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Reaction of sugar allyltins with aldehydes. A remarkable difference in reactivity between furanose and pyranose organometallic derivatives

Sławomir Jarosz,[a,*] Stanisław Skóra,[a] Katarzyna Szewczyk[a] and Zbigniew Ciunik[b]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland*
[b]*Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

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Abstract—The reaction of organometallic derivatives of monosaccharides with aldehydes catalyzed with $BF_3{\cdot}OEt_2$ was studied. A significant difference in reactivity between the pyranosidic and furanosidic allyltins was noted. The former reacted readily with aldehydes affording precursors of higher carbon sugars with very high stereoselectivity, while the latter underwent rearrangement with elimination of the stannyl moiety *prior* to reaction with the aldehyde.

1. Introduction

The synthesis of higher carbon sugars has gained considerable attention in the last decade. Such compounds may serve as non-metabolized analogs of sugars and may be used for the specific complexation of inorganic as well as organic cations (enantioselective complexation) or for studying conformational features. A number of methods leading to such molecules has been developed.[1]

In the past several years, we proposed a general methodology for the preparation of higher carbon sugars by coupling two sugar subunits[2] (Fig. 1).

Sugar phosphoranes[3] **1**, phosphonates[4] **2**, or vinyltin derivatives of monosaccharides[5] **4** were used as starting materials for the preparation of precursors **3** which are readily converted into higher carbon sugars[2] **5**.

We also applied the allyltin derivative **6** (which can be prepared by a method depicted in Fig. 2) for construction of a higher sugar skeleton (Fig. 2).[6] This organometallic compound reacted with sugar aldehyde **7** leading to the unsaturated alcohol **9** in the titanium chloride-catalyzed process. However, this reaction was capricious and afforded mainly unsaturated aldehyde **8**; for acceptable yields of the condensation product, an excess of the allyltin reagent had to be used.[6]

Although this decomposition process of allyltin derivatives (which may be performed in a strictly controlled manner[7]) opens a convenient route for the preparation of chiral, highly oxygenated cyclopentanes,[8] bicyclo[4.3.0]nonanes[9] and bicyclo[4.4.0]decanes[10] (Fig. 2), the formation of the dienoaldehyde (being an undesired side process) significantly lowers the yield of the higher carbon sugar precursors.

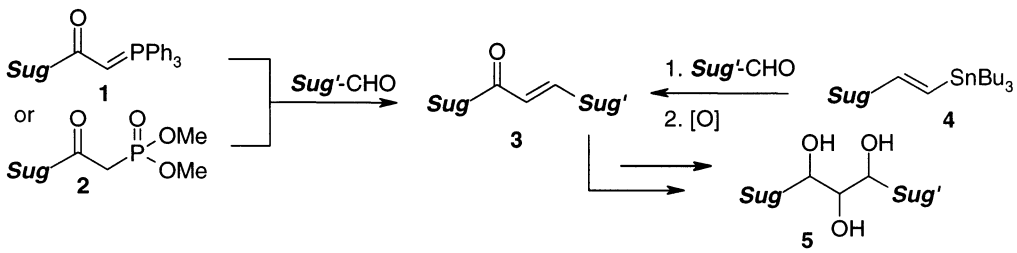

Figure 1. Methods for the preparation of higher carbon sugars.

* Corresponding author. E-mail: sljar@icho.edu.pl

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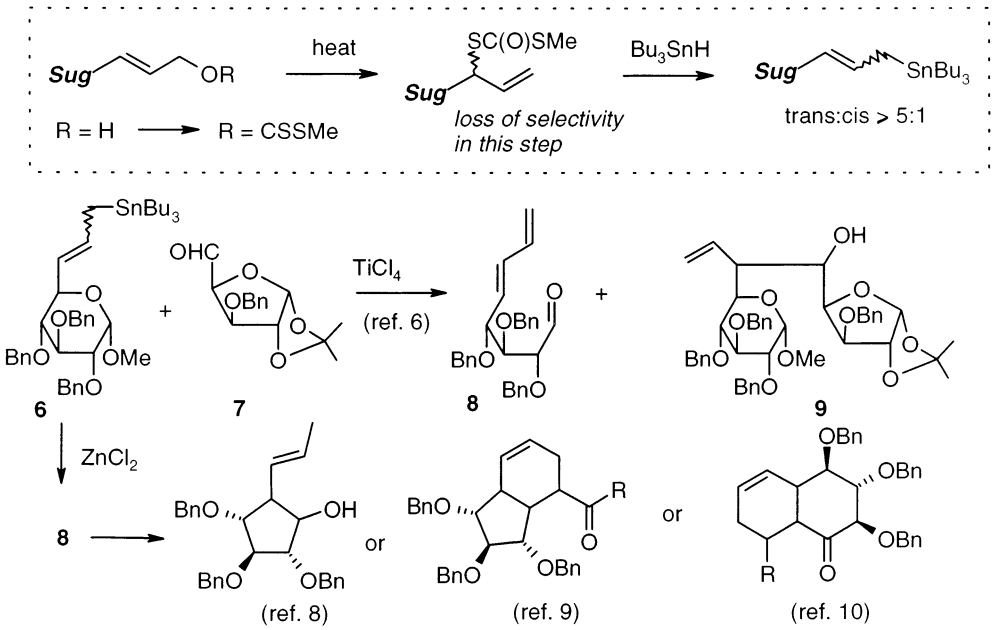


Figure 2. Preparation of sugar allyltins and their application in organic synthesis.

2. Results and discussion

The reaction of the allyltin derivatives with aldehydes can be performed either at high temperature,[11] under high pressure,[12] under radical conditions,[13] or may be catalyzed with a Lewis acid.[14] The relative configurations of the products (homoallylic alcohols) in the former two processes (Δt, Δp) depends on the geometry of the double bond of the starting allyltin derivative. It is, however, independent in an acid-catalyzed process.

The first two processes (Δt, Δp) proceed via a cyclic six-membered transition state in which the tin atom coordinates to a carbonyl group. It is evident, therefore, that both geometrical isomers must form different homoallylic alcohols (Fig. 3).

The reaction of organostannane reagents with aldehydes catalyzed with a Lewis acid proceeds through a different mechanism. The relatively low Lewis acidity of the tin atom in organostannanes compared to that of Lewis acids such as $TiCl_4$, $ZnBr_2$, $AlCl_3$ and BF_3, means that the carbonyl group is complexed by these Lewis acids but not tin. The open-chain model leading to the same *erythro* isomer—regardless of the configuration of starting allyltin—is, therefore, preferred[14] (Fig. 3).

Since sugar allyltin derivatives readily undergo decomposition on treatment with $TiCl_4$,[6] optimization of the conditions of the coupling process leading to a higher carbon sugar skeleton is required. Also, the reactivity of the pyranose- and furanose-derived organometallics

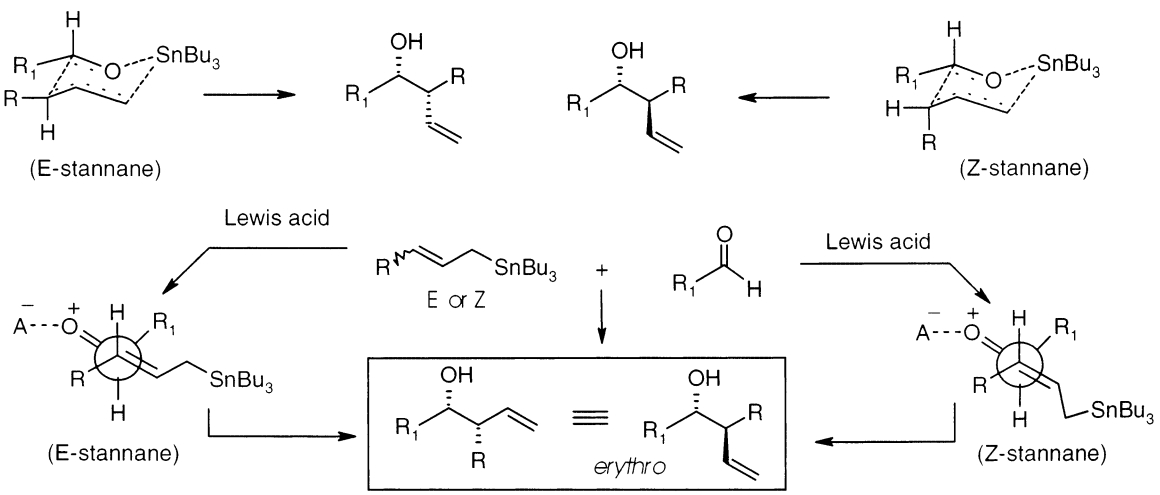


Figure 3. Stereochemical models for the reaction of allytins with aldehydes.

should be examined, since application of sugars with different size of the ring would extend the usefulness of the proposed method.

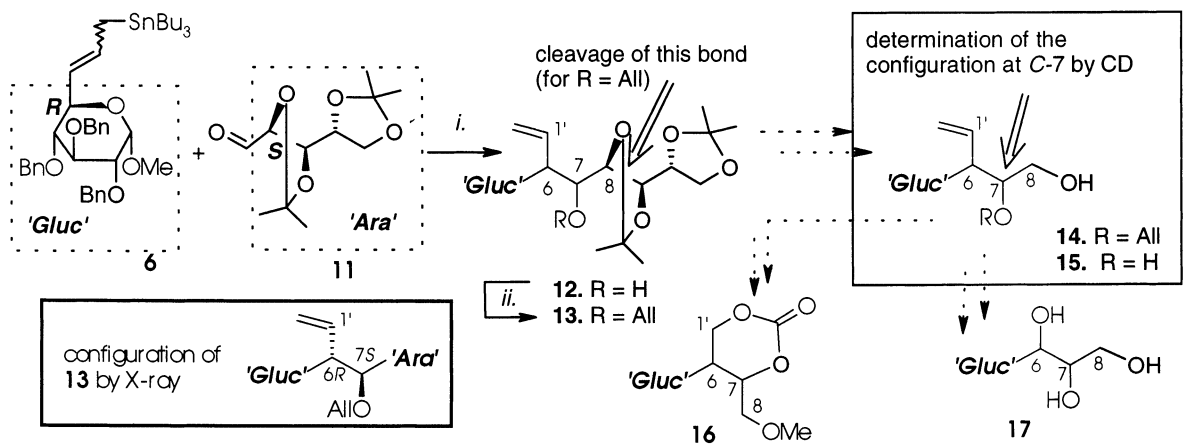
2.1. Reaction of the pyranose allyltins with aldehyde

Reaction of methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-tributylstannyl-oct-6-eno-α-D-*gluco*- or D-*manno*-1,5-pyranosides[7] (**6** in Scheme 1 or **10** in Scheme 2) with 2,3:4,5-di-*O*-isopropylidene-D-arabinose[15] **11** either at high temperature (140°C, boiling xylene) or under high pressure (11 kbar) did not provide the desired higher sugar precursors; the starting materials remained unreacted. These results showed unambiguously that the Lewis acid is needed to promote the coupling of sugar allyltin reagents with aldehydes. From several acids tested ($SnCl_4$, $TiCl_4$, $ZnBr_2$, $AlCl_3$, $BF_3{\cdot}OEt_2$), boron trifluoride etherate was found to be the reagent of choice. Reaction of the D-*gluco*-configurated derivative **6** with aldehyde **11** in the presence of $BF_3{\cdot}OEt_2$ gave 81% of the coupling product **12** as a single stereoisomer (Scheme 1). No decomposition of the allyltin derivative was seen using this promoter.

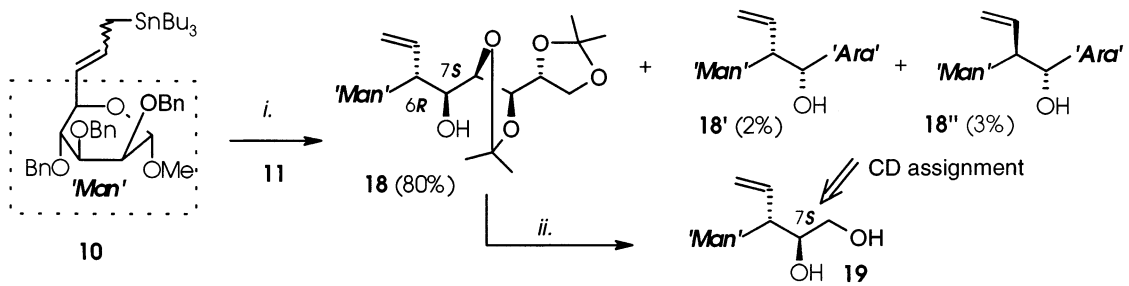
We assumed that, the configurations of the newly created stereogenic centers at C(6) and C(7) should be easily determined by the sequence of reactions shown in Scheme 1. Compound **12** could be converted into diol **15** by simple transformations, involving temporary protection of the free hydroxyl group at C(7), manipulations at the 'right' part of the molecule and finally deprotection. Diol **15** might be further converted into a known[16] octoside **17**, thus assigning the geometry at the newly created stereogenic C(6) and C(7) centers. Alternatively, the absolute configuration at the C(7) center in **15** might be assigned on the basis of the CD spectroscopy,[17] while the relative stereochemistry between the C(6) and C(7) centers could be established from NMR experiments performed on a cyclic derivative (e.g. **16**), which could be prepared from **15** by standard methods.

For the temporary protection of the hydroxyl group in **12** the allyl ether blocking group was chosen. This was based on its stability under a variety of reaction conditions and the possibility of its selective removal.[18] Fortunately, protection of the C(7)-OH as an allyl ether provided a crystalline derivative **13**, the configuration of which was determined by the X-ray analysis, thus avoiding a tedious degradation sequence. The ORTEP drawing of **13** is shown in Fig. 4.

An explanation of this very high selectivity is shown in Fig. 5. According to the model[14] proposed for reaction of allyltins with aldehydes catalyzed with a Lewis acid the *erythro* adduct (see Fig. 3) is preferred regardless of the configuration of the double bond of allyltin derivative. The attack of the pre-complexed aldehyde **11** may occur either 'from the front' or 'from behind' of the sugar ring of **6** (transition states **A** leading to the (6*R*,7*S*) isomer or **B** (→6*S*,7*R*) in Fig. 5). It can be clearly seen that attack from 'the front of the ring' is much more preferable to the alternative one, since in the transition state **B** severe steric repulsion between the isopropylidene group of aldehyde **11** and the allyltin fragment of **6** is noted. This interaction is much stronger than the Coulombic repulsion between the carbonyl group and the ring oxygen atom in approach **B**.



Scheme 1. (i) $BF_3{\cdot}OEt_2$, THF, −78°C, 81%; (ii) AllBr, NaH, DMF.



Scheme 2. (i) $BF_3{\cdot}OEt_2$, THF, −78°C; (ii) (a) AllBr, NaH, DMF; (b) MeOH, $H^{(+)}$; (c) $NaIO_4$, then $NaBH_4$; (d) deallylation.

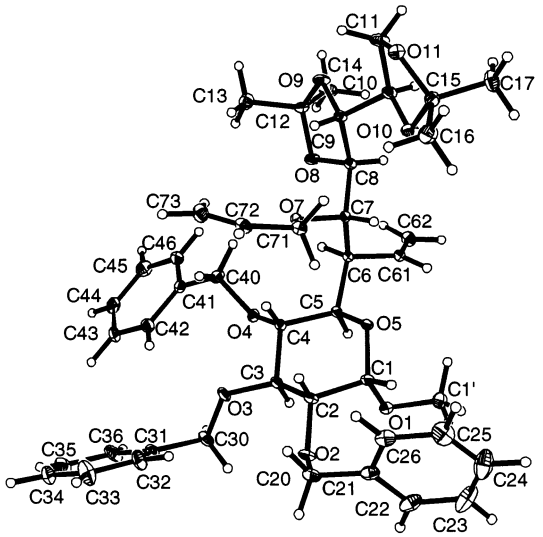


Figure 4. ORTEP dawing of compound **13**.

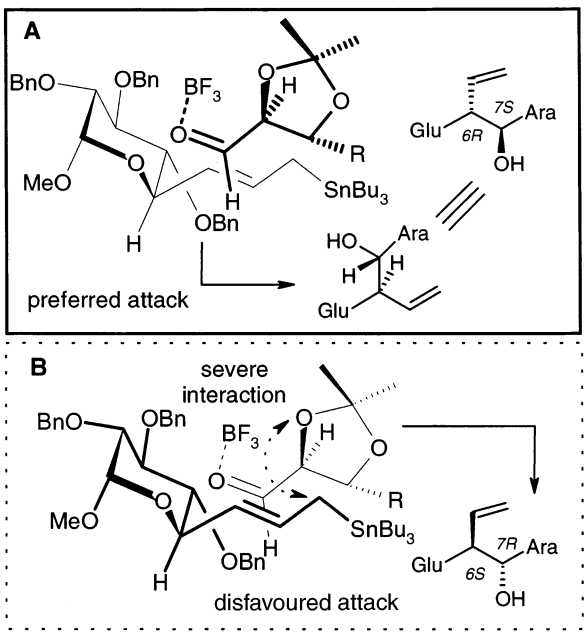


Figure 5. Preferred (**A**) and disfavoured (**B**) transition states in the reaction of **6** with aldehyde **11**.

Reaction of the D-*manno*-configured allyltin reagent **10** with aldehyde **11** (under the same conditions as for **6** and **11**) proceeded similarly, although the selectivity was slightly lower. The results are summarized in Scheme 2. Treatment of a mixture of **10** and **11** with boron trifluoride etherate afforded **18** in 80% yield together with small amounts of isomers **18′** and **18″**. It could be postulated that the configuration of the main isomer **18** has to be the same as that of **12**, because of only slight difference (at the distant stereogenic center) in the geometry of **6** and **10**.

This assumption was verified by the CD spectral assignment performed for the degradation product **19** (for its preparation, see Section 4). The positive Cotton effect at ca. 315 nm observed for the dimolybdenum complex

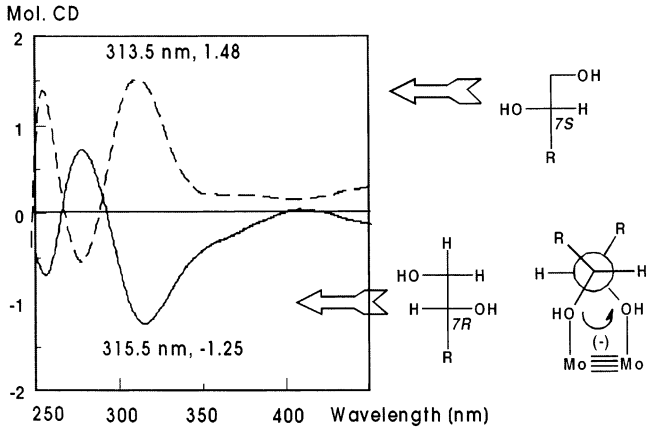


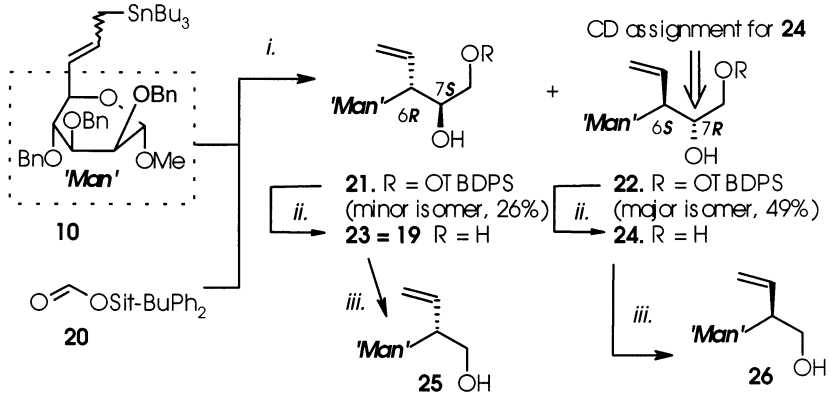
Figure 6. CD spectra of the molybdenum complexes of **19** (---) and **24** (—) in the *preferred threo* arrangement of the hydroxy groups. The negative sign of the Cotton effect at ca. 315 nm points to the 7*R* configuration (see Ref. 17).

of **19** pointed unambiguously to the (*S*)-configuration at the C(7) center (see Fig. 6).

Reaction of either **6** or **10** ((*R*)-configured at C(5) α- to the allyltin unit) with aldehyde **11** ((*S*)-configured α to the carbonyl group) represents a case in which both starting materials are chiral and may have influence on the steric course of this coupling process. The question, however, arises as to which component (allyltin or aldehyde) is responsible for the stereochemical outcome of the reaction. To solve this problem we performed the reaction of chiral allyltin **10** with the simplest achiral sugar-like derivative, *O*-*tert*-butyldiphenylsilyl glycol aldehyde[10b,19] **20**. The reaction of **10** with **20** catalyzed with $BF_3{\cdot}OEt_2$ afforded **21** in 26% yield and **22** in 49% yield (Scheme 3).

The relative configurations of both compounds were—as expected (see Fig. 3)—*erythro*, as determined by chemical and spectral correlations. Both compounds were deprotected with HF·py complex to the corresponding diols **23** and **24**. Compound **23** (obtained from *minor* isomer **21**) was identical to the previously obtained diol **19**, proving the (6*R*,7*S*)-configuration at the newly created stereogenic centers in **21**. Periodic acid cleavage of the C(7)–C(8) bond in **23** (=**19**) followed by reduction of the resulting aldehyde afforded alcohol **25**. The same sequence of reactions performed on **24** led to stereoisomer **26**, thus proving the opposite configuration at C(6) in **22**. The (7*R*)-configuration in the diol **24** was assigned on the basis of the CD spectra its dimolybdenum complex (see Fig. 6).

The selectivity of the coupling of the allyltin **10** with achiral aldehyde **20** was not particularly high. Moreover, the opposite product (than that obtained in reaction of **10** with the chiral aldehyde **11**) predominated. This means, that the chirality of the aldehyde (α-***S*** in **11**) is much more important for the stereochemical outcome of the coupling than the chirality of the allyltin derivative. The explanation is shown in Fig. 7.



Scheme 3. (i) $BF_3{\cdot}OEt_2$, THF, −78°C; (ii) HF·py in MeOH; (iii) $NaIO_4$, then $NaBH_4$.

The attack of activated aldehyde is more favored from 'behind the ring' than from the 'front' of the sugar allyltin, since in the latter there is an unfavorable interaction between the complexed carbonyl and the ring oxygen atom (Fig. 7). The differentiation of both sides of the sugar ring is not, however, particularly high and hence the selectivity of the coupling process is relatively low.

2.2. Reaction of furanose allyltins with aldehyde

Reaction of the furanose-derived allyltins with aldehydes catalyzed with a Lewis acid proceeded via a completely different pathway. Treatment of 3-*O*-benzyl-1,2-*O*-isopropylidene-5,6,7-trideoxy-7-tributylstannyl-hept-5-ene-α-D-*ribo*-1,4-furanose[7] **27** and aldehyde **11** with boron trifluoride etherate did not afford the expected product **28**, but a mixture of two compounds[†] with the molecular formula $C_{25}H_{34}O_8$, strongly suggesting the loss of a molecule of acetone. In the ^{13}C NMR spectrum of the main isomer only two isopropylidene groups were seen (at δ 110.9 and 109.5 ppm). Other signals at δ 136.0, 128.4, 127.8, 118.8 (=CH_2), 83.8, 78.5, 70.5, 27.4, and 26.7 ppm strongly resembled those observed in the spectrum of compound **29**[20] obtained from allyltin **27** by treatment with a Lewis acid in the absence of aldehyde.

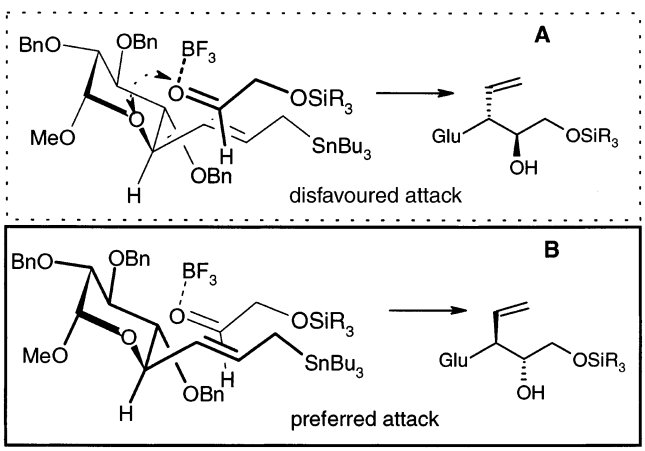


Figure 7. Preferred (**B**) and disfavoured (**A**) transition states in the reaction of **6** with aldehyde **20**.

These data suggested that the allyltin derivative decomposed prior to the reaction with aldehyde and the 'decomposed' species **30** reacted with the carbonyl group of **11** to give the disaccharide intermediate **31** (Scheme 4). Two possible pathways of stabilization of **31** (with the loss of the molecule of acetone) should be considered:

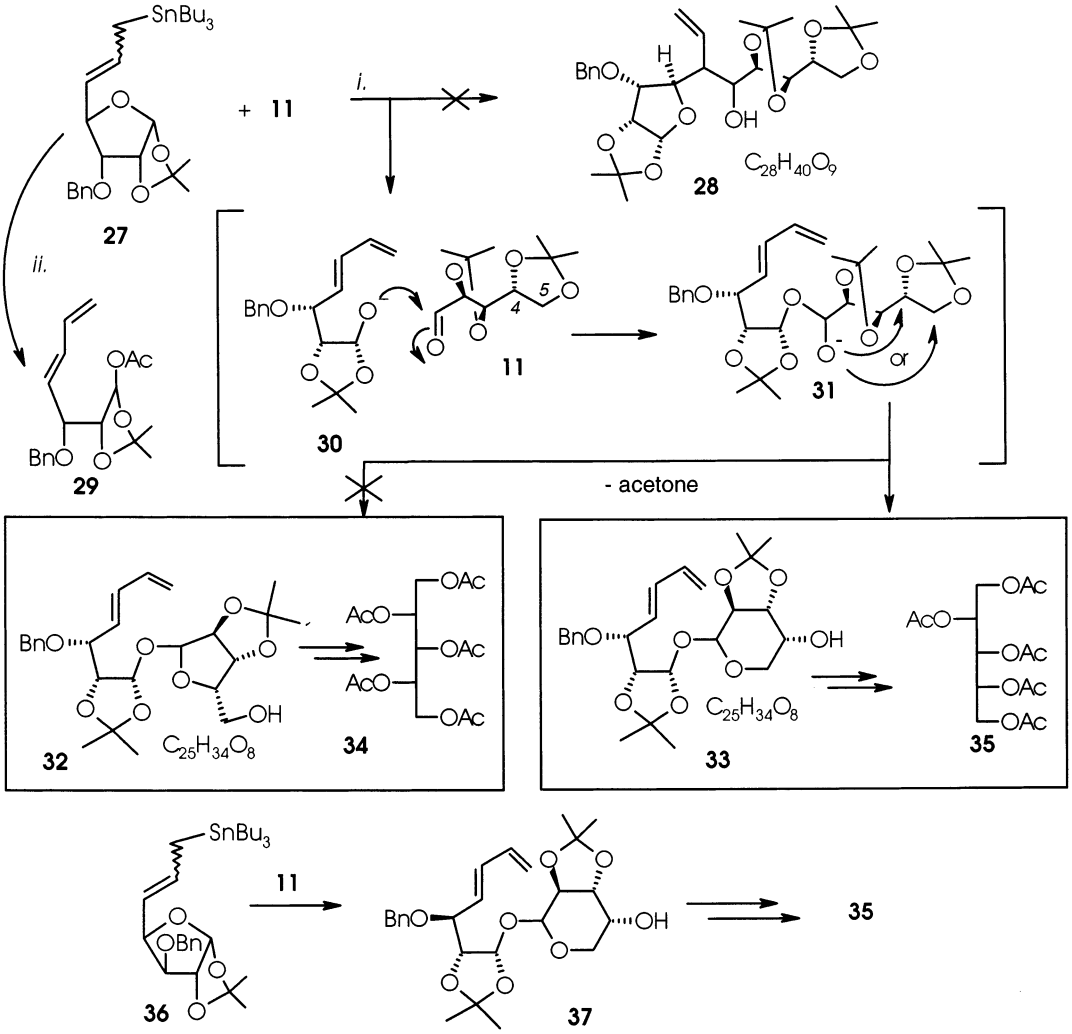
Attack of the oxygen anion on the C(4) position (what is connected with the inversion of the configuration at this tertiary center) leading to disaccharide **32** with a five-membered ring.

Attack of the oxygen anion on the C(5) position leading to disaccharide **33** containing a six-membered ring.

It is not easy to choose between those pathways analyzing only the NMR spectra of the products, however, the structures of the products (i.e. the size of the newly formed ring) can be unequivocally assigned by chemical correlations. Hydrolysis of the glycosydic linkage (with simultaneous removal of the isopropylidene groups) followed by reduction with $NaBH_4$ and acetylation should afford either penta-*O*-acetyl-xylitol[21] (**34**; from **32**) or penta-*O*-acetyl-D-arabinitol[21] (**35**; from **33**). Both model compounds are readily distinguishable by the ^{13}C NMR spectroscopy; only three signals of the pentitol chain were observed in the spectrum of xylitol **34** (at δ 61.8 (C-1,5), 69.04 (C-2,4), and 68.98 (C-3) ppm) and five signals for arabinitol **35** (at δ 61.6, 61.9 (C-1,5), 67.92, 67.97, and 68.23 (C-2,4,3) ppm).

In the spectrum of the product obtained by degradation of both isomers resulting from the coupling of **27** with **11** we were able to detect only the corresponding signals of the arabinitol **37**; no signals of xylitol **34** were seen. These results proved the structure **33** and

[†] Both compounds obtained in this reaction had similar NMR spectra suggesting that they were isomers.



Scheme 4. (i) $BF_3{\cdot}OEt_2$ −78°C; (ii) $ZnCl_2$, room temp. CH_2Cl_2, then Ac_2O.

excluded the alternative **32**. Reaction of the xylofuranose derivative **36**[20] with aldehyde **11** catalyzed with $BF_3{\cdot}OEt_2$ proceeded analogously and afforded the corresponding disaccharide **37** (as a mixture of isomers), the structure of which was also assigned by chemical degradation (Scheme 4).

3. Conclusion

The reaction of sugar allyltin derivatives of pyranoses with aldehydes catalyzed by $BF_3{\cdot}OEt_2$ is a convenient and highly stereoselective method for the synthesis of higher carbon sugars. The coupling process proceeds according to the open-chain model, widely accepted for such transformations.

The same reaction performed with the furanose-derived allyltins was unsuccessful as decomposition of the furanosyl ring by the Lewis acid catalyst was much faster than the desired coupling process.

4. Experimental

4.1. General

NMR spectra were recorded with a Bruker AM 500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si) unless otherwise stated. Most of the resonances were as signed by COSY (^1H–^1H) and/or HETCOR and DEPT correlations. The relative configurations of the protons were determined by NOE or NOESY experiments. Mass spectra were recorded with an AMD-604 (AMD Intectra GmbH, Germany); (LSIMS (*m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added)) mass spectrometer. Specific rotations were measured with a JASCO DIP digital polarimeter for chloroform solution ($c \sim 1.5$, unless otherwise stated) at room temperature. Column chromatography was performed on silica gel (Merck, 70–230 mesh). Organic solutions were dried over anhydrous magnesium or sodium sulfate.

Allyltin derivatives: methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-tributylstannyl-oct-6-eno-α-D-*gluco*-1,5-

pyranoside[7] **6**, methyl 2,3,4-tri-*O*-benzyl-6,7,8-trideoxy-8-tributylstannyl-6-eno-α-D-*manno*-1,5-pyranoside[7] **10**, 3-*O*-benzyl-1,2-*O*-isopropylidene-5,6,7-trideoxy-7-tributylstannyl-hept-5-ene-α-D-*ribo*-1,4-furanose[7] **27**, and 3-*O*-benzyl-1,2-*O*-iso-propylidene-5,6,7-trideoxy-7-tributylstannyl-hept-5-ene-α-D-*xylo*-1,4-furanose **36**,[20] were prepared according to literature methods. 2,3:4,5-Di-*O*-isopropylidene-D-arabinose[15] **11** was obtained by a periodate cleavage of 3,4:5,6-di-*O*-isopropylidene-D-glucitol readily available[22] from D-glucuronolactone.

4.2. Crystal data for compound 13

Crystal data for compound **13** are given in Table 1, together with refinement details. All measurements of crystal were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned at 65 mm from the KM4CCD camera. A total of 612 frames were measured at 0.75° intervals with a counting time of 30 s. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The structure was solved by direct methods (program SHELXS-97[23] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97[24] programs. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the $\Delta\rho$ maps and refined with isotropic thermal parameters.

Crystallographic data (excluding structure factors) for the structure of **13** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166869.

Table 1. Crystal data and structure refinement

Empirical formula	$C_{44}H_{56}O_{10}$
Formula weight	744.89
Temperature (K)	100(2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.773(2)
b (Å)	13.585(3)
c (Å)	13.888(3)
β (°)	111.90(3)
V (Å^{-3})	2060.9(7)
Z	2
D_{calcd} (Mg m^{-3})	1.200
μ (mm^{-1})	0.084
$F(000)$	800
Crystal size (mm)	$0.20\times0.20\times0.15$
Diffractometer	Kuma KM4CCD
θ Range for data collection (°)	3.47–28.75
Index ranges (°)	h: $-15\rightarrow15$
	k: $-13\rightarrow17$
	l: $-17\rightarrow18$
Reflections collected	14647
Independent reflections	7016 ($R_{int}=0.0150$)
Data/parameters	7016/711
Goodness-of-fit (F^2)	1.030
Final R_1/wR_2 indices ($I>2\sigma_I$)	0.0285/0.0702
Largest diff. peak/hole (e Å^{-3})	0.208/−0.196

4.3. Reaction of allyltin pyranosides with aldehydes

Sugar allyltin derivative **6** or **10** (3 mmol) and aldehyde **11** or **20** (3.5 mmol) was dissolved in methylene chloride (100 mL) under an argon atmosphere and cooled to −78°C. Boron trifluoride etherate (0.46 mL, 3.6 mmol) was added via syringe in one portion and the mixture was stirred for ca. 30 min (TLC monitoring in hexane:ethyl acetate, 4:1). Water (50 mL) was added, the organic layer was separated and the aqueous phase extracted with ethyl acetate (3×100 mL). The combined organic phase was washed with water (30 mL), brine (30 mL), dried, concentrated and the product(s) was isolated by column chromatography: hexane:ethyl acetate, 6:1.

- Reaction of **6** with **11** gave **12** (81%) as the only product.
- Reaction of **10** with **11** gave **18** (80%) and two side-products **18′** (2%) and **18″** (3%).
- Reaction of **10** with **20** gave **21** (26%) and **22** (49%).

4.3.1. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-8,9:10,11-di-*O*-isopropylidene-6-vinyl-α-D-*gluco*-D-*gulo*-D-*glycero*-undecoside 12. HRMS (LSIMS) m/z: 727.3453 [$C_{41}H_{52}NaO_{10}$ (M+Na$^+$) requires: 727.3458].

Acetate: $[\alpha]_D$ +1.7; ^{1}H NMR: δ 5.92 (ddd, $J_{1',6}$ 9.8, $J_{1',2'}$ 17.1, $J_{1',2'a}$ 9.9, H-1′), 5.32 (d, $J_{6,7}$ 9.0, H-7), 5.18 (dd, $J_{2',2'a}$ 1.0, H-2′), 5.12 (dd, H-2′a), 4.62 (d, $J_{1,2}$ 3.5, H-1), 4.28 (d, $J_{8,9}$ 6.6, H-8), 4.05 (m, H-10 and H-11), 3.90 (m, H-3 and H-11a), 3.73 (dd, $J_{4,5}$ 10.2, $J_{5,6}$ 2.1, H-5), 3.68 (dd, $J_{9,10}$ 6.8, H-9), 3.62 (dd, $J_{3,4}$ 8.7, H-4), 3.36 (H-2 and OCH_3), 3.21 (m, H-6), 2.06 (CH_3CO_2), 1.42, 1.36, 1.34 and 1.32 [2×C(CH_3)$_2$]; ^{13}C NMR: δ 169.7 (C=O), 136.6 (C-1′), 118.0 (C-2′), 109.7 and 109.5 [2×*C*(CH_3)$_2$], 97.5 (C-1), 82.3, 80.0, 79.8, 79.1, 77.2, 76.7, 72.5 and 71.2 (C-2,3,4,5,7,8,9,10), 75.6, 74.6 and 73.1 (3×*C*H$_2$Ph), 66.8 (C-11), 55.2 (OCH_3), 44.9 (C-6), 27.6, 26.8, 26.3 and 25.2 [2×C(*C*H$_3$)$_2$], 21.3 (*C*H$_3$CO$_2$).

This compound was allylated under standard conditions (AllBr, NaH in DMF) to afford methyl 7-*O*-allyl-2,3,4-tri-*O*-benzyl-6-deoxy-8,9:10,11-di-*O*-isopropylidene-6-vinyl-α-D-*gluco*-D-*gulo*-D-*glycero*-undecoside **15**; mp 104–105°C (heptane–ether). ^{13}C NMR: δ 137.4 and 134.6 (2×*C*H=CH$_2$), 117.7 and 115.8 (2×CH=*C*H$_2$), 109.5 and 108.6 [2×*C*(CH_3)$_2$], 97.9 (C-1), 82.6, 81.6, 80.0, 79.7, 77.2, 77.1, 77.6 and 72.7 (C-2,3,4,5,7,8,9,10), 75.4, 74.6, 73.2 and 72.7 (3×*C*H$_2$Ph+*C*H$_2$-CH=CH$_2$), 68.1 (C-11), 45.3 (C-6), 27.1, 26.7, 26.4 and 25.2 [2×C(*C*H$_3$)$_2$]

For the X-ray assignment, see Fig. 4.

4.3.2. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-8,9:10,11-di-*O*-isopropylidene-6-vinyl-α-D-*manno*-D-*gulo*-D-*glycero*-undecoside 18. HRMS (LSIMS) m/z: 727.3463 [$C_{41}H_{52}NaO_{10}$ (M+Na$^+$) requires: 727.3458].

Acetate: $[\alpha]_D$ −6.95 ($c=0.6$); ^{1}H NMR: δ 6.00 (ddd, $J_{1',6}$ 9.8, $J_{1',2'}$ 17.2, $J_{1',2'a}$ 10.2, H-1′), 5.37 (d, $J_{6,7}$ 9.6, H-7), 5.20 (dd, $J_{2',2'a}$ 1.2, H-2′), 5.13 (dd, H-2′a), 4.71 (d, $J_{1,2}$ 1.1, H-1), 4.34 (dd, $J_{7,8}$ 0.8, $J_{8,9}$ 5.2, H-8), 4.10 (dd, $J_{3,4}$ 9.0, $J_{4,5}$ 9.9, H-4), 4.02,(m, H-10 and H-11), 3.91 (m, H-11a), 3.73 (m, H-2, H-3 and H-9), 3.63 (dd, $J_{5,6}$ 1.6, H-5), 3.41 (m, H-6), 3.27 (OCH_3), 1.96 (CH_3CO_2), 1.41, 1.36, 1.36 and 1.32 [2×C(CH_3)$_2$]; ^{13}C NMR: δ 170.3 (C=O), 137.5 (C-1′), 118.0 (C-2′), 109.7 and 109.4 [2×*C*(CH_3)$_2$], 98.7 (C-1), 80.5, 78.9, 77.0, 76.9, 76.4, 75.8, 74.2 and 70.8 (C-2,3,4,5,7,8,9,10), 74.9, 73.0 and 72.1 (3×*C*H_2Ph), 66.4 (C-11), 54.7 (OCH_3), 43.6 (C-6), 27.6, 26.9, 26.4 and 25.3 [2×C(*C*H_3)$_2$], 21.3 (*C*H_3CO_2).

This compound was converted into its *p*-nitrobenzoate derivative by action of *p*-nitrobenzoyl chloride in pyridine; mp 84–85°C (heptane–ether). ^{13}C NMR: δ 163.4 (C=O), 137.0 (C-1′), 118.4 (C-2′), 109.7 and 109.2 [2×*C*(CH_3)$_2$], 98.8 (C-1), 80.4, 79.3, 77.0, 76.7, 76.5, 75.8, 73.7 and 72.0 (C-2,3,4,5,7,8,9,10), 74.7, 72.6 and 71.7 (3×*C*H_2Ph), 67.0 (C-11), 54.7 (OCH_3), 45.1 (C-6), 27.1 (double), 26.5 and 25.3 [2×C(*C*H_3)$_2$].

No crystal suitable for X-ray analysis could be obtained.

4.3.3. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-8,9:10,11-di-*O*-isopropylidene-6-vinyl-α-D-*manno*-D-*galacto*-D-*glycero*-undecoside 18′‡. HRMS (ESI) m/z: 727.3509 [$C_{41}H_{52}NaO_{10}$ (M+Na$^+$) requires: 727.3453].

Acetate: ^{1}H NMR: δ 6.01 (dt, $J_{1',6}$ 10.2, $J_{1',2'}$ 17.3, $J_{1',2'a}$ 10.2, H-1′), 5.37 (dd, $J_{6,7}$ 10.2, $J_{7,8}$ 1.6, H-7), 5.19 (dd, $J_{1',2'a}$ 2.2, H-2′), 5.06 (dd, H-2′a), 4.75 (d, $J_{1,2}$ 1.9, H-1), 4.40 (dd, $J_{8,9}$ 6.4, H-8), 4.11 (dd, $J_{10,11}$ 6.2, $J_{11,11a}$ 8.5, H-11), 3.98 (ddd, $J_{10,11a}$ 5.7, H-10), 3.90 (m, H-3, H-4, H-5, H-11a), 3.86 (dd, $J_{2,3}$ 2.0, H-2), 3.69 (dd, $J_{9,10}$ 8.5, H-9), 3.38 (OCH_3), 3.15 (t, H-6), 2.02 (CH_3CO_2), 1.46, 1.41, 1.36 and 1.24 [2×C(CH_3)$_2$]; ^{13}C NMR: δ 169.9 (C=O), 135.1 (C-1′), 119.8 (C-2′), 110.3 and 109.6 [2×*C*(CH_3)$_2$], 98.9 (C-1), 80.0, 78.8, 78.0, 77.5, 75.8, 74.4, 71.1 and 70.7 (C-2,3,4,5,7,8,9,10), 74.4, 72.2 and 71.9 (3×*C*H_2Ph), 67.8 (C-11), 55.3 (OCH_3), 46.9 (C-6), 28.0, 26.9, 26.5 and 25.3 [2×C(*C*H_3)$_2$], 21.2 (*C*H_3CO_2).

4.3.4. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-8,9:10,11-di-*O*-isopropylidene-6-vinyl-α-D-*manno*-D-talo-D-*glycero*-undecoside 18″. HRMS (LSIMS) m/z: 727.3443 [$C_{41}H_{52}NaO_{10}$ (M+Na$^+$) requires: 727.3458].

Acetate: ^{1}H NMR: δ 5.94 (dt, $J_{1',6}$ 10.2, $J_{1',2'}$ 17.4, $J_{1',2'a}$ 10.2, H-1′), 5.49 (dd, $J_{6,7}$ 9.3, $J_{7,8}$ 3.5, H-7), 5.31 (dd, $J_{2',2'a}$ 2.0, H-2′), 5.06 (dd, H-2′a), 4.64 (d, $J_{1,2}$ 2.0, H-1), 4.15 (dd, $J_{8,9}$ 6.3, H-8), 4.05 and 3.89 (2×m, H-3,4,5,9,10,11,11a), 3.73 (dd, $J_{2,3}$ 2.1, H-2), 3.30 (OCH_3), 3.10 (m, H-6), 2.10 (CH_3CO_2), 1.35, 1.33, 1.28 and 1.27 [2×C(CH_3)$_2$]; ^{13}C NMR: δ 134.2 (C-1′), 120.5 (C-2′), 109.6 and 109.0 [2×*C*(CH_3)$_2$], 99.1 (C-1), 80.7, 80.2, 77.5, 76.8, 75.0, 71.9 and 71.5 (C-2,3,4,5,7,8,9,10), 74.3, 72.2 and 71.9 (3×*C*H_2Ph), 66.9 (C-11), 55.5 (OCH_3), 44.7 (C-6), 27.2 (double), 26.4 and 25.6 [2×C(*C*H_3)$_2$], 21.3 (*C*H_3CO_2).

4.3.5. Methyl 2,3,4-tri-*O*-benzyl-8-*O*-*tert*-butyldiphenylsilyl-6-deoxy-6-vinyl-α-D-*manno*-D-*erythro*-octoside 21. This compound was characterized as diacetate **23-Ac**, after removal of the TBDPS block with a HF·py complex followed by reaction of resulting diol with Ac_2O/py. **23-Ac**: HRMS (LSIMS) m/z: 641.2727 [$C_{36}H_{42}NaO_9$ (M+Na$^+$) requires: 641.2727]. $[\alpha]_D$ +5.5; ^{1}H NMR: δ 5.87 (dt, $J_{1',6}$ 9.9 $J_{1',2'}$ 17.1, $J_{1'.2'a}$ 9.9, H-1′), 5.45 (ddd, $J_{6,7}$ 8.5, $J_{7,8}$ 2.3, $J_{7,8'}$ 6.5, H-7), 5.14 (m, H-2′), 4.69 (d, $J_{1,2}$ 1.54, H-1), 4.44 (dd, $J_{8,8a}$ 12.2, H-8), 4.09 (t, $J_{3,4}$ 9.5, $J_{4,5}$ 9.5, H-4), 4.02 (dd, H-8a), 3.79 (dd, $J_{2,3}$ 3.0, H-3), 3.73 (dd, H-2), 3.61 (dd, $J_{5,6}$ 1.6, H-5), 3.26 (OCH_3), 3.02 (m, H-6), 1.97 and 1.90 (2×CH_3CO_2); ^{13}C NMR: δ 170.7 and 170.0 (2×C=O), 135.9 (C-1′), 118.2 (C-2′), 98.6 (C-1), 80.4, 76.5, 75.1, 73.5 and 70.4 (C-2,3,4,5,7), 74.7, 72.7 and 71.9 (3×*C*H_2Ph), 64.6 (C-8), 54.8 (OCH_3), 43.8 (C-6), 21.1 and 20.7 (2×*C*H_3CO_2).

4.3.6. Methyl 2,3,4-tri-*O*-benzyl-8-*O*-*tert*-butyldiphenylsilyl-6-deoxy-6-vinyl-α-D-*manno*-L-*erythro*-octoside 22. Likewise this compound was characterized as diacetate **24-Ac**. HRMS (ESI) m/z: 641.2733 [$C_{36}H_{42}NaO_9$ (M+Na$^+$) requires: 641.2721]. $[\alpha]_D$ −10.7; ^{1}H NMR: δ 5.91 (dt, $J_{1',6}$ 10.2, $J_{1',2'}$ 10.2, $J_{1'.2'a}$ 17.3, H-1′), 5.31 (dd, $J_{2',2'a}$ 1.9, H-2′), 5.25 (ddd, $J_{6,7}$ 10.3, $J_{7,8}$ 2.4, $J_{7,8a}$ 5.2, H-7), 5.13 (dd, H-2′a), 4.66 (d, $J_{1,2}$ 2.3, H-1), 4.50 (dd, $J_{8,8a}$ 12.3, H-8), 3.96 (dd, H-8a), 3.88 (m, H-3 and H-4), 3.79 (dd, $J_{5,6}$ 1.4, H-5), 3.74 (t, $J_{2,3}$ 2.2, H-2), 3.22 (OCH_3), 3.02 (H-6), 2.06 and 2.03 (2×CH_3CO_2); ^{13}C NMR: δ 170.6 and 170.5 (2×C=O), 133.0 (C-1′), 121.3 (C-2′), 98.9 (C-1), 80.3, 75.4, 74.5, 70.1 and 69.5 (C-2,3,4,5,7), 74.8, 72.3 and 71.8 (3×*C*H_2Ph), 64.0 (C-8), 54.9 (OCH_3), 45.1 (C-6), 21.1 and 20.7 (2×*C*H_3CO_2).

For the CD assignment of the configuration at the C(7) center of the diol **24**, see Fig. 6.

4.4. Assignment of the configurations of 18, 21 and 22

4.4.1. Degradation of 18: methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-vinyl-α-D-*manno*-D-*erythro*-octoside 19. To a solution alcohol **18** (520 mg, 0.8 mmol) in DMF (25 mL) sodium hydride (60% dispersion in mineral oil, 100 mg) was added and the mixture was stirred for 30 min at rt under an argon atmosphere. Allyl bromide (0.15 mL, 1.7 mmol) was added, the mixture was stirred for another 2 h at rt, excess of hydride was decomposed by careful addition of water (2 mL) and the mixture was partitioned between water:ether. The organic phase was separated, dried, concentrated and the product was purified by column chromatography (hexane:ethyl acetate, 6:1).

The product was dissolved in THF/water (2:1, v/v, 25 mL) to which conc. H_2SO_4 (0.5 mL) was added, the mixture was heated under reflux for 16 h, cooled to rt and neutralized by addition of solid sodium bicarbonate. Sodium periodate (0.8 g) was added, the mixture

‡ The assignment of the configuration in **18′** and **18″** is tentative; for the more abundant isomer **18″** we proposed the alternative (to **18**) *erythro* structure, while for **18′** the *threo* one with the same configuration at the C(6) as in major isomer **18**.

was stirred for 1 h at room temperature and partitioned between brine (20 mL) and ethyl acetate (50 mL). The organic layer was separated, washed with water, and concentrated. The residue was dissolved in THF/methanol (1:1, v/v, 20 mL), the crude aldehyde was reduced with sodium borohydride (400 mg) for 3 h, and the product **19** was isolated by column chromatography (hexane:ethyl acetate, 2:1→1:1). The CD spectrum of the diol **19** is shown in Fig. 6. Acetylation of **19** afforded diacetate, the NMR spectrum of which was identical with **23-Ac**.

4.4.2. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-vinyl-α-D-*manno*-D-*glycero*-heptoside 25. Diol **23** (obtained from **21**, 200 mg, 0.37 mmol) was dissolved in ether (25 mL) to which sodium periodate (0.5 g) in water (10 mL) was added and the heterogeneous mixture was stirred for 30 min at room temperature. The organic layer was separated, washed with water, concentrated and the crude aldehyde was reduced with $NaBH_4$ (250 mg) under standard conditions to afford the title compound **25** which was characterized as acetate **25-Ac**: HRMS (ESI) m/z: 569.2552 [$C_{33}H_{38}NaO_7$ ($M+Na^+$) requires: 569.2510]. $[\alpha]_D$ 13.0; ^1H NMR (200 MHz): δ 5.91 (ddd, $J_{1',6}$ 8.5, $J_{1',2'}$ 10.2, $J_{1',2'a}$ 17.3, H-1′), 5.16 and 5.09 (2×m, both H-2′), 4.69 (d, $J_{1,2}$ 2.4, H-1), 4.34 (dd, $J_{6,7}$ 5.5, $J_{7,7a}$ 11.1, H-7), 4.24 (dd, $J_{6,7a}$ 7.7, H-7a), 3.92 (t, $J_{3,4}=J_{4,5}$ 9.0, H-4), 3.85 (m, H-5), 3.75 (dd, H-2), 3.65 (dd, $J_{2,3}$ 3.3, H-3), 3.26 (OCH_3), 2.87 (m, H-6), 2.00 (CH_3CO_2); ^{13}C NMR: δ 170.9 (C=O), 137.3 (C-1′), 116.5 (C-2′), 98.8 (C-1), 80.5, 76.0, 74.8 and 72.7 (C-2,3,4,5), 74.4, 72.5 and 72.1 (3×CH_2Ph), 63.8 (C-7), 54.7 (OCH_3), 43.7 (C-6), 21.1 (CH_3CO_2).

4.4.3. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-vinyl-α-D-*manno*-L-*glycero*-heptoside 26. Diol **24** (obtained from **22**, 200 mg) was converted in the same manner into **26** (170 mg), which was characterized as acetate **26-Ac**: HRMS (ESI) m/z: 569.2546 [$C_{33}H_{38}NaO_7$ ($M+Na^+$) requires: 569.2510]. ^1H NMR (200 MHz): δ 5.94 (ddd, $J_{1',6}$ 9.3, $J_{1',2'}$ 10.4, $J_{1',2'a}$ 17.2, H-1′), 5.27 and 5.19 (2×m, both H-2′), 4.20 (dd, $J_{6,7}$ 7.33, $J_{7,7a}$ 10.7, H-7), 4.13 (dd, $J_{6,7a}$ 8.4, H-7a), 3.92–3.74 (m, H-2,3,4,5), 3.27 (OCH_3), 3.00 (m, H-6), 2.03 (CH_3CO_2); ^{13}C NMR: δ 170.8 (C=O), 134.0 (C-1′), 119.9 (C-2′), 98.7 (C-1), 80.5, 75.5, 74.5 and 69.8 (C-2,3,4,5), 74.9, 72.4 and 71.9 (3×CH_2Ph), 64.5 (C-7), 54.5 (OCH_3), 43.3 (C-6), 20.0 (CH_3CO_2).

4.5. Reaction of allyltin furanosides with aldehyde 11

This reaction was performed in the same manner as for **6** and **10**, except that the products were purified using hexane:ethyl acetate, 4:1.

- Reaction of **27** with **11** gave **33** (72%; two pairs of isomers in the ratio 1:4)
  - Mixture of **33-I** and **33-II** in a 7:1 ratio
    HRMS (LSIMS) m/z: 485.2135 [$C_{25}H_{34}O_8Na$ ($M+Na^+$) requires: 485.2151].
    Main isomer: ^1H NMR: δ 6.48–6.17 (m, $J_{9,10}$ 14.4, $J_{11,12}$ 10.6, $J_{11,12a}$ 16.8, H-10 and H-11), 5.68–5.50 (dd, $J_{9,10}$ 14.4, $J_{8,9}$ 7.7, H-9), 1.44, 1.41, 1.39, 1.32 [2×$C(CH_3)_2$]; ^{13}C NMR: δ 135.9 135.5, 129.5 (C-9, C-10 and C-11), 118.5 (C-12), 110.5, 109.8 [2×$C(CH_3)_2$], 104.5 (C-6), 97.1 (C-5), 86.8, 80.9, 78.6, 77.2, 77.0 (C-8, C-7, C-4, C-3, C-2), 70.5 (C-1), 67.6 (CH_2Ph), 27.3, 26.7, 26.2, 25.2 [2×$C(CH_3)_2$].
  - Mixture of **33-III** and **33-IV** in a 4:1 ratio
    HRMS (LSIMS) m/z: 485.2145 [$C_{25}H_{34}O_8Na$ ($M+Na^+$) requires: 485.2151].
    Main isomer: ^1H NMR: δ 6.48–6.2 (m, $J_{9,10}$ 14.5, $J_{11,12}$ 10.5, H-10 and H-11), 5.7–5.55 (dd, $J_{9,10}$ 14.5, $J_{8,9}$ 7.3, H-9), 2×1.39, 1.36, 1.32 [2×$C(CH_3)_2$]; ^{13}C NMR: δ 135.8 135.4, 129.6 (C-9, C-10 and C-11), 118.5 (C-12), 110.8, 109.5 [2×$C(CH_3)_2$], 102.6 (C-6), 97.2 (C-5), 85.1, 78.6, 78.3, 77.2, 76.1 (C-8, C-7, C-4, C-3, C-2), 70.4 (C-1), 65.6 (CH_2Ph), 27.4, 26.9, 26.4, 25.2 [2×$C(CH_3)_2$].
    Minor isomer: ^{13}C NMR: δ 136.0 134.7, 130.6 (C-9, C-10 and C-11), 118.3 (C-12), 110.7, 109.6 [2×$C(CH_3)_2$], 102.8 (C-6), 94.5 (C-5), 82.5, 79.4, 77.3, 77.2, 76.8 (C-8, C-7, C-4, C-3, C-2), 71.0 (C-1), 67.5 (CH_2Ph), 2×27.2, 2×26.6 [2×$C(CH_3)_2$].
- Reaction of **36** with **11** gave **37** [92%; four isomers in the ratio 1 (single isomer):5 (three other compounds)]
  - Compound **37-I**
    HRMS (ESI) m/z: 485.2134 [$C_{25}H_{34}O_8Na$ ($M+Na^+$) requires: 485.2151]
    $[\alpha]_D$ +36.9; ^1H NMR: δ 6.48–6.17 (m, $J_{9,10}$ 14.5, $J_{11,12}$ 10.6, H-10 and H-11), 5.70–5.56 (dd, $J_{9,10}$ 14.5, $J_{8,9}$ 8.5, H-9), 1.43, 2×1.40, 1.32 [2×$C(CH_3)_2$]; ^{13}C NMR: δ 135.9 135.8, 128.9 (C-9, C-10 and C-11), 118.5 (C-12), 110.5, 109.7 [2×$C(CH_3)_2$], 104.7 (C-6), 96.6 (C-5), 86.7, 80.7, 78.2, 77.1, 76.8 (C-8, C-7, C-4, C-3, C-2), 70.1 (C-1), 67.4 (CH_2Ph), 27.1, 26.6, 26.1, 25.1 [2×$C(CH_3)_2$].
  - Mixture **37-II**, **37-III**, and **37-IV** in a 8:2:1 ratio
    HRMS (ESI) m/z: 485.2140 [$C_{25}H_{34}O_8Na$ ($M+Na^+$) requires: 485.2151].
    Main isomer: ^1H NMR: δ 6.48–6.18 (m, $J_{9,10}$ 14.6, $J_{11,12}$ 10.5, H-10 and H-11), 5.75–5.57 (m, $J_{9,10}$ 14.5, $J_{8,9}$ 7.5, H-9), 2×1.41, 2×1.40 [2×$C(CH_3)_2$]; ^{13}C NMR: δ 135.8, 135.5, 129.0 (C-9, C-10 and C-11), 118.6 (C-12), 110.7, 109.4 [2×$C(CH_3)_2$], 102.8 (C-6), 96.6 (C-5), 85.0, 78.4, 78.1, 77.1, 76.0 (C-8, C-7, C-4, C-3, C-2), 70.4 (C-1), 65.5 (CH_2Ph), 27.4, 27.0, 26.4, 25.3 [2×$C(CH_3)_2$].

4.6. Degradation of the products from reactions of furanose-allyltins with aldehyde 11

The appropriate disaccharide (ca. 1.5 mmol; from condensation of either **27** or **36** with **11**) was dissolved in THF (10 mL) and water (4 mL) to which conc. sulfuric acid (25 drops) was added. The mixture was stirred for 12 h at room temperature and neutralized by addition of triethylamine (0.8 mL). More water (2 mL) was added followed by $NaBH_4$ (ca. 50 mg), the mixture was stirred at room temperature for a further 3 h, and concentrated. The residue was dried by co-evaporation

with toluene (3×15 mL). The boronic species were removed by co-evaporation with methanol (3×15 mL) and the residue was finally dried by co-evaporation with toluene (10 mL). Pyridine (10 mL) was added followed by Ac_2O (5 mL) and DMAP (~50 mg). The mixture was stirred at room temperature for 2 h and concentrated. Ether (100 mL) was added to the residue, the organic layer was washed with water, brine, dried and concentrated and the pentitol derivative (identified with the standard prepared independently see Section 4.6) was isolated by column chromatography (hexane:ethyl acetate, 4:1→2:1)

In the ^{13}C NMR spectra of the products obtained from degradation of all stereoisomers derived from condensation of furanosidic allyltins with aldehyde **11** only signals characteristic for penta-*O*-acetyl-D-arabinitol were seen while no signals of the penta-*O*-acetyl-xylitol were visible.

4.7. Synthesis of models

4.7.1. Penta-*O*-acetyl-xylitol[21] 34. D-Xylose (0.5 g, 3.3 mmol) was dissolved in water (5 mL), reduced with $NaBH_4$ (60 mg) at rt for 1 h, concentrated and the residue was dried by co-evaporation with toluene (3×10 mL). Boron species were removed by co-evaporation with methanol (3×10 mL) and the residue was finally dried by co-evaporation with toluene (2×10 mL). Pyridine (10 mL) was added followed by Ac_2O (5 mL) and DMAP (~20 mg). The mixture was stirred at room temperature for 2 h and concentrated. Ether (50 mL) was added to the residue, the organic layer was washed with water, brine, dried and concentrated and the desired penta-*O*-acetyl xylitol was isolated by column chromatography (hexane:ethyl acetate, 4:1→2:1); yield 470 mg. ^1H NMR: δ 5.39 (d, *J* 5.3, H-3), 5.29 (ddd, *J* 4.3, 5.3 and 6.0, H-2 and H-4), 4.35 (dd, *J* 4.3 and 12.05, H-1 and H-5), 3.99 (dd, *J* 6.0 and 12.05, H-1a and H-5a), 2.11 (CH_3CO_2), 2.10 (2×CH_3CO_2), 2.06 (2×CH_3CO_2); ^{13}C NMR: δ 170.2 (2×C=O), 169.8 (2×C=O), 169.5 (C=O), 2×69.0 (C-2, C-4), 68.9 (C-3), 62.4 (C-1, C-5), 20.7 (double), 20.6 (double) and 20.5 (5×CH_3CO_2).

4.7.2. Penta-*O*-acetyl-D-arabinitol[21] 35. 2,3:4,5-Di-*O*-isopropylidene-D-arabinose[15] (**11**; 0.55 g, 2.4 mmol) was dissolved in methanol (5 mL) and reduced with $NaBH_4$ (150 mg) for 2 h. The product—isolated in usual way—was dissolved in methanol (10 mL) to which conc. H_2SO_4 (0.5 mL) was added and the mixture was stirred at rt for 48 h. The mixture was neutralized with Et_3N, concentrated, the residue was dried and acetylated (as for **34**) to give penta-*O*-acetyl-D-arabinitol (408 mg): ^1H NMR: δ 5.45–5.10 (m, H-2, H-3 and H-4), 4.34–3.86 (m, both H-1 and both H-5), 2.13, 2.08, 2.062, 2.06, 2.04 (5×CH_3CO_2); ^{13}C NMR: δ 170.1, 170.0, 169.7, 169.3, 169.2 (5×C=O), 68.0, 67.8 (double) (C-2, C-3 and C-4), 61.7, 61.4 (C-1 and C-5), 20.5, 3×20.4, 20.3 (5×CH_3CO_2).

References

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