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Synthesis and Reactivity of Sugar Allyltin Derivatives

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Thermal stability of primary sugar allyltin derivatives: Sug-CH=CH-CH_2SnBu_3 was studied. These organometallics with a pyranose ring are stable up to at least 214°C (boiling trichlorobenzene), while those with a furanose ring undergo already at 180°C a controlled decomposition with elimination of the tributylstannyl moiety and opening of the five-membered ring. The mechanism of this process is discussed.

Key words: sugars allyltin derivatives, rearrangement

One of the most useful methods for the synthesis of enantiomerically pure complex products is a derivatization of compounds, which are easily available in optically pure form (so-called chiron approach [1–5]). Very often simple sugars are sources of chirality. Recently we elaborated a convenient route to bicylo[4.3.0]-nonenes: **7-*E*** [6] or **7-*Z*** [7], as well as to *cis*-bicyclo[4.4.0]decenes **6** [8] from allyltin derivatives of simple sugars: **1** [9] and **4** [7]. These organometallic compounds are readily prepared from the corresponding sugar allylic derivatives: alcohol **2** or mesylate **3** (Fig. 1).

Primary allyltin derivatives **1**, upon treatment with a Lewis acid, undergo a controlled decomposition to dienoaldehydes **5** with the ***E***-configuration across the internal double bond regardless of the geometry (***E*** or ***Z***) of starting olefin **1** [9,10]. Interestingly, thermal decomposition of secondary isomers **4** (with the ***S*** configuration at the stereogenic center bearing the $-SnBu_3$ group) provides exclusively the ***Z***-dienoaldehydes **8** [7,11] (Fig. 1).

This result raised the question about thermal stability of isomeric sugar allyltins as well as about their behavior towards the Lewis acids.

RESULTS AND DISCUSSION

Since reactivity and stability of primary sugar allyltin derivatives may differ significantly from pyranoses to furanoses,*** we decided to study in detail the behavior

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*** For example: reaction of pyranose allyltins such as **1** with aldehydes catalyzed with a Lewis acid affords the expected homoallylic alcohols, while furanoses undergo decomposition under these conditions (ref. [12]).

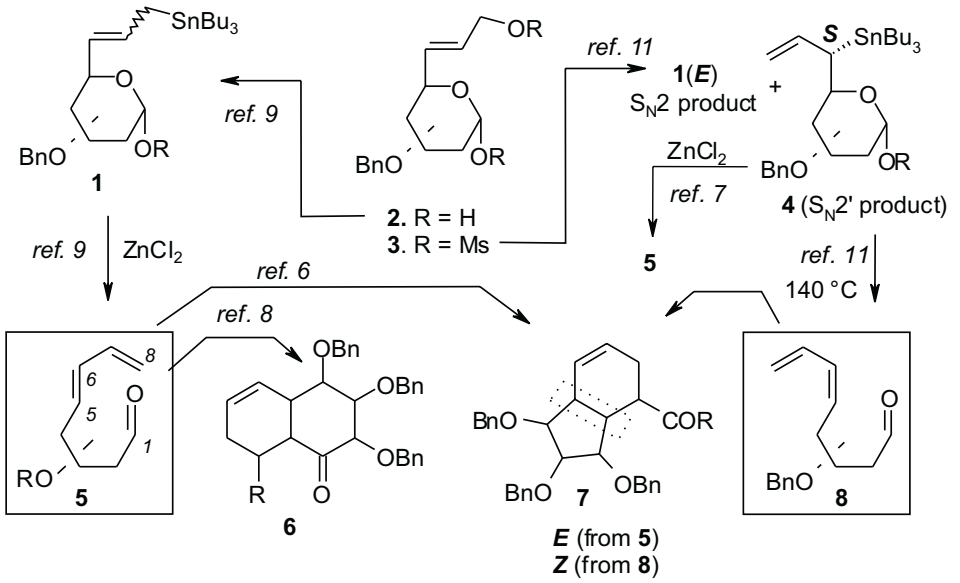


Figure 1. Application of sugar allyltin derivatives in organic synthesis.

of both types of isomers: these containing the 6-membered ring and those with the five-membered one. As pyranose representatives, diacetonogalactose derivatives have been selected. Compounds with five-membered ring are represented by ribofuranose derivatives.

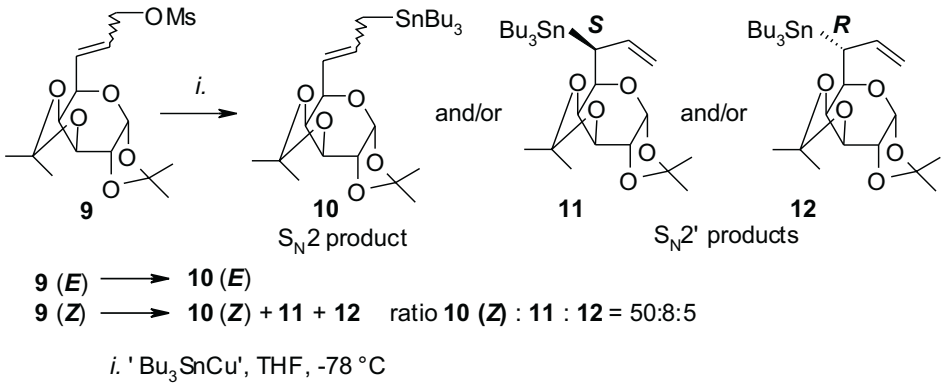
Preparation of sugar allyltin derivatives of 'diacetonogalactose'. Synthesis of sugar allyltins was realized by reaction of the corresponding allylic mesylates with tributyltin cuprate ('Bu_3SnCu'). This process opens a route to both: the primary or secondary derivatives *via* either the S_N2 or S_N2' reaction [10,11].

Although the 6,7-unsaturated galactose derivatives, existing in the chair conformation, are rather resistant towards the S_N2' substitution [10] (probably due to steric hindrance exerted by the oxygen atom at the C-4 position of the galactopyranose ring), the less sterically demanding compounds derived from 1,2:3,4-di-*O*-isopropylidene-D-galactose, in which the ring is highly distorted [13], might enable such process.

6,7-Dideoxy-1,2:3,4-di-*O*-isopropylidene-8-*O*-mesyl-α-D-*galacto*-oct-7(*E*)-eno-1,5-pyranose [15] (**9-*E***) upon reaction with 'Bu_3SnCu' [14] furnished exclusively the primary isomer **10-*E***. The *cis*-derivative [16] **9-*Z***, however, provided – besides the primary product **10-*Z*** – also the secondary isomers **11** and **12** under these conditions (Scheme 1).

Formation of both secondary products in comparable amounts in this S_N2' process (**11**:**12** = 8:5) was rather unexpected, since we found recently that the S_N2' reaction of other allylic sugar derivatives, such as methyl 2,3,4-tri-*O*-benzyl-α-D-*manno*-6,7-dideoxy-oct-7(*E*)-eno-pyranoside (**13**), with 'Bu_3SnCu' proceeded com-

Scheme 1



pletely stereoselectively and provided ***only one*** secondary isomer **14** with the ***S***-configuration at the newly created stereogenic center [11]. Moreover, the stereochemistry at this center did not depend on the geometry (***E*** or ***Z***) of starting olefin, as was proved by reaction of either **15-*E*** or **15-*Z*** with 'Bu_3SnCu'; both processes afforded (besides the primary allyltins) only one secondary isomer **16** [11] (Fig. 2).

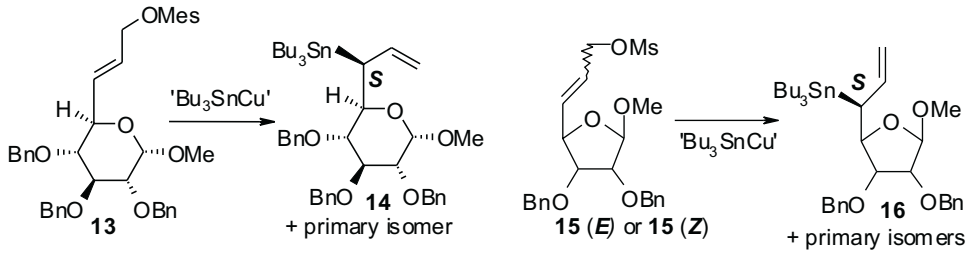
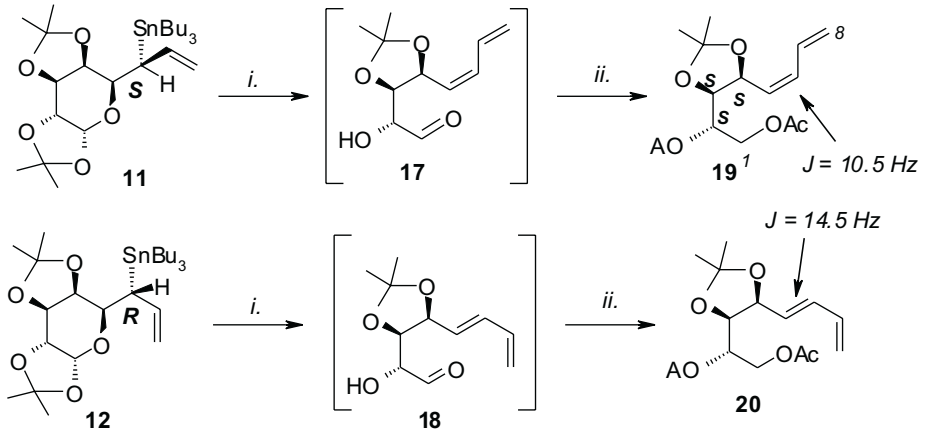


Figure 2. Stereoselective reaction of sugar allylic mesylates with 'Bu_3SnCu' (ref. 11).

Thermal stability of secondary sugar allyltin derivatives. Secondary sugar allyltins are thermally unstable and decompose at 140°C (boiling xylene) with elimination of the tributylstannyl moiety and opening of the sugar ring to the corresponding dienoaldehydes, according to the E-2 mechanism [11]. Such concerted decomposition might provide a valuable information about geometry of starting allyltins and should allow to assign their configuration; this problem is very difficult to solve by other direct methods [11,17].

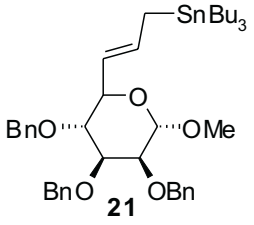
This method was used for determination of the configuration at the C-6 centers in isomers **11** and **12**; the results are shown in Scheme 2. Heating compound **11** at 140°C for 3 h resulted in formation of the ***Z***-diene **17** exclusively, while the same reaction performed for the opposite isomer **12** provided the ***E***-diene **18**. Assuming the concerted E-2 mechanism of this elimination [11], one can safely assign the ***S***-configuration to the main secondary isomer **11** and the ***R***-configuration to the minor one **12**.

Scheme 2



i. boiling xylene (140 °C), 2-3 h; *ii.* $NaBH_4$, then Ac_2O/py

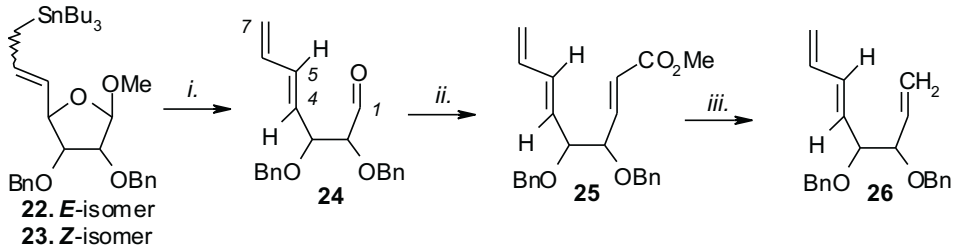
Thermal stability of the primary sugar allyltin derivatives. The secondary D-sugar allyltin derivatives decompose at high temperature (boiling xylene) with elimination of the tributylstannyl moiety and opening of the sugar ring, what leads to highly oxygenated dienoaldehydes. The configuration (***Z*** or ***E***) across the internal double bond depends on the configuration at the stereogenic center bearing the $-SnBu_3$ group in starting secondary allyltin derivative.



Primary sugar allyltins derived from pyranoses are thermally stable. Heating two representative compounds: ***E***-configurated **21** [9] or ***Z***-configurated **10-*Z*** at 214°C resulted in no change of the starting materials; not only decomposition products were not detected, but also there was no ***Z*→*E*** isomerization.

The furanose derivatives, however, are less thermally stable. Heating of methyl 2,3-di-*O*-benzyl-5,6,7-trideoxy-7-(tri-*n*-butylstannyl)-5(*E*)-, and 5(*Z*)-ene-β-D-*ribo*-hept-1,4-furanosides (**22** and **23**) [11] at 180°C induced their decomposition to the dienoaldehyde **24** with the ***E***-configuration across the C4–C5 bond. At such high temperature a significant polymerization of the unsaturated product was noted, so the dienoaldehyde **24** was isolated in a rather low yield. Its structure was proved on the basis of the NMR spectroscopy by comparison with the spectrum of the synthetic material with the ***E***-configuration across the internal double bond, which was prepared independently by a controlled decomposition of **22** with zinc chloride [18]. This compound was also characterized independently as triene **25** (see Scheme 3).

Scheme 3



i. 180 °C, 4 h; *ii.* $Ph_3P{=}CHCO_2Me$, rt; *iii.* 140 - 180 °C, 4 h

Interestingly, heating this compound (**25**) at high temperature (140–180°C) for several hours resulted in formation of another triene **26**, which had to arise from tandem hydrolysis (by traces of water) – decarboxylation reaction.

The observation, that both geometrical isomers of primary allyltin undergo a decomposition to the same product, surely needs a comment. Three hypotheses may be put forward. First one postulates, that the *trans*-dienoaldehyde **24** is a primary product in both decomposition reactions either of **22** or **23** (*route a* in Fig. 3). According to the second, the allyltin **23** rearranges into the thermodynamically more stable ***E***-olefin **22**, which further decomposes into ***E***-diene **24** (*route b*). Third one postulates, that the diene **27** (eventual primary product of decomposition of **23**) may isomerize into the ***E***-diene **24** at high temperature (*route c*). Two last hypotheses were excluded on the basis of the experiments shown in Scheme 4.

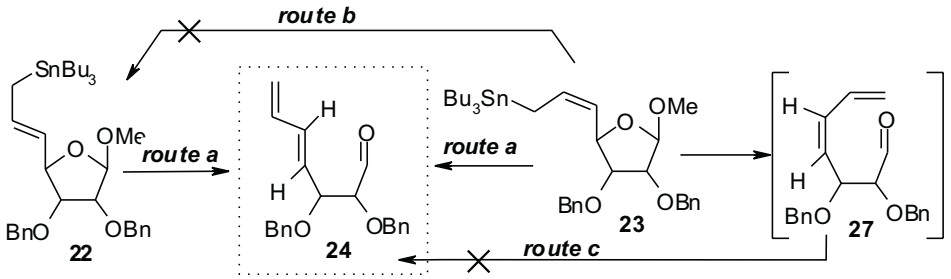
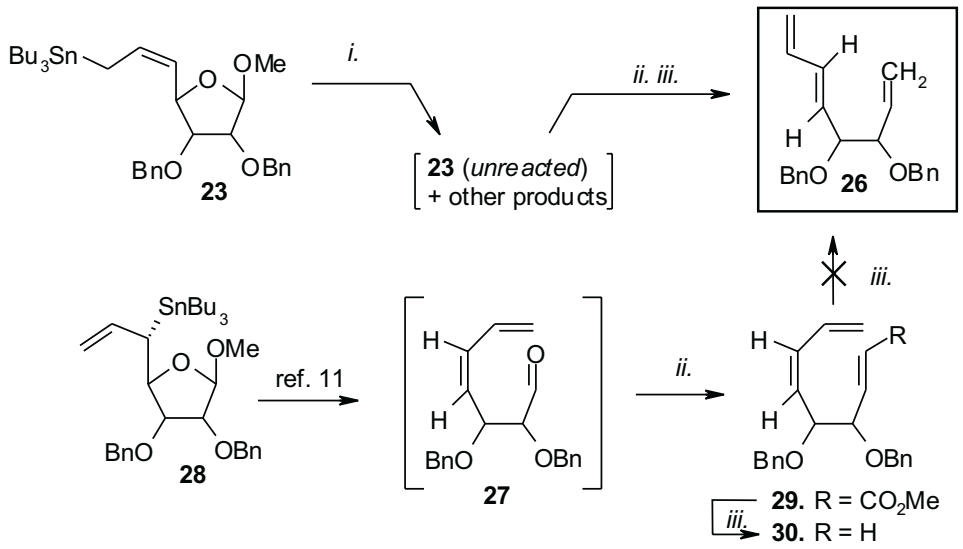


Figure 3. The possible pathways for thermal (180°C, 4 h) decomposition of primary sugar allyltis.

Heating of the *cis*-olefin **23** for 2 h at 180°C resulted in a partial decomposition; the recovered organometallic derivative had the ***Z***-configuration across the double bond, what pointed that under these conditions the isomerization **23→22** did not take place.

Alternatively, the *cis*-diene **27** (obtained acc. to [11] by thermal decomposition of the secondary allyltin **28**) was found to be configurationally stable at high temperature. Heating of its derivative **29** to 180°C for several hours left the internal double bond intact; only decarboxylation, leading to **30** (cf. **25→26** in Scheme 3) was noted.

Scheme 4



i. 180 °C, 2h; *ii*. $Ph_3P=CHCO_2Me$, rt, 1 h; *iii*. 140 - 180 °C, 4h

The conclusion is, that no isomerization at high temperature is, therefore, possible at either stage of decomposition process and the *trans*-dienoaldehyde **24** is a primary product in decomposition of either ***E***- or ***Z***-allyltins (**22** or **23**).

Therefore, the configuration of the internal double bond of the dienoaldehyde resulted from thermal decomposition of the primary furanose. Derived sugar allyltins did not depend on the geometry of the double bond of the starting allyltin derivative. This phenomenon may be explained by the models presented in Fig. 4; the conformations represented by picture **A** are much more favored over those depicted by drawing **B**.

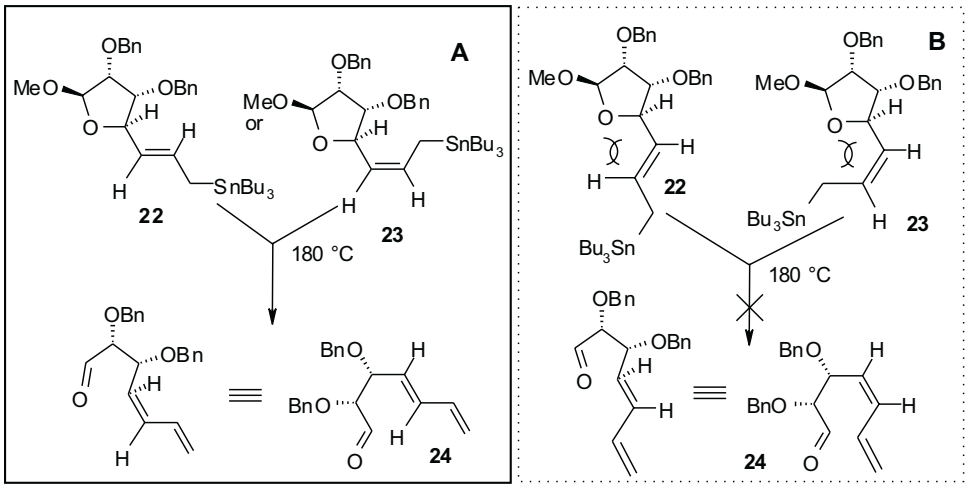


Figure 4. Stereochemical models for thermal decomposition of the primary allyltins **22** and **23**.

CONCLUSIONS

The primary sugar allyltin derivatives Sug-CH=CH-CH_2SnBu_3 with the six-membered ring (Sug = pyranose derivative) are thermally stable up to at least 214°C. Those with the five-membered ring (furanoses) decompose at 180°C with elimination of the tributylstannyl moiety and opening of the sugar ring. Dienoaldehydes CH_2=CH-CH=CH-$(CHOR)_2$CHO with the ***E***-geometry across the internal double bond are formed exclusively in this process. These results may be explained assuming the concerted mechanism for such elimination.

EXPERIMENTAL

Optical rotations were measured with a JASCO DIP 360 automatic polarimeter in chloroform at 20 +/– 2°C. NMR spectra were recorded with Varian Gemini AC-200 (200 MHz), Varian Mercury (400 MHz), or Bruker AM-500 (500 MHz) specrometers in $CDCl_3$ solutions with Me_4Si as an internal standard. ^{1}H and ^{13}C signals of aromatic groups occurred at the expected chemical shifts were omitted in the description of spectra. ^{13}C NMR spectra were recorded in the DEPT 135 mode. The proton and carbon resonances in the spectra of most compounds were assigned by the COSY and HETCOR correlations. Mass spectra were recorded on an AMD-604 mass spectrometer. HPLC was carried out on a Shimadzu instrument: central unit C-R4A, pump unit LC-8A, UV detector SPD-6A on a column Machery Nagel Nucleosil 100-7. TLC was performed on Silica Gel HF-254 ready plates and column chromatography on Silica Gel 230–400 or 70–230 mesh (E. Merck). Organic solutions were dried over anhydrous magnesium or sodium sulfate.

Reaction of diacetonogalactose derivatives with tributyltin cuprate. To a cooled (to –78°C) and stirred suspension of CuCN (270 mg, 3 mmol) in dry THF (10 mL) a solution of butyllithium in hexane (6 mmol) was added and the mixture was stirred for 10 min. To a slightly yellow solution of resulting organocuprate, tri-*n*-butyltin hydride (neat, 6 mmol) was added by a syringe at –78°C. After evolution of gas ceased the yellow mixture was stirred for 30 min at –78°C to yield a solution of crude tri-*n*-butyltin cuprate [14].

A solution of sugar electrophile, mesylate **9-*E*** [15] or **9-*Z*** [16] (364 mg, 1 mmol) in dry THF (5 mL) was added by a syringe to a solution of the above prepared tributyltin cuprate in THF and the mixture was stirred at –78°C until TLC showed disappearance of the starting material (hexane-ethyl acetate, 10:1). The mixture was diluted with ether (15 mL), aqueous saturated ammonium chloride (5 mL) was added and the mixture was stirred for 30 min at room temperature. Organic layer was separated, washed with water, dried and concentrated and the crude product was isolated by column chromatography (hexane-diethyl ether, 95:5 and then hexane-ethyl acetate, 15:1) and further purified by HPLC (hexane-ethyl acetate, 20:1).

- Reaction of **9-*E*** afforded only the primary allyltin **10-*E*** (340 mg, 61%).
- Reaction of **9-*Z*** afforded: **12** (28 mg, 5%), **10-*Z*** (273 mg, 49%) and **11** (45 mg, 8%).

1,2:3,4-Di-*O*-isopropylidene-6,7,8-trideoxy-8-tri-*n*-butylstannyl)-oct-6(*E*)-eno-α-D-*galacto*-1,5-pyranose (**10-*E***). Yield 61%; oil; $[\alpha]_D$ 23.5 (c 1.27); ^{1}H NMR (200 MHz) δ: 0.80 (m, 15H, 3×CH_2 and 3×CH_3), 1.20 (m, 6H, 3×CH_2), 2×1.25 (2×s, 2×3H, 2×CH_3), 1.39 (s, 3H, CH_3), 1.40 (m, 6H, 3×CH_2), 1.46 (s, 3H, CH_3), 1.70 (m, 2H, H-8a, H-8b), 4.04 (dd, 1H, J = 1.8 Hz, H-4), 4.11 (d, 1H, H-5), 4.18 (dd, 1H, J = 2.3 Hz, H-2), 4.50 (dd, 1H, J = 7.8 Hz, H-3), 5.34 (dd, 1H, J = 5.6 Hz, H-6), 5.46 (d, 1H, J = 5.1 Hz, H-1), 5.82 (ddd, 1H, J = 15.2 Hz, H-7); ^{13}C NMR (50 MHz) δ: 9.20 (3×CH_2), 13.62 (3×CH_3), 14.60 (CH_2), 24.18 (CH_3), 24.90 (CH_3), 25.94 (CH_3), 26.07 (CH_3), 27.24 (3×CH_2), 29.03 (3×CH_2), 69.37, 70.38, 70.87, and 74.01 (4×CH), 96.42 (CH, C-1), 107.99 and 108.72 (2×Cq), 120.49, 134.61 (2×CH, C-6,7); ESI (MeOH) m/z: 583 $(M+Na)^+$; HR-MS 583.2416 calculated for $C_{26}H_{48}O_5NaSn$, found 583.2454.

1,2:3,4-Di-*O*-isopropylidene-6,7,8-trideoxy-8-tri-*n*-butylstannyl)-oct-6(*Z*)-eno-α-D-*galacto*-1,5-pyranose (**10-*Z***). Yield 49%; oil; $[\alpha]_D$ –15.9 (c 1.06); ^{1}H NMR (400 MHz) δ: 0.90 (m, 15H, 3×CH_2 and 3×CH_3), 1.30 (m, 6H, 3×CH_2), 2×1.35 (2×s, 2×3H, 2×CH_3), 1.46 (m, 6H, 3×CH_2), 1.48 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.77 (ddd, 1H, J = 1.5 Hz, H-8b), 1.88 (ddd, 1H, J = 1.1, 11.4 Hz, H-8a), 4.13 (dd, 1H, J = 2.0 Hz, H-4), 4.30 (dd, 1H, J = 2.3 Hz, H-2), 4.58 (m, 1H, H-5), 4.59 (dd, 1H, J = 7.9 Hz, H-3), 5.34 (dd, 1H, J = 8.4 Hz, H-6), 5.56 (d,1H, J = 5.1 Hz, H-1), 5.83 (ddd, 1H, J = 9.5 Hz, H-7); ^{13}C NMR (100 MHz) δ: 9.35 (3×CH_2), 11.95 (CH_2), 13.68 (3×CH_3), 24.35 (CH_3), 24.89 (CH_3), 26.01 (CH_3), 26.27 (CH_3), 27.36 (3×CH_2), 29.11 (3×CH_2), 63.20, 70.24, 71.01, 73.32 (4×CH), 96.62 (CH, C-1), 107.99 and 108.92 (2×Cq), 118.58, 134.24 (2×CH, C-6,7); ESI (MeOH) m/z: 583 $(M+Na)^+$; HR-MS 583.2416 calculated for $C_{26}H_{48}O_5NaSn$, found 583.2436.

1,2:3,4-Di-*O*-isopropylidene-6,7,8-trideoxy-6(*S*)-(tri-*n*-butylstannyl)-oct-7-eno-α-D-*galacto*-1,5-pyranose (**11**). Yield 8%; oil; $[\alpha]_D$ –48.1 (c 0.73); ^{1}H NMR (400 MHz) δ: 0.89 (m, 15H, 3×CH_2 and 3×CH_3), 1.31 (m, 6H, 3×CH_2), 2×1.32 (2×s, 2×3H, 2×CH_3), 1.45 (s, 3H, CH_3), 1.49 (m, 6H, 3×CH_2), 1.54 (s, 3H, CH_3), 2.68 (dd, 1H, J = 10.6 Hz, H-6), 4.07 (dd, 1H, J = 1.6 Hz, H-4), 4.10 (dd, 1H, J = 11.1 Hz, H-5), 4.27 (dd, 1H, J = 2.2 Hz, H-2), 4.58 (dd, 1H, J = 7.9 Hz, H-3), 4.81 (dd, 1H, J = 0.7 Hz, H-8a), 4.90 (ddd, 1H, J = 1.4 Hz, H-8b), 5.57 (d, 1H, J = 5.1 Hz, H-1), 5.86 (ddd, 1H, J = 10.2, 16.8 Hz, H-7); ^{13}C NMR (100 Mhz) δ: 9.69 (3×CH_2), 13.65 (3×CH_3), 24.13 (CH_3), 24.93 (CH_3), 2×25.97 (2×CH_3), 27.50 (3×CH_2), 29.15 (3×CH_2), 34.29 (CH, C-6), 68.97 (CH, C-5), 70.31(CH, C-2), 71.53 (CH, C-3), 73.38 (CH, C-4), 97.10 (CH, C-1), 108.07 and 108.95 (2×Cq), 109.59 (CH_2, C-8), 139.21 (CH, C-7); ESI (MeOH) m/z: 583 $(M+Na)^+$; HR-MS 583.2416 calculated for $C_{26}H_{48}O_5NaSn$, found 583.2458.

1,2:3,4-Di-*O*-isopropylidene-6,7,8-trideoxy-6(*R*)-(tri-*n*-butylstannyl)-oct-7-eno-α-D-*galacto*-1,5-pyranose (**12**). Yield 5%; oil; $[\alpha]_D$ –23.8 (c 0.95); ^{1}H NMR (500 MHz) δ: 0.88 (m, 15H, 3×CH_2 and 3×CH_3), 1.29 (m, 6H, 3×CH_2), 1.32 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.49 (m, 6H, 3×CH_2), 1.54 (s, 3H, CH_3), 2.84 (dd, 1H, J = 10.1 Hz, H-6), 3.98 (dd, 1H, J = 10.5 Hz, H-5), 4.24 (dd, 1H, J = 1.8 Hz, H-4), 4.26 (dd, 1H, J = 2.3 Hz, H-2), 4.56 (dd, 1H, J = 7.9 Hz, H-3), 4.77 (d, 1H, J = 10.0 Hz, H-8a), 4.81 (d, 1H, J = 17.0 Hz, H-8b), 5.46 (d, 1H, J = 5.1 Hz, H-1), 5.86 (ddd, 1H, H-7); ^{13}C NMR (125 MHz) δ: 9.94 (3×CH_2), 13.77 (3×CH_3), 24.72 (CH_3), 24.97 (CH_3), 26.07 (CH_3), 26.08 (CH_3), 27.54 (3×CH_2), 29.17 (3×CH_2), 34.18 (CH, C-6), 69.00 (CH, C-5), 70.72 (CH, C-2), 71.26 (CH, C-3), 71.99 (CH, C-4), 96.85 (CH, C-1), 108.19 and 108.71 (2×Cq), 109.07 (CH_2, C-8), 138.56 (CH, C-7); ESI (MeOH) m/z: 583 $(M+Na)^+$; HR-MS 583.2416 calculated for $C_{26}H_{48}O_5NaSn$, found 583.2442.

Thermal decomposition of secondary sugar allyltins 11 and 12. A solution of the corresponding allyltin derivative **11** or **12** (30 mg, 0.053 mmol) was dissolved in dry xylene (3 mL) and boiled under reflux until TLC (hexane – ethyl acetate, 6:1) indicated disappearance of the starting material and formation of a new more polar product (1.5–2 h). The mixture was cooled to room temperature, concentrated and the residue was dissolved in methanol / water (8:1 v/v, 4.5 mL). Sodium borohydride (50 mg) was added and the mixture was stirred for 30 min at room temperature. Toluene (10 mL) was added and the mixture was concentrated to *ca* half volume. Water (0.5 mL) was added and the mixture was left over sodium sulfate (2 g) overnight. The mixture was filtered, concentrated and residue was co-evaporated twice with toluene and finally dissolved in toluene (6 mL). Triethylamine (3 mL) and acetic anhydride (1.5 mL) were added followed by a catalytic amount of DMAP (2 mg) and the mixture was kept at room temperature for 30 min. It was then concentrated in vacuum and the product was isolated by column chromatography (hexane – ethyl acetate, 10:1). From **11** the *cis*-diene **19** (3 mg, 19%) was obtained. Decomposition of **12** afforded **20** (2.5 mg, 16%).

1,2(*S*)-Di-*O*-acetyl-3(*S*),4(*S*)-*O*-isopropylidene-oct-5(Z),7-diene (**19**). Yield 18%; oil; ^{1}H NMR (500 MHz) δ: 1.25, 1.34 (2×s, 2×3H, 2×CH_3), 1.94, 2.06 (2×s, 2×3H, 2×CH_3), 4.11 (dd, 1H, J = 5.3, 12.2 Hz, H-1a), 4.32 (dd, 1H, J = 6.3, 8.7 Hz, H-3), 4.53 (dd, 1H, J = 2.4 Hz, H-1b), 5.01 (ddd, 1H, H-2), 5.15 (dd, 1H, J = 8.0 Hz, H-4), 5.24 (d, 1H, J = 10.5 Hz, H-8a), 5.30 (d, 1H, J = 16.5 Hz, H-8b), 5.41 (dd, 1H, H-5), 6.17 (dd, 1H, J = 10.5 Hz, H-6), 6.60 (ddd, 1H, J = 11.1 Hz, H-7); ESI (MeOH) m/z: 321 $(M+Na)^+$; HR-MS 321.1309 calculated for $C_{15}H_{22}O_6Na$, found 321.1311.

1,2(*S*)-Di-*O*-acetyl-3(*S*),4(*S*)-*O*-isopropylidene-octa-5(*E*),7-diene (**20**). Yield 16%; oil; $[\alpha]_D$ 4.5 (c 1.86); ^{1}H NMR (500 MHz) δ: 1.32, 1.53 (2×s, 2×3H, 2×CH_3), 2.04, 2.07 (2×s, 2×3H, 2×CH_3), 4.07 (dd, 1H, J = 6.7 Hz, H-1a), 4.28 (dd, 1H, J = 4.4, 6.0 Hz, H-3), 4.29 (dd, 1H, J = 11.8, 4.4 Hz, H-1b), 4.71 (dd,

1H, H-4), 5.07 (ddd, 1H, H-2), 5.15 (d, 1H, J = 9.1 Hz, H-8a), 5.25 (d, 1H, J = 14.2 Hz, H-8b), 5.61 (dd, 1H, J = 7.6, 14.2 Hz, H-5), 6.33 (m, 2H, H-6, H-7); ^{13}C NMR (125 MHz) δ: 20.69 (CH_3), 21.09 (CH_3), 25.50, 27.01 (2×CH_3), 62.96 (CH_2, C-1), 69.48 (CH, C-2), 76.35 (CH, C-3), 77.49 (CH, C-4), 109.39 (Cq), 118.97 (CH_2, C-8), 127.07 (CH, C-5), 134.78 and 135.70 (2×CH, C-6, C-7), 169.98 and 170.54 (2×C=O); ESI (MeOH) m/z: 321 $(M+Na)^+$; HR-MS 321.1309 calculated for $C_{15}H_{22}O_6Na$, found 321.1320.

Thermal decomposition of the primary pyranose sugar allyltins 10-*Z* and 21. The organometallic derivative **10-*Z*** or **21** (0.2 mmol) was dissolved in 1,2,4-trichloro-benzene (3 mL) and boiled under reflux for 4 h. After this time the starting material remained unchanged.

Thermal decomposition of the primary furanose sugar allyltins 22 and 23:

1. A 3:2 mixture of furanose derivatives **22** and **23** (180 mg, 0.28 mmol) was dissolved in dichlorobenzene (3 mL) and boiled under reflux for 3 h. After this time all starting material underwent decomposition (TLC in hexane – ethyl acetate, 5:1) to afford more polar product and large amounts of tars. The mixture was cooled to room temperature and the crude product was isolated by column chromatography (hexane – ethyl acetate, 100:1 to 6:1) to afford (18 mg, 0.056 mmol, 20%).
2. The same mixture of furanose derivatives **22** and **23** (180 mg, 0.28 mmol) was refluxed in dichlorobenzene (3 mL) for 3 h. After cooling to room temperature $Ph_3P{=}CHCO_2Me$ (139 mg, 0.42 mmol) was added and the mixture was left at room temp. overnight. The product **25** (24 mg, 23%, visible under the UV light) was isolated by column chromatography (hexane – ethyl acetate, 100:1 then 10:1). When the carboxylate **25** was heated in dichlorobenzene at 180°C for 8 h, less polar product was formed, which was isolated by column chromatography (hexane – ethyl acetate, 100:1 to 10:1) and identified as triene **26**.
3. Pure *cis*-derivative **23** (30 mg, 0.046 mmol) in dichlorobenzene (2 mL) was heated at 180°C for 2 h. The mixture was cooled to room temperature and $Ph_3P{=}CHCO_2Me$ (23 mg, 0.07 mmol) was added and left for 1 h at rt. Then it was heated at 140–180°C for 4 h. After cooling to rt the products were separated by column chromatography (hexane – ethyl acetate, 100:1 to remove dichlorobenzene and then 10:1) to afford *unreacted* **23** (6 mg) and triene **26** (1 mg, 8.3% calculated on consumed **23**).

2(*S*),3(*S*)-Di-*O*-benzyl-hepta-4(*E*),6-dienal (**24**). Yield 20%; oil; $[\alpha]_D$ –18.9 (c 0.86); ^{1}H NMR (200 MHz) δ: 3.90 (dd, 1H, J = 5.7 Hz, H-2), 4.18 (dd, 1H, J = 8.0 Hz, H-3), 4.40 and 4.64 (2×d, 2×1H, J = 12.1 Hz, CH_2), 5.18 (d, 1H, J = 9.8 Hz, H-7a), 5.27 (d, 1H, J = 17.8 Hz, H-8a), 5.71 (dd, 1H, J = 14.4 Hz, H-4), 6.32 (m, 2H, H-5, H-6), 9.62 (d, 1H, CHO); ^{13}C NMR (50 MHz) δ: 71.00 (CH_2), 73.60 (CH_2), 80.01 and 85.52 (2×CH_2, C-2, C-3), 119.46 (CH_2, C-7), 129.67, 136.18, 136.35 (3×CH, C-4,5,6), 202.15 (CHO); ESI (MeOH) m/z: 345 $(M+Na)^+$; HR-MS 345.1461 calculated for $C_{21}H_{22}O_3Na$, found 345.1482.

Methyl 4(*S*),5(*S*)-Di-*O*-benzyl-nona-2(*E*),6(*E*),8-trieneate (**25**). Yield 23%; oil; $[\alpha]_D$ –9.7 (c 1.27); ^{1}H NMR (500 MHz) δ: 3.76 (s, 3H, CH_3), 3.92 (dd, 1H, J = 5.6 Hz, H-5), 4.04 (dd, 1H, H-4), 4.39 and 4.46 (2×d, 2×1H, J = 12.0 Hz, CH_2), 2×4.60 (2×d, 2×1H, J = 12.1 Hz, CH_2), 5.15 (d, 1H, J = 9.9 Hz, H-9a), 5.25 (d, 1H, H-9b), 5.65 (dd, 1H, J = 7.8 Hz, H-6), 6.07 (d, 1H, H-2), 6.26 (dd, 1H, J = 10.6, 15.3 Hz, H-7), 6.37 (ddd, 1H, J = 17.0 Hz, H-8), 6.96 (dd, 1H, J = 6.0, 15.8 Hz, H-3); ^{13}C NMR (125 MHz) δ: 51.60 (CH_3, C-1), 71.62 (CH_2), 71.71 (CH_2), 80.35 and 81.20 (2×CH, C-4,5), 118.26 (CH_2, C-9), 123.01 (CH, C-2), 130.33 (CH, C-6), 135.16 (CH, C-8), 136.07 (CH, C-7), 137.82 and 138.11 (2×Cq), 145.46 (CH, C-3), 166.42 (C=O); ESI (MeOH) m/z: 401 $(M+Na)^+$; HR-MS 401.1723 calculated for $C_{24}H_{26}O_4Na$, found 401.1736.

3(*S*),4(*S*)-Di-*O*-benzyl-octa-1,5(*E*),7-triene (**26**). Yield 8%; oil; $[\alpha]_D$ –11.8 (c 1.02); ^{1}H NMR (500 MHz) δ: 3.86 (m, 1H, H-3), 3.90 (ddd, 1H, J = 0.8, 4.8, 7.8 Hz, H-4), 4.43 and 4.44 (2×d, 2×1H, J = 12.2 Hz, CH_2), 4.63 and 4.64 (2×d, 2×1H, J = 12.2 Hz, CH_2), 5.12 (dd, 1H, J = 1.6, 9.3 Hz, H-8a), 5.23 (dd, 1H, J = 1.1, 16.9 Hz, H-8b), 5.28 (ddd, 1H, J = 1.0, 1.8 Hz, H-1b), 5.31 (ddd, 1H, J = 0.8, 10.5 Hz, H-1a), 5.70 (ddd, 1H, J = 15.4 Hz, H-5), 5.85 (ddd, 1H, J = 7.4, 10.4 Hz, H-2) 6.24 (ddd, 1H, J = 10.9 Hz, H-6), 6.38 (ddd, 1H, H-7); ^{13}C NMR (125 MHz) δ: 2×70.51 (2×CH_2), 81.68 (CH, C-4), 82.51 (CH, C-3), 117.60 (CH_2, C-8), 118.64 (CH_2, C-1), 118.64, 121.14, 127.28, 128.11 (4×CH, C-2,5,6,7); ESI (MeOH) m/z: 343 $(M+Na)^+$; HR-MS 343.1669 calculated for $C_{22}H_{24}O_2Na$, found 343.1693.

Methyl 4(*S*),5(*S*)-di-*O*-benzyl-nona-2(*E*),6(*Z*),8-trieneate (**29**). Yield 71%; oil; $[\alpha]_D$ –28.9 (c 1.08); ^{1}H NMR (500 MHz) δ: 3.74 (s, 3H, CH3), 4.03 (ddd, 1H, J = 5.2 Hz, H-4), 4.37 (ddd, 1H, J = 0.8, 9.3 Hz, H-5), 4.39 and 4.46 (2×d, 2×1H, J = 12.0 Hz, CH_2), 2×4.61 (2×d, 2×1H, J = 12.1 Hz, CH_2), 5.16 (d, 1H, J =

11.0 Hz, H-9b), 5.27 (dd, 1H, J = 0.8, 16.7 Hz, H-9a), 5.42 (dd, 1H, H-6), 6.07 (dd, 1H, J = 1.3, 15.8 Hz, H-2), 6.29 (dd, 1H, J = 11.2 Hz, H-7), 6.44 (ddd, 1H, J = 0.8 Hz, H-8), 6.97 (dd, 1H, J =6.1, H-3); ^{13}C NMR (125 MHz) δ: 51.60 (CH_3, C-1), 70.30 (CH_2), 70.62 (CH_2), 76.14 (CH, C-5), 80.18 (CH, C-4), 119.99 (CH_2, C-9), 123.02 (CH, C-2), 128.24 (CH, C-6), 131.68 (CH, C-8), 134.18 (CH, C-7), 137.78 and 138.01 (2×Cq), 145.28 (CH, C-3), 166.42 (C=O); ESI (MeOH) m/z: 401 $(M+Na)^+$; HR-MS 401.1723 calculated for $C_{24}H_{26}O_4Na$, found 401.1738.

3(*S*),4(*S*)-Di-*O*-benzyl-octa-1,5(*Z*),7-triene (**30**). Yield 57%; oil; $[\alpha]_D$ –11.8 (c 1.02); ^{1}H NMR (500 MHz) δ: 3.88 (dd, 1H, J = 4.6 Hz, H-3), 4.36 (ddd, 1H, J = 0.8, 9.4 Hz, H-4), 4.42 and 4.44 (2×d, 2×1H, J = 12.8 Hz, CH_2), 4.64 and 4.65 (2×d, 2×1H, J = 12.2 Hz, CH_2), 5.15 (d, 1H, J = 10.1 Hz, H-8a), 5.27 (m, 3H, H-1a, H-1b, H-8b), 5.48 (dd, 1H, J = 10.3 Hz, H-5), 5.85 (ddd, 1H, J = 7.6, 10.4, 17.9 Hz, H-2), 6.27 (dd, 1H, J = 11.1 Hz, H-6), 6.49 (ddd, 1H, J = 0.9, 16.7 Hz, H-7); ^{13}C NMR (125 MHz) δ: 70.22 (CH_2), 70.50 (CH_2), 76.40 (CH, C-4), 82.54 (CH, C-3), 118.82 (CH_2, C-1), 119.37 (CH_2, C-8), 129.03, 132.09, 133.52, 135.42 (4×CH, C-2,5,6,7), 138.55 and 138.61 (2×Cq); ESI (MeOH) m/z: 343 $(M+Na)^+$; HR-MS 343.1669 calculated for $C_{22}H_{24}O_2Na$, found 343.1701.

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