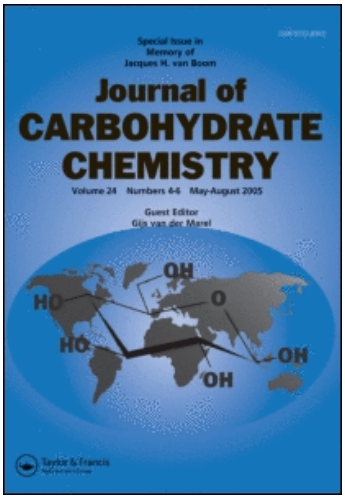

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THE ROLE OF THE C-3 SUBSTITUENT IN THE ASYMMETRIC DIHYDROXYLATION OF HEXO-5-ENOFURANOSIDES

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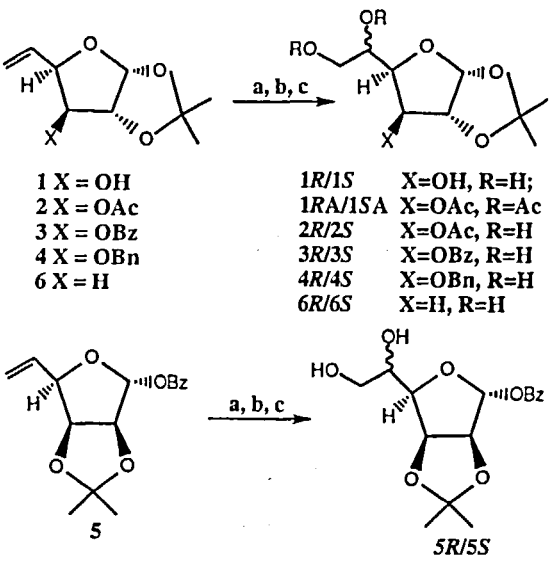
ABSTRACT

Asymmetric dihydroxylation of vinyl furanosides **1-6** by use of OsO_4, AD-mix-α® and β® is described yielding the corresponding hexofuranose sugars. Vinyl furanosides **2** and **3**, with an ester group at C-3, and vinyl manno furanoside **5** on asymmetric dihydroxylation with AD-mix-α® exhibited high ***R*** diastereoselectivity at C-5. Reversal in diastereoselectivity at C-5 was observed for the 3-deoxy vinyl furanoside **6** giving furanosaccharide **6*S*** with the ***S*** configuration at C-5.

INTRODUCTION

Recent advances in the catalytic asymmetric dihydroxylation (AD) of olefins by Sharpless have led to development of new systems such as AD-mixα® and AD-mixβ®, formulations that have simplified performing asymmetric dihydroxylation reactions on a millimolar scale in good to excellent enantiomeric excess.[1] Applicability of this process improvement was earlier demonstrated to a wide range of olefins.[1,2] Application of asymmetric dihydroxylation to anomeric C- and O-allyl carbohydrate derivatives has been earlier reported to show moderate diastereoselectivity.[3,4] Our interest lies in the utility of these reactions to synthesise L-sugars of synthetic and other wide ranging utilities.



Scheme 1. i) Catalytic reagent systems a,b and c; a=OsO_4/NMO/acetone-H_2O/ 0 °C/26 h; b=AD-mix-α/*t*-BuOH-H_2O/0 °C/96 h; c=AD-mix-β/*t*-BuOH-H_2O/0 °C/ 96 h

This study was intended to achieve the preparation of rare L-sugars by asymmetric dihydroxylation of vinyl furanose derivatives by choice of AD-mix (α/β)® reagents.

RESULTS AND DISCUSSION

We undertook study of asymmetric dihydroxylation of vinyl furanosides **1-6** by use of three catalytic reagent systems: **a)** OsO_4 - NMO - acetone - H_2O at 0 °C; b) AD mix α- *t*-BuOH-H_2O at 0 °C and **c)** AD mix β-*t*-BuOH-H_2O at 0 °C (Scheme 1).

Thus, 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-5-enofuranose **1**[5,6] on vicinal dihydroxylation with reagent system **a** gave an inseparable diastereomeric mixture of furanosaccharides **1*R*** (***R*** configuration at C-5) and **1*S*** (***S*** configuration at C-5) in a ratio of 1.4:1.0 as determined from the integration of the clearly distinguishable anomeric proton signals (Table, entry i) in the product ^1H NMR spectrum. In order to achieve good diastereoselectivity towards formation of a rare sugar with the ***S*** configuration at C-5, **1** was reacted with reagent system **b** to obtain a diastereomeric mixture **1*R*/1*S*** in a ratio of 2.1:1.0 where a marginal increase towards the formation of **1*R*** diastereomer was observed. Asymmetric dihydroxylation of **1** with catalytic reagent system **c** resulted in the formation of **1*R*/1*S*** in a ratio of 4.0:1.0 (entry i) indicating a marked increase in

Table. **Diastereomeric excesses of the diols obtained from catalytic asymmetric dihydroxylation (AD)[a]**

Entry	Olefin	OsO_4-NMO reagent **a** Ratio of diols[b] *R*:*S*	AD-mix-α® reagent **b** Ratio of diols *R*:*S*	AD-mix-β® reagent **c** Ratio of diols *R*:*S*
i	**1**	1.4 : 1.0	2.1 : 1.0	4.0 : 1.0
ii	**2**	1.6 : 1.0	9.0 : 1.0	4.0 : 1.0
iii	**3**	1.5 : 1.0	9.8 : 1.0	2.9 : 1.0
iv	**4**	2.7 : 1.0	3.0 : 1.0	2.0 : 1.0
v	**5**	4.0 : 1.0	11.0 : 2.0	2.5 : 1.0
vi	**6**	1.0 : 1.8	1.0 : 7.0	1.0 : 1.8

a. Diastereomeric excesses determined by ^{1}H NMR of diols and their corresponding diacetate derivatives. b. ***R*** and ***S*** configuration at C-5 was determined by comparison of ^{1}H NMR spectra with that of authentic diols and/or their diacetate derivatives.

diastereoselectivity. The diastereomeric mixture of **1*R* / 1*S*** derived from reagent system **a** was characterised by comparison of the ^{1}H NMR data with that from an authentic sample of **1*R*** [5,7] and from the chemical shift values of the anomeric protons. In the ^{1}H NMR spectrum of **1*R* /1*S*** two signals appeared for the anomeric proton (H-1) at δ 6.05 and δ 6.08, respectively, and in the authentic **1*R***[5,7] at δ 6.05. **1*R* /1*S*** was also characterised as the corresponding triacetate derivative **1*R*A/1*S*A**. In the ^{1}H NMR spectrum of **1*R*A/1*S*A** two signals appeared for H-6 protons at δ 4.10 and δ 3.90, respectively, and in the authentic **1*R*A**[7] H-6 appeared at δ 4.10.

In order to study the role of a C-3 substituent in asymmetric dihydroxylations, **1** was converted to 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-5-enofuranose **2**.[5,6] Asymmetric dihydroxylation of **2**, possessing an ester group, with reagent system **a** gave a diastereomeric mixture of **2*R*** (***R*** configuration at C-5) / **2*S*** (***S*** configuration at C-5) in a ratio of 1.6:1.0 (Table, entry ii). A similar reaction of **2** with catalytic system **b** resulted in the formation of **2*R* / 2*S*** diastereomers in a ratio of 9.0:1.0

indicating significant selectivity for the formation of a saccharide with ***R*** configuration at C-5. Reaction of **2** with reagent system **c** resulted in the formation of a diastereomeric mixture of ***2R /2S*** in a ratio of 4.0:1.0, characterised by comparison of ^{1}H NMR data with that of the distinct chemical shifts of the anomeric protons for authentic ***2R***.[5,7] In the ^{1}H NMR spectrum of ***2R /2S*** two signals appeared for anomeric proton (H-1) at δ 6.00, δ 5.95, respectively, while the anomeric proton in authentic ***2R***[5,7] appeared at δ 6.00. Thus, introduction of an electron withdrawing group at C-3 enhanced the formation of ***2R*** (entry ii). Reaction of 3-*O*-benzoyl derivative **3**[6] in reagent systems **a, b** and **c** resulted in the formation of ***3R***[7]***/3S*** diastereomers in a ratio of 1.5:1.0, 9.8:1.0 and 2.9:1.0 respectively (entry iii). Once again the effect of an electron withdrawing group at C-3 improved selectivity for the formation of a saccharide with ***R*** configuration at C-5 in reagent system **b**. The diastereomeric mixture ***3R /3S*** was characterised in analogous fashion to ***2R /2S*** from ^{1}H NMR data by comparison with that from authentic ***3R***.[7]

We then sought to reverse the diastereoselectivity in the AD reactions by protecting C3-OH as a benzyl ether. Asymmetric dihydroxylation of 3-*O*-benzyl derivative **4**[8] resulted in the formation of ***4R /4S*** in a ratio of 2.7:1.0, 3.0:1.0 and 2.0:1.0, respectively, in reagent systems **a-c** (entry iv). The diastereomeric mixture of ***4R /4S*** was characterised by comparison of the anomeric proton ^{1}H NMR data with that from the authentic ***4R***. In the ^{1}H NMR spectrum of ***4R /4S***, two anomeric proton (H-1) signals appeared at δ 5.89 and δ 5.96, respectively, and in the authentic ***4R***[9] the anomeric proton appeared at δ 5.89. The presence of an ether function at C-3 did not improve selectivity, the benzyl group being electron donating in contrast to acyl groups which are electron withdrawing.

Asymmetric dihydroxylation of 1-*O*-benzoyl-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-5-eno-furanoside (**5**) with reagent systems **a, b** and **c** gave ***5R /5S*** in a ratio of 4.0:1.0, 11.0:2.0 and 2.5:1.0, respectively (entry v). The diastereomeric mixture of ***5R /5S*** was characterised by comparison of the ^{1}H·NMR, H-1 and H-2 proton spectrum data with that from authentic ***5R***.[10] In the ^{1}H NMR spectrum of ***5R /5S*** two pairs of signals appeared for H-1,2 protons at δ 6.38, δ 6.41 and δ 4.83, δ 4.87, respectively. H-1,2 protons in the authentic ***5R*** appeared at δ 6.38 and δ 4.83, respectively. Once again selectivity for the formation of a saccharide with ***R*** configuration at C-5 was observed in reagent system **b**.

It was pertinent to assess the role of the substituent at C-3, hence the 3-deoxy derivative **6**[11] was prepared and subjected to asymmetric dihydroxylation using the three catalytic reagent systems **a,b** and **c**, respectively, to yield ***6R/6S***, respectively, in ratios of 1.0:1.8, 1.0:7.0 and 1.0:1.8 (entry vi), indicating a clear reversal of diastereoselectivity with the AD-mix-α® compared to vinyl furanoside **1-5**.

CONCLUSION

In conclusion, the C-3 substituent played a very significant role in asymmetric dihydroxylation of sugar vinyl furanoside derivatives. The presence of an ester group at C-3 resulted in the formation of saccharide with *R*-configuration at C-5 during the asymmetric dihydroxylation by use of AD mix-α reagent, while a benzyl ether group at C-3 hydroxyl did not exhibit good diastereoselectivity. Dramatic reversal in selectivity was observed for the 3-deoxy vinyl furanoside resulting in the formation of saccharide with *S*-configuration at C-5. Thus, the nature of the substituent at C-3 of vinyl furanosides plays a decisive role in asymmetric dihydroxylation of C-5,6-double bond.

EXPERIMENTAL

Typical procedure for the OsO_4 catalysed hydroxylation of olefins 1-6 (reagent system a). To a solution of ene (**1-6**) (1 mmol) in acetone : water (4:1, 4 mL) was added OsO_4 (0.02 mmol) and *N*-methylmorpholine-*N*-oxide (2 mmol) at 0 °C and the reaction mixture was stirred for 26 h. After completion of the reaction, acetone was removed on a rotary evaporator, saturated aqueous $NaHCO_3$ (5 mL) was added to the residue which was stirred for an additional 30 min. The reaction mixture was diluted with water (50 mL), extracted with ethyl acetate (50 mL), organic phase separated, dried (Na_2SO_4) and concentrated to give the diol (***1R/1S - 6R/6S***) in 85-90% yield. The mixtures were further purified by column chromatography and converted to the corresponding acetates for characterisation.

Typical procedure for the AD-mix-α / β catalysed hydroxylation of olefins 1-6 (reagent system b and c). To a mixture of AD-mix α or β (1.3 g) in *t*-BuOH:H_2O (1:1, 4 mL) at 0 °C was added the olefin (1 mmol) and the reaction mixture stirred for 96 h. Progress of the reaction was monitored by TLC. After completion of the reaction, solid sodium sulphite was added and the mixture was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was filtered through celite, the filtrate was concentrated under reduced pressure to yield a residue which was extracted with ethyl acetate (2x25 mL). Combined organic layers were dried (Na_2SO_4) and concentrated to obtain the diol (***1R /1S - 6R /6S***) in 86-95% yield. They were further purified by column chromatography.

A mixture of 1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (*1R / 1S*). Obtained from reagent system a. mp 140-142 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.41, 1.56 (2s, 6H, 2xCH_3), 3.60-4.20 (m, 4H, H-4,5,6,6'), 4.40 (d, 0.42H, J=3.6 Hz, H-3), 4.50 (d, 0.58H, H-3), 4.78 (d, 1H, J=4.0 Hz, H-2), 6.05 (d, 0.58 H, H-1), 6.08 (d, 0.42 H, H-1).

Anal. Calcd for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 49.26; H, 7.44.

Obtained from reagent system **b**. mp 138-141 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41, 1.56 (2s, 6H, 2xCH_3), 3.60-4.20 (m, 4H, H-4,5,6,6'), 4.40 (d, 0.33H, J=3.6 Hz, H-3), 4.50 (d, 0.67H, H-3), 4.78 (d, 1H, J=4.0 Hz, H-2), 6.05 (d, 0.68 H, H-1), 6.08 (d, 0.32 H, H-1).

Anal. Calcd for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 49.28; H, 7.39.

Obtained from reagent system **c**. mp 141-142 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41, 1.56 (2s, 6H, 2xCH_3), 3.60-4.20 (m, 4H, H-4,5,6,6'), 4.40 (d, 0.8H, J=3.6 Hz, H-3), 4.50 (d, 0.2H, H-3), 4.78 (d, 1H, J=4.0 Hz, H-2), 6.05 (d, 0.8 H, J=4.0 Hz, H-1), 6.08 (d, 0.2 H, H-1).

Anal. Calcd for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found: C, 49.18; H, 7.41.

A mixture of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (1*R*A/1*S*A). Obtained from reagent system **a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3, 1.52 (2s, 6H, 2xCH_3), 2.00, 2.05 (3s, 9H, 3xOCOCH_3), 3.90 (dd, 0.42H, J=12.2, J=5.7 Hz, H-6), 4.10 (dd, 0.58H, J=12.2, 5.7Hz, H-6), 4.20-4.60 (m, 3H, H-2,4,6'), 5.10-5.40 (m, 2H, H-3,5), 5.91 (d, 1H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.21; H, 6.32.

Obtained from reagent system **b**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30, 1.52 (2s, 6H, 2xCH_3), 2.00, 2.05 (3s, 9H, 3xOCOCH_3), 3.90 (dd, 0.33H, J=12.2, J=5.7 Hz, H-6), 4.10 (dd, 0.67H, J=12.2, 5.7Hz, H-6), 4.20-4.60 (m, 3H, H-2,4,6'), 5.10-5.40 (m, 2H, H-3,5), 5.91 (d, 1H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.24; H, 6.32.

Obtained from reagent system **c**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30, 1.52 (2s, 6H, 2xCH_3), 2.00, 2.05 (3s, 9H, 3xOCOCH_3), 3.90 (dd, 0.2H, J=12.2, J=5.7 Hz, H-6), 4.10 (dd, 0.8H, J=12.2, 5.7Hz, H-6), 4.20-4.60 (m, 3H, H-2,4,6'), 5.10-5.40 (m, 2H, H-3,5), 5.91 (d, 1H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.28; H, 6.55.

3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1*R*A).[7] To a solution of triol[7] (0.16 g, 0.72 mmol) in pyridine (1.5 mL) was added Ac_2O (0.6 mL) and the reaction mixture was stirred at room temperature for 2 h. After completion of the reaction the mixture was poured into water (100 mL) and extracted into diethyl ether (50 mL). The organic phase was separated, washed with water, concentrated to a residue that was filtered on a bed of silica gel (60-120 mesh) by eluting with hexane-ethyl acetate (2:1) giving the title compound (0.24 g, 94%) as a syrup. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30, 1.52 (2s, 6H, 2xCH_3), 2.00, 2.05 (3s, 9H, 3xOCOCH_3), 4.10 (dd, 1H, J=12.2 Hz,

$J_{5,6'}$=5.7 Hz, H-6'), 4.35 (dd, 1H, J=8.0 Hz, $J_{3,4}$=2.5 Hz, H-4), 4.44 (dd, 1H, J=2.5 Hz, J=2.3 Hz, H-2), 4.54 (dd, 1H, J=2.7 Hz, H-6), 5.18 (m, 1H, H-5), 5.33 (dd, 1H, H-3), 5.91 (d, 1H, H-1).

Anal. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40. Found: C, 52.11; H, 6.46.

A mixture of 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (2*R*/2*S*). Obtained from reagent system **a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 2.12 (s, 3H, $OCOCH_3$), 2.90-3.20 (bs, OH), 4.02-4.60 (m, 6H, H-2,3,4,5,6,6'), 5.95 (d, 0.39H, J=4.0 Hz, H-1), 6.00 (d, 0.61H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92. Found: C, 50.57; H, 7.03.

Obtained from reagent system **b**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 2.12 (s, 3H, $OCOCH_3$), 2.90-3.20 (bs, OH), 4.02-4.60 (m, 6H, H-2,3,4,5,6,6'), 5.95 (d, 0.1H, J=4.0 Hz, H-1), 6.00 (d, 0.9H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92. Found: C, 50.56; H, 7.10.

Obtained from reagent system **c**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 2.12 (s, 3H, $OCOCH_3$), 2.90-3.20 (bs, OH), 4.02-4.60 (m, 6H, H-2,3,4,5,6,6'), 5.95 (d, 0.2H, J=4.0 Hz, H-1), 6.00 (d, 0.8H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92. Found: C, 50.57; H, 6.99.

3-*O*-Acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2*R*).[5,7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 2.12 (s, 3H, $OCOCH_3$), 3.0-3.2 (bs, OH), 4.02-4.60 (m, 6H, H-2,3,4,5,6,6'), 6.0 (d, 1H, J=4.0 Hz, H-1).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.38; H, 6.92. Found: C, 50.47; H, 7.03.

A mixture of 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (3*R*/3*S*). Obtained from reagent system **a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33, 1.56 (2s, 6H, 2xCH_3), 3.60-4.70 (m, 5H, H-2,4,5,6,6'), 5.50 (d, 1H, J=6.0 Hz, H-3), 5.97 (d, 0.4H, H-1), 5.99 (d, 0.6 H, H-1), 7.40-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.47; H, 6.31.

Obtained from reagent system **b**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33, 1.56 (2s, 6H, 2xCH_3), 3.60-4.70 (m, 5H, H-2,4,5,6,6'), 5.50 (d, 1H, J=6.0 Hz, H-3), 5.97 (d, 0.1H, H-1), 5.99 (d, 0.9 H, H-1), 7.40-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.42; H, 6.31.

Obtained from reagent system **c**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33, 1.56 (2s, 6H, 2xCH_3), 3.6-4.7 (m, 5H, H-2,4,5,6,6'), 5.50 (d, 1H, J=6.0 Hz, H-3), 5.97 (d, 0.25H, H-1), 5.99 (d, 0.75 H, H-1), 7.40-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.38; H, 6.31.

3-*O*-Benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (3*R*).[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33, 1.56 (2s, 6H, 2xCH_3), 3.60-3.90 (m, 3H, H-5,6,6'), 4.25 (dd, 1H, J=7.1 Hz, J=2.5 Hz, H-4), 4.70 (d, 1H, $J_{1,2}$=4.1 Hz, H-2), 5.50 (d, 1H, H-3), 5.99 (d, 1H, H-1), 7.40-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.31; H, 6.25.

A mixture of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (4*R*/4*S*). Obtained from reagent system **a**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.50 (2s, 6H, 2xCH_3), 3.35 (bs, 2H, OH), 3.92-4.80 (m, 8H, H-2-6,6' and OCH_2Ph), 5.89 (d, 0.73H, H-1), 5.96 (d, 0.27H, H-1), 7.20-7.50 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 62.14; H, 7.23.

Obtained from reagent system **b**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.50 (2s, 6H, 2xCH_3), 3.35 (bs, 2H, OH), 3.92-4.80 (m, 8H, H-2-6,6' and O$\underline{CH_2}$Ph), 5.89 (d, 0.75H, H-1), 5.96 (d, 0.25H, H-1), 7.20-7.50 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 62.22; H, 7.21.

Obtained from reagent system **c**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.50 (2s, 6H, 2xCH_3), 3.35 (brs, 2H, OH), 3.92-4.80 (m, 8H, H-2-6,6' and O$\underline{CH_2}$Ph), 5.89 (d, 0.66H, H-1), 5.96 (d, 0.34H, H-1), 7.20-7.50 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 62.24; H, 7.27.

3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose(4*R*).[9] ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.5 (2s, 6H, 2xCH_3), 2.50 (brs, 1H, OH), 3.67 (dd, 1H, J=5.3 Hz, J=11.5 Hz, H-6'), 3.79 (dd, 1H, J=3.2 Hz, H-6), 3.95-4.20 (m, 3H, OH, H-3,4), 4.56 (d, 1H, J=4.1 Hz, H-2), 4.68 (dd, 2H, O$\underline{CH_2}$Ph), 5.89 (d, 1H, H-1), 7.2-7.5 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.99; H, 7.19.

1-*O*-Benzoyl-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-*lyxo*-hex-5-eno-furanoside (5). To a solution of compound **5*R***[10] (0.5 g, 1.5 mmol) in toluene (50 mL) was added triphenylphosphine (1.6 g, 6.1 mmol), imidazole (0.41 g, 6.1 mmol) and the reaction mixture stirred at 60 °C until a clear solution has resulted. To the above reaction mixture, iodine (1.56 g, 6.1 mmol) was added in small lots and then heated to reflux. After completion of the reaction, the reaction mixture was cooled to room temperature and 5% aqueous NaOH solution (15 ml) was added. Solvent was removed under reduced pressure to give a residue that was purified by column chromatography [SiO_2, 60-120 mesh, hexane-ethyl acetate (4:1)] yielding the title compound **5** (0.37 g, 83% yield) as a colourless syrup. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.52 (2s, 6H, 2xCH_3), 4.60 (dd,

1H, J=3.9 Hz, J=7.8 Hz, H-4), 4.70-4.90 (m, 2H, H-2,3), 5.32 (d, 1H, J=10.4 Hz, H-6), 5.45 (d, 1H, J=14.7 Hz, H-6'), 5.98 (ddd, 1H, H-5), 6.40 (s, 1H, H-1), 7.35-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.31; H, 6.28.

A mixture of 1-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-manno-/β-L-gulofuranoside (5*R*/5*S*). Obtained from reagent system **a**. ^1H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.40, 1.50, 1.54 (4s, 6H, 2xCH_3), 2.90 (d, 1H, J=6.0 Hz, OH), 3.60-4.30 (m, 4H, H-4,5,6,6'), 4.83 (d, 0.8 H, J=5.8 Hz, H-2), 4.87 (d, 0.2H, H-2), 4.92-5.05 (m, 1H, H-3), 6.38 (s, 0.8H, H-1), 6.41 (s, 0.2H, H-1), 7.42-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.24; H, 6.22. Found: C, 59.47; H, 6.31.

Obtained from reagent system **b**. ^1H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.40, 1.50, 1.54 (4s, 6H, 2xCH_3), 2.90 (d, 1H, J=6.0 Hz, OH), 3.60-4.30 (m, 4H, H-4,5,6,6'), 4.83 (d, 0.84 H, J=5.8 Hz, H-2), 4.87 (d, 0.16H, H-2), 4.92-5.05 (m, 1H, H-3), 6.38 (s, 0.8H, H-1), 6.41 (s, 0.2H, H-1), 7.42-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.24; H, 6.22. Found: C, 59.43; H, 6.31.

Obtained from reagent system **c**. ^1H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.40, 1.50, 1.54 (4s, 6H, 2xCH_3), 2.90 (d, 1H, J=6.0 Hz, OH), 3.60-4.30 (m, 4H, H-4,5,6,6'), 4.83 (d, 0.72 H, J=5.8 Hz, H-2), 4.87 (d, 0.28H, H-2), 4.92-5.05 (m, 1H, H-3), 6.38 (s, 0.71H, H-1), 6.41 (s, 0.29H, H-1), 7.42-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.24; H, 6.22. Found: C, 59.28; H, 6.24.

1-*O*-Benzoyl-2,3-*O*-isopropylidene-α-D-mannofuranoside (5*R*).[10] ^1H NMR (200 MHz, $CDCl_3$) δ 1.34, 1.54 (2s, 6H, 2xCH_3), 1.95 (brs, 1H, OH), 2.70 (brs, 1H, OH), 3.68 (dd, 1H, J=4.9 Hz, $J_{6,6'}$=11.2 Hz, H-6'), 3.84 (dd, 1H, J=3.0 Hz, H-6), 3.9-4.1 (m, 1H, H-5), 4.19 (dd, 1H, J=7.1 Hz, J=3.5 Hz, H-4), 4.83 (d, 1H, J=5.7 Hz, H-2), 4.96 (dd, 1H, H-3), 6.38 (s, 1H, H-1), 7.40-8.00 (m, 5H, H_{Ar}).

Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.24; H, 6.22. Found: C, 59.34; H, 6.32.

A mixture of 3-deoxy-1,2-*O*-isopropylidene-α-D-gluco-/β-L-idofuranose (6*R*/6*S*). Obtained from reagent system **a**. ^1H NMR (200 MHz, $CDCl_3$) δ1.32, 1.51(2s, 6H, 2xCH_3),1.70-2.12 (m, 2H, H-3,3'), 3.50-4.32 (m,4H,H-4,5,6,6'), 4.74 (dt,1H,J=3.9 Hz, H-2), 5.76(d, 0.65H, J=3.9 Hz, H-1), 5.80(d, 0.35H, J=3.9 Hz,H-1).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.14; H, 7.99.

Obtained from reagent system **b**. ^1H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 1.70-2.12 (m, 2H, H-3,3'), 3.50-4.32 (m, 4H, H-4,5,6,6'), 4.74 (dt, 1H, J=3.9 Hz, H-2), 5.76 (d, 0.88H, J=3.9 Hz, H-1), 5.80 (d, 0.12H, J=3.9 Hz, H-1).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.18; H, 7.99.

Obtained from reagent system **c**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 1.70-2.12 (m, 2H, H-3,3'), 3.50-4.32 (m, 4H, H-4,5,6,6'), 4.74 (dt, 1H, J=3.9 Hz, H-2), 5.76 (d, 0.64H, J=3.9 Hz, H-1), 5.80 (d, 0.36H, J=3.9 Hz, H-1).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.11; H, 8.02.

3-Deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (6*R*).[12] mp 75-77 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.51 (2s, 6H, 2xCH_3), 1.70-1.92 (m, 1H, H-3), 2.06 (dd, 1H, J=9.2, 3.9 Hz, H-3'), 2.38 (br.s, 1H, OH), 3.52-4.02 (m, 3H, H-5,6,6'), 4.18-4.30 (m, 1H, H-4), 4.74 (dt, 1H, J=3.9 Hz, H-2), 5.80 (d, 1H, J=3.9 Hz, H-1).

Anal. Calcd for $C_9H_{16}O_5$: C, 52.93; H, 7.90. Found: C, 53.04; H, 7.94.

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