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Migration of secondary *tert*-butyldimethylsilyl groups in cyclomalto-heptaose and -octaose derivatives

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Abstract

When 2,6-di-*O*-*tert*-butyldimethylsilylated cyclomalto-oligosaccharides (cyclodextrins) are treated with allyl or methyl iodide and NaH in dry tetrahydrofuran, O-2 → O-3 migration of the secondary 2-*O*-*tert*-butyldimethylsilyl groups occurs, leading to 2-*O*-alk(en)yl-3,6-di-*O*-*tert*-butyldimethylsilyl-cyclodextrin derivatives. The detection and identification of the reaction step during which migration occurred is described and possible mechanisms of migration are discussed.

Keywords: Migration of silyl groups; Cyclomaltoheptaose (β-cyclodextrin); Cyclomalto-octaose (γ-cyclodextrin)

1. Introduction

The *tert*-butyldimethylsilyl (TBDMS) group has proved to be a valuable protecting group in cyclodextrin (CD) chemistry [1] when selectively attached to the primary 6-OH groups of CD glucose residues. In 1982 the first preparation of heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl)-β-CD (2,6-TBDMS-β-CD) (**11**) was reported by Wife et al. [2]. Tabushi et al. [3] used 2,6-di-*O*-persilylation for the purification of a regiospecifically A,

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B capped β-CD (cyclomaltoheptaose) derivative. The preparation of 2,6-TBDMS-α-CD from α-CD was first reported by Bender and co-workers [4] in 1983, and modified by Stoddart and his co-workers [5] in 1988. Fügedi [1] reported the synthesis of 2,6-TBDMS-β-CD (**11**), applying slightly altered conditions. Recently, Coleman et al. [6] prepared the analogous 6-*O*- and 2,6-di-*O*-dimethylthexylsilyl (thexyl = 1,1,2-trimethylpropyl) derivatives of β-CD. When the present work was already in progress, Mosandl and co-workers [7] introduced **11** and the 2,6-TBDMS derivative (**2**) of γ-CD (cyclomalto-octaose) as chiral stationary phases in gas chromatography. All the syntheses cited above use the corresponding chlorosilane as the silylation reagent and imidazole or pyridine as catalyst in *N*,*N*-dimethylformamide (DMF) at elevated temperatures. In contrast to this, Blum and Aichholz [8] reported the synthesis of randomly silylated β-CD, using *N*-TBDMS-*N*-methyltrifluoroacetamide as the silylating agent.

Although a number of papers deal with the 2,6-di-*O*-persilylation of cyclodextrins, no publication of further chemical modification of these derivatives has come to our knowledge. This might hint at some difficulties when applying 2,6-TBDMS-CD as synthetic intermediates.

We investigated the synthetic potential of 2,6-TBDMS-γ- (**2**) and -β-CD (**11**) for selective introduction of substituents in position 3 of their glucose residues. CD derivatives of this type are especially suited as stationary phases for gas chromatography, because of the major influence of substituents in this position on separation ability and profile [9]. This goal was impaired substantially by encountering migration of the secondary TBDMS residues during alk(en)ylation of **2** and **11**.

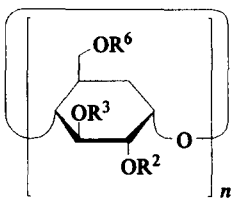
Migration of silyl groups — especially TBDMS — is a widely acknowledged phenomenon in carbohydrate [10–12] and ribonucleoside [13] chemistry. Taking into account the general problems of chemical modification of cyclodextrins caused by steric and statistical factors related to the torus structure and the large number of hydroxyl groups, the quantitative O-2 → O-3 TBDMS migration reported here, leading to symmetrically substituted migration products, is surprising. The results imply a thermodynamic driving force for TBDMS migration during the alk(en)ylation of 2,6-TBDMS)-γ- and -β-CD (**2** and **11**). The observed migration may be utilized for the selective introduction of substituents in position 2 of cyclodextrin glucose residues.

2. Results and discussion

Since it was rather difficult to establish unambiguous proof of the observed migration, the correct characterization of the disilyl starting materials as the 2,6-TBDMS-CD derivatives **2** and **11** was crucial. It is well established for cyclodextrins that primary hydroxyl groups in position 6 are substituted preferentially with the bulky TBDMS group [1]. Of the secondary hydroxyl groups it is generally known that the 2-hydroxyl groups are more acidic and thus more accessible to nucleophilic displacement reactions performed on electrophilic reagents under nearly neutral or basic conditions [14]. Hence, the reported formation of 2,6-TBDMS-CD derivatives is in agreement with expectations. In general, the specific reactivity of cyclodextrins is practically independent of the number of glucose residues forming their macrocyclic ring. Therefore, the characteriza-

tion by Bender and co-workers [4] and the confirmation by Stoddart and co-workers [5] of the previous assignments by NMR studies of 2,6-TBDMS-α-CD (**21**) on the basis of NOE difference spectroscopy and selective heteronuclear decoupling experiments can be generalized for the corresponding β- (**11**) and γ-cyclodextrin (**2**) derivatives.

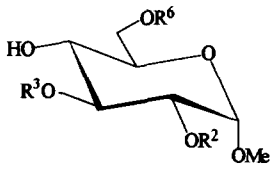
Per-2,6-di-*O*-silylation of γ- (**1**) and β-CD (**10**) with *tert*-butylchlorodimethylsilane, according to Fügedi [1], leads to 2,6-TBDMS-γ- (**2**) and -β-CD (**11**), respectively. The NMR data are recorded, because ^{1}H data were not previously reported, and ^{13}C signals were not assigned precisely. The assignments are supported by $^{1}H-^{1}H$ and $^{1}H-^{13}C$ COSY experiments. A cross-peak between the signal of the free OH groups and the H-3 protons can be observed in the $^{1}H-^{1}H$ COSY spectrum of **2** in $CDCl_3$, supporting 2,6-substitution. In the following graphic All = allyl; TBDMS = *tert*-butyldimethylsilyl.



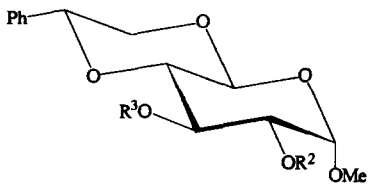
R^2	R^3	R^6	*n*		R^2	R^3	R^6	*n*	
H	H	H	8	**1**	All	H	H	7	**13**
TBDMS	H	TBDMS	8	**2**	All	Ac	Ac	7	**14**
All	TBDMS	TBDMS	8	**3**	All	Me	Me	7	**15**
All	H	H	8	**4**	H	Me	Me	7	**16**
All	Ac	Ac	8	**5**	Me	TBDMS	TBDMS	7	**17**
All	H	TBDMS	8	**6**	Me	H	H	7	**18**
Pr	TBDMS	TBDMS	8	**7**	Me	Ac	Ac	7	**19**
Pr	H	H	8	**8**	H	H	TBDMS	8	**20**
Pr	Ac	Ac	8	**9**	All	H	All	7	**21**
H	H	H	7	**10**	H	TBDMS	TBDMS	8	**22**
TBDMS	H	TBDMS	7	**11**	H	H	TBDMS	6	**23**
All	TBDMS	TBDMS	7	**12**					

When methyl α-D-glucopyranoside (**24**) was treated [11] with *tert*-butylchlorodimethylsilane, the reaction mixture contained 70% of the 2,6-di-TBDMS derivative (**25**) and 11% of the 3,6-di-TBDMS derivative (**26**), besides mono- and tri-silylated derivatives. Unfortunately, only partial ^{1}H-NMR data of the acetylated derivatives of **25**

and **26** were reported. Predominant substitution of the 2-hydroxy groups was also observed [12] for the selective silylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**27**) with *tert*-butyldiphenylsilyl (TBDPS) chloride. The 2-TBDPS derivative (**28**) and the 3-TBDPS derivative (**29**) of **27** are formed in a 94:6 ratio. In the following graphics TBDPS = *tert*-butyldiphenylsilyl.

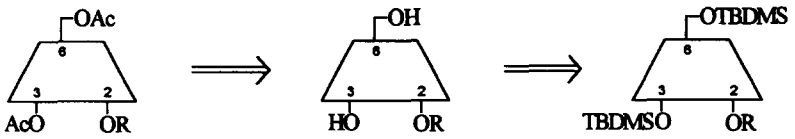


R^2	R^3	R^6	
H	H	H	**24**
TBDMS	H	TBDMS	**25**
H	TBDMS	TBDMS	**26**



R^2	R^3	
H	H	**27**
TBDPS	H	**28**
H	TBDPS	**29**
TBDMS	H	**30**
H	TBDMS	**31**
TBDMS	Me	**32**
Me	TBDMS	**33**

The per(*O*-allyl-di-*O*-*tert*-butyldimethylsilyl)-γ-cyclodextrin derived from 2,6-TBDMS-γ-CD (**2**) served as starting material for further syntheses [15], leading to



5 R = All, γ-CD	**4** R = All, γ-CD	**3** R = All, γ-CD
9 R = Pr, γ-CD	**8** R = Pr, γ-CD	**7** R = Pr, γ-CD
14 R = All, β-CD	**13** R = All, β-CD	**12** R = All, β-CD
19 R = Me, β-CD	**18** R = Me, β-CD	**17** R = Me, β-CD

Scheme 1. Retrosynthetic pathway of 3,6-di-*O*-acetyl-cyclodextrins.

products whose substitution patterns could only be explained by an interchange of the secondary hydroxyl substituents.

In order to identify the reaction step during which migration occurred, each *O*-R-di-*O*-TBDMS-cyclodextrin derivative (R = allyl, methyl, or propyl) was subjected to *O*-desilylation and subsequent acetylation. The observed acetyl shifts for the carbohydrate methine protons H-2 or H-3 should reveal the original site of the former TBDMS substituents.

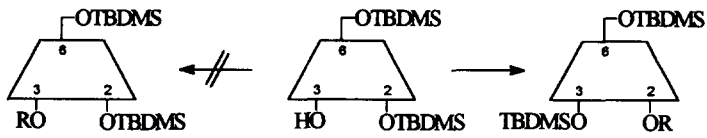
Scheme 1 shows the retrosynthetic pathway to 3,6-di-*O*-acetyl-2-*O*-alk(en)yl-cyclodextrins **5**, **9**, **14**, and **19**. To exclude possible allyl migration — prior to *O*-desilylation and subsequent acetylation — the allyl derivative (**3**) was hydrogenated and the final di-*O*-acetyl-*O*-propyl product was identified as per(3,6-di-*O*-acetyl-2-*O*-propyl)-γ-cyclodextrin (**9**).

The resulting one- and two-dimensional NMR spectra of the acetylated compounds (Table 1) show unambiguously the position of the former TBDMS substituents as the 3- and 6-hydroxy sites. This is proof for the migration occurring during the alk(en)ylation of 2,6-TBDMS-cyclodextrins (**2** and **11**), leading to the first reported cyclodextrin derivatives **3**, **7**, **12**, and **17** persilylated with TBDMS groups in positions 3 and 6 of their glucose residues.

The observed migration can be utilized for the general introduction of substituents in position 2 of cyclodextrin glucose residues. Per(2-*O*-allyl-3,6-di-*O*-*tert*-butyldimethylsilyl)-γ- (**3**) and -β-CD (**12**) were isolated in yields of 39% and 52%, respectively, and

Table 1
Selected ^{1}H NMR data for **5**, **9**, **14**, and **19**

Compound	Chemical shifts (δ)			
	H-2	H-3	H-6a	H-6b
5	3.38	5.25	4.46	4.33
9	3.35	5.29	4.51	4.35
14	3.38	5.23	4.51	4.31
19	3.32	5.23	4.54	4.31



R = All, Me

2 γ-CD

11 β-CD

3 R = All, γ-CD

12 R = All, β-CD

17 R = Me, β-CD

Scheme 2. Synthetic pathway to alk(en)ylation products of 2,6-TBDMS-cyclodextrins.

heptakis(3,6-di-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl)-β-CD (**17**) in 40% yield (Scheme 2).

O-Desilylation of **3** with tetrabutylammonium fluoride yielded 86% of crystalline octakis(2-*O*-allyl)-γ-cyclodextrin (**4**). Compounds **7**, **12**, and **17** were treated analogously; the product (**18**) of the latter was not purified prior to acetylation.

The cyclodextrin derivatives **4**, **8**, **13**, and **18** were conventionally acetylated with pyridine–acetic anhydride and 4-dimethylaminopyridine (DMAP), affording, for example, 83% of crystalline octakis(3,6-di-*O*-acetyl-2-*O*-allyl)-γ-cyclodextrin (**5**).

It was reported that when the 2-*O*-TBDPS-glucose derivative **28** was stirred [12] with potassium carbonate in methanol, the fast formation of a 2:1 mixture of the TBDPS derivatives of **29** and **28** occurred. When **2** was subjected to these conditions, after 1 h, a small amount of an unsymmetrically substituted (NMR) more polar derivative of **2** was isolated, lacking one TBDMS substituent as established by FAB mass spectrometry. After 2.5 h, a second, even more polar compound formed, which was unsymmetrically substituted as well but carried all of the original 16 TBDMS groups. Both products were not further characterized.

For further equilibration experiments methyl 4,6-*O*-benzylidene-2-*O*-TBDMS-α-D-glucopyranoside (**30**) and its 3-*O*-TBDMS isomer (**31**) were synthesized from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside according to Fügedi [1]. When submitted to alkaline methylation with NaH and MeI in THF, 98% of the rearranged 2-*O*-methyl derivative **33** was obtained from both the 2- and the 3-*O*-TBDMS derivative besides 2% of the 3-methyl ether **32**. Rearrangement was not observed when the methylation was performed with $MeOSO_2CF_3$ and 2,6-di-*tert*-butylpyridine in CH_2Cl_2. Equilibration of **30** and **31**, respectively, with NaH in THF rapidly gave a mixture of the 2-*O*- and 3-*O*-TBDMS regioisomers in a ratio of approximately 5:95. This indicates that the high regioselectivity observed in the alkylation reaction is essentially a result of thermodynamic control. In contrast, the β anomers of **30** and **31** in equivalent reactions yielded a 40:60 ratio of the regioisomers. Interestingly, the β-glucan cellulose showed no rearrangement under the alkaline methylation conditions [16].

The synthesis of 3,6-TBDMS-γ-CD (**22**) was attempted by removing the allyl groups from 2-allyl-3,6-TBDMS-γ-CD (**3**). No defined product could be isolated from this usually very facile two-step reaction [18,19].

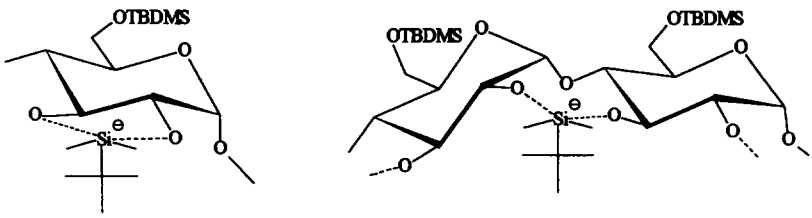


Fig. 1. Proposed mechanisms for intra- (left) and inter-glucosidic (right) 2-O → 3-O migration of TBDMS groups.

Other reactions of **2** and **11**, for example with acetic anhydride and 4-dimethylaminopyridine in pyridine, gave no symmetrically substituted products.

Selective silylation of **4** in position 6 with *tert*-butylchlorodimethylsilane in dry pyridine afforded 56% of octakis(2-*O*-allyl-6-*O*-TBDMS)-γ-cyclodextrin (**6**). Compound **6** is identical with the product of selective allylation of 6-TBDMS-γ-CD (**20**) carried out in accordance with selective allylation of β-CD (**10**) by Bergeron et al. [17], leading to heptakis(2,6-di-*O*-allyl)-β-CD (**21**), and is in agreement with results of selective allylation of 6-TBDMS-α-CD (**23**) by Stoddart and co-workers [5].

The 2-*O*-allyl-CD derivative **13** was methylated (NaH, MeI, DMF) to yield heptakis(2-*O*-allyl-3,6-di-*O*-methyl)-β-cyclodextrin (**15**), which after rearrangement [18] to the 2-*O*-propenyl derivative was cleaved [19] to the 3,6-di-*O*-methyl-β-CD derivative (**16**), also prepared by Takeo et al. [1] by another synthetic route. The physical data were in good agreement with the published results.

Taking into account the macrocyclic structure of the cyclodextrins, silyl migration might proceed intra- or inter-glucosidically (Fig. 1). Similar migrations have usually been reported for monosaccharide derivatives or other monomeric molecules. Although rather unlikely, interglucosidic migration might be possible, by analogy with the observed [20] bridging of benzylidene acetal groups of contiguous glucose residues in malto-oligosaccharide derivatives.

3. Experimental

General methods.—Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. Optical rotations were determined with Perkin–Elmer polarimeters, models 241 and 243. NMR spectra (^{1}H, 400 MHz; ^{13}C, 100.62 and 62.97 MHz) were recorded with Bruker WM 400 and 250 spectrometers, respectively. Allyl groups are assigned as an AMNXY system [5]. Analytical data for cyclodextrin derivatives were not obtained, because their complexation with solvents means that purity cannot be controlled in this way [21]. Purity was established by NMR spectroscopy and TLC. In some cases, FAB mass spectra [22] could be obtained (VG 70-250S, VG-Analytical, matrix: *m*-nitrobenzyl alcohol, collision gas: xenon); M + 1 refers to the ^{13}C-isotope peak. GCMS measurements were performed under electron impact (70 eV) conditions using a 25-m (0.25 mm i.d.) fused-silica capillary column

with CP-Sil 5 CB methyl polysiloxane phase. Chemical ionization mass spectra were obtained with ammonia as reactant gas on the same instrument. Organic solutions were dried over $MgSO_4$; TLC was performed on precoated plates of Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany). Column chromatography was performed at atmospheric pressure on Silica Gel 60 (70–230 mesh; E. Merck).

*Octakis(2,6-di-*O*-tert-butyldimethylsilyl)cyclomalto-octaose* (**2**).—γ-Cyclodextrin (**1**) was lyophilized and di-*tert*-butyldimethylsilylated essentially according to Fügedi's [1] preparation of the corresponding β-cyclodextrin derivative, with slightly higher excesses of chlorosilane and imidazole. A solution of **1** (5.0 g, 3.855 mmol), *tert*-butylchlorodimethylsilane (15.0 g, 99.5 mmol), and imidazole (13.0 g, 0.191 mol) was stirred for 40 h in dry DMF (120 mL) at 85 °C. The cooled reaction mixture was diluted with *n*-heptane and 1-butanol, and concentrated. The residue was partitioned with CH_2Cl_2 and water, and the organic phase was dried and concentrated. Column chromatography (75:1 toluene–EtOAc) of the residue gave **2** (8.17 g, 67.8%); mp 215–218 °C; TLC (30:1 *n*-hexane–EtOAc) R_f 0.54; $[\alpha]_D^{21}$ +48.4° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02, 0.03 (2 s, 48 H, 6-O-$SiMe_2$), 0.16, 0.17 (2 s, 48 H, 2-O-$SiMe_2$), 0.87 (s, 72 H, 2-O-$SiCMe_3$), 0.93 (s, 72 H, 2-O-$SiCMe_3$), 3.46 (dd, 8 H, $J_{4,5}$ 10.0 Hz, H-4), 3.55 (dd, 8 H, $J_{2,3}$ 9.7 Hz, H-2), 3.60 (ddd, 8 H, H-5), 3.68 (dd, 8 H, H-6b), 3.87 (dd, 8 H, $J_{3,4}$ 8.9 Hz, H-3), 3.99 (dd, 8 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.26 (s, 8 H, 3-OH, exchangeable with MeOH-d_4), and 4.95 (d, 8 H, $J_{1,2}$ 3.2 Hz, H-1); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ −4.9, −4.6 (6-O-$SiMe_2$), −4.1, −4.1 (2-O-$SiMe_2$), 18.7 (6-O-$SiCMe_3$), 19.2 (2-O-$SiCMe_3$), 26.2 (6-O-$SiCMe_3$), 26.6 (2-O-$SiCMe_3$), 62.4 (C-6), 72.3 (C-3), 72.5 (C-5), 75.4 (C-2), 81.4 (C-4), and 102.4 (C-1); $C_{144}H_{304}O_{40}Si_{16}$ 3125.34, FABMS: m/z_{calcd} 3121.8, m/z_{found} 3143.0 $[M + Na]^+$.

*Octakis(2-*O*-allyl-3,6-di-*O*-tert-butyldimethylsilyl)cyclomalto-octaose* (**3**).—To a stirred solution of **2** (8.09 g) and NaH (washed with *n*-pentane) (24 g) kept at 0 °C in dry THF (250 mL) was added allyl iodide (60 mL, 110.4 g). After 30 min, stirring was continued at room temperature for 2 days. Excess of NaH was then decomposed at 0 °C by the addition of MeOH. The reaction mixture was concentrated, the residue partitioned with *n*-hexane and water, and the organic phase dried and concentrated. Column chromatography (7:2 to 5:2 *n*-hexane–toluene, stepwise) of the residue afforded **3** (3.49 g, 39.1%); mp 125–128 °C; TLC (5:3 *n*-hexane–toluene) R_f 0.67; $[\alpha]_D^{21}$ +41.7° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (2 s, 48 H, 6-O-$SiMe_2$), 0.31 (2 s, 48 H, 3-O-$SiMe_2$), 0.89 (2 s, 144 H, 6-O- and 3-O-$SiCMe_3$), 3.25 (dd, 8 H, $J_{2,3}$ 6.5 Hz, H-2), 3.73 (m, dd, 16 H, H-5, H-6b), 3.76 (dd, 8 H, $J_{3,4}$ 5.6, $J_{4,5}$ 8.0 Hz, H-4), 3.99–4.15 (m, 32 H, $J_{A,Y}$ 6.0, $J_{X,Y}$ 12.8 Hz, H-3, H-6a, H-X, H-Y), 5.11 (m, 8 H, $J_{A,N}$ 10.8 Hz, H-N), 5.16 (d, 8 H, $J_{1,2}$ 2.4 Hz, H-1), 5.23 (m, 8 H, $J_{A,M}$ 17.6 Hz, H-M), 5.90 (m, 8 H, H-A); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ −4.9, −4.6, −3.6, and −3.4 (6-O- and 3-O-$SiMe_2$), 18.2 and 18.4 (6-O- and 3-O-$SiCMe_3$), 26.1 and 26.4 (6-O- and 3-O-$SiCMe_3$), 62.9 (C-6), 71.9 (α-CH_2-allyl), 72.9, 73.3, 77.2, and 78.6 (C-2,3,4,5), 96.5 (C-1), 116.8 (γ-CH_2-allyl), and 135.5 (β-CH-allyl).

*Octakis(2-*O*-allyl)cyclomalto-octaose* (**4**).—A solution of **3** (96 mg) and tetrabutylammonium fluoride trihydrate (75 mg) in 1:1 THF–DMF (1.2 mL) was stirred for 14 h at room temperature. The reaction mixture was diluted with 1-butanol and then concentrated, the residue dissolved in toluene, and the solution concentrated, to remove

residual solvent traces. Column chromatography (6:1 $CHCl_3$–MeOH) of the residue furnished **4**, contaminated with tetrabutylammonium salts. Therefore, the product was dissolved in MeOH (5 mL) and stirred with a mixed-bed anionic/cationic ion-exchange resin (1.5 g), Lewatit SM 703 (Bayer) for 2 h. The solution was filtered, concentrated, and repeatedly co-distilled with toluene, affording **4** (39.1 mg, 86.3%); mp 195 °C; TLC (2:1 $CHCl_3$–MeOH) R_f 0.53; $[\alpha]_D^{21}$ +103.6° (*c* 1, acetone); ^{1}H NMR (400 MHz, Me_2SO-d_6): δ 3.26 (dd, 8 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.4 Hz, H-2), 3.42 (dd, 8 H, $J_{3,4}$ 9.2 Hz, H-4), 3.56 (m, 8 H, H-5), 3.59–3.64 (m, 16 H, H-6a,6b), 3.76 (dd, 8 H, H-3), 4.18 (m, 8 H, $J_{A,Y}$ 6, $J_{X,Y}$ 12.6 Hz, H-Y), 4.26 (m, 8 H, $J_{A,X}$ 6.1 Hz, H-X), 4.55 (dd, 8 H, $J_{6\text{-OH},6a} = J_{6\text{-OH},6b}$ = 5.5 Hz, 6-OH), 4.76 (s, 8 H, 3-OH), 5.09 (d, 8 H, H-1), 5.17 (m, 8 H, $J_{A,N}$ 10.6 Hz, H-N), 5.30 (m, 8 H, $J_{A,M}$ 17.2 Hz, H-M), and 5.88 (m, 8 H, H-A); ^{13}C NMR (100.62 MHz, Me_2SO-d_6): δ 60.78 (C-6), 72.31 (C-5), 72.86 (α-CH_2-allyl), 73.27 (C-3), 80.35 (C-2), 80.77 (C-4), 99.69 (C-1), 118.33 (γ-CH_2-allyl), 135.72 (β-CH-allyl); $C_{72}H_{112}O_{40}$ 1617.66, FABMS: m/z_{calcd} 1616.7 $[M+H]^+$, m/z_{found} 1639.6 [M + Na].

*Octakis(3,6-di-*O*-acetyl-2-*O*-allyl)cyclomalto-octaose* (**5**).—A solution of **4** (40 mg) and 4-dimethylaminopyridine (8 mg) in 2:1 dry pyridine–Ac_2O was kept overnight in darkness. The mixture was co-distilled repeatedly with toluene, and the residue washed with $CHCl_3$ over silica gel and eluted with EtOAc, to afford **5** (47 mg, 83%); mp 108–111 °C; TLC (4:1 toluene–MeOH) R_f 0.33; $[\alpha]_D^{21}$ +92.4° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02, 2.08 (2 s, 48 H, Ac), 3.38 (dd, 8 H, $J_{1,2}$ 3.3, $J_{2,3}$ 9.5 Hz, H-2), 3.63 (dd, 8 H, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H-4), 3.97–4.13 (m, 24 H, $J_{A,X}$ 5.0, $J_{A,Y}$ 5.8, $J_{X,Y}$ 12.0 Hz, H-X, H-Y, H-5), 4.33 (dd, 8 H, $J_{5,6b}$ 4.6, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.46 (dd, 8 H, H-6a), 4.92 (d, 8 H, H-1), 5.17 (m, 8 H, $J_{A,N}$ 10.2 Hz, H-N), 5.25 (m, 16 H, $J_{A,M}$ 17.4 Hz, H-M, H-3), and 5.84 (m, 8 H, H-A); $C_{104}H_{144}O_{56}$ 2290.25, FABMS: m/z_{calcd} = 2288.8 $[M]^+$, m/z_{found} = 2313.0 $[M+1+Na]^+$.

*Octakis(2-*O*-allyl-6-*O*-tert-butyldimethylsilyl)cyclomalto-octaose* (**6**).—*(a)* A solution of **4** (1.59 g) and *tert*-butylchlorodimethylsilane (1.73 g) in dry pyridine (50 mL) was stirred for 5 min at 0 °C, then stirring was continued at room temperature. After 16, 19, and 22 h, *tert*-butylchlorodimethylsilane was added (220, 120, and 110 mg, respectively). The reaction was stopped after 36 h by the addition of water, the product extracted with toluene, the extract dried and concentrated, and the residue repeatedly co-distilled with toluene to remove traces of pyridine. Column chromatography (8:2 to 7:2 toluene–EtOAc, stepwise) of the residue afforded **6** (1.4 g, 56.3%).

(b) To a stirred solution of **20** (200 mg, prepared according to Fügedi [1]), BaO (0.5 g), and $Ba(OH)_2$ octahydrate (0.5 g) in a 1:1 mixture of dry Me_2SO–DMF (10 mL) was added allyl bromide (0.5 mL) at room temperature. After 3 days, the reaction was stopped by the addition of aq 25% ammonia (4 mL). After 20 min, the mixture was diluted with water. The crude product was extracted with CH_2Cl_2, and the extract washed with water, dried, concentrated, and subjected to high vacuum. Column chromatography (10:1 toluene–EtOAc) afforded **6** (23.6 mg, 10%); mp 195 °C; TLC (3:1 toluene–EtOAc) R_f 0.38; $[\alpha]_D^{21}$ +69.5° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.018, 0.023 (2 s, 48 H, $SiMe_2$), 0.87 (s, 72 H, Me_3C), 3.32 (dd, 8 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, H-2), 3.47 (dd, 8 H, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 3.58 (m, 8 H, H-5), 3.67 (m, 8 H, H-6a), 3.93 (dd, 8 H, $J_{5,6b}$ 2.4, $J_{6a,6b}$ 11.2 Hz, H-6b), 3.99 (dd, 8 H, H-3), 4.23 (m, 8 H,

J_{AY} 6.8, J_{XY} 12.8 Hz, H-Y), 4.48 (m, 8 H, J_{AX} 5.2 Hz, H-X), 4.85 (s, 8 H, 3-OH), 4.99 (d, 8 H, H-1), 5.21 (m, 8 H, J_{AN} 10.2 Hz, H-N), 5.29 (m, 8 H, J_{AM} 17.2 Hz, H-M), and 5.94 (m, 8 H, H-A); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ −5.25, −5.00 (6-O-$SiMe_2$), 18.28 (6-O-Si*C*Me_3), 25.88 (6-O-SiC*Me*$_3$), 61.87 (C-6), 71.74, 73.09, 79.67, 81.47 (C-2,3,4,5), 73.18 (α-CH_2-allyl), 100.74 (C-1), 118.17 (γ-CH_2-allyl), and 134.36 (β-CH-allyl).

*Octakis(3,6-di-*O-tert-*butyldimethylsilyl-2-*O-*propyl)cyclomalto-octaose* (**7**).—A solution of **3** (208 mg) in EtOAc was hydrogenated in the presence of 10% Pd–C (206 mg) for 1 h at 25 bar and room temperature, then filtered through Celite and concentrated. Column chromatography (8:1 to 6:1 *n*-hexane–toluene, stepwise) of the residue gave **7** (139.5 mg, 66.7%); mp 222–224 °C; TLC (12:5 *n*-hexane–toluene) R_f 0.73; $[\alpha]_D^{21}$ +60.2° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 48 H, 6-O-$SiMe_2$), 0.11, 0.12 (2 s, 48 H, 3-O-$SiMe_2$), 0.87 (t, 24 H, $J_{\beta,\gamma}$ 7 Hz, γ-CH_3), 0.88, 0.89 (2 s, 18 H, 6- and 3-O-SiCMe_3), 1.61 (m, 16 H, β-CH_2), 3.16 (dd, 8 H, $J_{2,3}$ 5.6 Hz, H-2), 3.37 (dd, 8 H, $J_{\alpha1,\alpha2}$ 15.16, $J_{\alpha1,\beta}$ 7.4 Hz, α1-CH_2), 3.53 (dd, 8 H, $J_{\alpha2,\beta}$ 8.0 Hz, α2-CH_2), 3.67–3.75 (m, 16 H, H-5,6b), 3.80 (dd, 8 H, $J_{3,4}$ 8.0, $J_{4,5}$ 6.8 Hz, H-4), 4.06 (dd, 8 H, H-3), 4.08 (m, 8 H, H-6a), and 5.30 (s, 8 H, H-1).

*Octakis(2-*O-*propyl)cyclomalto-octaose* (**8**).—A solution of **7** (120.5 mg) and tetrabutylammonium fluoride trihydrate (80 mg) in 1:1 THF–DMF (2 mL) was stirred overnight. Then it was diluted with THF (1 mL) and successively co-distilled with 1-butanol (1 mL) and toluene (1 mL). A solution of the residue and a mixed-bed anionic/cationic ion-exchange resin (2.0 g, Lewatit SM 703) in MeOH (5 mL) was stirred for 1 h. The resin was removed by filtration and the solution was concentrated and co-distilled with toluene, to afford **8** (56.8 mg, 99.7%); mp 290–293 °C; TLC (2:1 $CHCl_3$–MeOH R_f 0.54; $[\alpha]_D^{21}$ +72.6° (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, 24 H, $J_{\beta,\gamma}$ 7.4 Hz, γ-CH_3), 1.62 (m, 16 H, β-CH_2), 3.30 (dd, 8 H, $J_{3,4} = J_{4,5} = 9.16$ Hz, H-4), 3.36 (dd, 8 H, $J_{1,2}$ 4.0, $J_{2,3}$ 9.6 Hz, H-2), 3.60 (m, 8 H, α-CH_2), 3.70–3.80 (m, 16 H, H-5,6b), 3.85–3.98 (m, 24 H, α-CH_2, H-3, H-6a), 4.50 (s, 8 H, 6-OH), 4.90 (s, 8 H, 3-OH), and 4.91 (d, 8 H, H-1); ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ 10.62 (γ-CH_3), 23.48 (β-CH_2), 61.83 (C-6), 72.15 (C-5), 74.04 (C-3), 75.17 (α-CH_2), 81.03 (C-2), 84.16 (C-4), and 102.40 (C-1); $C_{72}H_{128}O_{40}$ 1633.78, FABMS: m/z_{calcd} 1632.8 $[M]^+$, m/z_{found} 1655.6 $[M + Na]^+$.

*Octakis(3,6-di-*O-*acetyl-2-*O-*propyl)cyclomalto-octaose* (**9**).—Treatment of **8** (52 mg) with 4-dimethylaminopyridine in pyridine–Ac_2O, as described for **5**, followed by column chromatography (8:8:1 $CHCl_3$–EtOAc–MeOH) gave **9** (15.8 mg, 21.5%); mp 99–101 °C; TLC (4:1 toluene–MeOH) R_f 0.36; $[\alpha]_D^{21}$ +95.3° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, acetone-d_6): δ 0.93 (t, 24 H, $J_{\beta,\gamma}$ 7.5 Hz, γ-CH_3), 1.58 (m, 16 H, β-CH_2), 2.04 and 2.08 (2 s, 48 H, Ac), 3.35 (dd, 8 H, $J_{1,2}$ 3.16, $J_{2,3}$ 9.8 Hz, H-2), 3.45 and 3.63 (2 m, 16 H, α-CH_2), 3.73 (dd, 8 H, $J_{3,4}$ 8.5, $J_{4,5}$ 9.6 Hz, H-4), 4.09 (m, 8 H, H-5), 4.35 (dd, 8 H, $J_{5,6b}$ 4.7, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.51 (dd, 8 H, $J_{5,6a}$ 2.0 Hz, H-6a), 5.07 (d, 8 H, H-1), and 5.29 (dd, 8 H, H-3); ^{13}C NMR (100.62 MHz, acetone-d_6): δ 10.09 (ϵ-CH_3), 20.22 and 20.61 (CO*Me*), 23.13 (β-CH_2), 63.52 (C-6), 70.07 (C-5), 71.87 (C-3), 72.91 (α-CH_2), 77.85 (C-4), 78.55 (C-2), 98.38 (C-1), 169.03, and 170.16 (C=O); $C_{104}H_{160}O_{56}$ 2306.38, FABMS (*m*-nitrobenzyl alcohol): m/z_{calcd} 2304.9 $[M]^+$, m/z_{found} 2329.4 $[M + 1 + Na]^+$.

Heptakis(2,6-di-O-tert-*butyldimethylsilyl)cyclomaltoheptaose* (**11**).—The disilylated derivative **11** was obtained by the treatment of lyophilized **10** (9.06 g, 6.86 mmol) and imidazole (20.02 g, 0.294 mol) in dry DMF with *tert*-butylchlorodimethylsilane (20 g, 0.133 mol, added portionwise) at 90 °C, as described for the preparation of **2** (with a slightly higher molar excess of imidazole and a slightly smaller excess of chlorosilane than applied by Fügedi [1], and a workup procedure basically according to Fügedi). Column chromatography (70:1 to 50:1 *n*-heptane–EtOAc) afforded **11** (15 g, 80%) (lit. [1] 66.1%); mp 280 °C; TLC (30:1 *n*-heptane–EtOAc) R_f 0.35; $[\alpha]_D^{21}$ +55.0° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (2 s, 42 H, 6-O-$SiMe_2$), 0.15 (2 s, 42 H, 2-O-$SiMe_2$), 0.88 (s, 63 H, 6-O-$SiCMe_3$), 0.91 (s, 63 H, 2-O-$SiCMe_3$), 3.43 (dd, 7 H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4), 3.52 (dd, 7 H, $J_{2,3}$ 9.5 Hz, H-2), 3.58 (ddd, 7 H, H-5), 3.64 (dd, 7 H, H-6b), 3.83 (dd, 7 H, H-3), 3.94 (dd, 7 H, $J_{5,6a}$ 2.6, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.40 (s, 7 H, 3-OH), and 4.82 (d, 7 H, $J_{1,2}$ 2.9 Hz, H-1); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.3, −5.0 (6-O-$SiMe_2$), −4.6, −4.5 (2-O-$SiMe_2$), 18.3 (6-O-Si*C*Me_3), 18.9 (2-O-Si*C*Me_3), 25.9 (6-O-SiC*Me*$_3$), 26.3 (2-O-SiC*Me*$_3$), 62.0 (C-6), 71.9, 72.2, 75.0 (C-2,3,5), 82.0 (C-4), and 102.6 (C-1); in excellent agreement with the reported 50-MHz ^{13}C NMR spectrum.

*Heptakis(2-*O-*allyl-3,6-di*-O-tert-*butyldimethylsilyl)cyclomaltoheptaose* (**12**).—Treatment of **11** (5.0 g) and NaH (12.1 g) in THF (100 mL) with allyl iodide (40.1 mL) for 3 days, as described for the preparation of **3**, gave, after column chromatography (7:2 to 6:2 *n*-heptane–toluene, stepwise), **12** (2.86 g, 52%); mp 221–225 °C; TLC (5:3 *n*-heptane–toluene) R_f 0.59; $[\alpha]_D^{21}$ +69.3° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 42 H, 6-O-$SiMe_2$), 0.06 (s, 42 H, 3-O-$SiMe_2$), 0.84 (s, 126 H, 6-O- and 3-O-$SiCMe_3$), 3.21 (dd, 7 H, H-2), 3.69 (dd, 7 H, $J_{5,6a}$ 2, $J_{6a,6b}$ 11 Hz, H-6b), 3.77 (ddd, 7 H, H-5), 3.86 (dd, 7 H, H-4), 4.02 (dd, 7 H, $J_{A,Y}$ 5.7, $J_{X,Y}$ 12.8 Hz, H-Y), 4.05–4.15 (m, 21 H, H-3, H-6a, H-X), 5.08–5.15 (m, 14 H, $J_{1,2}$ 2.4 Hz, H-1, H-N), 5.21 (m, 7 H, $J_{A,M}$ 17.6 Hz, H-M), 5.86 (m, 7 H, H-A); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.5, −5.2, −4.3, and −4.1 (6-O- and 3-O-$SiMe_2$), 17.6 and 17.7 (6-O- and 3-O-Si*C*Me_3), 25.5 and 25.8 (6-O- and 3-O-SiC*Me*$_3$), 61.9 (C-6), 71.1 (α-CH_2-allyl), 72.4 and 73.5 (C-3 and C-5), 76.6 (C-2 and C-4), 95.8 (C-1), 116.3 (γ-CH_2-allyl), and 135.0 (β-CH-allyl).

*Heptakis(2-*O-*allyl)cyclomaltoheptaose* (**13**).—Treatment of **12** (0.75 g) with tetrabutylammonium fluoride trihydrate (0.56 g) in 1:1 THF–DMF (10 mL) for 18 h at room temperature, as described for the preparation of **8**, gave, after column chromatography (4:1 $CHCl_3$–MeOH), **13** (0.306 g, 87%); mp 245 °C (dec); TLC (2:1 $CHCl_3$–MeOH) R_f 0.50; $[\alpha]_D^{21}$ +68.6° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, Me_2SO-d_6): δ 3.31 (dd, 7 H, H-2), 3.40 (dd, 7 H, H-4), 3.55 (m, 7 H, H-5), 3.59–3.69 (m, 14 H, H-6a,6b), 3.76 (dd, 7 H, $J_{2,3} \simeq J_{3,4} \simeq 9.2$ Hz, H-3), 4.20 (m, 7 H, $J_{A,Y}$ 6, $J_{X,Y}$ 12.7 Hz, H-Y), 4.33 (m, 7 H, $J_{A,X}$ 5.4 Hz, H-X), 4.46 (dd, 7 H, $J_{6\text{-OH},6a} = J_{6\text{-OH},6b} = 5.5$ Hz, 6-OH), 4.76 (s, 7 H, 3-OH), 4.96 (d, 7 H, $J_{1,2}$ 3.2 Hz, H-1), 5.20 (m, 7 H, $J_{A,N}$ 10.1 Hz, H-N), 5.31 (m, 7 H, $J_{A,M}$ 17.3 Hz, H-M), and 5.89 (m, 7 H, H-A); ^{13}C NMR (100.62 MHz, Me_2SO-d_6): δ 60.68 (C-6), 72.37 (C-5), 73.21 (α-CH_2-allyl), 73.60 (C-3), 80.19 (C-2), 82.98 (C-4), 101.06 (C-1), 118.58 (γ-CH_2-allyl), and 135.50 (β-CH-allyl); $C_{63}H_{98}O_{35}$ 1415.45, FABMS: m/z_{calcd} 1414.6 $[M]^+$, m/z_{found} 1437.1 $[M + Na]^+$.

Heptakis(3,6-di-O-*acetyl-2-*O-*allyl)cyclomaltoheptaose* (**14**).—A solution of **13** (30.3

mg) and 4-dimethylaminopyridine (20 mg) in 2:1 dry pyridine–Ac_2O was kept for 2 days at 70 °C, as described for the preparation of **5**. After co-distillation with toluene, a solution of the residue in $CHCl_3$ was washed with dilute (3%) HCl, satd aq NaCl, and water, dried, and concentrated. Silica gel filtration of the residue with EtOAc was followed by column chromatography (1:5 toluene–EtOAc), to afford **14** (20.5 mg, 48%); mp 228 °C; TLC (1:5 toluene–EtOAc) R_f 0.12; $[\alpha]_D^{21}$ +65.9° (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05, 2.11 (2 s, 42 H, Ac), 3.38 (dd, 7 H, $J_{2,3}$ 9.6 Hz, H-2), 3.63 (dd, 7 H, H-4), 4.01–4.12 (m, 21 H, H-X, H-Y, H-5), 4.34 (dd, 7 H, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.51 (dd, 7 H, H-6a), 4.91 (d, 7 H, $J_{1,2}$ 3.6 Hz, H-1), 5.17–5.31 (m, 21 H, H-3, H-N, H-M), and 5.85 (m, 7 H, H-A).

Heptakis(2-O-allyl-3,6-di-O-methyl)cyclomaltoheptaose (**15**).—To a stirred solution of **13** (113 mg, 0.08 mmol) in dry DMF (10 mL) at 0 °C were added NaH (0.54 g, 22.5 mmol, 80% in mineral oil, washed with *n*-pentane) and MeI (1.4 mL, 3.13 g, 22.5 mmol). After 2 h the temperature was raised to room temperature and stirring continued for 2 days. Excess of NaH was destroyed at 0 °C by the addition of MeOH. The solvents were coevaporated with added 1-butanol. A solution of the residue in $CHCl_3$ was washed with aq 10% NaS_2O_3, satd aq NaCl, and water, dried, and concentrated. Chromatography of the residue with two consecutive columns of silica gel (toluene–EtOAc: I, 10:1; II, 8:1) afforded **15** (96.9 mg, 84%); mp 310 °C (dec); TLC (5:1 toluene–EtOH) R_f 0.45; $[\alpha]_D^{21}$ +44.6° (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.34 (d, 7 H, $J_{1,2}$ 10 Hz, H-2), 3.37 (s, 21 H, O-Me), 3.50–3.59 (m, 14 H, H-3,6b), 3.60–3.68 (m, 28 H, H-4, O-Me), 3.80 (ddd, 7 H, $J_{4,5}$ 9.2 Hz, H-5), 3.85 (dd, 7 H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 10.2 Hz, H-6a), 4.14 (m, 7 H, $J_{A,Y}$ 5.2, $J_{X,Y}$ 12.8 Hz, H-Y), 4.23 (m, 7 H, $J_{A,X}$ 5.2 Hz, H-X), 5.09 (d, 7 H, $J_{1,2}$ 3.6 Hz, H-1), 5.14 (m, 7 H, $J_{A,N}$ 10.2 Hz, H-N), 5.30 (m, 7 H, $J_{A,M}$ 17.2 Hz, H-M), and 5.90 (m, 7 H, H-A); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 58.34 and 60.97 (2- and 6-O-Me), 70.30 and 70.85 (C-5 and C-6), 71.19 (α-CH_2-allyl), 78.92 and 79.13 (C-2 and C-4), 81.40 (C-3), 98.64 (C-1), 116.03 (γ-CH_2-allyl), and 134.75 (β-CH).

Heptakis(3,6-di-O-methyl)cyclomaltoheptaose (**16**).—A solution of **15** (57.5 mg, 0.036 mmol) with bis(methyldiphenylphosphine)(1,5-cyclooctadien)iridium(I) hexafluorophosphate (3 mg), activated with H_2, in dry THF (10 mL) was stirred for 18 h at room temperature. The mixture was diluted with THF and concentrated. The residue was dissolved in $CHCl_3$, and the solution filtered through Celite and concentrated. To a solution of the residue in 10:1 acetone–water (3 mL) were added HgO (70 mg), and $HgCl_2$ in 10:1 acetone–water (1 mL). The solution was diluted with THF (3 mL) and stirred for 90 min at room temperature. Upon further dilution with THF (2 mL), the mixture was filtered and concentrated. A solution of the residue in $CHCl_3$ was washed successively with aq 10% KI and water, dried, and concentrated. Column chromatography (6:1 toluene–EtOH) of the residue afforded **16** (26.0 mg, 0.02 mmol, 54%); mp 198 °C; TLC (5:3 toluene–EtOH) R_f 0.17; $[\alpha]_D^{21}$ +125.0° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (s, 21 H, O-Me), 3.50–3.58 (m, 14 H, H-3,5), 3.63–3.75 (m, 21 H, H-2,4,6b), 3.71 (s, 21 H, OMe), 3.78 (dd, 7 H, $J_{5,6a}$ 3.2, $J_{6a,6b}$ 9.2 Hz, H-6a), 4.82 (d, 7 H, $J_{2\text{-OH},2}$ 9.6 Hz, 2-OH), and 4.90 (d, 7 H, $J_{1,2}$ 3.4 Hz, H-1), in good agreement with previously reported partial 90-MHz NMR data; ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 58.5 (2- and 6-OMe), 70.2 (C-6), 71.1 and 73.0 (C-2 and C-4), 79.0 and 82.6

(C-3 and C-5), and 102.8 (C-1), in fair agreement with previously reported [1] 22.6-MHz NMR data; C-4 and C-5 were assigned in reversed order.

*Heptakis(3,6-di-*O*-tert-butyldimethylsilyl-2-*O*-methyl)cyclomaltoheptaose* (**17**).—Treatment of **11** (100 mg) and NaH (245 mg) in dry THF (5 mL) with MeI (0.64 mL), as described for the preparation of **3**, gave, after column chromatography (80:1 *n*-hexane–EtOAc, twice), **17** (43 mg, 40.5%); mp 228 °C; TLC (1:8 *n*-hexane–toluene) R_f 0.93; $[\alpha]_D^{21}$ +53.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 0.03 (s, 42 H, 6-O-SiMe_2), 0.09 and 0.10 (2 s, 42 H, 3-O-SiMe_2), 0.89 (2 s, 126 H, 6-O- and 3-O-SiCMe_3), 3.04 (dd, 7 H, $J_{2,3}$ 8.14 Hz, H-2), 3.35 (s, 21 H, 2-OMe), 3.70 (dd, 7 H, H-6a), 3.75–3.87 (m, 14 H, H-4,5), 4.13 (dd, 7 H, H-3), 4.21 (dd, 7 H, $J_{6a,6b}$ 11.3 Hz, H-6b), and 5.27 (d, 7 H, $J_{1,2}$ 3.6 Hz, H-1); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ −5.09, −4.77, −3.84, −3.76 (6-O- and 3-O-Si*Me*$_2$), 18.26, 18.36 (6-O- and 3-O-Si*C*Me_3), 25.98, 26.27 (6-O- and 3-O-SiCMe_3), 57.27 (2-OMe), 62.83 (C-6), 72.18 (C-5), 73.14 (C-3), 78.10 (C-4), 81.15 (C-2), and 96.16 (C-1).

*Heptakis(3,6-di-*O*-acetyl-2-*O*-methyl)cyclomaltoheptaose* (**19**).—Treatment of **17** (27.5 mg) with tetrabutylammonium fluoride (20 mg), as described for the preparation of **8**, gave the crude product **18**, which was acetylated according to the preparation of **5**, to give, after column chromatography (4:4:1 CH_2Cl_2–EtOAc–MeOH), **19** (9.8 mg, 47.4%); mp 144 °C; TLC (4:4:1 CH_2Cl_2–EtOAc–MeOH) R_f 0.31; $[\alpha]_D^{21}$ +89.4° (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (dd, 7 H, $J_{2,3}$ 10.2 Hz, H-2), 3.38, 3.39 (2 s, 42 H, Ac), 3.60 (dd, 7 H, H-4), 4.03–4.08 (m, 7 H, H-5), 4.31 (dd, 7 H, $J_{5,6b}$ 4.6 Hz, H-6b), 4.54 (dd, 7 H, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.94 (d, 7 H, $J_{1,2}$ 3.56 Hz, H-1), and 5.23 (dd, 7 H, $J_{3,4}$ 8.6 Hz, H-3); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 20.76, 20.89 (CO*Me*), 58.95 (2-OMe), 62.90 (C-6), 69.97 (C-5), 72.31 (C-3), 78.93 (C-4), 79.49 (C-2), 95.68 (C-1), and 170.35 (C=O).

*Methyl 4,6-*O*-benzylidene-2-*O*-tert-butyldimethylsilyl- and -3-*O*-tert-butyldimethylsilyl-α-*D*-glucopyranoside* (**30** *and* **31**).—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**27**) was converted into a mixture of **30** and **31** according to Fügedi [1]. The regioisomers were isolated by column chromatography on silica gel with 9:1 petroleum ether–EtOAc. MS (EI) (for m/z < 150, > 10%; for m/z > 150, > 5%): for **30**, m/z (% rel. int.) 41(16), 43(13), 45(16), 57(11), 59(22), 69(100), 73(55), 75(71), 77(21), 79(15), 89(44), 91(46), 105(31), 107(18), 116(17), 117(26), 129(50), 131(13), 147(15), 149(24), 155(8), 171(9), 173(18), 201(17), 215(9), 233(11), 397(17); for **31**, 43(20), 45(11), 59(15), 73(39), 75(56), 77(11), 91(28), 101(10), 105(18), 117(13), 129(100), 130(10), 131(14), 143(25), 149(31), 155(5), 159(9), 171(6), 173(8), 201(6), 265(16), 307(21). The molecular masses (396) were confirmed by CIMS. ^{1}H NMR (400 MHz, $CDCl_3$): for **30**, δ 0.14 (s, 6 H, 2-O-SiMe_2), 0.91 (s, 9 H, 2-O-SiCMe_3), 3.43 (s, 3 H, 1-OMe), 3.45–4.35 (6 H, H-2,3,4,5,6), 4.65 (d, 3.5 Hz, 1 H, H-1), 5.5 (s, 1 H, C*H*Ph), 7.3–7.5 (m, 5 H, Ph); for **31**, δ 0.02, 0.10 (2 s, 6 H, 3-O-SiMe_2), 0.85 (s, 9 H, 3-O-SiCMe_3), 3.38–4.3 (6 H, H-2,3,4,5,6), 4.80 (d, 3.5 Hz, 1 H, H-1), 5.5 (s, 1 H, C*H*Ph), 7.3–7.5 (m, 5 H, Ph); ^{13}C NMR (100.62 MHz, $CDCl_3$): for **30**, δ −4.71, −4.46 (2-O-SiMe_2), 18.23 (2-O-Si*C*Me_3), 25.79 (2-O-SiC*Me*$_3$), 55.57 (1-OMe), 62.30, 70.91, 74.22, 81.25 (C-2,3,4,5), 69.09 (C-6), 100.83, 101.88 (C-1, *C*HPh), 125.88, 126.31, 128.17, 129.12 (CH arom.), 137.23 (C, arom.); for **31**, δ −4.69, −4.30 (2-O-SiMe_2), 18.30 (3-O-Si*C*Me_3), 25.85 (3-O-SiC*Me*$_3$), 55.38 (1-OMe), 62.66, 73.19,

73.71, 81.76 (C-2,3,4,5), 69.03 (C-6), 100.10, 101.75 (C-1, *C*HPh), 125.88, 126.31, 128.17, 129.12 (CH arom.), 137.34 (C, arom.).

Methyl 4,6-O-benzylidene-2-O-tert-butyldimethylsilyl-3-O-methyl- and -3-O-tert-butyldimethylsilyl-2-O-methyl-α-D-glucopyranoside (**32** *and* **33**).—The identity of the methylation products **32** and **33** was proved by hydrolysis, reduction, acetylation, and GCMS of the resulting 2-*O*-methyl- or 3-*O*-methyl-D-glucitol acetates as described [16].

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