 H, H_B-C(3)), 3.96-4.08 (*m*, 2 H, H-C(9)), 4.12 (*q*, *J* = 7.2, 0.66H, CH_2 (ethyl acetate)), 4.18 (*dd*, *J* = 3.9, 6.4, 1 H, H-C(7)), 4.40 (*dd*, *J* = 6.4, 11.8, 1 H, H-C(8)), 4.50 (*d*, *J* = 5.9, 1 H, H-C(5)), 4.84 (*dd*, *J* = 3.9, 5.9, 1 H, H-C(6)), 5.96 (*s*, 1 H, H_A-C(2')), 6.08 (*s*, 1 H, H_B-C(2')); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.67, 23.85, 24.02, 25.05, 25.12, 33.98, 34.77, 35.67, 36.34 (each *t*, CH_2 (cyclohexyl)), 40.02 (*t*, C(3)), 60.33 (*t*, C(9)), 72.67, 79.69, 84.25 (each *d*, C(5, 6, 7, 8)), 104.98 (*s*, C(4)), 109.33, 113.63 (each *s*, C_q (cyclohexyl)), 117.29 (s, C(2)), 118.93 (*s*, C(1)), 135.20 (*t*, C(2')); MS (ei, 80 eV, 126 °C): 407(1.6), 406(10.9), 405(45.0), 377(2.7), 362(69.2), 290(3.1), 264(14.5), 204(5.4), 192(6.7), 160(10.2), 141(41.1), 112(6.8), 99(45.4), 97(21.7), 83(12.4), 81(49.7), 69(29.0), 55(100.00); Anal. calcd. for $C_{22}H_{31}NO_6$ x 0.33 $C_4H_9O_2$ (ethyl acetate) (434.86): C, 64.44; H, 7.80; N, 3.22; found: C, 64.23; H, 7.91; N, 3.12.

(2*S*)-2-Deoxy-2-(2'-hydroxyethyl)-4,5;7,8-di-*O*-isopropylidene-α-D-*manno*-3,6-furanoso-3-octulosonate-1,2'-lactone (21). – From **1** (0.26g, 1 mmol), **20** (0.25 g, 1.5 mmol) and SmI_2 (4 mmol) **21** (0.19 g, 55 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a white solid; mp 128-130 °C, $[\alpha]_D^{25}$ = + 16.1° (*c* = 1.0, $CHCl_3$), $[\alpha]_D^{25}$ = + 21.6° (*c* = 1.0, CH_3OH), R_F 0.14 (hexane/ethyl acetate 3:1), R_F 0.64 (hexane/ethyl acetate 1:1); IR (KBr): ν 3345*m*, 2987*m*, 2951*m*, 2903*w*, 1749*s*, 1457*m*, 1384*s*, 1369*m*, 1340*m*, 1290*m*, 1259*s*, 1216*s*, 1175*s*, 1098*s*, 1064*s*, 1032*s*, 1009*m*, 994*m*, 946*m*, 928*w*; ^1H NMR (300 MHz, $CDCl_3$): δ 1.31, 1.36, 1.43, 1.46 (each *s*, 3 H, CH_3 (isopropylidene)), 2.30-2.60 (*m*, 2 H, H-C(2')), 3.00 (*dd*, *J* = 9.0, 11.5, 2 H, H-C(2)), 3.90-4.21 (*m*, 4 H), 4.32-4.39 (*m*, 2 H), 4.59 (*d*, *J* = 5.9, 1 H, H-C(4)), 4.86 (*dd*, *J* = 3.9, 5.9, 1 H, H-C(5)), 5.54 (*s*, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.87, 25.11, 26.93 (each *q*, CH_3 (isopropylidene)), 26.08 (*t*, C(2')), 43.19 (*d*, C(2)), 66.96, 67.42 (each *t*, C(2') and C(8)), 73.05, 79.16, 79.75, 86.18 (each *d*, C(4,5,6,7)), 104.18 (*s*, C(3)), 109.31, 112.89 (each *s*, C_q (isopropylidene)), 178.79 (*s*, C(1)); MS (ei, 80 eV, 86 °C): 331(1.2), 330(6.8), 329(40.0), 271(5.5), 243(14.2), 211(5.4), 193(5.4), 179(8.6), 167(3.6), 145(26.0), 131(15.8), 113(23.9), 101(90.6); Anal. calcd. for $C_{16}H_{24}O_8$ (344.36): C, 55.81; H, 7.02; found: C, 55.84; H, 7.06.

Methyl 3,4;5,6-di-*O*-isopropylidene-2-*O*-methoxymethyl-D-gluconate (22). – To a solution of **24** (2.0 g, 6.9 mmol) in formaldehyde dimethylacetal (50 *ml*) under vigorous stirring P_2O_5 (3.0 g, 21.2 mmol)[34] was added in several portions and stirring was continued until TLC showed the complete disappearance of the starting material.[35] The reaction mixture was diluted with diethyl ether (50 *ml*), washed with an aqueous saturated solution of $NaHCO_3$ (20 *ml*), dried ($MgSO_4$) and the solvent was removed under reduced pressure. Chromatography (silica gel, hexane/ethyl acetate 5:1) afforded **22** (1.83 g, 80 %) as a white solid; mp 63-65 °C, $[\alpha]_D^{25}$ = + 79.2° (*c* = 1.0, $CHCl_3$), R_F 0.38 (hexane/ethyl acetate 3:1); IR (KBr): ν 2987*m*, 2960*m*, 2936*m*, 1752*s*, 1483*m*, 1459*m*, 1434*m*, 1384*s*, 1372*s*, 1254*s*, 1215*s*, 1150*s*, 1133*s*, 1072*s*, 1026*s*, 980*m*, 920*s*, 847*s*; ^1H NMR (300 MHz, $CDCl_3$): δ 1.35, 1.37, 1.41, 1.43 (each *s*, 3 H, CH_3 (isopropylidene)), 3.44, 3.80 (each *s*, 3 H, OCH_3), 3.92 (*dd*, *J* = 5.4, 8.2, 1 H, H_A-C(6)), 4.00 (*dd*, *J* = 6.9, 8.2, 1 H, H-C(4)), 4.05-4.11 (*m*, 1 H, H-C(5)), 4.18 (*dd*, *J* = 5.9, 8.3, 1 H, H_B-C(6)), 4.35 (*d*, *J* = 2.7, 1 H, H-C(2)), 4.38 (*dd*, *J* = 2.7, 6.9, 1 H, H-C(3)), 4.75 (*d*, *J* = 13.1,1H, H_A-C(2')), 4.78 (*d*, *J* = 13.1, 1 H, H_B-C(2')); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.16, 26.46, 26.70, 27.28 (each *q*, CH_3(isopropylidene)), 52.21, 56.58 (each *q*, OCH_3), 67.89 (*t*, C(6)), 74.54, 77.09, 80.62 (each *d*, C(2,3,4,5)), 96.70 (*t*, OCH_2O), 109.69, 110.25 (each *s*, C_q(isopropylidene)), 170.30 (*s*, C(1)); MS (ei, 80 eV, 64 °C): 319(58.0), 233(10.0), 201(18.9), 175(21.8), 143(94.3), 101(70.51), 85(22.3), 73(19.8), 59(36.9), 45(100.0); Anal. calcd. for $C_{15}H_{26}O_8$ (334.37): C, 53.88; H, 7.83; found: C, 53.96; H, 7.76.

***tert*-Butyl 2,3-dideoxy-4-hydroxy-4-(2-methylidene-*tert*-butoxycarbonylethyl)-2-methylidene-5-*O*-methoxymethyl-6,7;8,9-di-*O*-isopropylidene-D-*gluco*-nonanoate (23).** – From **22** (0.33 g, 1 mmol), **11** (0.33 g, 1.5 mmol) and SmI_2 (4 mmol) **23** (0.09 g, 15 %) was obtained after chromatography (hexane/ethyl acetate 20:1) as a colorless oil; unchanged **22** (0.21 g, 63 %) was recovered; $[\alpha]_D^{25}$ = + 7.8° (*c* = 1.4, $CHCl_3$), R_F 0.60 (hexane/ethyl acetate 3:1); IR (film): ν 3419*w*, 2980*s*, 2934*m*, 1728*s*, 1628*w*, 1393*m*, 1368*s*, 1329*s*, 1309*m*, 1252*m*, 1215*s*, 1157*s*, 1092*m*, 1064*s*, 1031*m*, 851*m*; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30, 1.34, 1.36, 1.39 (each *s*, 3 H, CH_3 (isopropylidene)), 1.45, 1.46 (each *s*, 9 H, CH_3 (*tert*-butyl)), 2.56 (*d*, *J* = 14.7, 1 H, H_A-C(3A)), 2.59 (*d*, *J* = 14.7, 1 H, H_B-C(3A)), 2.72 (*d*, *J* = 14.5, 1 H, H_A-C(3B)), 2.81 (*d*, *J* = 14.5, 1 H, H_B-C(3B)), 3.43 (*s*, 3 H, OCH_3), 3.71 (*d*, *J* = 1.4, 1 H, H-C(5)), 3.87-3.94 (*m*, 2H), 3.97-4.01(*m*, 1H), 4.04 (*s*, 1 H, OH), 4.11 (*dd*, *J* = 6.0, 8.4, 1 H), 4.20 (*dd*, *J* = 1.5, 7.4, 1 H), 4.71 (*d*, *J* = 6.4, 1 H, H_A-C(9)), 4.78 (*d*, *J* = 6.4, 1 H, H_B-C(9)), 5.61, 5.68 (each *s*, 1 H, H_A-C(2A') and H_A-C(2B')), 6.12 (*d*, *J* = 1.9, 1 H, H_B-C(2A')), 6.13 (*d*, *J* = 1.8, H_B-C(2B')); ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.38, 26.41, 26.90, 27.37 (each *q*, CH_3 (isopropylidene)), 28.03 (each *q*, CH_3 (*tert*-butyl)), 36.87, 38.00 (each *t*, C(3A) and C(3B)), 56.33 (*q*, OCH_3), 67.83 (*t*, C(9)), 76.14 (*t*, OCH_2O), 78.28 (2x), 78.98, 81.97 (each *d*, C(5, 6, 7, 8)), 80.55, 80.65 (each *s*,

C_q(*tert*-butyl)), 99.54 (*s*, C(4)), 109.55, 109.58 (each *s*, C_q (isopropylidene)), 127.49, 127.56 (each *t*, C(2A') and C(2B')), 138.33, 139.06 (*s*, C(2A) and C(2B)), 167.89, 168.38 (*s*, C(1A) and C(1B)); MS (ei, 80 eV, 113 °C): 571(2.0), 457(2.6), 427(3.5), 389(7.6), 357(14.1), 311(22.8), 255(33.8), 199(100.0); HRMS calcd. for $C_{30}H_{50}O_{11}$ (586.72): 586.3355; found: 586.3357; Anal. calcd. for $C_{30}H_{50}O_{11}$ (586.72): C, 61.41; H, 8.59; found: C, 61.58; H, 8.59.

***tert*-Butyl 3-*tert*-butoxycarbonylmethyl-2-deoxy-3-hydroxy-5,6;7,8-di-*O*-isopropylidene-4-*O*-methoxymethyl-D-*gluco*-octanoate (26).** – From **22** (0.33 g, 1 mmol), *tert*-butyl bromo-acetate (**25**) (0.29 g, 1.5 mmol) and SmI_2 (4 mmol) **26** (0.11 g, 20 %) was obtained after chromatography (hexane/ethyl acetate 10:1) as a white solid; unchanged **22** (0.17 g, 52 %) was recovered; mp 63-65 °C, $[\alpha]_D^{25}$ = + 24.5° (*c* = 1.0, $CHCl_3$), R_F 0.62 (hexane/ethyl acetate 3:1); IR (film): ν 3435*bw*, 2982*s*, 2935*m*, 1725*s*, 1652*w*, 1456*m*, 1393*m*, 1370*s*, 1256*s*, 1215*s*, 1155*s*, 1068*s*, 1027*s*, 846*m*; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30, 1.33, 1.38, 1.39 (each *s*, CH_3 (isopropylidene)), 1.44, 1.45 (each *s*, CH_3 (*tert*-butyl)), 2.65 (*d*, *J* = 15.4, 1 H, H_A-C(2A)), 2.71 (*d*, *J* = 15.4, 1 H, H_B-C(2A)), 2.74 (*d*, *J* = 15.6, 1 H, H_A-C(2B)), 2.86 (*d*, *J* = 15.6, 1 H, H_B-C(2B)), 3.41 (*s*, 3 H, OCH_3), 3.84 (*d*, *J* = 1.4, 1 H, H-C(4)), 3.88 (*dd*, *J* = 1.7, 3.6, 1 H), 3.90 (*dd*, *J* = 1.5, 4.1, 1 H), 3.99-4.04 (*m*, 2 H), 4.11 (*dd*, *J* = 1.9, 3.8, 1H), 4.13 (*dd*, *J* = 1.6, 4.4, 1 H), 4.17-4.19 (*m*, 1 H), 4.73 (*d*, *J* = 6.5, 1 H, H-C(8)), 4.79 (*d*, *J* = 6.5, 1 H, H_B-C(8)), 4.84 (*s*, 1 H, OH); ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.31, 26.34, 26.83, 27.38 (each *q*, CH_3 (isopropylidene)), 28.15 (2 x) (each *q*, CH_3 (*tert*-butyl)), 40.38, 41.85 (each *t*, C(2A) and C(2B)), 56.36 (*q*, OCH_3), 67.84 (*t*, C(8)), 75.01 (*t*, OCH_2O), 77.29, 78.00, 79.08, 82.03 (each *d*, C(4, 5, 6, 7)), 80.90, 80.93 (each *s*, C_q (*tert*-butyl)), 99.35 (*s*, C(3)), 109.73, 109.76 (each *s*, C_q (isopropylidene)), 170.81, 172.36 (each *s*, C(1A) and C(1B)); MS (ei, 80 eV, 131 °C): 520(1.1), 519(4.3), 405(7.2), 375(13.3), 347(3.9), 303(4.4), 259(18.1), 203(42.3), 191(18.6), 147(53.2), 143(16.2), 117(73.9), 101(29.4), 85(9.0), 73(8.0), 57(83.6), 45(100.0); Anal. calcd. for $C_{26}H_{46}O_{11}$ (534.64): C, 58.41; H, 8.67; found: C, 58.40; H, 8.63.

Methyl 2-bromo-2-deoxy-3,4;5,6-di-*O*-isopropylidene-D-mannonate (27). – To a solution of methyl 3,4;5,6-di-*O*-isopropylidene-D-gluconate (**24**) (8.0 g, 27.5 mmol), carbon-tetrabromide (20.2 g, 60.8 mmol) and imidazole (1.9 g, 28 mmol) in dry dichloromethane (20 *ml*) at 0 °C PPh_3 (16.6 g, 63.3 mmol) was added in several portions. Stirring was continued at 20°C for 20 h and then the reaction mixture was diluted with hexane/ethyl acetate (400 *ml*, 3:1) and the mixture was filtered through a layer (10 cm) of silica gel. The solvents were removed under diminished pressure and **27** (8.0 g, 82 %) was obtained as a colorless oil that crystallized after standing at -20 °C for several days; mp 39-41 °C, $[\alpha]_D^{25}$ = - 14.7° (*c* = 1.0, $CHCl_3$) [Lit.:[37] $[\alpha]_D^{25}$ = - 5.6°) (*c* = 1.0, $CHCl_3$)], R_F 0.63 (hexane/ethyl acetate 3:1); IR (film): ν 3000*s*, 2970*m*, 2950*m*, 2900*w*, 1755*s*, 1460*w*, 1450*m*, 1390*s*, 1380*s*, 1330*w*, 1275*s*, 1240*s*, 1165*s*, 1070*s*, 850*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35, 1.40, 1.42, 1.45 (each *s*, 3 H, CH_3 (isopropylidene)), 3.82 (*s*, 3 H, OCH_3), 3.98-4.02 (*m*, 1 H), 4.10-4.18 (*m*, 3H), 4.34 (*d*, *J* = 8.5, 1 H, H-C(2)), 4.54 (*dd*, *J* = 3.5, 8.5, 1 H, H-C(3)); ^{13}C NMR (63 MHz, $CDCl_3$): δ 26.33, 26.61, 28.37 (each *q*, CH_3 (isopropylidene)), 45.50 (*d*, C(2)), 53.13 (*q*, OCH_3), 66.67 (*t*, C(6)), 76.19, 80.14, 80.30 (each *d*, C(3,4,5)), 110.12, 111.60 (each *s*, C_q (isopropylidene)), 167.94 (s, C(1)); MS (ei, 80 eV, 111 °C): 339(18.3), 337(18.5), 253(4.3), 251(4.3), 221(2.4), 195(3.9), 193(4.5), 157(9.0), 101(94.4); Anal. calcd. for $C_{13}H_{21}O_6Br$ (353.21): C, 44.21; H, 5.99; Br, 22.62; found: C, 44.48; H, 6.09; Br, 22.79.

(2*E*) Methyl 2,3-dideoxy-5,6-*O*-isopropylidene-D-*erythro*-2-hexenoate (28). – To a solution of SmI_2 (0.1 M in dry THF, 40 *ml*) at 20°C a solution of **39** (0.53 g, 1.5 mmol) in THF (5 *ml*) was slowly added *via* a syringe and stirring was continued until the color of the reaction changed from deep blue to yellow. Usual work up (*vide supra*) followed by chromatography (silica gel, hexane/ethyl acetate 3:1) gave **28** (0.25 g, 77 %)

as a colorless oil; $[\alpha]_D^{25}$ = - 23.4° (*c* = 1.3, $CHCl_3$), R_F 0.19 (hexane/ethyl acetate 3:1), R_F 0.59 (hexane/ethyl acetate 1:1); IR (film): ν 3464*m*, 2988*m*, 2953*w*, 2890*w*, 1726*s*, 1661*m*, 1438*m*, 1382*m*, 1373*m*, 1315*m*, 1269*s*, 1215*m*, 1172*m*, 1122*m*, 1070*s*, 983*m*, 850*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36, 1.46 (each *s*, 3 H, CH_3 (isopropylidene)), 2.62 (*bs*, 1 H, OH), 3.75 (*s*, 3 H, OCH_3), 3.89 (*dd*, *J* = 6.2, 8.5, 1 H, H_A-C(6)), 3.96 (*dd*, *J* = 6.5, 8.5, 1 H, H_B-C(6)), 4.16 (*ddd*, *J* = 4.7, 6.2, 6.5, 1 H, H-C(5)), 4.45-4.47 (*m*, 1 H, H-C(4)), 6.18 (*dd*, *J* = 2.0, 15.7, 1 H, H-C(2)), 6.93 (*dd*, *J* = 4.1, 15.7, 1 H, H-C(3)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.01, 26.47 (each *q*, CH_3 (isopropylidene)), 51.71 (*q*, OCH_3), 64.72 (*t*, C(6)), 70.49 (*d*, C(4)), 77.36 (*d*, C(5)), 109.71 (C_q (isopropylidene), 121.60 (*d*, C(2)) 145.01 (*d*, C(3)), 166.44 (*d*, C(1)); MS (ei, 80 eV, 70 °C): 215(0.46), 201(3.7), 159(0.4), 141(12.0), 127(3.1), 116(1.9), 109(2.42), 101(58.0); Anal. calcd. for $C_{10}H_{16}O_5$ (216.23): C, 55.55; H, 7.46; found: C, 55.69; H, 7.39.

1-(1,4-Anhydro-2,3;5,6-di-*O*-isopropylidene-β-D-mannofuranosyl)-2,3;4,5-di-*O*-isopropylidene-α-D-mannofuranose (30). – To a solution of SmI_2 in THF (60 *ml*, 6 mmol) containing hexamethylphosphoric triamide (3 *ml*) at 20 °C a solution of **1** (0.77 g, 3 mmol) and **29** (0.89 g, 3 mmol)[38] in dry THF (5 *ml*) was slowly added *via* a syringe (the color of the mixture changed from purple to brown), stirring was continued for 30 min and then an aqueous solution of NH_4Cl (25 *ml*) was added. The reaction mixture was diluted with ethyl acetate, the organic layer was separated, washed in succession with a saturated aqueous solution of $NaHCO_3$ (10 *ml*) and brine (10 *ml*), dried ($MgSO_4$), the solvents were removed *in vacuo* and the residue subjected to chromatography (silica gel, hexane/ethyl acetate 5:1). **30** (0.32 g, 21.5 %) was obtained as a white solid; unchanged starting material **1** (0.37 g, 48 %) was recovered; mp 40-45 °C, $[\alpha]_D^{25}$ = - 8.8° (*c* = 1.2, $CHCl_3$), R_F 0.16 (hexane/ethyl acetate 3:1), R_F 0.72 (hexane/ethyl acetate 1:1); IR (film): ν 3445*bm*, 2987*s*, 2937*s*, 1739*m*, 1456*m*, 1373*s*, 1209*s*, 1162*s*, 1118*s*, 1066*s*, 974*m*, 946*m*, 923*m*, 891*m*, 848*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32, 1.33, 1.38, 1.39, 1.42, 1.43, 1.50, 1.53 (each *s*, 3 H, CH_3 (isopropylidene)), 3.95 (*dd*, *J* = 5.1, 8.6, 1 H), 4.03-4.12 (*m*, 5 H), 4.15 (*dd*, *J* = 3.8, 6.8, 1 H), 4.27 (*s*, 1 H, OH), 4.36-4.38 (*m*, 2 H), 4.66 (*d*, *J* = 5.9, 1 H), 4.68-4.71 (*m*, 1 H), 4.82 (*dd*, *J* = 3.8, 5.9, 1 H), 5.04 (*d*, *J* = 6.2, 1 H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 23.55, 24.17, 25.04, 25.16, 25.36, 25.98, 26.76, 26.80 (each *q*, CH_3 (isopropylidene)), 66.32, 66.37 (each *t*, C(1) and C(12)), 73.12, 73.74, 79.56, 79.64, 80.81, 82.62, 82.68, 84.78, 86.01 (each *d*, C(2, 3, 4, 5, 6) and C(8, 9, 10, 11)), 103.60 (*s*, C(7)), 108.92, 109.13, 112.22, 113.01 (*s*, C_q (isopropylidene)); MS (ei, 80 eV, 94 °C): 502(0.1), 487(57.7), 444(4.9), 429(4.8), 371(3.8), 313(3.9), 259(3.9), 236(4.3), 186(19.4), 145(12.4), 141(11.2), 111(21.6), 101(100.0); HRMS calcd. for $C_{24}H_{38}O_{11}$ (502.56): 502.2415; found: 502.2415; Anal. calcd. for $C_{24}H_{38}O_{11}$ (502.56): C, 57.36; H, 7.62; found: C, 57.28; H, 7.62.

4-Iodobutyl 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranoside (31). – To a solution of SmI_2 in THF (30 *ml*, 3 mmol) at 20°C a solution of **1** (0.59 g, 2.3 mmol) and **29** (0.37 g, 1.3 mmol) in THF (25 *ml*) was added and the color of the reaction mixture changed from deep blue to yellow. Stirring was continued for 3 h and then an aqueous, saturated solution of NH_4Cl (20 *ml*) was added. The aqueous phase was extracted with diethyl ether (5 x 30 *ml*), the combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The remaining red liquid was subjected to chromatography (silica gel, hexane/ethyl acetate 10:1); **31** (0.042g, 7.6 %) and **30** (0.019 g, 2.9 %) were obtained; unchanged starting material **1** was recovered (0.47 g, 79%); data for **31**: oil; $[\alpha]_D^{25}$ +20.4° (*c* = 0.2, $CHCl_3$); R_F 0.86 (hexane/ethyl acetate 3:1); IR (film): ν 2986*m*, 2936*m*, 2875*w*, 1380*m*, 1371*m*, 1260*m*, 1210*s*, 1162*m*, 1118*m*, 1085*s*, 1067*s*, 1023*m*, 979*w*, 890*w*, 849*m*, 823*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26-1.32 (*m*, 2 H, CH_2), 1.33 (*s*, 3 H, CH_3), 1.38 (*s*, 3 H; CH_3), 1.46 (*s*, 6 H, 2 x CH_3), 1.62-1.71 (*m*, 2 H, CH_2), 1.84-1.91 (*m*, 2 H, CH_2), 3.20 (*t*, *J* = 6.9, 2 H, CH_2I), 3.40 (*dt*, *J* = 6.2, 9.8, 1 H, H_A of OCH_2), 3.66 (*dt*, *J* = 6.2, 9.8, 1 H, H_B of OCH_2), 3.91 (*dd*, *J* = 3.6, 7.7, 1 H, H-C(4)), 4.07 (AB part of ABX system, ν_A = 4.03, *J* = 4.4, 8.7, ν_B = 4.11, *J* = 6.2, 8.7, 2 H, H-C(6)), 4.40 (*ddd*, *J* = 4.5, 6.2, 7.6, 1 H, H-C(5)), 4.58 (*d*, *J* = 5.9, 1 H, H-C(2)), 4.78 (*dd*, *J* = 3.6, 5.9, 1 H, H-C(3)),

4.96 (*s*, 1 H, H-C(1)); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.52, 25.17, 25.87, 26.90, (each *q*, CH_3), 26.31 (*t*, CH_2I), 30.22, 30.29 (each *t*, CH_2), 66.08, 66.83 (each *t*, OCH_2 and C(6)), 73.05, 79.42, 80.23, 84.95, (each *d*, C(2, 3, 4, 5)), 106.21 (*d*, C(1)), 109.05, 112.45, (each *s*, C_q (isopropylidene)); MS (ei, 80 eV, 112 °C): 427 (55.6), 214 (4.5), 183 (68.4), 156 (11.3), 141 (29.8), 126 (15.4), 101 (99.1), 55 (91.6), 43 (100.0); HRMS calcd. for $C_{16}H_{26}O_6I$ (441.27): 427.0616 (M-15); found: 427.0616; Anal. calcd. for C16H26O6I (441.27): C, 43.55; H, 5.94; found: C, 43.31; H, 5.81.

1-Cyclopropyl-2,3;5,6-di-*O*-isopropylidene-D-mannitol (32). – Samarium powder (0.7 g, 4.6 mmol) was suspended in dry THF (2.0 *ml*) and warmed to 50°C. Under vigorous stirring a solution of **1** (0.29 g, 1.1 mmol) and CH_2I_2 (0.25 *ml*, 3.1 mmol) in THF (8 *ml*) was very slowly added *via* a syringe (the reaction started after having added a few drops and waiting for 30 min). After completion of the addition stirring was continued (30 min at 50°C, then 2 h at 20°C), diluted aqueous hydrochloric acid (1:8, 5 *ml*) was added and the reaction mixture was extracted with diethyl ether (3 x 100 *ml*). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure and the residue subjected to chromatography to afford **32** (0.074 g, 24 %) as a white solid; mp 73-76 °C; $[\alpha]_D^{25}$ -23.7° (*c* = 0.5, $CHCl_3$); R_F 0.53 (hexane/ethyl acetate 1:1); IR (KBr): ν 3400*bm*, 2989*m*, 2936*w*, 1380*m*, 1372*m*, 1239*m*, 1215*m*, 1158*w*, 1131*w*, 1066*s*, 8856*w*, 850*w*, 822*w*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.56-0.69 (*m*, 2 H, H-C(cyclopropyl)), 0.91-1.02 (*m*, 2 H, H-C(cyclopropyl)), 1.37, 1.39, 1.42, 1.59 (each *s*, 3 H, CH_3), 3.63 (*d*, *J* = 8.0, 1H), 3.77-3.78 (*m*, 1 H), 3.86-3.90 (*m*, 1 H), 3.91 (*bs*, 1 H, OH), 4.08-4.15 (*m*, 3 H, OCH_2, OH), 4.42 (*d*, *J* = 8.0, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.06, 13.32, (each *t*, C(cyclopropyl)), 24.51, 25.29, 26.38, 26.95 (each *q*, CH_3), 52.88 (*s*), 67.18 (*t*, OCH_2), 70.28, 75.84, 75.97, 82.13 (each *d*), 108.36 (*s*), 109.20 (*s*), MS (ei, 80 eV, 53 °C): 273 (10.6), 197 (6.3), 155 (7.4), 101 (56.1), 59 (84.5), 43 (100.0); Anal. calcd. for $C_{14}H_{24}O_6$ (288.34): C, 58.32; H, 8.39; found: C, 58.10; H, 8.15.

2,3,5-Tri-*O*-benzyl-1-cyclopropyl-D-arabitol (33). – From **3** (0.42 g, 1 mmol), CH_2I_2 (0.25 *ml*, 3.1 mmol) and samarium powder (0.65 g, 4.3 mmol) after chromatographic purification (silica gel, hexane/ethyl acetate 5:1) **33** (0.086 g, 19 %) was obtained as a colorless oil; $[\alpha]_D^{25}$ -19.6° (*c* = 0.3, $CHCl_3$); R_F 0.21 (hexane/ethyl acetate 3:1); IR (film): ν 3420*bs*, 3088*m*, 3064*m*, 3031*m*, 3007*m*, 2869*s*, 1717*m*, 1497*m*, 1455*s*, 1393*m*, 1277*m*, 1209*s*, 1177*w*, 1071*s*, 1028*s*, 816*w*, 735*s*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.34-0.38, 0.50-0.58, 0.63-0.71, 0.90-0.96 (each *m*, 1 H, H-C(cyclopropyl)), 3.10 (*d*, *J* = 3.0, 2 H, H-C(1) and OH), 3.56 (*ddd*, *J* = 5.3, 9.7, 15.3, 2 H, H-C(4)), 3.80 (*dd*, *J* = 3.0, 5.9, 2 H, H-C(2) and OH), 4.16-4.22 (*m*, 1 H, H-C(3)), 4.50 (AB system, ν_A = 4.46, ν_B = 4.54, *J* = 11.6, 2 H, OCH_2), 4.65 (AB system, ν_A = 4.62, *J* = 11.1, *J* = 11.1, ν_B = 4.68, 2 H, OCH_2), 4.87 (*d*, *J* = 11.7, 2 H, OCH_2), 7.15-7.47 (*m*, 15 H, H-$C_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.15, 14.18 (each *t*), 54.06 (*s*), 69.78 (*d*), 70.85 (each *t*, OCH_2), 70.96, 73.21, 73.32, 80.96, 81.15 (each *d*), 127.56 127.61, 127.70, 127.80, 127.86, 127.89, 128.20, 128.21, 128.31 (each *d*, $CH_{arom.}$), 137.13, 137.54, 137.68 (each *s*, $C_{arom.}$); MS (ei, 80 eV, 166 °C): 430 (0.08), 339 (0.2), 322 (1.2), 249 (1.3), 233 (2.9), 219 (4.3), 181 (4.4), 163 (7.7), 143 (10.0), 105 (11.1), 91 (100.0); Anal. calcd. for $C_{35}H_{38}O_5$ (538.69): C, 78.04; H, 7.11; found: C, 79.92; H, 7.07.

(2*RS*)-2-Deoxy-2-(2'-hydroxyethyl)-4,5-*O*-isopropylidene-α-D-*threo*-3,6-furanoso-3-hexulosonate-1,2'-lactone (35). – From **15** (0.24 g, 1.5 mmol), **20** (0.37 g, 2.2 mmol) and SmI_2 (6 mmol) **35** (0.17, 47 %) was obtained after chromatography (hexane/ethyl acetate 3:1) as a colorless oil; $[\alpha]_D^{25}$ = - 59.5° (*c* = 1.2, $CHCl_3$), R_F 0.47 (hexane/ethyl acetate 1:1); IR (film): ν 3426*bm*, 2986*m* 2941*m*, 2885*w*, 1756*s*, 1676*w*, 1437*w*, 1419*w*, 1381*s*, 1273*m*, 1210*s*, 1163*s*, 1093*s*, 1058*s*, 1023*s*, 987*m*, 881*m*, 861*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31, 1.46 (each *s*, 3 H, CH_3 (isopropylidene)), 2.48 - 2.58 (*m*, 2 H, H-C(2')), 3.06 (*dd*, *J* = 9.3, 11.3, 1 H, H-C(2)), 3.98 (*d*, *J* =10.3, 1 H, H_A-C(6)), 4.08 (*dd*, *J* = 3.9, 10.3, 1 H, H_B-C(6)), 4.21 (*dd*, *J* = 7.2,

10.4, 2 H, H-C(2")), 4.56 (*d*, *J* = 6.0, 1 H, H-C(4)), 4.88 (*dd*, *J* = 3.5, 6.0, 1 H, H-C(5)), 5.41 (*s*, 1 H, OH); ^{13}C NMR (63 MHz, $CDCl_3$): δ 24.16, 25.72 (each *q*, CH_3 (isopropylidene)), 25.93 (*t*, C(2')), 43.26 (*d*, C(2)), 67.64 (*t*, C(6)), 71.02 (*t*, C(2")), 80.62 (*d*, C(5)), 85.64 (*d*, C(4)), 104.89 (*s*, C(3)), 112.60 (*s*, C_q (isopropylidene)), 179.01 (*s*, C(1)); MS (ei, 80 eV, 83 °C): 229(8.2), 186(10.4), 169(11.2), 168(13.2), 131(41.6), 114(7.3), 113(30.4), 99(5.8), 86(33.8), 85(27.9), 71(6.5), 69(24.6), 59(62.9), 55(22.6), 45(8.0), 43(100.0); Anal. calcd. for $C_{11}H_{16}O_6$ (244.24): C, 54.09, H; 6.60; found: C, 53.98; H, 6.89.

(2*RS*)-4,5,6,8-Tetra-*O*-benzyl-2-deoxy-2-(2'-hydroxyethyl)-α-D-*manno*-3,7-pyranoso-oct-3-ulosonate-1,2'-lactone (36). – From **9** (0.54 g, 1 mmol), **20** (0.25 g, 1.5 mmol) and SmI_2 (4 mmol) **36** (0.38 g, 61 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a white solid; mp 100-102 °C, $[\alpha]_D^{25}$ = + 6.1° (*c* = 1.3, $CHCl_3$), R_F 0.29 (hexane/ethyl acetate 3:1); IR (KBr): ν 3403*m*, 3064*w*, 3029*w*, 2915*m*, 2874*m*, 1760*s*, 1719*s*, 1497*m*, 1452*m*, 1386*m*, 1368*m*, 1222*m*, 1135*m*, 1109*s*, 1027*s*, 1015*s*, 741*m*, 734*m*, 698*s*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.16-2.26 (*m*, 1 H, H_A-C(2')), 2.54-2.71 (*m*, 1 H, H_B-C(2')), 2.75 (*dd*, *J* = 8.9, 10.7, 1 H, H-C(2)), 3.67 (*dd*, *J* = 1.7, 11.3, 1 H), 3.82 (*dd*, *J* =4.0, 11.3, 1 H), 3.95-4.00 (*ddd*, *J* =1.7, 4.0, 9.8, 2 H), 4.00-4.11 (*m*, 2 H), 4.20-4.28 (*m*, 2 H), 4.49 (*d*, *J* = 12.1, 1 H, part of AB system CH_2 (benzyl)), 4.58 (*d*, *J* = 11.4, 1 H, part of AB system CH_2 (benzyl)), 4.62 (*d*, *J* = 11.4, 1 H, part of AB system CH_2 (benzyl)), 4.63 (*d*, *J* = 12.1, 1 H, part of AB system CH_2 (benzyl)), 4.80 (*s*, 2 H, CH_2 (benzyl)), 4.87 (*d*, *J* = 11.0, 1 H, part of AB system CH_2 (benzyl)), 5.10 (*d*, *J* = 11.0, 1 H, part of AB system CH_2 (benzyl)), 5.67 (*bs*, 1 H, OH), 7.20-7.38 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (74 MHz, $CDCl_3$): δ 25.55 (*t*, C(2')), 45.67 (*d*, C(2)), 67.37, 69.06 (each *t*, C(2") and C(9)), 72.90, 73.08, 74.32, 74.90 (each *t*, CH_2 (benzyl)), 73.05, 74.45, 78.91, 81.28 (each *d*, C(4, 5, 6, 7)), 97.31 (*s*, C(3)), 127.18, 128.20 (each *d*, $CH_{arom.}$), 138.19, 138.30, 138.49 (each *s*, $C_{q\ arom.}$), 178.92 (*s*, C(1)); MS (ei, 80 eV, 185 °C): 448(1.0), 447(3.3), 355(0.5), 341(1.0), 267(0.4), 253(1.1), 235(0.3), 181(12.1), 163(8.2), 148(1.3), 107(6.9), 92(23.0), 91(100.0); Anal. calcd. for $C_{38}H_{40}O_8$ (624.73): C, 73.06, H, 6.45 found: C, 73.31, H, 6.52.

(2*S*)-4,5;7,8-Di-*O*-cyclohexylidene-2-deoxy-2-(2'-hydroxyethyl)-α-D-*manno*-3,6-furanoso-3-octulosonate-1,2'-lactone (37). –From **7** (0.34 g, 1 mmol), **20** (0.25 g, 1.5 mmol) and SmI_2 (4 mmol) **37** (0.23 g, 54 %) was obtained after chromatography (hexane/ethyl acetate 5:1) as a colorless oil; $[\alpha]_D^{25}$ = + 11.9° (*c* = 1.0, $CHCl_3$), R_F 0.31 (hexane/ethyl acetate 3:1); IR (film): ν 3418*m*, 2936*s*, 2861*m*, 1746*s*, 1450*m*, 1372*m*, 1164*s*, 1096*s*, 1042*s*, 996*m*, 948*m*, 928*m*; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (*t*, *J* = 7.1, 1 H, CH_3 (ethyl acetate)), 1.21-1.71 (*m*, 20 H, CH_2 (cyclohexyl)), 2.04 (*s*, 1 H, CH_3CO (ethyl acetate)), 2.38-2.57 (*m*, 2 H, H-C(2')), 3.04 (*dd*, *J* = 9.0, 11.5, 1 H, H-C(2)), 3.97 (*dd*, *J* = 5.4, 8.6, 1 H, H_A-C(8)), 4.03 (*dd*, *J* = 6.1, 8.6, 1 H, H_B-C(8)), 4.12 (*q*, *J* =7.1, 0.66 H, CH_2 (ethyl acetate)), 4.16-4.22 (*m*, 2 H), 4.35-4.44 (*m*, 2 H), 4.57 (*d*, *J* = 5.9, 1 H, H-C(4)), 4.83 (*dd*, *J* = 3.9, 5.9, 1 H, H-C(5)), 5.54 (*s*, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.51, 23.89, 23.98 (2 x), 25.05, 25.12, 26.03, 33.15, 34.85, 35.04, 36.35 (each *t*, CH_2 (cyclohexyl) and C(2')), 43.14 (*d*, C(2)), 66.16, 67.31 (each *t*, C(2") and C(8)), 72.66, 79.11, 79.51, 85.53 (each *d*, C(4,5,6,7)), 103.92 (*s*, C(3)), 109.38, 113.44 (each *s*, C_q (cyclohexylidene)), 178.55 (C(1)); MS (ei, 80 eV, 139 °C): 425(14.1), 424(58.6), 382(8.5), 381(40.4), 291(18.5), 283(11.2), 219(10.9), 211(12.0), 196(18.2), 157(30.9), 141(67.2), 113(15.2), 99(40.2), 98(26.0), 81(57.7), 69(48.6), 55(100.0); HRMS calcd. for $C_{22}H_{33}O_8$: 425.218; found: 425.219; Anal. calcd. for $C_{22}H_{32}O_8$ x 0.3 $C_4H_8O_2$ (ethyl acetate): C, 61.75; H, 7.70; found: C, 61.78; H, 7.95.

(2*RS*)-4,5,6,8-Tetra-*O*-benzyl-2-deoxy-2-(2'-hydroxyethyl)-α-D-*gluco*-3,7-pyranoso-oct-3-ulosonate-1,2'-lactone (38). – From **5** (0.54 g, 1 mmol), **20** (0.25 g, 1.5 mmol) and SmI_2 (4 mmol) **38** (0.46 g, 74 %) was obtained after chromatography (hexane/ethyl acetate 10:1) as a colorless oil; $[\alpha]_D^{25}$ = - 53.0° (*c* = 1.0, $CHCl_3$), R_F 0.42 (hexane/ethyl acetate 3:1); IR (film): ν 3425b*m*, 3089*w*, 3063*m*, 3030*m*, 3006*w*, 2916*s*, 2866*m*, 1749*s*, 1605*w*, 1586*w*, 1497*s*, 1454*s*, 1379*s*, 1363*s*, 1208*s*, 1182*s*, 1149*s*, 1088*s*, 1027*s*, 738*s*, 697*s*;

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89-0.97 (*m*, 1 H, H_A-C(2')), 1.58 (*s*, 1 H, OH), 1.88-2.04 (*m*, 1 H, H_B-C(2)), 2.84 (*t* , *J* = 9.8, 1 H, H-C(2)), 3.23 (*dd*, *J* = 1.7, 9.3, 1H), 3.57 (*dd*, *J* = 1.9, 9.3, 1H), 3.68-3.87 (*m*, 3H), 3.96-4.00 (*m*, 1 H), 4.08-4.21 (*m*, 2 H), 4.44, 4.51 (each *d*, *J* = 12.2, 1 H, AB system CH_2 (benzyl)); 4.63 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 4.70 (*d*, *J* = 12.2, 1 H, part of AB system CH_2 (benzyl)), 4.85 (*d*, *J* = 10.9, 1 H, part of AB system CH_2 (benzyl)), 4.95 (*d*, *J* = 2.0, 2 H), 5.54 (*s*, 1 H, OH), 7.19-7.40 (*m*, 20 H, $CH_{arom.}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.14 (*t*, C(2')), 43.74 (*d*, C(2)), 67.01, 68.32 (each *t*, C(2'') and C(8)), 71.39, 77.94, 78.24, 83.23 (each *d*, C(4, 5, 6, 7)), 73.02, 74.21, 74.87, 75.60 (each *t*, CH_2 (benzyl)), 97.65 (*s*, C(3)), 127.25-129.10 (each *d*, $CH_{arom.}$), 137.84, 138.06, 138.15, 138.29 (each *s*, $C_{q\ arom.}$), 178.93 (*s*, C(1)); MS (ei, 80 eV, 193 °C): 606(0.1), 533(0.2), 515(0.2), 447(0.8), 425(0.5), 409(0.5), 271(1.3), 253(5.2), 181(6.8), 163(2.2), 92(11.0), 91(100.0); Anal. calcd. for $C_{38}H_{40}O_8$ (624.73): C, 73.05, H, 6.45; found: C, 72.81, H, 6.51.

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REFERENCES AND NOTES

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cf. ref. 28). The thermodynamically more stable products are formed by subsequent anomerization reactions.

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