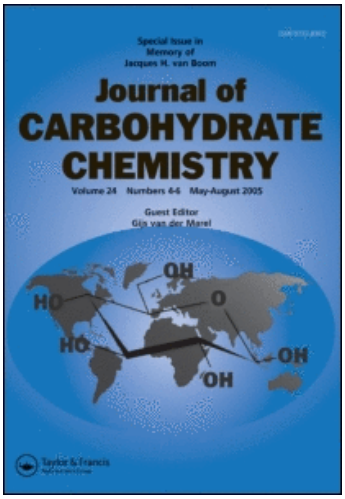

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Synthesis of the *Trans* and *Cis* Higher Sugar Allylic Alcohols—Direct Precursors of Dodecoses

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SYNTHESIS OF THE *TRANS* AND *CIS* HIGHER SUGAR ALLYLIC ALCOHOLS - DIRECT PRECURSORS OF DODECOSES

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ABSTRACT

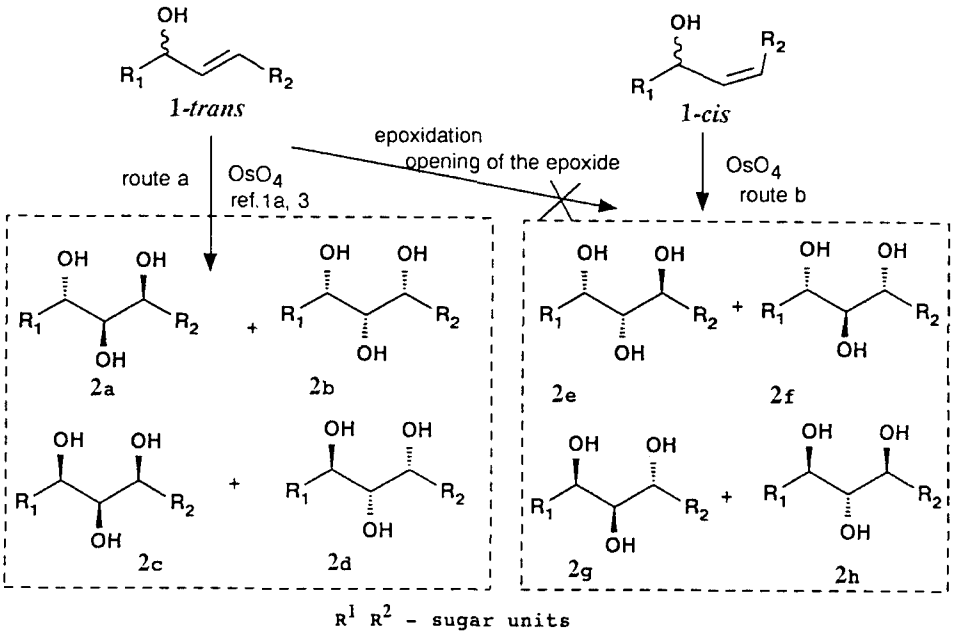
Reaction of 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6-ynopyranose (**3**) with 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodiulose (**4**) afforded two diastereoisomeric propargylic alcohols: **5a** (D-*glycero*, *R*) and **5b** (L-*glycero*, *S*) in 70% yield and in the 33:67 ratio. Hydrogenation of **5a** and **5b** over $Pd/BaSO_4$ gave *cis*-allylic alcohols **6a** and **6b**. Semireduction of the triple bond in **3** with tri-*n*-butyltin hydride afforded *trans*-olefin **7** which reacted with **4** yielding two diastereoisomeric *trans*-allylic alcohols: **8a** (D-*glycero*, *R*) and **8b** (L-*glycero*, *S*) in a 74% yield and a 72:28 ratio.

INTRODUCTION

The synthesis of sugars containing more than ten carbon atoms in the chain has gained considerable attention in the past few years,[1] since: *a)* the *C*-analogs of disaccharides (so-called *C*-disaccharides) may be regarded as unnatural glycosidase inhibitors, *b)* they are components of some antibiotics,[2] and *c)* the preparation of such complicated molecules presents a challenge for organic chemists.

Allylic alcohols substituted at both ends of the allylic system with different monosaccharide units are convenient precursors of higher carbon sugars. Stereoselective functionalization of the allylic bridge should afford eight isomeric triols **2a - 2h**. Recently we reported[1a,3] that osmylation of the *trans* higher sugar allylic alcohols (**1**) followed the empirical Kishi's rule[4]. Four (**2a - 2d**) of the eight possible triols were formed (route a in Scheme 1).

SCHEME 1

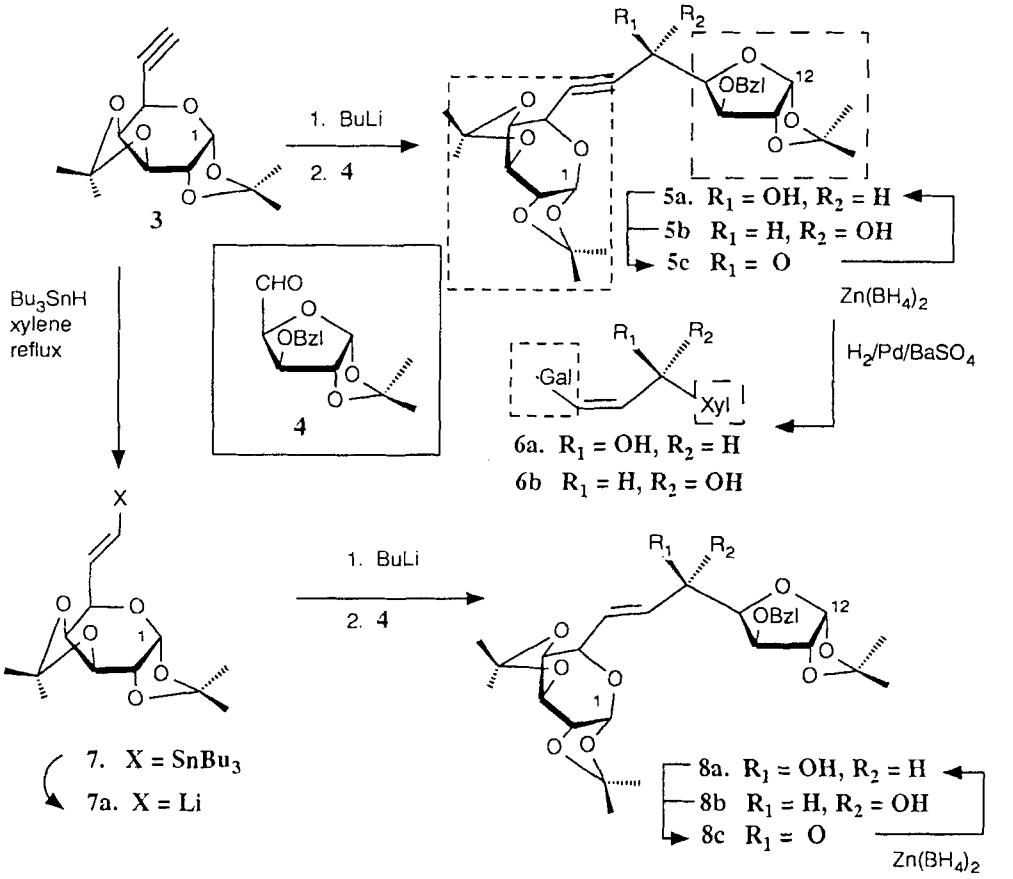


However, epoxidation of *trans*-**1** was troublesome[5] and the remaining four triols (**2e - 2h**) could not be obtained in this way. Synthesis of these compounds (**2e - 2h**), might eventually be achieved by osmylation of sugar-derived *cis* allylic alcohols (route b in Scheme 1).

RESULTS and DISCUSSION

To accomplish the synthesis of all eight isomeric higher sugars (resulting from the functionalization of the allylic fragment), a convenient route to the *trans* (*R* and *S*) and *cis* (*R* and *S*) allylic alcohols, substituted at both ends with different sugar units, is needed. For the model synthesis of such alcohols 6,7-dideoxy-1,2:3,4-di-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranose[6] (**3**) was chosen as starting material.

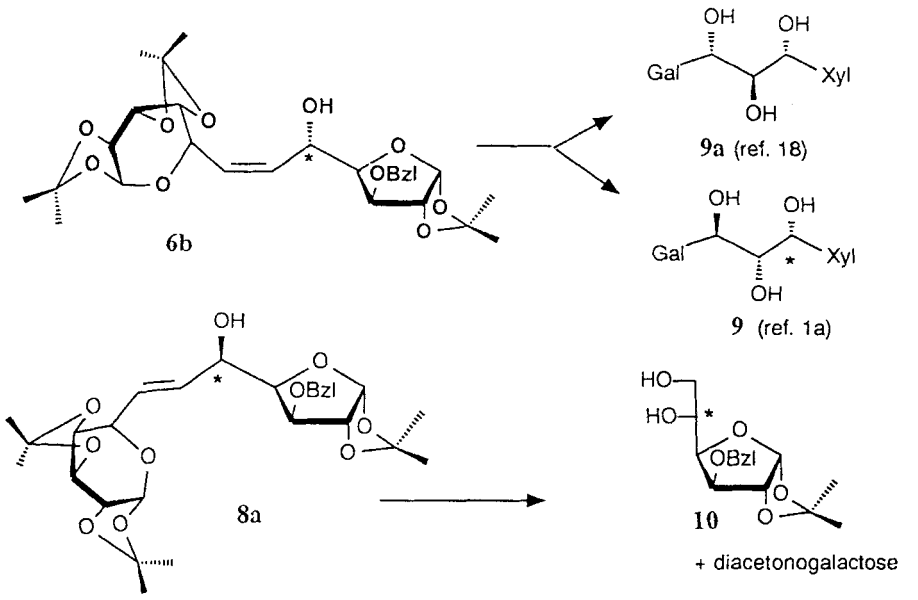
SCHEME 2



The anion generated from **3** reacted with 3-*O*-benzyl-1,2-*O*-isopropylidene- α -D-*xylo*-pentodiulose[7] (**4**) to afford a mixture of higher sugar propargylic alcohols **5a** (D-*glycero*, *R*) and **5b** (L-*glycero*, *S*) in 70% yield and in the 33:67 ratio (Scheme 2). These products were conveniently reduced (H_2/Pd/$BaSO_4$) to *cis* alcohols **6a** and **6b** (J_{olef} = 11 Hz). On the other hand, semireduction of the triple bond with tri-*n*-butyltin hydride[8] (in boiling xylene under an argon atmosphere, for 30 h) afforded the *trans*-vinyltin olefin **7** (together with a small amount of the *cis*-isomer). Treatment of **7** with butyllithium gave the sugar vinyl anion[8b] (**7a**) which reacted with **4** furnishing *trans* (J_{olef} = 15.5 Hz) higher sugar allylic alcohols **8a** (D-*glycero*, *R*) and **8b** (L-*glycero*, *S*) in a 74% yield and a 72:28 ratio.

Oxidation of **5a** and **5b** with the Jones reagent afforded the same ketone **5c**, while oxidation of **8a** and **8b** gave the same enone **8c**, proving that pairs **5a**,**5b** and **8a**,**8b** were diastereoisomers. Recently we reported that reduction of higher sugar enones (of the D-series)

SCHEME 3

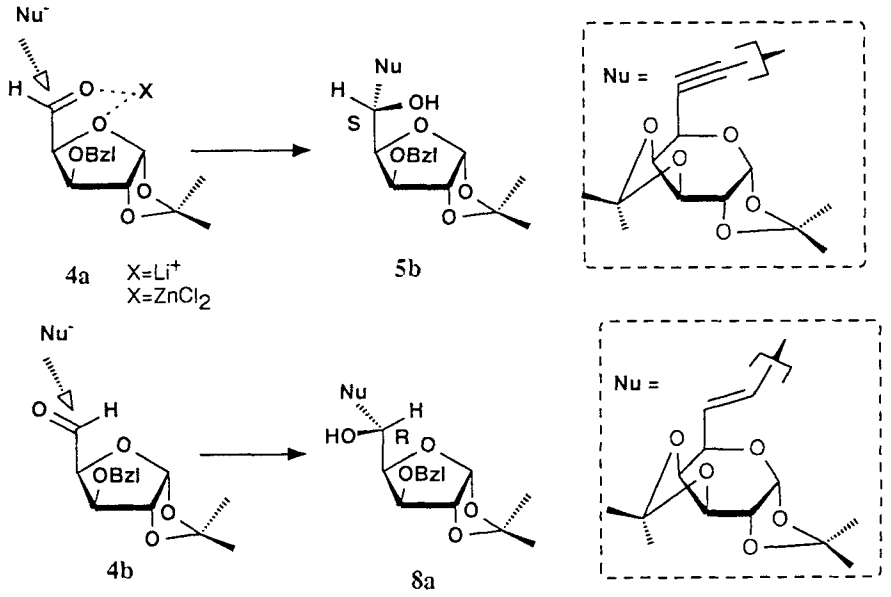


with zinc borohydride is highly stereoselective and affords allylic alcohols having the D-*glycero*-(*R*) configuration at the new chiral center.[9] We assumed, therefore, that the products of the reduction of **5c** and **8c** with zinc borohydride (**5a** and **8a**, respectively) should have *R*-configurations at the carbinol center.[9] This assumption was verified by chemical and spectral correlations performed for the major stereoisomers **6b** and **8a** (obtained in the condensation of either **3** or **7a** with **4**).

Osmylation of the *cis*-alcohol **6b** (OsO_4/NMO in THF) afforded (as one of the products) triol **9**, which was identical (^1H NMR, 500 MHz) with compound prepared independently,[1a] proving the *S*-configuration at the new chiral center. On the other hand, cleavage of the double bond in the *trans* isomer **8a** with ozone followed by reduction of the ozonide (first with triphenylphosphine then with $LiAlH_4$) afforded 3-*O*-benzyl-1,2-*O*-isopropylidene- α-D-glucofuranose,[10] suggesting formation of an *R*-configuration at the new chiral center in **8a**.

Stereoselectivity in reaction of the acetylene **3** with aldehyde **4** could be explained by complexation of the aldehyde with lithium cation,[11] fixing the conformation of the reacting molecule (Scheme 4, **4a**). Attack of nucleophile from the less hindered side of the carbonyl group afforded the *S*-stereoisomer (**5b**) as the main product. When a better complexing agent - zinc chloride - was used, the stereoselectivity was even higher;[12] the ratio of *S*:*R* isomers was

SCHEME 4



88:12. To explain the opposite stereoselectivity of the addition of vinyllithium **7a** to **4**, the non-complexed model (Scheme 4, **4b**) was used.[13] Attack of the nucleophile from the same side led to the ***R*** isomer **8a** as the main product.

EXPERIMENTAL

General. - All reactions with anions were performed under an argon atmosphere. ^{1}H NMR spectra were recorded with a Bruker AM-500 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). Column chromatography was performed on silica gel (Merck, 230-400 mesh and Maherey-Nagel, 70-270 mesh). Acetates **8a-Ac** and **8b-Ac** were prepared from parent alcohols by reaction with acetic anhydride in pyridine in the presence of *N,N*-dimethylaminopyridine (DMAP). For numering of protons see Scheme 2.

1,2:3,4:Di-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranose (3). To a solution of **1,2:3,4:di-*O*-isopropylidene- α -D-*galacto*-hexo-1,5-dialdose**[15] (10 g, 38.8 mmol), in dry benzene (500 mL), triphenylphosphine (4 equiv, 155 mmol, 40.6 g) and carbon tetrabromide (2 eqiuv, 77.6 mmol, 25.8 g) were added and the mixture was stirred overnight at room temperature. Precipitated triphenylphosphine oxide was filtered off, the filtrate was

concentrated to dryness, and the residue was dissolved in dry ether. Insoluble material (triphenylphosphine oxide) was filtered off and ether solution was concentrated to dryness. The residue was dissolved in dry tetrahydrofuran (300 mL) and cooled to -78 °C. A solution of *n*-BuLi (1.6 M in hexane, 2.4 equiv, 93 mmol, 58 mL) was added dropwise during 30 min and the resulting solution was stirred 2 h at -78 °C and 1 h at room temperature. Saturated ammonium chloride solution (100 mL) was added and the product was extracted with ether (3 x 200 mL). Purification of the crude material by column chromatography (hexane - acetone, 9:1 to 4:1) afforded acetylene **3**,[6] isolated as an oil (5.2 g, 20.47 mmol, 53% overall). ^{1}H NMR data: 5.56 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.33 (dd, 1 H, $J_{2,3}$ 2.5 Hz, **H-2**), 4.63 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.30 (dd, 1 H, $J_{4,5}$ 2.2 Hz, **H-4**), 4.61 (t, 1 H, $J_{5,7}$ 2.2 Hz, **H-5**), 2.54 (d, 1 H, **H-7**), 1.55, 1.54, 1.39 and 1.34 (4s, 2 x CMe_2).

Condensation of 1,2:3,4:di-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranose (3) with 3-*O*-benzyl-1,2-*O*-isopropylidene- α -D-*xylo*-pentodialdose (4). To a solution of **3** (360 mg, 1.41 mmol) in dry benzene (10 mL) at room temperature was added 1 M solution of $LiN(TMS)_2$ in tetrahydrofuran (1.7 mL, 1.2 equiv) and the resulting mixture was stirred for 40 min. Aldehyde **4** (470 mg, 1.7 mmol) in benzene (4 mL) was added dropwise, the mixture was stirred for another 40 min and quenched with *ca.* 5% aqueous ammonium chloride. The product was extracted with ether (3 x 20 mL) and column chromatography (hexane - ethyl acetate, 8:1 to 3:1) of the crude material afforded:

- 3-*O*-benzyl-6-*C*-(6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranos-6-ylidine)-1,2-*O*-isopropylidene- α -D-glucofuranose (**5b**, 178 mg, 0.34 mmol, 23.7%). ^{1}H NMR data: 5.55 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.36 (dd, 1 H, $J_{2,3}$ 2.5 Hz, **H-2**), 4.60 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.29 (dd, 1 H, $J_{4,5}$ 2.0 Hz, **H-4**), 4.65 (d, 1 H, $J_{8,9}$ 4.7 Hz, **H-8**), 4.36 (dd, 1 H, $J_{9,10}$ 3.6 Hz, **H-9**), 4.02 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.59 (d, 1 H, $J_{11,12}$ 3.6 Hz, **H-11**), 6.05 (d, 1 H, **H-12**), 1.54, 1.51, 1.49, 1.33, 1.31, and 1.24 (6 s, 18 H, 3 x CMe_2)

  Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.1; H, 6.8. Found: C, 62.9; H, 7.0.

- 3-*O*-benzyl-6-*C*-(6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranos-6-ylidine)-1,2-*O*-isopropylidene- β -L-idofuranose (**5a**, foam, 344 mg, 0.65 mmol, 46%). ^{1}H NMR data: 5.54 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.30 (dd, 1 H, $J_{2,3}$ 2.5 Hz, **H-2**), 4.57 (dd, 1 H, $J_{3,4}$ 8.5 Hz, **H-3**), 4.22 (dd, 1 H, $J_{4,5}$ 1.8 Hz, **H-4**), 4.81 (d, 1 H, $J_{8,9}$ 3.4 Hz, **H-8**), 4.39 (dd, 1 H, $J_{9,10}$ 3.6 Hz, **H-9**), 4.21 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.59 (d, 1 H, $J_{11,12}$ 3.7 Hz, **H-11**), 5.96 (d, 1 H, **H-12**), 1.54, 1.51, 1.49, 1.33, 1.31, and 1.24 (6 s, 18 H, 3 x CMe_2)

  Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.1; H, 6.8. Found: C, 63.0; H, 6.9.

Reaction of acetylene 3 with aldehyde 4 in the presence of zinc chloride. To a solution of aldehyde **4** (334 mg, 1.2 mmol) in dry THF (10 mL) a solution of $ZnCl_2$ in ether (0.5 M solution, 2.4 mL) was added and the mixture was kept at room temperature for 15 min. Then it was added dropwise to a solution of acetylene anion in benzene (generated from 244 mg, 0.96 mmol of **3** as described above), the mixture was stirred at room temperature for 45 min and then worked up as in the experiment without catalyst. Purification of the crude material by column chromatography afforded unreacted **3** (170 mg), **5a** (27 mg) and **5b** (198 mg).

Reaction of 1,2:3,4:di-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranose (3) with tri-*n*-butyltin hydride. To a solution of **3** (2.54 g, 10 mmol) in dry xylene, tri-*n*-butyltin hydride (3.3 mL, 1.2 equiv) was added, followed by a catalytic amount of azo-bis-isobutyronitrile (AIBN). The mixture was refluxed under an argon atmosphere until TLC (hexane - ethyl acetate, 3:1) showed disappearence of the starting material (*ca.* 8 h). The ^1H NMR spectrum of the crude product indicated the mixture of the *trans* ($\delta_{olef.}$ 6.28 and 6.05, $J_{olef.}$ 19.3 Hz) and *cis* ($\delta_{olef.}$ 6.55 and 6.12, $J_{olef.}$ 13.8 Hz) olefins in the ratio 1:4. Prolonged heating caused isomerisation of the *cis* olefin into the more stable *trans* isomer **7**, which was isolated by column chromatography (hexane - ether, 9:1) as a colorless oil (4.46 g, 8.18 mmol, 81.8%).

Reaction of 7 with aldehyde 4. To a cooled (to -78 °C) solution of **7** (1.286 g, 2.36 mmol) in dry tetrahydrofuran (20 mL), a solution of *n*-BuLi (1.6 M in hexane, 1.8 mL, 1.2 equiv) was added and the mixture was stirred at this temperature for 1 h. Aldehyde **4** (790 mg, 2.83 mmol, 1.2 equiv) in THF (10 mL) was added dropwise and the mixture was stirred for 1 h at -78 °C and 1 h at room temperature. Saturated ammonium chloride solution (5 mL) was added and the product was extracted with ether (3 x 25 mL). The organic phase was washed with water (2 x 10 mL), dried and concentrated and the product was purified by column chromatography (hexane - ethyl acetate, 5:1) to afford:

- 3-*O*-benzyl-6-*C*-[6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6(*E*)-enopyranos-6-ylidene]-1,2-*O*-isopropylidene- α -D-glucofuranose (**8a**, foam, 673 mg, 1.26 mmol, 53%) which was characterized as acetate **8a-Ac**. ^1H NMR data: 5.55 (d, 1 H, $J_{1,2}$ 5.1 Hz, **H-1**), 4.29 (dd, 1 H, $J_{2,3}$ 2.4 Hz, **H-2**), 4.57 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.15 (dd, 1 H, $J_{4,5}$ 2.0 Hz, **H-4**), 4.29 (m, 1 H, **H-5**), 5.92 (dd, 1 H, $J_{5,6}$ 3.8, $J_{6,7}$ 15.8 Hz, **H-6**), 5.87 (dd, 1 H, $J_{7,8}$ 5.0 Hz, **H-7**), 5.63 (dd, 1 H, $J_{8,9}$ 8.6 Hz, **H-8**), 4.22 (dd, 1 H, $J_{9,10}$ 3.3 Hz, **H-9**), 3.95 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.59 (d, 1 H, $J_{11,12}$ 3.7 Hz, **H-11**), 5.89 (d, 1 H, **H-12**), 1.92 (s, 3 H, **OAc**), 1.53, 1.49, 1.42, 1.33, 1.31, and 1.30 (6 s, 18 H, 3 x CMe_2).

Anal. Calcd for $C_{30}H_{40}O_{11}$: C, 62.5; H, 7.0. Found: C, 62.7; H, 7.1.

- 3-*O*-benzyl-5-*C*-[6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6(*E*)-enopyranos-6-ylidene]-1,2-*O*-isopropylidene- β -L-idofuranose (**8b**, oil, 261 mg, 0.49 mmol, 21%) which was characterized as acetate **8b-Ac**. ^{1}H NMR data: 5.57 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.30 (dd, 1 H, $J_{2,3}$ 2.3 Hz, **H-2**), 4.57 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.09 (dd, 1 H, $J_{4,5}$ 2.0 Hz, **H-4**), 4.29 (m, 1 H, **H-5**), 5.91 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,7}$ 15.5 Hz, **H-6**), 5.71 (dd, 1 H, $J_{7,8}$ 7.7 Hz, **H-7**), 5.74 (dd, 1 H, $J_{8,9}$ 1.6 Hz, **H-8**), 4.29 (dd, 1 H, $J_{9,10}$ 3.3 Hz, **H-9**), 3.92 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 5.89 (d, 1 H, $J_{11,12}$ 3.6 Hz **H-12**), 2.06 (s, 3 H, **OAc**), 1.48 (s, 6 H, **CMe$_2$**), 1.51, 1.33, 1.31, and 1.28 (4 s, 12 H, 2 x **CMe$_2$**).

Anal. Calcd for $C_{30}H_{40}O_{11}$: C, 62.5; H, 7.0. Found: C, 62.2; H, 6.9.

Reaction of vinyltin derivative 7 with 4 in the presence of zinc chloride. To a solution of aldehyde **4** (200 mg, 0.72 mmol) in dry THF (10 mL), a solution of $ZnCl_2$ in ether (0.5 M solution, 1.5 mL) was added and the mixture was kept at room temperature for 15 min. The mixture was then added dropwise to a solution of vinyl anion in THF at -78 °C (generated from 320 mg, 0.59 mmol of **7** as described above), and the resulting mixture stirred for 45 min at -78 °C and 15 min at room temperature, and then worked up as in the experiment without catalyst. Purification of the crude material by column chromatography (hexane - ethyl acetate, 4:1) afforded **8a** (72 mg) and **8b** (78 mg). A significant amount (50 mg) of the hydrolyzed product **7b** (X=H) was also isolated.

- **3-*O*-Benzyl-6-*C*-[6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6-ynopyranos-7-ylidine]-1,2-*O*-isopropylidene- α -D-*xylo*-hexofuranos-5-ulose (5c).** A solution of the propargylic alcohol (**5a** or **5b**, *ca.* 100 mg) in acetone (10 mL) was titrated with the Jones reagent[16] until TLC (hexane - ethyl acetate, 3:1) showed disappearence of the starting material and formation of a new, less polar compound that was visible under UV light. The mixture was diluted with ether (30 mL) washed with water (3 x 10 mL), dried and concentrated, and the product was isolated by column chromatography (hexane - ethyl acetate, 5:1) to give **5c** (oil, the yields in both reactions were *ca.* 85%). ^{1}H NMR data: 5.56 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.34 (dd, 1 H, $J_{2,3}$ 2.6 Hz, **H-2**), 4.61 (dd, 1 H, $J_{3,4}$ 7.7 H, **H-3**), 4.26 (dd, 1 H, $J_{4,5}$ 2.1 Hz, **H-4**), 4.74 (d, 1 H, **H-5**), 4.99 (d, 1 H, $J_{9,10}$ 3.6 Hz, **H-9**), 4.55 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.60 (d, 1 H, $J_{11,12}$ 3.6, **H-11**), 6.07 (d, 1 H, **H-12**), 1.55, 1.48, 1.41, 1.34, 1.31, and 1.26 (6 s, 18 H, 3 x **CMe$_2$**).

Anal. Calcd for $C_{28}H_{34}O_{10}$: C, 63.4; H, 6.5. Found: C, 63.3; H, 6.7.

3-*O*-Benzyl-6-*C*-[6,7-dideoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6(*E*)-enopyranos-7-ylidine]-1,2-*O*-isopropylidene- α -D-*xylo*-hexofuranos-5-ulose (8c). The oxidation

reaction was performed in the same manner as for **5a** and **5b** to give **8c** (oil, 85 mg from **8a** and 80 mg **8b**). ^{1}H NMR data: 5.61 (d, 1 H, $J_{1,2}$ 5.0 Hz, **H-1**), 4.35 (dd, 1 H, $J_{2,3}$ 2.4 Hz, **H-2**), 4.63 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.27 (dd, 1 H, $J_{4,5}$ 2.1 Hz, **H-4**), 4.47 (m, 1 H, **H-5**), 6.96 (dd, 1 H, $J_{5,6}$ 4.1, $J_{6,7}$ 15.6 Hz, **H-6**), 6.83 (dd, 1 H, $J_{5,7}$ 1.7 Hz, **H-7**), 4.85 (d, 1 H, $J_{9,10}$ 3.4 Hz, **H-9**), 4.34 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.58 (d, 1 H, $J_{11,12}$ 3.6, **H-11**), 6.10 (d, 1 H, $J_{11,12}$ 3.6 Hz **H-12**), 1.51, 1.48, 1.37, 1.35, 1.32, and 1.28 (6 s, 18 H, 3 x CMe_2).

Anal. Calcd for $C_{28}H_{36}O_{10}$ H_2O: C, 61.1; H, 7.0. Found: C, 61.3; H, 7.1.

Reduction of propargylic alcohols 5a and 5b. A solution of **5a** or **5b** (*ca.* 500 mg) in dry benzene (30 mL) was hydrogenated in the presence of $Pd/BaSO_4$ until the theoretical amount of hydrogen was consumed. The catalyst was filtered off and the crude product was purified by column chromatography (hexane - ethyl acetate, 3:1) to give **6a** (92% yield) or **6b** (95% yield).

- 3-*O*-benzyl-6-*C*-[6-deoxy-1,2-*O*-isopropylidene- α-D-*galacto*-hept-6(*Z*)-enopyranos-6-ylidene]-1,2-*O*-isopropylidene- α -D-glucofuranose (**6a**). ^{1}H NMR data: 5.53 (d, 1 H, $J_{1,2}$ 5.1 Hz, **H-1**), 4.30 (dd, 1 H, $J_{2,3}$ 2.4 Hz, **H-2**), 4.59 (dd, 1 H, $J_{3,4}$ 7.8 Hz, **H-3**), 4.23 (dd, 1 H, $J_{4,5}$ 1.9 Hz, **H-4**), 5.76 (dd, 1 H, $J_{5,6}$ 1.3, $J_{6,7}$ 11.4 Hz, **H-6**), 5.69 (dd, 1 H, $J_{7,8}$ 6.8 Hz, **H-7**), 4.20 (dd, 1 H, $J_{9,10}$ 3.4 Hz, **H-9**), 4.16 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.62 (d, 1 H, $J_{11,12}$ 3.9 Hz, **H-11**), 5.89 (d, 1 H, **H-12**), 1.55, 1.48, 1.41, 1.34, 1.31, and 1.26 (6 s, 18 H, 3 x CMe_2)

Anal. Calcd for $C_{28}H_{38}O_{10}$: C, 62.9; H, 7.2. Found: C, 63.1; H, 7.3

- 3-*O*-benzyl-5-*C*-[6-deoxy-1,2-*O*-isopropylidene- α -D-*galacto*-hept-6(*Z*)-enopyranos-6-ylidene]-1,2-*O*-isopropylidene- β -L-idofuranose (**6b**). ^{1}H NMR data: 5.50 (d, 1 H, $J_{1,2}$ 5.1 Hz, **H-1**), 4.24 (dd, 1 H, $J_{2,3}$ 2.4 Hz, **H-2**), 4.44 (dd, 1 H, $J_{3,4}$ 7.9 Hz, **H-3**), 4.08 (dd, 1 H, $J_{4,5}$ 2.1 Hz, **H-4**), 5.71 (dd, 1 H, $J_{5,6}$ 7.5, $J_{6,7}$ 11.6 Hz, **H-6**), 5.62 (dd, 1 H, $J_{7,8}$ 7.2 Hz, **H-7**), 4.75 (t, 1 H, $J_{8,9}$ 7.2 Hz, **H-8**), 4.18 (dd, 1 H, $J_{9,10}$ 3.4 Hz, **H-9**), 3.92 (d, 1 H, $J_{10,11}$ 0 Hz, **H-10**), 4.59 (d, 1 H, $J_{11,12}$ 3.8 Hz, **H-11**), 5.95 (d, 1 H, **H-12**), 1.53, 1.49, 1.46, 1.33, 1.32, and 1.26 (6 s, 18 H, 3 x CMe_2).

Anal. Calcd for $C_{28}H_{38}O_{10}$: C, 62.9; H, 7.2. Found: C, 63.0; H, 7.4

Reduction of ketone 5c with zinc borohydride. To a solution of **5c** (150 mg, 0.28 mmol) in dry ether at 0 °C was added a solution of zinc borohydride[17] (0.3 mL of *ca.* 1.0 M solution in ether) and the reaction was stirred at 0 °C for 30 min. The excess of hydride was decomposed with water and the product was purified by column chromatography (hexane - ethyl acetate, 5:1) to afford **5a** (120 mg) and **5b** (10 mg).

Reduction of ketone 8c with zinc borohydride. This reaction was performed analogously as above to give **8a** (85%) and **8b** (4%).

Determination of the configuration of 6b. This reaction was performed according to reference 3. To a solution of **6b** in THF (5 mL), *tert*-butyl alcohol (0.3 mL) and water (0.1 mL) *N*-methylmorpholine-*N*-oxide (50 mg) was added followed by catalytic amount of osmium tetraoxide (0.2 mL of *ca.* 2% solution in *tert*-butyl alcohol). The mixture was stirred at room temperature for 2 days, diluted with methanol (5 mL) and OsO_4 was decomposed with sodium hydrogen sulfite (3 mL of 40% solution in water). Column chromatography (hexane - ethyl acetate, 3:2) of the crude material afforded:

- 3-*O*-benzyl-6-*C*-(1,2-*O*-isopropylidene-D-*glycero*- α -D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-L-*glycero*- β -L-*ido*-hexofuranose[18] (**9a**, 90 mg),
- 3-*O*-benzyl-6-*C*-(1,2-*O*-isopropylidene-L-*glycero*- α --D-*galacto*-hexopyranos-6-yl)-1,2-*O*-isopropylidene-D-*glycero*- β -L-*ido*-hexofuranose (**9**, 14 mg). The ^{1}H NMR spectrum of this compound was identical with the spectrum of **9** prepared according to reference 1a.

Determination of the configuration of 8a. Olefin **8a** (110 mg, 0.21 mmol) was dissolved in methylene chloride and cooled to -78 °C. Ozone was passed through the solution until the blue color persisted (5 min.). Triphenylphosphine (200 mg) was added, the mixture was kept 30 min at room temperature, and the solution was concentrated to dryness. The residue was dissolved in dry THF (10 mL) and reduced with lithium aluminum hydride (20 mg). Usual work-up followed by column chromatography (hexane - ethyl acetate, 3:1 to 1:1) afforded: 1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose (39 mg, 0.15 mmol, 71%) and 3-*O*-benzyl-1,2-*O*-isopropylidene- α -D-glucofuranose[10] (**10**, 48 mg, 0.155 mmol, 74%). The ^{1}H NMR spectra of both degradation products were identical with the spectra of compounds prepared independantly.

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