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# SYNTHESES OF KIJANIMICIN OLIGOSACCHARIDES

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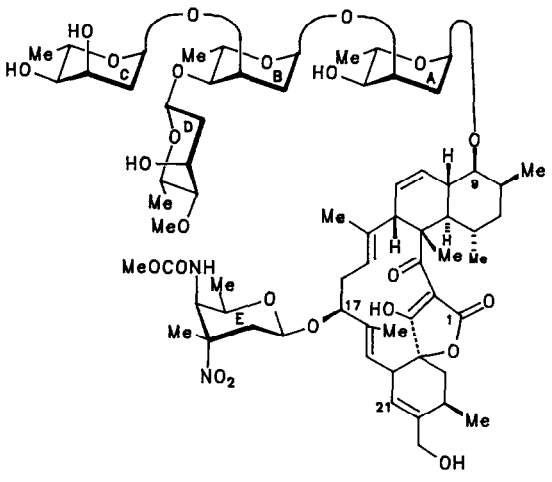
*A b s t r a c t* - Various di- and trisaccharide precursors of the kijanimicin tetrasaccharide were prepared by the **N**-iodosuccinimide glycosylation procedure employing regioselectively blocked L-digitoxosides and L-digitoxals. Assumed 1,3-neighboring group participations were studied in acid- and silver or mercury salt-promoted glycosylations with selectively functionalized digitoxoses or their glycosyl chlorides. No evidence for enhanced $\beta$:$\alpha$-ratios exceeding that of previous glycosylations in 2-deoxy-ribo components could be observed. A straightforward sequential synthetic approach applied both the studied glycosylation methods, and thus a synthesis of the blocked D C B-A tetrasaccharide of kijanimicin was achieved. Throughout structures and conformations of the oligosaccharides were assigned by extensive $^1$H NMR spectroscopy.

The macrolide antibiotic Kijanimicin (**1**) was isolated as the turnover product of *Actinomadura kijanata* from kenian soil[2,3] and the structure most elegantly elucidated by Mallams et al.[4] It was demonstrated to show antitumor activity as well as activity against malaria and anaerobic bacteria.[5,6] Owing to corresponding activities as well as the novel tetronic acid lactone structures kijanimicin, the tetrocarcines and antlermycines may belong to a new subgroup of antibiotics all of which contain L-digitoxose in the sugar parts.

In addition to the stereochemically pretentious macrolide part kijanimicin (**1**) contains a number of saccharide units. Among these the novel methyl-branched nitro-amino sugar E (in **1**), named D-kijanose could be structurally verified both by synthesis[7] and X-ray structure analysis.[8] At position 9-OH of the aglycone a tetrasaccharide is attached which comprises of only L-digitoxose units. The C, B, and A parts are interglycosidically bound by $\alpha$,1→3-linkages, however, the terminal D unit occurs as a 4-methyl ether and shows a $\beta$,1→4-linkage to the branching unit B.

Synthetic approaches to this tetrasaccharide are not described, however, shortly after isolation of **1** the synthesis of L-digitoxose was

*Scheme* 1



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reported from chiral carbonyl derivatives,[9] from L-rhamnose,[10] and a particular attractive one from calcium gluconate.[11]

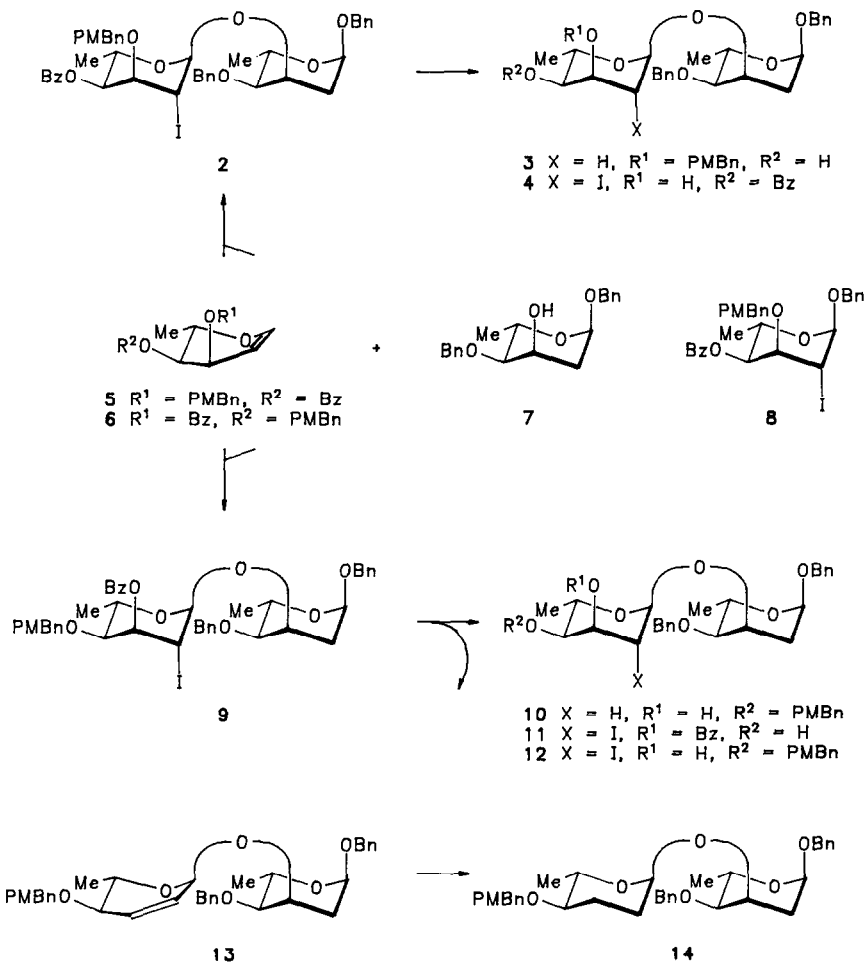
## RESULTS AND DISCUSSION

By straightforward retrosynthesis evidence was obtained that owing to the branch at unit B a sequential preparation of a kijanimicin trisaccharide would require not less than three different blocking groups which may be cleaved selectively. Such a required blocking group strategy resulted in a complex series of synthetic possibilities. However, the easy access to selectively protected monosaccharide precursors allowed a broad variation of synthetic studies by application of derivatives with varying reactivity.

Ideally suited to construct the $\alpha$,1→3-linkages would be the **N**-iodosuccinimide procedure.[12] By such an approach the A-B-C trisaccharide precursor should be available which, finally, was to be glycosylated with a monosaccharide derivative to introduce the D unit in the $\beta$-mode.

In fact both p-methoxy-benzylated L-digitoxals **5** and **6**[13] could be subjected to an **N**-iodosuccinimide glycosylation with benzyl L-digitoxoside (**7**)[14] having an unblocked OH-group at C-3. Even though **7** showed only a limited nucleophilicity in both cases exclusively the α,1→3-disaccharides **2** (40 %) and **9** (43 %) resulted. In contrast to average yields the α-selectivity was high. As an interesting side product in reaction of **5** and **7** the benzyl glycoside **8** was obtained in 15 % yield. Its formation can be assumed to occur by a preferred nucleophilic attack of a benzyloxy group (1- or 3-OBn) instead of the 3-OH group of **7** at the iodonium intermediate

**Scheme 2**



formed from **5**. Comparatively high electrofugal properties of benzyl ether groups were observed previously in tetrahydrofuran cyclizations from γ-benzyloxy olefins with halonium sources.[15]

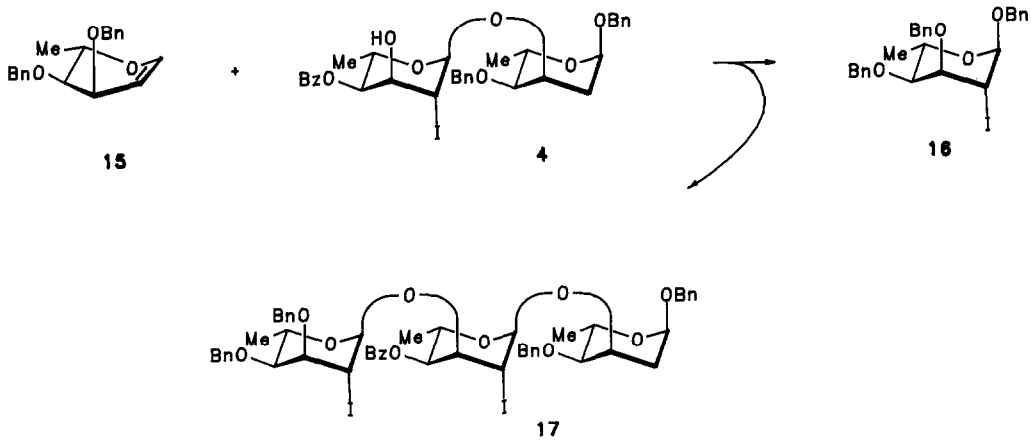
Both the isomers **2** and **9** represent potential B-A disaccharide precursors to further attach the C or D sugar units at positions 3' or 4'. By hydrogenation in the presence of triethylamine and a subsequent Zemplén transesterification derivative **3** was obtained in good yields. Quite selective and smooth was the deblocking of the p-methoxy benzyl function with 2,3-dicyano-4,6-dichloro-p-benzoquinone (DDQ)[16] which gave the disaccharide derivative **4**.

As before, treatment of **9** with DDQ smoothly gave **11**. On the other hand hydrogenation performed as above followed by transesterification led to the tetradeoxy disaccharide **10**. After diligent separation in addition to **10** the olefin disaccharide **13** and its hydrogenation product **14** could be isolated in minor amounts, and structurally assigned. Obviously the trans arrangement of the 2'-iodo and 3'-OBz groups in the L-*altro* configurated nonreducing sugar unit of **9** is particularly prone for attack by hydride in the surface of the palladium catalyst to foster a trans elimination. Attempts for an improved access from **9** to **10** by inversion of the two reactions did not meet with success. Surprisingly, the alkaline cleavage of the 3'-benzoate function required rather drastic conditions to give compound **12**. However, this in turn could not be hydrogenated to **10**, and also the reductive deiodination with nickel boride[17] failed. As will be discussed later, the amazingly low reactivity can be correlated with the unusual conformation of this derivative.

It was of interest to use the disaccharide **4** for another **N**-iodosuccinimide glycosylation to achieve the synthesis of a C-B-A trisaccharide precursor. By treatment of **4** with a 2.4 molar excess dibenzyl L-digitoxal **15**[13] and NIS the desired compound **17** could be obtained in only 21 % yield after extensive purification steps. Approximately 70 % of the disaccharide **4** was recovered unreacted, however, as an additional product the iodinated benzyl glycoside **16** was isolated in 57 % yield based on the glycal **15**. As discussed above the formation of **16** must be interpreted as an internal attack of a benzyloxy function of **15** on the iodonium intermediate obtained from NIS and **15**. In fact, treatment of the glycal with NIS without additon of another nucleophile showed the formation of **16** among other products. Obviously, the nucleophilic attack of the 3'-hydroxy group was overcome by

a benzyloxy function, and again we attribute this feature to unfavourable conformational effects such as 1,3-diaxial interactions in the nonreducing sugar unit of **4**.

**Scheme 3**




Even though the trisaccharide **17** with a 3'-benzoyl function could be suited as a precursor for the construction of the tetrasaccharide, the comparatively unfavorable yield suggested another approach.

However, the attachment of the sugar unit D in a $\beta$,1→4-linkage required a different methodolgy and will be discussed first. Based on recently disclosed findings the 1,2-cis addition of phenylselenyl[18] or sulfenyl chlorides[19] to the double bond of glycals occured predominantly from the $\alpha$-face. Transformation of the additon product into the trichloroacetimidate gave a precursor ideally suited for 2-deoxy-$\beta$-glycoside synthesis.[19] Previous to these studies we preferred the application of 1,2-dibromo precursors prepared by the dibromomethyl methyl ether reaction (DBE reaction).[20-22] This approach gave convincing results for the synthesis of 2-deoxy-$\beta$-glycosides in the *arabino*[21,23-25] and the *lyxo*[26] series, however, it cannot be applied in the *xylo* or *ribo* series. Recently, a novel conception for $\beta$-glycosylation in the latter series was proposed which made use of 1,3-neighboring group participations,[27] and it was of interest to

test its application for this problem.

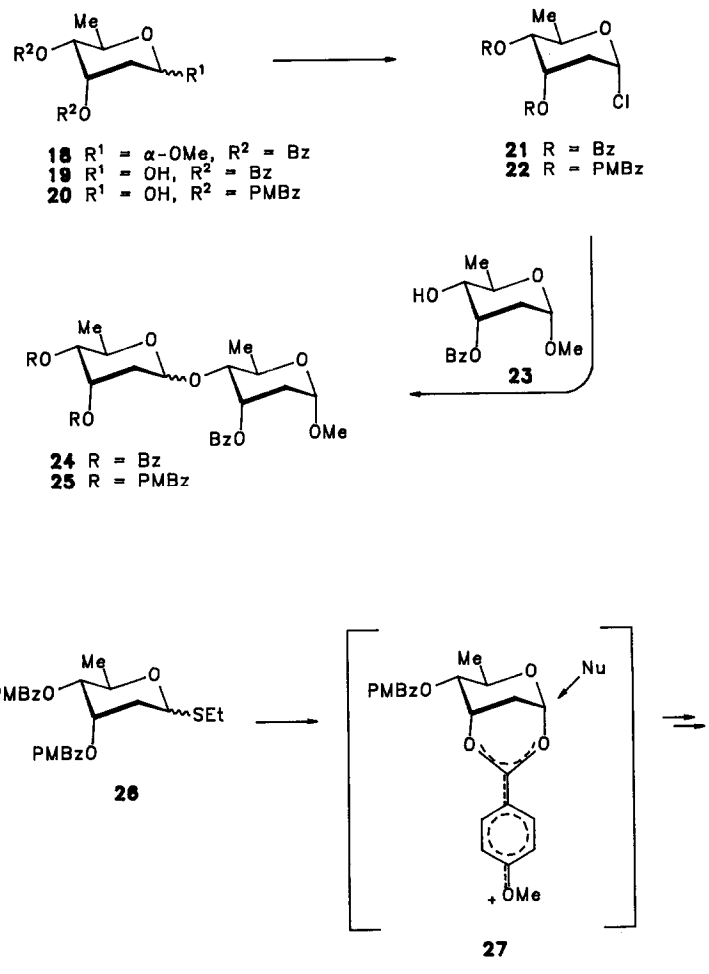
Model experiments made use of available D-digitoxose precursors. Methyl α-D-digitoxoside (**18**)[28] was subjected to mild acid hydrolysis and gave the crystalline anomeric mixture of benzoylated digitoxose pyranoses (**19**). Similarly, the p-methoxy-benzoylated analogues **20**[27] could be obtained. Treatment of **19** or **20** with oxalyl chloride in the presence of catalytic amounts of dimethyl formamide could be used as a very mild method for synthesis of the highly reactive glycosides **21** and **22**, respectively. As previously described for the preparation of carboxylic acid chlorides,[29] the reactive intermediate in this type of reactions is supposed to be a type of Vilsmeier salt.

Both labile glycosyl chlorides could be characterized by $^1$H NMR spectroscopy, and glycosylation with the selectively blocked digitoxoside **23** and silver trifluoromethane sulfonate (silver triflate, AgOTf) as promoter (cf. ref[31]) gave both 1→4-linked disaccharide derivatives[30] in 66 % isolated yield in the ratio **24α:24β** = 1:0.7. In a corresponding reaction with the 3-O-p-methoxy-benzoylated glycosyl chloride **22** the anomeric disaccharide mixture resulted in 69 % isolated yield and a ratio of **25α:25β** = 1:1.4. Further, the reaction of **22** and **23** was performed under Helferich conditions[32] [$Hg(CN)_2/HgBr_2$] at room temperature to give 62 % of the anomeric mixture in the same ratio **25α:25β** = 1:1.4 as determined by $^1$H NMR.

These findings are to be discussed in comparison with the glycosylations of Wiesner et al. in the total synthesis of digitoxin. Even though the glycosylation of the p-methoxy-benzoylated species **22** led to a somewhat minor enhancement of the anomeric ratio in favour of the β-component if compared with the benzoylated precursor **21**, this cannot compete with the high selectivity as described by Wiesner et al. They generated the oxocarbenium species by mercury-assisted sovolysis of both anomeric ethylthio glycosides **26**[27] seperately and therefore assume a participation by the 3-acyl group towards a p-methoxy benzoxonium intermediate **27**, which underwent stereoselective nucleophilic attack from the β-face. Accordingly, the oxocarbenium ion intermediates generated from **21** and **22** by promotion with silver triflate should be of corresponding structure and reactivity. In order to exclude any external effects of catalysts Helferich conditions were applied which make use of mercury salts and thus simulate the generation of the oxonium intermediate as in ref.[27] However, even then the ratio of the β-anomer did not increase considerably.

The $\alpha/\beta$-ratios obtained here resemble our previous findings in the synthesis of digitoxosides from digitoxosyl halides. Other recent contributions also reported much lower stereoselectivities both by use of digitoxosyl halides as well as mercury assisted generation of active species via thioalkyl digitoxosides.[35] Thus a 1,3-neighboring group participation of a p-methoxy benzoyl function in ribopyranose derivatives could not be supported. The striking stereoselectivities reported earlier[27] may be understood in connection with particular steric requirements exerted by a higher thermodynamic stability of glycosides in digitoxigenylmono- and disaccharides.

**Scheme 4**




**18** $R^1$ = α-OMe, $R^2$ = Bz
**19** $R^1$ = OH, $R^2$ = Bz
**20** $R^1$ = OH, $R^2$ = PMBz

**21** R = Bz
**22** R = PMBz

**24** R = Bz
**25** R = PMBz

**26**

**27**

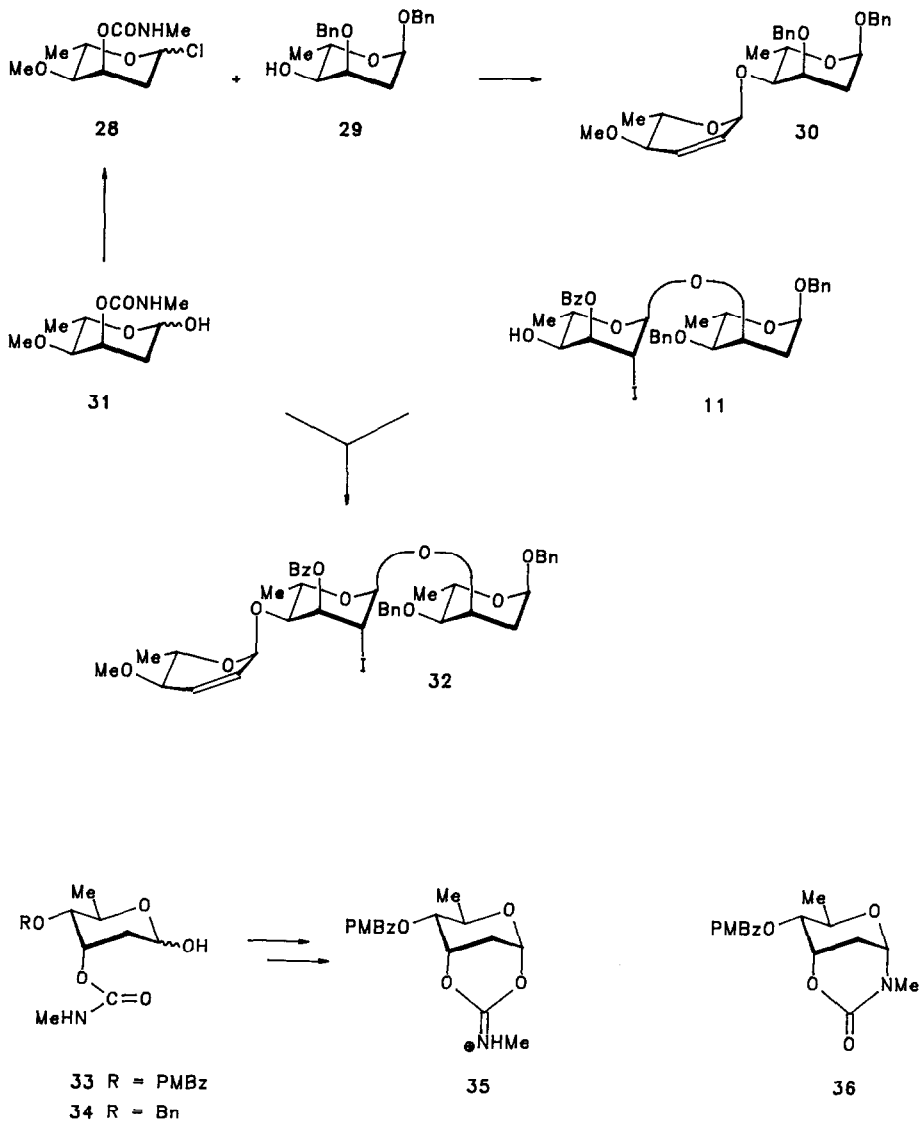
Another most attractive glycosyl halide in the *ribo* series carries a carbamate group in the 3 position. Therefore the anomerically unblocked species **31**[14] was treated with oxalyl chloride under DMF catalysis to afford the glycosyl chloride **28**. By in situ-reaction with the L-digitoxoside **29**[14] at -30°C and silver triflate promotion the unsaturated α,1→4-linked disaccharide **30** was obtained in 20 % yield. Approximately 50 % of the components did not react as evidenced by recovering 52 % of **29** after workup. Similarly, the reaction under Helferich conditions gave **30** in only 20 % yield as well.

In a further approach an acid promoted glycosylation of the selectively unblocked disaccharide **11** was checked employing the 3-carbamate **31**[14] as D unit glycosyl donor. As observed by tlc the reaction only proceeded by molar consumption of p-toluene sulfonic acid (p-TsOH). After quenching and purification the unsaturated trisaccharide **32** was obtained as the sole product in addition to recovered starting material. The assignment of α-configurations for both newly formed interglycosidic linkages in **30** and **32** is based on comparison of their $^1$H NMR spectra to data of the corresponding hex-2-enopyranosides described in ref.[34]

Previously Wiesner et al.[27] reported on the acid-catalyzed glycosylation of the carbamate **33** with digitoxigenin to give a 47 % yield of the glycosides in a ratio α:β = 1:7. Again a 1,3-bridged intermediate such as **35** was considered to be responsible to direct a predominating substitution from the β-face. Indeed, isolation of the 1,3-carbonate-bridged **N**-methyl α-*ribo*-hexopyranosyl amine **36**, as well as some previous mechanistic suggestions[36,37] seem to favour such an assumption. However, for the same reaction applied to the 4-O-benzyl analogue **34** the study reported a ratio α:β = 1:1.3, and with **26** this ratio dropped to α:β = 1:1.5. Attempts to explain these findings quote steric factors in the glycosyl donor or the digitoxigenyl mono- and disaccharides.

In the present case both different glycosylation procedures using carbamates were characterized by an easy elimination of the carbamoyl function which lead to olefin sugars, carbon dioxide and methylamine. Whereas there was no evidence for a bridged intermediate similar to **35**, it remained uncertain at which stage the elimination would occur. The exclusive formation of unsaturated α-glycosides may point to hex-2-enopyranosyl intermediates which in turn were substituted stereoselectively from

Scheme 5


OCONHMe
Me
MeO
O
Cl
28
BnO
OBn
HO
29
30
OH
31
BzO
HO
BnO
I
11
32
RO
C=O
MeHN
33 R = PMBz
34 R = Bn
PMBzO
NHMe
35
NMe
36

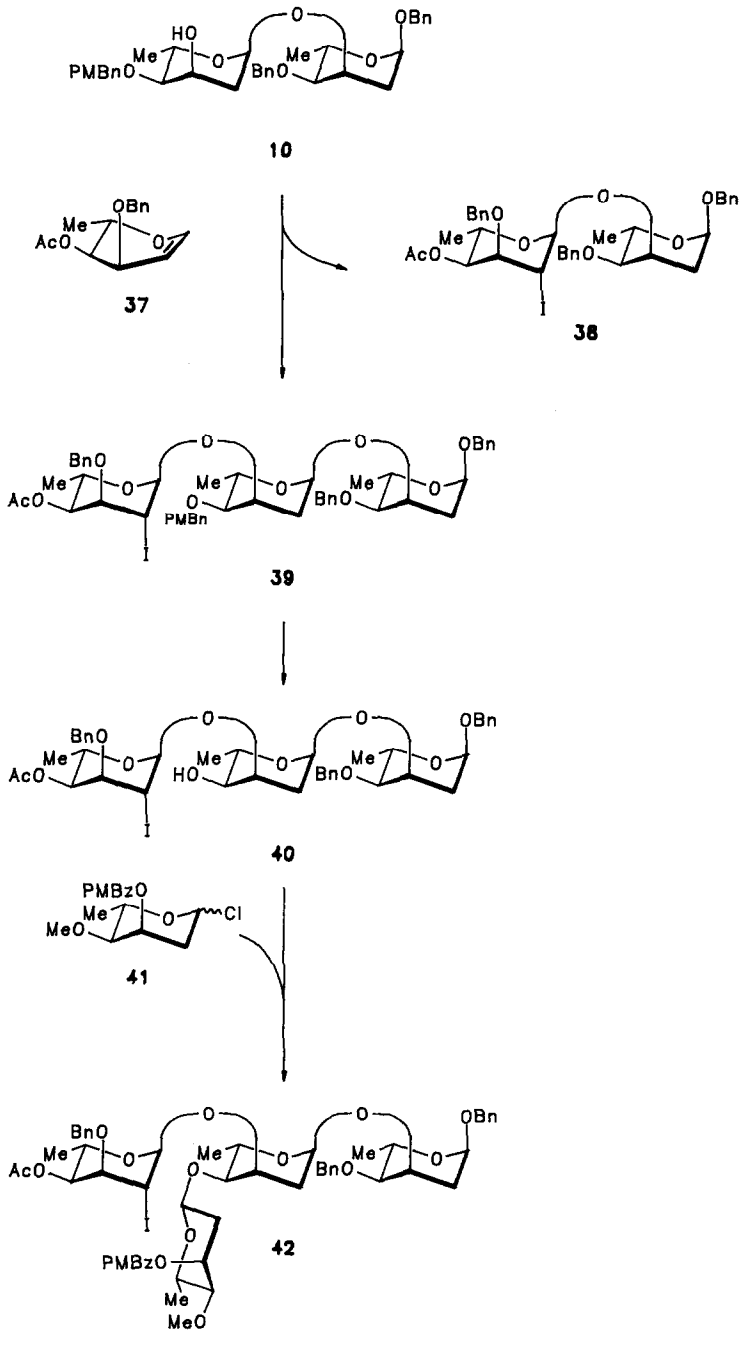
the α-face. Altogether, these results show the limits for application of carbamoyl derivatives in Koenigs-Knorr type as well as acid-promoted glycosylations.

Even though a 1,3-diaxial arrangement of an unblocked 3'-OH group and the α-anomerically attached sugar as in disaccharide **10** was shown to exhibit only limited reactivity in **N**-iodosuccinimide glycosylations, this still presented the most straightforward access to the target α,1→3 linked oligomers. Thus treatment of the digitoxal **37**[13] with NIS and **10** gave the trisaccharide **39** in 24 % yield. As a side product (cf. schemes 2 and 3) the disaccharide **38** was obtained in 24 % yield (based on **10**) as well. Obviously in this case the iodonium ion was attacked by the interglycosidic oxygen of **10**. Similar to the above discussed substitution by benzyloxy groups (cf. ref.[15]) here substantial electrofugal properties of the released oxocarbenium ion of the nonreducing sugar part in **10** can be assumed to favour such a reaction. On treatment of the trisaccharide **39** with DDQ a smooth cleavage of the p-methoxy-benzyl ether function gave the solid C-B-A precursor **40**.

For the final steps the 3-O-methoxy-benzoyl analogue of **31**[14] was used as glycosyl donor , and transferred into the *ribo*-hexopyranosyl chloride **41**. This in turn was subjected to a silver triflate promoted glycosylation at -35°C as before. Following HPLC separations the hydroxy component **40** was recovered in 46 % yield and two minor fractions obtained in an enriched state. One of these contained the component **42** with the D sugar unit attached to the 4'-position (unit B) as the β anomer ($J_{1,2}$ = 8.1, $J_{1,2e}$ = 4.0 Hz). It could be completely analyzed by $^1$H NMR (2D-COSY) and unequivocally assigned. The other fraction presumably contained the corresponding tetrasaccharide with an α,1→4-linked D unit.

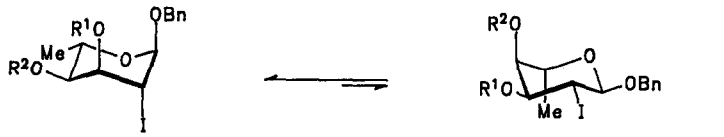
Thus the first synthesis of the kijanimicin tetrasaccharide in a protected form could be achieved. Doubtless an approach along a corresponding conception would need several improvements, in particular with respect to yields. Recently, alternative and improved accesses to precursors of the decisive D-B disaccharide unit were studied and will be reported in due course.[38]

**Scheme 6**

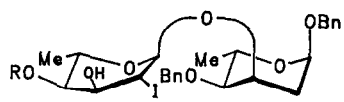


Finally, some conformational effects of α-digitoxosides should be discussed. Both the monosaccharide glycosides **8** and **16** show a conformational equilibrium of $^{1}C_{4}$(L)- and $^{4}C_{1}$(L)-chair conformations. As observed in the coupling constants and depicted in scheme 7 the former still prevailed. The disaccharide derivative **12** and also the corresponding 4'-benzyl ether **43**[39] show half chair conformations in the nonreducing rings. Neither hydrogenation nor reduction of the iodo function in **12** nor NIS glycosylation of **43** could be achieved.[39] This failure of a reaction at position 2 may be correlated with the adopted conformation.

**Scheme 7**




**8** $R^1$ = PMBn, $R^2$ = Bz
**16** $R^1$ = $R^2$ = Bn




**12** R = PMBn
**43** R = Bn

Generally in the *ribo* series, an easy interchange of chair and half chair conformations can be observed. Indeed, this may be facilitated by additional 1,3-diaxial interactions as in these α-glycosides. Previously only one 2-deoxy-*ribo* derivative was proven to show a conformational equilibrium,[40] however, for 2-iodo substituted derivatives such as **8** and **16** and also a digitoxigenyl 2-deoxy-2-iodo-digitoxoside[34] this effect is observed more often.

Altogether, subtle changes in the substitution pattern drastically influenced the conformations. For instance, the disaccharide derivative **4** which differs from **12** and **43** only by a 4'-ester function showed a completely normal $^{1}C_{4}$(L)-chair conformation in its nonreducing ring unit. Observations of this kind give evidence that particular spatial as well as electronic interactions may have to be considered in addition to 1,3-diaxial interactions and steric effects in order to understand subtle conformational changes in these oligosaccharides.

## EXPERIMENTAL

**General.** - Reactions were followed by TLC on DC-Alufolien Kieselgel $GF_{254}$ (Merck), detection was by u.v. and/or spraying with 10 % ethanolic $H_2SO_4$ and charring. Preparative layer chromatography (PLC): Fertigplatten Kieselgel 60 $F_{254}$ (Merck). Column chromatography: Kieselgel 60, 70-230 mesh (Merck). HPLC: LiChrosorb Si 60, 7µm (Knauer) on columns 8×500 mm, flow rate: 2.0-2.5 mL/min. Gel permeation chromatography: Bio-Beads S-X2 (Bio-Rad Laboratories); eluent: toluene; flow rate: 7-12 drops/min. Melting points (uncorrected) were determined on Leitz and Reichert heating table microscopes, optical rotations with Perkin-Elmer polarimeter 241. NMR spectra were recorded on a Bruker WM 300. Chemical shifts are given downfield to TMS as standard. All described trisaccharides were unequivocally assigned by 2D-COSY spectroscopy (standard conditions, Bruker software 1984/85). If necessary, the other compounds were assigned by either 2D-COSY or spin decoupling. Glycoside synthesis were generally performed in a nitrogen atmosphere under strict exclusion of light and moisture.

Formation of Glycosyl Chlorides for Glycoside Syntheses (General Procedure I, GP I). - Under a nitrogen cover the anhydrous hexose derivative (1.0 mmol) was dissolved in anhydrous dichloromethane (15 mL) and stirred for 30 min in the presence of molecular sieves (4 Å) and dimethyl formamide (only a catalytic amount should be used, since the chlorides tend to eliminate HCl easily). Following addition of oxalyl chloride (1.2 mmol) stirring was continued at room temperature for 10-60 min. Both the developing gases and the solvent were evaporated with a vigorous stream of nitrogen, and the remaining glycosyl chloride used immediately for glycosylation.

Workup of N-Iodosuccinimide Glycosylations (General Procedure II, GP II). - The reaction mixture was evaporated to dryness *in vacuo*, the remaining material dissolved in dichloromethane, and washed with aqueous sodium thiosulfate. The washings were reextracted with dichloromethane, the combined organic layers dried ($MgSO_4$) and evaporated *in vacuo*.

Benzyl 3-O-[4-O-Benzoyl-2,6-dideoxy-2-iodo-3-O-(p-methoxybenzyl)-α-L-altropyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (2). - A solution of glycal 5[13] (319 mg, 0.90 mmol) and the digitoxoside 7[14] (200 mg, 0.61 mmmol) in anhydrous acetonitrile (4 mL) was stirred with molecular sieves 4 Å for 30 min, and then a solution of N-iodosuccinimide (243 mg, 1.08 mmol) in acetonitrile (3mL) added within 15 min. Stirring was continued overnight at room temperature and workup followed GP II. Purification was performed by column chromatography (ethyl acetate - toluene, 1:15) to afford 199 mg (40 %), colourless syrup; $[\alpha]_D^{20}$ = -121.4°

(c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.90 (dd, 1-H), 1.68 (ddd, 2a-H), 2.29 (ddd, 2e-H), 4.32 (ddd~q, 3-H), 3.17 (dd, 4-H), 4.63 (dq, 5-H), 1.25 (d, 3H, 6-$CH_3$), 5.34 (brs, 1'-H), 4.42 (dd, 2'-H), 4.07 (dd~t, 3'-H), 5.37 (dd, 4'-H), 4.30 (dq, 5'-H), 1.14 (d, 3H, 6'-$CH_3$), 3.70 (s, 3H, $OCH_3$), 3.96, 4.37, 4.45, 4.49, 4.69 and 4.73 (3 AB, 6H, Aryl-C$H_2$), 6.59, 7.07, 7.30 and 7.91 (each mc, 19H, Aryl-H); $J_{1,2a}$ = 4.1, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.4, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.3, $J_{1',2'}$ = 1.1, $J_{2',3'}$ = 3.0, $J_{3',4'}$ = 3.1, $J_{4',5'}$ = 9.4, $J_{5',6'}$ = 6.5, $J_{A,B}$ = 11.4, 11.4 and 11.6 Hz. Anal. Calcd for $C_{41}H_{45}IO_9$ (808.7): C, 60.89; H, 5.61. Found: C, 60.52; H, 5.56.

In addition a mixture of **5** and Benzyl 4-O-Benzoyl-2,6-dideoxy-2-iodo-3-O-(p-methoxybenzyl)-α-L-altropyranoside (**8**) was obtained, 79 mg (ratio **5**:**8** = 1:2); corresponding to 15 % yield of **8** (calculation based on **7**) characterized by NMR spectroscopy. $^1$H NMR (300 MHz, $CDCl_3$): δ = 5.14 (d, 1-H), 4.42 (dd, 2-H), 4.10 (dd, 3-H), 5.41 (dd, 4-H), 4.46 (dq, 5-H), 1.28 (d, 3H, 6-$CH_3$), 3.82 (s, 3H, $OCH_3$), 4.50, 4.54, 4.56 and 4.78 (2 AB, 4H, Aryl-C$H_2$), 6.69, 7.33 and 7.93 (each mc, 14H, Aryl-H); $J_{1,2}$ = 3.6, $J_{2,3}$ = 5.9, $J_{3,4}$ = 3.3, $J_{4,5}$ = 7.0, $J_{5,6}$ = 6.6, $J_{A,B}$ = 11.9 and 11.9 Hz.

Benzyl 3-O-[3-O-(p-Methoxybenzyl-)2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**3**). - To a solution of **2** (199 mg, 0.25 mmol) in anhydrous dimethoxyethane (7mL) was added triethylamine (60 µl, 0.4 mmol) and palladium on charcoal (10 %, 30 mg). The mixture was stirred and hydrogenated for 24 h at room temperature, then filtered over celite, and taken to dryness. The syrup was dissolved in anhydrous methanol (5 mL) and stirred with sodium methanolate (10 mg) for 30 h. Following neutralization (Amberlite IR 120, $H^+$), filtration and evaporation methyl benzoate was removed azeotropically with water. The residue was purified by column chromatography (ethyl acetate-toluene, 1:15); yield 88.9 mg (63 %), colourless syrup: $[\alpha]_D^{20}$ = -175.2° (c = 1.1, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.86 (dd, 1-H), 1.66 (ddd, 2a-H), 2.28 (ddd, 2e-H), 4.34 (ddd~q, 3-H), 3.17 (dd, 4-H), 4.32 (dq, 5-H), 1.25 (d, 3H, 6-$CH_3$), 5.00 (dd, 1'-H), 1.65 (ddd, 2a'-H), 2.27 (ddd, 2e'-H), 3.72 (ddd~q, 3'-H), 3.18 (dd, 4'-H), 4.14 (dq, 5'-H), 1.16 (d, 3H, 6'-$CH_3$), 2.52 (d, 4'-OH), 3.77 (s, 3H, $OCH_3$), 3.96, 4.39, 4.47, 4.61, 4.62 and 4.75 (3 AB, 6H, Aryl-C$H_2$), 7.26 (mc, 14H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.4, $J_{3,4}$ = 2.9, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.4, $J_{1',2a'}$ = 1.0, $J_{1',2e'}$ = 4.2, $J_{2a',2e'}$ = 15.0, $J_{2a',3'}$ = 3.2, $J_{2e',3'}$ = .2, $J_{3',4'}$ = 2.7, $J_{3',4'-OH}$ = 10.6, $J_{4',5'}$ = 9.4, $J_{5',6'}$ = 6.4, $J_{A,B}$ = 11.6, 11.8 and 12.0 Hz. Anal. Calcd for $C_{34}H_{42}O_8$ (578.7): C, 70.56; H, 7.31. Found: C, 70.48; H, 7.28.

Benzyl 3-O-(4-O-Benzoyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (4) - A solution of 2 (69 mg, 0.085 mmol) in dichloromethane (1 mL) and water (0.1 mL) was stirred with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 24 mg, 0.105 mmol) for 3 h, then diluted with dichloromethane (2 mL), filtred, and evaporated. Purification by column chromatography gave 41 mg (70 %), colourless syrup; $[\alpha]_D^{20}$ = -121.1° (c = 1.4, chloroform); $^1$H NMR (300 MHz, $C_6D_6$): δ = 4.53 (dd, 1-H), 1.04 (ddd, 2a-H), 1.74 (dddd, 2e-H), 3.88 (ddd~q, 3-H), 2.81 (dd, 4-H), 4.23 (dq, 5-H), 1.21 (d, 3H, 6-$CH_3$), 5.28 (br s, 1'-H), 4.37 (mc, 2H, 2'-H and 3'-H), 5.91 (dd, 4'-H), 4.46 (dq, 5'-H), 1.24 (d, 3H, 6'-$CH_3$), 4.10, 4.19, 4.39 and 4.57 (2 AB, 4H, Aryl-$CH_2$), 7.18 and 8.13 (each mc, 15H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ = 0.8, $J_{2a,2e}$ = 15.6, $J_{2a,3}$ = 2.9, $J_{2e,3}$ = 3.2, $J_{3,4}$ = 3.0, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.3, $J_{1',2'}$ ≃ 0.8, $J_{3',4'}$ = 2.9, $J_{4',5'}$ = 10.3, $J_{5',6'}$ = 6.3, $J_{A,B}$ = 11.9 and 12.0 Hz. Anal. Calcd for $C_{33}H_{37}IO_8$ (688.6): C, 57.56; H, 5.42. Found: C, 57.35; H, 5.44.

Benzyl 3-O-[3-O-Benzoyl-2,6-dideoxy-2-iodo-4-O-(p-methoxybenzoyl)-α-L-altropyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (9). - A solution of glycal 6[13] (716 mg, 2.02 mmol) and digitoxoside 7[14] (486 mg, 1.48 mmol) in anhydrous acetonitrile (6 mL) was stirred with molecular sieves 3 A for 30 min, followed by dropwise addition of N-iodosuccinimide (545 mg, 2.42 mmol) in acetonitrile (6 mL) added within 30 min. The mixture was left overnight at room temperature and worked up following GP II. Column chromatography (ethyl acetate-toluene, 1:20) gave 571 mg (48 %), colourless syrup; $[\alpha]_D^{20}$ = -130.0° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.78 (dd, 1-H), 1.58 (ddd, 2a-H), 2.16 (ddd, 2e-H), 4.33 (ddd~q, 3-H), 2.82 (dd, 4-H), 4.14 (dq, 5-H), 1.14 (d, 3H, 6-$CH_3$), 5.22 (dq, 1'-H), 4.28 (dd, 2'-H), 5.73 (dd~t, 3'-H), 3.95 (dd, 4'-H), 4.54 (dq, 5'-H), 1.20 (d, 3H, 6'-$CH_3$), 3.76 (s, 3H, $OCOCH_3$), 4.20, 4.35, 4.48, 4.48, 4.59 and 4.75 (3 AB, 6H, Aryl-$CH_2$), 6.81, 7.26 and 8.24 (each mc, 19H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 2.6, $J_{2e,3}$= 3.0, $J_{3,4}$ = 2.7, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.3, $J_{1',2'}$ ≃ 0.6, $J_{2',3'}$ = 2.6, $J_{3',4'}$ = 2.8, $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.4, $J_{A,B}$ = 11.2, 11.4 and 12.0 Hz. Anal. Calcd for $C_{41}H_{45}IO_9$ (808.7): C, 60.89; H, 5.61. Found: C, 61.01; H, 5.63.

Benzyl 3-O-[4-O-(p-Methoxybenzyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (10). - A solution of 9 (437 mg, 0.54 mmol) and triethylamine (120 μL, 0.81 mmol) in dimethoxyethane (5 mL) was stirred with palladium/charcoal (10 %, 50 mg) for 10 h under a hydrogen cover at room temperature. The mixture was filtered over silica gel, washed with ethyl acetate and evaporated. The remaining syrup was dissolved in methanol (7 mL) and treated with sodium methylate (40 mg) for 30 h at room temperature, and another 24 h at 55°C. Following further

workup as for 3 the residue was purified by chromatography (ethyl acetate-toluene, 1:5); yield: 209 mg (66 %), colourless syrup: $[\alpha]_D^{20}$ = -172.0° (c = 1.4, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.81 (dd, 1-H), 1.62 (ddd, 2a-H), 2.23 (ddd, 2e-H), 4.18 (ddd~q, 3-H), 3.12 (dd, 4-H[a)]), 4.21 (dq, 5-H[b)]), 1.18 (d, 3H, 6-$CH_3$[c)]), 5.13 (dd, 1'-H), 1.71 (ddd~dt, 2a'-H), 2.06 (ddd, 2e'-H), 4.14 (dddd~dq, 3'-H), 2.98 (dd, 4'-H[a)]), 4.16 (dq, 5'-H[b)]), 1.19 (d, 3H, 6'-$CH_3$[c)]), 3.79 (s, 3H, $OCH_3$), 3.98 (d, 3'-OH), 4.37, 4.44, 4.50, 4.65, 4.67 and 4.68 (3 AB, 6H, Aryl-C$H_2$), 6.86 and 7.30 (each mc, 14H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ ≃ 0.8, $J_{2a,2e}$ = 15.1, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.7, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.2, $J_{1',2a'}$ = 3.3, $J_{1',2e'}$ = 0.8, $J_{2a',2e'}$ = 14.2, $J_{2a',3'}$ = 3.3, $J_{2e',3'}$ = 3.3, $J_{3',3'\text{-OH}}$ =10.3, $J_{3',4'}$ = 2.6, $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.0, $J_{A,B}$ = 11.8, 11.9 and 12.0 Hz. [a),b),c)] Signals may be inverted.

Anal. Calcd for $C_{34}H_{42}O_8$ (578.7): C, 70.57; H, 7.32. Found: C, 71.10; H, 7.25.

In addition 20 mg (7 %) of the disaccharide derivative **14** and 49.8 mg of a mixture of **13** and **14** (ratio **13**:**14** = 1:2) were isolated and subsequently separated by PLC (ethyl acetate-toluene, 1:5).

Benzyl 3-O-[4-O-(p-Methoxybenzyl)-2,3,6-trideoxy-α-L-erythro-hex-2-enopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**13**). - Yield: 14.1 mg (5 %), mp. 71-73°C, $[\alpha]_D^{20}$ = -127.8° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): 4.86 (dd, 1-H), 1.66 (ddd, 2a-H), 2.33 (ddd, 2e-H), 4.41 (ddd~q, 3-H), 3.18 (dd, 4-H), 4.32 (dq, 5-H), 1.25 (d, 3H, 6-$CH_3$), 5.21 (br s, 1'-H), 5.94 (ddd~dt, 2'-H), 5.62 (ddd, 3'-H), 3.65 (dddd≈dq, 4'-H), 3.99 (dq, 5'-H), 1.23 (d, 3H, 6'-$CH_3$), 3.81 (s, 3H, $OCH_3$), 4.37, 4.44, 4.49, 4.56, 4.74 and 4.75 (3 AB, 6H, Aryl-C$H_2$), 6.82 and 7.24 (each mc, 14H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.1, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.3, $J_{3,4}$ = 2.9, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.3, $J_{1',2'}$ = 1.4, $J_{1',3'}$ = 2.6, $J_{1',4'}$ = 1.4, $J_{2',3'}$ = 10.1, $J_{2',4'}$ = 1.4, $J_{3',4'}$ = 2.0, $J_{4',5'}$ = 8.8, $J_{5',6'}$ = 6.2, $J_{A,B}$ = 11.9, 12.0 and 12.0 Hz. Anal. Calcd for $C_{34}H_{40}O_7$ (560.7): C, 72.83; H, 7.19. Found: C, 72.78; H, 7.20.

Benzyl 3-O-[4-O-(p-Methoxybenzyl)-2,3,6-trideoxy-α-L-erythro-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**14**). - Total yield: 54 mg (18 %), colourless syrup; $[\alpha]_D^{20}$ = -127.8° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.85 (dd, 1-H), 1.69 (ddd, 2a-H), 2.28 (ddd, 2e-H), 4.26 (ddd~q, 3-H), 3.18 (dd, 4-H), 4.65 (dq, 5-H), 1.19 (d, 3H, 6-$CH_3$), 4.99 (dd, 1'-H), 1.61 (mc, 2a'-H), 1.87 (mc, 3H, 2e'-H, 3a'-H and 3e'-H), 3.04 (ddd, 4'-H), 3.95 (dq, 5'-H), 1.23 (d, 3H, 6'-$CH_3$), 3.79 (s, 3H, $OCH_3$), 4.37, 4.44, 4.50, 4.65, 4.67 and 4.68 (3 AB, 6H, Aryl-C$H_2$), 6.86 and 7.30 (mc, 14H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.4, $J_{1a,2e}$ = 15.0,

$J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.8, $J_{3,4}$ = 3.0, $J_{4,5}$ = 9.0, $J_{5,6}$ = 6.4, $J_{1',2a'}$ = 3.2, $J_{1',2e'}$ = 0.8, $J_{3a',4'}$ = 10.1, $J_{3e',4'}$ = 4.8, $J_{4',5'}$ = 9.0, $J_{5',6'}$ = 6.3, $J_{A,B}$ = 11.4, 11.9 and 12.0 Hz. Anal Calcd for $C_{34}H_{42}O_7$ (562.7): C, 72.57; H, 7.52. Found: C, 72.32; H, 7.41.

Benzyl 3-O-(3-O-Benzoyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (11). - A solution of **9** (87 mg, 0.10 mmol) in dichloromethane (1mL) and water (100 µL) was stirred with DDQ (38 mg, 0.13 mmol) for 3 h at room temperature. Following dilution with $CH_2Cl_2$ (2 mL), filtration, and evaporation, the residue was purified by chromatography (ethyl acetate-toluene, 1:10); yield: 50.2 mg (68 %), colour-less syrup; $[\alpha]_D^{20}$ = -133.9° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.74 (dd, 1-H), 1.58 (ddd, 2a-H), 2.15 (ddd, 2e-H), 4.33 (ddd~q, 3-H), 3.12 (dd, 4-H), 4.03 (dq, 5-H), 1.40 (d, 3H, 6-$CH_3$), 5.24 (d, 1'-H), 4.37 (dd, 2'-H), 5.42 (dd~t, 3'-H), 4.13 (br ddd, 4'-H), 4.36 (dq, 5'-H), 1.29 (d, 3H, 6'-$CH_3$), 1.83 (br d, 4'-OH), 4.18, 4.40, 4.51 and 4.70 (2 AB, 4H, Aryl-$CH_2$), 7.31 and 8.16 (each mc, 15 H, Aryl-H); $J_{1,2a}$ = 4.3, $J_{1,2e}$ = 0.8, $J_{2a,2e}$ = 15.2, $J_{2a,3}$ = 2.7, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.4, $J_{1',2'}$ = 0.8, $J_{2',3'}$ = 2.7, $J_{3',4'}$ = 3.0, $J_{4',4'\text{-OH}}$ = 8.6, $J_{4',5'}$ = 9.7, $J_{5',6'}$ = 6.4, $J_{A,B}$ = 11.6 and 11.8 Hz. Anal. Calcd for $C_{33}H_{37}IO_8$ (688.6): C, 57.56; H, 5.42. Found: C, 57.47; H, 5.39.

Benzyl 3-O-[2,6-Dideoxy-2-iodo-4-O-(p-methoxybenzyl)-α-L-altropyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (12). - A solution of **9** (44 mg, 0.05 mmol) in anhydrous methanol (2 mL) was stirred with sodium methanolate (50 mg) for 3 d at room temperature. Following neutralization (Amberlite IR 120 $H^+$), workup as for **3**, and filtration over silica gel to give 30 mg (78 %), colourless syrup; $[\alpha]_D^{20}$ = -123.6° (c = 1.5, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.87 (dd, 1-H), 1.68 (dd, 2a-H), 2.32 (ddd, 2e-H), 4.42 (ddd~q, 3-H), 3.20 (dd, 4-H), 4.39 (dq, 5-H), 1.24 (d, 3H, 6-$CH_3$), 5.15 (d, 1'-H), 3.28 (dd, 2'-H), 3.34 (dd, 3'-H), 3.38 (dd, 4'-H), 4.05 (dq, 5'-H), 1.13 (d, 3H, 6'-$CH_3$), 3.80 (s, 3H, $OCH_3$), 4.35, 4.47, 4.60, 4.66, 4.75 and 4.78 (3 AB, 6H, Aryl-$CH_2$), 6.87 and 7.28 (mc, 14H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.2, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 4.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 8.9, $J_{5,6}$ = 6.2, $J_{1',2'}$ = 3.0, $J_{2',3'}$ = 4.0, $J_{3',4'}$ = 1.0, $J_{4',5'}$ = 9.0, $J_{5',6'}$ = 6.2, $J_{A,B}$ = 11.4, 12.0 and 12.0 Hz. Anal. Calcd for $C_{34}H_{41}IO_8$ (704.6): C, 57.96; H, 5.86. Found: C, 58.05; H, 5.90.

Benzyl 3-O-[3-O-(3-4-Di-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-4-O-benzoyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (17). - A solution of glycal **15**[13] (38 mg, 0.12 mmol), disaccharide **4** (35 mg,0.05 mmol) and N-iodosuccinimide (33 mg,

0.15 mmol) in anhydrous acetonitrile (1 mL) was concentrated to a syrup by a continuous stream of nitrogen. After 1 h at room temperature an additional amount of **15** (24 mg, 0.08 mmol) and N-iodosuccinimide (26 mg, 0.09 mmol) in acetonitrile (1 mL) were added, treated as above, and then left at room temperature for 1 d. Following workup (GP II) the residue was separated by HPLC (ethyl acetate-toluene, 1:15). In addition to recovered disaccharide **4** (24.2 mg, 69 %) a mixture (48 mg) of **16** and **17** were obtained. These were separated by gel permeation chromatography.
**17**: Yield: 10.1 mg (21 %), colourless syrup; $[\alpha]_D^{20}$ = -95.4° (c = 0.6, chloroform); $^1$H NMR (300 MHz, $CDCl_3$) : δ = 4.81 (dd,1-H), 1.57 (ddd, 2a-H), 2.25 (ddd, 2e-H), 4.30 (mq, 3-H), 3.14 (dd, 4-H), 4.38 (dq, 5-H), 1.54 (d, 3H, 6-$CH_3$), 5.31 (brs, 1'-H), 4.34 (dd, 2'-H), 4.31 (mc, 3'-H), 5.57 (dd, 4'-H), 4.78 (dq, 5'-H), 1.42 (d, 3H, 6'-$CH_3$), 5.12 (brs, 1''-H), 4.77 (dd, 2''-H), 4.05 (dd~t,3''-H), 3.75 (dd, 4''-H), 4.09 (dq, 5''-H), 0.88 (d, 3H,6''-$CH_3$), 4.29, 4.33, 4.37, 4.43, 4.47, 4.62 and 4.78 (4 AB, 8H, Aryl-$CH_2$), 7.22 and 7.97 (mc, 25H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.2, $J_{2a,3}$ = 2.6, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.7, $J_{4,5}$ = 9.3, $J_{5,6}$ = 6.2, $J_{1',2'}$ = 0.8, $J_{2',3'}$ = 2.8, $J_{3',4'}$ = 2.6, $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.4, $J_{1'',2''}$ = 0.8, $J_{2'',3''}$ = 2.6, $J_{3'',4''}$ = 2.7, $J_{4'',5''}$ = 9.4, $J_{5'',6''}$ = 6.4, $J_{AB}$ = 12.0, 11.2, 11.8 and 11.9 Hz. Anal. Calcd for $C_{53}H_{58}I_2O_{11}$ (1124.8): C, 56.69; H, 5.20. Found: C, 55.96; H, 5.16.

Benzyl 3,4-Di-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranoside (**16**). - Yield: 29.8 mg (57 %) (based on 31 mg of **15**; half the amount of **15** since self condensation is presumed), colourless syrup, $[\alpha]_D^{20}$ = -65.5° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 5.21 (d, 1-H), 4.43 (dd, 2-H), 3.90 (dd, 3-H), 3.72 (dd, 4-H), 4.37 (dq, 5-H), 1.22 (d, 3H, 6-$CH_3$), 4.39, 4.43, 4.47, 4.64 (2 AB, 4H, Aryl-$CH_2$), 4.52 (d, 2H, Aryl-$CH_2$), 7.29 (mc, 15H, Aryl-H); $J_{1,2}$ = 2.9, $J_{2,3}$ = 4.4, $J_{3,4}$ = 2.9, $J_{4,5}$ = 7.9, $J_{5,6}$ = 6.4, $J_{A,B}$ = 11.9, 12.0 and 12.0 Hz. Anal. Calcd for $C_{27}H_{29}IO_4$ (544.4): C, 59.57; H, 5.37. Found: C, 59.24; H, 5.28.

3,4-Di-O-benzoyl-2,6-dideoxy-D-hexopyranose (**19**). - Compound **18**[28] (1.0 g, 2.9 mmol) was dissolved in aqueous acetic acid (50 %, 30 mL) and refluxed for 6 h. Following evaporation and repeated codestillation with toluene the residue was purified by chromatography (ethyl acetate-toluene, 1:3); yield: 677 mg (70 %), **19α**:**19β** = 1:2 ($^1$H NMR), m. p. 123°C, $[\alpha]_D^{20}$ = +141.3° (c = 1.5, chloroform).

**19α**: $^1$H NMR (300 MHz, $C_6D_6$): δ = 4.94 (dd, 1-H), 1.58 (ddd~dt, 2a-H), 1.92 (ddd, 2e-H), 5.84 (ddd~q, 3-H), 5.12 (dd, 4-H), 4.76 (dq, 5-H), 1.24 (d, 3H, 6-$CH_3$), 3.11 (d, 1-OH), 7.97 and 8.20 (each mc, 10H, Aryl-H); $J_{1,2a}$ = 3.8, $J_{1,2e}$ = 1.6, $J_{1,1\text{-OH}}$ = 5.4, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.9, $J_{2e,3}$ = 4.0, $J_{3,4}$ = 3.0, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.4 Hz.

**19β**: $^1$H NMR (300 MHz, $C_6D_6$) δ = 5.15 (ddd, 1-H), 1.64 (ddd, 2a-H), 2.02 (ddd, 2e-H), 5.90 (ddd~q, 3-H), 5.08 (dd, 4-H), 4.19 (dq, 5-H), 1.26 (d, 3H, 6-$CH_3$), 3.40 (d, 1-OH), 7.09 and 8.03 (each mc, 10H, Aryl-H); $J_{1,2a}$ = 9.6, $J_{1,2e}$ = 2.0, $J_{1,1\text{-OH}}$ = 6.4, $J_{2a,2e}$ = 11.2, $J_{2a,3}$ = 2.8, $J_{2e,3}$ = 3.7, $J_{3,4}$ = 3.0, $J_{4,5}$ = 10.0, $J_{5,6}$ = 6.4 Hz. Anal. Calcd for $C_{20}H_{20}O_6$ (356.4): C, 67.41; H, 5.66. Found: C, 67.10; H, 5.57.

Methyl 4-O-(3,4-Di-O-benzoyl-2,6-dideoxy-α- and -β-D-ribo-hexopyranosyl)-3-O-benzoyl-2,6-dideoxy-α-D-ribo-hexopyranoside (**24α** and **24β**). - Following GP I compound **19** (44.5 mg, 0.12 mmol) was transferred into the glycosyl chloride **21** (characterized by $^1$H NMR[35]) and this in situ treated with a solution of **23**[30] (19 mg, 0.08 mmol) in anhydrous benzene/dichloromethane (3:1, 2.0 mL). In the presence of pulverized molecular sieves (4 Å, Merck 6106) at -30°C silver trifluoromethane sulfonate (30 mg) was added and stirred another 2 h. The mixture was stirred overnight and gradually warmed to room temperature. Following dilution with $CH_2Cl_2$ filtration over silica gel, washing with aqueous $Na_2S_2O_3$ - and $NaHCO_3$ solutions and drying ($MgSO_4$) evaporation gave a syrup which was separated by chromatography (ethyl acetate-toluene, 1:5).

First the amorphous β-compound **24β** was eluted: yield: 12 mg (28 %), softening range 57-62°C, $[\alpha]_D^{20}$ = 165.6° (c = 0.3, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.70 (dd, 1-H), 2.01 (ddd~dt, 2a-H), 2.32 (ddd, 2e-H), 5.56 (ddd~q, 3-H), 3.52 (dd, 4-H), 4.33 (dq, 5-H), 1.29 (d, 3H, 6-$CH_3$), 5.04 (dd, 1'-H), 2.00 (ddd, 2a'-H), 2.24 (ddd, 2e'-H), 5.74 (ddd~q, 3'-H), 4.86 (dd, 4'-H), 4.19 (dq, 5'-H), 1.18 (d, 3H, 6'-$CH_3$), 3.29 (s, 3H, $OCH_3$), 7.35, 7.83, 7.97 and 8.07 (each mc, 15H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.3, $J_{2e,3}$ = 3.2, $J_{3,4}$ = 3.1, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.3, $J_{1',2a'}$ = 9.4, $J_{1',2e'}$ = 2.0, $J_{2a',2e'}$ = 14.4, $J_{2a',3'}$ = 3.0, $J_{2e',3'}$ = 3.6, $J_{3',4'}$ = 3.0, $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.3 Hz.

Second fraction: amorphous α-compound **24α**: yield 16.4 mg (38 %), softening range 49-52°C, $[\alpha]_D^{20}$ = 190.8° (c = 0.4, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.75 (dd, 1-H), 2.04 (ddd~dt, 2a-H), 2.19 (ddd, 2e-H), 5.53 (ddd~q, 3-H), 3.62 (dd, 4-H), 4.34 (dq, 5-H), 1.37 (d, 3H, 6-$CH_3$), 5.15 (dd, 1'-H), 2.14 (mc, 2H, 2a'-H and 2e'-H), 5.65 (ddd~q, 3'-H), 4.98 (dd, 4'-H), 4.53 (dq, 5'-H), 1.24 (d, 3H, 6'-$CH_3$), 3.34 (s, 3H, $OCH_3$), 7.33, 7.85, 7.90 and 7.94 (each mc, 15H, Aryl-H); $J_{1,2a}$ = 4.4, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.8, $J_{2e,3}$ = 3.4, $J_{3,4}$ = 3.9, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.2, $J_{1',2a'}$ = 3.2, $J_{1',2e'}$ = 2.2, $J_{2a',3'}$ ≃ 3.2, $J_{2e',3'}$ ≃ 3.2, $J_{3',4'}$ = 3.0, $J_{4',5'}$ = 9.8, $J_{5',6'}$ = 6.4 Hz. Anal. Calcd for $C_{34}H_{36}O_{10}$ (604.6): C, 67.54; H, 6.00. Found for **24α**: C, 67.89; H, 6.05. Found for **24β**: C, 67.49; H, 5.95.

Methyl 4-O-[(3,4-Di-O-p-methoxybenzoyl)-2,6-dideoxy-α- and -β-D-ribo-hexopyranosyl]-3-O-benzoyl-2,6-dideoxy-α-D-ribo-hexopyranoside (**25α** and **25β**). - a) Following GP I compound **20**[27] (38 mg, 0.09 mmol) was transferred into the glycosyl chloride **22** ($^1$H NMR showed identical data as reported for the L-enantioner[13]) and this in situ treated with a solution of **23**[30] (19 mg, 0.08 mmol) in anhydrous benzene/dichloromethane (3:1, 2 mL). In the presence of pulverized molecular sieves (4 Å, Merck 6106) at -30°C silver triflate (30 mg) was added and further processed and worked up as for the preparation of **24α/β**. From chloroform/n-hexane the β-compound **25β** crystallized (12 mg). The remaining raw material was subjected to PLC (ethyl acetate-toluene, 1:5) to give another 7.1 mg (15 %) of **25β** and 13.9 mg (29 %) of **25α**. Total yield: **25α**: 13.9 mg (29 %), **25β**: 19.1 mg (40 %); ratio 1:1.4.

b) Following GP I compound **20**[27] (38 mg, 00.9 mmol) was transferred into the glycosyl chloride **22**[35] and in situ treated with a solution of **23**[30] (15 mg, 0.05 mmol) in anhydrous dichloromethane (2 mL). Pulverized molecular sieves (4 Å, Merck 6106), $Hg(CN)_2$ (60 mg), and $HgBr_2$ (15 mg) were added and the mixture stirred overnight at room temperature. Following filtration over celite the solution was washed with aqueous $NaHCO_3$ and NaI solutions, dried ($MgSO_4$) and evaporated. The raw material was characterized by $^1$H NMR; yield 62 %, ratio **25α**:**25β** = 1:1.4.

Compound **25α**: colourless syrup, $[\alpha]_D^{20}$ = 131.6° (c = 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.75 (dd, 1-H), 2.09 (ddd~dt, 2a-H), 2.20 (ddd, 2e-H), 5.64 (ddd~q, 3-H), 3.62 (dd, 4-H), 4.19 (dq, 5-H), 1.38 (d, 3H, 6-$CH_3$), 5.13 (dd, 1'-H), 2.12 (mc, 2H, 2a'-H and 2e'-H), 5.48 (ddd~q, 3'-H), 4.95 (dd, 4'-H), 4.50 (dd, 5'-H), 1.23 (d, 3H, 6'-$CH_3$), 3.41 (s, 3H, $OCH_3$), 3.79 and 3.85 (each s, each 3H, Aryl-$OCH_3$), 6.80, 7.29, 7.43, 7.81, 7.94 (each mc, 13H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ = 1.1, $J_{2a,2e}$ = 14.9, $J_{2a,3}$ = 3.7, $J_{2e,3}$ = 3.4, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.3, $J_{5,6}$ = 6.3, $J_{1',2a'}$ = 3.1, $J_{1',2e'}$ = 1.7, $J_{3',4'}$ = 3.1, $J_{4',5'}$ = 9.9, $J_{5',6'}$ = 6.3 Hz.

Compound **25β**: m. p. 224-226°C, $[\alpha]_D^{20}$ = 113.4° (c= 1.0, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.70 (dd, 1-H), 2.00 (ddd, 2a-H), 2.33 (ddd, 2e-H), 5.57 (ddd~q, 3-H), 3.51 (dd, 4-H), 4.33 (dq, 5-H), 1.30 (d, 3H, 6-$CH_3$), 5.03 (dd, 1'-H), 1.98 (ddd, 2a'-H), 2.22 (ddd, 2e'-H), 5.69 (ddd~q, 3'-H), 4.82 (dd, 4'-H), 4.17 (dq, 5'-H), 1.17 (d, 3H, 6'-$CH_3$), 3.34 (s, 3H, $OCH_3$), 3.79 and 3.88 (each s, each 3H, Aryl-$OCH_3$), 6.77, 6.95, 7.20, 7.34, 7.76, 7.95, 8.06 (each mc, 13H, Aryl-H); $J_{1,2a}$ = 4.2, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.6, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 3.1, $J_{4,5}$ = 9.4, $J_{5,6}$ = 6.4, $J_{1',2a'}$ = 8.6, $J_{1',2e'}$ = 2.2, $J_{2a',2e'}$ = 14.3, $J_{2a,3}$ = 2.9, $J_{2e,3}$ = 3.6, $J_{3',4'}$ = 3.0, $J_{4',5'}$ = 9.8, $J_{5',6'}$ = 6.3 Hz. Anal. Calcd for $C_{36}H_{40}O_{12}$ (664.7): C,

65.05; H, 6.06. Found for **25α**: C, 65.12; H, 6.08. Found for **25β**: C, 64.84; H, 5.97.

Benzyl 4-O-(2,3,6-Tridesoxy-4-O-methyl-α-L-erythro-hex-2-enopyranosyl)-3-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**30**). - a) According to GP I the urethane derivative **31**[14] (26.5 mg, 0.12 mmol) was transformed into the glycosyl chloride **28**. In situ this was mixed with a solution of compound **29**[14] (26 mg, 0.08 mmol) in anhydrous dichloromethane (2 mL), molecular sieves (4 Å, Merck 6106) added, cooled to -30°C and treated with silver triflate (40 mg). Overnight the mixture was gradually warmed to room temperature, worked up as described for the preparations of **24α/β** and separated by column chromatography (ethyl acetate-toluene, 1:10). Yield: 7.3 mg (20 %) of **30** and 13.3 mg (51 %) of **29** recovered.
b) Similarly **31**[14] (22 mg, 0.10 mmol) was treated as in GP I to give the glycosyl chloride **28**. In situ addition of **29**[14] (24 mg, 0.07 mmol) in anhydrous dichloromethane (2 mL), pulverized molecular sieves (4 Å, Merck 6101), $Hg(CN)_2$ (40 mg), and $HgBr_2$ (15 mg), followed by stirring overnight at room temperature, workup as for **25α/β** (method b), and chromatography as above gave 7 mg (20 %) of **30** with 11 mg (46 %) of **29** recovered.
**30**: colourless syrup, $[\alpha]_D^{20}$ = -135.9° (c = 1.4, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.89 (dd, 1-H), 1.73 (ddd, 2a-H), 2.35 (ddd, 2e-H), 3.92 (ddd~q, 3-H), 3.56 (dd, 4-H), 4.31 (dq, 5-H), 1.23 (d, 3H, 6-$CH_3$), 4.96 (br s, 1'-H), 6.04 (ddd~dt, 2'-H), 5.93 (ddd~dt, 3'-H), 3.44 (dddd~dq, 4'-H), 3.81 (dq, 5'-H), 1.26 (d, 3H, 6'-$CH_3$), 3.38 (s, 3H, $OCH_3$), 4.42, 4.49, 4.76 and 4.86 (2 AB, 4H, Aryl-$CH_2$), 7.28 (mc, 10H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.2, $J_{2a,2e}$ = 15.6, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.9, $J_{3,4}$ = 2.9, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.2, $J_{1',2'}$ = 1.4, $J_{1',3'}$ = 2.8, $J_{1',4'}$ = 1.6, $J_{2',3'}$ = 10.2, $J_{2',4'}$ = 1.6, $J_{3',4'}$ = 2.0, $J_{4',5'}$ = 8.9, $J_{5',6'}$ = 6.2, $J_{A,B}$ = 12.0 and 12.0 Hz. Anal. Calcd for $C_{27}H_{34}O_6$ (454.5): C, 71.34; H, 7.54. Found: C, 71.42; H, 7.56.

Benzyl 3-O-[4-O-(4-O-Methyl-2,3,6-trideoxy-α-L-erythro-hex-2-enopyranosyl)-3-O-benzoyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**32**). - A solution of compounds **31**[14] (23 mg, 0.11 mmol) and **11** (41 mg, 0.06 mmol) in anhydrous dichloromethane/benzene (1:1, 1 mL) was stirred with molecular sieves (4 Å). Under nitrogen anhydrous p-toluene sulfonic acid (5 mg, 0.03 mmol) was added and stirred at room temperature for 2 h. Following TLC check another p-TsOH (6 mg, 0.04 mmol) was added and stirring continued for 1.5 h. The cooled reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution

(1 mL) and extracted with dichloromethane. After drying ($MgSO_4$) separation was performed by gel permeation chromatography, and the individual fractions were finally purified by HPLC (ethyl acetate-toluene, 1:5). Yield of **32**: 13 mg (27 %), recovered urethane **31**: 12.7 mg (55 %), recovered; disaccharide **11**: 21 mg (51 %). Trisaccharide **32**: colourless syrup, $[\alpha]_D^{20}$ = -136.0° (c = 0.5, chloroform); $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.81 (dd, 1-H), 1.61 (ddd, 2a-H), 2.19 (ddd, 2e-H), 4.34 (ddd~q, 3-H), 3.16 (dd, 4-H), 4.27 (dq, 5-H), 1.23 (d, 3H, 6-$CH_3$), 5.25 (br s, 1'-H), 4.16 (d, 2'-H), 5.64 (dd~t, 3'-H), 4.27 (dd, 4'-H), 4.49 (dq, 5'-H), 1.21 (d, 3H, 6'-$CH_3$), 5.04 (br s, 1"-H), 5.94 (ddd~dt, 2"-H), 5.48 (ddd~dt, 3"-H), 3.40 (ddd~dq, 4"-H), 3.69 (dq, 5"-H), 1.27 (d, 3H,6"-$CH_3$), 3.34 (s, 3H, $OCH_3$), 4.22, 4.49, 4.51 and 4.74 (2 AB, 4H, Aryl-C$H_2$), 7.27 and 8.22 (each mc, 15H, Aryl-H); $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 0.7, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 2.2, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.3, $J_{1',2'} \approx 0.5$, $J_{2',3'}$ = 2.5, $J_{3',4'}$ = 2.9, $J_{4',5'}$ = 10.0, $J_{5',6'}$ = 6.3, $J_{1",2"}$ = 1.2, $J_{1",3"}$ = 2.6, $J_{1",4"}$ = 1.5, $J_{2",3"}$ = 10.2, $J_{2",4"}$ = 1.4, $J_{3",4"}$ = 1.4, $J_{4",5"}$ = 9.0, $J_{5",6"}$ = 6.3, $J_{A,B}$ = 11.8 and 12.2 Hz. Anal. Calcd for $C_{40}H_{47}IO_{10}$ (814.7): C, 58.97; H, 5.81. Found: C, 58.83; H, 5.79.

Benzyl 3-O-[3-O-(4-O-Acetyl-3-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-2,6-dideoxy-4-O-(p-methoxybenzyl)-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**39**). - A solution of disaccharide **10** (205 mg, 0.35 mmol), glycal **37**[13] (139 mg, 0.52 mmol) and N-iodosuccinimide (131 mg, 0.58 mmol) in anhydrous acetonitrile (1 mL) was stirred for 12 h at room temperature. Following workup (GP II) separation was done by HPLC (ethyl acetate-toluene, 1:10). Yield: 81.8 mg (24 %), colourless syrup, $[\alpha]_D^{20}$ = -153.8° (c = 1.0, chloroform); $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.81 (dd, 1-H), 1.51 (ddd, 2a-H), 2.28 (ddd, 2e-H), 4.29 (dd~q, 3-H), 3.14 (dd, 4-H); 4.46 (mc, 5-H), 1.39 (d, 3H, 6-$CH_3$[a)]), 4.99 (dd, 1'-H), 1.44 (ddd, 2a'-H), 2.16 (ddd, 2e'-H), 4.19 (ddd~q, 3'-H), 3.10 (dd, 4'-H), 4.42 (dq, 5'-H), 1.24 (d, 3H, 6'-$CH_3$[a)]), 5.41 (brs, 1"-H), 4.68 (dd, 2"-H), 4.10 (dd~t, 3"-H), 5.27 (dd, 4"-H), 4.46 (dq, 5"-H), 1.17 (d, 3H, 6"-$CH_3$[a)]), 2.01 (s, 3H, $OCOCH_3$), 3.77 (s, 3H, $OCH_3$), 4.07, 4.34, 4.37, 4.41, 4.54, 4.55, 4.56 and 4.81 (4 AB, 8H, Aryl-C$H_2$), 6.77 and 7.25 (each mc, 19H, Aryl-H); $J_{1,2a}$ = 4.1, $J_{1,2e}$ = 0.8, $J_{2a,2e}$ = 15.2, $J_{2a,3}$ = 2.8, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.3, $J_{5,6}$ = 6.2, $J_{1',2a'}$ = 4.3, $J_{1',2e'}$ = 0.9, $J_{2a',2e'}$ = 15.3, $J_{2a',3'}$ = 3.0, $J_{2e',3'}$ = 3.3, $J_{3',4'}$ = 2.6, $J_{4',5'}$ = 9.1, $J_{5',6'}$ = 6.3, $J_{1",2"}$ = 0.8, $J_{2",3"}$ = 2.8, $J_{3",4"}$ = 3.0, $J_{4",5"}$ = 9.6, $J_{5",6"}$ = 6.2, $J_{AB}$ = 11.6, 11.8, 11.9 and 12.0 Hz; [a)] assignment may be inverted. Anal. Calcd for $C_{49}H_{59}IO_{12}$ (966.9): C, 60.87; H, 6.15. Found: C, 61.21; H, 6.20.

In addition Benzyl 3-O-(4-O-Acetyl-3-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**38**) was isolated. Yield: 60 mg (24 % based on **10**); colourless syrup; $[\alpha]_D^{20}$ = -131.7° (c = 1.06, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.87 (dd, 1-H), 1.68 (ddd, 2a-H), 2.26 (ddd, 2e-H), 4.27 (ddd~q, 3-H), 3.13 (dd, 4-H), 4.25 (dq, 5-H), 1.21 (d, 3H, 6-$CH_3$), 5.28 (br s, 1'-H), 4.41 (dd, 2'-H), 3.95 (dd~t, 3'-H), 5.16 (dd, 4'-H), 4.51 (dq, 5'-H), 1.11 (d, 3H, 6'-$CH_3$), 1.99 (s, 3H, $OCOCH_3$), 4.04, 4.43, 4.44, 4.47, 4.65 and 4.71 (3 AB, 6H, Aryl-$CH_2$), 7.31 (mc, 15H, Aryl-H); $J_{1,2a}$ = 4.4, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 14.8, $J_{2a,3}$ = 3.0, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.0, $J_{5,6}$ = 6.3, $J_{1',2'}$ = 0.8, $J_{2',3'}$ = 2.8, $J_{3',4'}$ = 3.1, $J_{4',5'}$ = 9.1, $J_{5',6'}$ = 6.4, $J_{A,B}$ = 11.9, 11.9 and 12.0 Hz. Anal. Calcd for $C_{35}H_{41}IO_8$ (716.6): C, 58.66; H, 5.77. Found: C, 58.78; H, 5.79.

Benzyl 3-O-[3-O-(4-O-Acetyl-3-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**40**). - A solution of **39** (70.4 mg, 0.073 mmol) in dichloromethane (2 mL) and water (0.3 mL) was stirred with DDQ (20 mg, 0.088 mmol) for 50 min at room temperature, then filtered and purified chromatographically (ethyl acetate-toluene, 1:3). Yield: 43.1 mg (70 %), m. p. 155-163°C (amorphous, from toluene); $[\alpha]_D^{20}$ = -141.3° (c = 1.1, chloroform); $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.83 (dd, 1-H), 1.59 (ddd, 2a-H), 2.27 (ddd, 2e-H), 4.35 (ddd~q, 3-H), 3.19 (dd, 4-H), 4.40 (dq, 5-H), 1.44 (d, 3H, 6-$CH_3$[a]), 4.99 (dd, 1"-H), 1.53 (ddd, 2a"-H), 2.06 (ddd, 2e'-H) 3.91 (ddd~q, 3'-H), 3.09 (ddd, 4'-H), 4.04 (dq, 5'-H), 1.19 (d, 3H, 6'-$CH_3$[a]), 5.34 (brs, 1"-H), 4.52 (dd, 2"-H), 4.02 (dd~t, 3"-H), 5.26 (dd, 4"-H), 4.15 (dq, 5"-H), 1.18 (d, 3H, 6"-$CH_3$), 2.01 (s, 3H, $OCOCH_3$), 2.77 (d, 4'-OH), 4.03, 4.29, 4.43, 4.54, 4.75 and 4.77 (3 AB, 6H, Aryl-$CH_2$), 7.27 (mc, 15H, Aryl-H); $J_{1,2a}$ = 4.3, $J_{1,2e}$ = 0.7, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 2.6, $J_{2e,3}$ = 3.0, $J_{3,4}$ = 2.7, $J_{4,5}$ = 9.3, $J_{5,6}$ = 6.2, $J_{1',2a'}$ = 4.3, $J_{1',2e'}$ = 0.8, $J_{2a',2e'}$ = 15.2, $J_{2a',3'}$ = 2.8, $J_{2e',3'}$ = 2.8, $J_{3',4'}$ = 3.1, $J_{4',5'}$ = 9.5, $J_{5',6'}$ = 6.3, $J_{1",2"}$ = 0.8, $J_{2",3"}$ = 2.9, $J_{3",4"}$ = 3.1, $J_{4",5"}$ = 10.0, $J_{5",6"}$ = 6.3, $J_{4',4'\text{-OH}}$ = 12.6, $J_{A,B}$ = 11.4, 11.9 and 12.0 Hz; [a]assignment my be inverted. Anal. Calcd for $C_{41}H_{51}IO_{11}$ (846.7): C, 58.16; H, 6.07. Found: C, 58.03; H, 6.03.

Benzyl 3-O-[3-O-(4-O-Acetyl-3-O-benzyl-2,6-dideoxy-2-iodo-α-L-altropyranosyl)-4-O-(2,6-dideoxy-4-O-methyl-3-O-(p-methoxybenzyl)-β-L-ribo-hexopyranosyl)-2,6-dideoxy-α-L-ribo-hexopyranosyl]-4-O-benzyl-2,6-dideoxy-α-L-ribo-hexopyranoside (**42**). - Following GP I 2,6-dideoxy-4-O-methyl-3-O-(p-methoxybenzoyl)-α- and β-L-ribo-hexopyranose[14] (23.6 mg, 0.08 mmol) was transformed into the glycosyl chloride **41**. In situ this was treated with **40** (34 mg, 0.04 mmol) dissolved in anhydrous $CH_2Cl_2/C_6H_6$ (2:1, 2 mL) in the presence of pulverized molcular sieves (4 A, Merck 6106), and the mixture cooled to -35°C. Following addition of silver triflate (20 mg) this temperature was maintained for 1 h, and then the mixture gradually warmed to room temperature overnight under stirring. Workup was as for compounds **24**, and the residue was separated by HPLC (ethyl acetate-toluene, 1:5). In addition to 15.6 mg (46 %) recovered **40**, 2.5 mg (5 %) of a mixture of **40** and **42** (ratio 1:2) and 1.0 mg of a mixture of **40** and presumably the α, 1'''→3' isomer of **42** was characterized by $^1$H NMR spectroscopy. $^1$H NMR (300 MHz, $CDCl_3$): pyranose unit A: δ = 4.80 (dd, 1-H), 1.52 (mc, 2a-H), 2.26 (ddd, 2e-H), 4.25 (mc, 3-H), 3.04 (dd, 4-H), 4.37 (mc, 5-H), 1.30 (d, 3H, 6-$CH_3$); unit B: 5.04 (dd, 1-H), 1.54 (mc, 2a-H), 2.03 (ddd, 2e-H), 4.20 (mc, 3-H), 3.46 (dd, 4-H), 4.29 (mc, 5-H), 1.29 (d, 3H, 6-$CH_3$); unit C: 5.32 (br s, 1-H), 4.49 (dd, 2-H), 3.86 (dd~t, 3-H), 5.03 (dd, 4-H), 4.15 (mc, 5-H), 1.15 (d, 3H, 6-$CH_3$); unit D: 4.98 (dd, 1-H), 1.91 (ddd, 2a-H), 2.15 (mc, 2e-H), 5.55 (dd~q, 3-H), 2.99 (dd, 4-H), 4.19 (mc, 5-H), 1.26 (d, 3H, 6-$CH_3$); 1.97 (s, 3H, $OCOCH_3$, 3.33 and 3.85 (each s, 3H, $OCH_3$), 4.76, 4.74, 4.51, 4.38, 4.28 and 4.26 (3 AB, 6H, Aryl-$CH_2$), 6.78, 7.22 and 7.93 (mc, Aryl-H); unit A: $J_{1,2a}$ = 4.0, $J_{1,2e}$ = 1.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.2; unit B: $J_{1,2a}$ = 4.1, $J_{1,2e}$ ≃ 0.8, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ ≃ 3.0, $J_{2e,3}$ ≃ 3.0, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.0, $J_{5,6}$ = 6.2; unit C: $J_{1,2}$ ≃ 0.8, $J_{2,3}$ = 2.8, $J_{3,4}$ = 3.0, $J_{4,5}$ = 9.6, $J_{5,6}$ = 6.3; unit D: $J_{1,2a}$ = 9.1, $J_{1,2e}$ = 4.0, $J_{2a,2e}$ = 15.0, $J_{2a,3}$ = 3.4, $J_{2e,3}$ ≃ 3.0, $J_{3,4}$ = 3.0, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.1; $J_{A,B}$ = 11.8, 11.9 and 12.0 Hz.

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