Carbohydrate Research, 220 (1991) 79–92
Elsevier Science Publishers B.V., Amsterdam

Reaction of pyranoid and furanoid aldonolactones with chloromethyltrimethylsilane-derived reagents

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(Received January 5th, 1991; accepted for publication March 4th, 1991)

ABSTRACT

Reaction of pyranoid and furanoid aldonolactones with trimethylsilylmethyl-lithium provides a convenient route to carbon-chain-elongated methyl ketones. Reaction of the lactones with chloro(trimethylsilyl)methyl-lithium gives the corresponding chloromethylketones.

INTRODUCTION

Chloromethyltrimethylsilane (**1**) has unique properties which give rise to many applications in synthesis[1]. Reaction of **1** with lithium metal[2,3] or *tert*-butyl-lithium[1] results in Cl/Li-exchange and the formation of trimethylsilylmethyl-lithium (**2**). Reaction of esters with **2** followed by protodesilylation provides a convenient route for converting an ester into a carbon-chain-elongated methyl ketone[4], since reactions of lactones with Grignard reagents often[5] lead to some disubstitution. The difference in products obtained either from the organolithium or the Grignard reagent can be rationalised in terms of protection of the intermediate ketone function from further nucleophilic attack by competitive lithium enolate formation[6,7] of the α-trimethylsilylketone[4]. On the other hand, a second equivalent of the Grignard reagent can be added by premixing the α-silyl Grignard reagent with anhydrous cerium(III) chloride[8,9]. We now report on the reaction of **2** with pyranoid and furanoid aldonolactones.

RESULTS AND DISCUSSION

Reaction of 2,3:5,6-di-*O*-isopropylidene-D-mannono-1,4-lactone (**3**) with **2** at −70° afforded a 1:1 equilibrium mixture of the acyclic product **4** and the hemiacetal **5**. The presence of **4** in the mixture was indicated by the ^{13}C signal of the carbonyl carbon at 177.54 p.p.m. and the i.r. band for CO at 1680 cm^{-1}.

The ^{29}Si-n.m.r. spectrum of the mixture contained two signals at δ −1.09 and 2.16. On adding trifluoroacetic acid, both lines quickly decreased, an additional signal

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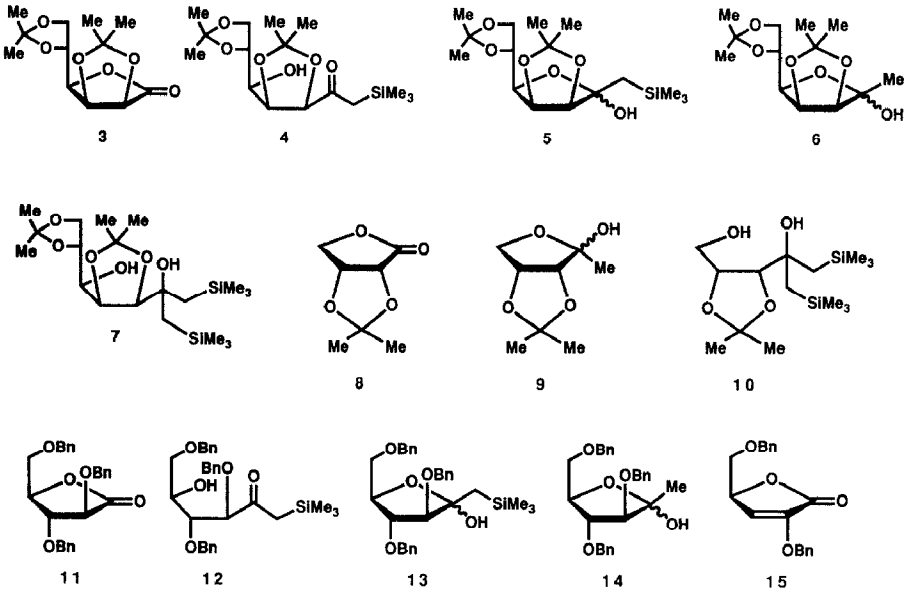
0008-6215/91/$ 03.50

at δ 7.26 corresponding to hexamethyldisiloxane[10] was detected, and the ^{1}H- and ^{13}C-n.m.r. spectra revealed the formation of 1-deoxy-3,4:6,7-di-*O*-isopropylidene-D-*manno*-2-heptulofuranose (**6**). Treatment of **4/5** with silica gel also gave **6** (63%). The formation of **6** can be explained either by a protodesilylation process[1] or a Brook rearrangement[11,12] followed by protodesilylation. Similar ulofuranoses have been prepared by Wittig reactions[13] or by the action of lithium dialkylcuprates[14]. 1-Deoxy-D-*altro*-heptulose and its pyranoid 2,7-anhydride have been isolated from cultures of *Bacillus pumilus*[15], whereas a pyranoid 1-deoxy-D-*galacto*-heptulose has been obtained from the corresponding 2,6-anhydro-hept-1-enitol by the action of a β-galactosidase[16] or from a 2,6-anhydro-1-deoxy-1-diazo-D-*glycero*-L-*manno*-heptitol by degradation with alkali[17].



In addition to **4/5**, small quantities of **7** were isolated from the reaction mixture, the formation of which results from a two-fold attack of **2** on the lactone carbonyl group. Compound **7** can be obtained as the major product by reaction of **3** with an excess of **2**.

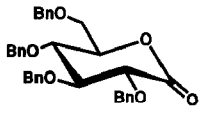
Similarly, 2,3-*O*-isopropylidene-D-erythronolactone[18] (**8**) afforded, on reaction with an equimolar amount of **2** followed by chromatography, 58% of **9**, whereas use of an excess of **2** again favoured the formation of the bis(trimethylsilylmethyl)-D-*erythro*-pentitol derivative **10**. Both **7** and **10** are excellent starting materials for the synthesis of carbohydrate-derived allylsilanes[8,19], an aspect which is being investigated.

2,3,5-Tri-*O*-benzyl-D-arabinono-1,4-lactone[20] (**11**) reacted with **2** to afford 27% of the mixture **12/13** and 31% of **14**. In addition, a small proportion of the elimination product[21] **15** was isolated, the extent of formation of which could be increased to 62% by raising the temperature of the reaction. The butenolide **15**, the formation of which was due to an elimination reaction caused by the basicity of the reagent, and analogues that

have a different pattern of protecting groups[22] are precursors for the synthesis of milbemycins[23] and avermectins[24].

Treatment of 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone[25] (**16**) with **2** yielded, *via* **18**, 62% of the desired compound **17** together with 15% of **19**. The acetylated analogue of **17** has been prepared by the reaction of trimethylsilylated D-glucono-1,5-lactone with 2-lithio-1,3-dithiane followed by deprotection and desulfuration[26].

Treatment of crude **18** with thionyl chloride–methanol gave the glycoside **20**. Although this reaction yielded only one anomer, its anomeric configuration could not be assigned as described for the acetylated analogue[27]. The yields of this glycosidation procedure decreased when secondary alcohols were used.



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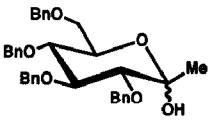

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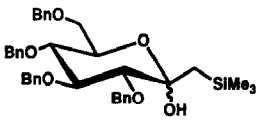

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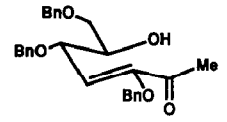

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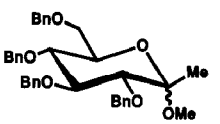

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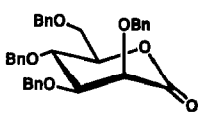

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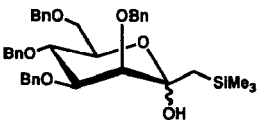

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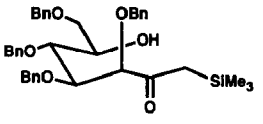

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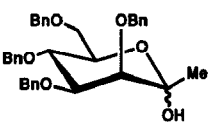

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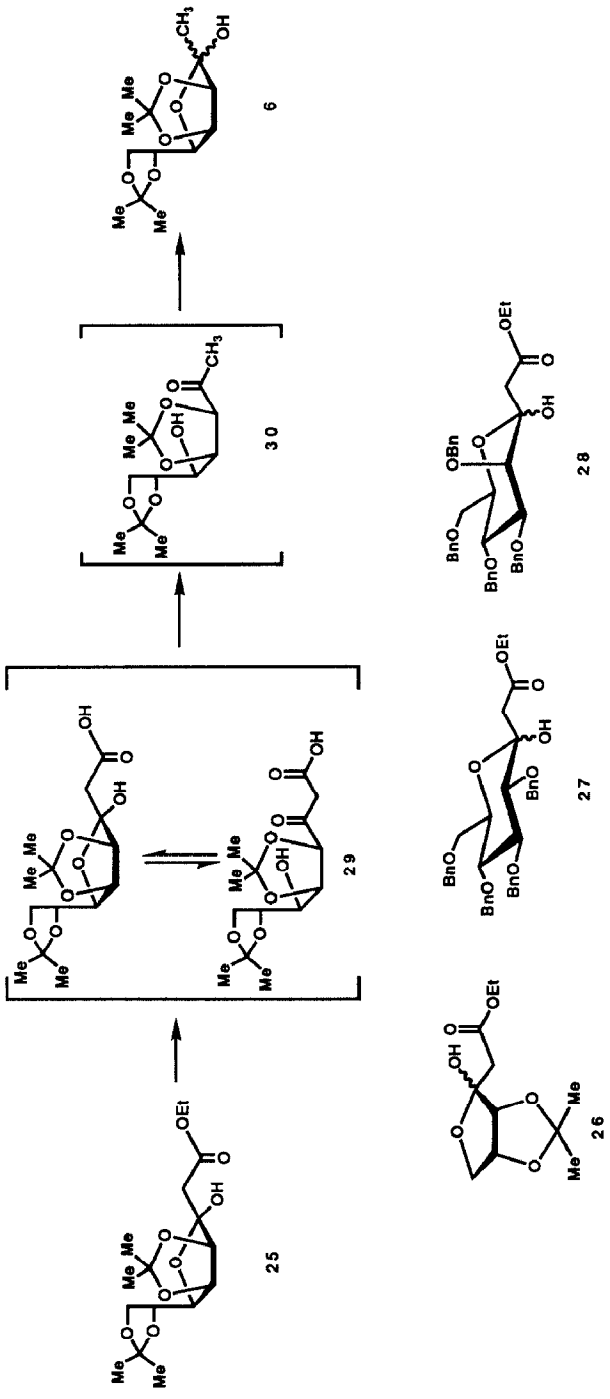
Reaction of 2,3,4,6-tetra-*O*-benzyl-D-mannono-1,5-lactone[28] (**21**) with **2** yielded the hemiacetal **22** (19%) and the acyclic derivative **23** (28%). On storage for several hours at room temperature, solutions of **22** or **23** equilibrated to 1:1.5–2 mixtures of **22** and **23**. Treatment of either **22** or **23** or the equilibrium mixture with silica gel afforded **24** (70–80%), which was also obtained by chromatography of the crude **22/23** mixture.

The structures of **6**, **9**, **17**, and **24** were proved independently. The chain-elongated products **25–28**, which can be prepared conveniently by reaction of **3**, **8**, **16**, or **21**, respectively, with either ethyl bromoacetate and the zinc/silver graphite surface compound in a Reformatzky-type manner[29] or with ethyl trimethylsilylacetate–tetrabutylammonium fluoride[30], are supposed to exist in an equilibrium with their corresponding acyclic forms. As exemplified for **25**, hydrolysis of the ester moiety followed by a ketonic decarboxylation[31,32] of the intermediate **29** yielded **30**, which formed the more stable cyclic hemiacetal **6**. Similarly, **26–28** afforded **9**, **17**, and **24** in yields of 86, 76, and 58%, respectively. Analogues prepared by a different route[33] have been used as starting materials for the synthesis of deoxyfuconojirimycin[34] and of *C*-disaccharides[35].

Chloro(trimethylsilyl)methyl-lithium (**31**) can be prepared *in situ* by the reaction of chloromethyltrimethylsilane with *sec*-butyl-lithium in the presence of *N,N,N′,N′*-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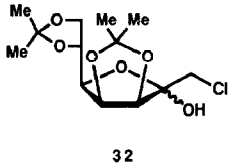
tetramethylethylenediamine through deprotonation of the chloromethyl carbon atom. Compound **31** is well known for its reaction with aldehydes and ketones to give, *via* intermediate chlorohydrins, epoxyalkylsilanes by elimination of lithium chloride[36]. These epoxides may be hydrolysed to produce chain-elongated aldehydes.

Reaction of **3** with two mol of **31** provided convenient access to 1-chloro-1-deoxy-3,4,6,7-di-*O*-isopropylidene-α-D-*manno*-2-heptulofuranose (**32**, 81%). ^{1}H-N.m.r. experiments indicated this reaction to proceed *via* a mixture of the corresponding 1-chloro-1-*C*-trimethylsilyl-2-ulofuranoses and the acyclic 1-chloro-1-deoxy-1-*C*-trimethylsilyl-2-hexuloses, all of these intermediates being too unstable for isolation. The structure of **32** was established by a broad i.r. band for the hydroxyl at 3400 cm^{-1}, and the anomeric hydroxyl group (HO-2, δ 1.67) was exchangeable with D_2O. Although the 400-MHz ^{1}H-n.m.r. spectrum of **32** was crowded, all the signals could be assigned and, by means of a ^{1}H–^{13}C-heteronuclear shift correlation[37], unambiguous assignment of all the ^{13}C resonances of the sugar backbone could be achieved.

Although the stereochemistry at the new chiral centre in **32** has not yet been determined, AM1 calculations[38] on the two possible isomers indicate a strong preference for the α-D-*manno* product. The formation of the product can be rationalised by assuming either a direct protodesilylation of the intermediate chlorohydrin species or a Brook rearrangement followed by desilylation.

In an analogous manner, **8**, **16**, and **21** afforded **33**, **34**, and **35** in yields of 72, 69, and 64%, respectively.

From the reaction of **11**, 23% of the mixture **36/37** was obtained by flash-column chromatography. The ^{13}C-n.m.r. and the i.r. spectra of this mixture clearly revealed acyclic diastereomers **36** and hemiacetalic stereomers **37**. Treatment of this mixture with silica gel or acid, or on prolonged storage of solutions in chloroform at room temperature, gave 3,4,6-tri-*O*-benzyl-1-chloro-1-deoxy-D-*arabino*-2-hexulofuranose (**38**), which was obtained in higher yield (84%) by direct chromatography of the crude reaction mixture.



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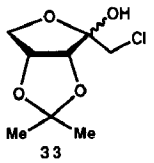

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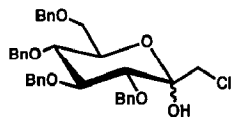

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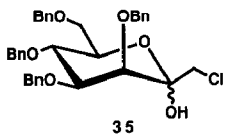

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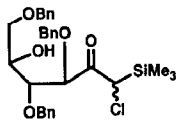

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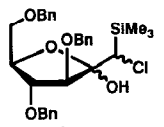

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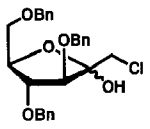

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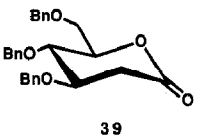

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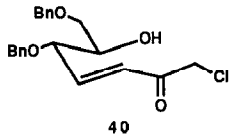

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Regardless of alterations in the conditions, the deoxylactone[39] **39** reacted with **31** to give the α,β-unsaturated ketone **40**. Due to the large $J_{H\text{-}3,H\text{-}4}$ value (16 Hz), the *E* configuration was assigned to **40**.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were obtained with a Perkin–Elmer 243 polarimeter. N.m.r. spectra for solutions in $CDCl_3$ (internal Me_4Si) were recorded with Bruker AM250 and AM400 instruments, i.r. spectra (3% solution in chloroform) with a Perkin–Elmer 298 spectrometer, and c.i. (isobutane)-mass spectra with a Varian 112S instrument. T.l.c. was performed on silica gel plates (Merck, 5554), and column chromatography on silica gel (Merck).

*1-Deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-trimethylsilyl-*D*-manno-2-heptulose* (**4**) *and 1-deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-trimethysilyl-α-*D*-manno-2-heptulofuranose* (**5**). — To a solution of **3** (0.3 g, 1.16 mmol) in dry tetrahydrofuran (10 mL) at −70° was slowly added a M solution of **2** (1.2 mL, 1.2 mmol) in pentane *via* a syringe. Stirring was continued at −70° for 30 min, and the mixture was poured into ice-cold aqueous ammonium chloride (20 mL) and extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed quickly with ice–water and brine (5 mL each), then dried ($MgSO_4$). The solvent was evaporated (<30°) and toluene (2 × 10 mL) was evaporated from the residue to leave a crude oily mixture (220 mg, 54.7%) of **4** and **5**. Flash-column chromatography (hexane–ethyl acetate, 3:1) of a sample gave an oil which was shown by i.r. and n.m.r. spectroscopy to consist of a rapidly equilibrating 1:1 mixture of **4** and **5**, R_f 0.54, $[\alpha]_D^{25}$ +56° (*c* 1.1, chloroform); ν_{max} 3600 (brs), 3560 (m), 2980 (s), 2950 (s), 2900 (m), 2840 (w), 1680 (s), 1450 (m), 1370 (s), 1315 (w), 1220 (s), 1150 (s), 1065 (s), 1010 (m), 850 (s) cm^{-1}. N.m.r. data: ^1H, δ 0.09, 0.13 (2 s, each 4.5 H, Me_3Si), 1.19, 1.20, 1.21, 1.24 (4 s, each 1.5 H), 1.25 (d, 0.5 H, *J* 14.8 Hz), 1.27, 1.32, 1.34, 1.46 (4 s, each 1.5 H), 1.58 (bs, 0.5 H, exchangeable with D_2O), 1.59 (s, 1.5 H), 2.00, 2.08 (2 dd, each 0.5 H, *J* 0.8 and 9.9 Hz), 2.24 (d, 0.5 H, *J* 3.9 Hz), 2.94 (d, 0.5 H, *J* 9.9 Hz), 3.53–3.55 (m, 0.5 H), 3.82–3.89, 4.20–4.27 (2 m, each 1.5 H), 4.63 (dd, 0.5 H, *J* 0.8 and 8.6 Hz), 4.81 (dd, 0.5 H, *J* 3.9 and 5.9 Hz); ^{13}C, δ −0.88 (q), −0.11 (q), 24.21 (q), 24.57 (q), 25.25 (q), 25.35 (q), 25.97 (q), 26.29 (q), 26.79 (q), 26.89 (q), 35.70 (t), 66.76 (t), 67.05 (t), 69.36 (d), 73.29 (d), 75.82 (d), 77.62 (d), 78.58 (d), 80.31 (d), 80.47 (d), 85.38 (d), 107.91 (s), 108.97 (s), 109.34 (s), 109.65 (s), 112.45 (s), 177.54 (s); ^{29}Si (74.46 MHz), δ −1.09 and 2.16; δ 7.26 after the addition of trifluoroacetic acid. Mass spectrum: *m/z* 347 (M^+ + 1), 329 ($M^+ - H_2O + 1$).

Anal. Calc. for $C_{16}H_{30}O_6Si$ (346.50): C, 55.46; H, 8.73; Si, 8.11. Found: C, 55.67; H, 8.91; Si, 8.24.

In addition, **7** (32 mg, 6.3%), R_f 0.61, was obtained as a side product, m.p. 145–146°, $[\alpha]_D^{25}$ −49° (*c* 0.1, chloroform).

*1-Deoxy-3,4:6,7-di-*O*-isopropylidene-*D*-manno-2-heptulofuranose* (**6**). — *(a) By decarboxylation of* **25**. — Compound **25** (0.6 g, 1.73 mmol) and potassium hydroxide

(0.29 g, 3.56 mmol) were stirred at room temperature in 4:1 methanol–water (2 mL) for 6 h. The mixture was neutralised with acetic acid and exhaustively extracted with ethyl acetate, the extract was washed with cold water and brine (5 mL each), and the solvent was evaporated. A solution of the remaining syrup in toluene (5 mL) was boiled under reflux for 2 h. Evaporation of the solvent then gave a syrup which was subjected to chromatography to afford **6** (0.43 g, 90.5%), R_F (toluene–ethyl acetate, 3:1) 0.35, m.p. 102–104°, $[\alpha]_D^{25}$ +10.3° (*c* 1.1, chloroform).

(b) From **4/5**. — The crude mixture of **4/5** (200 mg, 0.58 mmol) was subjected to column chromatography (hexane–ethyl acetate, 3:1), to afford **6** (100 mg, 63%), m.p. 102–104°, $[\alpha]_D^{25}$ +10.5° (*c* 0.9, chloroform). N.m.r. data: ^{1}H, δ 1.33, 1.37, 1.44, 1.47, 1.49 (5 s, each 3 H, 5 CH_3), 2.67 (s, 1 H, exchangeable with D_2O, OH), 4.00 (dd, 1 H, *J* 4.7 and 8.7 Hz, H-7a), 4.06 (dd, 1 H, *J* 6.0 and 8.7 Hz, H-7b), 4.10 (dd, 1 H, *J* 3.7 and 7.3 Hz, H-5), 4.38 (ddd, 1 H, *J* 4.7, 6.0, and 7.3 Hz, H-6), 4.44 (d, 1 H, *J* 5.8 Hz, H-3), 4.82 (dd, 1 H, *J* 3.7 and 5.8 Hz, H-4); ^{13}C, δ 22.25 (q), 24.50 (q), 25.16 (q), 25.91 (q), 26.83 (q), 66.58 (t), 73.29 (d), 78.83 (d), 80.45 (d), 105.30 (s), 109.06 (s), 112.58 (s). Mass spectrum: *m/z* 275 (M^+ + 1).

Anal. Calc. for $C_{13}H_{22}O_6$ (274.32): C, 56.92; H, 8.08. Found: C, 57.10; H, 8.27.

*1-Deoxy-3,4:6,7-di-*O*-isopropylidene-1-*C*-trimethylsilyl-2-C-(trimethylsilylmethyl)-*D*-gluco-hepitol* (**7**). — Prepared from **3** (0.3 g, 1.16 mmol) and **2** (2.2 mL, 2.2 mmol), by the procedure for the preparation of **4/5** followed by column chromatography (hexane–ethyl acetate, 3:1), **7** (0.24 g, 47.5%) had R_F 0.61, m.p. 145–146°, $[\alpha]_D^{25}$ −49° (*c* 0.1, chloroform). N.m.r. data: ^{1}H, δ 0.10, 0.13 (2 s, each 9 H, 2 Me_3Si), 1.06, 1.17 (2 d, each 1 H, *J* 14.8 Hz, H-1a,1b), 1.35 (d, 1 H, *J* 7 Hz, H-1′b), 1.36, 1.39, 1.41, 1.54 (4 s, each 3 H, 4 CH_3), 1.55 (d, 1 H, *J* 7.0 Hz, H-1′a), 2.42 (bs, 1 H, exchangeable with D_2O, OH), 3.79 (d, 1 H, *J* 7.4 Hz, exchangeable with D_2O, HO-5), 4.01–4.17 (m, 5 H), 3.39 (d, *J* 6.8 Hz, 1 H); ^{13}C, δ 0.55, 0.67 (2 q, 2 Me_3Si), 25.34, 25.73, 26.46, 27.05 (4 q, 4 CH_3), 27.28 (t, CH_2Si), 33.51 (t, CH_2Si), 67.59 (t, C-7), 70.88 (d), 75.57 (d), 75.69 (s, C-2), 76.71 (d), 83.48 (d), 108.07 (s), 109.05 (s).

Anal. Calc. for $C_{20}H_{42}O_6Si_2$ (434.73): C, 55.26; H, 9.74; Si, 12.92. Found: C, 55.49; H, 9.55; Si, 12.99.

*1-Deoxy-3,4-*O*-isopropylidene-*D*-erythro-2-pentulofuranose* (**9**). — *(a) By decarboxylation of* **26**. Prepared from **26** (0.4 g, 1.6 mmol) and potassium hydroxide (0.28 g, 3.56 mmol), following the procedure given for **6** (from **25**), **9** (0.24 g, 85.7%) was obtained as an oil, R_F (toluene–ethyl acetate, 3:1) 0.25, $[\alpha]_D^{25}$ −66° (*c* 1.5, chloroform).

(b) From **8**. Prepared from **8** (330 mg, 2.09 mmol) and **2** (2.1 mL, 2.1 mmol), following the procedure given for **6** (from **3**), **9** (210 mg, 57.8%) was obtained as an oil, $[\alpha]_D^{25}$ −65° (*c* 1, chloroform). N.m.r. data: ^{1}H, δ 1.33, 1.49, 1.54 (3 s, each 3 H, 3 CH_3), 2.10 (s, 1 H, exchangeable with D_2O, OH), 3.93 (d, 1 H, *J* 10.2 Hz, H-5a), 4.02 (dd, 1 H, *J* 3.7 and 10.2 Hz, H-5b), 4.41 (d, 1 H, *J* 5.9 Hz, H-3), 4.89 (dd, 1 H, *J* 3.7 and 5.9 Hz, H-4); ^{13}C, δ 22.32 (q), 26.26 (q), 26.75 (q), 70.95 (t), 80.84 (d), 84.98 (d), 105.92 (s), 110.73 (s), 112.37 (s). Mass spectrum: *m/z* 157 ($M^+ - H_2O$ + 1).

Anal. Calc. for $C_8H_{14}O_4$ (174.20): C, 55.16; H, 8.10. Found: C, 55.32; H, 8.19.

*1-Deoxy-3,4-*O*-isopropylidene-1-*C*-trimethylsilyl-2-*C*-(trimethylsilylmethyl)-*D*-*

erythro-*pentitol* (**10**). — Prepared from **8** (330 mg, 2.09 mmol) and **2** (4.2 mL, 4.2 mmol), following the procedure given for **7** (from **3**), **10** (405 mg, 58%) was obtained as an oil, R_f (hexane–ethyl acetate, 3:1) 0.31, $[\alpha]_D^{25}$ −40° (*c* 0.4, chloroform). N.m.r. data: ^{1}H, δ 0.10, 0.11 (2 s, each 9 H, 2 Me_3Si), 1.00, 1.20 (2 d, each 1 H, *J* 14.8 Hz, 2 CH_2Si), 1.28 (s, 2 H, CH_2Si), 1.37, 1.49 (2 s, each 3 H, 2 CH_3), 2.29, 3.12 (2 bs, each 1 H, exchangeable with D_2O, 2 OH), 3.62–3.65, 3.76–3.78 (2 m, each 1 H, H-5a,5b), 3.91 (d, 1 H, *J* 5.4 Hz, H-3), 4.22 (dd, 1 H, *J* 5.4 and 12.0 Hz, H-4); ^{13}C, δ 0.57 (q, Me_3Si), 0.74 (q, Me_3Si), 26.18 (q, CH_3), 27.48 (t, CH_2Si), 28.33 (q, CH_3), 32.22 (t, CH_2Si), 61.98 (t), 75.81 (s), 78.24 (d), 84.01 (d), 107.81 (s).

Anal. Calc. for $C_{15}H_{34}O_4Si_2$ (334.61): C, 53.84; H, 10.24; Si, 16.79. Found: C, 53.94; H, 10.03; Si, 16.64.

3,4,6-Tri-O-*benzyl-1-deoxy-1*-C-*trimethylsilyl*-D-arabino-*2-hexulose* (**12**), *3,4,6-tri*-O-*benzyl-1-deoxy-1*-C-*trimethylsilyl*-D-arabino-*2-hexulofuranose* (**13**), *and 3,4,6-tri*-O-*benzyl-1-deoxy*-D-arabino-*2-hexulofuranose* (**14**). — Prepared from **11** (0.4 g, 0.956 mmol) and **2** (1 mL, 1.0 mmol), an inseparable 1:2 mixture (n.m.r. data) of **12/13** (90 mg, 27%) was obtained, after reaction for 4 h at −60° followed by flash-column chromatography (hexane–ethyl acetate, 3:1), as an oil, R_f 0.42, $[\alpha]_D^{25}$ −7.2° (*c* 1.6, chloroform). N.m.r. data: ^{1}H, both isomers, δ 0.08, 0.11 (2 s, 9 H), 1.60, 2.48 (2 bs, exchangeable with D_2O, 2 OH), 3.55–3.62 (m), 3.99, 4.35 (2 bd, *J* 2.7 Hz), 4.58–4.88 (m), 7.20–7.42 (m, 15 H, 3 Ph); minor isomer, 4.64, 4.78, 5.07 (3 d, *J* 11.6 Hz); major isomer, 3.76, 3.91 (2 d, *J* 14.2 Hz), 4.44, 4.85 (2 d, *J* 11.6 Hz). Mass spectrum: *m/z* 507 (M^+ + 1). The product was too unstable for elemental analysis.

In addition, **11** (280 mg) was recovered.

Column chromatography of the crude mixture gave **14** (90 mg, 31%), as an oil, R_f 0.38, $[\alpha]_D^{25}$ +21° (*c* 2, chloroform). N.m.r. data: ^{1}H, δ 1.53 (s, 3 H, CH_3), 2.6 (bs, 1 H, exchangeable with D_2O, OH), 3.49, 3.59 (2 dd, each 1 H, *J* 4.6 and 10.1 Hz, H-6a,6b), 3.86 (d, 1 H, *J* 4.8 Hz, H-3), 4.08 (ddd, 1 H, *J* 4.5, 4.6, and 4.9 Hz, H-5), 4.17 (dd, 1 H, *J* 4.8 and 4.9 Hz, H-4), 4.51, 4.52, 4.57, 4.59, 4.64, 4.71 (6 d, each 1 H, *J* 11.7–11.9 Hz, 3 PhCH_2), 7.24–7.39 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{27}H_{30}O_5$ (434.54): C, 74.63; H, 6.96. Found: C, 74.89; H, 6.75.

In addition, **15** (4–5%) was isolated; R_f 0.35, $[\alpha]_D^{25}$ −1.5° (*c* 0.4, chloroform).

2,5-Di-O-*benzyl-3-deoxy*-D-glycero-*pent-2-enono-1,4-lactone* (**15**). — Treatment of **11** (0.5 g, 1.2 mmol) with **2** (1.2 mL, 1.2 mmol) for 1 h at −60° and additional stirring at room temperature for 1 h, followed by the usual work-up and chromatography, afforded **15** (230 mg, 62%) as an oil which was crystallised from di-isopropyl ether; R_f 0.35, m.p. 90–92°, $[\alpha]_D^{25}$ −2.0° (*c* 1.3, chloroform); lit.[21] m.p. 91.5–92.5°, $[\alpha]_D^{25}$ −1.7° (*c* 2, chloroform). N.m.r. data: ^{1}H, δ 3.60, 3.63 (2 dd, each 1 H, *J* 5.2 and 10.5 Hz, H-5a,5b), 4.53, 4.58, 4.98 (3 d, each 1 H, *J* 12.0 Hz, 1.5 PhCH_2), 5.03 (dt, 1 H, *J* 2.1 and 5.2 Hz, H-4), 5.04 (d, 1 H, *J* 12.0 Hz, 0.5 PhCH_2), 6.09 (d, 1 H, *J* 2.1 Hz, H-3), 7.25–7.40 (m, 10 H, 2 Ph); ^{13}C, δ 70.60 (t, C-5), 72.85 (t, OBn), 73.67 (t, OBn), 77.64 (d, C-4), 115.32 (d, C-2), 127.60 (d), 127.69 (d), 127.90 (d), 128.31 (d), 128.47 (d), 128.54 (d), 128.65 (d), 134.68 (s), 137.35 (s), 146.48 (s, C-3), 167.28 (s, C-1).

Anal. Calc. for $C_{19}H_{18}O_4$ (310.35): C, 73.53; H, 5.85. Found: C, 73.69; H, 5.64.

A mixture (100 mg) of **12/13** was obtained on further elution.

*3,4,5,7-Tetra-*O*-benzyl-1-deoxy-*D-gluco*-2-heptulopyranose* (**17**). — Prepared from **16** (320 mg, 0.51 mmol), following the procedure given for **6** (from **3**), **17** (215 mg, 76%) was obtained as an oil, $[\alpha]_D^{25}$ +13° (*c* 0.4, chloroform). N.m.r. data: ^{1}H, δ 1.42 (s, 3 H, CH_3), 2.60 (bs, 1 H, exchangeable with D_2O, OH), 3.37 (d, 1 H, *J* 9.2 Hz, H-3), 3.64 (dd, 1 H, *J* 9.2 and 9.4 Hz, H-4), 3.69 (dd, 1 H, *J* 1.7 and 10.8 Hz, H-7a), 3.73 (dd, 1 H, *J* 4.1 and 10.8 Hz, H-7b), 3.96 (dd, *J* 9.3 and 9.4 Hz, H-5), 4.01 (ddd, 1 H, *J* 1.7, 4.1, and 9.3 Hz, H-6), 4.53, 4.56, 4.63, 4.70, 4.83, 4.88, 4.92, 4.94 (8 d, each 1 H, *J* 12.3, 10.8, 12.3, 11.0, 10.8, 12.5, 12.5, and 11.0 Hz, 4 PhCH_2), 7.15–7.40 (m, 20 H, 4 Ph); ^{13}C, δ 26.54 (q), 68.80 (t), 71.50 (d), 73.39 (t), 74.82 (t), 75.55 (t), 75.65 (t), 78.41 (d), 83.16 (d), 83.60 (d), 97.33 (s), 127.19 (d), 127.57 (d), 127.64 (d), 127.73 (d), 127.82 (d), 128.07 (d), 128.27 (d), 128.33 (d), 128.39 (d), 138.24 (s), 138.46 (s), 138.63 (s).

Anal. Calc. for $C_{35}H_{38}O_6$ (554.69): C, 75.79; H, 6.91; Found: 76.00; H, 6.81.

Compound **17** *and (Z)-3,5,7-tri-*O*-benzyl-1,4-dideoxy-*D-erythro*-2-hept-3-enulose* (**19**). — To a solution of **16** (0.5 g, 0.93 mmol) in anhydrous tetrahydrofuran (10 mL) at −70° was slowly added **2** (1 mL, 1.0 mmol) *via* a syringe. Stirring was continued for 1 h at −60° then 3 h at −20°. The mixture was poured into ice-cold saturated aqueous ammonium chloride (20 mL) and extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed quickly with ice–water and brine (5 mL each), then dried ($MgSO_4$), the solvent was evaporated (<30°), and toluene (2 × 10 mL) was evaporated from the residue. The resulting syrup (crude **18**) was chromatographed (hexane–ethyl acetate, 3:1) to yield **17** (320 mg, 62.2%), R_F 0.31, and **19** (60 mg, 15%), R_F 0.18, as oils.

Compound **17** had $[\alpha]_D^{25}$ +13° (*c* 0.3, chloroform).

Compound **19** had $[\alpha]_D^{25}$ −7.3° (*c* 0.3, chloroform). N.m.r. data: ^{1}H, δ 2.26 (s, 3 H, CH_3), 2.27 (bs, 1 H, exchangeable with D_2O, OH), 3.45–3.49 (m, 2 H, H-7a,7b), 3.84 (ddd, 1 H, *J* 5.0, 5.2, and 9.8 Hz, H-6), 4.21, 4.35 (2 d, each 1 H, *J* 11.8 Hz, PhCH_2), 4.42 (dd, 1 H, *J* 5.0 and 9.2 Hz, H-5), 4.44 (s, 2 H, PhCH_2), 4.81, 4.87 (2 d, each 1 H, *J* 11.3 Hz, PhCH_2), 6.06 (d, 1 H, *J* 9.1 Hz, H-4), 7.10–7.40 (m, 15 H, 3 Ph); ^{13}C, δ 26.43 (q), 70.47 (t), 71.09 (t), 72.10 (d), 72.17 (d), 73.38 (t), 73.89 (d), 126.04 (d), 127.76 (d), 127.85 (d), 128.31 (d), 128.49 (d), 128.68 (d), 136.78 (s), 137.89 (s), 137.99 (s), 154.47 (s), 192.13 (s).

Anal. Calc. for $C_{28}H_{30}O_5$ (446.55): C, 75.31; H, 6.77. Found: C, 75.07; H, 6.59.

*3,4,5,7-Tetra-*O*-benzyl-1-deoxy-1-*C*-trimethylsilyl-*D-gluco*-2-heptulopyranose* (**18**). — As described for the preparation of **17**, a solution of **16** (0.5 g, 0.93 mmol) was treated with **2** (1 mL, 1.0 mmol). The crude product (500 mg) was subjected to flash-column chromatography (silica gel deactivated with 0.5% of triethylamine; hexane–ethyl acetate, 3:1) to afford **18** (99 mg, 17%) as an oil, R_F 0.51. Further elution gave **17** (258 mg, 50%), R_F 0.3.

Compound **18** had $[\alpha]_D^{25}$ +14° (*c* 2.7, chloroform). N.m.r. data: ^{1}H, δ 0.0 (s, 9 H, Me_3Si), 1.06, 1.16 (2 d, each 1 H, *J* 14.7 Hz, H-1a,1b), 3.28 (d, 1 H, *J* 9.2 Hz, H-3), 3.57 (dd, 1 H, *J* 1.8 and 10.5 Hz, H-7a), 3.63 (t, 1 H, *J* 9.6 Hz, H-5), 3.70 (dd, 1 H, *J* 3.7, 10.5 Hz, H-7b), 3.86 (t, *J* 9.2 Hz, H-4), 3.91 (ddd, *J* 1.9, 3.6, and 10.1 Hz, H-6), 4.43, 4.45, 4.48, 4.56, 4.67, 4.79, 4.81, 4.89 (8 d, each 1 H, *J* 10.8, 10.5, 10.8, 11.4, 11.2, 11.2, 11.6,

and 11.2 Hz, 4 PhCH_2), 7.10–7.27 (m, 20 H, 4 Ph); ^{13}C, δ 0.23 (q, Me_3Si), 29.11 (t, C-1), 69.15 (t), 73.41 (d), 74.80 (t), 75.55 (t), 75.58 (t), 75.60 (t), 78.42 (d), 83.99 (d), 84.42 (d), 99.71 (s, C-2), 125.28 (d), 127.21 (d), 127.46 (d), 127.58 (d), 127.68 (d), 127.75 (d), 127.94 (d), 128.06 (d), 128.21 (d), 128.25 (d), 128.38 (d), 128.50 (d), 128.56 (d), 129.00 (d), 138.11 (s), 138.33 (s), 138.45 (s), 138.72 (s).

Anal. Calc. for $C_{38}H_{46}O_6Si$ (626.87): C, 72.81; H, 7.40; Si, 4.48. Found: C, 72.99; H, 7.49; Si, 4.64.

*Methyl 3,4,5,7-tetra-*O*-benzyl-1-*C*-methyl-*D*-gluco-2-heptulopyranoside* (**20**). — To a solution of **18** (188 mg, 0.3 mmol) in dry methanol (5 mL) was added thionyl chloride (44 μL, 0.6 mmol) at 0° under argon. The solution was stirred for 30 min at room temperature, the solvent was evaporated, a solution of the residue in dichloromethane (15 mL) was washed with saturated aqueous sodium hydrogencarbonate and brine (2 mL each), then dried (Na_2SO_4), and the solvent was evaporated. The residue was subjected to flash-column chromatography (hexane–ethyl acetate, 3:1) to afford **20** (152 mg, 89%), as an oil, $[\alpha]_D^{25}$ +19° (*c* 1, chloroform), R_F 0.34. N.m.r. data: ^{1}H, δ 1.24, 3.20 (2 s, each 3 H, 2 CH_3), 3.33 (d, 1 H, *J* 9.4 Hz), 3.55–3.70 (m, 4 H), 4.00–4.10 (m, 1 H), 4.45–4.72, 4.80–4.95 (2 m, each 4 H), 7.10–7.35 (m, 20 H, 4 Ph); ^{13}C, δ 19.91 (q), 47.85 (t, C-7), 71.45 (d), 73.34 (t), 74.87 (t), 75.49 (t), 75.64 (t), 78.55 (d), 83.29 (d), 83.75 (d), 100.26 (s, C-2), 127.29 (d), 127.51 (d), 127.59 (d), 127.71 (d), 127.78 (d), 128.26 (d), 128.33 (d), 137.91 (s), 138.17 (s), 138.16 (s), 138.69 (s). Mass spectrum *m/z* 569 (M^+ + 1).

Anal. Calc. for $C_{36}H_{40}O_6$ (568.72): C, 76.03; H, 7.09. Found: C, 76.29; H, 7.00.

*3,4,5,7-Tetra-*O*-benzyl-1-deoxy-1-*C*-trimethylsilyl-*D*-manno-2-heptulopyranose* (**22**) *and 3,4,5,7-tetra-*O*-benzyl-1-deoxy-1-*C*-trimethylsilyl-*D*-manno-2-heptulose* (**23**). — Prepared from **21** (0.4 g, 0.74 mmol) and **2** (0.75 mL, 0.75 mmol) following the procedure given for **18**. **22** (90 mg, 19%), R_F (hexane–ethyl acetate, 3:1) 0.57, was obtained after column chromatography as an oil, $[\alpha]_D^{25}$ +1.7° (*c* 2, chloroform). N.m.r. data: ^{1}H, δ 0.07 (s, 9 H, Me_3Si), 2.68 (d, 1 H, *J* 5.7 Hz, exchangeable with D_2O, OH), 3.60 (dd, 1 H, *J* 5.1 and 9.7 Hz, H-7a), 3.65 (dd, 1 H, *J* 3.2 and 9.7 Hz, H-7b), 3.67, 3.83 (2 d, each 1 H, *J* 14.1 Hz, H-1a,1b), 3.84 (dd, 1 H, *J* 3.4 and 8.0 Hz, H-5), 4.06 (dddd, 1 H, *J* 3.2, 5.1, 5.7, and 8.0 Hz, H-6), 4.17 (dd, 1 H, *J* 3.4 and 6.8 Hz, H-4), 4.33 (d, 1 H, *J* 6.8 Hz, H-3), 4.32, 4.44, 4.47, 4.50, 4.52, 4.59, 4.62, 4.66 (8 d, each 1 H, *J* 11.4, 11.6, 11.9, 11.6, 11.9, 9.2, 9.2, and 11.4 Hz, 4 PhCH_2), 7.17–7.36 (m, 20 H, 4 Ph); ^{13}C, δ −3.09 (q), 58.21 (t), 70.15 (d), 71.01 (t), 72.19 (t), 73.27 (t), 73.87 (t), 74.13 (t), 78.36 (d), 79.67 (d), 127.49 (d), 127.65 (d), 127.78 (d), 127.83 (d), 127.87 (d), 128.01 (d), 128.17 (d), 128.32 (d), 128.43 (d), 137.04 (s), 137.97 (s), 138.03 (s), 138.23 (s), 172.11 (s). Mass spectrum: *m/z* 627 (M^+ + 1).

Anal. Calc. for $C_{38}H_{46}O_6Si$ (626.87): C, 72.81; H, 7.40; Si, 4.48. Found: C, 73.09; H, 7.15; Si, 4.72.

Further elution afforded **23** (130 mg, 28%, R_F 0.47), as an oil, $[\alpha]_D^{25}$ +27° (*c* 2.5, chloroform); ν_{max} 3580 (bs), 3080 (m), 3060 (m), 3000 (m), 2950 (s), 2900 (m), 2860 (s), 1680 (s), 1490 (m), 1450 (s), 1380 (m), 1360 (m), 1250 (s), 1090 (s), 1030 (m) cm^{-1}. N.m.r. data: ^{1}H, δ 0.07 (s, 9H, Me_3Si), 2.30, 2.51 (2 d, each 1 H, *J* 11.0 Hz, H-1a,1b), 2.82 (d, 1 H, *J* 5.4 Hz, exchangeable with D_2O, OH), 3.61 (dd, 1 H, *J* 5.0 and 9.7 Hz, H-7a), 3.63 (dd, 1

H, *J* 3.5 and 9.7 Hz, H-7b), 3.85 (dd, 1 H, *J* 4.2 and 7.6 Hz, H-5), 4.06 (dddd, 1 H, *J* 3.5, 5.0, 5.4, and 7.6 Hz, H-6), 4.15 (dd, 1 H, *J* 4.2 and 5.1 Hz, H-4), 4.23 (d, 1 H, *J* 5.1 Hz, H-3), 4.41, 4.50, 4.54 (3 d, each 1 H, *J* 11.1–11.2 Hz, 1.5 PhCH_2), 4.55 (s, 2 H, PhCH_2), 4.58, 4.63, 4.67 (3 d, each 1 H, *J* 11.1–11.4 Hz, 1.5 PhCH_2), 7.15–7.40 (m, 20 H, 4 Ph). Mass spectrum: *m/z* 627 ($M^+ + 1$). Compound **23** was too unstable for elemental analysis.

Storage of solutions of **22** or **23** gave 1:1.5–2 equilibrium mixtures of **22/23**.

Further elution gave **24** (120 mg, 29%), R_F 0.40.

Chromatography of **22** or **23**, or equilibrated mixtures **22/23**, again afforded **24** (70–80%).

*3,4,5,7-Tetra-*O*-benzyl-1-deoxy-*D-manno*-2-heptulopyranose* (**24**). — *(a) By reaction with* **2**. Prepared from **21** (0.5 g, 0.93 mmol) following the procedure for **17**, **24** (300 mg, 58%) was obtained as an oil, $[\alpha]_D^{25}$ +12° (*c* 1.7, chloroform).

(b) By decarboxylation. Prepared from **28** (320 mg, 0.51 mmol), as described for **17** (from **27**), **24** (201 mg, 71%) was obtained as an oil, $[\alpha]_D^{25}$ +12° (*c* 2.15, chloroform). N.m.r. data: ^{1}H, δ 1.46 (s, 3 H, CH_3), 2.90 (bs, 1 H, exchangeable with D_2O, OH), 3.69–3.76 (m, 2 H), 3.98 (d, 1 H, *J* 9.7 Hz), 4.02 (ddd, 1 H, *J* 2.0, 6.3, and 10.0 Hz, H-6), 4.18 (dd, 1 H, *J* 2.8 and 9.4 Hz), 4.45 (d, 1 H, *J* 9.4 Hz, H-3), 4.52, 4.58, 4.59, 4.63, 4.72 (5 d, each 1 H, *J* 10.8, 10.8, 12.3, 12.3, and 11.6 Hz, 2.5 PhCH_2), 4.79 (s, 2 H, PhCH_2), 5.01 (d, 1 H, *J* 11.6 Hz, 0.5 PhCH_2), 7.19–7.43 (m, 20 H, 4 Ph); ^{13}C, δ 26.38 (q, C-1), 69.86 (t, C-7), 72.61 (t), 62.73 (t), 73.43 (d), 74.81 (t), 74.97 (t), 75.19 (d), 78.28 (d), 81.55 (d), 98.15 (s, C-2), 127.25 (d), 127.42 (d), 127.58 (d), 127.79 (d), 127.88 (d), 127.97 (d), 128.07 (d), 128.13 (d), 128.13 (d), 128.23 (d), 128.33 (d), 128.43 (d), 128.51 (d), 128.65 (d), 128.69 (d), 138.37 (s), 138.51 (s), 138.65 (s), 138.73 (s).

Anal. Calc. for $C_{35}H_{38}O_6$ (554.69): C, 75.79; H, 6.91. Found: C, 75.93; H, 6.75.

General procedure for the reaction of lactones with chloro(trimethylsilyl)methyllithium (**31**). — To a solution of chloromethyltrimethylsilane (**1**; 0.28 mL, 2 mmol) in dry tetrahydrofuran (10 mL) at −70° under argon was slowly added a solution of *sec*-butyllithium [1.6 mL, 1.4M in cyclohexane–isopentane (92/8)] *via* a syringe. The mixture was stirred for 5 min, *N,N,N′,N′*-tetramethylethylenediamine (0.33 mL, 2.2 mmol) was added, and stirring at −60° was continued for 30 min. A solution (1 mmol/mL) of the lactone (1 mmol) in tetrahydrofuran was added and the mixture stirred at the given temperature until complete disappearance of the lactone (t.l.c.; hexane–ethyl acetate, 3:1). The mixture was then poured with stirring into ice-cold, saturated aqueous ammonium chloride (10 mL) and extracted with ethyl acetate (5 × 20 mL). The combined extracts were washed with cold water and brine (5 mL each), then dried ($MgSO_4$), the solvent was evaporated, and toluene (2 × 20 mL) was evaporated from the residue. The resulting syrup was subjected to either flash-column or column chromatography (hexane–ethyl acetate, 3:1) to afford the product.

*1-Chloro-1-deoxy-3,4:6,7-di-*O*-isopropylidene-*α*-*D*-manno-2-heptulofuranose* (**32**). — Prepared from **3** (0.6 g, 3 mmol), **32** (0.75 g, 81%) was obtained, after reaction for 10 min at −50°, as an oil, R_F 0.26, $[\alpha]_D^{25}$ −1.4° (*c* 1.3, chloroform). N.m.r. data: ^{1}H, δ 1.33, 1.38, 1.45, 1.48 (4 s, each 3 H, 4 CH_3), 1.67 (bs, 1 H, exchangeable with D_2O, OH),

3.76 (s, 2 H, H-1a,1b), 4.02 (dd, 1 H, *J* 4.4 and 8.8 Hz, H-7a), 4.08 (dd, 1 H, *J* 6.1 and 8.8 Hz, H-7b), 4.10 (dd, 1 H, *J* 3.7 and 7.9 Hz, H-5), 4.37 (ddd, 1 H, *J* 4.4, 6.1, and 7.9 Hz, H-6), 4.59 (d, 1 H, *J* 5.8 Hz, H-3), 4.88 (dd, 1 H, *J* 3.7 and 5.8 Hz, H-4); ^{13}C, δ 24.21 (q), 25.01 (q), 25.67 (q), 26.69 (q), 47.05 (t, C-1), 66.50 (t, C-7), 72.83 (d, C-5), 79.48 (d, C-6), 80.19 (d, C-4), 84.84 (d, C-3), 103.57 (s), 109.09 (s), 112.95 (s).

Anal. Calc. for $C_{13}H_{21}ClO_6$ (308.76): C, 50.57: H, 6.86; Cl, 11.48. Found: C, 50.69; H, 6.96; Cl, 11.56.

*1-Chloro-1-deoxy-3,4-*O*-isopropylidene-*D-erythro*-2-pentulofuranose* (**33**). — Prepared from **8** (0.47 g, 3 mmol), **33** (0.445 g, 72%) was obtained, after reaction for 10 min at $-40°$, as an oil, R_F 0.40, $[\alpha]_D^{25}$ $-48.5°$ (*c* 0.95, chloroform). N.m.r. data: ^{1}H, δ 1.31, 1.47 (2 s, each 3 H, 2 CH_3), 3.10 (bs, 1 H, exchangeable with D_2O, OH), 3.81 (s, 2 H, H-1a,1b), 4.0 (part of ABq, 1 H, *J* 10.5 Hz, H-5a), 4.05 (part of ABq, 1 H, *J* 3.5 and 10.5 Hz, H-5b), 4.54 (d, 1 H, *J* 5.6 Hz, H-3), 4.91 (dd, 1 H, *J* 3.5 and 5.6 Hz, H-4); ^{13}C, δ 24.62 (q), 26.05 (q), 47.49 (t), 71.47 (t), 80.68 (d), 84.58 (d), 104.16 (s), 112.84 (s).

Anal. Calc. for $C_8H_{13}ClO_4$ (208.64): C, 46.05; H, 6.28; Cl, 16.99. Found: C, 46.21; H, 6.50; Cl, 17.23.

*3,4,5,7-Tetra-*O*-benzyl-1-chloro-1-deoxy-*D-gluco*-2-heptulopyranose* (**34**). — Prepared from **16** (0.54 g, 1 mmol), **34** (0.41 g, 69%) was obtained, after reaction for 1 h at $-50°$ and 3 h at room temperature, as an oil, R_f 0.48, $[\alpha]_D^{25}$ $+19°$ (*c* 1.4, chloroform). N.m.r. data: ^{1}H, δ 3.20 (bs, 1 H, exchangeable with D_2O, OH), 3.40 and 3.59 (ABq, 2 H, *J* 11.3 Hz, H-1a,1b), 3.70 (dd, 1 H, *J* 1.7 and 11.2 Hz, H-7a), 3.72 (dd, 1 H, *J* 9.0 and 10.0 Hz, H-4), 3.80 (dd, 1 H, *J* 3.9 and 11.2 Hz, H-7b), 3.99 (ddd, 1 H, *J* 1.7, 3.9, and 9.6 Hz, H-6), 4.04 (dd, 1 H, *J* 9.0 and 9.6 Hz, H-5), 4.56, 4.63, 4.67, 4.70, 4.84, 4.89 (6 d, each 1 H, *J* 12.3, 10.8, 12.3, 11.2, 10.8, and 11.0 Hz, 3 PhCH_2), 4.92 (d, 1 H, *J* 10.0 Hz, H-3), 4.95, 4.96 (2 d, each 1 H, *J* 11.0 and 11.2 Hz, PhCH_2), 7.19–7.38 (m, 20 H, 4 Ph); ^{13}C, δ 48.06 (t), 68.34 (t), 72.29 (d), 73.39 (t), 74.96 (t), 75.42 (t), 75.64 (t), 78.12 (d), 78.79 (d), 83.50 (d), 104.80 (s), 127.44 (d), 127.52 (d), 127.73 (d), 127.85 (d), 127.93 (d), 128.15 (d), 128.30 (d), 128.39 (d), 128.45 (d), 128.56 (d), 137.45 (s), 138.09 (s), 138.31 (s), 138.39 (s).

Anal. Calc. for $C_{35}H_{37}ClO_6$ (589.13): C, 71.36; H, 6.33; Cl, 6.02. Found: C, 71.59; H, 6.21; Cl, 6.12.

*3,4,5,7-Tetra-*O*-benzyl-1-chloro-1-deoxy-*D-manno*-2-heptulopyranose* (**35**). — Prepared from **21** (0.54 g, 1 mmol), **35** (0.38 g, 64%) was obtained, after reaction for 1 h at $-50°$ and 30 min at room temperature, as an oil, R_F 0.46, $[\alpha]_D^{25}$ $+6.8°$ (*c* 1.35, chloroform). N.m.r. data: ^{1}H, δ 3.03 (s, 1 H, exchangeable with D_2O, OH), 3.66 (d, 1 H, *J* 11.3 Hz, H-1a), 3.82 (s, 2 H), 3.84 (d, 1 H, *J* 11.3 Hz, H-1b), 4.04 (d, 1 H, *J* 2.7 Hz), 4.05–4.08 (m, 2 H), 4.24 (m, 1 H), 4.60–4.85 (m, 4 H), 4.89 (s, 2 H), 4.97 (d, 1 H, *J* 10.8 Hz), 5.14 (d, 1 H, *J* 11.3 Hz), 7.20–7.60 (m, 20 H, 4 Ph); ^{13}C, δ 49.74 (t, C-1), 69.31 (t, C-7), 72.86 (t), 73.38 (t), 73.43 (d), 74.77 (t), 74.93 (d), 75.06 (t), 76.03 (d), 81.55 (d), 96.89 (s, C-2), 127.00 (d), 127.44 (d), 127.53 (d), 127.59 (d), 127.66 (d), 127.77 (d), 127.86 (d), 128.09 (d), 128.23 (d), 128.32 (d), 128.45 (d), 128.50 (d), 128.99 (d), 138.18 (s), 138.25 (s), 138.44 (s), 138.85 (s).

Anal. Calc. for $C_{35}H_{37}ClO_6$ (589.13): C, 71.36; H, 6.33; Cl, 6.02. Found: C, 71.62; H, 6.14; Cl, 6.20.

(*1*RS)-*3,4,6-Tri*-O-*benzyl-1-chloro-1-deoxy-1*-C-*trimethylsilyl*-D-arabino-*2-hexulose* (**36**), (*1*RS)-*3,4,6-tri*-O-*benzyl-1-chloro-1-deoxy-1*-C-*trimethylsilyl*-D-arabino-*2-hexulofuranose* (**37**), *and 3,4,6-tri*-O-*benzyl-1-chloro-1-deoxy*-D-arabino-*2-hexulofuranose* (**38**). — Prepared from **11** (0.5 g, 1.2 mmol), **36/37** (150 mg, 23%) (rapidly equilibrating, n.m.r. data), R_F 0.67, was obtained after flash-column chromatography as an oil. N.m.r. data: ^{1}H, δ −0.05, −0.14, and −0.19 (3 s, ratios 4.5:2.5:1, 9 H), 1.0 and 1.6 (2 s, exchangeable with D_2O, 2 OH), 3.4–4.8 (m, 12 H), 7.1–7.5 (m, 15 H); ^{13}C, δ 184.58 (s, CO), 110.34, 106.74, 104.64, 102.52 (s). The mixture **36/37** was too unstable for elemental analysis.

Further elution afforded **38** (230 mg, 41%), as an oily mixture of two isomers in the ratio 1.4–1.8:1 (^{1}H-n.m.r. data), R_F 0.39, $[\alpha]_D^{25}$ +12.5° (*c* 0.9, chloroform). N.m.r. data: ^{1}H, δ 1.64 (bs, exchangeable with D_2O, OH), 3.48–3.66 (m), 3.75 and 3.79 (ABq, *J* 11.2 Hz), 3.97 (dd, *J* 1.4 and 2.8 Hz, minor isomer), 4.03 (d, *J* 1.4 Hz, minor isomer), 4.11–4.18 (m), 4.23 (d, *J* 4.2 Hz, major isomer), 4.50–4.60 (m), 4.64 and 4.68 (ABq, *J* 11.6 Hz), 7.23–7.38 (m, 15 H, 3 Ph); ^{13}C, both isomers, δ 127.63 (d), 127.68 (d), 127.76 (d), 127.91 (d), 127.96 (d), 128.09 (d), 128.29 (d), 128.37 (d), 128.47 (d), 128.61 (d), 137.02 (s), 137.44 (s), 137.47 (s); minor isomer, 46.12, 69.83, 71.82, 72.17, 73.23 (5 t), 82.09, 82.76, 85.39 (3 d), 105.44 (s); major isomer, 46.60, 70.19, 72.09, 72.88, 73.42 (5 t), 80.59, 83.00, 83.10 (3 d), 102.51 (s).

Anal. Calc. for $C_{27}H_{29}ClO_5$ (468.98): C, 69.15; H, 6.23; Cl, 7.56. Found: C, 69.37; H, 6.09; Cl, 7.64.

Alternatively, the crude mixture was subjected to column chromatography, to allow the isolation of **38** (470 mg, 84%). Treatment of ethyl acetate solutions of **36/37** with silica gel afforded **38** (80–90%).

(E)-*5,7-Di*-O-*benzyl-1-chloro-1,3,4-trideoxy*-D-erythro-*2-hept-3-enulose* (**40**). — Prepared from **39** (0.2 g, 0.46 mmol), **40** (130 mg, 75%) was obtained, after reaction for 2 h at −60°, as an oil, R_F 0.15, $[\alpha]_D^{25}$ +24° (*c* 0.6, chloroform); ν_{max} 3090 (w), 3060 (w), 3040 (w), 3000 (m), 2929 (m), 2860 (m), 1695 (m), 1630 (m), 1490 (w), 1450 (m), 1370 (m), 1090 (s), 1070 (s), 1025 (m) cm^{-1}. N.m.r. data: ^{1}H, δ 2.50 (bd, 1 H, *J* 5.0 Hz, exchangeable with D_2O, HO-6), 3.57 (dd, 1 H, *J* 4.5 and 9.6 Hz, H-7a), 3.61 (dd, 1 H, *J* 5.4 and 9.6 Hz, H-7b), 3.91 (dddd, 1 H, *J* 4.5, 5.0, 5.4, and 6.0 Hz, H-6), 4.14 (dt, 1 H, *J* 1.3 and 6.0 Hz, H-5), 4.21 (s, 2 H, H-1a,1b), 4.43 (d, 1 H, *J* 11.5 Hz, 0.5 PhCH_2), 4.52 (s, 2 H, PhCH_2), 4.61 (d, 1 H, *J* 11.5 Hz, 0.5 PhCH_2), 6.52 (dd, 1 H, *J* 1.3 and 16.0 Hz, H-3), 6.97 (dd, 1 H, *J* 6.0 and 16.0 Hz, H-4), 7.27 (m, 10 H, 2 Ph); ^{13}C, δ 47.02 (t, C-1), 70.27 (t, C-7), 72.13 (t), 72.37 (d), 73.61 (t), 78.94 (d), 127.82 (d), 127.89 (d), 127.99 (d), 128.06 (d), 128.15 (d, C-3), 128.60 (d), 138.12 (s), 138.45 (s), 145.99 (d, C-4), 191.20 (s, C-2).

Anal. Calc. for $C_{21}H_{23}ClO_4$ (374.87): C, 67.29; H, 6.18; Cl, 9.46. Found: C, 67.53; H, 6.39; Cl, 9.60.

ACKNOWLEDGMENTS

We thank Professor Dr. R. Neidlein (Pharmazeutisch-Chemisches Institut, Universität Heidelberg) for his encouragement, D. Nanz (Organisch-Chemisches Institut,

Universität Zürich) for recording the ^{29}Si-n.m.r. spectra, Boehringer Ingelheim for support, Perkin–Elmer for providing a polarimeter, and IBM (Munich) for computational support.

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