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Preparation of Some Acetylated Deoxy-pento- and -hexofuranoses and their Deacetylation

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Acetylated 2-deoxy-, 3-deoxy-, 2,3-dideoxy- and 2,3,6-trideoxy-furanoses have been prepared by reduction of the corresponding acetylated deoxyaldonolactones with disiamylborane. An improved procedure for the isolation of the reduced products is described. Deacetylation of the acetylated 3-deoxy- and 2,3-dideoxy-furanoses with methanolic sodium methoxide proceeds smoothly to give the unsubstituted deoxy sugars. Acetylated 2-deoxyfuranoses may, however, undergo elimination–addition reactions under these conditions to give 2-deoxy-3-*O*-methyl-sugars. This complication can be avoided by using the weaker bases potassium cyanide or magnesium oxide.

In previous papers the preparation of a number of acetylated mono-, di- and tri-deoxy-pentono- and -hexono-1,4-lactones has been described.[1–4] The reduction of such lactones may yield the corresponding acetylated furanoses, which are of potential synthetic use, e.g., for the synthesis of nucleoside analogues[5] or for the preparation of free deoxy sugars by deacetylation.

Unprotected aldonolactones have been reduced to the corresponding hemiacetals with several reagents such as sodium amalgam,[6] sodium borohydride,[7] bis(2-butyl)aluminium hydride[8] (DIBAL) or bis(3-methyl-2-butyl)borane (disiamylborane).[5] For the reduction of acylated lactones only disiamylborane can be used since the other three reagents will cleave off the acyl groups. Reduction of acetylated and benzoylated aldonolactones with disiamylborane was first described by Kohn *et al.*,[5] who used this reagent to prepare a number of benzoylated hexofuranoses. They also synthesized 2,3,5,6-tetra-*O*-acetyl-D-galactofuranose in 83% yield by reduction of the corresponding acetylated lactone. Dyong *et al.*, on the other hand, reported that they obtained complex mixtures of products on reduction of tetra-*O*-acetyl-D-galactono-1,4-lactone and some acetylated deoxyhexonolactones with disiamylborane.[9]

When a lactone is reduced with disiamylborane an addition of the latter to the double bond of the carbonyl group takes place. Subsequent hydrolysis then gives the hemiacetal and disiamylborinic acid.[5] In the normal procedure used to isolate the product the borinic acid is oxidized by simultaneous addition of hydrogen peroxide and aqueous sodium hydroxide, keeping the pH at 7.[5,8] This converts the borinic acid into boric acid and 3-methyl-2-butanol, both of which are easily removed by evaporation. In our opinion this procedure should not be used for the reduction of acylated lactones, because the addition of sodium hydroxide is likely to cause partial deacylation, even with careful control of pH, and this may explain the mixture of products obtained in some cases.[9] We have now found that the disiamylborinic acid can be completely removed from the reaction mixture simply by coevaporation with water and with methanol.

Results and discussion

To achieve complete reduction of an acetylated aldonolactone it is necessary to use two to four times the calculated amount of disiamylborane and a reaction time of about 18 h at room temperature. Acetylated 2-deoxy- and 2,3-dideoxy-lactones are reduced relatively easily, whereas 3-deoxy-lactones require more time and more reagent to be reduced completely. Thus the acetylated 2,6-dideoxy-D- and -L-*arabino*-hexofuranoses (**1** and **3**, respectively), the 2,6-dideoxy-L-*ribo*- (**5**) and the 2,3,6-trideoxy-D-*erythro*-hexofuranose (**9a**) were all obtained in virtually quantitative yields by reduction of the corresponding acetylated lactones. For complete formation of the acetylated 2-deoxy-L-*ribo*-hexofuranose (**7a**) a 40 h reaction time was necessary under the same conditions. The synthesis of the acetylated 3-deoxy-D-*threo*-pentofuranose (**10a**), 3-deoxy-D-*arabino*-hexofuranose (**11a**), 3-deoxy-D-*xylo*-hexofuranose (**12a**), 3-deoxy- and 3,6-dideoxy-D-*gluco*-heptofuranose (**13a** and **13b**, respectively), from the corresponding lactones, required four equivalents of disiamylborane and a 48–72 h reaction time for complete reduction. The electronegative acetoxy

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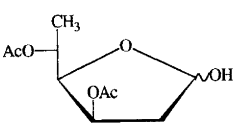
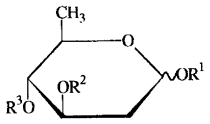


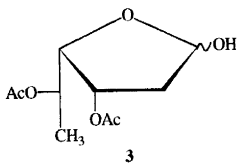
1



2

a) $R^1=R^2=R^3=H$; b) $R^1=R^3=H$, $R^2=CH_3$

c) $R^1=CH_3$, $R^2=R^3=H$; d) $R^1=CH_3$, $R^2=R^3=p\text{-}NO_2Bz$



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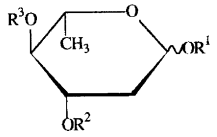
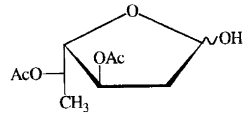


4

a) $R^1=R^2=R^3=H$; b) $R^1=R^3=H$, $R^2=CH_3$

c) $R^1=CH_3$, $R^2=R^3=p\text{-}NO_2Bz$



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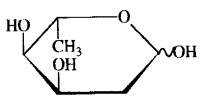
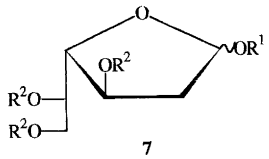


6

Scheme 1.

groups probably inhibit the reaction of the electrophilic borane with the carbonyl group of the lactone, and this becomes more pronounced when an acetoxy group is present at the 2-position.



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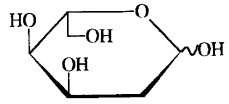
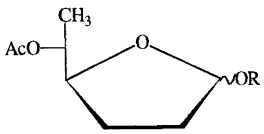


8

a) $R^1=H$, $R^2=Ac$

b) $R^1=CH_3$, $R^2=H$



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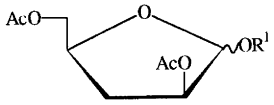
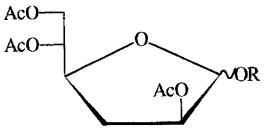


10

a) R=H; b) R=OBz

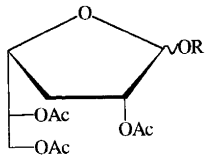
a) R=H; b) R=OBz

Scheme 2.



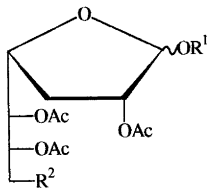
11

a) R=H; b) R=OBz



12

a) R=H; b) R=OBz



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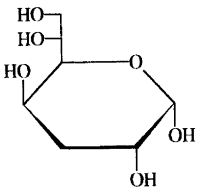

14

a) $R^1=H$, $R^2=OAc$

b) $R^1=R^2=H$; c) $R^1=p\text{-}NO_2Bz$, $R^2=H$

Scheme 3.

Some of the acetylated furanoses, prepared as described above, were deacetylated in order to obtain the corresponding free sugars. Acetylated 3-deoxy- and 2,3-dideoxy-furanoses were readily deacetylated with catalytic amounts of sodium methoxide in methanol to give high yields of the free sugars. Deacetylation of acetylated 2-deoxyfuranoses, on the other hand, gave mixtures of products which contained *O*-methyl groups. Thus deacetylation of 3,5-di-*O*-acetyl-2,6-dideoxy-D-*arabino*-hexofuranose (**1**) gave a mixture of the expected 2,6-dideoxy-D-*arabino*-hexose (**2a**) and 2,6-dideoxy-3-*O*-methyl-D-*arabino*-hexose (oleandrose, **2b**); the latter was isolated in 39% yield. The formation of **2b** must proceed via elimination of the 3-*O*-acetyl group from the aldehyde form of **1** and subsequent addition of a methoxy group to the resulting unsaturated aldehyde. Apparently the addition was, in this case, highly stereoselective since no isomeric product was observed. Deacetylation of **5** and **7a** with methoxide gave mixtures of *O*-methyl derivatives. However, all the acetylated furanoses could be deacetylated smoothly when the less basic reagents, potassium cyanide[10] or magnesium oxide[11] were used.

Experimental

Melting points are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. NMR spectra were recorded on Bruker AC-250 or AM-500 instruments. Tetramethylsilane was used as an internal reference for $CDCl_3$ solutions and dioxane (67.4 ppm) for ^{13}C NMR spectra measured in D_2O solutions. Unless

otherwise stated NMR spectra were measured for samples in $CDCl_3$ solution. Chromatographic separations were performed on columns of silica gel using the flash technique.

*3,5-Di-*O*-acetyl-2,6-dideoxy-α-*D*-*arabino*-hexofuranose (α-**1**).* A solution of disiamylborane was prepared by addition of 2-methyl-2-butene (6.9 ml, 65 mmol) in CH_2Cl_2 (15 ml) to borane–dimethyl sulfide complex (3.2 ml, 34 mmol) in CH_2Cl_2 (10 ml) at 0°C under an N_2 atmosphere.[12] After 2.5 h 3,5-di-*O*-acetyl-2,6-dideoxy-D-*arabino*-hexono-1,4-lactone[1] (2.5 g, 11 mmol) in CH_2Cl_2 (10 ml) was added and the mixture was kept at 20°C for 18 h. Water (10 ml) was then added and the mixture was stirred for 1 h. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were concentrated and the residue was coevaporated three times with 20 ml portions of water at 40°C (to remove the borinic acid) and three times with MeOH, to leave the title compound as a syrup (2.5 g, 100%), which crystallized from Et_2O–pentane to give 2.2 g (88%) of α-**1**, m.p. 75–78°C. Recrystallization gave a product with m.p. 83–85°C, $[\alpha]_D^{20}$ +41.1→ +16.8° (*c* 3.2, $CHCl_3$). Anal. $C_{10}H_{16}O_6$: C, H. ^{1}H NMR: δ 5.70 (dd, 1 H, $J_{1,2}$ 3.8 Hz, $J_{1,2'}$ 5.5, H-1), 5.48 (ddd, 1 H, $J_{3,4}$ 3.8, H-3), 5.04 (dq, 1 H, $J_{5,6}$ 6.0, H-5), 4.14 (dd, 1 H, $J_{4,5}$ 8.5, H-4), 2.24 (m, 1 H, $J_{2,2'}$ 14.7, $J_{2,3}$ 5.3, H-2), 2.21 (m, 1 H, $J_{2',3}$ 2.2, H-2′), 2.00, 1.98 (OAc), 1.31 (d, 3 H, H-6). ^{13}C NMR: δ 97.8 (C-1), 81.1 (C-4), 72.7, 67.4 (C-3,5), 41.3 (C-2), 21.0, 20.8 (OAc), 17.7 (C-6).

*3,5-Di-*O*-acetyl-2,6-dideoxy-L-*arabino*-hexofuranose (**3**).* was prepared in 75% yield as described above from 3,5-di-*O*-acetyl-2,5-dideoxy-L-*arabino*-hexono-1,4-lactone,[1] m.p. 74–78°C. Recrystallization gave a product with m.p. 81–83°C, $[\alpha]_D^{20}$ −40.8→ −16.5° (*c* 2, $CHCl_3$). Anal. $C_{10}H_{16}O_6$: C, H. ^{1}H and ^{13}C NMR spectra were identical with those of **1**.

*3,5-Di-*O*-acetyl-2,6-dideoxy-L-*ribo*-hexofuranose (**5**).* Reduction of 3,5-di-*O*-acetyl-2,6-dideoxy-L-*ribo*-hexono-1,4-lactone[3] (1.5 g, 6.52 mmol) with disiamylborane (27.4 mmol) for 18 h as described above gave 1.45 g (96%) of crude **5**, which was chromatographed twice, using first Et_2O and the EtOAc as eluents, to give **5** as a syrup, $[\alpha]_D^{20}$ −34.6→ −43.1° (*c* 5, $CHCl_3$). Anal. $C_{10}H_{16}O_6$: C, H. ^{1}H NMR, α-**5**: δ 5.52 (dd, 1 H, $J_{1,2}$ 5.0 Hz, $J_{1,2'}$ 0.5, H-1), 5.16 (ddd, 1 H, $J_{3,4}$ 3.0, H-3), 4.94 (dq, 1 H, $J_{5,6}$ 6.5, H-5), 4.17 (dd, 1 H, $J_{4,5}$ 4.2, H-4), 2.28 (ddd, 1 H, $J_{2,2'}$ 14.5, $J_{2,3}$ 7.5, H-2), 1.93 (m, 1 H, $J_{2',3}$ 1.5, H-2′), 2.05, 1.95 (OAc), 1.20, (d, 3 H, H-6). ^{13}C NMR, α-**5**: δ 98.1 (C-1), 84.7 (C-4), 73.3, 69.6 (C-3,5), 39.4 (C-2), 20.7, 20.6 (OAc), 15.5 (C-6). ^{1}H NMR, β-**5**: δ 5.55 (dd, 1 H, $J_{1,2}$ 3.9 Hz, $J_{1,2'}$ 5.7, H-1), 5.29 (dt, 1 H, $J_{3,4}$ 3.0, H-3), 5.02 (dd, 1 H, $J_{5,6}$ 6.7, H-5), 3.89 (dd, 1 H, $J_{4,5}$ 6.0, H-4), 2.19 (ddd, 1 H, $J_{2,2'}$ 14.2, $J_{2,3}$ 6.8, H-2), 2.08 (m, 1 H, $J_{2',3}$ 6.6, H-2′), 2.01, 1.95 (OAc), 1.23 (dd, 3 H, H-6). ^{13}C NMR, β-**5**: δ 98.5 (C-1), 85.3 (C-4), 74.2, 69.9 (C-3,5), 39.3 (C-2), 20.8, 20.7 (OAc), 15.5 (C-6).

*3,5,6-Tri-*O*-acetyl-2-deoxy-L-*ribo*-hexofuranose (**7a**).* Reduction of 3,5,6-tri-*O*-acetyl-2-deoxy-L-*ribo*-hexono-1,4-lactone[3] (2.5 g, 8.7 mmol) with disiamylborane (35 mmol) for 42 h at 20°C gave 2.5 g (100%) of **7a**, pure as seen from its NMR spectra. With shorter reaction time or less reagent unreduced lactone remained present. Chromatography using first Et_2O and then EtOAc as eluents gave an analytical sample of **7a** as a syrup, $[\alpha]_D^{20}$ −13.9→ −18.7° (*c* 4.2, $CHCl_3$). Anal. $C_{12}H_{18}O_8$: C, H. ^{1}H NMR, α-**7a**: δ 5.55 (dd, 1 H, $J_{1,2}$ 5.0 Hz, $J_{1,2'}$ 1.0, H-1), 5.25 (ddd, 1 H, $J_{3,4}$ 2.5, H-3), 5.04 (m, 1 H, $J_{5,6}$ 3.2, $J_{5,6'}$ 6.0, H-5), 4.37 (dd, 1 H, $J_{6,6'}$ 12.0, H-6), 4.31 (m, 1 H, $J_{4,5}$ 6.5, $J_{4,6'}$ 2.0, H-4), 4.11 (ddd, 1 H, H-6′), 2.30 (m, 1 H, $J_{2,3}$ 1.5, H-2), 2.10 (m, 1 H, $J_{2',3}$ 7.0, H-2′), 2.10, 2.00 (3 OAc); ^{13}C NMR, α-**7a**: δ 98.8 (C-1), 81.5 (C-4), 74.9, 70.9 (C-3,5), 62.5 (C-6), 39.2 (C-2), 20.6, 20.5, 20.4 (OAc); ^{1}H NMR, β-**7a**: δ 5.65 (dd, 1 H, $J_{1,2}$ 5.5 Hz, $J_{1,2'}$ 3.2, H-1), 5.32 (ddd, 1 H, $J_{3,4}$ 2.5, H-3), 5.17 (dd, 1 H, $J_{5,6}$ 3.0, $J_{5,6'}$ 5.5, H-5), 4.43 (dd, 1 H, $J_{6,6'}$ 12.0, H-6), 4.18 (ddd, 1 H, H-6′), 4.08 (m, 1 H, $J_{4,5}$ 7.8, $J_{4,6}$ 1.5, H-4), 2.30 (m, 1 H, $J_{2,2'}$ 14.5, $J_{2,3}$ 7.0, H-2), 2.17 (ddd, 1 H, $J_{2',3}$ 5.5, H-2′), 2.10, 2.00 (OAc); ^{13}C NMR, β-**7a**: δ 98.1 (C-1), 81.5 (C-4), 73.6, 70.3 (C-3,5), 62.3 (C-6), 39.0 (C-2), 20.7, 20.6, 20.3 (OAc).

*5-*O*-Acetyl-2,3,6-trideoxy-D-*erythro*-hexofuranose (**9a**).* Reduction of 5-*O*-acetyl-2,3,6-trideoxy-D-*erythro*-hexono-1,4-lactone[2] (1.5 g, 8.7 mmol) with disiamylborane (27 mmol) for 16 h at 20°C as described above gave 1.5 g (100%) of syrupy **9a** in an α:β ration of 5:6. ^{13}C NMR, α-**9a**: δ 98.2 (C-1), 79.2 (C-4), 71.1 (C-5), 32.0 (C-2), 24.1 (C-3), 15.2 (C-6); β-**9a**, 97.8 (C-1), 81.6 (C-4), 71.3 (C-5), 32.8 (C-2), 24.3 (C-3), 15.5 (C-6). The product readily undergoes self-condensation to form mixtures of 1:1-linked disaccharides; it should therefore be used immediately after preparation.

*5-*O*-Acetyl-1-*O*-benzoyl-2,3,6-trideoxy-α-D-*erythro*-hexofuranose (α-**9b**).* Treatment of **9a** (0.55 g) with benzoyl chloride (1.2 ml) in pyridine (10 ml) followed by processing in the usual way gave 0.82 g (93%) of product. Column chromatography using Et_2O–pentane (1:1) as the eluent gave 230 mg (26%) of α-**9b**, m.p. 64–66°C. Recrystallization from pentane gave a product with m.p. 70–71°C, $[\alpha]_D^{20}$ +57.7° (*c* 0.6, $CHCl_3$). Anal. $C_{15}H_{18}O_5$: C, H. ^{1}H NMR: δ 8.1–7.4 (5 H, Bz), 6.59 (br d, 1 H, $J_{1,2}$ 4.0 Hz, $J_{1,2'}$ ca. 0, H-1), 4.98 (dq, 1 H, $J_{5,6}$ 6.5, H-5), 4.34 (dt, 1 H, $J_{4,5}$ 4.5, H-4), 2.3–2.1 (m, 3 H, $J_{3,4}$ 7.5, H-2,2′, H-3), 2.05 (s, 3 H, OAc), 1.88–1.95 (m, 1 H, H-3′), 1.22 (d, 3 H, H-6). ^{13}C NMR: δ 99.6 (C-1), 81.4 (C-4), 71.0 (C-5), 31.4 (C-2), 23.7 (C-3), 21.0 (OAc), 15.6 (C-6).

*2,5-Di-*O*-acetyl-3-deoxy-D-*threo*-pentofuranose (**10a**).* 2,5-Di-*O*-acetyl-3-deoxy-D-*threo*-pentono-1,4-lactone[2] (1.0 g, 4.6 mmol) was reduced with disiamylborane (18.5 mmol)

for 72 h at 20°C to give 1.0 g (100%) of **10a** as a syrup. When only 3 equiv. of the borane had been used 20% of unreduced lactone remained. ^{13}C NMR α-**10a**: δ 100.6 (C-1), 77.8, 75.5 (C-2,4), 66.2 (C-5), 31.5 (C-3), 20.7, 20.5 (OAc); β-**10a**: δ 94.1 (C-1), 73.7, 72.9 (C-2,4), 67.0 (C-5), 29.4 (C-3), 21.4, 20.9 (OAc).

2,5-Di-O-*acetyl-1*-O-*benzoyl-3-deoxy*-α-D-threo-*pentofuranose* (α-**10b**). Benzoylation of crude **10a** (560 mg) with benzoyl chloride in pyridine followed by chromatography, using Et_2O–pentane as the eluent, yielded 400 mg (48%) of α-**10b** as a colourless syrup, $[\alpha]_D^{20}$ +78.0° (*c* 1.5, $CHCl_3$). Anal. $C_{16}H_{18}O_7$: C, H. ^{1}H NMR: δ 8.1–7.3 (5 H, Ph), 6.48 (s, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.53 (dd, 1 H, $J_{2,3}$ 1.9, $J_{2,3'}$ 6.5, H-2), 4.61 (m, 1 H, $J_{4,5}$ 4.5, $J_{4,5'}$ 7.0, H-4), 4.23 (dd, 1 H, $J_{5,5'}$ 11.5, H-5), 4.16 (dd, 1 H, H-5′), 2.66 (ddd, 1 H, $J_{3,3'}$ 14.5, $J_{3,4}$ 8.5, H-3), 1.98 (ddd, 1 H, $J_{3',4}$ 5.0, H-3′). ^{13}C NMR: δ 100.3 (C-1), 77.4, 76.5 (C-2,4), 65.6 (C-5), 32.0 (C-3), 20.6, 20.5 (OAc).

2,5,6-Tri-O-*acetyl-3-deoxy*-D-arabino-*hexofuranose* (**11a**). Reduction of 2,5,6-tri-*O*-acetyl-3-deoxy-D-*arabino*-hexono-1,4-lactone[2] (2.0 g, 6.9 mmol) with disiamylborane (20.8 mmol) for 4 days gave 2.0 g (100%) of **11a** in an α:β ratio of 7:1. ^{13}C NMR, α-**11a**: δ 100.5 (C-1), 77.6, 75.8, 72.2 (C-2,4,5), 62.5 (C-6), 31.1 (C-3), 20.7, 20.6, 20.4 (OAc); β-**11a**: δ 94.2 (C-1), 73.8, 72.9, 72.7 (C-2,4,5), 62.5 (C-6), 29.6 (C-3), 20.7–20.4 (3 OAc).

2,5,6-Tri-O-*acetyl-1*-O-*benzoyl-3-deoxy*-α-D-arabino-*hexofuranose* (α-**11b**). Benzoylation of **11a** (400 mg) with benzoyl chloride in pyridine gave 500 mg of a product which was purified by chromatography, using Et_2O–pentane (3:2) as the eluent, to give α-**11b** as a colourless syrup, $[\alpha]_D^{20}$ +75° (*c* 0.9, $CHCl_3$). Anal. $C_{19}H_{22}O_9$: C, H. ^{1}H NMR: δ 8.0–7.4 (5 H, Bz), 6.46 (s, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.30 (dd, 1 H, $J_{2,3}$ 8.5, $J_{2,3'}$ 1.5, H-2), 5.16 (dt, 1 H, $J_{5,6}$ 3.0, $J_{5,6'}$ 6.0, H-5), 4.50 (dd, 1 H, $J_{6,6'}$ 12.0, H-6), 4.48 (m, 1 H, $J_{4,5}$ 6.5, H-4), 4.12 (dd, 1 H, H-6′), 2.60 (ddd, 1 H, $J_{3,4}$ 2.0, H-3), 2.10, 2.07, 2.02 (OAc), 1.99 (dd, 1 H, $J_{3',4}$ 7.0, H-3′). ^{13}C NMR: δ 133.4–128.3 (Bz), 100.2 (C-1), 77.8, 76.5, 72.0 (C-2,4,5), 62.3 (C-6), 31.7 (C-3), 20.8, 20.6 (3 OAc).

2,5,6-Tri-O-*acetyl-3-deoxy*-D-xylo-*hexofuranose* (**12a**). was prepared from 2,5,6-tri-*O*-acetyl-3-deoxy-D-*xylo*-hexono-1,4-lactone[2] (2.0 g, 6.9 mmol) by reduction with disiamylborane (27.6 mmol) for 48 h. The crude product (2.1 g, 100%) was an α:β mixture (ratio 1:5). ^{13}C NMR, α-**12a**: δ 94.1 (C-1), 74.2, 73.5, 72.9 (C-2,4,5), 62.4 (C-6), 29.0 (C-3), 20.7–29.4 (3 OAc); β-**12a**: δ 100.4 (C-1), 77.6, 75.8, 71.7 (C-2,4,5), 62.8 (C-6), 31.1 (C-3), 20.7, 20.6, 20.4 (OAc).

2,5,6-Tri-O-*acetyl-1*-O-*benzoyl-3-deoxy*-β-D-xylo-*hexofuranose* (β-**12b**). Benzoylation of **12a** (600 mg) gave 800 mg (97%) of a product which was chromatographed, using Et_2O–pentane (2:1) as the eluent, to give β-**12b**, colourless syrup, $[\alpha]_D^{20}$ −28.6° (*c* 1, $CHCl_3$). Anal. $C_{19}H_{22}O_9$: C, H. ^{1}H NMR: δ 8.0–7.4 (Bz), 6.46 (s, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.33 (dd, 1 H, $J_{2,3}$ 6.5, $J_{2,3'}$ 2.0, H-2), 5.25 (ddd, 1 H, $J_{5,6}$ 3.5, $J_{5,6'}$ 7.0, H-5), 4.54 (dt, 1 H, $J_{4,5}$ 5.5, H-4), 4.37 (dd, 1 H, $J_{6,6'}$ 12.0, H-6), 4.16 (dd, 1 H, H-6′), 2.65 (ddd, 1 H, $J_{3,3'}$ 15.0, $J_{3,4}$ 9.0, H-3), 2.12 (2 OAc), 2.03 (OAc), 1.91 (ddd, 1 H, $J_{3',4}$ 6.0, H-3′); ^{13}C NMR: δ 133.3–128.2 (Bz), 100.1 (C-1), 77.8, 76.5, 71.2 (C-2,4,5), 62.7 (C-6), 31.5 (C-3), 20.6, 20.4 (OAc).

2,5,6,7-Tetra-O-*acetyl-3-deoxy*-β-D-gluco-*heptofuranose* (**13a**). 2,5,6,7-Tetra-*O*-acetyl-3-deoxy-D-*gluco*-heptono-1,4-lactone[4] (3.0 g, 8.3 mmol) was reduced with disiamylborane (33.2 mmol) for 48 h to give 3.1 g (100%) of **13** which crystallized from EtOAc–pentane to give 2.1 g (70%) of β-**13a**, m.p. 78–84°C. Recrystallization gave a product with m.p. 80.5–82°C, $[\alpha]_D^{20}$ −10.2→−2.8° (*c* 1.5, $CHCl_3$). Anal. $C_{15}H_{22}O_{10}$: C, H. ^{1}H NMR: δ 5.40 (br s, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.30 (t, 1 H, $J_{5,6}$ 6.0, H-5), 5.23 (dt, 1 H, $J_{6,7}$ 2.5, $J_{6,7'}$ 6.0, H-6), 5.05 (dd, 1 H, $J_{2,3}$ 7.0, $J_{2,3'}$ 2.0, H-2), 4.48 (dt, 1 H, $J_{4,5}$ 5.0, H-4), 4.40 (dd, 1 H, $J_{7,7'}$ 12.0, H-7), 4.20 (dd, 1 H, H-7′), 2.55 (ddd, 1 H, $J_{3,3'}$ 14.5, $J_{3,4}$ 8.0, H-3), 2.13–2.06 (4 OAc), 1.76 (ddd, 1 H, $J_{3',4}$ 6.0, H-3′); ^{13}C NMR: δ 100.3 (C-1), 77.8, 75.3 (C-2,4), 71.1, 70.3 (C-5,6), 61.7 (C-7), 31.3 (C-3), 20.7–20.4 (4 OAc).

2,5,6-Tri-O-*acetyl-3,7-dideoxy*-D-gluco-*heptofuranose* (**13b**). Reduction of 2,5,6-tri-*O*-acetyl-3,7-dideoxy-D-*gluco*-heptono-1,4-lactone[4] (2.0 g, 6.62 mmol) with disiamylborane (27.2 mmol) for 48 h gave 2.1 g (100%) of **13b** (α,β-ratio 1:5) as a syrup. ^{13}C NMR: α-**13b**: δ 94.1 (C-1), 76.3, 74.4, 72.7, 68.3 (C-2,4,5,6), 29.4 (C-3), 20.8–20.5 (3 OAc), 14.7 (C-7); β-**13b**: δ 100.3 (C-1), 78.0 (C-4), 75.8, 74.3, 69.9 (C-2,5,6), 31.8 (C-3), 20.8–20.5 (3 OAc), 14.9 (C-7).

2,5,6-Tri-O-*acetyl-3,7-dideoxy-1*-O-p-*nitrobenzoyl*-β-D-gluco-*heptofuranose* (β-**13c**). Treatment of crude **13b** (0.85 g) with *p*-nitrobenzoyl chloride (1.5 g) in pyridine (10 ml) and processing in the usual manner followed by chromatography with Et_2O–pentane as the eluent gave 310 mg (25%) of β-**13c**, m.p. 73–81°C. Recrystallization from EtOAc–pentane gave a product with m.p. 85–86°C, $[\alpha]_D^{20}$ +35.7° (*c* 1, $CHCl_3$). Anal. $C_{20}H_{23}NO_{11}$: C, H, N. ^{1}H NMR: δ 8.3–8.1 (4 H, ArH), 6.46 (s, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.35 (dd, 1 H, $J_{2,3}$ 6.5, $J_{2,3'}$ 2.5, H-2), 5.25 (dd, 1 H, $J_{5,6}$ 3.8, H-5), 5.03 (dq, 1 H, $J_{6,7}$ 6.5, H-6), 4.46 (dt, 1 H, $J_{4,5}$ 6.0, H-4), 2.63 (p, 1 H, $J_{3,3'}$ 14.0, $J_{3,4}$ 8.0, H-3), 2.15, 2.13, 2.00 (3 OAc), 1.98 (ddd, 1 H, $J_{3',4}$ 6.0, H-3′), 1.26 (d, 3 H, H-7). ^{13}C NMR: δ 134.8–123.5 (Bz), 101.2 (C-1), 78.6, 76.8, 73.9, 69.2 (C-2,4,5,6), 32.2 (C-3), 20.9–20.8 (3 OAc), 14.9 (C-7).

2,6-Dideoxy-3-O-*methyl*-D-arabino-*hexopyranose* (D-*oleandrose*, **2b**). To a solution of **1** (2.0 g) in MeOH (70 ml) was added 1 M methanolic sodium methoxide (18 ml, 2 mol equiv.). The solution was stirred for 2 h and then

neutralized with ion-exchange resin (Amberlite IR-120, H^+) and concentrated. The residue (1.4 g) was chromatographed twice using first Et_2O–MeOH (9:1) and then 2% MeOH in Et_2O as the eluent. The first fraction gave 480 mg (36%) of **2b** as a syrup. ^1H NMR, α-**2b**: δ 5.27 (br d, 1 H, $J_{1,2}$ 1.5 Hz, $J_{1,2'}$ 3.5, H-1), 3.87 (dq, 1 H, $J_{5,6}$ 6.0, H-5), 3.53 (ddd, 1 H, $J_{3,4}$ 9.0, H-3), 3.35 (s, 3 H, OMe), 3.09 (t, 1 H, $J_{4,5}$ 9.0, H-4), 2.22 (ddd, 1 H, $J_{2,2'}$ 12.5, $J_{2,3}$ 11.5, H-2), 1.43 (ddd, 1 H, $J_{2',3}$ 3.5, H-2′), 1.22 (d, 3 H, H-6); ^{13}C NMR, α-**2b**: δ 91.7 (C-1), 77.8, 75.8 (C-3,4), 67.4 (C-5), 56.3 (OMe), 33.9 (C-2), 17.7 (C-6). ^1H NMR, β-**2b**: δ 4.74 (dd, 1 H, $J_{1,2}$ 2.0 Hz, $J_{1,2'}$ 9.5, H-1), 3.48–3.24 (m, 2 H, H-4,5), 3.35 (s, 3 H, OMe), 3.15 (ddd, 1 H, $J_{3,4}$ 13.0, H-3), 2.23 (ddd, 1 H, $J_{2,2'}$ 12.0, $J_{2,3}$ 5.0, H-2), 1.35 (ddd, 1 H, $J_{2',3}$ 11.2, H-2′), 1.28 (d, 3 H, $J_{5,6}$ 6.0, H-6); ^{13}C NMR, β-**2b**: δ 93.7 (C-1), 80.4, 74.9 (C-3,4), 71.6 (C-5), 56.2 (OMe), 36.3 (C-2), 17.6 (C-6).

The second fraction gave 520 mg (39%) of 2,6-dideoxy-D-*arabino*-hexopyranose (D-olivose) (**2a**) as a syrupy α,β-mixture. A ^{13}C NMR spectrum was identical with that reported previously.[1]

*2,6-Dideoxy-3-*O*-methyl-*D-arabino-*hexonic acid phenylhydrazide*. To crude **2b** (200 mg) in water (3.4 ml) was added bromine (0.09 ml) and the mixture was kept for 18 h. The excess of bromine was then removed with air and the solution was neutralized with silver carbonate, filtered and concentrated. The residue was heated at 100°C with phenylhydrazine (0.12 ml) for 0.5 h. Addition of Et_2O precipitated the title compound, which was recrystallized from EtOH, m.p. 133.5–135°C, $[\alpha]_D^{20}$ −19.9° (*c* 0.4, MeOH); (lit.[13] for the L-enantiomer m.p. 135–136°C, $[\alpha]_D$ +20.3°). Anal. $C_{13}H_{20}N_2O_4$: C, H. ^{13}C NMR (D_2O): δ 173.5 (C-1), 130.2–114.2 (Ph), 78.4, 77.5 (C-3,4), 67.6 (C-5), 59.8 (OMe), 36.6 (C-2), 19.3 (C-6).

*Methyl 2,6-dideoxy-3,4-di-*O-p-*nitrobenzoyl-α-D-*arabino-*hexopyranoside (α-***2d***)*. A solution of **1** (700 mg) in MeOH (45 ml) containing KCN (98 mg, 0.5 mol equiv.) was kept overnight. It was then neutralized with an acidic ion-exchange resin (Amberlite IR-120, H^+) and concentrated leaving 410 mg (92%) of 2,6-dideoxy-D-*arabino*-hexose (**2a**), pure as seen from its ^{13}C NMR spectrum. The product was kept overnight in MeOH (10 ml) which contained 3 drops of sulfuric acid. The solution was then neutralized with barium carbonate, filtered and concentrated to leave 400 mg of methyl 2,6-dideoxy-α,β-D-*arabino*-hexopyranoside (**2c**), (α:β ratio 5:1). Subsequent *p*-nitrobenzoylation in pyridine gave 1.0 g (88%) of crude **2d**. Chromatography with Et_2O–pentane (1.1) as the eluent yielded α-**2d**, m.p. 149–150°C, $[\alpha]_D^{20}$ −71° (*c* 0.7, $CHCl_3$); (lit.[1] m.p. 149–151°C, $[\alpha]_D$ −72°).

When **1** (230 mg) was stirred in MeOH (15 ml) with MgO (1.0 g) for 72 h, then filtered and concentrated, 130 mg (88%) of **2a** were obtained. A ^{13}C NMR spectrum showed no other products.

*2,6-Dideoxy-3-*O*-methyl-L-*arabino-*hexopyranose (L-oleandrose,* **4b***)*. Reaction of **3** with methanolic sodium methoxide as described above for the D-enantiomer followed by chromatography gave 38% of **4b**. Oxidation and subsequent reaction with phenylhydrazine as described above yielded 2,6-dideoxy-3-*O*-methyl-L-*arabino*-hexonic acid phenylhydrazide, m.p. 134–135°C, $[\alpha]_D^{20}$ +20.0° (*c* 0.4, MeOH); (lit.[13] m.p. 135–136°C, $[\alpha]_D$ +20.3°).

A second fraction gave 30% of 2,6-dideoxy-L-*arabino*-hexopyranose (L-olivose, **4a**). It was converted into methyl 2,6-dideoxy-3,4-di-*O*-*p*-nitrobenzoyl-α-L-*arabino*-hexopyranoside (α-**4c**) as described above for α-**2d**, m.p. 150–151°C, $[\alpha]_D^{20}$ +70.9° (*c* 0.7, $CHCl_3$). Anal. $C_{21}H_{20}N_2O_{10}$: C, H, N. ^1H and ^{13}C NMR spectra were identical with those of α-**2d**.

*2,6-Dideoxy-L-*ribo-*hexose (L-digitoxose* **6***)*. A solution of **5** (270 mg) in MeOH (15 ml) was stirred with KCN (37 mg) for 2.5 h. The solution was then neutralized with Amberlite IR-120(H^+), filtered and concentrated. The residue (160 mg, 94%) contained only **6** as seen from its ^{13}C NMR spectrum.[3] Recrystallization from acetone gave a product with m.p. 104–105°C, $[\alpha]_D^{20}$ −46.8° (*c* 0.5, H_2O); (lit.[14] m.p. 105–107°C, $[\alpha]_D$ −47.0°).

When the deacetylation of **5** was carried out with sodium methoxide (0.2 mol equiv.) in MeOH as described above the main product was **6** in admixture with ca. 20% of an *O*-methyl derivative.

*2-Deoxy-β-L-*ribo-*hexopyranose (β-***8***)*. A solution of **7a** (800 mg) was treated with KCN as described above to give 460 mg (100%) of **8**. A ^{13}C NMR spectrum showed that it was a mixture of the α- and β-pyranoses and small amounts of the furanoses. Crystallization from EtOH gave 100 mg (22%) of β-**8**, m.p. 135–137°C. Recrystallization gave a product with m.p. 136–137°C, $[\alpha]_D^{20}$ −49.4→−55.5° (*c* 0.6, H_2O); (lit.[15] for the D-enantiomer, m.p. 135–136°C, $[\alpha]_D$ +57.9°). Anal. $C_6H_{12}O_5$: C, H. ^{13}C NMR (D_2O): δ 92.4 (C-1), 74.5 (C-4), 68.3, 67.7 (C-3,5), 62.3 (C-6), 38.9 (C-2).

*2,3,6-Trideoxy-D-*erythro-*hexose (amicetose)* was obtained by treatment of **9a** (500 mg) in MeOH (20 ml) with 1 M methanolic sodium methoxide (0.7 ml, 0.25 mol equiv.) for 1 h followed by neutralisation and concentration as described above. The product was a mixture of furanoses and pyranoses as seen from the ^{13}C NMR spectrum. Treatment with 2,4-dinitrophenylhydrazine in 2 M hydrochloric acid precipitated 2,3,6-trideoxy-D-*erythro*-hexose 2,4-dinitrophenylhydrazone, which was recrystallized from MeOH–benzene, m.p. 151–152°C, $[\alpha]_D^{20}$ −9.8° (*c* 0.5, pyridine); (lit.[16] m.p. 152–153°C, $[\alpha]_D$ −10.0°).

*3-Deoxy-α-D-*gluco-*heptopyranose (***14***)*. Treatment of **13a** (1.7 g), 4.5 mmol) with sodium methoxide (4.5 mmol) in MeOH (45 ml) for 50 min, followed by neutralisation and evaporation, gave a syrup which crystallized from EtOH–water to give 500 mg (55%) of **14**, m.p. 115–120°C.

Recrystallization from 2-propanol gave a product with m.p. 126–128 °C, $[\alpha]_D^{20}$ +55.0→+9.6° (*c* 1.5, H_2O); {lit.[17] m.p. 126–128 °C, $[\alpha]_D$ +10° (equil.)}.

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