Carbohydrate Research, 187 (1989) 203–221
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SELECTIVE CHEMICAL MODIFICATION OF CYCLOMALTO-OLIGOSACCHARIDES *via tert*-BUTYLDIMETHYLSILYLATION

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(Received August 9th, 1988; accepted for publication, November 12th, 1988)

ABSTRACT

Selective reaction of cyclomaltoheptaose and cyclomalto-octaose with *tert*-butylchlorodimethylsilane in *N,N*-dimethylformamide in the presence of imidazole gave the heptakis(6-*O*-*tert*-butyldimethylsilyl) (**21**) and octakis(6-*O*-*tert*-butyldimethylsilyl) (**27**) derivatives in yields of 70 and 67%, respectively. The twelve partially methylated regioisomers of cyclomalto-oligosaccharides, namely, hexakis(2- and 3-*O*-methyl, and 2,6- and 3,6-di-*O*-methyl)cyclomaltohexaoses, heptakis(2-, 3-, and 6-*O*-methyl and 2,3-, 2,6- and 3,6-di-*O*-methyl)cyclomaltoheptaoses, and octakis(6-*O*-methyl and 2,3-di-*O*-methyl)cyclomalto-octaoses, have been prepared crystalline by unambiguous routes using hexakis(6-*O*-*tert*-butyldimethylsilyl)cyclomaltohexaose (**2**), **21**, and **27**, respectively, as the key intermediates. The synthesis of several heptakis- and octakis-(6-substituted) derivatives of cyclomalto-heptaose and -octaose is also described.

INTRODUCTION

Selective chemical modification of cyclomalto-oligosaccharides (cyclodextrins, cycloamyloses) involves problems originating from the steric and statistical factors imposed by the torus structures and the large number of hydroxyl groups[1–4]. We have reported[5] an efficient method for the preparation of several hexakis(6-substituted) and hexakis(2,3-disubstituted) derivatives of cyclomaltohexaose (**1**), using the hexakis(6-*O*-*tert*-butyldimethylsilyl) derivative **2** as the key intermediate. As a further extension of our studies of the chemical modifiation of cyclomalto-oligosaccharides[5–8], we now report the preparation of hexakis[2- (**4**) and 3-*O*-methyl (**13**) and 2,6- (**9**) and 3,6-di-*O*-methyl (**16**)] derivatives of **1** starting from **2**[5], and the synthesis of derivatives of cyclomaltoheptaose (**20**) and cyclomalto-octaose (**26**) by application of reaction sequences analogous to those worked out for the synthesis of the derivatives of **1**.

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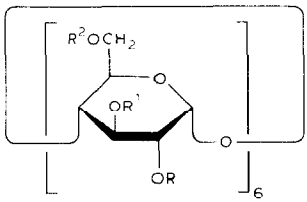
0008-6215/89/$ 03.50



	R	R¹	R²
1	H	H	H
2	H	H	X
3	Me	H	X
4	Me	H	H
5	Me	Allyl	X
6	Me	Bzl	X
7	Me	Allyl	H
8	Me	Allyl	Me
9	Me	H	Me
10	Bzl	H	X
11	Bzl	Me	X
12	Bzl	Me	H
13	H	Me	H
14	Bzl	H	H
15	Bzl	Me	Me
16	H	Me	Me
17	Bz	Bz	H
18	H	H	Me
19	Me	Me	H

X = *tert*-butyldimethylsilyl

RESULTS AND DISCUSSION

Selective methylation of **2** with 9 mol of methyl iodide in *N,N*-dimethylformamide in the presence of barium oxide and barium hydroxide[9] for 4 h at room temperature gave a mixture, column chromatography of which afforded 42% of the crystalline hexakis(6-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl) derivative **3**. Attempts to synthesise **3** *via* dibutyl-[10] and tributyl-stannylations[11] of **2** or by the phase-transfer method[12] were unsuccessful. The reactions were sluggish and incomplete and gave mixtures of partially methylated derivatives containing a small proportion of **3**. *O*-Desilylation of **3** with tetrabutylammonium fluoride[13] in oxolane afforded crystalline **4**. The identity of **4** and the structures of all the partially methylated derivatives described below were confirmed by ^{13}C-n.m.r. spectroscopy and by g.l.c. after hydrolysis and conversion of the products into the partially methylated D-glucitol acetates.

Alkylation of **3** (sparingly soluble in *N,N*-dimethylformamide) with allyl bromide in oxolane in the presence of sodium hydride[14] gave the hexakis(3-*O*-allyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl) derivative **5**. With the aim of obtaining the hexakis(3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl) derivative **6**, an attempted benzylation of **3** with benzyl bromide under conditions similar to those used for the preparation of **5** gave a mixture of partially benzylated derivatives; the use of tetrabutylammonium iodide as catalyst[15] was also ineffective. *O*-Desilylation of **5** with fluoride ion[13] afforded the hexakis(3-*O*-allyl-2-*O*-methyl) derivative **7**, which was methylated with methyl iodide in *N,N*-dimethylformamide in the presence of sodium hydride[14] to yield the hexakis(3-*O*-allyl-2,6-di-*O*-methyl) derivative **8**. The

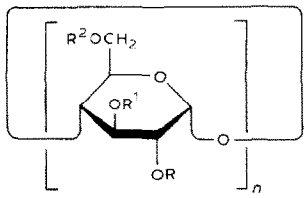
allyl groups in **8** were removed by rearrangement first to the propenyl ethers with tris(triphenylphosphine)rhodium(I) chloride[16,17] in the presence of 1,4-diazabicyclo[2.2.2]octane[16], followed by hydrolysis with mercuric chloride and mercuric oxide[18], to give crystalline **9**. Casu *et al.*[19,20] obtained **9** containing a small proportion of products with a higher degree of substitution by methylation of **1** with methyl sulfate and barium oxide in *N,N*-dimethylformamide and methyl sulfoxide[9]. Boger *et al.*[1] have optimised the reaction and isolation conditions of **9** by modification of the original procedure[19].

Partial benzylation of **2** with 7.2 mol of benzyl bromide in *N,N*-dimethylformamide in the presence of barium oxide and barium hydroxide[9] for 18 h at room temperature gave, after column chromatography, 46% of the hexakis(2-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl) derivative **10** which, with methyl iodide and sodium hydride in *N,N*-dimethylformamide and oxolane, afforded the hexakis(2-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl) derivative **11**. *O*-Desilylation of **11**, as above, afforded the hexakis(2-*O*-benzyl-3-*O*-methyl) derivative **12**, which was hydrogenolysed (Pd/C) to give crystalline **13**, thereby proving the structure of **10**. *O*-Desilylation of **10** afforded the hexakis(2-*O*-benzyl) derivative **14**, which was methylated[14] to give the hexakis(2-*O*-benzyl-3,6-di-*O*-methyl) derivative **15**. Catalytic hydrogenolysis of **15** furnished crystalline **16**.

Since **2** was found in the previous paper[5] and from the results obtained above to be a useful intermediate for the selective modification of **1**, the synthesis was investigated of the derivatives of **20** and **26**, analogous to those obtained above and previously[5] for **1**, using heptakis(6-*O*-*tert*-butyldimethylsilyl)cyclomaltoheptaose (**21**) and octakis(6-*O*-*tert*-butyldimethylsilyl)cyclomalto-octaose (**27**). Lipták *et al.*[2] reported the selective reaction of **20** with 7.7 mol of *tert*-butylchlorodimethylsilane in pyridine, followed by acetylation, to give the heptakis(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl) derivative **22**, which was saponified to provide **21**, and then methylated to afford the heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl) derivative **23**, hydrolysis of which with dilute acid yielded the heptakis(2,3-di-*O*-methyl) derivative **24**. However, the details of the isolation of **21**–**24**, and their physical constants, have not been reported.

Treatment of dried[5] **20** with 7.7 mol of *tert*-butylchlorodimethylsilane in *N,N*-dimethylformamide in the presence of imidazole[13] for 2.5 h at room temperature, as for **1**[5], gave, after column chromatography, 70% of crystalline **21**, the ^{13}C-n.m.r. spectrum of which reflected the seven-fold symmetry[1,3,5,21]. Acetylation[5] of **21** with acetic anhydride–pyridine for 4 h at 100° provided **22**. Methylation of **21** with methyl iodide and sodium hydride in oxolane afforded **23**, *O*-desilylation of which gave crystalline **24**. A similar reaction of **20** with 26 mol of the silylating reagent in *N,N*-dimethylformamide in the presence of imidazole at 90° and then at room temperature was reported[22] to give 42% of the heptakis(2,6-di-*O*-*tert*-butyldimethylsilyl) derivative **25**.

Likewise, selective *tert*-butyldimethylsilylation of **26** with 8.8 mol of the reagent in *N,N*-dimethylformamide in the presence of imidazole afforded crystal-



	n	R	R1	R2		n	R	R1	R2
20	7	H	H	H	36	8	H	H	Me
21	7	H	H	X	37	7	Me	H	X
22	7	Ac	Ac	X	38	7	Me	H	H
23	7	Me	Me	X	39	7	Me	Allyl	X
24	7	Me	Me	H	40	7	Me	Allyl	H
25	7	X	H	X	41	7	Me	Allyl	Me
26	8	H	H	H	42	7	Me	H	Me
27	8	H	H	X	43	7	Bzl	H	X
28	8	Ac	Ac	X	44	7	Bzl	Me	X
29	8	Me	Me	X	45	7	Bzl	Me	H
30	8	Me	Me	H	46	7	H	Me	H
31	7	Ac	Ac	H	47	7	Allyl	H	Allyl
32	8	Ac	Ac	H	48	7	Bzl	H	H
33	7	Ac	Ac	Me	49	7	Bzl	Me	Me
34	7	H	H	Me	50	7	H	Me	Me
35	8	Ac	Ac	Me					

X = *tert*-butyldimethylsilyl

line **27** (67% after column chromatography), which was converted into the octakis(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl) derivative **28**. Methylation of **27** with methyl iodide and sodium hydride in oxolane afforded the octakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl) derivative **29**, *O*-desilylation of which gave the crystalline octakis(2,3-di-*O*-methyl) derivative **30**. The ^{13}C-n.m.r. spectrum of **27** in $CDCl_3$ did not show the eight-fold symmetry expected[1,3,5,21], whereas each of the ^{13}C-n.m.r. spectra of **28** and **29** in the same solvent contained signals for only six skeleton carbons, which suggested a distortion of the macrocyclic ring of **27** in the solvent.

In contrast to the easy allylation and benzylation of all HO-2,3 in **2**[5], attempted alkylation of **21** and **27** under similar conditions gave a mixture of partially alkylated derivatives. Increasing the amounts of the reagents did not yield the fully alkylated derivatives and, at prolonged elevated temperatures, extensive cleavage of the silyl groups occurred.

O-Desilylation of **22** and **28** with boron trifluoride etherate[5,23] in dichloromethane afforded the heptakis((2,3-di-*O*-acetyl) and octakis(2,3-di-*O*-acetyl) derivatives **31** and **32**, respectively. The ^{13}C-n.m.r. spectra of **31** and **32** in $(CD_3)_2SO$ (but not in $CDCl_3$) showed the expected seven- and eight-fold symmetry,

respectively. Boger *et al.*[1] have observed a similar solvent effect of the hexakis(2,3-di-*O*-benzoyl) derivative **17** and, on the basis of the i.r. spectra and optical rotations, suggested different conformations of **17** in the two solvents. However, the optical rotations of **31** and **32** measured in the two solvents were almost identical. Methylation of **31** with methyl trifluoromethanesulfonate (triflate) in dichloromethane in the presence of 2,6-di-*tert*-butyl-4-methylpyridine[24] gave the heptakis(2,3-di-*O*-acetyl-6-*O*-methyl) derivative **33**, *O*-deacetylation of which afforded the crystalline heptakis(6-*O*-methyl) derivative **34**. Similarly, methylation[24] of **32** (→ **35**), followed by *O*-deacetylation, provided the crystalline octakis(6-*O*-methyl) derivative **36**.

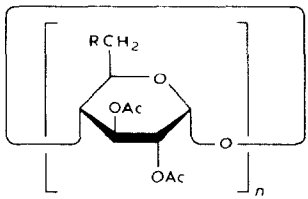
Partial methylation of **21**, as for **2**, gave the heptakis(6-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl) derivative **37** (61% after column chromatography), *O*-desilylation of which provided the crystalline heptakis(2-*O*-methyl) derivative **38**. However, the physical constants of **38** differed from those reported[7]. The previous route to **38**, which involved the sequence selective methylation of the heptakis(6-bromo-6-deoxy) derivative **53**, nucleophilic displacement with benzoate ion, and saponification[7], requires re-investigation because ^{13}C-n.m.r. spectroscopy was not used to determine the structure of each intermediate.

The heptakis(2,6-di-*O*-methyl) derivative **42** was prepared from **37** by a reaction sequence (→ **39** → **40** → **41** → **42**) similar to that described for the preparation of **9**. Several research groups[1,19,20,25] have obtained **42** by selective methylation of **20**, according to the Kuhn method[9] or modifications thereof. However, Koizumi *et al.*[26] found (t.l.c., h.p.l.c.) **42** obtained by these workers[19,25] to be contaminated with derivatives having higher degrees of substitution and pure **42** was obtainable only by preparative h.p.l.c.

Selective benzylation of **21**, as for **2**, afforded the heptakis(2-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl) derivative **43** (68% after column chromatography), which was converted into the crystalline heptakis(3-*O*-methyl) derivative **46** by the sequence methylation (→ **44**), *O*-desilylation (→**45**), and catalytic hydrogenolysis. Bergeron *et al.*[27] have reported the synthesis of **46** from the heptakis(2,6-di-*O*-allyl) derivative **47**, but gave no physical constants. *O*-Desilylation of **43** (→ **48**), methylation (→ **49**), and hydrogenolysis afforded the crystalline heptakis(3,6-di-*O*-methyl) derivative **50**. In order to obtain the octakis(2-*O*-alkyl) derivative of **27**, attempted selective methylation and benzylation of **27**, under conditions similar to those used for **2** and **21**, gave complex mixtures of the products that were difficult to fractionate by column chromatography. Thus, together with the previous synthesis[5] of the hexakis[6-*O*-methyl (**18**) and 2,3-di-*O*-methyl (**19**)] derivatives, the preparation is now completed of all the regioisomeric hexakis- and heptakis(mono- and di-*O*-methyl) derivatives of **1** and **20** and of the regioisomers **30** and **36** of **26**. The complexing and catalytic properties[20,25,28] of these derivatives will be of interest.

Methanesulfonylation of **31** and **32** gave the heptakis(2,3-di-*O*-acetyl-6-*O*-methylsulfonyl)[29,30] and octakis(2,3-di-*O*-acetyl-6-*O*-methylsulfonyl) derivatives **51**

and **52**, respectively. Nucleophilic displacements of **51** with sodium bromide, sodium iodide, lithium chloride, and sodium azide in *N,N*-dimethylformamide afforded **53**[6], the heptakis[6-deoxy-6-iodo[30] (**54**), 6-chloro-6-deoxy (**55**), and 6-azido-6-deoxy[1] (**56**)] derivatives, respectively, of the tetradeca-acetates of **20**. Reductive dehalogenation of **54** in 1,4-dioxane–methanol in the presence of Pd/C and triethylamine provided the heptakis(2,3-di-*O*-acetyl-6-deoxy) derivative[6] **57**. Similarly, **52** underwent nucleophilic displacement with the iodide, bromide, chloride, and azide ions in *N,N*-dimethylformamide to afford the octakis[6-deoxy-6-iodo (**58**), 6-bromo-6-deoxy[6] (**59**), 6-chloro-6-deoxy (**60**), and 6-azido-6-deoxy (**61**)] derivatives, respectively, of the hexadeca-acetates of **26**. Compound **58** was reductively dehalogenated to furnish the octakis(2,3-di-*O*-acetyl-6-deoxy) derivative[6] **62**. Compounds **51, 53, 54, 57, 59**, and **62**, obtained previously by alternative routes, were not purified by column chromatography.



	n	R		*n*	R
51	7	OMs	**57**	7	H
52	8	OMs	**58**	8	I
53	7	Br	**59**	8	Br
54	7	I	**60**	8	Cl
55	7	Cl	**61**	8	N_3
56	7	N_3	**62**	8	H

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with an Applied Electronic polarimeter Model MP-1T. N.m.r. spectra (^1H, 90 MHz; ^{13}C, 22.6 MHz) were recorded with a Hitachi R-90H spectrometer for solutions in $CDCl_3$ and $(CD_3)_2SO$ (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-4-silapentanoate-d_4). I.r. spectra were recorded with a Nicolet 5SXC FT-IR spectrometer in potassium bromide pellets. Correct analytical data were not obtained for most of the derivatives of **20** and **26**, because of their highly hygroscopic nature and their complexation with solvents[20,31], but their purity was established by t.l.c. and n.m.r. spectroscopy. The purity of the partially methylated derivatives was also confirmed by g.l.c.[32] after hydrolysis with 2M trifluoroacetic acid (sealed tube, 18 h, 100°), borohydride reduction, and acetylation. Organic

solutions were dried over anhydrous sodium sulfate. Solutions were concentrated at <50° under diminished pressure. T.l.c. was performed on silica gel (7734, Merck) with detection by charring with sulfuric acid. Column chromatography was performed on Waco Gel C-300. Compounds **20** and **26** were dried as described[5].

Hexakis(6-O-tert-butyldimethylsilyl-2-O-methyl)cyclomaltohexaose (**3**). — Methyl iodide (0.67 mL, 10.8 mmol) was added at 5° to a solution of **2** (2.0 g, 1.2 mmol) in *N,N*-dimethylformamide (60 mL) containing barium oxide (3.0 g) and barium hydroxide octahydrate (1.5 g). The mixture was stirred for 4 h at room temperature, and the inorganic material was collected on a pad of Celite and washed with chloroform. The combined filtrate and washings were neutralised with dilute sulfuric acid and concentrated. A solution of the residue in chloroform was washed successively with water, aqueous sodium thiosulfate, and water, dried, and concentrated. Column chromatography (4:1 → 1:1 benzene–ethyl acetate, stepwise) of the residue gave **3** (0.88 g, 42%), m.p. 260–263° (from methanol), $[\alpha]_D^{18}$ +78° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.98 (d, 6 H, $J_{1,2}$ 2.9 Hz, H-1), 4.92 (s, 6 H, exchangeable with D_2O, HO-3), 3.69 (s, 18 H, 6 OMe), 3.25 (dd, 6 H, $J_{2,3}$ 9.7 Hz, H-2), 0.88 [s, 54 H, 6 $(CH_3)_3C$], and 0.05 [s, 36 H, 6 $(CH_3)_2Si$]; ^{13}C, δ 100.5 (C-1), 82.4 (C-4), 81.9 (C-2), 73.5 and 71.65 (C-3,5), 61.9 (C-6), 60.0 (OMe), 25.9 [$(CH_3)_3C$], 18.4 [$(CH_3)_3C$], and −5.1 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{13}H_{26}O_5Si)_6$: C, 53.76; H, 9.02. Found: C, 53.92; H, 9.22.

Hexakis(2-O-methyl)cyclomaltohexaose (**4**). — M Tetrabutylammonium fluoride in oxolane (0.9 mL) was added to a solution of **3** (0.22 g) in oxolane (3 mL), and the mixture was boiled for 2 h under reflux and then concentrated. A solution of the residue in dichloromethane was washed with brine, dried, and concentrated. Column chromatography (9:1 → 4:1 chloroform–methanol, stepwise) of the residue afforded **4** (0.11 g, 85%), m.p. ~345° (dec.) (from methanol), $[\alpha]_D^{18}$ +111° (*c* 0.8, dimethyl sulfoxide). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 4.99 (s, 6 H, H-1), 4.67 (s, 6 H, exchangeable with D_2O, HO-3), 4.45 (s, 6 H, exchangeable with D_2O, HO-6), and 3.49 (s, 18 H, 6 OMe); ^{13}C, δ 99.5 (C-1), 82.6 (C-4), 81.4 (C-2), 72.7 and 71.5 (C-3,5), 59.9 (C-6), and 59.1 (OMe).

Anal. Calc. for $(C_7H_{12}O_5)_6$: C, 47.72; H, 6.87. Found: C, 48.03; H, 6.95.

Hexakis(3-O-allyl-6-O-tert-butyldimethylsilyl-2-O-methyl)cyclomaltohexaose (**5**). — Sodium hydride (0.62 g; 50% mineral oil) was added at 0° to a solution of **4** (1.26 g) in oxolane (18 mL), and the mixture was stirred for 2 h at room temperature and then cooled to 0°. Allyl bromide (1.1 mL) was added dropwise and the mixture was stirred overnight at room temperature. Methanol was then added to decompose the excess of hydride, the solvents were evaporated, and a solution of the residue in dichloromethane was washed with water, dried, and concentrated. The residue was subjected to column chromatography (20:1 hexane–ethyl acetate), to give **5** (1.43 g, 82%), m.p. 196–201° (from methanol), $[\alpha]_D^{19}$ +99° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.31–5.94 (m, 6 H, –CH=), 5.09 (d, 6 H, $J_{1,2}$ 2.2 Hz, H-1), 3.50 (s, 18 H, 6 OMe), 0.87 [s, 54 H, 6 $(CH_3)_3C$], and 0.05 [s, 36 H, 6 $(CH_3)_2Si$]; ^{13}C, δ 136.5 and 116.0 ($CH=CH_2$), 99.2 (C-1), 82.3 (C-4), 80.4 and 79.4

(C-2,3), 74.8 (CH_2=CH–CH_2), 72.5 (C-5), 62.4 (C-6), 58.6 (OMe), 25.9 [$(CH_3)_3C$], 18.2 [$(CH_3)_3C$], and −4.8 and −5.1 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{16}H_{30}O_5Si)_6$: C, 58.14; H, 9.15. Found: C, 58.40; H, 9.29.

Hexakis(3-O-allyl-2-O-methyl)cyclomaltohexaose (**7**). — A solution of **5** (1.26 g) in oxolane (20 mL) was boiled for 2 h under reflux with M tetrabutylammonium fluoride in oxolane (4.6 mL) and processed as described for the preparation of **4**. Column chromatography (9:1 → 4:1 chloroform–methanol, stepwise) of the product afforded **7** (0.68 g, 83%), m.p. 131–139° (from ethanol), $[\alpha]_D^{18}$ +130° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.23–5.86 (m, 6 H, –CH=), 5.07 (s, 6 H, H-1), and 3.47 (s, 18 H, 6 OMe); ^{13}C, δ 136.2 and 115.8 (CH=CH_2), 98.6 (C-1), 81.7, 81.4, and 79.7 (C-2,3,4), 74.6 (CH_2=CH–CH_2), 73.1 (C-5), 62.3 (C-6), and 58.9 (OMe).

Anal. Calc. for $(C_{10}H_{16}O_5)_6$: C, 55.46; H, 7.46. Found: C, 55.35; H, 7.67.

Hexakis(3-O-allyl-2,6-di-O-methyl)cyclomaltohexaose (**8**). — A solution of **7** (0.55 g) in *N,N*-dimethylformamide (7 mL) was stirred with sodium hydride (0.19 g; 50% mineral oil) for 1 h at room temperature and then cooled to 0°. Methyl iodide (1 mL) was added dropwise and the mixture was processed as described for the preparation of **5**. Column chromatography (19:1 benzene–ethyl acetate) of the product gave **8** (0.51 g, 86%), m.p. 99–104° (from light petrolcum), $[\alpha]_D^{19}$ +133° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.28–5.91 (m, 6 H, –CH=), 5.05 (d, 6 H, $J_{1,2}$ 3.1 Hz, H-1), and 3.46 and 3.39 (2 s, each 18 H, 12 OMe); ^{13}C, δ 136.5 and 115.9 (CH=CH_2), 100.1 (C-1), 82.3 (2 C) (C-2,4), 78.8 (C-3), 74.7 (CH_2=CH–CH_2), 71.5 (C-6), 71.3 (C-5), and 58.85 and 58.75 (OMe).

Anal. Calc. for $(C_{11}H_{18}O_5)_6$: C, 57.38; H, 7.88. Found: C, 57.55; H, 7.76.

Hexakis(2,6-di-O-methyl)cyclomaltohexaose (**9**). — A mixture of **8** (0.39 g), tris(triphenylphosphine)rhodium(I) chloride (0.1 g), and 1,4-diazabicyclo[2.2.2]-octane (0.3 g) in 8:3:1 ethanol–toluene–water (15 mL) was stirred overnight under reflux and then concentrated. The residue was extracted with chloroform, and the extract was washed successively with brine, cold M hydrochloric acid, aqueous sodium hydrogencarbonate, and brine, dried, and concentrated. To a solution of the residue in 4:1 acetone–water (5 mL) was added mercuric oxide (0.1 g), followed by a solution of mercuric chloride (0.1 g) in 9:1 acetone–water (2 mL). The suspension was stirred for 30 min at room temperature, the solids were removed by filtration, and the filtrate was concentrated. A solution of the residue in chloroform was washed successively with brine, aqueous potassium iodide, and brine, dried, and concentrated. Column chromatography (99:1 → 49:1 chloroform–methanol, stepwise) of the residue gave **9** (0.24 g, 75%), m.p. 301–306° (dec.) (from methanol), $[\alpha]_D^{20}$ +118° (*c* 1.6, chloroform), $[\alpha]_D^{18}$ +152.5° (*c* 1.5, water); lit.[1] $[\alpha]_D^{22}$ +118.3° (chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.97 (d, 6 H, $J_{1,2}$ 3.3 Hz, H-1), 4.84 (s, 6 H, exchangeable with D_2O, HO-3), and 3.62 and 3.41 (2 s, each 18 H, 12 OMe); ^{13}C, δ 100.8 (C-1), 83.5 (C-4), 81.7 (C-2), 73.5 (C-3), 70.5 (C-6), 71.2 (C-5), and 60.1 and 59.1 (OMe).

Anal. Calc. for $(C_8H_{14}O_5)_6$: C, 50.52; H, 7.42. Found: C, 50.40; H, 7.27.

*Hexakis(2-O-benzyl-6-O-*tert*-butyldimethylsilyl)cyclomaltohexaose* (**10**). — Benzyl bromide (1.53 mL, 13 mmol) was added to a mixture of **2** (3.0 g, 1.8 mmol), barium oxide (4.5 g), and barium hydroxide octahydrate (2.25 g) in *N,N*-dimethylformamide (90 mL). The mixture was stirred for 18 h at room temperature, followed by addition of methanol (3 mL) to destroy the excess of benzyl bromide. After being stirred for 1 h, the mixture was filtered through a bed of Celite which was washed with chloroform. The combined filtrate and washings were neutralised with dilute sulfuric acid and most of the solvents were evaporated. A solution of the residue in chloroform was washed with water, dried, and concentrated. Column chromatography (25:1 → 10:1 benzene–ethyl acetate, stepwise) of the residue afforded **10** (1.83 g, 46%), m.p. 204–206° (from ethanol), $[\alpha]_D^{18}$ +48° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.35 (s, 30 H, 6 Ph), 4.85 (ABq, 12 H, J 11.8 Hz, 6 PhCH_2), 0.85 [s, 54 H, 6 $(CH_3)_3C$], and −0.01 [s, 36 H, 6 $(CH_3)_2Si$]; ^{13}C, δ 137.7 (aromatic C-1), 101.2 (C-1), 82.4 (C-4), 78.1 (C-2), 73.9 and 71.5 (C-3,5), 73.8 (PhCH_2), 61.9 (C-6), 25.9 [$(CH_3)_3C$], 18.4 [$(CH_3)_3C$], and −5.2 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{19}H_{30}O_5Si)_6$: C, 62.26; H, 8.25. Found: C, 62.48; H, 8.40.

*Hexakis(2-O-benzyl-6-O-*tert*-butyldimethylsilyl-3-O-methyl)cyclomaltohexaose* (**11**). — A solution of **10** (1.21 g) in *N,N*-dimethylformamide (4 mL) and oxolane (10 mL) was treated with sodium hydride (0.48 g; 50% mineral oil), followed by methyl iodide (1.2 mL), and processed as described for the preparation of **5**. Column chromatography (10:1 hexane–ethyl acetate) of the product gave **11** (1.11 g, 88%), m.p. 183–188° (from ethanol), $[\alpha]_D^{18}$ +85° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.48–7.22 (m, 30 H, 6 Ph), 5.02 (d, 6 H, $J_{1,2}$ 2.9 Hz, H-1), 3.50 (s, 18 H, 6 OMe), 0.85 [s, 54 H, 6 $(CH_3)_3C$], and 0.01 [s, 36 H, 6 $(CH_3)_2Si$]; ^{13}C, δ 138.9 (aromatic C-1), 99.85 (C-1). 81.6 (C-4), 80.8 and 80.3 (C-2,3), 72.6 (C-5), 72.2 (PhCH_2), 62.35 (C-6), 61.7 (OMe), 25.9 [$(CH_3)_3C$], 18.3 [$(CH_3)_3C$], and −5.1 and −4.8 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{20}H_{32}O_5Si)_6$: C, 63.12; H, 8.48. Found: C, 63.21; H, 8.71.

Hexakis(2-O-benzyl-3-O-methyl)cyclomaltohexaose (**12**). — A solution of **11** (0.97 g) in oxolane (5 mL) was treated with M tetrabutylammonium fluoride in oxolane (5 mL) and processed as described for the preparation of **4**. Column chromatography (20:1 benzene–ethanol) of the product afforded **12** (0.58 g, 85%), m.p. 131–137° (from methanol), $[\alpha]_D^{18}$ +128° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.44–7.19 (m, 30 H, 6 Ph), 5.00 (d, 6 H, $J_{1,2}$ 2.9 Hz, H-1), and 3.52 (s, 18 H, 6 OMe); ^{13}C, δ 138.8 (aromatic C-1), 99.1 (C-1), 82.1 (C-4), 81.4 and 79.9 (C-2,3), 73.0 (C-5), 72.5 (PhCH_2), 62.2 (C-6), and 61.7 (OMe).

Anal. Calc. for $(C_{14}H_{18}O_5)_6$: C, 63.15; H, 6.81. Found: C, 63.04; H, 7.01.

Hexakis(3-O-methyl)cyclomaltohexaose (**13**). — A solution of **12** (0.42 g) in 1:1 methanol–acetic acid (10 mL) was hydrogenated in the presence of 10% Pd/C (0.5 g) at atmospheric pressure for 1 day at room temperature and then filtered through a layer of Celite which was washed with methanol. The combined filtrate and washings were concentrated and the residue was crystallised from aqueous methanol to give **13** (0.24 g, 86%), m.p. 295–297° (dec.), $[\alpha]_D^{18}$ +141° (*c* 1.2,

water). N.m.r. data (D_2O): ^1H, δ 4.90 (s, 6 H, H-1) and 3.51 (s, 18 H, 6 OMe); ^{13}C, δ 102.4 (C-1), 83.6 (C-4), 79.7 (C-3), 73.6 and 72.7 (C-2,5), 62.0 (C-6), and 60.1 (OMe).

Anal. Calc. for $(C_7H_{12}O_5)_6$: C, 47.72; H, 6.87. Found: C, 47.60; H, 6.78.

Hexakis(2-O-benzyl)cyclomaltohexaose (**14**). — Treatment of **10** (0.85 g) in oxolane (8 mL) with M tetrabutylammonium fluoride in oxolane (2.8 mL) as described for the preparation of **4**, followed by column chromatography (15:1 chloroform–methanol) of the product, gave **14** (0.48 g, 83%), m.p. 237–242° (from chloroform–hexane), $[\alpha]_D^{18}$ +46° (*c* 0.7, chloroform). ^{13}C-n.m.r. data ($CDCl_3$): δ 137.6 (aromatic C-1), 101.0 (C-1), 84.0 (C-4), 78.2 (C-2), 74.1 and 71.9 (C-3,5), 73.6 ($PhCH_2$), and 61.3 (C-6).

Hexakis(2-O-benzyl-3,6-di-O-methyl)cyclomaltohexaose (**15**). — A solution of **14** (0.38 g) in *N,N*-dimethylformamide (5 mL) was treated with sodium hydride (0.3 g; 50% mineral oil), followed by methyl iodide (1 mL), and processed as described for the preparation of **5**. Column chromatography (99:1 → 49:1 benzene–ethanol, stepwise) of the product afforded **15** (0.38 g, 90%), m.p. 174–175° (from methanol), $[\alpha]_D^{18}$ +112° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.52–7.23 (m, 30 H, 6 Ph), 4.96 (d, 6 H, $J_{1,2}$ 2.9 Hz, H-1), and 3.55 and 3.36 (2 s, each 18 H, 12 OMe); ^{13}C, δ 138.8 (aromatic C-1), 100.7 (C-1), 82.4 (C-4), 81.5 and 80.0 (C-2,3), 72.2 ($PhCH_2$), 71.5 (C-6), 71.2 (C-5), and 61.9 and 58.8 (OMe).

Anal. Calc. for $(C_{15}H_{20}O_5)_6$: C, 64.27; H, 7.19. Found: C, 64.01; H, 7.11.

Hexakis(3,6-di-O-methyl)cyclomaltohexaose (**16**). — Hydrogenolysis of **15** (0.28 g) in acetic acid (6 mL) in the presence of 10% Pd/C (0.3 g), as described for **12**, followed by column chromatography (9:1 benzene–ethanol) of the product, afforded **16** (0.16 g, 84%), m.p. 224–227° (from ethanol), $[\alpha]_D^{18}$ +157.5° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.89 (s, 6 H, H-1), 4.14 (s, 6 H, exchangeable with D_2O, HO-2), and 3.72 and 3.42 (2 s, each 18 H, 12 OMe); ^{13}C, δ 103.1 (C-1), 83.2 (C-4), 79.5 (C-3), 73.3 and 71.5 (C-2,5), 71.0 (C-6), and 59.1 and 59.0 (OMe).

Anal. Calc. for $(C_8H_{14}O_5)_6$: C, 50.52; H, 7.42. Found: C, 50.30; H, 7.61.

Heptakis(6-O-tert-butyldimethylsilyl)cyclomaltoheptaose (**21**). — To a stirred mixture of dried[5] **20** (11.0 g, 9.7 mmol) and imidazole (10.15 g, 0.15 mol) in dry *N,N*-dimethylformamide (350 mL) was added, dropwise during 30 min at room temperature, a solution of *tert*-butylchlorodimethylsilane (11.25 g, 74.6 mmol) in anhydrous *N,N*-dimethylformamide (100 mL). The mixture was stirred for 2.5 h at room temperature, at which time t.l.c. (50:10:1 chloroform–methanol–water) showed the presence of **21** as a major product (R_F 0.31), together with some minor ones. Processing of the mixture as described previously[5], followed by column chromatography (8:1 → 4:1 chloroform–methanol, stepwise) of the product, afforded **21** (13.11 g, 70%), m.p. 299–302° (dec.) (from ethanol), $[\alpha]_D^{22}$ +113° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.05 (C-1), 81.2 (C-4), 73.45 (2 C) and 72.6 (C-2,3,5), 61.7 (C-6), 25.9 [$(CH_3)_3C$], 18.3 [$(CH_3)_3C$], and −5.0 and −5.15 [$(CH_3)_2Si$].

Heptakis(2,3-di-O-acetyl-6-O-tert-butyldimethylsilyl)cyclomaltoheptaose (**22**). — A solution of **21** (3.55 g) in acetic anhydride (30 mL) and pyridine (40 mL) was stirred for 4 h at 100° and then concentrated; the last traces of the solvents were removed by coevaporation of toluene. Column chromatography (49:1 benzene–ethanol) of the residue afforded amorphous **22** (4.63 g, 93%), $[\alpha]_D^{25}$ +82° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.23 (d, 7 H, $J_{1,2}$ 3.5 Hz, H-1), 4.76 (dd, 7 H, $J_{2,3}$ 10.0 Hz, H-2), 2.06 and 2.05 (2 s, each 21 H, 14 OAc), 0.89 [s, 63 H, 7 $(CH_3)_3C$], and 0.06 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 170.5 and 169.3 (C=O), 96.5 (C-1), 75.25 (C-4), 71.9, 71.5, and 71.25 (C-2,3,5), 61.9 (C-6), 25.9 [$(CH_3)_3C$], 20.9 and 20.7 ($COCH_3$), 18.3 [$(CH_3)_3C$], and −4.9 and −5.2 [$(CH_3)_2Si$].

Heptakis(6-O-tert-butyldimethylsilyl-2,3-di-O-methyl)cyclomaltoheptaose (**23**). — A solution of **21** (0.88 g) in oxolane (20 mL) was treated with sodium hydride (0.9 g; 50% mineral oil), followed by methyl iodide (2 mL), and processed as described for the preparation of **5**. Column chromatography (4:1 hexane–ethyl acetate) of the product gave amorphous **23** (0.82 g, 85%), $[\alpha]_D^{26}$ +97° (*c* 1.45, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.20 (d, 7 H, $J_{1,2}$ 3.3 Hz, H-1), 3.67 and 3.51 (2 s, each 21 H, 14 OMe), 0.88 [s, 63 H, 7 $(CH_3)_3C$], and 0.03 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 98.1 (C-1), 82.3, 82.0, and 78.6 (C-2,3,4), 72.2 (C-5), 62.3 (C-6), 61.4 and 58.6 (OMe), 25.95 [$(CH_3)_3C$], 18.3 [$(CH_3)_3C$], and −4.8 and −5.1 [$(CH_3)_2Si$].

Heptakis(2,3-di-O-methyl)cyclomaltoheptaose (**24**). — *O*-Desilylation of **23** (0.69 g), as described for the preparation of **4**, followed by column chromatography (8:1 chloroform–methanol and then 40:10:0.1 chloroform–methanol–water) of the product, afforded **24** (0.35 g, 81%), m.p. 168–172° after softening at ~164° (from ether–light petroleum), $[\alpha]_D^{24}$ +176° (*c* 1.2, chloroform), $[\alpha]_D^{24}$ +153° (*c* 1,2 water). N.m.r. data (D_2O): ^1H, δ 5.13 (d, 7 H, $J_{1,2}$ 2.4 Hz, H-1), and 3.62 and 3.48 (2 s, each 21 H, 14 OMe); ^{13}C, δ 100.4 (C-1), 83.1 (C-4), 82.4 and 81.4 (C-2,3), 73.7 (C-5), 62.1 (C-6), and 62.4 and 59.7 (OMe).

Octakis(6-O-tert-butyldimethylsilyl)cyclomalto-octaose (**27**). — The product obtained by treatment of a mixture of **26** (7.0 g, 5.4 mmol) and imidazole (6.46 g, 95 mmol) in *N,N*-dimethylformamide (210 mL) with a solution of *tert*-butylchlorodimethylsilane (7.16 g, 47.5 mmol) in *N,N*-dimethylformamide (70 mL) for 2.5 h at room temperature, as described for the preparation of **21**, was subjected to column chromatography (8:1 → 4:1 chloroform–methanol and 40:10:0.1 chloroform–methanol–water, stepwise) to give **26** (7.98 g, 67%), m.p. 264.5–267° (from chloroform–methanol), $[\alpha]_D^{26}$ +117.5° (*c* 1.5, chloroform); R_F 0.21 (t.l.c. in 50:10:1 chloroform–methanol–water).

Octakis(2,3-di-O-acetyl-6-O-tert-butyldimethylsilyl)cyclomalto-octaose (**28**). — Acetylation of **27** (2.51 g), as described for **21**, followed by column chromatography (49:1 → 24:1 benzene–ethanol, stepwise) of the product, afforded amorphous **28** (2.95 g, 90%), $[\alpha]_D^{26}$ +98° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.31 (d, 8 H, $J_{1,2}$ 3.1 Hz, H-1), 4.73 (dd, 8 H, $J_{2,3}$ 10.1 Hz, H-2), 2.07 (s, 48 H, 16 OAc), 0.89 [s, 72 H, 8 $(CH_3)_3C$], and 0.06 [s, 48 H, 8 $(CH_3)_2Si$]; ^{13}C, δ 170.4

and 169.3 (C=O), 95.5 (C-1), 73.9 (C-4), 71.6, 71.5, and 70.9 (C-2,3,5), 61.8 (C-6), 25.9 [$(CH_3)_3C$], 20.9 and 20.6 ($COCH_3$), 18.35 [$(CH_3)_3C$], and −4.9 and −5.2 [$(CH_3)_2Si$].

Octakis(6-O-tert-butyldimethylsilyl-2,3-di-O-methyl)cyclomalto-octaose (**29**). — Methylation of **27** (0.74 g), as described for **21**, followed by column chromatography (4:1 → 3:2 hexane–ethyl acetate, stepwise) of the product, gave amorphous **29** (0.70 g, 86%), $[\alpha]_D^{26}$ +97° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.32 (d, 8 H, $J_{1,2}$ 3.3 Hz, H-1), 3.71 and 3.55 (2 s, each 24 H, 16 OMe), 0.88 [s, 72 H, 8 $(CH_3)_3C$], and 0.03 [s, 48 H, 8 $(CH_3)_2Si$)]; ^{13}C, δ 97.7 (C-1), 82.2, 82.0, and 77.9 (C-2,3,4), 72.35 (C-5), 62.35 (C-6), 61.5 and 58.7 (OMe), 25.95 [$(CH_3)_3C$], 18.75 [$(CH_3)_3C$], and −4.8 and −5.1 [$(CH_3)_2Si$].

Octakis(2,3-di-O-methyl)cyclomalto-octaose (**30**). — *O*-Desilylation of **29** (0.54 g), as described for the preparation of **4**, followed by column chromatography (8:1 chloroform and then 40:10:1 chloroform–methanol–water) of the product, afforded **30** (0.28 g, 82%), m.p. 181–185° (from chloroform–hexane), $[\alpha]_D^{26}$ +168° (*c* 1.4, chloroform), $[\alpha]_D^{24}$ +169° (*c* 1.4, water). N.m.r. data (D_2O): ^1H, δ 5.38 (d, 8 H, $J_{1,2}$ 3.1 Hz, H-1), and 3.60 and 3.53 (2 s, 24 H, 16 OMe); ^{13}C, δ 98.7 (C-1), 83.5 (C-4), 82.9 and 77.4 (C-2,3), 73.5 (C-5), 63.0 (C-6), and 61.6 and 60.9 (OMe).

Heptakis((2,3-di-O-acetyl)cyclomaltoheptaose (**31**). — To a solution of **22** (3.37 g) in dichloromethane (40 mL) was added 47% boron trifluoride etherate in ether (3.4 mL). The mixture was stirred for 6 h at room temperature, diluted with dichloromethane, and poured into ice–water. The organic layer was separated, washed successively with water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Column chromatography (7:1 → 4:1 chloroform–methanol, stepwise) of the residue gave **31** (1.68 g, 73%), m.p. 184–188° (from dichloromethane–ether). $[\alpha]_D^{26}$ +115° (*c* 1.45, chloroform), $[\alpha]_D^{26}$ +115° (*c* 1.45, dimethyl sulfoxide). ^{13}C-N.m.r. data [$(CD_3)_2SO$]: δ 169.85 and 169.0 (C=O), 95.8 (C-1), 75.15 (C-4), 71.9, 70.55, and 70.5 (C-2,3,5), 59.6 (C-6), and 20.5 and 20.4 ($COCH_3$).

Octakis(2,3-di-O-acetyl)cyclomalto-octaose (**32**). — *O*-Desilylation of **28** (1.98 g), as described for **22**, followed by column chromatography (7:1 → 5:1 chloroform–methanol, stepwise) of the product, gave **32** (0.95 g, 70%), m.p. 199–206° (from dichloromethane–hexane), $[\alpha]_D^{25}$ +122° (*c* 1.6, chloroform), $[\alpha]_D^{26}$ +119° (*c* 1.4, dimethyl sulfoxide). ^{13}C-N.m.r. data [$(CD_3)_2SO$]: δ 169.8 and 169.0 (C=O), 95.3 (C-1), 74.15 (C-4), 71.9, 70.7, and 70.2 (C-2,3,5), 59.5 (C-6), and 20.5 and 20.3 ($COCH_3$).

Heptakis(2,3-di-O-acetyl-6-O-methyl)cyclomaltoheptaose (**33**). — A mixture of **31** (0.39 g), methyl triflate (0.9 mL), and 2,6-di-*tert*-butyl-4-methylpyridine (2.27 g) in dichloromethane (10 mL) was heated in a sealed tube for 2.5 h at 80° and then cooled. Methanol (5 mL) was added, and the mixture was kept for 30 min at room temperature and then concentrated. A solution of the residue in chloroform was washed successively with water, cold 5% hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Column chromatography

(19:1 → 9:1 benzene–ethanol, stepwise) of the residue gave **33** (0.37 g, 90%), m.p. 133–140° (from methanol), $[\alpha]_D^{18}$ +108° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.36 (t, 7 H, $J_{3,4}$ 8.7 Hz, H-3), 5.14 (d, 7 H, $J_{1,2}$ 3.3 Hz, H-1), 4.81 (dd, 7 H, $J_{2,3}$ 9.7 Hz, H-2), 3.41 (s, 21 H, 7 OMe), and 2.07 (s, 42 H, 14 OAc); ^{13}C, δ 170.4 and 169.2 (C=O), 96.5 (C-1), 75.9 (C-4), 71.3 and 70.8 (3 C) (C-2,3,5,6), 59.1 (OMe), and 20.8 and 20.7 ($COCH_3$).

Anal. Calc. for $(C_{11}H_{16}O_7)_7$: C, 50.77; H, 6.20. Found: C, 50.41; H, 6.10.

Heptakis(6-O-methyl)cyclomaltoheptaose (**34**). — A solution of **33** (0.26 g) in methanol (10 mL) was treated with methanolic M sodium methoxide (0.01 mL) and kept for 1 h at room temperature. Water (10 mL) was added, and the solution was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Crystallisation of the residue from methanol afforded **34** (0.16 g, 89%), m.p. 303–310° (dec.), $[\alpha]_D^{20}$ +166° (*c* 0.85, water). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 4.78 (s, 7 H, H-1) and 3.24 (s, 21 H, 7 OMe); ^{13}C, δ 102.0 (C-1), 82.0 (C-4), 72.7, 72.0, and 70.1 (C-2,3,5), 70.7 (C-6), and 57.5 (OMe).

Octakis(2,3-di-O-acetyl-6-O-methyl)cyclomalto-octaose (**35**). — Treatment of **32** (0.31 g) with methyl triflate (0.7 mL) and 2,6-di-*tert*-butyl-4-methylpyridine (1.81 g) in dichloromethane (10 mL), followed by column chromatography, as described for the preparation of **33**, gave **35** (0.29 g, 88%), m.p. 148–154° (from light petroleum–ether), $[\alpha]_D^{18}$ +130° (*c* 0.7, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.21 (d, 8 H, $J_{1,2}$ 2.3 Hz, H-1), 4.76 (dd, 8 H, $J_{2,3}$ 9.9 Hz, H-2), 3.39 (s, 24 H, 8 OMe), and 2.08 (s, 48 H, 16 OAc); ^{13}C, δ 170.4 and 169.3 (C=O), 95.8 (C-1), 74.4 (C-4), 71.2 and 70.3 (3 C) (C-2,3,5,6), 59.1 (OMe), and 20.9 and 20.7 ($COCH_3$).

Anal. Calc. for $(C_{11}H_{16}O_7)_8$: C, 50.77; H, 6.20. Found: C, 50.45; H, 6.37.

Octakis(6-O-methyl)cyclomalto-octaose (**36**). — *O*-Deacetylation of **35** (0.19 g), as described for **33**, gave **36** (0.12 g, 92%), m.p. 296–301° (dec.) (from aqueous methanol), $[\alpha]_D^{18}$ +174° (*c* 1.2, water). N.m.r. data (D_2O): ^1H, δ 5.09 (d, 8 H, $J_{1,2}$ 2.6 Hz, H-1) and 3.40 (s, 24 H, 8 OMe); ^{13}C, δ 104.0 (C-1), 83.0 (C-4), 75.3, 74.6, and 72.9 (2 C) (C-2,3,5,6), and 60.8 (OMe).

Heptakis(6-O-tert-butyldimethylsilyl-2-O-methyl)cyclomaltoheptaose (**37**). — A mixture of **21** (2.5 g, 1.3 mmol), barium oxide (3.75 g), and barium hydroxide octahydrate (1.88 g) in *N,N*-dimethylformamide (75 mL) was treated with methyl iodide (0.84 mL, 13.5 mmol) for 4 h at room temperature and then processed as described for the preparation of **3**. Column chromatography (2:1 → 1:1 benzene–ethyl acetate, stepwise) of the product gave **37** (1.60 g, 61%), m.p. 217–221° (from methanol), $[\alpha]_D^{18}$ +76° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.01 (d, 7 H, $J_{1,2}$ 3.3 Hz, H-1), 3.21 (dd, 7 H, $J_{2,3}$ 9.3 Hz, H-2), 5.09 (s, 7 H, exchangeable with D_2O, HO-3), 3.69 (s, 21 H, 7 OMe), 0.88 [s, 63 H, 7 $(CH_3)_3C$], and 0.04 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 100.5 (C-1), 82.3 and 82.2 (C-2,4), 73.1 and 71.7 (C-3,5), 61.7 (C-6), 60.1 (OMe), 25.9 [$(CH_3)_3C$], 18.3 [$(CH_3)_3C$], and −5.0 and −5.2 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{13}H_{26}O_5Si)_7$: C, 53.76; H, 9.02. Found: C, 53.95; H, 8.88.

Heptakis(2-O-methyl)cyclomaltoheptaose (**38**). — *O*-Desilylation of **37** (0.25

g), followed by column chromatography of the product, as described for the preparation of **4**, gave **38** (0.13 g, 87%), m.p. 318–323° (dec.) (from methanol), $[\alpha]_D^{18}$ +115° (*c* 0.8, dimethyl sulfoxide). N.m.r. data [$(CD_3)_2SO$]: ^1H, δ 5.00 (s, 7 H, H-1) and 3.51 (s, 21 H, 7 OMe); ^{13}C, δ 99.5 (C-1), 81.9 and 81.7 (C-2,4), 72.6 and 71.3 (C-3,5), 59.7 (C-6), and 59.2 (OMe).

*Heptakis(3-O-allyl-6-O-*tert*-butyldimethylsilyl-2-O-methyl)cyclomaltoheptaose* (**39**). — A solution of **37** (1.35 g) in oxolane (15 mL) and *N,N*-dimethylformamide (1.5 mL) was treated with sodium hydride (0.67 g; 50% mineral oil), followed by allyl bromide (1.5 mL), and processed as described for the preparation of **5**. Column chromatography (20:1 hexane–ethyl acetate) of the product afforded amorphous **39** (1.29 g, 84%), $[\alpha]_D^{19}$ +87° (*c* 1.45, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.25–5.93 (m, 7 H, –CH=), 5.07 (s, 7 H, H-1), 3.52 (s, 21 H, 7 OMe), 0.88 [s, 63 H, 7 $(CH_3)_3C$], and 0.03 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 136.2 and 115.9 ($CH=CH_2$), 98.1 (C-1), 82.1 (C-4), 80.3 and 78.3 (C-2,3), 74.8 ($CH_2=CH-CH_2$), 72.2 (C-5), 62.4 (C-6), 59.0 (OMe), 25.9 [$(CH_3)_3C$], 18.3 [$(CH_3)_3C$], and −4.7 and −5.1 [$(CH_3)_2Si$].

Heptakis(3-O-allyl-2-O-methyl)cyclomaltoheptaose (**40**). — *O*-Desilylation of **39** (1.11 g), as described for the preparation of **4**, followed by column chromatography (9:1 → 4:1 chloroform–methanol, stepwise) of the product, gave **40** (0.62 g, 85%), m.p. 205–215° (from ethanol), $[\alpha]_D^{19}$ +124° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.18–5.82 (m, 7 H, –CH=), 5.05 (s, 7 H, H-1), and 3.47 (s, 21 H, 7 OMe); ^{13}C, δ 136.0 and 115.7 ($CH=CH_2$), 98.5 (C-1), 81.6 (C-4), 80.0 (2 C) (C-2,3), 74.4 ($CH_2=CH-CH_2$), 72.6 (C-5), 61.6 (C-6), and 59.1 (OMe).

Anal. Calc. for $(C_{10}H_{16}O_5)_7$: C, 55.46; H, 7.46. Found: C, 55.18; H, 7.60.

Heptakis(3-O-allyl-2,6-di-O-methyl)cyclomaltoheptaose (**41**). — Methylation of **40** (0.58 g) as described for **7**, followed by column chromatography (19:1 benzene–ethanol) of the product, afforded amorphous **41** (0.54 g, 87%), $[\alpha]_D^{19}$ +124° (*c* 1.0, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 6.20–5.83 (m, 7 H, –CH=), 5.05 (s, 7 H, H-1), and 3.48 and 3.37 (2 s, each 21 H, 14 OMe); ^{13}C, δ 136.0 and 115.6 ($CH=CH_2$), 98.6 (C-1), 81.8 (C-4), 80.1 and 79.6 (C-2,3), 74.5 ($CH_2=CH-CH_2$), 72.6 (C-6), 71.5 (C-5), and 54.1 and 58.9 (OMe).

Heptakis(2,6-di-O-methyl)cyclomaltoheptaose (**42**). — *O*-Deallylation of **41** (0.41 g) followed by column chromatography, as described for **8**, afforded **42** (0.24 g, 71%), m.p. 300–305° (dec.) (from methanol), $[\alpha]_D^{23}$ +122° (*c* 1.3, chloroform), $[\alpha]_D^{23}$ +156° (*c* 1.6, water); lit.[26] m.p. 276° (dec.) (from water), $[\alpha]_D^{23}$ +116.1° (*c* 1, chloroform), $[\alpha]_D^{23}$ +155.4° (*c* 1, water), N.m.r. data ($CDCl_3$): ^1H, δ 5.05 (s, 7 H, exchangeable with D_2O, HO-3), 4.96 (d, 7 H, $J_{1,2}$ 3.5 Hz, H-1), 3.29 (dd, 7 H, $J_{2,3}$ 9.7 Hz, H-2), and 3.64 and 3.40 (2 s, each 21 H, 14 OMe); ^{13}C, δ 101.3 (C-1), 83.6 (C-4), 82.1 (C-2), 73.2 (C-3), 70.9 (C-6), 70.3 (C-5), and 60.2 and 58.9 (OMe).

*Heptakis(2-O-benzyl-6-O-*tert*-butyldimethylsilyl)cyclomaltoheptaose* (**43**). — A mixture of **21** (3.52 g, 1.8 mmol), barium oxide (5.28 g), and barium hydroxide octahydrate (2.64 g) in *N,N*-dimethylformamide (100 mL) was stirred with benzyl bromide (1.8 mL, 15.3 mmol) for 18 h at room temperature and then processed as

described for the preparation of **10**. Column chromatography (25:1 → 10:1 benzene–ethyl acetate, stepwise) of the product gave **43** (3.17 g, 68%), m.p. 210–212° (from ethanol), $[\alpha]_D^{18}$ +46° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.37 (s, 35 H, 7 Ph), 4.86 (ABq 14 H, *J* 12.0 Hz, 7 PhCH_2), 0.84 [s, 63 H, 7 $(CH_3)_3C$], and −0.02 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 137.7 (aromatic C-1), 101.2 (C-1), 82.4 (C-4), 79.1 (C-2), 73.9 (PhCH$_2$), 73.5 and 71.7 (C-3,5), 61.7 (C-6), 25.9 [(CH_3)$_3$C], 18.3 [(CH_3)$_3$*C*], and −5.1 and −5.2 [$(CH_3)_2Si$].

Anal. Calc. for $(C_{19}H_{30}O_5Si)_7$: C, 62.26; H, 8.25. Found: C, 62.47; H, 7.98.

*Heptakis(2-O-benzyl-6-O-*tert*-butyldimethylsilyl-3-O-methyl)cyclomaltoheptaose* (**44**). — Methylation of **43** (1.12 g) as described for **10**, followed by column chromatography (20:1 → 10:1 hexane–ethyl acetate, stepwise) of the product, gave amorphous **44** (0.97 g, 84%), $[\alpha]_D^{18}$ +79.5° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.52–7.21 (m, 35 H, 7 Ph), 5.27 (d, 7 H, $J_{1,2}$ 2.4 Hz, H-1), 3.58 (s, 21 H, 7 OMe), 0.88 [s, 63 H, 7 $(CH_3)_3C$], and 0.03 [s, 42 H, 7 $(CH_3)_2Si$]; ^{13}C, δ 138.8 (aromatic C-1), 98.3 (C-1), 82.1 (C-4), 79.9 (C-2), 78.3 (C-3), 72.4 (2 C) (C-5, PhCH$_2$), 62.4 (C-6), 61.3 (OMe), 26.9 [(CH_3)$_3$C], 18.3 [(CH_3)$_3$*C*], and −4.8 and −5.1 [$(CH_3)_2Si$].

Heptakis(2-O-benzyl-3-O-methyl)cyclomaltoheptaose (**45**). — *O*-Desilylation of **44** (0.95 g) followed by column chromatography, as described for **11**, afforded **45** (0.55 g, 82%), $[\alpha]_D^{18}$ +109° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.36–7.23 (m, 35 H, 7 Ph), 5.04 (s, 7 H, H-1), and 3.50 (s, 21 H, 7 OMe); ^{13}C, δ 138.75 (aromatic C-1), 98.8 (C-1), 82.2 (C-4), 80.0 and 79.5 (C-2,3), 72.6 (2 C) (C-5, PhCH$_2$), 61.7 (C-6), and 61.3 (OMe). This compound crystallised from ethanol as needles, but the crystals did not show a definite m.p.

Heptakis(3-O-methyl)cyclomaltoheptaose (**46**). — Hydrogenolysis of **45** (0.42 g), as described for **12**, afforded **46** (0.25 g, 89%), m.p. 222–229° (dec.) (from methanol–ether), $[\alpha]_D^{18}$ +141° (*c* 1.2, water). N.m.r. data (D_2O): ^1H, δ 4.81 (s, 7 H, H-1) and 3.43 (s, 21 H, 7 OMe); ^{13}C, δ 101.7 (C-1), 83.1 (C-4), 78.5 (C-3), 72.7 (2 C) (C-2,5), 60.9 (C-6), and 60.1 (OMe).

Heptakis(2-O-benzyl)cyclomaltoheptaose (**48**). — *O*-Desilylation of **43** (0.77 g) as described for **10**, followed by column chromatography (15:1 → 9:1 chloroform–methanol, stepwise) of the product, gave **48** (0.45 g, 85%), m.p. 198–205° (from methanol–ether), $[\alpha]_D^{18}$ +62° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 137.4 (aromatic C-1), 101.7 (C-1), 83.7 (C-4), 78.4 (C-2), 73.9 (2 C) and 71.7 (C-3,5, PhCH$_2$), and 61.6 (C-6).

Heptakis(2-O-benzyl-3,6-di-O-methyl)-cyclomaltoheptaose (**49**). — Methylation of **48** (0.34 g) followed by column chromatography, as described for **14**, afforded amorphous **49** (0.34 g, 89%), $[\alpha]_D^{18}$ +84° (*c* 0.8, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 7.44–7.18 (m, 35 H, 7 Ph), 5.05 (d, 7 H, $J_{1,2}$ 3.1 Hz, H-1), and 3.55 and 3.32 (2 s, each 21 H, 14 OMe); ^{13}C, δ 138.7 (aromatic C-1), 99.2 (C-1), 82.1 (C-4), 79.6 and 79.5 (C-2,3), 72.65 (PhCH$_2$), 71.4 (C-6), 71.0 (C-5), and 61.3 (OMe).

Heptakis(3,6-di-O-methyl)cyclomaltoheptaose (**50**). — Hydrogenolysis of **49**

(0.24 g) followed by column chromatography, as described for **15**, gave **50** (0.14 g, 88%), m.p. 208–213° (from chloroform–hexane), $[\alpha]_D^{18}$ +144.5° (*c* 1.2, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.89 (s, 7 H, H-1), and 3.70 and 3.40 (2 s, each 21 H, 14 OMe); ^{13}C, δ 103.2 (C-1), 83.1 (C-4), 79.5 (C-3), 73.6 and 71.6 (C-2,5), 70.7 (C-6), and 59.2 and 58.9 (OMe).

Anal. Calc. for $(C_8H_{14}O_5)_7$: C, 50.52; H, 7.42. Found: C, 50.66; H, 7.56.

Heptakis(2,3-di-O-acetyl-6-O-methylsulfonyl)cyclomaltoheptaose (**51**). — A solution of **31** (2.16 g) in pyridine (15 mL) was cooled to −10°, treated with methanesulfonyl chloride (1.36 mL), and kept overnight at 5°. The mixture was poured into ice–water, and the precipitate formed was filtered off, washed with cold water, and dissolved in chloroform. The solution was washed with water, dried, and concentrated. The residue was subjected to column chromatography (9:1 → 17:3 benzene–ethanol, stepwise) to give amorphous **51** (2.51 g, 88%), $[\alpha]_D^{25}$ +108° (*c* 1.55, chloroform); lit.[29,30] m.p. 165° (dec.), $[\alpha]_D$ +114° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.36 (t, 7 H, $J_{3,4}$ ~9 Hz, H-3), 5.17 (d, 7 H, $J_{1,2}$ 3.7 Hz, H-1), 4.81 (dd, 7 H, $J_{2,3}$ 10.1 Hz, H-2), 3.82 (t, 7 H, $J_{4,5}$ ~9 Hz, H-4), 3.12 (s, 21 H, 7 OMs), and 2.08 and 2.06 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.2 and 169.2 (C=O), 96.8 (C-1), 76.1 (C-4), 70.2 (2 C) and 69.6 (C-2,3,5), 68.5 (C-6), 37.4 (CH_3SO_2), and 20.7 ($COCH_3$).

Anal. Calc. for $(C_{11}H_{16}O_9S)_7$: C, 40.74; H, 4.97. Found: C, 40.90; H, 5.10.

Octakis(2,3-di-O-acetyl-6-O-methylsulfonyl)cyclomalto-octaose (**52**). — Treatment of **32** (2.28 g) in pyridine (17 mL) with methanesulfonyl chloride (1.5 mL) followed by column chromatography of the product, as just described, afforded **52** (2.34 g, 78%), m.p. 173–179° (from methanol–acetone), $[\alpha]_D^{26}$ +127° (*c* 1.55, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.52 (t, 8 H, $J_{3,4}$ ~9 Hz, H-3), 5.24 (s, 8 H, H-1), 3.82 (t, 8 H, $J_{4,5}$ 9.0 Hz, H-4), 3.11 (s, 24 H, 8 OMs), and 2.09 (s, 48 H, 16 OAc); ^{13}C, δ 170.2 and 169.3 (C=O), 96.8 (C-1), 75.5 (C-4), 71.2, 69.7, and 69.2 (C-2,3,5), 68.6 (C-6), 37.2 (CH_3SO_2), and 20.8 ($COCH_3$).

Anal. Calc. for $(C_{11}H_{16}O_9S)_7$: C, 40.74; H, 4.97. Found: C, 40.55; H, 5.19.

Heptakis(2,3-di-O-acetyl-6-bromo-6-deoxy)cyclomaltoheptaose (**53**). — A solution of **51** (0.33 g) in *N,N*-dimethylformamide (5 mL) was stirred with sodium bromide (0.4 g) for 3 h at 100°. The mixture was concentrated and the residue was partitioned between chloroform and water. The organic layer was separated, washed with water, dried, and concentrated. Column chromatography (49:1 → 19:1 benzene–ethanol, stepwise) of the residue gave **53** (0.27 g, 84%), m.p. 193–198° (from methanol–dichloromethane), $[\alpha]_D^{26}$ +98° (*c* 1.6, chloroform); lit.[6] m.p. 193–195°, $[\alpha]_D^{25}$ +100° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.35 (dd, 7 H, $J_{3,4}$ 8.4 Hz, H-3), 5.22 (d, 7 H, $J_{1,2}$ 3.6 Hz, H-1), 4.83 (dd, 7 H, $J_{2,3}$ 9.8 Hz, H-2), 3.76 (t, 7 H, $J_{3,4}$ ~9 Hz, H-4), and 2.08 and 2.06 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.2 and 169.2 (C=O), 96.5 (C-1), 78.5 (C-4), 70.3 (3 C) (C-2,3,5), 33.3 (C-6), and 20.7 ($COCH_3$).

Anal. Calc. for $(C_{10}H_{13}BrO_6)_7$: C, 38.86; H, 4.24. Found: C, 38.77; H, 4.45.

Heptakis(2,3-di-O-acetyl-6-deoxy-6-iodo)cyclomaltoheptaose (**54**). — Treat-

ment of **51** (0.48 g) in *N,N*-dimethylformamide (10 mL) with sodium iodide (0.6 g) followed by column chromatography of the product, as described for **53**, gave amorphous **54** (0.43 g, 81%), $[\alpha]_D^{26}$ +78° (*c* 1.5, chloroform); lit.[30] m.p. 172–177° $[\alpha]_D^{24}$ +84° (*c* 0.1, methanol). N.m.r. data ($CDCl_3$): ^1H, δ 5.35 (dd, 7 H, $J_{3,4}$ 7.6 Hz, H-3), 5.20 (d, 7 H, $J_{1,2}$ 3.7 Hz, H-1), 4.82 (dd, 7 H, $J_{2,3}$ 9.9 Hz, H-2), and 2.08 and 2.05 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.3 and 169.1 (C=O), 96.5 (C-1), 80.5 (C-4), 70.3 and 70.2 (2 C) (C-2,3,5), 20.7 ($COCH_3$), and 7.95 (C-6).

Heptakis(2,3-di-O-acetyl-6-chloro-6-deoxy)cyclomaltoheptaose (**55**). — Treatment of **51** (0.31 g) in *N,N*-dimethylformamide (7 mL) with lithium chloride (0.4 g) followed by column chromatography, as described for **53**, afforded **55** (0.22 g, 88%), m.p. 179–182° (from ethanol–dichloromethane), $[\alpha]_D^{26}$ +102° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.36 (dd, 7 H, $J_{3,4}$ 8.8 Hz, H-3), 5.21 (d, 7 H, $J_{1,2}$ 3.5 Hz, H-1), 4.83 (d, 7 H, $J_{2,3}$ 9.9 Hz, H-2), 3.81 (t, 7 H, $J_{4,5}$ 8.8 Hz, H-4), and 2.08 and 2.06 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.2 and 169.25 (C=O), 96.5 (C-1), 77.2 (C-4), 70.9, 70.4, and 70.25 (C-2,3,5), 44.5 (C-6), and 20.7 ($COCH_3$).

Anal. Calc. for $(C_{10}H_{13}ClO_6)_7$: C, 45.38; H, 4.95. Found: C, 45.50; H, 5.12.

Heptakis(2,3-di-O-acetyl-6-azido-6-deoxy)cyclomaltoheptaose (**56**). — Compound **51** (0.44 g) was stirred in *N,N*-dimethylformamide (7 mL) with sodium azide (0.5 g) for 4 h at 80°, and processed as described for **53**. Column chromatography (19:1 benzene–ethanol) of the product afforded amorphous **56** (0.30 g, 81%), $[\alpha]_D^{26}$ +139° (*c* 1.5, chloroform); ν_{max} 2097 cm^{-1} (N_3). N.m.r. data ($CDCl_3$): ^1H, δ 5.30 (t, 7 H, $J_{3,4}$ ~8 Hz, H-3), 5.10 (d, 7 H, $J_{1,2}$ 3.5 Hz, H-1), 4.81 (dd, 7 H, $J_{2,3}$ 9.9 Hz, H-2), and 2.08 and 2.06 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.3 and 169.2 (C=O), 96.6 (C-1), 77.0 (C-4), 70.9, 70.6, and 70.3 (C-2,3,5), 51.5 (C-6), and 20.7 ($COCH_3$).

Heptakis(2,3-di-O-acetyl-6-deoxy)cyclomaltoheptaose (**57**). — A solution of **54** (0.28 g) in 2:1 1,4-dioxane–methanol (15 mL) containing triethylamine (0.2 mL) was hydrogenated in the presence of 10% Pd/C (0.35 g) at atmospheric pressure overnight at room temperature, then filtered through a Celite pad, and concentrated. A solution of the residue in chloroform was washed successively with water, cold 5% hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Column chromatography (19:1 benzene–ethanol) of the residue gave **57** (0.15 g, 83%), m.p. 162–165° (from 2-propanol–ethanol), $[\alpha]_D^{25}$ +111° (*c* 1.5, chloroform); lit.[6] m.p. 193–195°, $[\alpha]_D^{25}$ +100° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.29 (t, 7 H, $J_{3,4}$ ~9 Hz, H-3), 5.00 (d, 7 H, $J_{1,2}$ 3.5 Hz, H-1), 4.77 (dd, 7 H, $J_{2,3}$ 9.9 Hz, H-2), 3.35 (t, 7 H, $J_{4,5}$ 8.6 Hz, H-4), 1.40 (d, 21 H, $J_{5,6}$ 5.7 Hz, 7 CH_3), and 2.07 and 2.05 (2 s, each 21 H, 14 OAc); ^{13}C, δ 170.6 and 169.2 (C=O), 96.5 (C-1), 82.5 (C-4), 71.1 (2 C) and 67.2 (C-2,3,5), 20.8 ($COCH_3$), and 18.0 (C-6).

Anal. Calc. for $(C_{10}H_{14}O_6)_7$: C, 52.17; H, 6.13. Found: C, 52.46; H, 6.19.

Octakis(2,3-di-O-acetyl-6-deoxy-6-iodo)cyclomalto-octaose (**58**). — Treatment of **52** (0.55 g) with sodium iodide in *N,N*-dimethylformamide followed by column chromatography, as described for **53**, gave amorphous **58** (0.50 g, 83%),

$[\alpha]_D^{26}$ +94° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.34 (t, 8 H, $J_{3,4}$ 9.6 Hz, H-3), 5.24 (d, 8 H, $J_{1,2}$ 3.2 Hz, H-1), 4.77 (dd, 8 H, $J_{2,3}$ 9.9 Hz, H-2), and 2.09 and 2.06 (2 s, each 24 H, 16 OAc); ^{13}C, δ 170.0 and 169.0 (C=O), 96.1 (C-1), 79.55 (C-4), 70.6, 70.3, and 69.7 (C-2,3,5), 20.7 and 20.6 ($COCH_3$), and 7.7 (C-6).

Octakis(2,3-di-O-acetyl-6-bromo-6-deoxy)cyclomalto-octaose (**59**). — Treatment of **52** (0.41 g) with sodium bromide in *N,N*-dimethylformamide followed by column chromatography of the product, as described for **53**, afforded **59** (0.32 g, 82%), m.p.184–188° (from methanol–ethanol), $[\alpha]_D^{26}$ +100° (*c* 1.6, chloroform); lit.[6] m.p. 196–199°, $[\alpha]_D^{25}$ +112° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.35 (t, 8 H, $J_{3,4}$ 9.7 Hz, H-3), 5.28 (d, 8 H, $J_{1,2}$ 3.3 Hz, H-1), 4.77 (dd, 8 H, $J_{2,3}$ 10.1 Hz, H-2), and 2.08 and 2.07 (2 s, each 24 H, 16 OAc); ^{13}C, δ 170.2 and 169.2 (C=O), 95.95 (C-1), 77.3 (C-4), 70.5, 70.4, and 69.9 (C-2,3,5), 33.3 (C-6), and 20.7 and 20.6 ($COCH_3$).

Anal. Calc. for $(C_{10}H_{13}BrO_6)_8$: C, 38.86; H, 4.24. Found: C, 38.98; H, 4.10.

Octakis(2,3-di-O-acetyl-6-chloro-6-deoxy)cyclomalto-octaose (**60**). — Treatment of **52** (0.37 g) with lithium chloride in *N,N*-dimethylformamide followed by column chromatography of the product, as described for **53**, gave amorphous **60** (0.26 g, 83%), $[\alpha]_D^{26}$ +116° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.36 (t, 8 H, $J_{3,4}$ 9.5 Hz, H-3), 5.27 (d, 8 H, $J_{1,2}$ 3.1 Hz, H-1), 4.78 (dd, 8 H, $J_{2,3}$ 9.9 Hz, H-2), and 2.08 (s, 48 H, 16 OAc); ^{13}C, δ 170.2 and 169.2 (C=O), 96.0 (C-1), 76.0 (C-4), 70.8, 70.6, and 70.0 (C-2,3,5), 44.45 (C-6), and 20.8 and 20.6 ($COCH_3$).

Octakis(2,3-di-O-acetyl-6-azido-6-deoxy)cyclomalto-octaose (**61**). — Treatment of **52** (0.48 g) with sodium azide in *N,N*-dimethylformamide followed by column chromatography of the product, as described for **56**, gave amorphous **61** (0.32 g, 80%), $[\alpha]_D^{26}$ +157° (*c* 1.5, chloroform); ν_{max} 2100 cm^{-1} (N_3). N.m.r. data ($CDCl_3$): ^1H, δ 5.52 (t, 8 H, $J_{3,4}$ 9.0 Hz, H-3), 5.16 (d, 8 H, $J_{1,2}$ 3.3 Hz, H-1), 4.77 (dd, 8 H, $J_{2,3}$ 9.9 Hz, H-2), and 2.08 (s, 48 H, 16 OAc); ^{13}C, δ 170.2 and 169.25 (C=O), 96.2 (C-1), 75.9 (C-4), 71.0, 70.6, and 70.2 (C-2,3,5), and 51.3 (C-6).

Octakis(2,3-di-O-acetyl-6-deoxy)cyclomalto-octaose (**62**). — Reductive dehalogenation of **58** (0.36 g) followed by column chromatography of the product, as described for **57**, gave **62** (0.19 g, 83%), m.p. 207–210° (from 2-propanol–acetone), $[\alpha]_D^{26}$ +127° (*c* 1.6, chloroform); lit.[6] m.p. 196–198°, $[\alpha]_D^{25}$ +112° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.29 (t, 8 H, $J_{3,4}$ ~9 Hz, H-3), 5.04 (d, 8 H, $J_{1,2}$ 3.5 Hz, H-1), 4.74 (dd, 8 H, $J_{2,3}$ 9.8 Hz, H-2), 3.35 (t, 8 H, $J_{4,5}$ 8.8 Hz, H-4), 1.38 (d, 24 H, $J_{5,6}$ 5.9 Hz, 8 CH_3), and 2.07 and 2.05 (s, 48 H, 16 OAc); ^{13}C, δ 170.6 and 169.3 (C=O), 96.2 (C-1), 81.4 (C-4), 71.35, 70.9, and 67.35 (C-2,3,5), 20.9 and 20.8 ($COCH_3$), and 18.0 (C-6).

Anal. Calc. for $(C_{10}H_{14}O_6)_8$: C, 52.17; H, 6.13. Found: C, 52.40; H, 6.22.

ACKNOWLEDGMENTS

We thank Sanraku Inc. for a supply of cyclomalto-oligosaccharides, and the Ministry of Education, Science, and Culture of Japan for a Grant-in-Aid for Scientific Research.

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