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Stereocontrolled Synthesis of *C*-Glycosides: Further Studies on the Organolithium Reagents Derived from 2-Deoxy-D-Glucose and D-Glucose

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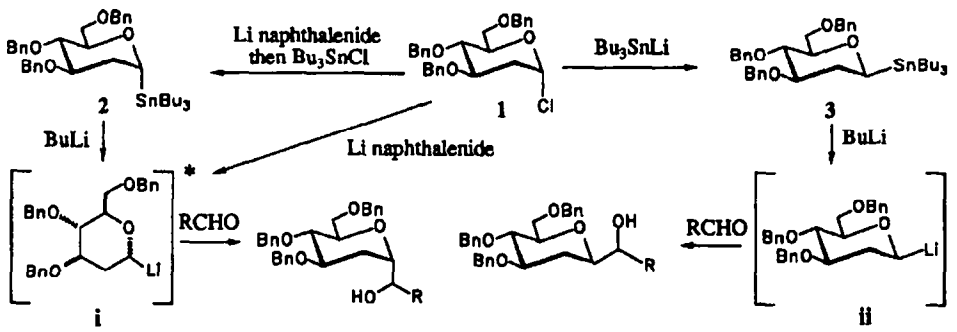
Abstract—The addition of α- and β-2-deoxy-D-glucopyranosyl lithium reagents **i** and **ii** to prochiral aldehydes is a *syn*-selective process, synthetically useful only with the α-lithio reagent **i** (*syn:anti* selectivity of ~10:1 with saturated aldehydes). This has been demonstrated by using propionaldehyde and converting the *syn*-isomers of both series to an easily identified acyclic *meso*-chain (α-series) or a C_2 symmetric acyclic chain (β-series). The preparation of α- and β-D-glucopyranosyl dilithio reagents **26** and **27** is possible but a notable decrease in efficiency and facial selectivity is observed in coupling reactions with model aldehydes.

Introduction

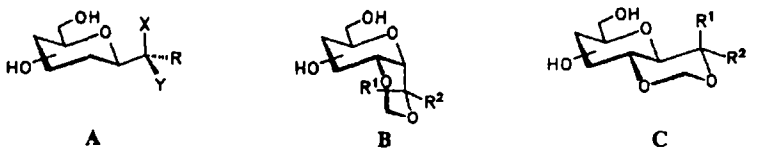
The importance of *C*-glycosides, not only as structural subunits of a variety of natural products but as mimics of biologically relevant *O*-glycosides, has stimulated the discovery of a wide-range of synthetic methods for their construction.[1] Targeting the assembly of *O*-glycoside mimics as possible glycoenzyme regulators[2] or more generally as artificial ligands usable in biological recognition studies[3] is now a growing concern for potential use in medicinal chemistry.

All possible synthetic strategies including anomeric carbocations, carbanions, radicals and carbenes have been intensively exploited over the past decade[1] to realize the direct formation of a carbon–carbon bond at the anomeric center of carbohydrates.

For the preparation of *C*-glycopyranosyl compounds, we have shown that a stereodefined umpolung at the anomeric center is possible via the stereoselective construction of the corresponding α and β anomeric stannanes, a strategy limited to the 2-deoxy series[4] (Scheme I). The transmetallation of the isomeric stannanes led to the organolithium reagents **i** and **ii** configurationally stable[4,5] at low temperature which reacted with electrophiles with retention of the configuration. The seemingly unnecessary route to lithium reagent **i** via anomeric stannane **2** instead of directly using the reductive lithiation product of chloride **1**[6] was justified because of the higher coupling efficiencies obtained with carbonyl compounds using this protocol and because of the possibility of modifying **i** for its condensation with α,β-unsaturated ketones[7] or epoxides.[8] Addition of these lithium reagents to prochiral carbonyl compounds provided varying degrees of diastereofacial selectivity which was left undefined in the previous study.[4] The absolute configuration of the exocyclic asymmetric center produced in the coupling reactions has now been established and we present an extension of this work to the *gluco* series. The extra-functionality at C-7 can be considered a useful means of producing restricted (see **A**) or fixed (see **B** and **C**) '*exo*-anomeric conformations' expected to influence biological activity (see the following scheme).



Scheme I. *This representation denotes that the conformation of **i** is presently unknown. For the sake of convenience, the α-*C*-glycosides reported are drawn in the $^4C_1$(D) chair conformation. However, a substantial conformational distortion from the chair was observed for most of them.



A B C

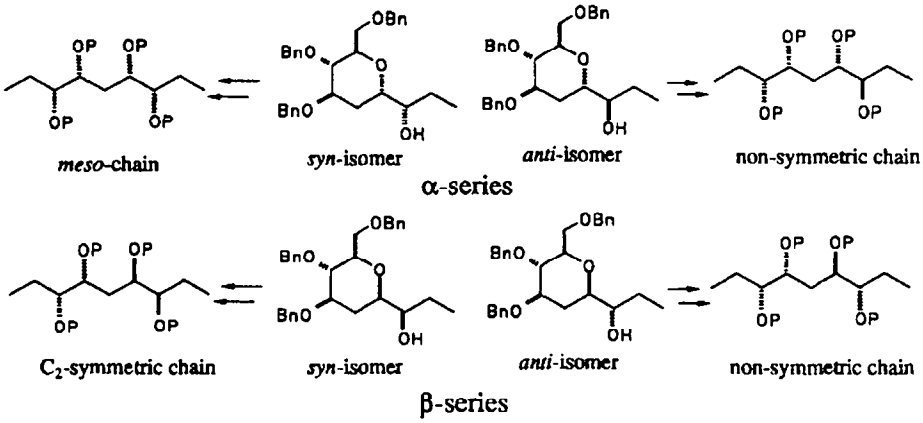
Results and Discussion

Facial enantioselection in the 2-deoxy gluco series

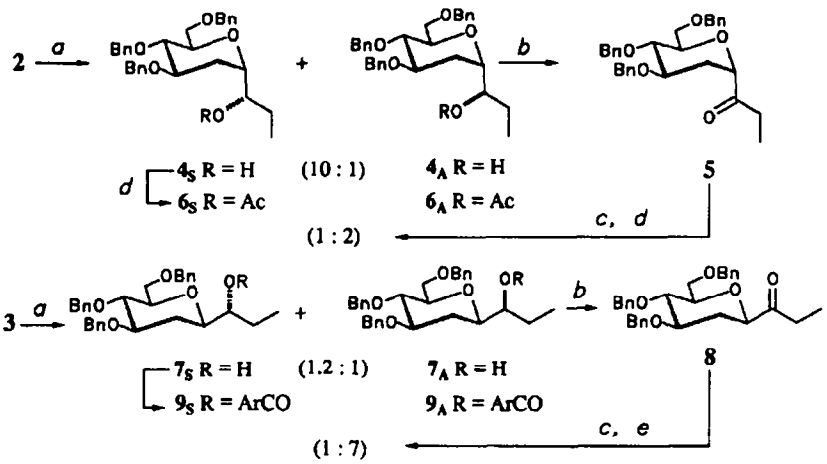
The difficulty establishing the configuration of the exocyclic asymmetric center directly by NMR analysis especially in the α-series led us to consider a sequence of transformations leading to acyclic chains. Using propionaldehyde as the electrophilic partner of the anomeric lithiated series combined with a conversion of the C-5–C-6 carbons of the hexose to an ethyl group would lead to easily differentiated chains as illustrated in Scheme II. Thus the *syn*-isomers in both series would produce a *meso*-chain (α-series) or a C_2-symmetric chain (β-series) readily identified by NMR spectroscopy. This sequence offered the further advantage of probing the transformation of the cyclic systems to stereodefined acyclic chains, useful precursors for other synthetic objectives.

Treatment of the glycosylstannanes **2** and **3**[4] with butyl lithium in THF at −78 °C, followed after 5 min by the addition of propionaldehyde (1.5 equiv) provided the α-*C*-glycosides $\mathbf{4_S}$ and $\mathbf{4_A}$ (*syn:anti* isomeric ratio,[9] 10:1, see below) and the β-*C*-glucosides $\mathbf{7_S}$ and $\mathbf{7_A}$ (*syn:anti* isomeric ratio, 1.2:1, see below), respectively (Scheme III).

That $\mathbf{4_S}$ and $\mathbf{4_A}$ were diastereoisomers at the exocyclic asymmetric center was readily established by oxidation to a single ketone **5**. The $J_{1,2ax}$, $J_{1,2eq}$, $J_{2ax,3}$ coupling constant values (5.8, 3.0 and 10.1 Hz), as shown by the ^{1}H NMR spectrum of ketone **5**, are consistent with an α-oriented side chain. Similarly isomers $\mathbf{7_S}$ and $\mathbf{7_A}$



Scheme II.

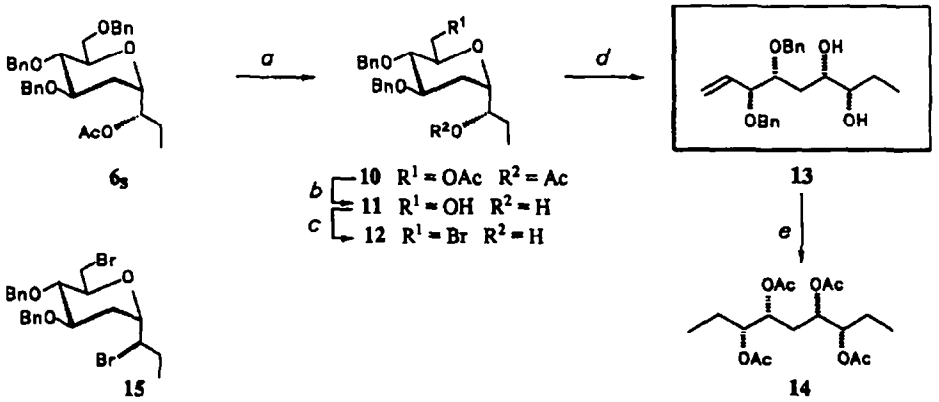


Scheme III. (a) BuLi, THF, −78 ° C then EtCHO ($\mathbf{4_S}$ + $\mathbf{4_A}$, 72 %; $\mathbf{7_S}$ + $\mathbf{7_A}$, 68 %; (b) PCC, AcONa, MS 4A, CH_2Cl_2 (**5**, 81 %; **8**, 86 %); (c) $Zn(BH_4)_2$, Et_2O, −20 °C ($\mathbf{4_S}$ + $\mathbf{4_A}$, 95 %; $\mathbf{7_S}$ + $\mathbf{7_A}$, 90 %); (d) Ac_2O, pyr, 93 %; (e) 3,5-dinitrobenzoylchloride, pyr, 96 %.

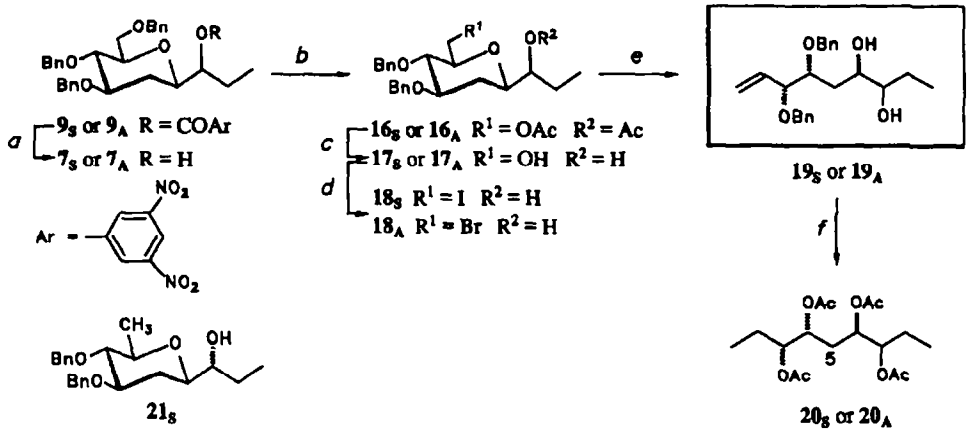
furnished a single ketone **8** with a β-oriented substituent deduced from the ^{1}H NMR spectrum ($J_{1,2ax}$ and $J_{1,2eq}$ of ~12.5 and 2.2 Hz, respectively).

For preparative purposes, isomeric α-*C*-glycosides $\mathbf{4_S}$ and $\mathbf{4_A}$ were separated as their mono-*O*-acetates $\mathbf{6_S}$ and $\mathbf{6_A}$ whereas β-*C*-glycosides $\mathbf{7_S}$ and $\mathbf{7_A}$ were easily separated only after a 3,5-dinitrobenzoylation to afford $\mathbf{9_S}$ and $\mathbf{9_A}$. At this stage, ketones **5** and **8** were reduced with zinc borohydride[5c,10,11] to alcohols **4** and **7**. The stereoselectivity noted in the coupling reactions was reversed in these reductions ($\mathbf{4_S}$:$\mathbf{4_A}$ isomeric ratio, 1:2 and $\mathbf{7_S}$:$\mathbf{7_A}$ isomeric ratio, 1:7, unoptimized conditions), a simple operation which suggested that the major isomers in the coupling reaction were the *syn*-isomers.†

In the α-series, a sequence of transformations was conducted on the major isomer $\mathbf{6_S}$ (Scheme IV). Acetolysis of the primary benzyl group and deacetylation provided the diol **11** in 90 % yield. Treatment of the diol **11** with CBr_4–PPh_3–pyridine[12] did produce the expected primary bromide **12** (58 % yield) but accompanied by the dibromide **15** (22 % yield). Opening of the ring system in **12** by activated zinc[13] furnished the ethylenic acyclic chain **13** with high efficiency. This non-symmetric chain, readily usable in other synthetic transformations, was converted to the optically inactive tetra-*O*-acetate **14**, easily identified as a *meso*-chain by ^{1}H NMR spectroscopy (see Experimental). The *S*-configuration of the exocyclic asymmetric center then follows, defining a selective attack on the *re*-face of the aldehyde by the asymmetric nucleophile (*syn* selection).[9]



Scheme IV. (a) CF_3COOH, Ac_2O, 0 °C, 92 %; (b) MeONa, MeOH, rt, 97 %; (c) CBr_4, PPh_3 pyr, 58 %; (d) Zn, aqueous *n*PrOH, 80 °C, 93 %; (e) H_2, Pd/C, MeOH then Ac_2O, pyr, 88 %.



Scheme V. (a) MeONa, MeOH, rt (7_S, 92 %; 7_A, 87 %); (b)CF_3COOH, Ac_2O, 0 °C (16_S, 87 %; 16_A, 92 %); (c) MeONa, MeOH, rt (17s, 96 %; 17_A, 98 %); (d) for 18_S: I_2, imidazole, PPh_3, 60 °C, 68 %; for 18_A: CBr_4, PPh_3, pyr, 0 °C, 75 %; (e) BuLi, THF, -78 °C (19_S, 79 %; 19_A, 80 %); (f) H_2, Pd/C, MeOH then Ac_2O, pyr (20_S, 82 %; 20_A, 81 %).

†It is assumed that the reduction proceeds via a cyclic transition state in which zinc coordinates the carbonyl and the endocyclic oxygen (1,2-asymmetric induction) with the hydride delivery occurring *anti* to the C-2 carbon atom (carbohydrate numbering) thus giving selectively the *anti*-isomers.

The same synthetic route performed on the β-*C*-glycosides 7_S and 7_A required that some steps be adjusted for maximum efficiency (Scheme V). First, halogenation of crystalline diol 17_S with the CBr_4–PPh_3–pyridine system furnished a mixture of the expected primary bromide (18_S, R^1 = Br, 48 %) and the corresponding dibromo compound (10–20 %). The best yield (68 %) was obtained using the Garegg procedure[14] (I_2, imidazole, PPh_3; 15 % of the diiodo compound was still formed under these conditions). Secondly, opening of the tetrahydropyran ring in iodide 18_S or bromide 18_A with activated zinc in aqueous propanol did not proceed well, giving a 1:1 mixture (90 %) of the acyclic product 19_S or 19_A and the reduction product (21_S or its *anti* isomer). Compound 21_S was the only one formed using the Rieke reagent.[15] However, treatment of 18_S or 18_A with butyl lithium gave the C_9-acyclic chains 19_S or 19_A in 79 and 80 % yields, respectively. Hydrogenolysis and acetylation of 19_S furnished an optically active ($[\alpha]_D^{20}$ +62 °) tetra-*O*-acetate 20_S showing a simplified ^1H NMR spectrum (2 singlets for the 4 acetyl groups for example, see Experimental) representative of a C_2-symmetric chain with a homotopic center at C-5. The absolute configuration of the exocyclic asymmetric center in 20_S is thus *R*, pointing to a slightly *syn* selective process in the coupling reaction (e.g. a *slightly* selective attack on the *si*-face of the aldehyde by the β-lithiated anomeric species). As a confirmation of this, diastereoisomer 20_A ($[\alpha]_D^{20}$ +28°) showed a ^1H NMR spectrum diagnostic of a non-symmetric acyclic chain (see Experimental).

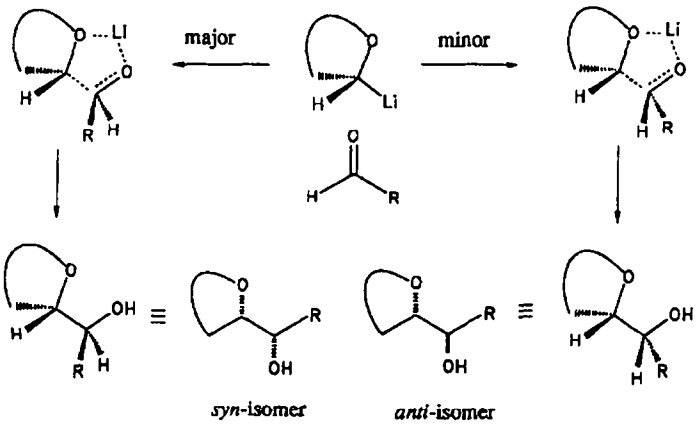
The diastereoselectivity observed can easily be explained by considering the two possible diastereoisomeric transition structures[5c] (shown in Scheme VI for the α-series) with the major path being the one in which the R group of the aldehyde and the C-2 of the sugar are *anti* in the cyclic structure. If chelation is not a major contributing factor, the steric empirical model proposed by Bassindale *et al.*[16] will predict the same selectivity taking the C-2 carbon atom as the largest carbanion ligand.

Anomeric organolithium compounds in the gluco *series*

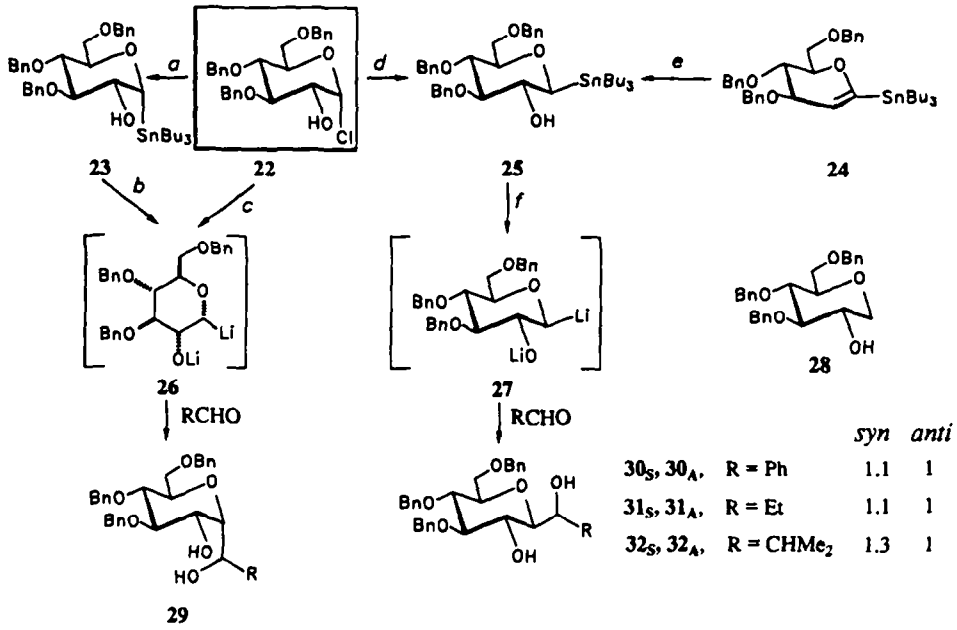
Following the work we described in the 2-deoxy *gluco* series, a more difficult task was to find a similar solution in the *gluco* series, that is, one capable of generating a β-oxygenated organolithium compound. With an alkoxy group at the C-2 carbon atom, these types of lithiated species will eliminate[6,17] even when a stabilizing substituent like a phenylsulfinyl[18] or a phenylsulfonyl group[19] is present at the anomeric center and this property has been utilized to prepare the corresponding glycals. Further, a trimethylsilyloxy group at position 2 will either rearrange to the corresponding pyranosyltrimethylsilane[20] (1,3 *O* to *C* silyl migration in the *gluco* or *galacto* series with an α-oriented organolithium compound) or be eliminated (*manno* series). Elimination could be retarded or prevented by a lithioalkoxy group at C-2 (that is, the production of a dianion) and such species have been used in C–C bond forming reactions.[21,22]

For this purpose, crystalline chloride **22**, easily produced from D-glucose[23] appeared to be a convenient precursor. Formation of the lithium alkoxide at position 2 by butyl lithium treatment of chloride **22** at –78 °C followed by a reductive lithiation at the anomeric center (3 equiv. of lithium naphthalenide) and stannylation furnished, however, an unacceptable yield of stannane **23** (20 %). Tin–lithium exchange by treatment with an excess of butyl lithium (2.5 equiv.; the exchange needed ~30 min at –78 °C in this case) did produce the dilithio compound **26** as evidenced by the formation of the α-*C*-glycoside **29** (R = Ph,[22] 30–40 % yield) after the addition of benzaldehyde. As a consequence of the low tin–lithium exchange rate, the major byproduct was the protonated product 1,5-anhydro-3,4,6-tri-*O*-benzyl-D-glucitol **28**. No glycal was formed (e.g. β-elimination of 'Li_2O') under these conditions.

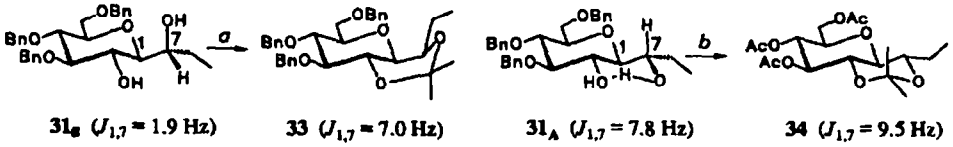
By reductive lithiation of chloride **22** to the dilithio compound **26** and treatment with aldehydes, Wittman and Kessler[22] very recently obtained remarkable coupling yields (e.g. **29**, R = Ph, 70 % yield), simply



Scheme VI.



Scheme VII. (a) BuLi, 1.1 equiv. then Li naphthalenide, 3 equiv. then Bu_3SnCl, THF, –78 °C, 20 %; (b) BuLi, 2.5 equiv. then RCHO; (c) see Wittman and Kessler, ref. 22; (d) Bu_3SnLi or BuLi, 1.1 equiv. then Bu_3SnLi, 20–30 %; (e) BH3·THF, rt, 2.5 h then H_2O_2, aq. NaOH work-up, 82 %; (f) BuLi, 2.5 equiv., HMPA, 1 equiv., –78 °C, 20 min then RCHO (**30**, 56 %; **31**, 51 %; **32**, 50 %).



Scheme VIII. (a) $Me_2C(OMe)_2$, TsOH, DMF, rt, 65 %; (b) see (a) then H_2, Pd/C, MeOH; Ac_2O, pyr, 83 %.

by cooling down the reaction medium to –100 °C, thus offering an efficient solution for the synthesis of α-*C*-glycosides **29**.

Following the procedure described in the 2-deoxy series,[4] a low yield (20–30 %) was also obtained for the isomeric β-stannane **25** by treating chloride **22** either directly with an excess of tributylstannyl lithium[5a] (2 to 5 equiv.) at 0 °C in THF or with butyl lithium (1 equiv. at –78 °C) then with Bu_3SnLi (1 equiv. or more). A more reliable, although lengthier, route to stannane **25** relied on a hydroboration–oxidation sequence on vinylic stannane **24**[19] which provided stereoselectively stannane **25** in 82 % yield. The β-orientation of the stannyl group was readily indicated by its ^1H NMR spectrum which showed the H_1 (δ 3.44) axially oriented ($J_{1,2}$ = 11.1 Hz with satellites, $J_{1,Sn}$ = 12 Hz, arising from the extra coupling with the ^{117}Sn and ^{119}Sn nuclei) in a $^4C_1$ (D) chair conformation ($J_{2,3}$, $J_{3,4}$ and $J_{4,5}$ of 8.5, 8.5 and 9.8 Hz, respectively).

Treatment of stannane **25** in THF at –78 °C with 2.2 equiv. of butyl lithium led to incomplete tin–lithium exchange as observed in the α-series and in contrast with the almost instantaneous transmetallation observed in the 2-deoxy series (~20 % of the stannane remained after 20 min). The rate of exchange could be accelerated by adding 1 equiv. of HMPA before the butyl lithium treatment. Further addition of benzaldehyde, propionaldehyde and iso-butyraldehyde on the presumed dilithio compound **27** afforded the expected diastereoisomeric β-*C*-glycosides **30** (56 %, isomeric ratio, 1.1:1), **31** (51 %, isomeric ratio, 1.1:1) and **32** (50 %, isomeric ratio, 1.3:1). Some of stannane **25** was recovered and again, the major by-product (20–30 %) was the protonated product **28**.

In contrast to the α-*C*-glycosides of the 2-deoxy series, isomers $\mathbf{31_S}$, $\mathbf{31_A}$ and $\mathbf{32_S}$, $\mathbf{32_A}$ were easily separated by flash chromatography. A comparison of the $J_{1,7}$ values (1.5–1.9 Hz) of the coupling constants obtained from the ^1H NMR spectra of the (slightly) major isomers $\mathbf{31_S}$ and $\mathbf{32_S}$ and those of the minor isomers $\mathbf{31_A}$ and $\mathbf{32_A}$ (6.5–7.8 Hz) suggested that $\mathbf{31_S}$ and $\mathbf{32_S}$ were the *syn*-isomers and $\mathbf{31_A}$ and $\mathbf{32_A}$ the *anti*-isomers.† The ethyl or *i*-propyl group and the C-2 carbon atom (carbohydrate numbering) of the tetrahydropyran ring are antiperiplanar in a conformation close to the staggered

†Compounds $\mathbf{31_S}$ and $\mathbf{31_A}$ have already been prepared[26] by hydroboration of the corresponding 1-C hydroxyalkylated glycals and the absolute configuration at the exocyclic asymmetric center defined by isopropylidene formation (see **33**).

ones shown for $\mathbf{31_S}$ and $\mathbf{31_A}$ (Scheme VIII). For the *anti*-isomers $\mathbf{31_A}$ and $\mathbf{32_A}$ the staggered conformation may be stabilized by hydrogen bonding.[8a,24]

This interpretation was confirmed by the values of the coupling constants $J_{1,7}$ found for the isopropylidene derivatives $\mathbf{33}^+$ ($J_{1,7}$ = 7.0 Hz, only compatible with a boat conformation of the dioxane ring which avoids the unfavorable 1,3-diaxial interactions between the axial methyl substituent of the isopropylidene group and the ethyl group in a chair conformation) and **34** ($J_{1,7}$ = 9.5 Hz, chair conformation of the dioxane ring).

This rather unselective coupling process with aldehydes and the β-dilithio compound **27** was also reported by Whittman and Kessler[22] for the α-dilithio compound **26**. With the α-lithiated anomeric species, and taking isobutyraldehyde as the electrophilic partner, the *syn:anti* selectivity of ~10:1 observed in the 2-deoxy *gluco* series[4] (nucleophile **i**) drops to ~1:1 in the *gluco* series (nucleophile **26**).[22] The same is true to a lesser extent going from the β-2-deoxy lithio compound **ii** (facial selectivity of 3:1 with isobutyraldehyde)[4] to the β-lithio compound **27** (facial selectivity of 1.3:1 with isobutyraldehyde). A competitive chelation of the aldehyde oxygen by the lithium atom at O-2 could lead to a six-membered transition state which would favor the formation of the *anti*-isomer and thus explain an essentially unselective process as compared with the 2-deoxy series. A similar type of unselective coupling reaction (isomeric ratio, 1:1) was recently observed in the preparation of **37** (16 % yield) by de Pouilly *et al.*[25] via the samariated anomeric species derived from the sulfone **35** (Scheme IX). That the counter ion (Li^+ or Na^+) at the O-2 oxygen atom of the anomeric anion is detrimental to the facial selectivity is strongly suggested by the stereoselective construction of only one isomer (24 % yield) when R at O-2 is a benzyl group[25] (see **36** → **38**, Scheme IX). The configuration of the exocyclic asymmetric center in **38** was not defined by the authors. In keeping with the observations described above, however, the singlet for H-7 reported in the ^1H NMR spectrum (very small value of $J_{1,7}$) indicates a *syn*-isomer in which C-2 of the ring and the *t*-butyl group are antiperiplanar in a conformation close to the staggered conformation shown in **38**.

This work clarifies the stereochemical course of the coupling reactions involving some anomeric lithio compounds with aldehydes. With the notable exception of the α-2-deoxy organolithium **i**, the facial enantioselectivity of the asymmetric lithio compounds **ii**, **26** and **27** are well below a level useful enough for synthetic projects where the *stereoselective* construction of 1,2-diol derivatives in a single step is desired. Improvements in both diastereoselectivity and efficiency are, however, feasible by suitable modifications and we will report progress along these lines in due course.

Experimental

For General Methods see reference 4.

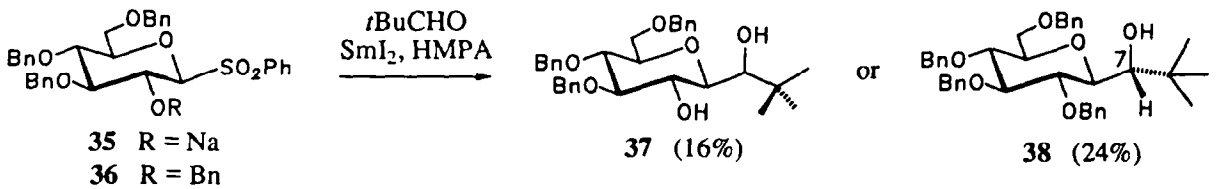
*1-(3,4,6-Tri-O-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-1-propanol* ($\mathbf{4_S}$, $\mathbf{4_A}$)

To a stirred solution of stannane **2**[4] (2.56 g, 3.62 mmol) in THF (8 mL) at −78 °C under Ar was added butyl lithium (1.6 M in hexanes, 1.1 equiv.). After stirring for 5 min, propionaldehyde (0.4 mL, 1.5 equiv.) was added. After 45 min, the solution was treated with NH_4Cl, diluted with ethyl ether and water, and the organic phase was extracted twice with sat. aqueous NH_4Cl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by column chromatography (10:1, CH_2Cl_2:AcOEt) to give $\mathbf{4_S}$, $\mathbf{4_A}$ (1.24 g, 72 %).

^1H NMR; $\mathbf{4_S}$: δ 0.98 (t, 3H, J = 7.4 Hz, CH_3), 1.36–1.49 (2 m, 2H, CH_2), 1.74 (ddd, 1H, $J_{1,2}$ = 4.2, $J_{2,3}$ = 6.9, $J_{2,2'}$ = 13.9 Hz, H-2), 1.965 (ddd, 1H, $J_{2',3}$ = 4.2, $J_{1,2'}$ = 7.0 Hz, H-2'), 2.60 (bs, 1H, OH), 3.50 (t, 1H, $J_{3,4} = J_{4,5}$ = 5.8 Hz, H-4), 3.56 (m, 1H, H-7), 3.67 (dd, 1H, $J_{5,6}$ = 4.4, $J_{6,6'}$ = 10.1Hz, H-6), 3.66–3.77 (2 m, 2H, H-1,3), 3.77 (dd, 1H, $J_{5,6'}$ = 6.1 Hz, H-6'), 3.965 (dt, 1H, H-5); $\mathbf{4_A}$: δ 2.19 (ddd, 1H, $J_{1,2}$ = 3.9, $J_{2,3}$ = 8.4, $J_{2,2'}$ = 13.8 Hz, H-2), 2.36 (ddd, 1H, $J_{2',3}$ = 5.7, $J_{1,2'}$ = 7.4 Hz, H-2'); $\mathbf{4_S}$:$\mathbf{4_A}$, isomeric ratio, ~10:1. Anal. calcd for $C_{30}H_{36}O_5$: C 75.60, H 7.61. Found: C 75.52, H 7.49.

*1-(3,4,6-Tri-O-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-1-propanone* (**5**)

A solution of $\mathbf{4_S}$, $\mathbf{4_A}$ (393 mg, 0.82 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of pyridinium chlorochromate (530 mg, 3 equiv.) in CH_2Cl_2 (3 mL) containing molecular sieves (4 Å) and sodium acetate (330 mg). Stirring was continued until complete oxidation (TLC), then ethyl ether was added. The suspension was stirred for an additional 15 min, filtered through a bed of Celite and the insoluble material was washed several times with ethyl ether. Evaporation of



35 R = Na
36 R = Bn

37 (16%)

38 (24%)

Scheme IX.

the combined filtrate and washings gave a residue which was purified by column chromatography (5:1, hexanes:AcOEt) to afford **5** (316 mg, 81 %), $[\alpha]_D^{20}$ +20 ° (*c* 1.57, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.04 (t, 3H, *J* = 7.3 Hz, CH_3), 1.755 (ddd, 1H, $J_{1,2a}$ = 5.8, $J_{2a,3}$ = 10.1, $J_{2a,2e}$ = 13.3 Hz, H-2a), 2.59 (ddd, 1H, $J_{1,2e}$ = 3.0, $J_{2e,3}$ = 4.8 Hz, H-2e), 2.605 (m, 2H, CH_2CO), 3.47 (m, 1H, $J_{5,6} = J_{5,6'}$ = 3.2, $J_{4,5}$ ~ 7.5 Hz, H-5), 3.51 (t, 1H, $J_{3,4}$ ~ 7.5 Hz, H-4), 3.645 (ddd, 1H, H-3), 3.72 (d, 2H, H-6,6'). Anal. calcd for $C_{30}H_{34}O_5$: C 75.92, H 7.22. Found: C 75.73, H 7.30.

*[1S]-1-Acetoxy-1-(3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-*arabino*-hexopyranosyl)propane (**6S**)* and *its 1R isomer (**6A**)*

*From **4S**, **4A***. Acetylation of **4S**, **4A** (1.03 g, 2.16 mmol) in pyridine (6 mL) and acetic anhydride (1.5 mL), standard work-up and column chromatography (10:1 → 3:1, hexanes:AcOEt) gave successively **6A** (91 mg, 8 %) and **6S** (949 mg, 85 %). **6A**, $[\alpha]_D^{20}$ +12 ° (*c* 2.35, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.885 (t, 3H, *J* = 7.5 Hz, CH_3), 1.56 and 1.80 (2 m, 2H, CH_2), 1.71 (ddd, 1H, $J_{1,2}$ = 4.8, $J_{2,3}$ = 9.1, $J_{2,2'}$ = 13.8 Hz, H-2), 1.975 (dt, $J_{1,2'} = J_{2',3}$ = 4.5 Hz, H-2'), 2.05 (s, 3H, CH_3CO), 3.53 (t, 1H, $J_{3,4} = J_{4,5}$ = 7.2 Hz, H-4), 3.675 (dd, 1H, $J_{5,6}$ = 6.5, $J_{6,6'}$ = 11.4 Hz, H-6), 3.705 (m, 1H, H-5), 3.71 (dd, 1H, $J_{5,6}$ = 2.0 Hz, H-6'), 3.845 (ddd, 1H, $J_{1,7}$ = 8.8 Hz, H-1), 3.895 (ddd, 1H, $J_{3,4}$ = 7.2 Hz, H-3), 5.105 (dt, 1H, J_{7,CH_2} = 3.4 and 8.8 Hz, H-7). Anal. calcd for $C_{32}H_{38}O_6$: C 74.11, H, 7.38. Found: C 74.07, H 7.45.

6S, $[\alpha]_D^{20}$ +25 ° (*c* 1.33, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.875 (t, 3H, *J* = 7.5 Hz, CH-3), 1.55 (m, 2H, CH_2), 1.75 (ddd, 1H, $J_{2,3}$ = 5.0, $J_{1,2}$ = 8.3, $J_{2,2'}$ = 13.6 Hz, H-2), 1.97 (ddd, 1H, $J_{1,2'}$ = 4.0, $J_{2',3}$ = 5.4 Hz, H-2'), 2.01 (s, 3H, CH_3CO), 3.545 (t, 1H, $J_{3,4} = J_{4,5}$ = 6.7 Hz, H-4), 3.62 (dd, 1H, $J_{5,6}$ = 3.9, $J_{6,6'}$ = 10.6 Hz, H-6), 3.71 (ddd, 1H, $J_{5,6'}$ = 5.0 Hz, H-5), 3.75 (ddd, 1H, H-6'), 3.94 (ddd, 1H, H-3), 3.945 (ddd, 1H, $J_{1,7}$ 6.4 Hz H-1), 5.005 (ddd, $J_{7,CH2}$ 5.1 and 7.9 Hz, H-7). Anal. calcd for $C_{32}H_{38}O_6$: C 74.11, H 7.38. Found: C 74.18, H 7.44.

*From **5***. To a stirred solution of ketone **5** (32 mg, 0.067 mmol) in ethyl ether (1 mL) at –78 °C under Ar was added $Zn(BH_4)_2$[10] (0.1 M in ethyl ether, 0.5 equiv. mol). After 30 min, MeOH and NH_4Cl were added, the reaction mixture was diluted with ethyl ether and the solvents were evaporated several times with MeOH. Ethyl ether was added and the organic layer was washed with sat. aqueous NH_4Cl, water, sat. aqueous NaCl and concentrated *in vacuo*. The dried residue was acetylated as described above to give, after column chromatography (5:1, hexanes:AcOEt) **6S**, **6A** (33.5 mg, 95 %), **6S**:**6A** isomeric ratio of 1:2 as determined by ^1H NMR.

*1-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-1-propanol (**7S**,**7A**)*

*From **3***. The procedure utilized for **2** with **3**[4] (4.0 g, 5.65 mmol) and propionaldehyde (0.55 mL, 1.3 equiv.) gave, after column chromatography (10:1, CH_2Cl_2:AcOEt), isomeric alcohols **7S**, **7A** (1.83 g, 68 %). For ^1H NMR, see below. Anal. calcd for $C_{30}H_{36}O_5$: C 75.60, H 7.61. Found: C 75.82, H 7.88.

*From **9S** or **9A***. Ester **9S** (1.11 g, 1.65 mmol) in solution in anhydrous MeOH was treated for 2 h at 0 °C with a catalytic amount of MeONa. Standard work-up (ethyl ether extraction, washing of the organic phase with water, sat. NaCl, drying with $MgSO_4$ and concentration) afforded, after column chromatography (3:1, hexanes:AcOEt), alcohol **7S** (725 mg, 92 %) $[\alpha]_D^{20}$ +14.2 (*c* 0.85, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.4 Hz, CH_3), 1.49 (dt, 1H, $J_{1,2a} = J_{2a,3}$ = 11.4, $J_{2a,2e}$ = 12.9 Hz, H-2a), 2.095 (ddd, 1H, $J_{1,2e}$ = 2.1, $J_{2e,3}$ = 5.0 Hz, H-2e), 3.23 (ddd, 1H, $J_{1,7}$ = 6.3 Hz, H-1), 3.40 (dt, 1H, $J_{5,6}$ ~ $J_{5,6'}$ ~ 3.2, $J_{4,5}$ = 9.5 Hz, H-5), 3.45 (ddd, 1H, J_{7,CH_2} = 3.8 and 8.2 Hz, H-7), 3.52 (t, 1H, $J_{3,4}$ ~ 9 Hz, H-3), 3.68 (ddd, 1H, H-3), 3.72 (m, 2H, H-6,6'). Anal. calcd for $C_{30}H_{36}O_5$: C 75.60, H 7.61. Found: C 75.80, H 7.80.

Deacylation of ester **9A** (812 mg, 1.21 mmol) following the above procedure provided **7A** (501 mg, 87 %) $[\alpha]_D^{20}$ + 11.5 ° (*c* 1.03, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.98 (t, 3H, *J* = 7.6 Hz, CH_3), 1.46 (m, 2H, CH_2), 1.595 (dt, $J_{1,2a} = J_{2a,3}$ ~ 11.9, $J_{2a,2e}$ = 12.9 Hz, H-2a), 2.11 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 5.3 Hz, H-2e), 3.34 (ddd, 1H, $J_{1,7}$ = 4.0 Hz, H-1), 3.42–3.49 and 3.63–3.75 (2 m, 6H, H-3,4,6,6',7).

*1-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-*arabino*-hexopyranosyl)-1-propanone (**8**)*

Oxidation of **7S**, **7A** (70 mg, 0.147 mmol) according to the procedure used for **5** gave, after column chromatography (6:1, hexanes:AcOEt), ketone **8** (60 mg, 86 %) $[\alpha]_D^{20}$ +39 ° (*c* 2.80, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.05 (t, 3H, *J* 7.1 Hz, CH_3), 1.49 (q, 1H, $J_{1,2a}$ ~ $J_{2a,2e}$ ~ $J_{2a,3}$ ~ 12.5 Hz, H-2a), 2.465 (ddd, 1H, $J_{1,2e}$ = 2.2, $J_{2e,3}$ = 5.1 Hz, H-2e), 2.685 (q, 2H, *J* = 7.1 Hz, CH_2CO), 3.45 (m, 1H, H-5), 3.49 (t, 1H, $J_{3,4} = J_{4,5}$ = 8.1 Hz, H-4), 3.70 (ddd, 1H, H-3), 3.70–3.78 (m, 2H, H-6,6'), 3.82 (dd, 1H, H-1). Anal. calcd for $C_{30}H_{34}O_5$: C 75.92, H 7.22. Found: C 75.98, H 7.38.

*[1R]-1-(3,5-Dinitrobenzoyloxy)-1-(3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-arabino-*hexopyranosyl)propane (**9S**)* and *its 1S isomer (**9A**)*

*From **7S** and **7A***. Acylation of alcohols **7S** and **7A** (1.60 g, 3.36 mmol) in pyridine (4 mL) with 3,5-dinitrobenzoyl chloride (1.5 equiv.) at rt for 3 h followed by a standard work-up and column chromatography (3:1, hexanes:AcOEt) gave successively **9S** (1.19 g) and **9A** (0.97 g) in a total yield of 96 %, isomeric ratio, ~1.2:1. **9S**, $[\alpha]_D^{20}$ +5.9 ° (*c* 2.7, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.505 (q, 1H, $J_{1,2a}$ ~ $J_{2a,2e}$ ~ $J_{2a,3}$ 12.2 Hz, H-2a), 1.83 (m, 2H, J_{7,CH_2} = 5.0 and 8.3 Hz, CH_2), 2.15 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 4.9 Hz, H-

2e), 3.60 (ddd, 1H, $J_{1,7}$ = 5.6 Hz, H-1), 3.62–3.75 (m, 3H, H-3,4,5), 5.23 (ddd, 1H, H-7). Anal. calcd for $C_{37}H_{38}N_2O_{10}$: C 66.26, H 5.71. Found: C 65.97, H 5.51.

9_A, $[\alpha]_D^{20}$ +5.9 ° (*c* 4.38, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.61 (q, 1H, $J_{1,2a} \sim J_{2a,2e} \sim J_{2a,3} \sim$ 12.5 Hz, H-2a), 1.84 (m, 2H, CH_2), 2.18 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 5.1 Hz, H-2e), 3.425 (ddd, 1H, $J_{5,6}$ = 2.0, $J_{5,6'}$ = 4.0, $J_{4,5}$ = 9.5 Hz, H-5), 3.555 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-4), 3.61 (ddd, 1H, $J_{1,7}$ = 4.5 Hz, H-1), 3.68 (ddd, 1H, H-3), 3.69 (dd, 1H, $J_{6,6'}$ = 11.3 Hz, H-6), 3.76 (dd, 1H, H-6'), 5.32 (dt, 1H, J_{7,CH_2} = 6.7 Hz, H-7). Anal. calcd for $C_{37}H_{38}N_2O_{10}$: C 66.26, H 5.71. Found: C 65.97, H 5.51.

From 8. Ketone **8** (21 mg, 0.044 mmol) treated under the conditions described above (**5** → **4_S**, **4_A**) provided, after column chromatography (10:1, CH_2Cl_2:AcOEt) **7_S**, **7_A** (20 mg, 95 %). Acylation as above with 3,5-dinitrobenzoyl chloride furnished, after column chromatography (4:1, hexanes:AcOEt), **9_S**, **9_A** (26.5 mg), **9_S:9_A** isomeric ratio of 1:7 as determined by ^1H NMR.

*[1S]-1-Acetoxy-1-(6-O-acetyl-3,4-di-O-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)propane (**10**)*

Trifluoroacetic acid (1.5 mL) was added to a stirred solution of **6_S** (798 mg, 1.54 mmol) in acetic anhydride (4 mL) cooled to 0 °C, then the reaction was followed by TLC (3:1, hexanes:AcOEt). After 3 h at 0 °C, the reaction mixture was diluted with ethyl ether, washed with cold water, sat. aqueous $NaHCO_3$ and NaCl. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (8:1 → 4:1, hexanes:AcOEt) to give **10** (666 mg, 92 %), $[\alpha]_D^{20}$ +28.5 ° (*c* 1.47, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, *J* = 7.5 Hz, CH_3), 1.55 (m, 2H, CH_2), 1.735 (ddd, 1H, $J_{1,2a}$ = 4.9, $J_{2a,3}$ = 7.8, $J_{2a,2e}$ = 14.0 Hz, H-2a), 1.97 (ddd, 1H, $J_{2e,3}$ = 4.0, $J_{1,2e}$ = 6.1 Hz, H-2e), 2.03 and 2.05 (2 s, 6H, 2 CH_3CO), 3.375 (dd, 1H, $J_{3,4}$ = 6.0, $J_{4,5}$ = 6.3 Hz, H-4), 3.745 (ddd, 1H, H-3), 3.95 (dt, 1H, $J_{1,7}$ = 6.0 Hz, H-1), 4.015 (ddd, 1H, $J_{5,6}$ = 3.1, $J_{5,6'}$ = 6.7 Hz, H-5), 4.13 (dd, 1H, $J_{6,6'}$ = 12.0 Hz, H-6), 4.42 (dd, 1H, H-6'), 4.98 (dt, 1H, J_{7,CH_2} = 6.0 and 7.7 Hz, H-7). Anal. calcd for $C_{27}H_{34}O_7$: C 68.92, H 7.28. Found: C 69.12, H 7.20.

*[1S]-1-(3,4-Di-O-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-1-propanol* (**11**)

Deacetylation of **10** (632 mg, 1.34 mmol) in anhydrous methanol (10 mL) with a catalytic amount of MeONa at rt provided, after a standard work-up and column chromatography (20:1, CH_2Cl_2:MeOH), **11** (502 mg, 97 %), $[\alpha]_D^{20}$ +10.5 ° (*c* 3.65, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.43 (m, 2H, CH_2), 1.74 (ddd, 1H, $J_{1,2}$ = 4.6, $J_{2,3}$ = 7.7, $J_{2,2'}$ = 14.0 Hz, H-2), 2.01 (ddd, 1H, $J_{2',3}$ = 4.0, $J_{1,2'}$ = 6.3, H-2'), 2.10 and 2.50 (2 bs, 2H, 2 OH), 3.43 (t, 1H, $J_{3,4} = J_{4,5}$ = 6.0 Hz, H-4), 3.59 (dt, 1H, $J_{1,7}$ = 8.0, J_{7,CH_2} = 3.6 and 8.0 Hz, H-7), 3.685 (dd, 1H, $J_{5,6}$ = 3.2, $J_{6,6'}$ = 11.5 Hz, H-6), 3.71–3.83 (m, 2H, H-1,5), 3.76 (ddd, 1H, H-3), 3.905 (dd, 1H, $J_{5,6'}$ = 6.2 Hz, H-6'). Anal. calcd for $C_{23}H_{30}O_5$: C 71.48, H 7.82. Found: C 71.51, H 7.92.

*[1S]-1-(3,4-Di-O-benzyl-6-bromo-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-1-propanol (**12**)*

Triphenylphosphine (415 mg, 2.3 equiv.) and, after 5 min, carbon tetrabromide (263 mg, 1.15 equiv.) were successively added to a cooled (0 °C) solution of **11** (266 mg, 0.69 mmol) in pyridine (1.5 mL). After being stirred overnight at 4 °C, MeOH (1 mL) was added to the reaction mixture. The solvents were evaporated *in vacuo*, and the residue was purified by column chromatography (30:1 → 10:1, CH_2Cl_2:AcOEt). Dibromide **15** eluted first (77 mg, 22 %), then **12** (181 mg, 58 %), $[\alpha]_D^{20}$ ~0 ° (*c* 3.45, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.4 Hz, CH_3), 1.45 (m, 2H, CH_2), 1.73 (ddd, 1H, $J_{2,3}$ = 3.9, $J_{1,2}$ = 6.1, $J_{2,2'}$ = 13.9 Hz, H-2), 1.98 (ddd, 1H, $J_{1,2'}$ = 3.8, $J_{2',3}$ = 8.3 Hz, H-2'), 2.50 (bs, 1H, OH), 3.51 (t, 1H, $J_{3,4} = J_{4,5}$ = 4.8 Hz, H-4), 3.62–3.73 (m, 3H, H-6,6',7), 3.78 (dt, 1H, $J_{1,7}$ = 6.1, H-1), 4.01 (dt, 1H, $J_{5,6}$ = 4.8, $J_{5,6'}$ = 7.5 Hz, H-5). Anal. calcd for $C_{23}H_{29}BrO_4$: C 61.47, H 6.50. Found: C 61.73, H 6.73.

*[3R,4R,6S,7S]-3,4-Dibenzyloxy-6,7-dihydroxynon-1-ene (**13**)*

Activated zinc (50 equiv.) was added to a solution of **12** (163 mg, 0.36 mmol) in aqueous *n*-propanol (93:7, v/v, 10 mL). The stirred reaction mixture was heated at 80 °C for 1.5 h, cooled, filtered through a bed of Celite and the insoluble material was washed with MeOH. The filtrate and washings were concentrated *in vacuo* and the residue was purified by column chromatography (10:1, CH_2Cl_2:MeOH) to give **13** (121 mg, 90 %), $[\alpha]_D^{20}$ +12 ° (*c* 1.51, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.96 (t, 3H, *J* = 7.5 Hz, CH_3), 1.47 (m, 2H, H-8,8'), 1.69 (dt, 1H, $J_{4,5} = J_{5,6}$ = 9.7, $J_{5,5'}$ = 14.8 Hz, H-5), 1.79 (ddd, 1H, $J_{5',6}$ = 2.7, $J_{4,5'}$ = 4.1 Hz, H-5'), 2.265 (d, 1H, $J_{7,OH}$ = 5.8 Hz, OH-7), 3.245 (m, 1H, $J_{6,7}$ = 4.5, $J_{7,8}$ = 9.0, $J_{7,8'}$ = 9.9 Hz, H-7), 3.53 (d, 1H, $J_{6,OH}$ = 2.3 Hz, OH-6), 3.61 (m, 1H, H-6), 3.82 (ddd, 1H, $J_{3,4}$ = 5.4 Hz, H-4), 4.025 (m, 1H, $J_{1,3} \sim 1$, $J_{2,3}$ = 7.2 Hz, H-3), 5.34 (dt, 1H, $J_{1,1'}$ = 1.6, $J_{1,2}$ = 17.3 Hz, H-1), 5.38 (dd, 1H, $J_{1',2}$ = 10.2 Hz, H-1'), 5.825 (ddd, 1H, H-2). Anal. calcd for $C_{23}H_{30}O_4$: C 74.56, H 8.16. Found: C 74.28, H 8.16.

*[3R,4R,6S,7S]-3,4,6,7-Tetraacetoxynonane (**14**)*

A solution of **13** (80 mg, 0.22 mmol) in methanol (1 mL) containing 10 % Pd C (~ 5 mg) under H_2 was stirred for 1 h at rt. The mixture was filtered through Celite, and the insoluble material washed with several portions of methanol. Evaporation to dryness of the combined filtrate and washings gave a residue, a part of which was purified by column chromatography (9:1, CH_2Cl_2:MeOH) to obtain an analytically pure sample of

the tetrol, $[\alpha]_D^{20}$ 0 (*c* 1.7, MeOH). Anal. calcd for $C_9H_{20}O_4$: C 56.23, H 10.48. Found: C 56.41, H 10.31.

Most of the previous residue, acetylated under standard conditions (pyridine, acetic anhydride) afforded, after column chromatography (4:1, hexanes:AcOEt), **14** (69 mg, 88 % from **13**), $[\alpha]_D^{20}$ 0 ° (*c* 2.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.87 (t, 6H, $J_{1,2(8,9)}$ = 7.5 Hz, H-1,9), 1.56 (m, 4H, $J_{2,3(7,8)}$ = 6.2, $J_{2',3(7,8')}$ = 7.5 Hz, H-2,2',8,8'), 1.74 (m, 2H, $J_{4,5(5',6)}$ = 2.2, $J_{4,5'(5,6)}$ = 6.5 Hz, H-5,5'), 2.095 and 2.105 (2 s, 12H, 4 Ac), 4.95–5.08 (m, 4 H, H-3,4,6,7). Anal. calcd for $C_{17}H_{28}O_8$: C 56.65, H 7.83. Found: C 56.71, H 7.70.

*[1R]-1-Acetoxy-1-(6-O-acetyl-3,4-di-O-benzyl-2-deoxy-β-D-*arabino-*hexopyranosyl)propane (**16**$_S$)*

Acetolysis of **7**$_S$ (710 mg, 1.49 mmol) under the conditions described for the preparation of **10** gave, after purification by column chromatography (4:1, hexanes:AcOEt), **16**$_S$ (610 mg, 87 %), $[\alpha]_D^{20}$ +33.5 ° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, *J* = 7.4 Hz, CH_3), 1.48 (q, 1H, $J_{1,2a} = J_{2a,2e} = J_{2a,3}$ = 12.2 Hz, H-2a), 1.64 (m, 2H, CH_2), 2.06 (ddd, 1H, $J_{1,2e}$ = 1.9, $J_{2e,3}$ = 5.7 Hz, H-2e), 2.03 and 2.095 (2 s, 6H, 2 Ac), 3.34–3.44 (m, 2H, H-4,5), 3.44 (ddd, 1H, $J_{1,7}$ = 4.3 Hz, H-1), 3.69 (ddd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 4.20 (dd, 1H, $J_{5,6}$ = 5.0, $J_{6,6'}$ = 11.8 Hz, H-6), 4.33 (dd, 1H, $J_{5,6'}$ = 1.7, H-6'), 4.865 (dt, 1H, J_{7,CH_2} 4.3 and 8.2 Hz, H-7). Anal. calcd for $C_{27}H_{34}O_7$: C 68.92, H 7.29. Found: C 68.96, H 7.31.

*[1S]-1-Acetoxy-1-(6-O-acetyl-3,4-di-O-benzyl-2-deoxy-β-D-*arabino-*hexopyranosyl)propane (**16**$_A$)*

Acetolysis of **7**$_A$ (490 mg, 1.03 mmol) as above gave, after column chromatography (3:1 → 2:1, hexanes: AcOEt), **16**$_A$ (442 mg, 92 %), $[\alpha]_D^{20}$ –6.3 ° (*c* 0.95, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 7.5 Hz, CH_3), 1.445 (dt, 1H, $J_{1,2a} = J_{2a,3}$ = 11.2, $J_{2a,2e}$ = 11.9 Hz, H-2a), 1.66 (m, 2H, J_{7,CH_2} = 4.1 and 8.3 Hz, CH_2), 2.025 and 2.065 (2 s, 6 H, 2 Ac), 2.125 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 5.1 Hz, H-2e), 3.34–3.44 (m, 3H, H-1,4,5), 3.655 (ddd, 1H, $J_{3,4}$ = 8.6 Hz, H-3), 4.22 (dd, 1H, $J_{5,6}$ = 4.6, $J_{6,6'}$ = 11.8 Hz, H-6), 4.32 (dd, 1H, $J_{5,6'}$ = 1.9 Hz, H-6'), 4.82 (ddd, 1H, $J_{1,7}$ 5.9 Hz, H-7). Anal. calcd for $C_{27}H_{34}O_7$: C 68.92, H 7.29. Found: C 68.88, H 7.19.

*[1R]-1-(3,4-Di-O-benzyl-2-deoxy-β-D-*arabino-*hexopyranosyl)-1-propanol (**17**$_S$)*

Deacetylation of **16**$_S$ (555 mg, 1.18 mmol) as described for the preparation of **11** gave, after column chromatography (20:1, CH_2Cl_2:MeOH), **17**$_S$ (437 mg, 96 %), $[\alpha]_D^{20}$ +6.5 ° (*c* 1.25, $CHCl_3$), mp: 94 °C (ethyl ether:hexanes). ^1H NMR ($CDCl_3$): δ 0.985 (t, 3H, *J* = 7.5 Hz, CH_3), 1.48 (m, 2H, CH_2), 1.49 (m, 1H, $J_{2a,3}$ = 11.2, $J_{1,2a}$ = 11.8, $J_{2a,2e}$ = 12.9 Hz, H-2a), 2.10 (ddd, 1H, $J_{1,2e}$ = 1.9, $J_{2e,3}$ = 5.1 Hz, H-2e), 3.295 (ddd, 1H, $J_{1,7}$ = 6.0 Hz, H-1), 3.305 (ddd, 1H, $J_{5,6}$ = 3.0, $J_{5,6'}$ = 4.5, $J_{4,5}$ = 9.5 Hz, H-5), 3.42 (ddd, 1H, J_{7,CH_2} = 2.0 and 8.2 Hz, H-7), 3.455 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-4), 3.705 (ddd, 1H, H-3), 3.72 (dd, 1H, $J_{6,6'}$ = 12.1 Hz, H-6'), 3.86 (dd, 1H, H-6). Anal. calcd for $C_{23}H_{30}O_5$: C 71.48, H 7.82. Found: C 71.60, H 7.81.

*[1S]-1-(3,4-Di-O-benzyl-2-deoxy-β-D-*arabino-*hexopyranosyl)-1-propanol (**17**$_A$)*

Deacetylation of **16**$_A$ (431 mg, 0.92 mmol) as above gave, after column chromatography (20:1, CH_2Cl_2: MeOH), **17**$_A$ (349 mg, 98 %), $[\alpha]_D^{20}$ +0.7 ° (*c* 1.03, $CHCl_3$), mp: 91–92 °C (ethyl ether:hexanes). ^1H NMR ($CDCl_3$): δ 0.985 (t, 3H, *J* = 7.4 Hz, CH_3), 1.47 (m, 2H, CH_2), 1.565 (dt, 1H, $J_{1,2a} = J_{2a,3}$ = 11.5, $J_{2a,2e}$ = 12.5 Hz, H-2a), 2.15 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 5.1 Hz, H-2e), 3.335 (ddd, 1H, $J_{5,6'}$ = 2.9, $J_{5,6}$ = 5.1, $J_{4,5}$ = 9.0 Hz, H-5), 3.37 (ddd, 1H, $J_{1,7}$ = 4.5 Hz, H-1), 3.42 (dd, 1H, $J_{3,4}$ = 8.5 Hz, H-4), 3.63 (dt, 1H, J_{7,CH_2} = 4.5 and 8.5 Hz, H-7), 3.69 (dd, 1H, H-3), 3.85 (dd, 1H, H-6'). Anal. calcd for $C_{23}H_{30}O_5$: C 71.48, H 7.82. Found: C 71.43, H 7.63.

*[1R]-1-(3,4-di-O-benzyl-2,6-dideoxy-6-iodo-β-D-*arabino-*hexopyranosyl)-1-propanol (**18**$_S$)*

A solution of **17**$_S$ (198 mg, 0.51 mmol) in toluene (15 mL) containing triphenylphosphine (204 mg, 1.5 equiv.) and imidazole (106 mg, 3 equiv.) was distilled until a final volume of 1.5 mL was reached. The temperature of the solution was adjusted to 55 °C and iodine (143 mg, 1.1 equiv.) was then added. After 30 min the reaction mixture was diluted with ethyl ether and the organic layer was washed with sat. aqueous sodium sulfite, water, sat. aqueous NaCl, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (15:1, CH_2Cl_2:AcOEt). The 6,7-diiodo compound (46 mg, 15 %) eluted first, then **18**$_S$ (172 mg, 68 %), $[\alpha]_D^{20}$ +20.5 ° (*c* 2.38, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 1.00 (t, 3H, *J* = 7.4 Hz, CH_3), 1.53 (m, 1H, $J_{1,2a}$ = 11.5, $J_{2a,2e} \sim J_{2a,3} \sim$ 13.0 Hz, H-2a), 1.55 (m, 2H, CH_2), 2.12 (ddd, 1H, $J_{1,2e}$ = 2.0, $J_{2e,3}$ = 5.0 Hz, H-2e), 2.45 (bs, 1H, OH), 3.07 (ddd, $J_{5,6'}$ = 2.7, $J_{5,6}$ = 6.8, $J_{4,5}$ = 9.0 Hz, H-5), 3.295 (dd, 1H, $J_{3,4}$ = 8.4 Hz, H-4), 3.305 (dd, 1H, $J_{6,6'}$ = 10.5 Hz, H-6), 3.31 (ddd, 1H, $J_{1,7}$ = 6.0 Hz, H-1), 3.43 (ddd, 1H, $J_{7,CH2}$ = 4.0 and 8.2 Hz, H-7), 3.525 (dd, 1H, H-6'), 3.72 (ddd, 1H, H-3). Anal. calcd for $C_{23}H_{29}IO_4$: C 55.65, H 5.89. Found: C 55.94, H 5.92.

*[1S]-1-(3,4-Di-O-benzyl-6-bromo-2,6-dideoxy-β-D-*arabino-*hexopyranosyl)-1-propanol (**18**$_A$)*

Halogenation of diol **17**$_A$ (160 mg, 0.41 mmol) as described for the preparation of **12** gave, after column chromatography (30:1 → 15:1, CH_2Cl_2:AcOEt), the 6,7-dibromo product (25 mg, 12 %) and **18**$_A$ (139 mg, 75 %), $[\alpha]_D^{20}$ +8.5 ° (*c* 1.56, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.985 (t, 3H, *J* = 7.4 Hz, CH_3), 1.48 (m, 2H, CH_2), 1.59

(dt, $J_{1,2a} \sim J_{2a,3} \sim 12.0$, $J_{2a,2e} = 12.8$ Hz, H-2a), 2.145 (ddd, 1H, $J_{1,2e} = 2.0$, $J_{2e,3} = 5.0$ Hz, H-2e), 3.38 (ddd, 1H, $J_{1,7} = 4.0$ Hz, H-1), 3.41 (ddd, 1H, $J_{5,6'} = 2.5$, $J_{5,6} = 4.5$, $J_{4,5} = 8.6$ Hz, H-5), 3.455 (dd, 1H, $J_{3,4} = 8.1$ Hz, H-4), 3.585 (dd, 1H, $J_{6,6'} = 11.0$ Hz, H-6), 3.625 (m, 1H, H-7), 3.66 (dd, 1H, H-6'), 3.70 (ddd, 1H, H-3). Anal. calcd for $C_{23}H_{29}BrO_4$: C 61.47, H 6.50. Found: C 61.30, H 6.49.

*[3R,4R,6R,7R]-3,4-Dibenzyloxy-6,7-dihydroxynon-1-ene (**19**$_S$)*

To a solution of **18**$_S$ (130 mg, 0.26 mmol) in THF at –78 °C under Ar was added BuLi (1.5 M in hexanes, 0.36 mL, 2.1 equiv.). After 10 min, ammonium chloride was added and the temperature was raised to –20 °C. The reaction mixture was diluted with ethyl ether and the organic layer was washed with sat. aqueous sodium sulfite, sat. NH_4Cl, sat. NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (10:1, CH_2Cl_2:AcOEt) to give **19**$_S$ (78 mg, 80 %), $[\alpha]_D^{20}$ +24.5 (*c* 1.46, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.935 (t, 3H, $J = 7.5$ Hz, CH_3), 1.42 (m, 2H, H-8,8'), 1.58 (ddd, 1H, $J_{5,6} = 2.7$, $J_{4,5} = 8.6$, $J_{5,5'} = 14.5$ Hz, H-5), 1.74 (ddd, 1H, $J_{5',6} = 9.7$ Hz, H-5'), 2.46 (bs, 2H, 2 OH), 3.24 (dt, 1H, $J_{6,7} = 5.0$, $J_{7,8} = J_{7,8'} = 8.0$ Hz, H-7), 3.60 (ddd, 1H, H-6), 3.815 (ddd, 1H, $J_{3,4} = 6.0$ Hz, H-4), 3.995 (m, 1H, $J_{2,3} = 7.3$ Hz, H-3), 5.32 (m, 1H, $J_{1,3} \sim 1$, $J_{1,1'} = 2.1$, $J_{1,2} = 17.1$ Hz, H-1), 5.35 (dd, $J_{1',2} = 10.9$ Hz, H-1'), 5.80 (ddd, 1H, H-2). Anal. calcd for $C_{23}H_{30}O_4$: C 74.56, H 8.16. Found: C 74.59, H 7.92.

*[3R,4R,6R,7S]-3,4-Dibenzyloxy-6,7-dihydroxynon-1-ene (**19**$_A$)*

Treatment of **18**$_A$ (67 mg, 0.15 mmol) as described above for **18**$_S$ gave, after column chromatography (10:1, CH_2Cl_2:AcOEt), **19**$_A$ (44 mg, 80 %), $[\alpha]_D^{20}$ +13.3 ° (*c* 1.14, $CHCl_3$), mp: 54–55 °C (ethyl ether:hexanes). ^1H NMR ($CDCl_3$): δ 0.95 (t, 3H, $J = 7.5$ Hz, CH_3), 1.40 (m, 2H, H-8,8'), 1.57 (ddd, 1H, $J_{4,5} = 7.6$, $J_{5,6} = 7.7$, $J_{5,5'} = 14.6$ Hz, H-5), 1.75 (ddd, 1H, $J_{4,5'} = 3.8$, $J_{5',6} = 10.3$ Hz, H-5'), 1.92 (d, 1H, $J_{7,OH} = 4.0$ Hz, OH-7), 2.75 (d, 1H, $J_{6,OH} = 4.5$ Hz, OH-6), 3.49 (m, 1H, $J_{6,7} = 4.0$, $J_{7,8} = 8.4$ Hz, H-7), 3.745 (m, 1H, H-6), 3.825 (ddd, 1H, $J_{3,4} = 6.5$, H-4), 4.02 (dd, 1H, $J_{2,3} = 7.4$ Hz, H-3), 5.33 (m, 1H, $J_{1,3} \sim 0.8$, $J_{1,1'} = 2.4$, $J_{1,2} = 16.9$ Hz, H-1), 5.355 (dd, 1H, $J_{1',2} = 10.8$ Hz, H-1'), 5.80 (ddd, 1H, H-2). Anal. calcd for $C_{23}H_{30}O_4$: C 74.56, H 8.16. Found: C 74.71, H 8.30.

*[3R,4R,6R,7R]-3,4,6,7-Tetraacetoxynonane (**20**$_S$)*

Treatment of **19**$_S$ (44 mg, 0.12 mmol) using the same conditions described for the preparation of **14** gave, after column chromatography (12:1, CH_2Cl_2:AcOEt), **20**$_S$ (35 mg, 82 %), $[\alpha]_D^{20}$ +62 ° (*c* 1.38, $CHCl_3$), mp: 83 °C (ethyl ether:hexanes). ^1H NMR ($CDCl_3$): δ 0.89 (t, 6H, $J_{1,2(8,9)} = 7.5$ Hz, H-1,9), 1.54 (m, 4 H, $J_{2,3(7,8)} = 5.5$, $J_{2',3(7,8')} = 8.0$ Hz, H-2,2',8,8'), 1.765 (dd, 2H, $J_{4,5(5',6)} = 5.9$, $J_{4,5'(5,6)} = 7.9$ Hz, H-5,5'), 2.065 and 2.09 (2 s, 12H, 4 Ac), 4.87 (ddd, 2H, $J_{3,4(6,7)} = 4.0$, H-3,7), 5.08 (ddd, 2H, H-4,6). Anal. calcd for $C_{17}H_{28}O_8$: C 56.65, H 7.83. Found: C 56.54, H 7.60.

*[3R,4R,6R,7S]-3,4,6,7-Tetraacetoxynonane (**20**$_A$)*

Treatment of **19**$_A$ (33 mg, 0.09 mmol) under the same conditions described for the preparation of **14** gave the tetrol derivative, $[\alpha]_D^{20}$ +30 ° (*c* 0.89, MeOH), mp: 123 °C (CH_2Cl_2:MeOH) and, after column chromatography (12:1 → 7:1, CH_2Cl_2:AcOEt), **20**$_A$ (26 mg, 81 %), $[\alpha]_D^{20}$ + 28.3 ° (*c* 0.60, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.90 and 0.905 (2t, 6H, $J = 7.4$ Hz, 2 CH_3-1,9), 1.55 (m, 4H, $J = 4.1$ and 7.4 Hz, H-2,2',8,8'), 1.79 (m, 2H, $J_{4,5(5',6)} = 2.2$, $J_{4,5'(5,6)} = 4.1$, $J_{5,5'} = 10.0$ Hz, H-5,5'), 2.015, 2.055, 2.065 and 2.105 (4s, 12H, 4 Ac), 4.89 (ddd, 1H, $J_{7,8} = 1.7$, $J_{7,8'} = 4.1$, $J_{6,7} = 8.1$ Hz, H-7), 4.93 (ddd, 1H, $J_{3,4} = 3.2$ Hz, H-4), 4.96 (ddd, 1H, $J_{2,3} = 1.7$, $J_{2',3} = 4.1$ Hz, H-3), 5.14 (ddd, 1H, H-6). Anal. calcd for $C_{17}H_{28}O_4$: C 56.65, H 7.83. Found: C 56.75, H 7.59.

*Tributyl-(3,4,6-tri-O-benzyl-β-D-gluco-hexopyranosyl)-stannane (**25**)*

*From **22**.* To a stirred solution of chloride **22**[23] (486 mg, 1.04 mmol) in THF (2 mL) at –78 °C under Ar were added successively butyl lithium (1.6 M in hexanes, 1 equiv.) and after 3 min tributylstannyl lithium[5a] (0.4 M in THF, 5.2 mL, 2 equiv.). The temperature was raised to 0 °C and after 30 min more tributylstannyl lithium (1 equiv.) was added. After 1 h at 0 °C, NH_4Cl was added and the mixture was diluted with ethyl ether. The organic layer was washed with water, sat. aqueous NH_4Cl, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (hexanes then 12:1 hexanes:AcOEt) of the residue provided **25** (201 mg, 27 %).

*From **24**.* To a stirred solution of vinylic stannane **24**[19] (635 mg, 0.90 mmol) in THF (2.5 mL) at rt under Ar was added 1 M borane–THF (2 equiv.). After stirring at rt for 2.5 h (0.5 equiv. of borane was added after 1 h), 3 M NaOH (2 equiv.) and 10 M H_2O_2 (6 equiv.) were added at 0°C. Stirring was continued for 1 h and the mixture was concentrated *in vacuo*. The mixture was diluted with ethyl ether and the organic layer was washed with water, sat. NH_4Cl, sat. NaCl, dried ($MgSO_4$) and the solvent evaporated. The residue was purified by column chromatography (hexanes then 15:1 → 10:1, hexanes:AcOEt) to give **25** (533 mg, 82 %).

25: $[\alpha]_D^{20}$ –0.6 ° (*c* 4.30, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.91 (m, 12H, 4 CH_3), 1.30 and 1.52 (2 m, 24 H, 12 CH_2), 2.06 (d, 1H, $J_{2,OH} = 3.0$ Hz, OH), 3.30 (ddd, 1H, $J_{5,6} = 2.2$, $J_{5,6'} = 4.8$, $J_{4,5} = 9.8$ Hz, H-5), 3.39 (t, 1H, $J_{2,3} = J_{3,4} = 8.5$ Hz, H-3), 3.435 (d, 1H, $J_{1,2} = 11.0$ Hz, H-1), 3.61 (dd, 1H, H-4), 3.685 (dd, 1H, $J_{6,6'} = 11.9$ Hz, H-6), 3.73 (dd, 1H, H-6'), 3.74 (ddd, 1H, H-2), $^{117,119}Sn$ satellites for H-1: $J_{Sn,1} = 12$ Hz. Anal. calcd for $C_{39}H_{56}O_5Sn$: C 64.74, H 7.80. Found: C 64.54, H 7.86.

Phenyl (3,4,6-tri-O-benzyl-β-D-gluco-hexopyranosyl)-methanol (**30$_S$**, **30$_A$**)

To a stirred solution of stannane **25** (94 mg, 0.13 mmol) in THF (0.5 mL) at –78 °C under Ar was added HMPA (1 equiv.) then butyl lithium (1.5 M in hexanes; 2.5 equiv., 1 fast and 1.5 in 5 min). After stirring for 20 min, benzaldehyde (40 μL, 3 equiv.) was added. After 30 min at –78 °C, a work-up as described for the preparation of **4** and column chromatography (6:1 → 1:1, CH_2Cl_2:AcOEt) provided in the elution order stannane **25** (6.2 mg, 7 %), the protonated product **28**[25] (11 mg, 17 %) and **30$_S$**, **30$_A$** (39 mg, 56 %). ^{1}H NMR ($CDCl_3$): δ 1.88, 2.68 and 2.82 (3 bs, OH), 3.40–3.70 non analyzable pattern, 3.78 (bt, $J_{1,2} \sim J_{2,3} \sim 9$ Hz, H-2 both isomers), 7.20–7.42 (m, 20H, arom). Isomeric ratio was obtained from the singlets at 2.68 (one isomer) and 2.82 (other isomer). Anal. calcd for $C_{34}H_{36}O_6$: C 75.53, H, 6.71. Found: C 75.62, H 6.91.

[1R]-1-(3,4,6-Tri-O-benzyl-β-D-gluco-hexopyranosyl)-1-propanol (31$_S$) and its [1S] isomer (31$_A$)

The procedure described for the preparation of **30** with **25** (120 mg, 0.16 mmol) and propionaldehyde (39 μL, 3 equiv.) provided, after column chromatography (6:1 → 1:1, CH_2Cl_2:AcOEt), in the elution order stannane **25** (12 mg, 10 %), **28** (16 mg, 22 %), **31$_A$** (19.5 mg, 24 %) and **31$_S$** (22.5 mg, 27 %).

31$_A$: $[\alpha]_D^{20}$ +22 ° (*c* 2.10, $CHCl_3$) mp: 105 °C; lit.[26], mp: 106 °C, $[\alpha]_D^{20}$ +23.6 ° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.53 and 1.77 (2 m, 2H, CH_2), 1.60 (bs, 1H, OH), 2.87 (bs, 1H, OH), 3.16 (dd, 1H, $J_{1,7}$ = 6.5, $J_{1,2}$ = 9.2 Hz, H-1), 3.43 (dt, 1H, $J_{5,6} \sim J_{5,6'} \sim 3.3$, $J_{4,5}$ = 9.0 Hz, H-5), 3.53 (dd, 1H, $J_{3,4}$ = 8.6 Hz, H-4), 3.60 (t, 1H, $J_{2,3}$ = 8.6 Hz, H-3), 3.64 (t, 1H, H-2), 3.69 (m, 2H, H-6,6'), 3.735 (ddd, 1H, J_{7,CH_2} = 3.2 and 8.4 Hz, H-7). Anal. calcd for $C_{30}H_{36}O_6$: C 73.14, H 7.37. Found: C 73.02, H 7.48.

31$_S$: $[\alpha]_D^{20}$ +22 ° (*c* 2.30, $CHCl_3$). mp: 137 °C; lit.[26] mp: 139 °C, $[\alpha]_D^{20}$ +35.4 ° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3H, *J* = 7.5 Hz, CH_3), 1.62 (m, 2H, CH_2), 2.0 and 2.45 (2 bs, 2H, 2 OH), 3.16 (dd, 1H, $J_{1,7}$ = 1.9, $J_{1,2}$ = 9.9 Hz, H-1), 3.455 (dt, 1H, $J_{5,6} \sim J_{5,6'} \sim 3$ Hz, $J_{4,5}$ = 9.8 Hz, H-5), 3.52 and 3.58 (2 t, 2H, *J* ~ 9 Hz, H-3,4), 3.70 (m, 2H, H-6,6'), 3.71 (m, 1H, H-7), 3.75 (bt, 1H, $J_{2,3} \sim 9$ Hz, H-2). Anal. calcd for $C_{30}H_{36}O_6$: C 73.14, H, 7.37. Found: C 73.30, H 7.45.

[1R]-1-(3,4,6-Tri-O-benzyl-β-D-gluco-hexopyranosyl)-2-methylpropan-1-ol (32$_S$) and its [1S] isomer (32$_A$)

The procedure described for the preparation of **30** with **25** (146 mg, 0.20 mmol) and iso-butyraldehyde (55 μL, 3 equiv.) provided, after column chromatography (CH_2Cl_2 then 10:1 → 1:1, CH_2Cl_2:AcOEt), in the elution order, stannane **25** (24 mg, 16 %), **32$_A$** (21 mg, 21 %), the protonated product **28** (17 mg, 19 %) and **32$_S$** (29 mg, 29 %).

32$_A$: $[\alpha]_D^{20}$ +17 ° (*c* 0.8, $CHCl_3$) mp: 96 °C. ^{1}H NMR ($CDCl_3$): δ 0.91 and 1.00 (2 d, 6H, *J* = 7.8 Hz, 2 CH_3), 2.03 and 2.68 (2 bs, 2H, 2 OH), 2.12 (m, 1H, $J_{CH,7}$ = 3.3 Hz, C*H*Me$_2$), 3.20 (dd, 1H, $J_{1,7}$ = 7.8, $J_{1,2}$ = 9.1 Hz, H-1), 3.42 (m, 1H, $J_{5,6}$ = 2.5, $J_{5,6'}$ = 4.0, $J_{4,5}$ = 9.5 Hz, H-5), 3.56 and 3.62 (2 t, 2H, *J* ~ 9 Hz, H-3,4), 3.68 (dd, 1H, H-7), 3.69 (m, 2H, H-6,6'), 3.71 (t, 1H, H-2). Anal. calcd for $C_{31}H_{38}O_6$: C 73.49, H 7.56. Found: C 73.58, H 7.70.

32$_S$: $[\alpha]_D^{20}$ +18 ° (*c* 1.05, $CHCl_3$) mp: 153 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 and 1.03 (2 d, 6 H, *J* = 7.5 Hz, 2 CH_3), 1.77 (bs, 1H, OH), 1.87 (m, 1H, C*H*Me$_2$), 2.62 (bs, 1H, OH), 3.29 (dd, 1H, $J_{1,7}$ = 1.5, $J_{1,2}$ = 9.5 Hz, H-1), 3.40 (d, 1H, $J_{7,CH}$ = 8.3 Hz, H-7), 3.45 (dt, 1H, $J_{5,6} = J_{5,6'}$ = 3.1, $J_{4,5}$ = 9.2 Hz, H-5), 3.44 and 3.60 (2 t, 2H, *J* ~ 9.0 Hz, H-3,4), 3.70 (m, 2H, H-6,6'), 3.78 (t, 1H, H-2). Anal. calcd for $C_{31}H_{38}O_6$: C 73.49, H 7.56. Found: C 73.69, H 7.64.

Preparation of the isopropylidene derivative **33**

To a stirred solution of **31$_S$** (25 mg, 0.05 mmol) in DMF (0.3 mL) and 2,2-dimethoxypropane (0.2 mL) was added *p*-toluene sulfonic acid (~1 mg). After 5 h at rt, the reaction mixture was neutralized with Et_3N and concentrated. Purification of the residue by column chromatography (10:1 → 8:1, hexanes: AcOEt) provided **33** (18 mg, 65 %). lit.[26] $[\alpha]_D^{20}$ +8.7 ° (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.375 and 1.46 (2 s, 6H, CMe_2), 1.64 and 1.77 (2 m, 2H, J_{7,CH_2} = 5.5 and 8.9 Hz, CH_2), 3.445 (dd, 1H, $J_{1,7}$ = 7.0, $J_{1,2}$ = 9.5 Hz, H-1), 3.455 (ddd, 1H, $J_{5,6}$ = 2.6, $J_{5,6'}$ = 4.1, $J_{4,5}$ = 9.8 Hz, H-5), 3.51–3.77 (m, 5 H, H-2,3,4,6,6'), 3.99 (ddd, 1H, H-7). Anal. calcd for $C_{33}H_{40}O_6$: C 74.41, H 7.57. Found: C 74.72, H 7.69.

Preparation of the isopropylidene derivative **34**

Diol **31$_A$** (25 mg, 0.05 mmol) treated as above provided, after column chromatography (10:1, hexanes:AcOEt), the isopropylidene derivative (23 mg, 85 %). Hydrogenolysis and acetylation under standard conditions (see preparation of **14**) on the isopropylidene derivative (5 mg) furnished, after column chromatography (3:1, hexanes:AcOEt), **34** (3.5 mg, ~ quant.) mp: 117 °C. ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 3H, *J* = 7.5 Hz, CH_3), 1.38 and 1.46 (2 s, 6H, CMe_2), 1.80 (m, 2H, CH_2), 2.025, 2.045 and 2.08 (3 s, 9H, 3 Ac), 2.965 (t, 1H, $J_{1,2} = J_{1,7}$ = 9.5 Hz), 3.66 (dd, 1H, J_{7,CH_2} = 2.2 and 5.0 Hz, H-7), 3.665 (m, 1H, $J_{5,6}$ = 2.3, $J_{5,6'}$ = 5.1, $J_{4,5}$ = 9.5 Hz, H-5), 3.70 (t, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 4.045 (dd, 1H, $J_{6,6'}$ = 12.5 Hz, H-6), 4.03 (dd, 1H, H-6'), 5.02 (t, 1H, $J_{3,4}$ = 9.5 Hz), 5.12 (t, 1H, H-3). MS (d.c.i. mode using ammonia on a Ribermag R10-10 instrument) m/z: 406 (M + 18), 389 (M + 1).

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