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Reaction of sugar allyltins with aldehydes under high pressure

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Abstract—High-pressure reactions of allyltin derivatives of furanoses with sugar aldehydes affords *threo*-homoallylic alcohols regardless of the configuration (*Z* or *E*) across the double bond of the starting allyltin. Reaction of methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-hept-5-(*Z*)-eno-β-D-ribofuranoside **13*Z*** with 2,3:4,5-di-*O*-isopropylidene-D-arabinose **6** was highly stereoselective and afforded only one *threo*-homoallylic alcohol **14**, while the same process with *E*-organometallic **13*E*** furnished both *threo*-alcohols: **14** and **15** in the ratio 36:64. This result does not agree with the widely accepted six-membered (chair) transition state, which predicts the *threo*-isomers for the reaction of the *E*-allyltin and *erythro* for the *Z*-isomers; however, this result may be explained by a twisted six-membered transition state.

1. Introduction

Higher carbon sugars are attractive targets with their synthesis gaining considerable interest over the last decade. A number of methods leading to such complicated molecules have been developed.[1] Over the past several years, we have proposed a general methodology for the preparation of higher carbon sugars by coupling of two sugar sub-units.[2] Precursor **3** can be readily obtained from sugar phosphoranes[3] **1**, phosphonates [4] **2**, or vinyltin derivatives of monosaccharides[5] **4** (Fig. 1).

Other types of higher sugar precursors, homoallylic alcohols flanked at both ends with sugar moieties (e.g., **8** in Fig. 2), have recently been prepared by us via a boron trifluoride catalyzed addition of sugar allyltins to sugar aldehydes (Fig. 2).[6] Only the catalyst $BF_3{\cdot}OEt_2$ was suitable for such transformation; the pyranose derivatives (e.g., **5**) reacted readily with aldehydes providing the products (e.g., **8**) in high yields and with very high diastereoselectivities.[6] The use of other Lewis acids was connected with the decomposition of sugar allyltins; this process can be controlled thus providing useful chiral synthons, *E*-dienoaldehydes (e.g., **7**),[7] as starting materials in stereocontrolled syntheses of carbobicyclic derivatives such as **9**[8] or **10**.[9]

However, the furanose allyltin derivatives did not react with the aldehydes in the same way as the pyranoses; in the presence of $BF_3{\cdot}OEt_2$ they underwent decomposition prior to the reaction with the aldehyde.[6] Acid catalysis for the formation of compounds of type **12** should, therefore, be avoided and other conditions have to be evaluated to achieve this transformation (Fig. 3).

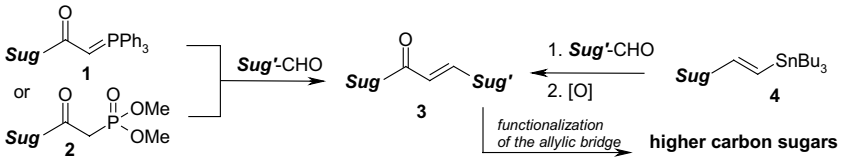

Figure 1. Methods for the preparation of higher carbon sugars using Wittig-type and stannyl methodology.

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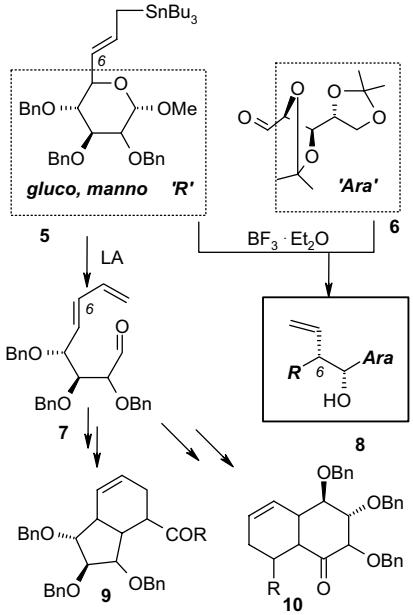


Figure 2. Behavior of sugar allytins toward Lewis acids in (a) the absence and (b) the presence of aldehydes.

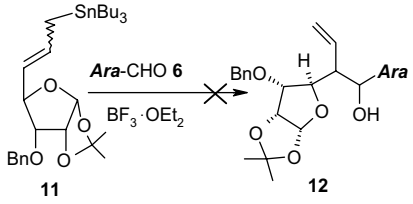


Figure 3.

2. Results and discussion

2.1. Reaction of geometrical isomers (*E* and *Z*) of sugar allyltins with aldehydes under high pressure

The reaction of allylstannanes with aldehydes is usually catalyzed by Lewis acids.[10] It can be performed successfully at high temperature,[11] high pressure,[12] or under radical conditions.[13] The relative configurations of the products (homoallylic alcohols) in the former two processes (Δt, Δp) depend on the geometry of the double bond of the starting allyltin. It is, however, independent of the 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. 4-**I**). Reaction of organostannanes with aldehydes catalyzed by a Lewis acid proceeds through a different mechanism. The acidity of the tin atom on the organostannanes is much lower than that of any Lewis acid used, hence the carbonyl group is complexed by a Lewis acid and not tin. The open-chain model leading to the same *erythro*-isomer, regardless of the configuration of starting allyltin, is, therefore, preferred[10] (Fig. 4-**II**).

We decided to study this process using furanose-derived allyltins: Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butyl)stannyl-hept-5-(*E*)- and 5-(*Z*)-eno-β-D-ribofuranosides, **13*E***, and **13*Z***, respectively.[14] According to the models presented in Figure 4, the *Z*-organometallic **13*Z*** should afford the *erythro*- and the **13*E*** derivative furnish the *threo*-isomers.

The reaction of a readily available mixture of both olefins, **13*E*/13*Z*** (2:1), with 2,3:4,5-di-*O*-isopropylidene-

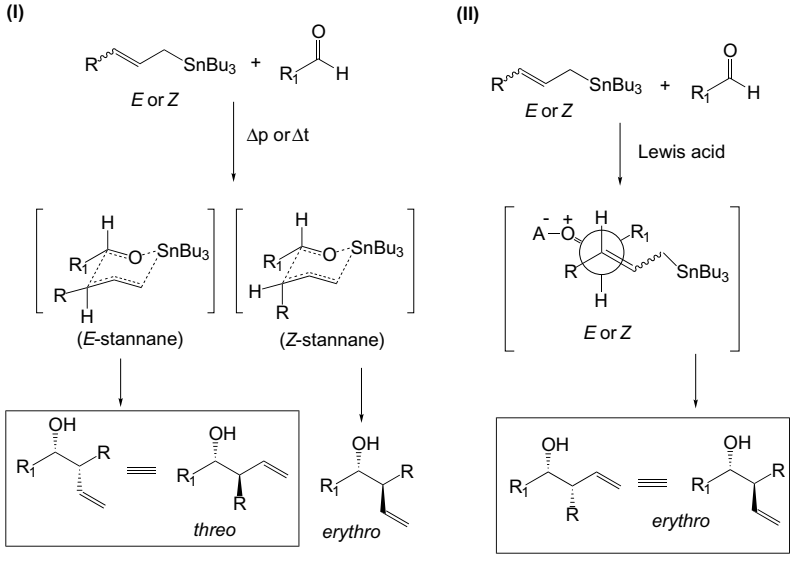
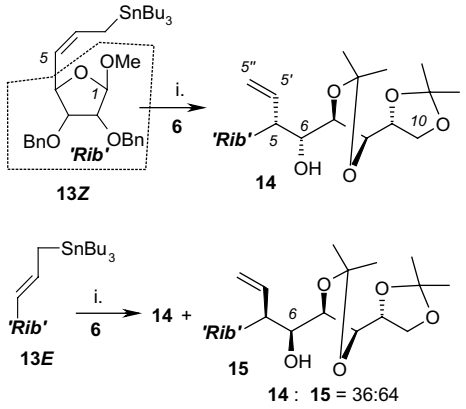


Figure 4. Stereochemical models for the reaction of allyltins with aldehydes under high-pressure **I** and catalyzed by Lewis acids **II**.

D-arabinose **6** was conducted under high pressure and elevated temperature for 7 days affording a mixture of two homoallylic alcohols **14** and **15** (ratio: 58:42, overall yield 93%), to which unexpectedly the *threo*-configurations were assigned.[†] This observation raised a question about the mechanism of this process, which according to a widely accepted model (Fig. 4), should lead to stereoisomers with different relative configurations. We performed, therefore a high-pressure reaction of aldehyde **6** with pure geometrical isomers **13*Z*** and **13*E*** with the results shown in Scheme 1.



Scheme 1. Reagents and conditions: (i) 13 kbar, 57 °C, CH_2Cl_2, 7 days.

The **13*Z***-isomer upon reaction with aldehyde **6** afforded only one stereoisomeric *threo*-homoallylic alcohol **14** in 97% yield. In the reaction of the **13*E***-isomer with **6**, the stereoselectivity was much lower with both *threo*-adducts **14** and **15** being formed in a 36:64 ratio (overall yield 91%). Although the *threo*-product(s) was to be expected from high pressure reactions of the *E*-isomers according to mechanism of this process (Fig. 4-**I**), it is hard to explain the formation of such a product with the same relative stereochemistry from the *Z*-isomer under these conditions, unless another mechanism is considered.

2.2. Determination of the configurations of adducts 14 and 15

The configuration of both isomers **14** and **15** was established by X-ray crystallography and chemical correlations. Fortunately, isomer **15** (obtained in the reaction of **13*E*** with aldehyde **6**) was crystalline; its structure was determined by the X-ray method as shown in Figure 5.

Having proven the configuration of isomer **15**, it was relatively easy to assign the structure of the product **14**. The geometry at the C5 center in **14** was easily determined when the stereogenic center at C6 was destroyed. Oxidation of **14** with PCC gave ketone **16**, while oxidation of **15** gave the stereoisomer **17**, thus proving opposite configurations for both homoallylic alcohols at the C5 atom (Scheme 2).

[†] For determination of the configuration of **14** and **15** see Section 2.2.

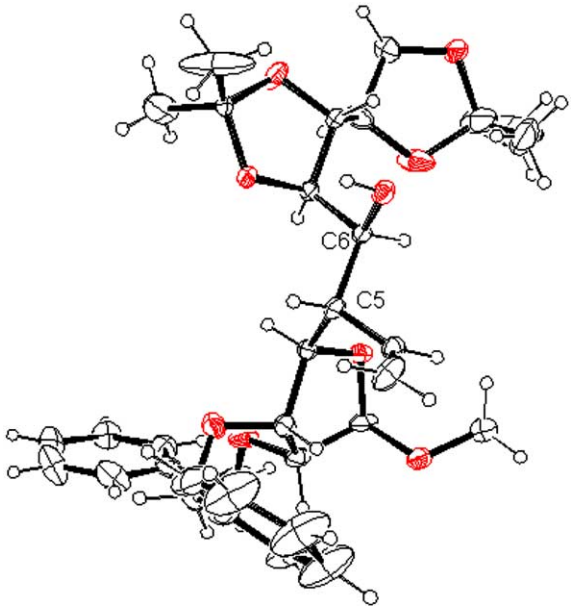


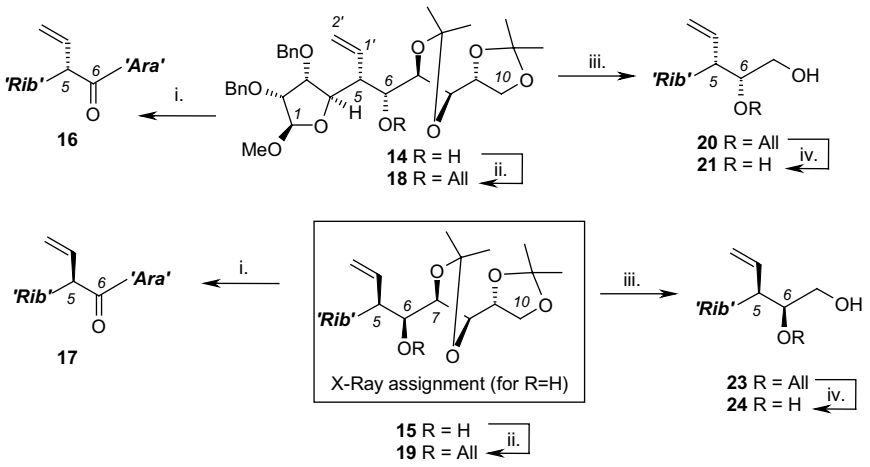
Figure 5. ORTEP drawing of **15**.

On the other hand, the absolute configuration of the diols can be conveniently established by CD spectroscopy; the sign of the Cotton effect of the complexes of the diols with molybdenum tetraacetate allows precise determination of the geometry of the stereogenic centers;[15,16] both adducts **14** and **15** were, therefore, converted into the diols **21** and **24** (Scheme 2).

First the free hydroxyl group was blocked as an allyl ether, because of its stability under a wide variety of reaction conditions and the possibility of its selective removal.[17] Next both isopropylidene protecting functions were removed by hydrolysis and the resulting tetraol subjected to periodate cleavage. Reduction of the resulting aldehydes with sodium borohydride afforded alcohols **20** and **23**, respectively. The allyl block was then removed under standard conditions providing diols **21** and **24**. The CD spectra of the complexes of these diols with dimolybdenum tetraacetate shown in Figure 6 clearly indicated at the C6 center an (*S*)-configuration for **24** and an (*R*)-configuration for **21**.[16]

3. Stereochemical models for the reaction of sugar allyltins with aldehydes under high pressure

The formation of *threo*-adducts **14** and **15** from *E*-organometallic **13*E*** can be explained using the cyclic model for such a reaction as shown in Figure 4. The formation of *threo*-adduct **14** from the *Z*-isomer is more difficult to explain, since according to this cyclic model, the *Z*-organometallics should provide the *erythro*-adducts. The possibility that the *Z*-isomer undergoes isomerization to ***13E*** prior to reaction with the aldehyde should be also excluded, since **13*E*** upon reaction with **6** gives *threo*-adducts with low stereoselectivity (**14**/**15** = 36:64), while selectivity in reaction of **13*Z*** is very high (97% of only one stereoisomer **14**). The cyclic



Scheme 2. Reagents and conditions: (i) PCC, $(CH_2Cl)_2$, 80 °C (58% for **14** and 60% for **15**); (ii) AllBr, NaH, DMF; (iii) (1) H^+, THF/H_2O; (2) $NaIO_4$, Et_2O; (3) $NaBH_4$, MeOH; (iv) Pd/C, *p*-TsOH, MeOH; (iv) Pd/C, *p*-TsOH, MeOH, 50 °C.

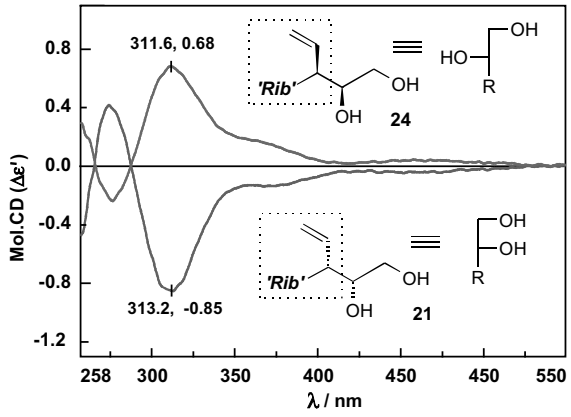


Figure 6. The CD spectra of the complexes of **21** and **24** with $Mo_2(OAc)_4$.

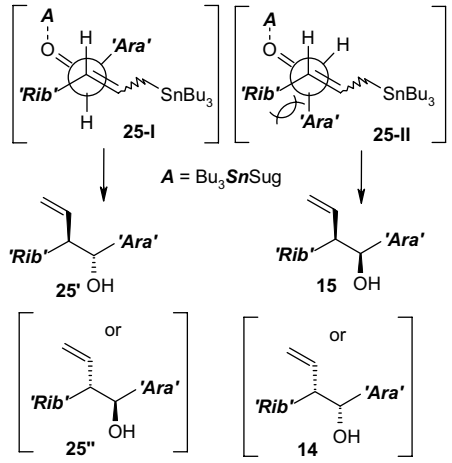


Figure 7. Stereochemical open-chain models in the Yamamoto reaction.

model, widely accepted for such processes does not explain the results obtained in the reaction of **13** with **6** and has to be excluded.

Tetraorganostannanes are very weak Lewis acids, but their acidity can be increased under high pressure. The process studied by us could therefore be regarded as acid catalyzed with the Lewis acid being a part of the reacting molecules (Sug-*Sn*Bu_3). In the open-chain, an antiperiplanar model of the acid-catalyzed Yamamoto reaction (**25-I**; Lewis acid = second molecule of organostannane **13**) adducts with the relative *erythro*-configuration is expected.[10] The high-pressure reaction of **13*Z*** with **6**, however, afforded the *threo*-product **14** exclusively.

This could result from another open-chain transition state having an antiperiplanar arrangement of the carbonyl and allylstannane groups: **25-II**; this is, however, very unlikely due to severe steric repulsions between the arabinose and ribose units (Fig. 7).

Recently, Nishigaichi and Takuwa demonstrated that the stereochemistry of an acid-catalyzed reaction of alkoxy-aldehydes with allyltin derivatives is dependent on the nature of the acid. The nonchelating $BF_3{\cdot}OEt_2$ predominantly provided the *syn* (or *erythro*) adducts, while $TiCl_4$ afforded the *anti* (*threo*) homoallylic alcohols as the major products. To explain these results they proposed an alternative open-chain model, in which the carbonyl group and the allylstannane moiety are in synclinal relation.[18]

The exclusive formation of the *threo*-homoallylic alcohols in a high-pressure reaction of isomeric sugar allyltins **13*Z*** and **13*E*** with aldehyde **6** may be explained by a slightly modified model of Nishigaichi and Takuwa. In this model one can postulate, that olefinic (allyltin) and carbonyl fragments of both reacting molecules are synclinal to each other, and this arrangement is stabilized by complexation of the tin atom (present in the molecule of **13**) to the carbonyl oxygen atom.[‡] The transition

[‡] Although tetraorganostannanes are very weak Lewis acids (they do not react with aldehydes without activation), their acidity increases under high pressure.

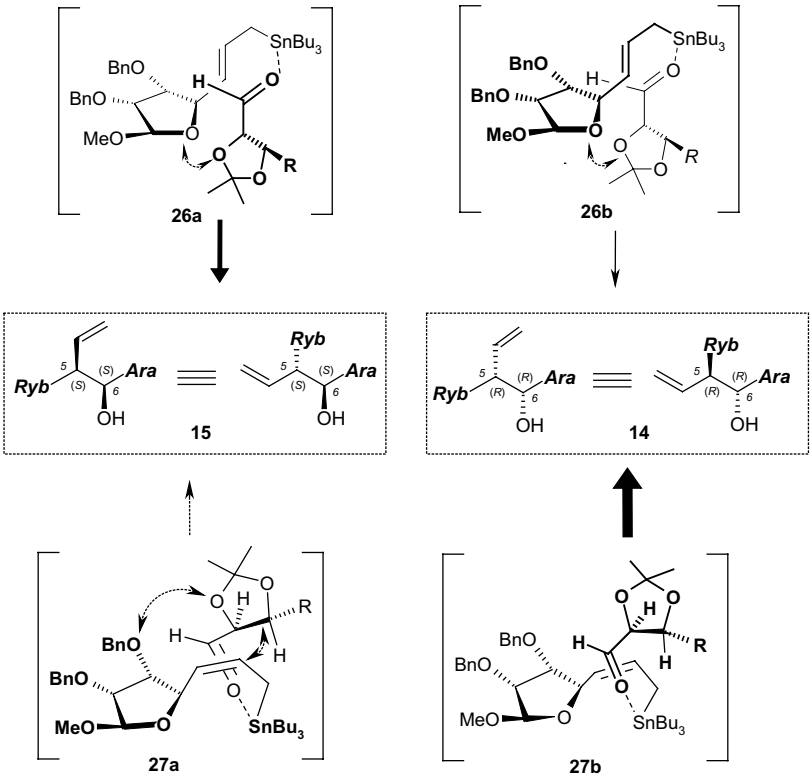


Figure 8. Stereochemical models for the high-pressure reaction of isomeric allylstannanes **13*Z*** and **13*E*** with aldehyde **6**.

states for the reaction of the *E*-oraganostannane **13*E*** with the aldehyde are represented by the drawings **26a** and **26b** in Figure 8. Both of them should provide the *threo*-adducts **14** and **15**. Analysis of the models indicates, that the steric interaction in these transition states are comparable, and no significant differentiation between them should be expected. In fact, reaction of **13*E*** with **6** afforded **14** and **15** in the ratio 36:64.

For the reaction of the **13*Z***-isomer, another two transition states can be drawn: **27a** and **27b**, both leading either to **14** or **15**. The unfavorable steric and Coulombic repulsions are much lower in **27b** than in **27a** meaning the former (leading to **14**) should be highly favored. This assumption is in full agreement with the experimental observations; only one *threo*-stereoisomeric homoallylic alcohol **14** was formed in a high-pressure reaction of **13*Z*** with **6**.

4. Conclusion

The reaction of sugar allyltin derivatives of furanoses can only be successfully achieved under high pressure (13 kbar) and at elevated temperature. This process proceeds not according to the widely accepted cyclic chair transition state, but to a highly distorted model with the synclinal arrangement of the carbonyl and vinyl fragments. According to such model homoallylic alcohols, the relative *threo*-configurations are formed regardless of the geometry across the double bond (*E* or *Z*) in the allyltin derivative. The reaction of the *Z*-organometallic with an aldehyde was highly stereoselective and furnished only one homoallylic alcohol, while the reaction of the *E*-isomer provided both *threo*-products with low selectivity.

5. Experimental

5.1. 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 assigned by COSY (^1H–^1H) and/or HETCOR, and DEPT correlations. The ^1H- and ^{13}C-aromatic resonances occurring at typical δ values were omitted for simplicity. The relative configurations of the protons were determined by 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 spectrometers. Optical rotations were measured with a JASCO DIP Digital Polarimeter for chloroform solution ($c \approx 1.5$, unless otherwise stated) at room temperature. CD Spectra were measured between 650 and 230 nm at room temperature with a Jasco J715 spectropolarimeter using DMSO solutions in cells of 0.2 path length (spectral band width 1 nm, sensitivity 10×10^{-6} or 20×10^{-6} ΔA unit/nm). Depending on the

S/N-ratio, the λ-scan speed was 0.2 or 0.5 nm/s. For CD measurements, the chiral diol (1–3 mg) was dissolved in a solution of the stock $[Mo_2(OAc)_4]$ complex (6–7 mg) in DMSO (10 mL) so that the molar ratio of the stock complex to the diol was about 1:0.3–1:0.7. As the true concentrations of the individual optically active complexes are not known, apparent $\Delta\varepsilon'$ values are given, calculated from the total ligand concentration and assuming 100% complexation. $[Mo_2(OAc)_4]$ and DMSO (Uvasol) were commercially available from Fluka AG and E. Merck, respectively, and used without further purification.

Column chromatography was performed on silica gel (Merck, 70–230 mesh). Organic solutions were dried over anhydrous magnesium or sodium sulfate.

Methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butyl)-stannyl-hept-5-(*E*)- and 5-(*Z*)-eno-β-D-ribofuranosides (**13*E*** and **13*Z***, respectively) were prepared according to Ref. 14. 2,3:4,5-Di-*O*-isopropylidene-D-arabinose[19] **6** was obtained by periodate cleavage of 3,4:5,6-di-*O*-isopropylidene-D-glucitol, readily available[20] from D-gluconolactone.

5.2. High-pressure reaction of organostannanes 13*E* and 13*Z* with aldehyde 6

A solution of organostannane **13** (1 mmol) and aldehyde **6** (0.95 mmol) in methylene chloride (10 mL) was placed in a piston–cylinder type apparatus[21] and kept under 13 kbar hydrostatic pressure at 57 °C for 7 days. After this time the solvent was evaporated to dryness and the residue chromatographed [first with hexane–diethyl ether, 500:1 (to remove all impurities containing tin) and hexane–ethyl acetate, 6:1] to afford pure isomers.

- Reaction of **13*Z*** afforded **14** in 97% yield.
- Reaction of **13*E*** afforded **14** (33%) and **15** (58%).
- Reaction of a 2:1 mixture **13*E*/13*Z*** afforded **14** (54%) and **15** (39%). When this process was stopped after ca. 50% conversion (3 days) the proportion of **14/15** was 3:2 (^{1}H NMR estimation; integration of the signal of OMe at δ: 3.33 and 3.32 ppm for **14** and **15**, respectively) with the initial ratio of *E*:*Z*-isomeric tins **13** was preserved (δ OMe = 3.34 and 3.32 ppm for the *E* and *Z*-isomers), which indicated that no *Z* to *E*-isomerization took place during the high-pressure reaction.

5.2.1. Methyl 2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*R*)-vinyl-β-D-*ribo*-D-*manno*-deca-1,4-furanoside 14. $[\alpha]_D = +8.6$; ^{1}H NMR (for numbering see Scheme 2) δ: 5.86 (m, 1H, $J_{1',2a'}$ 9.7 Hz, H-1′), 5.20 (m, 2H, H-2a′,H-2b′), 4.95 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.62 and 4.54 (2 × d, 2 × 1H, $J_{A,B}$ 11.9 Hz, CH_2C$_6$H$_5$), 4.33(m, 3H, H-4, CH_2C$_6$H$_5$), 4.17 (dd, 1H, $J_{10a,b}$ 8.5 Hz, $J_{9,10a}$ 6.1 Hz, H-10a), 4.05 (m, 1H, H-9), 3.99 (m, 2H, H-6, H-10b), 3.94 (dd, 1H, $J_{2,3}$ 4.7 Hz, $J_{3,4}$ 5.4 Hz, H-3), 3.85 (dd, 1H, H-2), 3.77 (dd, 1H, $J_{7,8}$ 9.0 Hz, $J_{8,9}$ 7.9 Hz H-8), 3.71 (dd, 1H, $J_{6,7}$ 8.8 Hz, H-7), 3.43 (br s, 1H, O*H*), 3.33 (s, 3H, OCH_3), 2.53 (m, 1H, H-5), 1.44, 1.35, 1.33, 1.32 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR (125 MHz) δ: 2 × 137.9 (2 × C$_{q\ benzyl}$), 133.7 (C-1′), 118.9 (C-2′), 110.2, 108.9 [2 × *C*(CH$_3$)], 106.5 (C-1), 81.8 (C-8), 81.4 (C-3), 80.4 (C-4), 2 × 80.3 (C-2, C-7), 76.2 (C-9), 72.2, 72.0 (2 × *C*H$_2$C$_6$H$_5$), 71.6 (C-9), 67.8 (C-10), 54.9 (O*C*H$_3$), 53.2 (C-5), 26.9, 26.7, 26.3, 25.1 [2 × C(*C*H$_3$)]. Anal. Calcd for $C_{33}H_{44}O_9$: C, 67.78; H, 7.58. Found: C, 67.64; H 7.51.

5.2.2. Methyl 2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*S*)-vinyl-β-D-*ribo*-D-*gluco*-deca-1,4-furanoside 15. (ORTEP Fig. 6). $[\alpha]_D = +16.6$; ^{1}H NMR (200 MHz) δ: 5.85 (ddd, 1H, $J_{1',2a'}$ 10.1 Hz, $J_{1',2b'}$ 17.0 Hz H-1′), 5.22 (d, 1H, H-2a′) 5.05 (d, 1H, H-2b′), 4.95 (s, 1H, H-1), 4.58 (m, 4H, 2 × CH_2C$_6$H$_5$), 4.39 (dd, 1H, $J_{3,4}$ 7.1 Hz, $J_{4,5}$ 4.5 Hz, H-4), 4.18–3.72 (m, 7H, H-3, H-6, H-7, H-8, H-9, H-10a, H-10b), 3.77 (d, 1H, $J_{2,3}$ 4.5 Hz, H-2), 3.32 (s, 3H, OCH_3), 2.52 (m, 1H, H-5), 2.47 (br s, 1H, O*H*), 1.39, 21.37, 1.33 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR (125 MHz) δ: 2 × 137.7 (2 × C$_{q\ benzyl}$), 134.3 (C-1′), 119.7 (C-2′), 109.7, 109.5 [2 × *C*(CH$_3$)], 105.9 (C-1), 81.4 (C-4), 80.4 (C-8), 79.2 and 79.0 (C-2, C-3), 78.4 (C-7), 76.9 (C-9), 72.3, 72.2 (2 × *C*H$_2$C$_6$H$_5$), 71.3 (C-6), 67.5 (C-10), 55.0 (O*C*H$_3$), 49.5 (C-5), 27.5, 27.3, 26.6, 25.5 [2 × C(*C*H$_3$)]. Anal. Calcd for $C_{33}H_{44}O_9$: C, 67.78; H, 7.58. Found: C 67.80; H 7.49.

5.3. Crystal assignment for 15

Crystallographic data for the structure of **15** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No CCDC 232692. Diffraction data were collected at 100 K by using a Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. Structure was solved by direct methods (SHELXS-97) and refined on F^2 by full-matrix least-squares method (SHELXL-97). The structure contains two symmetry independent molecules of **15** both having the same absolute configuration and the water molecule bind via hydrogen bonds to the one molecule of **15**. Water molecule was refined with occupancy 0.25. Formula: $2C_{33}H_{44}O_9{\cdot}0.25H_2O$, monoclinic, space group $P2_1$, $a = 9.0470(2)$, $b = 23.9720(7)$, $c = 14.9150(4)$ Å, $\beta = 98.646(2)^\circ$, $V = 3197.92(15)$ Å^3, $Z = 2$, $F(000) = 1261$, $\mu(\text{MoK}\alpha) = 0.088\ \text{mm}^{-1}$, $R_1 = 0.0652$ [$I > 2\sigma(I)$], $wR^2 = 0.1439$ for all data.

5.4. Oxidation of alcohols 14 and 15

To a solution of alcohol **14** or **15** (0.1 mmol) in ethylene dichloride (2 mL), pyridinum chlorochromate (PCC, 43 mg, 0.2 mmol) was added and the heterogeneous mixture stirred at 80 °C until TLC (hexane–ethyl acetate, 4:1) indicated disappearance of the starting material and the formation of a new less polar product (2 h). The mixture was cooled, diluted with methylene chloride (2 mL), filtered through Celite, and the crude product purified by column chromatography (hexane–ethyl acetate, 4:1).

5.4.1. Methyl 2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*R*)-vinyl-6-oxo-β-D-*ribo*-D-*arabino*-deca-1,4-furanoside 16. Obtained from **14** in 58% yield from **14**. $[\alpha]_D = -53.1$; ^{1}H NMR δ: 5.71 (ddd, 1H, $J_{1',2a'}$ 10.0 Hz, $J_{1',2b'}$ 17.1 Hz, H-1′), 5.29 (dd, 1H, H-2b′), 5.21 (dd, 1H, $J_{2a',2b'}$ 1.4 Hz, H-2a′), 4.87 (dd, 1H, $J_{1,2}$ 1.4 Hz, H-1), 4.62 (dd, 1H,$J_{3,4}$ 6.4 Hz, $J_{4,5}$ 10.0 Hz, H-4), 4.61, 4.54 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.55 (d, 1H, $J_{7,8}$ 6.0 Hz, H-7), 4.42 (br s, 2H, CH_2C$_6$H$_5$), 4.30 (dd, 1H, $J_{8,9}$ 6.3 Hz, H-8), 4.19 (ddd, 1H,$J_{9,10b}$ 5.6 Hz, H-9), 4.08 (dd, 1H, $J_{9,10a}$ 6.4 Hz,$J_{10a,b}$ 8.6 Hz, H-10a), 3.92 (dd, 1H, H-10b), 3.89 (dd, 1H, $J_{2,3}$ 4.7 Hz, H-3), 3.82 (dd, 1H, $J_{1',5}$ 9.7 Hz, H-5), 3.78 (dd, 1H, H-2), 3.32 (s, 3H, OCH_3), 1.44, 1.41, 1.37, 1.34 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR δ: 206.3 (C=O), 137.7, 137.6 (2 × C$_{q\ benzyl}$), 131.7 (C-1′), 120.1 (C-2′), 111.4, 109.8 [2 × *C*(CH$_3$)], 106.6 (C-1), 81.9 (C-7), 80.5 (C-3), 80.4 (C-4), 79.5 (C-2), 77.4 (C-8), 76.5 (C-9), 72.2, 72.1 (2 × *C*H$_2$C$_6$H$_5$), 66.5 (C-10), 59.7 (C-5), 55.6 (O*C*H$_3$), 27.2, 26.4, 26.3, 25.2 [2 × C(*C*H$_3$)]; *m*/*z*: 605.2701 [C$_{33}$H$_{42}$O$_9$Na (M+Na$^+$) requires: 605.2726].

5.4.2. Methyl 2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*S*)-vinyl-6-oxo-β-D-*ribo*-D-*arabino*-deca-1,4-furanoside 17. Obtained from **15** in 60% yield. $[\alpha]_D = +32.2$; ^{1}H NMR δ: 5.86 (ddd, 1H, $J_{1',2a'}$ 10.0 Hz, $J_{1',2b'}$ 17.2 Hz, H-1′), 5.23 (dd, 1H, $J_{2a',2b'}$ 1.5 Hz, H-2a′), 5.03 (dd, 1H, H-2b′), 4.86 (s, 1H, H-1), 4.62 and 4.59 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.58 (dd, 1H, H-4), 4.56, 4.54 (2 × d, 2 × 1H, $J_{A,B}$ 11.8 Hz, CH_2C$_6$H$_5$), 4.46 (d, 1H, H-7), 4.19 (dd, 1H, $J_{7,8}$ 6.6 Hz, H-8), 4.14 (ddd, 1H,$J_{8,9}$ 5.8 Hz, H-9), 4.06 (dd, 1H, $J_{9,10a}$ 6.3 Hz, H-10a), 4.00 (dd, 1H, $J_{3,4}$ 7.1 Hz, H-3), 3.91 (dd, 1H, $J_{1',5}$ 9.9 Hz, $J_{4,5}$ 5.2 Hz, H-5), 3.89 (dd, 1H, $J_{10a,10b}$ 8.6 Hz, $J_{9,10b}$ 6.2 Hz, H-10b), 3.78 (dd, 1H, $J_{1,2}$ 0.6 Hz, $J_{2,3}$ 4.6 Hz, H-2), 3.31 (s, 3H, OCH_3), 1.43, 1.37, 1.34, 1.32 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR δ: 207.2 (C=O), 137.8, 137.7 (2 × C$_{q\ benzyl}$), 132.3 (C-1′), 120.2 (C-2′), 111.5, 109.8 [2 × *C*(CH$_3$)], 106.3 (C-1), 82.0 (C-7), 80.2 (C-4), 80.4 (C-4), 79.5 (C-2), 78.8 (C-3), 78.1 (C-8), 76.4 (C-9), 72.2. 72.1 (2 × *C*H$_2$C$_6$H$_5$), 66.5 (C-10), 55.8 (C-5), 55.3 (O*C*H$_3$), 27.2, 26.4, 26.3, 25.2 [2 × C(*C*H$_3$)]; *m*/*z*: 605.2707 [C$_{33}$H$_{42}$O$_9$Na (M+Na$^+$) requires: 605.2726].

5.5. Conversion of adducts 14 and 15 into the diols 21 and 24

5.5.1. Methyl 6-*O*-allyl-2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*R*)-vinyl-β-D-*ribo*-D-*manno*-deca-1,4-furanoside 18. To a solution of alcohol **14** (2 mmol) in dry DMF (30 mL), sodium hydride (50% suspension in mineral oil; 3 mmol) was added followed by a catalytic amount of imidazole (20 mg), and the mixture stirred for 30 min. Allyl bromide (0.26 mL, 3.0 mmol) was then added dropwise and stirring prolonged for another 30 min. Excess hydride was decomposed with water (0.5 mL) and the mixture partitioned between water (30 mL) and ether (100 mL). The organic phase was separated, washed with water (15 mL), dried, and concentrated and crude product **18** isolated by column chromatography (hexane–ethyl acetate, 5:1). Yield: 89%; $[\alpha]_D = -6.0$; ^{1}H NMR δ: 5.90 (m, 1H, $J_{2'',3a'}$ 10.9 Hz, $J_{2'',3''}$ 17.2 Hz, H-2″[§]), 5.77 (ddd, 1H, $J_{1',2a'}$ 10.3 Hz, $J_{1',2b'}$ 17.2 Hz, $J_{1',5}$ 9.8 Hz, H-1′), 5.27 (m, 1H, $J_{3a'',3b''}$ 1.5 Hz, H-3b″), 5.20 (dd, 1H, $J_{2a',2b'}$ 2.2 Hz, H-2a′), 5.18 (dd, 1H, H-2b′), 5.13 (m, 1H, H-3a″), 4.92 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1), 4.63, 4.55 (2 × d, 2 × 1H, $J_{A,B}$ 12.1 Hz, CH_2C$_6$H$_5$), 4.42, 4.39 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.30 (dd, 1H, $J_{1a'',1b''}$ 12.3 Hz, $J_{1a'',2''}$ 5.2 Hz, H-1a″), 4.22 (m, 3H, H-4, H-8, H-9), 4.13 (dd, 1H, $J_{1b'',2''}$ 6.0 Hz, H-1b″), 4.01 (dd, 1H, $J_{10a,b}$ 8.1 Hz, $J_{9,10a}$ 6.5 Hz, H-10a), 3.95 (dd, 1H, $J_{9,10b}$ 7.2 Hz, H-10b), 3.89 (dd, 1H, $J_{3,4}$ 5.4 Hz, H-3), 3.84 (dd, 1H, $J_{5,6}$ 1.4 Hz, $J_{6,7}$ 9.0 Hz, H-6), 3.83 (dd, 1H, $J_{2,3}$ 4.7 Hz, H-2), 3.73 (dd, 1H, $J_{7,8}$ 6.0 Hz, H-7), 3.33 (s, 3H, OCH_3), 2.46 (m, 1H, H-5), 1.42, 1.37, 1.36, 1.34 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR δ: 137.8, 137.7 (2 × C$_{q\ benzyl}$), 134.6 (C-2″), 133.9 (C-1′), 119.1 (C-2′), 116.9 (C-3″), 109.6 and 109.3 [2 × *C*(CH$_3$)], 106.6 (C-1), 81.9 (C-3), 80.2 and 80.0 (C-2, C-4, C-6, C-8), 77.8 (C-7), 76.2 (C-9), 74.0 (C-1″), 72.3 and 72.2 (2 × *C*H$_2$C$_6$H$_5$), 65.2 (C-10), 55.2 (O*C*H$_3$), 53.3 (C-5), 27.7, 27.5, 26.3, 25.4 [2 × C(*C*H$_3$)]; ESI (MeOH) *m*/*z*: 647.3221 [C$_{36}$H$_{48}$O$_9$Na (M+Na$^+$) requires: 647.3191].

5.5.2. Methyl 6-*O*-allyl-2,3-di-*O*-benzyl-5-deoxy-7,8:9,10-di-*O*-isopropylidene-(5*S*)-vinyl-β-D-*ribo*-D-*gluco*-deca-1,4-furanoside 19. Was obtained analogously from **15** in 79% yield. $[\alpha]_D = +12.3$; ^{1}H NMR δ: 5.89 (m, 2H, H-1′, H-2″), 5.21 (m, 1H, $J_{2'',3b''}$ 17.2 Hz, $J_{1'',3b''}$ 3.4 Hz, H-3b″), 5.15 (dd, 1H, $J_{1',2a'}$ 10.3 Hz, $J_{2a',2b'} = -2.1$ Hz, H-2a′), 5.07 (dd, 1H, $J_{1',2b'}$ 17.3 Hz, H-2b′), 5.06 (m, 1H, $J_{2'',3a''}$ 9.0 Hz, H-3a″), 4.89 (d, 1H, $J_{1,2}$ 0.7 Hz, H-1), 4.65, 4.59 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.55 and 4.43 (2 × d, 2 × 1H, $J_{A,B}$ 11.8 Hz, CH_2C$_6$H$_5$), 4.37 (dd, 1H, $J_{3,4}$ 7.2 Hz, $J_{4,5}$ 4.8 Hz, H-4), 4.15 (dd, 1H, $J_{6,7}$ 4.6 Hz, $J_{7,8}$ 7.0 Hz, H-7), 4.12 (m, 3H, H-1a″, H-1b″, H-10b), 4.07 (m, 1H, H-9), 3.97 (dd, 1H, $J_{2,3}$ 4.8 Hz, H-3), 3.89 (dd, 1H, $J_{9,10a}$ 6.4 Hz, $J_{10a,b}$ 8.1 Hz, H-10a), 3.85 (dd, 1H, $J_{8,9}$ 7.3 Hz, H-8), 3.79 (dd, 1H, H-2), 3.59 (dd, 1H, $J_{5,6}$ 5.6 Hz, H-6), 3.33 (s, 3H, OCH_3), 2.68 (ddd, 1H, $J_{1',5}$ 10.1 Hz, H-5), 1.41, 1.37, 1.35, 1.34 {4 × s, 4 × 3H, [2 × C(CH_3)]}; ^{13}C NMR (125 MHz) δ: 137.9 and 137.8 (2 × C$_{q\ benzyl}$), 135.3, 135.2 (C-1′, C-2″), 119.1 (C-2′), 115.9 (C-3″), 109.6, 109.2 [2 × *C*(CH$_3$)], 106.0 (C-1), 81.1 (C-7), 81.0 (C-4), 79.7 (C-2), 79.3 (C-3), 78.9 (C-6), 78.2 (C-8), 77.0 (C-9), 73.3 (C-1″), 72.3 and 72.2 (2 × *C*H$_2$C$_6$H$_5$), 67.7 (C-10), 55.1 (O*C*H$_3$), 49.5 (C-5), 27.3, 27.2, 26.4, 25.4 [2 × C(*C*H$_3$)]; ESI (MeOH) *m*/*z*: 647.3213 [C$_{36}$H$_{48}$O$_9$Na (M+Na$^+$) requires: 647.3191].

5.5.3. Methyl 6-*O*-allyl-2,3-di-*O*-benzyl-5-deoxy-5-vinyl-β-D-*ribo*-L-*threo*-hept-1,4-furanoside 20. Compound **18** (360 mg, 0.57 mmol) was dissolved in a mixture of THF/water (2:1, 25 mL) containing concentrated sulfuric acid (0.25 mL) and boiled under reflux for 20 h. After cooling to room temperature it was neutralized with triethyl amine. To this solution of a tetraol, diethyl ether

[§] Description bis (″) refers to the allylic blocking group.

(10 mL) was added followed by sodium periodate (460 mg, 2.3 mmol), and the mixture stirred vigorously for 30 min at rt. This was diluted with ether (30 mL), and then washed with brine (15 mL) and water (15 mL). Crude aldehyde was reduced with sodium borohydride (40 mg, 0.086 mmol) under standard conditions. Chromatographic purification (hexane–ethyl acetate, 4:1–2:1) afforded alcohol **20** in 70% overall yield (180 mg, 0.4 mmol). $[\alpha]_D = -19.1$; ^{1}H NMR δ: 5.94 (m, 1H, H-2″), 5.79 (ddd, 1H, H-1′), 5.27 (m, 1H, $J_{2'',3b''}$ 17.2 Hz, H-3b″), 5.15 (m, 1H, $J_{2'',3a''}$ 10.4 Hz, H-3a″), 5.13 (dd, 1H, $J_{1',2a'}$ 10.0 Hz, $J_{2a',2b'}$ 2.0 Hz, H-2a′), 5.08 (dd, 1H, $J_{1',2b'}$ 17.2 Hz, H-2b′), 4.92 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.63, 4.55 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.93 (s, 2H, CH_2C$_6$H$_5$), 4.33 (dd, 1H, $J_{3,4}$ 5.9 Hz, $J_{4,5}$ 10.3 Hz, H-4), 4.19 (m, 1H, $J_{1a'',2''}$ 5.3 Hz, $J_{1a'',3b''}$ 1.7 Hz, H-1a″), 4.14 (m, 1H, $J_{1a'',1b'}$ 12.7 Hz, $J_{1b'',2''}$ 6.0 Hz, $J_{1b'',3a''}$ 1.3 Hz, H-1b″), 3.89 (dd, 1H, $J_{2,3}$ 4.8 Hz, H-3), 3.83 (dd, 1H, H-2), 3.82 (m, 1H, H-6), 3.65 (m, 1H, H-7a), 3.56 (m, 1H, H-7b), 3.34 (s, 3H, OCH_3), 2.16 (ddd, 1H, $J_{5,6}$ 2.9 Hz, $J_{1',5}$ 10.2 Hz, H-5), 1.83 (m, 1H, OH); ^{13}C NMR δ: 2 × 137.7 (2 × C$_{q\ benzyl}$), 135.2 (C-2″), 134.6 (C-1′), 118.2 (C-2′), 116.8 (C-3″), 106.7 (C-1), 81.5 (C-3), 80.3 (C-4), 80.1 (C-2), 79.1 (C-6), 72.9 (C-1″), 72.3, 72.1 (2 × CH$_2$C$_6$H$_5$), 64.1 (C-7), 55.2 (OCH$_3$), 53.9 (C-5); m/z (ESI): 477.2230 [C$_{27}$H$_{34}$O$_6$Na (M+Na$^+$) requires: 477.2248]. Anal. Calcd for C$_{27}$H$_{34}$O$_6$: C, 71.34; H, 7.53. Found: C, 71.58; H 7.60.

5.5.4. Methyl 6-*O*-allyl-2,3-di-*O*-benzyl-5-deoxy-5-vinyl-β-D-*ribo*-D-*threo*-hept-1,4-furanoside 23. Prepared analogously from **19** in 80% overall yield. $[\alpha]_D = +48.3$; ^{1}H NMR δ: 5.91 (m, 1H, H-2″), 5.73 (ddd, 1H, H-1′), 5.25 (m, 1H, $J_{2'',3b''}$ 17.2 Hz, $J_{3a'',3b''}$ 1.6 Hz, H-3b″), 5.14 (m, 1H, $J_{2'',3a''}$ 0.3 Hz, H-3a″), 5.13 (dd, 1H, $J_{1',2a'}$ 10.3 Hz, $J_{2a',2b'}$ 2.0 Hz, H-2a′), 4.94 (dd, 1H, $J_{1',2b'}$ 17.2 Hz, H-2b′), 4.83 (s, 1H, H-1), 4.66, 4.59 (2 × d, 2 × 1H, $J_{A,B}$ 12.1 Hz, CH_2C$_6$H$_5$), 4.56, 4.37 (2 × d, 2 × 1H, $J_{A,B}$ 11.9 Hz, CH_2C$_6$H$_5$), 4.39 (dd, 1H, $J_{3,4}$ 8.2 Hz, $J_{4,5}$ 3.3 Hz, H-4), 4.12 (m, 1H, $J_{1a'',1b''}$ 14.0 Hz, $J_{1a'',2''}$ 5.5 Hz, H-1a″), 4.02 (m, 1H, $J_{1b'',2''}$ 5.9 Hz, H-1b″), 3.91 (dd, 1H, $J_{2,3}$ 4.6 Hz, H-3), 3.76 (d, 1H, H-2), 3.69 (m, 2H, H-7a, H-7b), 3.31 (s, 3H, OCH_3), 2.51 (ddd, 1H, $J_{5,6}$ 5.3 Hz, $J_{1',5}$ 9.1 Hz, H-5), 2.24 (m, 1H, OH); ^{13}C NMR δ: 137.8, 137.7 (2 × C$_{q\ benzyl}$), 135.1 (C-2″), 134.3 (C-1′), 119.3 (C-3″), 116.8 (C-2′), 106.1 (C-1), 81.0 (C-6), 79.0 (C-2), 79.0 (C-4), 78.9 (C-3), 72.35, 72.3 (2CH$_2$C$_6$H$_5$), 71.2 (C-1″), 62.3 (C-7), 55.2 (OCH$_3$), 48.1 (C-5). m/z (ESI): 477.2243 [C$_{27}$H$_{34}$O$_6$Na (M+Na$^+$) requires: 477.2248].

5.5.5. Methyl 2,3-di-*O*-benzyl-5-deoxy-5-vinyl-β-D-*ribo*-L-*threo*-hept-1,4-furanoside 21. Allyl ether **20** (0.1 mmol) was dissolved in a mixture of methanol/water (5/0.5 mL), to which Pd/C (50 mg), and *p*-toluenesulfonic acid were added and the mixture heated at 45–50 °C for 2 h. This was then cooled to rt, diluted with methanol (5 mL) and passed through Celite. The filtrate was neutralized with Et$_3$N, concentrated, and the residue purified by column chromatography (hexane–ethyl acetate 1:1–1:2) to afford diol **21** as an oil in 44% overall yield. $[\alpha]_D = +10.1$; ^{1}H NMR δ: 5.82 (ddd, 1H, H-1′), 5.20 (dd, 1H, $J_{1',2a'}$ 10.3 Hz, $J_{2a',2b'}$ 1.9 Hz, H-2a′), 5.15 (dd, 1H, $J_{1',2b'}$ 17.2 Hz, H-2b′), 4.89 (s, 1H, H-1), 4.63, 4.56 (2 × d, 2 × 1H, $J_{A,B}$ 11.9 Hz, CH_2C$_6$H$_5$), 4.45, 4.41 (2 × d, 2 × 1H, $J_{A,B}$ 11.3 Hz, CH_2C$_6$H$_5$), 4.28 (dd, 1H, H-4), 3.94 (dd, 1H, $J_{3,4}$ 7.0 Hz, H3), 3.89 (m, 1H, H-6), 3.82 (d, 1H, $J_{2,3}$ 4.6 Hz, H-2), 3.61 (m, 2H, H-7a, H-7b), 3.34 (s, 3H, OCH_3), 2.77 (d, 1H, $J_{6,OH}$ 4.1 Hz, OH), 2.31 (ddd, 1H, $J_{5,6}$ 3.7 Hz, H-5), 2.03 (m, 1H, OH); ^{13}C NMR δ: 137.6 and 137.3 (2 × C$_{q\ benzyl}$), 133.8 (C-1′), 119.1 (C-2′), 105.4 (C-1), 81.3 (C-4), 80.1 (C-3), 79.4 (C-2), 72.4 (C-6), 72.35, 72.3 (2 × CH$_2$C$_6$H$_5$), 65.1 (C-7), 55.5 (OCH$_3$), 52.3 (C-5). m/z (ESI): 437.1958 C$_{24}$H$_{30}$O$_6$Na (M+Na$^+$) requires: 437.1935].

5.5.6. Methyl 2,3-di-*O*-benzyl-5-deoxy-5-vinyl-β-D-*ribo*-D-*threo*-hept-1,4-furanoside 24. Obtained analogously from **23** in 54% overall yield. $[\alpha]_D = +30.5$; ^{1}H NMR δ: 5.79 (ddd, 1H, H1′), 5.20 (dd, 1H, $J_{1',2a'}$ 0.3 Hz, $J_{2a',2b'}$ 2.0 Hz, H-2a′), 4.97 (dd, 1H, $J_{1',2b'}$ 17.3 Hz, H-2b′), 4.86 (s, 1H, H-1), 4.66, 4.59 (2 × d, 2 × 1H, $J_{A,B}$ 12.0 Hz, CH_2C$_6$H$_5$), 4.55, 4.38 (2 × d, 2 × 1H, $J_{A,B}$ 11.7 Hz, CH_2C$_6$H$_5$), 4.37 dd, 1H, $J_{4,5}$ 3.7 Hz, H-4), 3.96 (dd, 1H, $J_{3,4}$ 8.5 Hz, H-3), 3.91 (m, 1H, H-6), 3.78 (d, 1H, $J_{2,3}$ 4.5 Hz, H-2), 3.62 (m, 1H, H-7a), 3.55 (ddd, 1H, $J_{6,7b}$ 7.9 Hz, $J_{7a,b}$ 11.9 Hz, $J_{7b,OH}$ 4.0 Hz, H-7b), 3.32 (s, 3H, OCH_3), 2.91 (d, 1H, $J_{6,OH}$ 2.8 Hz, OH), 2.32 (ddd, 1H, $J_{5,6}$ 3.9 Hz, $J_{5,1'}$ 9.9 Hz, H-5), 2.08 (br s, 1H, OH); ^{13}C NMR δ: 137.6, 137.4 (2 × C$_{q\ benzyl}$), 133.2 (C-1′), 120.0 (C-2′), 106.1 (C-1), 81.6 (C-4), 78.7 and 78.6 (C-2, C-3), 73.4 (C-6), 72.50, and 72.4 (2 × CH$_2$C$_6$H$_5$), 64.4 (C-7), 55.2 (OCH$_3$), 49.2 (C-5). m/z (ESI): 437.1948 C$_{24}$H$_{30}$O$_6$Na (M+Na$^+$) requires: 437.1935].

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