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Mercuration-Reductive Demercuration of Glycals: a Mild and Convenient Entry to 2-Deoxy-Sugars.

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Abstract: Protected glycals, derived from mono-, di- and tri-saccharides, were easily and efficiently converted into the corresponding 2-deoxy-sugars, by reaction with mercuric(II) acetate/sodium borohydride in a polar solvent at 0 °C. The mild and non acidic reaction conditions permit the survival of acid-labile groups, such as silyl ethers. © 1998 Elsevier Science Ltd. All rights reserved.

2-Deoxy-sugars are versatile building blocks in organic chemistry for many purposes, particularly in the synthesis of biologically active natural products.[1] As a rule, glycals have been proven to be the most valuable source for the synthesis of 2-deoxy-sugars and several methodologies are currently available.[1,2]

Benzyl-protected glycals are usually converted by acids into the corresponding 2-deoxy-sugars.[2] However, many protecting groups are acid sensitive.

Over the past years, mercuration-reductive demercuration has been extensively employed in carbohydrate chemistry for many purposes.[3] In particular, this sequence has been used to convert glycals into glycosides[4] and as a means of accessing mixed acetals.[5] However, this methodology has been rarely and occasionally described for obtaining 2-deoxy-sugars: the only reported applications concern the conversion of 1,4-anhydro-2-deoxy-5,6-*O*-isopropylidene-D-*arabino*-hex-1-enitol into the 2-deoxy-derivative and two similar molecules.[6] More recently and in spite of the above reported method, the transformation of a protected D-galactose into the corresponding 2-deoxy-derivative has been achieved by a multistep sequence, such as the addition of phenylsulfenyl chloride to the protected glycal, the ensuing hydrolysis of the chloride group and then the reductive removal of thiophenyl group by treatment with *n*-Bu_3SnH/AIBN.[2]

To our knowledge, hydration through the mercuration-demercuration strategy has not been exploited fully to date in the conversion of glycals into 2-deoxy-sugars.[7]

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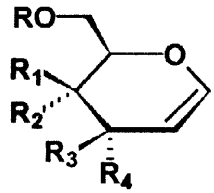
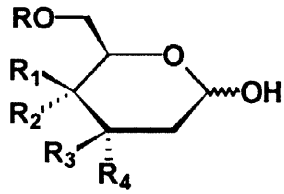
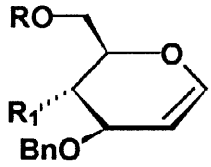
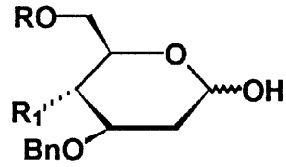
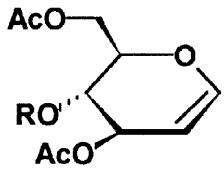
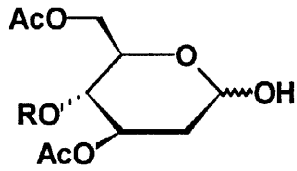
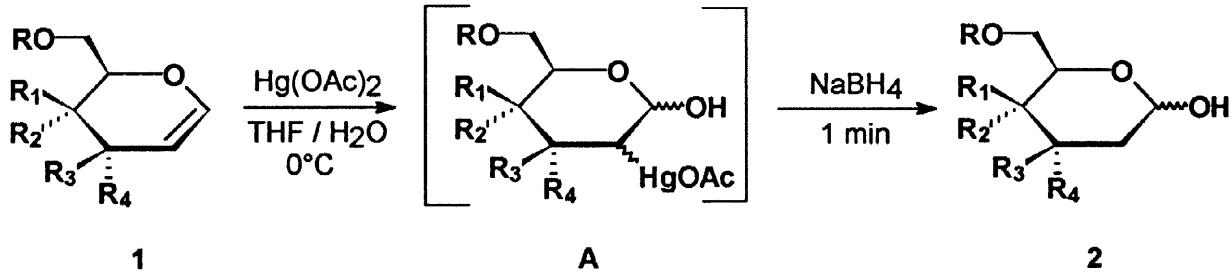
The lack of a systematic study prompted us to investigate this reaction as a general protocol for obtaining 2-deoxy-sugars, particularly for more complex structures, such as glycals derived from di- and tri-saccharides.

We report herein our findings that the mercuration-reductive demercuration sequence can be utilised as a general, mild and efficient method to prepare 2-deoxy-sugars from glycals. The overall transformation is a fast, one pot formal Markownikoff addition of H_2O to the cyclic enol-ethers under non-acidic conditions, which must be considered an interesting outcome. All the reactions have been performed at 0 °C, in a 1:4 H_2O/THF solvent mixture for the mercuration, whereas a 4:1 H_2O/THF ratio has been employed to accomplish the subsequent reductive step. (Table 1)

Table 1. Synthesis of 2-deoxy-sugars **2** from glycals **1** by mercuration-demercuration

Entry	1			2		Yield (%)
						
a	R=Bn	R_1=H	R_2=OBn	R_3=Bn	R_4=H	87
b	R=Ac	R_1=H	R_2=OAc	R_3=OAc	R_4=H	86
c	R=TIPS	R_1=OAc	R_2=H	R_3=OTIPS	R_4=H	90
d	R=Bn	R_1=OBn	R_2=H	R_3=OBn	R_4=H	84
e	R=Ac	R_1=OAc	R_2=H	R_3=OAc	R_4=H	88
f	R=Bn	R_1=H	R_2=OBn	R_3=H	R_4=OBn	84
						
g	R=(tetra-*O*-benzyl-α-D-galactopyranosyl); R_1=OBn					86
h	R=Bn; R_1=O(tetra-*O*-benzyl-β-D-glucopyranosyl)					91
i	R= Bn ; R_1=O(tetra-*O*-benzyl-β-D-galactopyranosyl)					86
						
j	R= Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-(2,3,6-tri-*O*-acetyl)-α-D-glucopyranosyl					93

The results can be explained by referring to the previously proposed mechanism for these reactions, with the formation of a reactive intermediate, such as **A**, by the electrophilic addition of mercuric(II) acetate to the cyclic enol-ether **1**, and followed then by intermolecular assistance of the solvent.[8] (Scheme 1)



1 **A** **2**

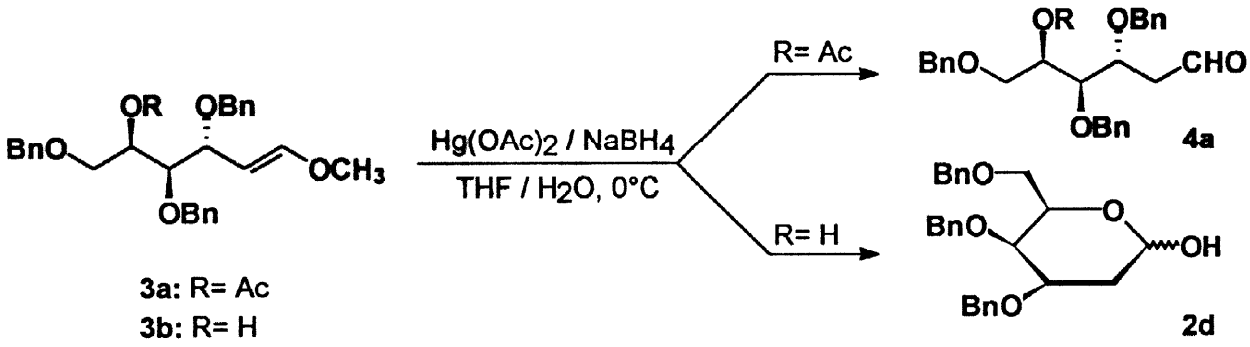
Scheme 1

Both solvent composition and reaction temperature play a pivotal role on the outcome of the subsequent reductive demercuration.[9] The best results were obtained by carrying out the reactions at 0 °C in a strong polar medium, which would favour the demercuration of the intermediate organomercurial **A** into 2-deoxy-sugars **2** by reaction with sodium borohydride. In fact, the reduction times point out a very fast demercuration rate (1 min) and the observed effect of the solvent, which can be explained in terms of the mechanism involving solvent-cage reactions, is consistent with these data.[9]

Different experimental conditions, such as either the solvent polarity or the reaction temperatures or longer reduction times, give rise to the formation of side-products, stemming from competing ionic and/or radical reactions.[9]

A recent report describes the conversion of alkyl enol-ethers into the corresponding alcohols by treatment with $Hg(OAc)_2$ at 0 °C in a near 2:1 H_2O/THF solvent mixture and leaving the reaction at room temperature after reduction with $NaBH_4$.[10] However, the crucial role played by the experimental conditions was witnessed by a parallel experiment carried out using an alkyl enol-ether, such as 5-*O*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-1-*O*-methyl-D-*lyxo*-hex-1-enitol **3a**,[11] which was easily converted into the saturated aldehyde **4a** in a 88% yield by reaction with $Hg(OAc)_2/NaBH_4$ in a 4:1 H_2O/THF solvent mixture at 0 °C, without the formation of the alcoholic derivative. Interestingly, the reaction sequence performed on **3b** (R=H) spontaneously led to the formation of 3,4,6-tri-*O*-benzyl-2-deoxy-D-galactose **2d** in very high yields (90%), by intramolecular ring closure of the aldehydic function. (Scheme 2)

The procedure is of high synthetic value, and it shows a wide generality, as demonstrated by the variety of protected glycals, such as D-glucal derivatives **1a-b**, D-galactal derivatives **1c-e** and tri-*O*-benzyl-D-allal (**1f**), that can be converted into 2-deoxy-sugars. More complex compounds, such as the perbenzylated derivatives of D-melibial **1g**, D-cellobial **1h**, D-lactal **1i** and the peracetylated derivative of D-maltotrial **1j** were cleanly converted into the corresponding 2-deoxy-derivatives.



Scheme 2

It is worth noting that these compounds represent a challenging target not easily available. More significantly, the non-acidic conditions are consistent with the presence of acid-sensitive protecting groups, such as silyl ethers, (entry 1c), which survive the experimental conditions. Moreover, the reaction can be successfully applied to linear alkyl enol-ethers, such as 3a, providing directly only the aldehydic compound. This result can be considered a useful synthetic goal, since it allows to avoid oftentimes troublesome oxidation steps of the primary alcoholic function in compounds with several stereogenic centres. Particularly, all the chiral centres have been conserved, while the acidic treatment gives rise quantitatively to the formation of the corresponding α,β-unsaturated aldehydes, losing a chiral centre.[11b]

In conclusion, we have developed a general, one-pot method for the synthesis of 2-deoxy-sugars from glycals under non acidic conditions. Our studies broaden the utility of the mercuration-reductive demercuration sequence, opening new routes to synthetic applications in organic chemistry. We continue to investigate other aspects of this reaction and its mechanism.

Experimental Section

General Experimental: All common solvents and reagents were purchased and used as received. Reactions were monitored on TLC (silica gel 60 F_{254}, Merck). Detection was performed using UV light (all *O*-benzyl derivatives) or sulfuric acid (all glycals or glycosyl moieties). Chromatographies were performed using silica gel 60 (230-400 mesh) and eluted with the solvent mentioned. ^{1}H-NMR spectra were recorded either at 200 or 300 MHz in $CDCl_3$ soln, and ^{13}C-NMR were recorded either at 50.3 or 75.4 MHz in $CDCl_3$ soln. As criteria of identity and degree of purity, we utilised TLC, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis.

Starting Materials.-All glycals **1a-f** were prepared following standard procedures.[12] The glycosyl glycals **1g-j** were prepared following known procedures from their corresponding di- or trisaccharides.[13]

Typical experimental procedure: a solution of the protected glycal **1** (0.12 mmol) in 4 ml of THF was cooled to 0 °C and treated with 0.18 mmol of $Hg(OAc)_2$ dissolved in H_2O (1 ml). After disappearance of the substrate, detected on TLC (generally 30 min), the mixture was diluted with 15 ml of H_2O, reaching a 4:1 H_2O/THF ratio solvent. Then, at 0 °C, 0.72 mmol of $NaBH_4$ were added and after 1 min the reaction mixture

was treated with bubbling CO_2 until pH ~7. The suspension was extracted twice with EtOAc (50 mlx2). The combined extracts were washed with brine and dried (Na_2SO_4). After evaporation of the solvent, the crude 2-deoxy-sugars **2** were chromatographed on silica gel (hexane-ether). Yields are calculated after purification.

3,4,6-Tri-*O*-benzyl-2-deoxy-D-*arabino*-hexopyranose (2a) [2b]

From 3,4,6-tri-*O*-benzyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol, **1a** (D-glucal derivative, 100 mg, 0,24 mmol): 90 mg, 0.21 mmol (87 %), colourless oil. ^{13}C-NMR ($CDCl_3$, δ): 139.10, 139.06, 138.89, 138.36, 128.89, 128.83, 128.51, 128.44, 128.17, 128.09 (CH_2Ph); 94.61, 92.60 (C1); 79.68, 79.07, 77.54, 75.42, 72.29, 71.22, 69.81, 69.72 (C3, C4, C5, C6); 75.42, 75.31, 73.95 ($\underline{C}H_2Ph$); 36.37, 35.97 (C2). Anal.Calcd. for $C_{27}H_{30}O_5$: C, 74.65, H, 6.91. Found: C, 74.23, H, 6.20.

3,4,6-Tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranose (2b) [14]

From 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol **1b** (D-glucal derivative, 100 mg, 0.37 mmol): 92 mg, 0.32 mmol (86 %), colourless oil. ^{1}H-NMR ($CDCl_3$, δ): 5.44 (H-C1, bs); 2.45-1.75 (2H-C2, m); 2.11-2.0 ($\underline{C}H_3CO$, s). ^{13}C-NMR ($CDCl_3$, δ): 171.37, 170.77, 170.48 ($CH_3\underline{C}O$); 94.35, 92.21 (C1); 72.62, 70.91, 69.66, 69.26, 69.16, 68.50, 62.93 (C3, C4, C5, C6); 37.95, 35.53 (C2); 21.49, 21.42, 21.26, 21.08 ($\underline{C}H_3CO$). Anal. Calcd. for $C_{12}H_{18}O_8$: C, 52.90, H, 6.67. Found: C, 52.88, H, 6.16.

4-*O*-Acetyl-1,5-anhydro-2-deoxy-3,6-di-*O*-TIPS-D-*lyxo*-hex-1-enitol (1c)

A solution of 1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (D-galactal, 100 mg, 0.68 mmol) in DMF (3 ml) was treated with imidazole (143 mg, 2.1 mmol) and with TIPSCl (270 mg, 1.4 mmol). The resulting mixture was stirred at r.t. under N_2 for 12 h, diluted with water and extracted twice with ethyl acetate (50 mlx2). The organic phase, washed with brine until neutrality, was dried (Na_2SO_4). After the evaporation, the residue was chromatographed on silica gel (hexane-ether 95:5) to give 1,5-anhydro-2-deoxy-3,6-di-*O*-TIPS-D-*lyxo*-hex-1-enitol as colourless oil (282 mg, 0.612 mmol, 92% yield). Then a portion of this material (100 mg, 0.22 mmol), dissolved in pyridine (1 ml), was stirred overnight at r.t. with Ac_2O (0.5 ml). After the addition of methanol at 0 °C (2 ml, 5 min.), the solution was diluted with ethyl acetate (50 ml), cooled with ice, washed with HCl 6N (4 ml) and then brine until neutrality, dried (Na_2SO_4) and evaporated, giving 4-*O*-acetyl-1,5-anhydro-2-deoxy-3,6-di-*O*-TIPS-D-*lyxo*-hex-1-enitol (**1c**) as a crude colourless oil in quantitative yield. ^{13}C-NMR spectrum ($CDCl_3$, δ): 169.98 ($\underline{C}OCH_3$); 143.24 (C1); 103.69 (C2); 76.30 (C5); 66.29, 66.56 (C3, C4); 61.37 (C6); 20.83 ($\underline{C}H_3CO$); 17.79 ($\underline{C}HSi$); 12.06, 11.78 [$(\underline{C}H_3)_2CHSi$]. Anal. Calcd. for $C_{26}H_{52}O_5Si_2$: C, 62.40, H, 10.40. Found: C, 60.39, H, 10.07.

4-*O*-Acetyl-2-deoxy-3,6-di-*O*-TIPS-D-*lyxo*-hexopyranose (2c)

From 4-*O*-acetyl-1,5-anhydro-2-deoxy-3,6-di-*O*-TIPS-D-*lyxo*-hex-1-enitol **1c** (D-galactal derivative, 100 mg, 0.20 mmol); 93.2 mg, 0.18 mmol (90 %), colourless oil.^{13}C-NMR spectrum ($CDCl_3$, δ): 169.95 ($CH_3\underline{C}O$); 94.39, 92.68 (C1); 74.59, 70.41, 69.64, 68.51, 67.89, 64.79, 62.36, 61.86 (C3, C4, C5, C6); 37.97, 34.53 (C2);

20.58 (CH$_3$CO); 17.87 (CHSi); 12.13, 11.84 [(CH$_3$)$_2$CHSi]. Anal. Calcd. for $C_{26}H_{54}O_6Si_2$: C, 60.23, H, 10.42. Found: C, 60.20, H, 10.12.

3,4,6-Tri-*O*-benzyl-2-deoxy-D-*lyxo*-hexopyranose (2d)

From 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*lyxo*-hex-1-enitol, **1d** (D-galactal derivative, 100 mg, 0.24 mmol): 88 mg, 0.20 mmol (84 %), colourless oil. From 3,4,6-tri-*O*-benzyl-2-deoxy-1-*O*-methyl-D-*lyxo*-hex-1-enitol, **3b** (100 mg, 0.22 mmol): 89 mg, 0.20 mmol (90 %), colourless oil. ^{1}H-NMR ($CDCl_3$, δ): 5.46 (1H, bd, $J_{1,2}$=3,5Hz); 5.00-4.39 (6H, 3CH$_2$Ph, fs,); 4.12 (1H, pt, $J_{4,3}$=$J_{4,5}$=7Hz); 4.0 (H-C3, m); 3.65-3.40 (2H-C6, fs); 2.27-1.92 (2H-C2, m).^{13}C-NMR ($CDCl_3$, δ): 138.45, 138.36, 137.67, 128.27, 128.22, 128.08, 128.02, 127.61, 127.53, 127.44, 127.40, 127.16 (CH$_2$Ph); 94.54, 92.39 (C1); 74.19, 73.99, 73.29 (CH$_2$Ph), 72.97, 71.65, 70.31, 70.08, 69.79, 69.0 (C3, C4, C5, C6); 34.24, 30.92 (C2). Anal.Calcd. for $C_{27}H_{30}O_5$: C, 74.65, H, 6.91. Found: C, 74.61, H, 6.25.

3,4,6-Tri-*O*-acetyl-2-deoxy-D-*lyxo*-hexopyranose (2e)

From 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol **1e** (D-galactal derivative, 100 mg, 0.37 mmol): 94 mg, 0.32 mmol (88 %), colourless oil. ^{13}C-NMR ($CDCl_3$, δ): 171.25, 170.60, 170.22 (CH$_3$CO); 94.28, 91.85 (C1); 67.32, 65.95, 64.45, 62.82, 62.51, 62.02 (C3, C4, C5, C6); 35.82, 31.45 (C2); 21.39, 21.20, 21.16, 21.08 (CH$_3$CO). Anal. Calcd. for $C_{12}H_{18}O_8$: C, 52.90, H, 6.67. Found: C, 52.89, H, 6.10.

3,4,6-Tri-*O*-benzyl-2-deoxy-D-*ribo*-hexopyranose (2f)

From 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*ribo*-hex-1-enitol, **1f** (D-allal derivative, 100 mg, 0.24 mmol): 89 mg, 0.20 mmol (84 %), colourless oil. ^{13}C-NMR ($CDCl_3$, δ): 138.95, 138.69, 138.56, 138.44, 129.05, 128.88, 128.49, 128.45, 128.32, 128.23, 128.14 (CH$_2$Ph); 93.05, 92.77 (C1); 75.78, 75.58, 72.05, 71.85, 71.61, 70.23, 69.55, 67.12 (C3, C4, C5, C6); 74.11, 73.80, 73.11, 72.33 (CH$_2$Ph); 36.69, 34.47 (C2). Anal.Calcd. for $C_{27}H_{30}O_5$: C, 74.65, H, 6.91. Found: C, 74.64, H, 6.18.

3,4-Di-*O*-benzyl-2-deoxy-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-D-glucopyranose (2g)

From 1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-D-*arabino*-hex-1-enitol **1g** (D-melibial derivative, 100 mg, 0.12 mmol): 88 mg, 0.10 mmol (86 %),colourless oil. ^{1}H NMR ($CDCl_3$, δ): 5.30 (H-C1, m); 4.90-4.30 (6H, 3CH$_2$Ph, bm); 4.18 (H-C4, bm); 4.0 (H-C3, m); 3.75 (2H-C6, m); 3.53 (H-C5, fs); 2.35-1.45 (2H-C2, m). ^{13}C-NMR ($CDCl_3$, δ): 138.95, 138.69, 138.56, 138.44, 129.05, 128.88, 128.49, 128.45, 128.32, 128.23, 128.14 (CH$_2$Ph); 100.12, 99.0 (C1' acetal); 93.05, 92.77 (C1 hemiacetal); 75.78, 75.58, 74.11, 74.03, 73.80, 73.11, 72.33, 72.05, 71.85, 71.61, 70.23, 69.55, 67.12 (C3, C4, C5, C6, C2', C3', C4', C5', C6', CH$_2$Ph); 36.69, 34.47 (C2). Anal. Calcd. for $C_{54}H_{58}O_{10}$: C, 74.82, H, 6.69. Found: C, 74.84, H, 6.41.

3,6-Di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-D-glucopyranose (2h)

From 1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-glucopyranosyl)-D-*arabino*-hex-1-enitol **1h** (D-cellobial derivative, 100 mg, 0.12 mmol): 91 mg, 0.11 mmol (91 %), colourless oil. ^{1}H-NMR

($CDCl_3$, δ): 5.39 (H, bs, hemiacetal); 2.37-1.55 (2H-C2, m). ^{13}C-NMR ($CDCl_3$, δ): 139.34, 138.54, 138.45, 138.30, 138.20, 137.87, 128.34, 128.24, 128.10, 127.91, 127.80, 127.69, 127.40 (CH_2Ph); 102.72, 102.56 (C1' acetal); 93.94, 91.81 (C1 hemiacetal); 84.81, 82.66, 78.60, 76.18, 75.49, 75.39, 73.92, 73.83, 72.85, 72.38, 69.36, 69.24, 63.52 (C3, C4, C5, C6, C2', C3', C4', C5', C6', CH_2Ph); 37.80, 35.76 (C2). Anal. Calcd. for $C_{54}H_{58}O_{10}$: C, 74.82, H, 6.69. Found: C, 74.80, H, 6.13.

3,6-Di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucopyranose (2i)

From 1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-*arabino*-hex-1-enitol **1i** (D-lactal derivative, 100 mg, 0.12 mmol): 89 mg, 0.10 mmol (86 %), colourless oil. ^{13}C-NMR ($CDCl_3$, δ): 138.91, 138.69, 138.62, 138.50, 137.92, 128.29, 128.24, 128.13, 128.09, 127.97, 127.89, 127.80, 127.68, 127.50, 127.38, 127.31 (CH_2Ph); 103.23 (C1' acetal); 94.25, 91.87 (C1 hemiacetal); 82.65, 79.36, 78.33, 76.20, 74.92, 74.73, 73.46, 73.36, 73.05, 72.85, 72.49, 70.82, 69.03, 68.35 (C3, C4, C5, C6, C2', C3', C4', C5', C6', CH_2Ph); 37.91, 35.73 (C2). Anal. Calcd. for $C_{54}H_{58}O_{10}$: C, 74.82, H, 6.69. Found: C, 74.81, H, 6.50.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-deoxy-D-glucopyranose (2j)

From 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol, **1j** (D-maltotrial derivative, 100 mg, 0.12 mmol): 97 mg, 0.11 mmol (93 %), colourless oil. ^{13}C-NMR spectra ($CDCl_3$, δ): 171.37, 170.95, 170.62, 170.52, 170.36, 170.29, 169.96 (CH_3CO); 96.12, 95.99 (C1', C1" acetals); 93.81, 91.67 (C1 hemiacetal); 77.75, 74.51, 73.18, 72.91, 72.62, 72.34, 71.73, 71.07, 70.56, 69.85, 69.19, 68.90, 68.35, 64.12, 62.68, 61.81 (C3, C4, C5, C6, C2', C3', C4', C5', C6', C2", C3", C4", C5", C6"); 37.66, 35.37 (C2). Anal. Calcd. for $C_{36}H_{50}O_{24}$: C, 49.88, H, 5.77. Found: C, 49.88, H, 5.32.

5-*O*-Acetyl-1-al-3,4,6-tri-*O*-benzyl-2-deoxy-D-*lyxo*-hexanitol (4a)

From 5-*O*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-1-*O*-methyl-D-*lyxo*-hex-1-enitol, **3a** (100 mg, 0.20 mmol): 84 mg, 0.18 mmol (88 %), colourless oil, $[\alpha]_D^{20}$ = - 40.2° (c=2.1, $CHCl_3$). ^{1}H-NMR spectra ($CDCl_3$, δ): 9.75 (1H, CHO, bs); 5.25 (1H, q, $J_{5.6a}$=$J_{5.4}$=4.4Hz); 4.70-4.40 (6H, 3CH_2Ph, fs); 4.15 (H, q, $J_{4.5}$=$J_{4.3}$=4.1Hz); 3.94 (H, t, $J_{3.4}$=$J_{3.2a}$=3.0Hz); 3.60 (2H-C6, fs); 2.75 (2H-C2, m); 2.05 (CH_3CO, s). ^{13}C-NMR spectra ($CDCl_3$, δ): 201.0 (CHO); 170.87 (CH_3CO); 138.33, 138.13, 128.95, 128.89, 128.78, 128.50, 128.34 (CH_2Ph); 78.67, 75.24, 74.99, 73.84, 72.65, 72.38, 68.65 (C3, C4, C5, C6, CH_2Ph); 45.65 (C2); 21.58 (CH_3CO). Anal. Calcd. for $C_{29}H_{32}O_6$: C, 73.10, H, 6.72. Found: C, 73.08, H, 6.24.

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