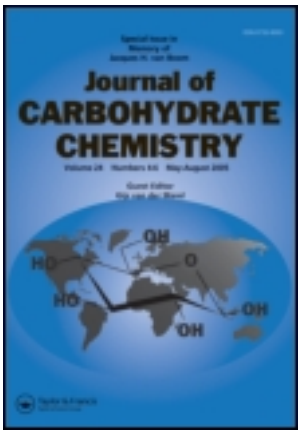

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

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Published online: 27 Feb 2008.

To cite this article: Slawomir Jarosz , Mateusz Mach & Jadwiga Frelek (2000) Synthesis and Structural Analysis of Higher Analogs of Sucrose, Journal of Carbohydrate Chemistry, 19:6, 693-715, DOI: 10.1080/07328300008544111

To link to this article: http://dx.doi.org/10.1080/07328300008544111

J. CARBOHYDRATE CHEMISTRY, 19(6), 693–715 (2000)

SYNTHESIS AND STRUCTURAL ANALYSIS OF HIGHER ANALOGS OF SUCROSE

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Received July 23, 1999 - Final Form February 22, 2000

ABSTRACT

Three sucrose monoalcohols with free hydroxyl groups at C-1', C-6, and C-6' (**1**, **4**, and **6**) were prepared selectively and in good yield from 2,3,3',4,4'-penta-*O*-benzylsucrose. These compounds were oxidized to aldehydes and reacted with stabilized ylide, $Ph_3P{=}CHCO_2Me$ to afford appropriate α,β-unsaturated esters **10**, **11**, and **12**. Each olefin was *cis*-hydroxylated with OsO_4/NMO to stereoisomeric diols **13/14**, **15/16**, and **17/18**, configurations of which were assigned by chemical correlation and CD evaluation. Stereoselectivity of the osmylation reaction was surprisingly low (*ca* 3:2), especially as compared to a similar process performed on simple derivatives of 6,7-unsaturated methyl glycosides for which the ratio of isomeric diols was assigned as 10:1. The osmylation of **11** (derivative homologated by a C_2-unit at the glucose part) did not obey Kishi's rule. Horner-Emmons reaction of sucrose aldehyde **7** with a sugar-derived phosphonate **22** afforded α,β-unsaturated derivative **24**, homologated by a C_7-unit at the glucose end.

INTRODUCTION

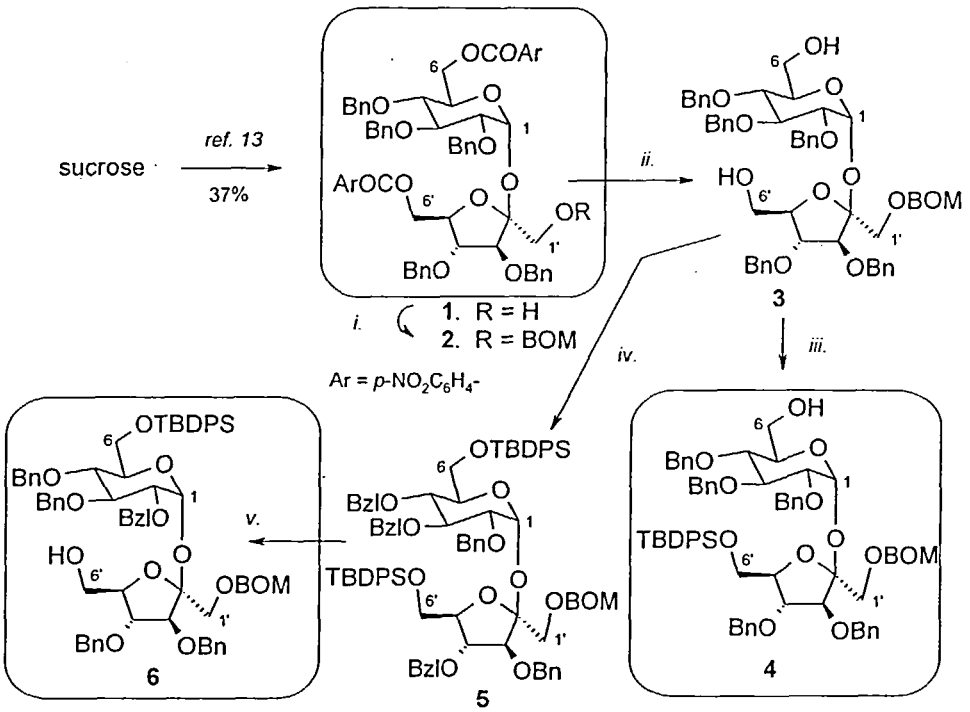
Selective mono-protection of sucrose, with eight free hydroxyl groups, is a significant challenge for chemists.[1] Only differentiation between the primary and secondary hydroxyl groups is rather straightforward and 1',6,6'-tri-*O*-tritylsucrose is prepared readily in good yield by reaction of sucrose with a large excess of trityl chloride.[2] However, differentiation between primary hydroxyl groups with this reagent is not possible; reaction of sucrose with 1 equivalent of trityl chloride affords a mixture consisting of two mono- (at C-6 and C-6') and di-protected (at C-6,6') derivatives in low yield.[1] Selective silylation can be achieved with bulky silyl chlorides; silylation of a free sucrose with *tert*-butyldiphenylsilyl chloride is, to a large extent, regioselective and - depending on the stoichiometry and reaction conditions - the 6'-mono-, 6,6'-di-, and 1',6,6'-tri-substituted derivatives are obtained in good yields.[3] Esterification of free sucrose with bulky pivaloyl chloride affords a mixture of C-6, and C-6' mono- and disubstituted derivatives.[4] 6-*O*-Acetylsucrose[5] can be obtained in 40% yield by selective acetylation of a free sugar at -40 °C. Enzymatic acylation of sucrose selectively protects neopentyl-like 1'-OH to give 1'-*O*-acylsucroses,[6] while 6'-*O*-acylsucroses may be obtained by action of 3-acyl-5-methyl-1,3,4-thiadiazole-2(3H)-thiones on sucrose in the presence of strong organic bases (*e.g.*, DABCO).[7] Conversion of the most reactive primary hydroxyl groups at C-6, C-6' into difluoride,[8] dichloride,[9] dibromide,[10] and diiodide[11] was also described. Another serious problem encountered in chemical transformations of sucrose is the sensitivity of the glycosidic linkage towards acids; it is cleaved completely within 30 min in 0.1% methanolic hydrogen chloride.[12]

As a part of an on-going program directed towards modified sucrose derivatives, we elaborated a convenient method for the preparation of 2,3, 3',4,4'-penta-*O*-benzylsucrose from the free disaccharide in 50% overall yield.[13] Surprisingly, this compound has been not known, although the benzyl protecting groups are widely used in carbohydrate chemistry.[14] This convenient starting material has been converted in 73% yield into 2,3,3',4,4'-penta-*O*-benzyl-6,6'-di-*O*-*p*-nitrobenzoylsucrose[13] (**1**).

RESULTS AND DISCUSSION

The synthesis of the higher analogs of sucrose started from this readily available

intermediate **1**. Methods for the preparation of two other sucrose monoalcohols protected at the C-1' position with the easily removable, under neutral conditions, benzyloxymethyl group (BOM) essentially followed those published earlier by us for the preparation of the 1'-MOM derivatives.[15]

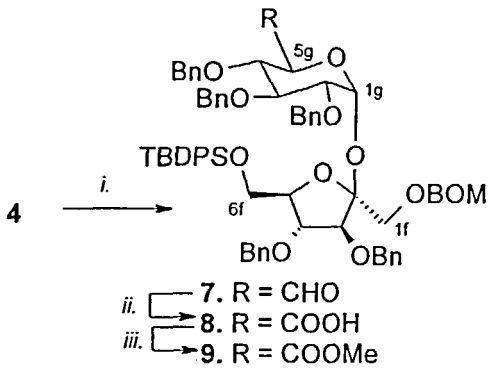


Scheme 1. *i.* BOMCl, py, 80%; *ii.* MeONa, MeOH, 72%; *iii.* TBDPSCl (1 equiv.), CH_2Cl_2, DMAP, iPr_2NEt, 80%; *iv.* TBDPSCl (3 equiv.), DMF, NaH, 95%; *v.* HF- py, 68%

Treatment of **1** with benzyloxymethyl chloride in pyridine afforded 80% of fully protected derivative **2**. Removal of the ester functions from **2** under Zemplen's conditions furnished diol **3** in good yield, in which two remaining primary hydroxyl groups (at C-6,6') could be differentiated with bulky silyl reagents. Treatment of **3** with *tert*-butyldiphenylsilyl chloride (TBDPSCl) afforded 69% (or 80% calculated on consumed **2**) of **4** with the free 6-OH and 11% of the disubstituted compound **5**. The last monoalcohol **6** (with the 6'-OH free) was prepared by selective desilylation of **5** using an excess of HF/pyridine complex in methanol; no formation of **4** has been noted. Thus, alcohol **6** could be obtained in good overall yield, since the intermediate **5** could be prepared from diol **3** almost quantitatively

by reaction of the dianion of **3** with an excess of *tert*-butyldiphenylsilyl chloride (Scheme 1). These results are consistent with our previous observations.[15]

Although it was difficult to assign the structures of alcohols **4** and **6** directly from their NMR spectra, it could be done unequivocally from the ^{1}H NMR spectrum of methyl uronate **9** obtained from **4** (Scheme 2). The highly downfield shifted signal of H-5g (the 'glucose part') in the spectrum of **9** (^{1}H-^{1}H COSY) was observed as a doublet with the only coupling to the H-4g of the glucose ring (δ = 4.98 ppm, $J_{4,5}$ = 9.0 Hz). Compound **4**, therefore, had the 6-OH free, and, consequently, the remaining alcohol **6** had the 6'-OH position unprotected.



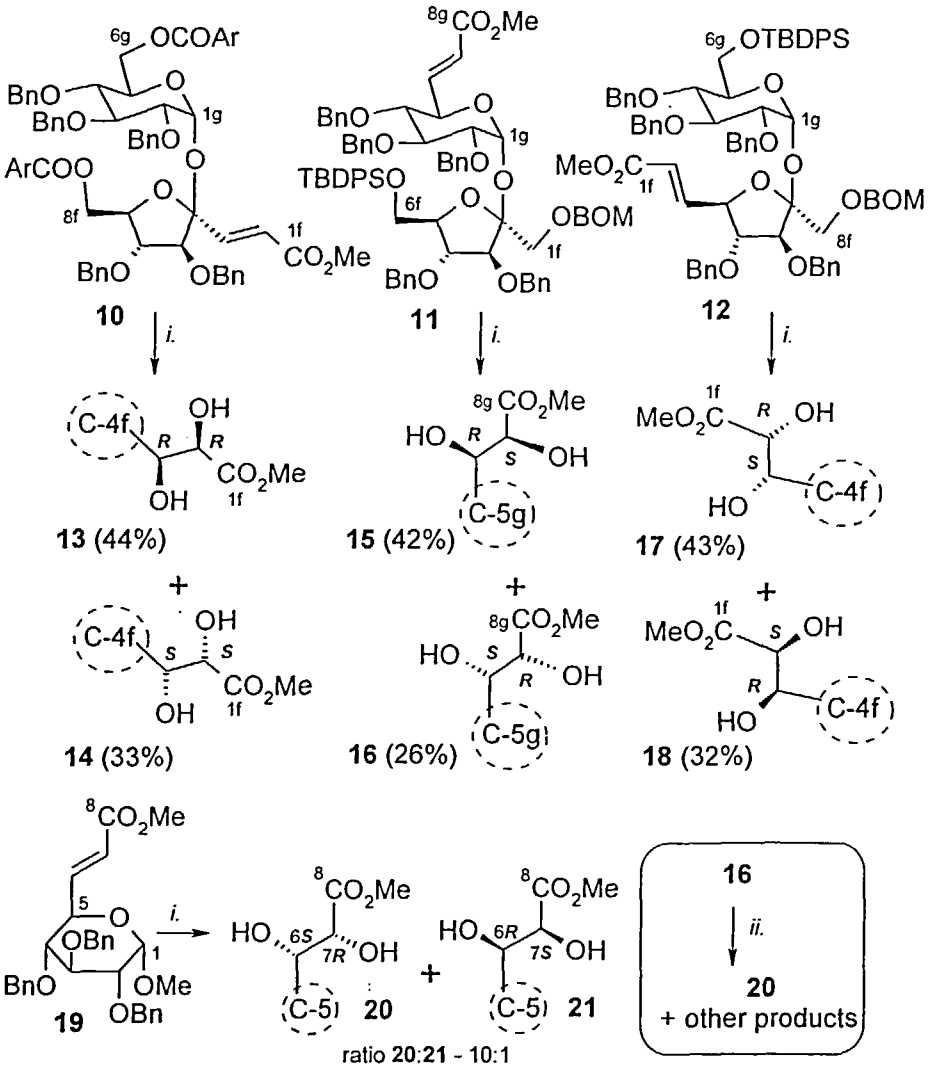
Scheme 2. *i.* Swern oxidation; *ii.* Jones oxidation; *iii.* CH_2N_2, 63% overall

Regioselective preparation of higher analogs of sucrose

Specifically blocked derivatives: **1**, **4**, and **6**, were used for the regioselective preparation of modified sucroses. Oxidation of the hydroxyl group to an aldehyde followed by reaction with methoxycarbonyl-methylenetriphenylphosphorane (Ph_3P=CH-CO_2Me) gave the corresponding α,β-unsaturated esters **10, 11, 12** with the *trans* configuration of the double bond ($J_{olef.}$ = 16 Hz). *Cis*-hydroxylation of these olefins with OsO_4/NMO[16] furnished three pairs of diastereoisomeric diols **13/14, 15/16** and **17/18** (Scheme 3). The selectivity of the osmylation of **10-12** was surprisingly low (*ca* 3:2) especially as compared to a similar reaction performed for methyl [(*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-α-D-*gluco*-oct-6-enopyranosid]uronate (**19**) which gave two diastereoisomeric products **20** and **21** in the ratio 10:1[17] (Scheme 3).

Determination of the configuration of higher sucroses

The configuration of the products of osmylation of α-alkoxy(hydroxy)-olefins can usually be assigned on the basis of so-called Kishi's rule[18] according to which the relative



Scheme 3. *i.* OsO_4, NMO, THF, ^{t}BuOH, water; *ii.* HCl in MeOH;

configuration of the hydroxylated product at Cα and the pre-existing hydroxy(alkoxy) group is *erythro*. However, this assignment may be done safely *only* when the selectivity is high (at least 3-4:1); for higher sucroses **13-18** another method(s) must be found. Configuration at the new chiral centers in diols **15** and **16** can be easily assigned by chemical degradation. Cleavage of the glycosydic linkage in **15** or **16** with acidic methanol should afford the methyl α/β-octopyranosides (from the homologated 'glucose' part) and α/β-fructofuranosides. The configuration of such α-octo-pyranosides is known.[17]

Methanolysis of the minor isomer **16** afforded a mixture of compounds from which the L-*threo* isomer **20** (identical with that prepared according to Brimacombe,[17] *see* Scheme 3) was isolated, proving the L-*threo* [6(*S*),7(*R*)] configuration at C-6,C-7; therefore, the configuration of the major isomer **15** was assigned as D-*threo* [6(*R*),7(*S*)].

Such degradation would be difficult to perform for the products of osmylation of **10** and **12**, since no models are available. We turned our attention, therefore, to the indirect CD method involving dimolybdenum tetraacetate as an auxiliary chromophore. As we have shown, the dimolybdenum tetraacetate [$Mo_2(OAc)_4$] is especially useful for the determination of the absolute configuration of *vic*-glycols.[19] The acetate ligands of [$Mo_2(OAc)_4$] can be easily exchanged in solution by chiral 1,2-diols. The optically active *in situ* complexes thus formed show several Cotton effects (CEs) within the absorption bands of the metal cluster and the CD obtained depends solely on the chirality of the ligand applied. The great advantage of this bidentate bonding is that the conformational freedom of the ligand is significantly restricted, if it is not completely fixed. The complex forces flexible molecules, like, *e.g.*, aliphatic ones, into only one single conformation, which leads to more interpretable CD spectra and often also to larger Cotton effects. In addition, it is noteworthy that this restriction of the conformational freedom makes an absolute configurational assignment possible on the basis of the chiroptical data alone.

With dimolybdenum tetraacetate and *vic*-diols, in general, three Cotton effects, namely, around 390 nm, 340 nm, and 310 nm have been found the most useful for the determination of the sign of the torsional angle of the complexing glycol. This in turn is induced by the absolute configuration of the glycol moiety. As have been proved with many *vic*-glycols of rigid conformation, a positive torsional angle in the (OH)-C-C-(OH) moiety leads to a positive CE around 300 nm, and a negative torsional angle leads to a negative CE in the same range. No exception to this rule has as yet been found. In most CD spectra the 400 nm Cotton effect has the same sign. The 350 nm Cotton effect is opposite to both of these and is often detectable just as a minimum between two CD maxima.

The same helicity rule applies to aliphatic *vic*-glycols. Open chain *sec-sec vic*-diols can adopt two conformations having a torsional angle (OH)-C-C-(OH) of ±60°. In one the C-C-C-C torsional angle is 180°, in the other ±60°. It was experimentally found[20]

that the latter (shown in Fig 1) conformation is preferred in complexes with $[Mo_2(OAc)_4]$. In these cases, for steric reasons, the conformation of the diol must be fixed so that each O-C-C-R moiety of glycol adopts an antiperiplanar conformation (Figure 1).

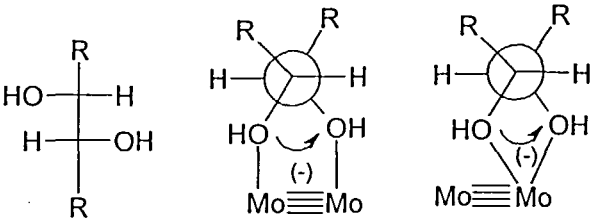


Figure 1 Preferred antiperiplanar conformation of an aliphatic 1,2-diol when complexed onto a Mo-cluster with negative torsional angle to give a negative CE at *ca.* 300 nm ("parallel" - middle and "perpendicular" - right complexation mode).

This means that the bulky R-groups point away from the rest of the complex. This seems very reasonable since only in such a conformation, the bigger group R avoids steric interaction with the still present acetate ligands in the stock complex.

Application of this CD method for diols **15/16** (configuration assigned by chemical degradation) and **20/21** (Brimacombe's compounds)[17] showed the validity of these rules for such carbohydrate diols. The same configurations: 6(*R*),7(*S*) for **15** and **21** and 6(*S*),7(*R*) for **16** and **20** were assigned by the CD method and chemical degradation (see Table 1). We reasoned, therefore, that this CD method might be used safely for determination of the configuration of diols resulting from osmylation of **10** and **12**.

All CD data of compounds **13** - **21** are shown in the Table. The negative sign of the Cotton effect at *ca.* 300 nm in compounds **15**, **18**, and **21** points to a negative sign of the torsion angle in the (HO)-C-C-(OH) unit whereas the positive sign of the same CE in **16**, **17**, and **20** corresponds to a positive torsional angle in the (HO)-C-C-(OH) moiety. Assuming the preferred conformation for these compounds to be the one with an antiperiplanar arrangement of both hydroxyl groups with respect to bulky substituents (Figure 2), the absolute configuration of compounds **15** and **18** can be determined as C-6(*R*), C-7(*S*) and C-2(*S*), C-3(*R*), respectivety, on the basis of their negative (OH)-C-C-(OH) torsional angle.

Table. CD data of diols **13** - **21** with $[Mo_2(OAc)_4]$ in DMSO. Values are given as (λ [nm] ($\Delta\varepsilon$'))

Comp.	Band I	Band II	Band III	Configuration
13	----	343.5 (-0.79)	394.5 (0.17)	C-2(*R*), C-3(*R*)
13a	296.8 (1.32)	349.8 (-1.53)	413.2 (0.27)	
14	----	351.0 (0.24)	403.5 (-0.13)	C-2(*S*), C-3(*S*)
14a	298.8 (-1.49)	343.8 (2.90)	408.4 (-0.85)	
15	301.0 (-2.34)	347.0 (2.35)	399.5 (-0.95)	C-6(*R*), C-7(*S*)
16	300.0 (1.64)	345.5 (-1.37)	396.0 (0.47)	C-6(*S*), C-7(*R*)
17	298.5 (0.70)	344.5 (-0.67)	403.0 (0.27)	C-2(*R*), C-3(*S*)
18	294.0 (-0.46)	344.0 (1.02)	402.5 (-0.25)	C-2(*S*), C-3(*R*)
20	302.8 (1.42)	348.0 (-0.81)	399.0 (0.52)	C-6 (*S*), C-7 (*R*)
21	307.8 (-1.90)	350.6 (0.68)	396.8 (-0.55)	C-6 (*R*), C-7 (*S*)

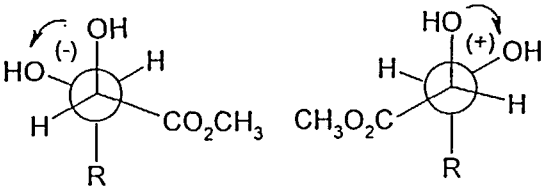


Figure 2 Preferred antiperiplanar arrangement of hydroxyl groups and bulky substituents R and CO_2CH_3 in **15** and **18** leading to a negative torsional angle of (OH)-C-C-(OH) unit (left) and in **16** and **17** with a positive (OH)-C-C-(OH) torsional angle (right).

In contrast, the positive sign of the (HO)-C-C-(OH) torsional angle allows determination of the absolute configuration of the stereogenic centers at C-6 and C-7 (or C-2 and C-3) in **16** and **17** as C-6(*S*), C-7(*R*) and C-2(*R*), C-3(*S*), respectively. An example of CD spectra of two diastereoisomers **15** and **16** is shown in Figure 3. In the CD spectra of Mo-complexes of compounds **13** and **14**, the 300 nm band is not visible, since it is buried beneath a strong absorption of a *p*-nitrobenzoic group. However, taking into account the aforementioned regularity, that in most cases the 400 nm and 300 nm CD band have the same signs, we have assigned the absolute configuration at C-2 and C-3 as ***R*** in compound **13** and ***S*** in compound **14**. In order to prove this prediction, we

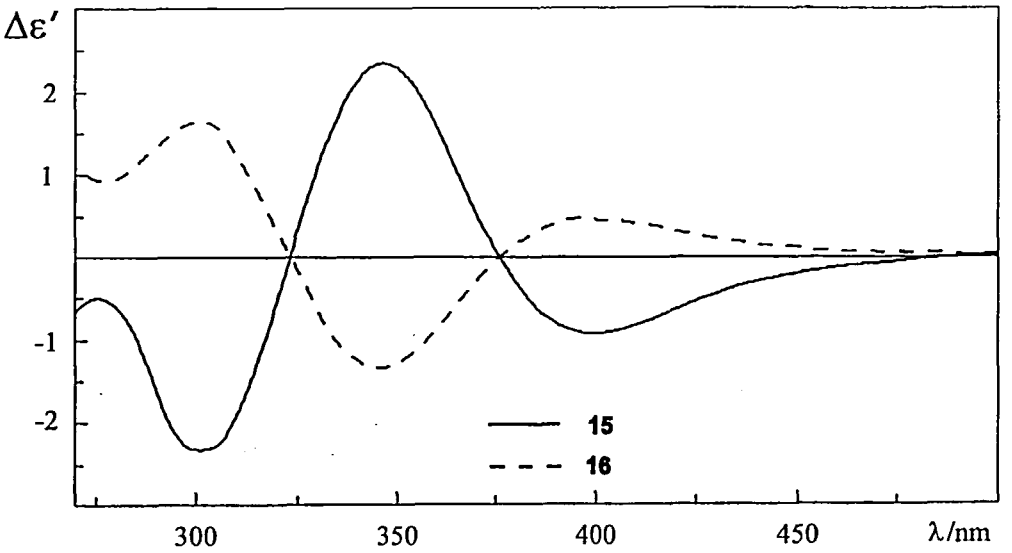


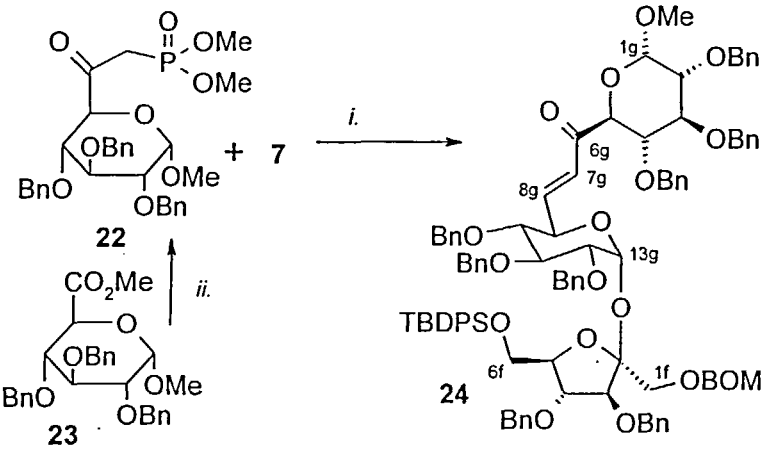
Figure 3 CD spectra of diastereoisomeric diols **15** and **16**.

have carried out a hydrolysis (under Zemplen's conditions) of the *p*-nitrobenzoic ester functions yielding compounds **13a** and **14a**, respectively. In the CD spectrum of **13a** the well separated and distinctly visible 300 nm band is positive, which is consistent with our assumption for compound **13**. In the case of **14a**, the 300 nm band is negative, again in accordance with our expectation. These results fully support our prediction for **13** and **14** and confirm the validity of the helicity rule for configurational and conformational assignment of *vic*-glycols by circular dichroism in the presence of dimolybdenum tetraacetate [$Mo_2(OAc)_4$].

Homologation of sucrose by a C_7-unit at the C6 end

The easy access to the selectively protected derivatives: **1**, **4**, and **6** opens also a convenient route to higher analogs of sucrose according to the methodology proposed by us for the preparation of higher carbon sugars. Recently, the C_{21}-dialdoses were prepared by reaction of sugar derived phosphonates with sugar aldehydes.[21] Application of this methodology in the chemistry of sucrose is shown in Scheme 4. Oxidation of the mono-alcohol **4** with the C6-OH free, afforded aldehyde **7** (*cf.* Scheme 2) which, upon treatment with sugar phosphonate **22** (readily available from appropriate methyl uronate **23** and

dimethyl methylphoshonate anion according to the literature method[21,22]) furnished the unsaturated ulose **24**. The *trans* geometry of the double bond was assigned from the ^{1}H NMR spectrum of **24** in which the large coupling constant between olefinic protons ($J_{olef.}$ = 15.7 Hz) was observed.



Scheme 4. *i.* K_2CO_3, 18-crown-6, toluene, r.t., 82%
ii. $MeP(O)(OMe)_2$, BuLi, THF, 91%

CONCLUSION

The convenient method for the preparation of selectively protected (with the easily removable - under neutral conditions - protecting groups) sucrose monoalcohols is described. Although, the selective protection of the 6'-OH could be rather expected on the basis of literature data, the ***selective*** deprotection of this position (→ **6**) is noteworthy. Such monoalcohols are useful starting materials for modified sucroses, compounds homologated by two (or even more) carbon atoms at either terminal position.

The results of the osmylation of α,β-unsaturated esters derived from homologation of sucrose at the C-6, C-6' and C-1' positions dramatically differ from those observed for simple sugars. The stereoselectivity is much lower (3:2 for all derivatives of sucrose *vs* 10:1 for **19**) and for osmylation of **11**, the well established Kishi's rule is not obeyed.

The configuration of higher sucrose diols can be conveniently assigned from the circular dichroism spectra of chiral Mo-complexes formed *in situ* with *vic*-diols; this is a very powerful and fast technique for studying the absolute chiralities of such systems, and

especially useful when only small amounts of the substance are available. An additional advantage of this *in situ* method is that it avoids derivatization, isolation and purification.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Bruker AM 500 spectrometer for solutions in benzene-d_6 (internal Me_4Si) unless otherwise stated. Assignment of the signals (in ^{1}H and ^{13}C spectra) were made by appropriate COSY (^{1}H-^{1}H and ^{1}H-^{13}C) and DEPT experiments. Mass spectra (LSIMS; *m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added) were recorded with an AMD-604 apparatus. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 for solutions in $CHCl_3$ (c = 1). Column chromatography was performed on silica gel (Merck, 70-230 or 230-400 mesh). 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 diol was about 1:0.3 to 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 were used without further purification. THF and methylene chloride were distilled from potassium or calcium hydride, respectively, prior to use. Dry toluene and benzene were stored over sodium wire. For chromatography purposes a fraction of mineral oil with boiling point in range 70 – 90 °C was used as mixture of hexanes. All solutions were dried over anhydrous sodium sulfate. Acetylation reactions were performed under standard conditions: acetic anhydride, TEA, DMAP as a catalyst in dry methylene chloride.

2,3,3',4,4'-Penta-*O*-benzyl-1'-*O*-benzyloxymethyl-6,6'-di-*p*-nitrobenzoylsucrose (2). 2,3,3',4,4'-penta-*O*-benzyl-6,6'-di-*O*-*p*-nitrobenzoylsucrose[13] (**1**; 17.5 g, 16 mmol) was dissolved in pyridine (50 mL) containing a catalytic amount of DMAP (0.1 g). To the

refluxing reaction mixture (under an argon atmosphere) pure benzyloxymethyl chloride (8.9 mL, 64 mmol, prepared directly before use) was added and reflux was prolonged for 2 h. Pyridine was distilled off, the product was extracted with diethyl ether and the organic layer was washed with water, brine and dried. Column chromatography (hexane - ethyl acetate 6:1 to 3:1) afforded 2,3,3',4,4'-penta-*O*-benzyl-1'-*O*-benzyloxy- methyl-6,6'-di-*p*-nitrobenzoylsucrose (**2**) (15.5 g, 80%). [α] +50.7°. ^{1}H NMR δ 5.88 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.69 (dd, 1H, $J_{5,6a}$ = 2.0, $J_{6a,6b}$ = 11.9 Hz, H-6a), 4.65 (d, 1H, $J_{3',4'}$ = 7.1 Hz, H-3'), 4.64 - 4.44 [m, 14H, OCH_2O (BOM), 4xCH_2Ph, H-5, H-5', H-6'a and H-6'b), 4.37 (dd, 1H, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.33 - 4.27 (m, 2H, H-3,4'), 3.98 and 3.91 (AB of both H-1', 2H, J_{AB} = 11.2 Hz), 3.63 (dd, 1H, $J_{3,4}$ = 9.0, $J_{4,5}$ = 10.0 Hz, H-4), 3.56 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2); ^{13}C NMR δ 164.5, 164.4 (2×C=O), 105.3 (C-2'), 95.0 (OCH_2O), 90.2 (C-1), 84.3 (C-3'), 82.6 (C-4'), 82.0 (C-5'), 80.1 (C-2), 78.8 (C-3), 77.4 (C-4), 75.9, 75.0, 73.7, 72.9, 72.7 (5×OCH_2Ph), 70.1 (C-5), 69.8 (OCH_2Ph, BOM), 69.6 (C-1'), 66.0 (C-6'), 64.6 (C-6); *m/z*: 1233 ($M + Na^+$).

Anal. Calcd for $C_{69}H_{66}N_2O_{16}·H_2O$: C, 67.42; H, 5.58, N, 2.28. Found: C, 67.59; H, 5.30, N, 2.03.

2,3,3',4,4'-Penta-*O*-benzyl-1'-*O*-benzyloxymethylsucrose (3). A solution of **2** (15.5 g, 12.8 mmol) in THF (15 mL) was added to methanol (60 mL) containing MeONa (2.3 g) and the reaction mixture was stirred for 1 h at rt. The solvent was evaporated and the crude product was extracted with ethyl acetate. Purification by column chromatography (hexanes - ethyl acetate 3:1 to 1:1) afforded title compound **3** (7.5 g, 64%; when this reaction sequence was performed on a larger scale (68 mmol) without purification of intermediate **2**, total yield of **3** from **1** increased to 72%). [α] +25.7°. *m/z*: 935 [$M(C_{55}H_{60}O_{12}) + Na^+$]. This compound was characterized as a diacetate: [α] +43.2°. ^{1}H NMR δ 5.87 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.67 - 4.54 [m, 8H, 4H of OCH_2Ph, 2H of OCH_2O (BOM), H-3', H-6'a], 4.54 - 4.36 [m, 7H, OCH_2Ph (BOM), 1H of benzyl group, H-5, H-6a, H-5', H-6'b], 4.33 - 4.20 (m, 3H, H-3, H-6b, H-4'), 3.92 and 3.88 (AB of both H-1', 2H, J_{AB} = 11.2 Hz), 3.56 (dd, 1H, $J_{3,4}$ = 8.5, $J_{4,5}$ = 10.0 Hz, H-4), 3.54 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 1.73 and 1.67 (2s, 3H, 2×OAc); ^{13}C NMR δ 170.1 (2×C=O), 104.8 (C-2'), 94.9 (OCH_2O), 89.8 (C-1), 84.2 (C-3'), 82.5 (C-4'), 82.0 (C-5'), 80.1 (C-2), 79.0 (C-3), 77.9 (C-4), 75.6, 75.0, 73.2, 72.9, 72.6 (5×OCH_2Ph), 69.9 (C-5, C-1'), 69.6 (OCH_2Ph, BOM), 65.0 (C-6'), 63.4 (C-6), 20.5 and 20.4 (2×OAc).

Anal. Calcd for $C_{59}H_{64}O_{14}$: C, 71.07; H, 6.47. Found: C, 70.86; H, 6.70.

2,3,3',4,4'-Penta-*O*-benzyl-1'-*O*-benzyloxymethyl-6'-*O*-*t*-butyldiphenylsilylsucrose (4). To a stirred solution of diol **3** (10.7 g, 11.7 mmol) in dry dichloromethane (100 mL), containing diisopropylethylamine (6 mL, 35.1 mmol) and DMAP (0.7 g, 0.6 mmol) *t*-bultyldiphenylchlorosilane (3.6 mL, 14.1 mmol) was added at rt with a syringe pump (at a rate of 0.14 mL/h) and stirring was prolonged for an additional 12 h. Ethyl acetate and water were added, the organic layer was separated, washed with water, brine, dried and concentrated. Column chromatography (hexanes - ethyl acetate 9:1 to 1:2) afforded **5** (1.79 g, 14%) and desired monoalcohol **4** (9.31 g, 80% calculated on consumed **3**). [α] +28.8°. *m/z*: 1173 [$M(C_{71}H_{78}O_{12}Si) + Na^+$]. This compound was characterized as an acetate: [α] +32.5°. ^{1}H NMR δ 6.09 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.68 - 4.66 (m, 2H, H-3', H-4'), 4.47 - 4.42 (m, 2H, $J_{6a,6b}$ = 11.3 Hz, H-5, H-6a,), 4.26 [ddd (broad), 1H, H-5'], 4.22 (dd, 1H, H-3), 4.17 - 4.12 (m, 3H, $J_{5,6b}$ = 4.0 Hz, H-6b, both H-6'), 3.96 [s (broad), 2H, both H-1'], 3.61 (dd, 1H, $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.7 Hz, H-4), 3.57 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 1.68 (s, 3H, OAc), 1.17 (s, 9H, *t*-Bu); ^{13}C NMR δ 169.9 (C=O), 104.6 (C-2'), 94.9 (OCH_2O), 89.4 (C-1), 84.5 (C-3'), 82.6 (C-3), 81.64 (C-5'), 81.58, (C-4'), 80.6 (C-2), 78.0 (C-4), 75.6, 74.9, 73.5, 72.9, 72.6 (5×OCH_2Ph), 70.3 (C-1'), 69.8 (C-5), 69.6 (OCH_2Ph, BOM), 65.1 (C-6'), 63.3 (C-6), 27.2 [$C(\underline{C}H_3)_3$], 20.6 (OAc), 19.5 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{73}H_{80}O_{13}Si$: C, 73.64; H, 6.76. Found: C, 73.34; H, 6.91.

2,3,3',4,4'-Penta-*O*-benzyl-1'-*O*-benzyloxymethyl-6,6'-di-*O*-*t*-butyldiphenylsilylsucrose (5). To a solution of diol **3** (2.0 g, 2.2 mmol) in dry THF (30 mL) containing a catalytic amount (*ca.* 50 mg) of imidazole, sodium hydride (50% suspension in mineral oil; 0.5 g, 10.4 mmol) was added and the mixture was stirred at room temperature for 0.5 h. *t*-Butyldiphenylchlorosilane (1.4 mL, 5.5 mmol) was added and stirring was prolonged for 12 h. Diethyl ether and water were added, the organic layer was separated, washed with water, dried and concentrated. Column chromatography (hexane - ethyl acetate 9:1 to 6:1) gave desired product **5** (2.9 g, 95%) [α] +27.7°. ^{1}H NMR δ 6.13 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.71 and 4.65 [AB of OCH_2O (BOM), 2H, J_{AB} = 6.5 Hz], 4.62 (d, 1H, $J_{3',4'}$ = 7.4 Hz, H-3'), 4.54 - 4.49 (m, 5H, 4H OCH_2Ph, H-5'), 4.32 - 4.28 (m, 2H, $J_{4',5'}$ = 7.5 Hz, H-4', H-5), 4.27 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 4.21 - 4.18 (m, 2H, H-6a, H-6b), 4.14 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 4.02 and 3.97 (AB of both H-1', 2H, J_{AB} = 11.1 Hz), 3.89 (dd, 1H, $J_{6'a,6'b}$ = 11.5, $J_{5',6'a}$ = 2.4 Hz, H-6'a), 3.80 (dd, 1H, $J_{5',6'b}$ = 1.1 Hz, H-6'b), 3.71 (dd, 1H, $J_{2,3}$ = 9.6 Hz,

H-2), 1.173, 1.169 (2×*t*-Bu); ^{13}C NMR δ 105.0 (C-2'), 96.4 (OCH_2O), 90.2 (C-1), 84.7 (C-3'), 82.9 (C-3), 82.4 (C-5'), 81.7 (C-4'), 81.1 (C-2), 78.0 (C-4), 75.8, 75.1, 73.5, 72.8, 72.6 (5×OCH_2Ph), 72.3 (C-5), 70.3 (C-1'), 69.6 (OCH_2Ph, BOM), 65.5 (C-6), 63.0 (C-6'), 27.3, 27.2 [2×C($\underline{C}H_3)_3$], 19.6, 19.5 [2×$\underline{C}(CH_3)_3$]; *m/z*: 1411 (M+ Na^+).

Anal. Calcd for $C_{87}H_{96}O_{12}Si_2$: C, 75.18; H, 6.96. Found: C, 74.99; H, 6.80.

2,3,3',4,4'-Penta-*O*-benzyl-1'-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilylsucrose (6). To a solution of **5** (1.48 g, 1.06 mmol) in MeOH - Et_2O (70 mL 4:1v\v), HF-Py complex (1M in methanol; 80 mL) was added and the reaction mixture was stirred at rt for 10 h (TLC monitoring in hexane - ethyl acetate, 3:1). Ethyl acetate and water were added, the organic layer was separated, washed with water, brine, dried, and concentrated. Column chromatography (hexanes - ethyl acetate 9:1 to 1:2) afforded the desired product **6** (0.564 g, 68% calculated on consumed **5**) [α] +24.6°; *m/z*: 1173 [M(C H O Si) + Na^+] and **3** (0.0987 g, 15%). Acetate of **6**: [α] +27.3°. ^{1}H NMR δ 6.00 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.66 - 4.52 [m, 7H, 3H of OCH_2Ph, OCH_2O (BOM), H-6'a, H-3' $J_{3',4'}$ = 7.6 Hz), 4.49 - 4.42 (m, 5H, 2x OCH_2Ph, H-6'b), 4.36 - 4.26 (m, 4H, H-3, H-5, H-4', H-5'), 4.16 (dd, 1H, $J_{3,4}$ = 9.4, $J_{4,5}$ = 9.6 Hz, H-4), 3.99 (dd, 1H, $J_{5,6a}$ = 2.4, $J_{6a,6b}$ = 11.6 Hz, H-6a), 3.94 and 3.89 (AB of both H-1', 2H, J_{AB} =11.2 Hz), 3.89 (dd, 1H, $J_{5,6b}$ = 1.3 Hz, H-6b), 3.69 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 1.72 (s, OAc), 1.18 (s, 9H, *t*-Bu); ^{13}C NMR δ 170.1 (C=O), 104.8 (C-2'), 95.0 (OCH_2O), 90.1 (C-1), 84.2 (C-3'), 82.8 (C-3), 81.9 (C-4'), 80.7 (C-2), 78.8 (C-5'), 78.0 (C-4), 75.8, 74.2, 73.2, 72.9, 72.7 (5×OCH_2Ph), 72.5 (C-5), 70.3 (C-1'), 69.7 (OCH_2Ph, BOM), 64.8 (C6'), 63.0 (C-6), 27.2 [C($\underline{C}H_3)_3$], 20.6 (OAc), 19.6 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{73}H_{80}O_{13}Si$: C, 73.64; H, 6.76. Found: C, 73.24; H, 6.69.

Methyl (3,4-di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔1)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid)uronate (9). Oxidation of **4** to aldehyde **7** was achieved by a Swern procedure.[23] Thus, to a stirred solution of oxalyl chloride (0.3 mL, 3.5 mmol) in dry dichloromethane (8 mL) at -78 °C, DMSO (1 mL, 14 mmol) was carefully added followed by a solution of alcohol **4** (1 mmol) in dichloromethane (5 mL). After 15 min triethylamine (1 mL, 7.2 mmol) was added, the mixture was stirred for an additional 15 min and allowed to reach rt. Crude **7** was extracted with diethyl ether, the organic layer was washed twice with water, 1% aqueous HCl, water, saturated $NaHCO_3$, water, brine and dried. Evaporation of the solvents left crude aldehyde

which was oxidized to uronic acid **8** with the Jones[24] reagent and converted (with diazomethane) into methyl ester **9**. Crude product was isolated by column chromatography (hexanes - ethyl acetate 6:1 to 3:1) as an oil (0.750 g) in 63% overall yield (three steps) from **4**. [α] +25.5°. ^{1}H NMR δ 5.94 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1g), 4.98 (d, 1H, $J_{4,5}$ = 9.0 Hz, H-5g), 4.66 (d, 1H, $J_{3,4}$ = 7.5 Hz, H-3f), ~4.58 (H-4f and CH_2Ph), 4.37 (m, 1H, H-5f), 4.25 (dd, 1H, $J_{6a,6b}$ = 11.2, $J_{5,6a}$ = 6.0 Hz, H-6fa), 4.22 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3g), 4.16 (dd, 1H, $J_{5,6b}$ = 3.7 Hz, H-6fb), 4.06 (dd, 1H, H-4g), 3.93 and 3.87 (AB of both H-1f, 2H, J_{AB} = 11.2 Hz), 3.53 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2g), 3.22 (s, 3H, CO_2CH_3), 1.17 (s, 9H, *t*-Bu); ^{13}C NMR δ 170.2 (C-6g), 104.8 (C-2f), 94.9 (OCH_2O), 90.3 (C-1g), 84.1 (C-3f), 82.5 (C-4f), 82.3 (C-5f), 82.0 (C-3g), 80.2 (C-2g), 80.0 (C-4g), 75.6, 75.1, 73.09, 72.98, 72.92 (5×OCH_2Ph), 71.4 (C-5g), 69.8 (C-1f), 69.5 (OCH_2Ph, BOM), 65.6 (C-6f), 51.6 ($CO_2\underline{C}H_3$), 27.1 [$C(\underline{C}H_3)_3$], 19.5 [$\underline{C}(CH_3)_3$]. *m/z*: 1201 (M+ Na^+).

Anal. Calcd for $C_{72}H_{78}O_{13}Si$: C, 73.32; H, 6.67. Found: C, 72.87; H, 6.68.

General procedure for elongation of sucrose at terminal positions by a C_2-unit. Appropriate aldehyde [prepared by a Swern oxidation of alcohols: **1**, **4**, or **6** (1 mmol)] and methoxycarbonylmethylene-triphenylphosphorane (0.384 g, 1.2 mmol) were dissolved in dry benzene (30 mL) and stirred at rt for 24 h. The solvent was evaporated, and the crude α,β-unsaturated ester (**10**, **11**, and **12**, respectively) was isolated by column chromatography (hexane - ethyl acetate 4:1 to 2:1).

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzoyl-α-D-glucopyranosyl)-(1↔4)-[(*E*)-5,6-di-*O*-benzyl-2,3-dideoxy-8-*O*-*p*-nitrobenzoyl-β-D-*arabino*-oct-2-eno-4-ulofuranosid]onate (10). (82%); [α] +52.4°. ^{1}H NMR δ 7.32 (d, 1H, $J_{2,3}$ = 15.5 Hz, H-3f), 6.63 (d, 1H, H-2f), 5.56 (d, 1H, $J_{1,2}$ = 3.4.Hz, H-1g), 4.76 (dd, 1H, $J_{6a,6b}$ = 12.0, $J_{5,6a}$ = 2.2 Hz, H-6ga), 4.56 - 4.51 (m, 3H, H-6gb, H-8fa, H-8fb), 4.49 - 4.42 (m, 3H, OCH_2Ph and H-5g), 4.34 (dd, 1H, $J_{6,7}$ = 6.8 Hz, H-6f), 4.30 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3g), 4.24 (center of multiplet, 1H, H-5g), 3.98 (d, 1H, $J_{5,6}$ = 6.6 Hz, H-5f), 3.65 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4g), 3.53 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2g), 3.39 (s, 3H, CO_2CH_3); ^{13}C NMR δ 166.8, 165.1, 165.0 (3×C=O), 128.3 (C-3f), 124.7 (C-2f), 105.5 (C-4f), 92.9 (C-1g), 89.9 (C-5f), 83.6 (C-6f), 83.0 (C-3g), 80.9 (C-2g), 79.6 (C-7f), 78.4 (C-4g), 76.5, 75.8, 74.1, 73.8, 73.3 (5×OCH_2Ph), 71.3 (C-5g), 66.9 (C-8f), 65.0 (C-6g), 52.1 ($CO_2\underline{C}H_3$). *m/z*: 1167 (M + Na^+).

Anal. Calcd for $C_{64}H_{60}N_2O_{18}$: C, 67.13; H, 5.28; N, 2.45. Found: C, 67.27; H, 5.09; N, 2.61.

Methyl (3,4-di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-fructofuranosyl)-(2↔1)-[(*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-*α*-D-*gluco*-oct-6-eno-1,5-pyranosid]uronate (11). (88%); [α] +32.6°. ^{1}H NMR δ ~7.28 (H-6, and aromatics), 6.35 (dd, 1H, $J_{6,7}$ = 15.8 Hz, H-7g), 6.11 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1g), 4.96 (ddd, 1H, $J_{5,6}$ = 4.3 Hz, H-5g), 4.64 - 4.62 (m, 2H, H-3f, H-4f), 4.23 - 4.19 (m, 2H, H-3g, H-5f), 4.11(dd, 1H, $J_{6a,6b}$ = 11.5, $J_{5,6a}$ = 3.6 Hz, H-6fa), 4.06 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, H-6fb), 3.93 and 3.89 (AB of both H-1f, 2H, J_{AB} = 11.1 Hz), 3.55 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2g), 3.41 (s, 3H, CO_2CH_3), 3.26 (dd, 1H, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 9.0 Hz, H-4g), 1.19 (s, 9H, *t*-Bu); ^{13}C NMR δ 166.5 (C-8g), ~128.1 (C-6g, and aromatics), 121.5 (C-7g), 104.6 (C-2f), 95.0 (OCH_2O), 89.2 (C-1g), 84.2 (C-3f), 82.4 (C-3g), 82.3 (C-4g), 81.5 (C-4f, C-5f), 80.4 (C-2g), 75.6, 75.3, 73.4, 73.0, 72.7 (5×OCH_2Ph), 70.5 (C-5g), 70.4 (C-1f), 69.6 (OCH_2Ph of BOM), 64.7 (C-6f), 51.0 ($CO_2\underline{C}H_3$), 27.2 [$C(\underline{C}H_3)_3$], 19.5 [$\underline{C}(CH_3)_3$]. *m/z*: 1227 ($M + Na^+$).

Anal. Calcd for $C_{74}H_{80}O_{13}Si$: C, 73.73; H, 6.69. Found: C, 73.49; H, 6.77.

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-*α*-D-glucopyranosyl)-(1↔7)-[(*E*)-5,6-di-*O*-benzyl-8-*O*-benzyloxymethyl-2,3-dideoxy-*β*-D-*lyxo*-oct-2-eno-7-ulofuranosid]onate (12). (80%); [α] +43.5°. ^{1}H NMR δ 7.38 (dd, 1H, $J_{3,4}$ = 5.5 Hz, H-3f), 6.29 (dd, 1H, $J_{2,3}$ = 15.7, $J_{2,4}$ = 1.3 Hz, H-2f), 5.87 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1g), 4.60 (dd, 1H, $J_{4,5}$ = $J_{5,6}$ = 7.9 Hz, H-5f), 4.55 (ddd, 1H, H-4f), 4.41 (d, 1H, H-6f), 4.36 (ddd, 1H, H-5g), 4.34 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3g), 4.16 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4g), 4.03 (dd, 1H, $J_{6a,6b}$ = 11.6, $J_{5,6a}$ = 2.5 Hz, H-6ga), 3.98 (dd, 1H, $J_{5,6b}$ = 1.4 Hz, H-6gb), 3.97 and 3.91 (AB of both H-8f, 2H, J_{AB} = 11.3 Hz), 3.65 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2g), 3.32 (s, 3H, CO_2CH_3), 1.20 (s, 9H, *t*-Bu); ^{13}C NMR δ 166.0 (C-1f), ~127.5 (C-3f and aromatics), 123.0 (C-2f), 104.9 (C-7f), 95.1 (OCH_2O), 90.7 (C-1g), 85.3 (C-6f), 84.1 (C-5f), 82.7 (C-3g), 80.8 (C-2g), 79.7 (C-4f), 78.0 (C-4g), 75.8, 75.1, 73.3, 73.2, 72.8 (5×OCH_2Ph), 72.7 (C-5g), 69.8 (C-8f), 69.7 (OCH_2Ph, BOM), 63.2 (C-6g), 51.2 ($CO_2\underline{C}H_3$), 27.2 [$C(\underline{C}H_3)_3$], 19.6 [$\underline{C}(CH_3)_3$]. *m/z*: 1227 ($M + Na^+$).

Anal. Calcd for $C_{74}H_{80}O_{13}Si$: C, 73.73; H, 6.69. Found: C, 73.54; H, 6.81.

Dimethyl (methyl 2,3,4-tri-*O*-benzyl-D-*gluco*-heptopyranos-6-ulos-7-yl)phosphonate (22). To a stirred solution of methyl dimethylphosphonate (0.104 g, 89 μL, 0.838 mmol) in dry THF (5 mL) at -78 °C, 2.5M BuLi (334 μL) was added. After 15 min compound **23** (0.137 g, 0.279 mmol) in THF (2 mL) was added, stirring was continued for

an additional 20 min at -78 °C and the mixture was allowed to reach rt.TLC (hexane - ethyl acetate, 2:1) showed disappearance of a starting material and formation of a new, very polar product. The mixture was partitioned between ethyl acetate and brine, the organic layer was separated, washed twice with water, dried, concentrated, and the crude product was isolated by column chromatography (hexane - ethyl acetate 2:1 to 1:3) to afford **22** (0.148 g, 91%). [α] +11.4°. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.64 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.40 (d, 1H, $J_{4,5}$ = 9.9 Hz, H-5), 4.07 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 3.77 [d, 3H, $J_{P,H}$ = 11.4 Hz, P(OMe)], 3.74 [d, 3H, $J_{P,H}$ = 11.3 Hz, P(OMe)], 3.67 (dd, 1H, H-4), 3.55 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 3.47 (s, 3H, OMe), 3.41 - 3.10 (m, 2H, H-7a, H-7b); ^{13}C NMR (200 MHz, $CDCl_3$) δ 198.5 (d, $J_{C\text{-}6,\,P}$ = 6.6 Hz, C-6), 98.6 (C-1), 81.8 (C-3), 79.3 (C-2), 78.8 (C-4), 73.8 (C-5), 75.9, 75.0, 73.6 (3×OCH_2Ph), 55.5 (OMe), 53.1 (d, $J_{C,P}$ = 7.1 Hz, P(OMe)), 52.9 [d, $J_{C,P}$ = 6.8 Hz, P(OMe)], 49.1 (d, $J_{C\text{-}7,P}$ = 128.8 Hz, C-7). *m/z*: 607.2074 [M($C_{31}H_{37}O_9P$) + Na^+= 607.2073].

Methyl (3,4-di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔13)-[(*E*)-2,3,4,10,11,12-hexa-*O*-benzyl-7,8-dideoxy-β-L-*gulo*-α-D-*gluco*-tridekadialdo-7-eno-6-ulo-1,5:9,13-dipyranoside] (24). Phosphonate **22** (0.124 g, 0.212 mmol), aldehyde **7** (0.125 g, 0.109 mmol) and 18-crown-6 (0.336 g, 1.272 mmol) were dissolved in dry toluene (10 mL) to which anhydrous potassium carbonate (0.088 g, 0.638 mmol) was added and the mixture was stirred overnight at rt. TLC (hexane - ethyl acetate, 3:1) showed disappearance of the aldehyde and formation of a new product that was visible under UV light. Ethyl acetate was added, the organic phase was washed twice with water, dried, concentrated, and the crude product was purified by column chromatography (hexane - ethyl acetate 6:1 to 3:1) to give **24** (0.142 g, 82%). [α] +35.0°. ^{1}H NMR (500 MHz, $CDCl_3$, *inter alia*) δ 6.96 (dd, 1H, $J_{8,9}$ = 4.4, $J_{7,8}$ = 15.7 Hz, H-8g), 6.55 (dd, 1H, $J_{7,9}$ = 1.8 Hz, H-7g), 5.96 (d, 1H, $J_{12,13}$ = 3.7 Hz, H-13g), 4.68 (H-9g), 4.21 (d, 1H, $J_{4,5}$ = 9.8 Hz, H-5g), 4.03 - 3.84 (m, 5H, H-11g, H-4f, H-6fa, H-6fb and H-3g), 3.79 and 3.69 (AB of both H-1f, J_{AB} = 11.2 Hz), 3.60 (dd, 1H, $J_{3,4}$ = 9.1 Hz, H-4g), 3.43 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, H-2g), 3.37 (dd, 1H, $J_{11,12}$ = 9.8 Hz, H-12g), 3.09 (s, 3H, OCH_3), 3.07 (dd, 1H, $J_{10,11}$ = 8.9, $J_{9,10}$ = 10.0 Hz, H-10g), 1.07 (s, 9H, *t*-Bu); ^{13}C NMR (500 MHz, $CDCl_3$) δ 194.7 (C-6g), 145.0 (C-8g), 126.1 (C-7g), 104.2 (C-2f), 98.5 (C-1g), 94.8 (OCH_2O), 88.8 (C-13g), 84.0, 81.61 (C-11g), 81.55, 81.47 (C-10g), 81.2, 80.7, 79.7

(C-12g), 79,4 (C-2g), 79.2 (C-4g), 75.7, 75.6, 74.7 (2xC), 73.4, 73,19 (6×OCH_2Ph), 73.17 (C-5g), 72.9, 72.0 (2×OCH_2Ph), 70.0 (C-9g), 69.8 (C-1f), 69.5 (OCH_2Ph, BOM), 64.0 (C-6f), 55.5 (OCH_3), 26.9 [$C(\underline{C}H_3)_3$], 19.2 [$\underline{C}(CH_3)_3$]. *m/z*: 1630 ($M + Na^+$).

Anal. Calcd for $C_{100}H_{106}O_{17}Si$: C, 73.86; H, 6.64. Found: C, 73.88; H, 6.88.

General procedure for osmylation reaction. Appropriate α,β - unsaturated ester (**10**, **11** or **12**, 1 mmol) was dissolved in a mixture of THF (8 mL), *t*-butyl alcohol (0.8 mL) and water (0.1 mL). *N*-Methylmorpholine-*N*-oxide (0.160 g, 1.2 mmol) and osmium tetraoxide (0.5 mL of a ~2% solution in *t*-butyl alcohol) were added and reaction mixture was stirred at rt until TLC (hexane - ethyl acetate, 2:1) showed disappearance of the starting material and formation of new products (24 - 48 h). Methanol (20 mL) and saturated sodium hydrogensulfite (3 mL) were added and the reaction mixture was stirred vigorously for 30 min. Products were extracted with ethyl acetate, the organic layer was washed twice with water, dried, concentrated, and crude products were separated by careful column chromatography (hexane - ethyl acetate, 4:1 to 2:1).

Osmylation of 10 afforded 13 and 14:

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzoyl-α-D-glucopyranosyl)-(1↔4)-(5,6-di-*O*-benzyl-8-*O*-*p*-nitrobenzoyl-β-D-*glycero*-D-*galacto*-oct-4-ulofuranosid)onate (13). (44%); [α] +73.0°; *m/z*: 1201 [$M(C_{64}H_{62}N_2O_{20}) + Na^+$]. This compound was characterized as a diacetate: [α] +56.4°. ^{1}H NMR δ 6.35 (d, 1H, $J_{2,3}$ = 2.0 Hz, H-3f), 6.07 (d, 1H, H-2f), 5.81 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1g), 4.76 (d, 1H, $J_{5,6}$ = 5.1 Hz, H-5f), 4.63 (dd, 1H, H-5g), 4.54 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 2.2 Hz, H-6ga), 4.47 (dd, 1H, $J_{6,7}$ = 6.6 Hz, H-6f), 4.41 (dd, 1H, $J_{8a,8b}$ = 12.4, $J_{7,8a}$ = 5.7 Hz, H-8fa), 4.35 (dd, 1H, $J_{7,8b}$ = 3.5 Hz, H-8fb), 4.32 (dd, 1H, H-3g), 4.12 (ddd, 1H, H-7f), 4.00 (dd, 1H, $J_{5,6b}$ = 3.1 Hz, H-6gb), 3.59 (dd, 1H, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4g), 3.54 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2g), 3.39 (s, 3H, CO_2CH_3), 1.83, 1.79 (2×s, 6H, 2xOAc); ^{13}C NMR δ 170.5, 169.9, 169.4, 164.91, 164.90 (5×C=O), 105.4 (C-4f), 91.0 (C-1g), 85.7 (C-5f), 83.36, 83.33 (C-3g,C-6f), 80.0 (C-7f), 79.9 (C-2g), 78.4 (C-4g), 76.7, 75.6 (2×OCH_2Ph), 74.8 (C-2f), 74.5, 73.9, 73.7 (3×OCH_2Ph), 71.5 (C-3f), 71.0 (C-5g), 65.3 (C-8f), 64.7 (C-6g), 53.0 ($CO_2\underline{C}H_3$), 21.2, 21.1 (2×OAc).

Anal. Calcd for $C_{68}H_{66}N_2O_{22}$: C, 64.65; H, 5.27; N, 2.22. Found: C, 64.39; H, 5.28; N, 2.01.

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzoyl-α-D-glucopyranosyl)-(1↔4)-5,6-di-*O*-benzyl-8-*O*-*p*-nitrobenzoyl-β-D-*glycero*-D-*ido*-oct-4-ulofuranosid)onate (14). (33%); [α] +61.2°; *m/z*: 1201 [M($C_{64}H_{62}N_2O_{20}$) + Na^+]. Diacetate: [α] +74.6°. ^{1}H NMR δ 6.46 (d, 1H, $J_{2,3}$ = 1.2 Hz, H-3f), 6.02 (d, 1H, H-2f), 5.82 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1g), 4.76 - 4.58 [m, 9H, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 2.1 Hz, 3xCH_2Ph, H-6ga, H-5g, H-6f], 4.49 (d, 1H, $J_{5,6}$ = 8.1 Hz, H-5f), 4.46 (dd, broad, 1H, $J_{8a,8b}$ = 10.1 Hz, H-8fa), 4.43 (dd, broad, 1H, H-8fb), 4.37 (t, 1H, $J_{2,3} = J_{3,4}$ = 9.3 Hz, H-3g), 4.14 (ddd, broad, 1H, H-7f), 4.07 (dd, 1H, $J_{5,6b}$ = 2.6 Hz, H-6gb), 3.59 (dd, 1H, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.9 Hz, H-4g), 3.50 (s, 3H, CO_2CH_3), 3.49 (dd, 1H, H-2g), 1.82, 1.78 2×(s, 3H, OAc); ^{13}C NMR δ 170.3, 170.2, 169.9, 164.96, 164.92 (5×C=O), 104.8 (C-4f), 90.9 (C-1g), 85.3 (C-5f), 83.6 (C-3g), 80.0 (C-6f), 79.2 (C-2g), 78.7 (C-7f), 78.3 (C-4g), 76.7, 75.7, 75.0, 74.1 (4×OCH_2Ph), 74.0 (C-2f), 73.7 (OCH_2Ph), 71.2 (C-5g), 70.4 (C-3f), 64.8 (C-8f), 64.5 (C-6g), 53.2 ($CO_2\underline{C}H_3$), 21.3, 20.9 (2×OAc).

Anal. Calcd for $C_{68}H_{66}N_2O_{22}\cdot H_2O$: C, 64.65; H, 5.27; N, 2.22. Found: C, 64.39; H, 5.28; N, 2.01.

Osmylation of 11 afforded 15 and 16:

Methyl (3,4-di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔1)-(2,3,4-tri-*O*-benzyl-α-D-*threo*-D-*gluco*-oct-1,5-pyranosid)uronate (15). (42%); [α] +18.1°. *m/z*: 1261 [M($C_{74}H_{82}O_{18}Si$) + Na^+]. This compound was characterized as a diacetate: [α] +17.4°. ^{1}H NMR δ 6.12 (dd, 1H, $J_{5,6}$ = 3.6 Hz, H-6g), 6.09 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1g), 5.78 (d, 1H, $J_{6,7}$ = 3.9 Hz, H-7g), 4.75 - 4.60 [m, 10H, 5H of CH_2Ph, OCH_2O, H-5g, H-3f, H-4f], 4.33 (ddd, broad, 1H, H-5f), 4.27 - 4.20 (m, 3H, H-3g, H-6fa, H-6fb), 4.04 and 4.01 (AB of both H-1f, 2H, J_{AB} = 11.1 Hz), 3.71 (dd, 1H, $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.8 Hz, H-4g), 3.57 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2g), 3.35 (s, 3H, CO_2CH_3), 1.78, 1.76 (2s, 6H, 2xOAc), 1.19 (s, 9H, *t*-Bu); ^{13}C NMR δ 170.5, 170.2, 169.4 (3×C=O), 106.4 (C-2f), 95.6 (OCH_2O), 91.2 (C-1g), 85.0 (C-3f), 83.8 (C-4f), 83.2 (C-5f), 83.0 (C-3g), 81.2 (C-2g), 79.5 (C-4g), 76.4, 75.8, 74.0, 73.5, 73.2 (5×OCH_2Ph), 71.9 (C-7g), 71.4 (C-5g), 70.8 (C-6g), 70.4 (OCH_2Ph, BOM), 69.6 (C-1f), 66.2 (C-6f), 52.9 ($CO_2\underline{C}H_3$), 27.9 [$C(\underline{C}H_3)_3$], 21.0 (2×OAc), 20.5 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{78}H_{86}O_{17}Si$: C, 70.78; H, 6.55. Found: C, 70.39; H, 6.75.

Methyl (3,4-di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔1)-(2,3,4-tri-*O*-benzyl-β-L-*threo*-D-*gluco*-oct-1,5-pyranosid)u-

ronate (16). (26%); [α] +22.6°; *m/z*: 1261 [M($C_{74}H_{82}O_{18}Si$) + Na^+]. This compound was characterized as a diacetate: [α] +13.0°. ^1H NMR δ 6.10 (t, 1H, $J_{5,6} = J_{6,7}$ = 3.2 Hz, H-6g), 5.91 - 5.89 (m, 2H, H-1g, H-7g), 4.96 (d, 1H, H-3f), 4.71 - 4.36 [m, 10H, (6H, benzyl signals + 2H, OCH_2O + 2H, OCH_2Ph (BOM)], 4.61 (dd, 1H, H-5g), 4.48 (dd, 1H, H-4f), 4.40 (ddd, 1H, H-5f), 4.38 (m, 1H, $J_{5,6a}$ = 6.2 Hz, H-6fa), 4.28 (dd, 1H, $J_{6a,6b}$ = 10.4, $J_{5,6b}$ = 4.5 Hz, H-6fb). 4.18 (dd, 1H, $J_{3,4}$ = 8.9 Hz, H-3g), 3.98 and 3.93 (AB of both H-1f, 2H, J_{AB} = 11.3 Hz), 3.78 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4g), 3.53 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.8 Hz, H-2g), 3.38 (s, 3H, CO_2CH_3), 1.78, 1.69 2×(s, 3H, OAc), 1.17 (s, 9H, *t*-Bu); ^{13}C NMR δ 170.5, 170.3, 169.8 (3×C=O), 105.9 (C-2f), 95.6 (OCH_2O), 91.3 (C-1g), 85.0 (C-3f), 84.5 (C-4f), 83.5 (C-5f), 83.0 (C-3g), 80.9 (C-2g), 79.9 (C-4g), 76.3, 75.6, 73.9, 73.7, 73.4 (5×OCH_2Ph), 72.7 (C-6g), 72.5 (C-5g), 70.7 (C-7g), 70.3 (OCH_2Ph, BOM), 69.6 (C-1f), 67.3 (C-6f), 52.9 ($CO_2\underline{C}H_3$), 27.9 [$C(\underline{C}H_3)_3$], 21.15, 21.13 (2×OAc), 20.2 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{78}H_{86}O_{17}Si$: C, 70.78; H, 6.55. Found: C, 70.34; H, 6.89.

Osmylation of 12 afforded 17 and 18:

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1↔7)-(5,6-di-*O*-benzyl-8-*O*-benzyloxymethyl-β-D-*glycero*-L-*altro*-oct-2-eno-7-ulofuranosid)onate (17). (43%); [α] +13.2°; *m/z*: 1261 [M($C_{74}H_{82}O_{18}Si$) + Na^+]. This compound was characterized as a diacetate: [α] +9.4°. ^1H NMR δ 6.22 (dd, 1H, $J_{3,4}$ = 8.3, $J_{2,3}$ = 1.0 Hz, H-3f), 6.01 - 5.99 (m, 2H, H-1g, H-2f), 4.70 - 4.45 (m, 12H, 3xCH_2Ph, OCH_2O, H-6f, H-5f, H-4f, H-3g), 4.32 (d, broad, 1H, $J_{4,5}$ = 9.8 Hz, H-5g), 4.21 - 4.10 (m, 5H, 1H of benzyl signal, H-6ga, H-8fa, H-4g, H-6gb) 3,97 (second part of AB of both H-8f, 1H, J_{AB} = 11.5 Hz, H-8fb), 3.62 (dd, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.6 Hz, H-2g), 3.46 (s, 3H, CO_2CH_3), 1.68, 1.67 (2× OAc), 1.23 (s, 9H, *t*-Bu); ^{13}C NMR δ 169.7, 169.3, 168.8 (3×C=O), 105.9 (C-7f), 95.0 (OCH_2O), 92.4 (C-1g), 86.0 (C-6f), 85.5 (C-5f), 82.6 (C-3g), 81.4 (C-2g), 78.7 (C-4f), 78.1 (C-4g), 76.0, 75.3 (2×OCH_2Ph), 73.7 (C-3f), 73.5, 73.1, 72.8 (3×OCH_2Ph), 72.7 (C-5g), 71.1 (C-2f), 69.7 (OCH_2Ph, BOM), 67.3 (C-8f), 63.1 (C-6g), 52.3 ($CO_2\underline{C}H_3$), 27.2 [$C(\underline{C}H_3)_3$] 20.4, 20.0 (2×OAc), 19.6 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{78}H_{86}O_{17}Si$: C, 70.78; H, 6.55. Found: C, 70.59; H, 6.74

Methyl (2,3,4-tri-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl)-(1↔7)-(5,6-di-*O*-benzyl-8-*O*-benzyloxymethyl-β-D-*glycero*-L-*gluco*-oct-2-eno-7-ulofuranosid)onate (18). (32%); [α] +19.5°; *m/z*: 1261 [M($C_{74}H_{82}O_{18}Si$) + Na^+]. This

compound was characterized as a diacetate: [α] +38.0°. ^{1}H NMR δ 6.29 - 6.25 (m, 2H, H-1g, H-3f), 5.64 (d, 1H, $J_{2,3}$ = 2.4 Hz, H-2f), 4.72 - 4.50 (m, 11H, 5H of benzyl signals, OCH_2O, H-6f, H-5f, H-4f, H-3g), 4.36 (d, broad, 1H, $J_{4,5}$ = 10.0 Hz, H-5g), 4.14 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-4g), 4.04 and 3.96 (AB of both H-8f, 2H, J_{AB} = 11.4 Hz), 3.92 (d, broad, 1H, $J_{6a,6b}$ = 11.7 Hz, H-6ga), 3.89 (d, broad, 1H, H-6gb), 3.75 (dd, 1H, $J_{1,2}$ = 3.7, $J_{2,3}$ = 9.7 Hz, H-2g), 3.38 (s, 3H, CO_2CH_3), 1.80, 1.62 (2xOAc), 1.18 (s, 9H, *t*-Bu); ^{13}C NMR δ 169.80, 169.76, 167.8 (3×C=O), 105.2 (C-7f), 95.0 (OCH_2O), 90.5 (C-1g), 85.4 (C-6f), 82.6 (C-3g), 81.6 (C-5f), 80.8 (C-2g), 78.2 (C-4f), 77.9 (C-4g), 76.0, 75.0, 73.7, 72.8 (4×OCH_2Ph) 72.7 (C-3f), 72.5 (C-5g), 72.1 (OCH_2Ph), 71.7 (C-2f), 69.9 (C-8f), 69.7 (OCH_2Ph, BOM), 63.2 (C-6g), 52.3 ($CO_2\underline{C}H_3$), 27.2 [$C(\underline{C}H_3)_3$], 20.4, 19.9 (2×OAc), 19.6 [$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{78}H_{86}O_{17}Si$: C, 70.78; H, 6.55. Found: C, 70.66; H, 6.80.

Determination of the configuration of 16 by chemical degradation. The Brimacombe model compounds, diols **20** and **21**[17] were prepared by osmylation of **19**. The CD data of these diols are shown in the Table. Selected NMR signals (200 MHz, $CDCl_3$):

Methyl (2,3,4-tri-*O*-benzyl-*β*-L-*threo*-D-*gluco*-oct-1,5-pyranosid)uronate (20): ^{1}H NMR δ 3.77 (s, 3H, OMe), 3.42 (s, 3H, CO_2Me); ^{13}C NMR (without aromatics) δ 173.6, 97.6, 81.9 (double intensity), 80.0, 75.6, 74.9, 74.8, 73.2, 70.0, 66.5, 55.4, 52.5.

Methyl (2,3,4-tri-*O*-benzyl-*α*-D-*threo*-D-*gluco*-oct-1,5-pyranosid)uronate (21): ^{1}H NMR δ 3.78 (s, 3H, OMe), 3.38 (s, 3H, CO_2Me); ^{13}C NMR (without aromatics) δ 173.3, 98.6, 81.7, 79.6, 77.4, 75.6, 75.1, 73.4, 71.4, 69.9, 69.8, 55.7, 52.7.

Compound **16** (0.200 g, 0.16 mmol) was dissolved in Et_2O (10 mL), to which a 5% solution of hydrochloric acid in MeOH (5 mL) was added and reaction mixture was stirred at rt for 24 h. Products of hydrolysis were extracted with ethyl acetate, the organic layer was washed with water, aqueous sodium bicarbonate, water, brine and dried. From the post-reaction mixture the desired octoses were identified by comparison with synthetic **20** and **21** (TLC; hexanes - ethyl acetate, 1:1) and isolated by column chromatography as inseparable mixture of α/β-anomers (0.064 g, 72%).

In the NMR spectra (200 MHz, $CDCl_3$) of this mixture the signals of **20** were found (δ_H: 3.42; δ_C: 66.6, 97.7, 173.5), while no signals characteristic for **21** were seen.

ACKNOWLEDGEMENTS

This work was partially supported by the Grant No **3 T09A 119 16** from the Polish State Committee for Scientific Research.

REFERENCES AND NOTES

1. A. H. Haines, *Adv. Carbohydr. Chem. Biochem.*, **33**, 11 (1976); R. Khan, *Pure Appl. Chem.*, **56**, 833 (1984); *Carbohydrates as Organic Raw Materials*, F. W. Lichtenthaler, Ed., VCH Verlagsgesellschaft mbH (1991).
2. T. Otake, *Bull. Chem. Soc. Jpn.*, **43**, 3199 (1970); L. Hough, K. S. Mufti, and R. Khan, *Carbohydr. Res.*, **21**, 144 (1972).
3. K. Horst, C. K. Lee, and R. Khan, *Carbohydr. Res.*, **101**, 31 (1982).
4. M. S. Chowdhary, L. Hough, and A. C. Richardson, *J. Chem. Soc., Chem. Comm.*, 664 (1978); *item., J. Chem. Soc., Perkin Trans. 1*, 419 (1984).
5. R. Khan and K. S. Mufti, U.K. Pat., 2,079,749 (1980); *Chem. Abstr.*, **96**, 163112j (1982).
6. S. Riva, J. Chopineau, A. P. G. Kieboom, and A. M. Klibanov, *J. Am. Chem. Soc.*, **110**, 584 (1988).
7. C. Chauvin and D. Plusquellec, *Tetrahedron Lett.*, **32**, 3495 (1991).
8. J. N. Zikopoulos, S. H. Eklund, and J. F. Robyt, *Carbohydr. Res.*, **104**, 245 (1982).
9. R. Khan, C. L. Bhardwaj, K. S. Mufti, and M. R. Jenner, *Carbohydr. Res.*, **78**, 185 (1980); Ch.-Ch. Chen, R. L. Whistler, and J. R. Daniel, *Carbohydr. Res.*, **117**, 318 (1983); A. de Raadt and A. E. Stuetz, *Tetrahedron Lett.*, **33**, 189 (1992).
10. M. K. Bhattacharjee and R. M. Mayer, *Carbohydr. Res.*, **142**, 277 (1985).
11. L. Hough, L. V. Sinchareonkul, A. C. Richardson, F. Akhtar, and M. G. Drew, *Carbohydr. Res.*, **174**, 145 (1988).
12. C. B. Purves and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 1973 (1934).
13. S. Jarosz, *J. Carbohydr. Chem.*, **15**, 73 (1996).
14. A related modified compound: 6,6'-dideoxy-6,6'-diazido-1',2,3,3',4,4'-hexa-*O*-benzylsucrose was prepared by benzylation of 6,6'-dideoxy-6,6'-diazido-sucrose [G. Gradnig, G. Legler, and A. E. Stuetz, *Carbohydr. Res.*, **287**, 49 (1996)].
15. S. Jarosz and M. Mach, *J. Carbohydr. Chem.*, **16**, 1111 (1997).
16. V. Van Rheenen, R. C. Kelly, and D. Y. Cha, *Tetrahedron Lett.*, **17**, 1973 (1976); S. Jarosz, *Carbohydr. Res.*, **224**, 73 (1992).
17. J. S. Brimacombe and G. McDonald, *Carbohydr. Res.*, **194**, c4 (1989); J. S. Brimacombe, G. McDonald, and A. M. Rahman, *Carbohydr. Res.*, **205**, 422 (1990).
18. J. K. Cha, W. J. Christ, and Y. Kishi, *Tetrahedron*, **40**, 2247 (1984).
19. J. Frelek, Z. Majer, A. Perkowska, G. Snatzke, I. Vlahov, and U. Wagner,. *Pure Appl. Chem.*, **57**, 441 (1985); A. Liptak, J. Frelek, G. Snatzke, and I. Vlahov, *Carbohydr. Res.*, **164**, 149 (1987); J. Frelek, Z. Pakulski, and A. Zamojski, *Tetrahedron: Asymmetry*, 7, 1363 (1996).

20. J. Frelek and G. Snatzke, *Fresenius' J. Anal. Chem.*, **316**, 261 (1983); J. Frelek, M. Geiger and W. Voelter, *Curr. Org. Chem.*, **2**, 197 (1998).
21. S. Jarosz, P. Sałański, and M. Mach, *Tetrahedron*, **54**, 2583 (1998) and references therein.
22. Y. Ojikawa, T. Tanaka, and O. Yonemitsu, *Tetrahedron Lett.*, **27**, 3647 (1986); K. Horita, S. Nagato, Y. Ojikawa, and O. Yonemitsu, *Tetrahedron Lett.*, **28**, 3253 (1987); *see also*: K. C. Nicolaou, R. A. Daines, T. K. Chakraborty, and Y. Ogawa, *J. Am. Chem. Soc.*, **110**, 4685 (1988); T. Yamanoi, T. Akiyama, E. Ishida, H. Abe, M. Anemiya, and T. Inazu, *Chem. Lett.*, 335 (1989).
23. A. J. Mancuso, S.-L. Huang, and D. Swern, *J. Org. Chem.*, **43**, 2480 (1978).
24. K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).