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SYNTHESIS OF 6-*O*-α-D-GLUCOPYRANOSYLCYCLOMALTOHEPTAOSE*†

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ABSTRACT

(2,3-Di-*O*-acetyl)hexakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose was prepared by reaction of cyclomaltoheptaose with *tert*-butyldimethylsilyl chloride in pyridine followed by acetylation and desilylation. Glycosylation with 2,3,4,6-tetra-*O*-benzyl-1-*O*-trichloroacetimidoyl-α-D-glucopyranose, using trifluoromethanesulfonic acid as catalyst, and removal of the protecting groups from the product then afforded the title compound.

INTRODUCTION

Cyclomalto-oligosaccharides (cyclodextrins, cycloamyloses) with one or more branches at position 6 consisting of an α-D-glucopyranosyl unit or a (1→4)-α-D-glucan are formed as minor products during the action of *Bacillus macerans* cycloamylose glucanotransferase on starch[1]. These glycosylated cyclomalto-oligosaccharides were used[2,3] as specific enzyme substrates in the study of glycogen-storage disease type III, but were not available readily[1-4] and were poorly characterised. Although improved procedures have been reported[5-7], the isolation of these compounds from the mother liquor of large-scale preparation of cyclomalto-oligosaccharides still remains tedious. In order to simplify the isolation procedures, the side chains are shortened enzymically and glucosylated cyclomalto-oligosaccharides are isolated.

The need for glucosylated derivatives arose in our studies of the enzymic degradation of cyclomalto-oligosaccharides[8,9], and we now report on the synthesis of 6-*O*-α-D-glucopyranosylcyclomaltoheptaose (1).

After this work was completed, enzymic syntheses of branched cyclomalto-oligosaccharides were reported[10-12].

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* Dedicated to Professor Rezsö Bognár in the year of his 75th birthday.
† *Note added in proof:* After submission of this manuscript, Dr. Kenichi Takeo informed us in a personal communication that the synthesis of 6-*O*-α-D-glucopyranosylcyclomaltohexaose was accomplished by him (*J. Carbohydr. Chem.*, submitted).
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RESULTS AND DISCUSSION

For the synthesis of **1**, a partially protected cyclomaltoheptaose derivative having one hydroxyl group (HO-6) unsubstituted was required as a glycosyl acceptor. Despite the large number of chemically modified cyclomalto-oligosaccharide derivatives[13,14], only one compound of this kind, namely, (2,3-di-*O*-benzoyl)-tetrakis(2,3-di-*O*-benzoyl-6-*O*-trityl)bis(2,3,6-tri-*O*-benzoyl)cyclomaltoheptaose[15] has been reported*, the relative arrangement of differently substituted rings is unknown, and the compound could be a mixture of isomers.

Regioselective substitution of all the primary hydroxyl groups of cyclomaltoheptaose can be achieved easily by reaction with *tert*-butyldimethylsilyl chloride in pyridine[13]. Under the commonly used conditions[17] (imidazole in *N,N*-dimethylformamide), substitution of both the primary and the secondary hydroxyl groups of monosaccharides[18] and of cyclomalto-oligosaccharides[19–21] occurs. However, with pyridine as solvent, regioselectivities similar to that of tritylation can be obtained[22,23]

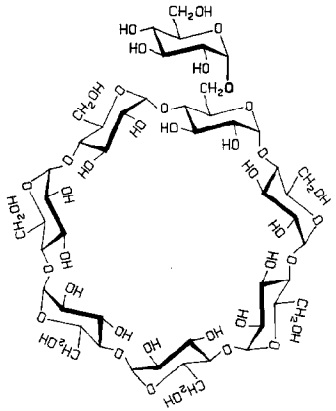
The reaction of dry cyclomaltoheptaose with 1.25 mol of *tert*-butyldimethylsilyl chloride in pyridine was followed by t.l.c., and the product was acetylated when the formation of the mono(*tert*-butyldimethylsilyl) derivative was judged to be optimal. In order to achieve complete acetylation, the addition of 4-dimethylaminopyridine and heating was necessary. Column chromatography of the mixture afforded 40% of (2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)hexakis(2,3,6-tri-*O*-acetyl)-cyclomaltoheptaose (**2**). In the ^{1}H-n.m.r. spectrum** of **2**, sharp singlets of the *tert*-butyldimethylsilyl group at 0.87 and 0.06 p.p.m., with the correct integration intensities relative to those of the signals for the acetyl groups, were observed. In the ^{13}C-n.m.r. spectrum, one of the signals (61.0 p.p.m.) for C-6 was separated from the others (62.3–62.7 p.p.m.), indicating the site of silylation.

In addition to **2**, a mixture of multiply *tert*-butyldimethylsilylated compounds, tris(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)tetrakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose, two bis(*tert*-butyldimethylsilyl) derivatives, and heptakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose[24] (**3**), were obtained. The degree and site of *tert*-butyldimethylsilylation were determined from the ^{1}H- and ^{13}C-n.m.r. spectra, respectively. The relative arrangement of the *tert*-butyldimethylsilylated glucose moieties was not established.

Treatment of **2** with tetrabutylammonium fluoride or acid afforded the required glycosyl acceptor **4**. Halide-ion catalysed glycosylation[25] of **4** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide[26] (**5**), readily prepared by bromination[26] of methyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[27] (**6**), was slow, and with a 6-fold excess of **5** only 3% of the glucosylated derivative **7** could be isolated after reaction for 9 days. Halide-ion catalysed glycosylations are not effi-

* An unpublished synthesis of another compound is mentioned in ref. 16.

** It is to be noted that **2** and related substituted cyclomalto-oligosaccharides are asymmetric, and so every proton and carbon atom is heterotopic and therefore potentially anisochronous.



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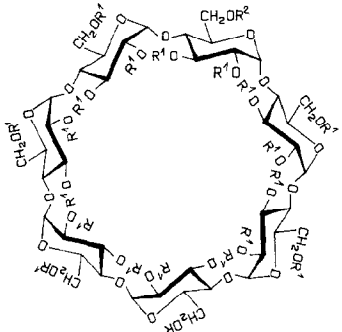
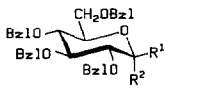
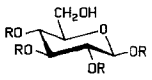


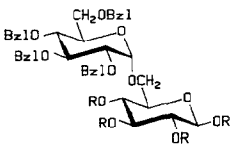
2 R^1 = Ac, R^2 = Bu^tMe_2Si
3 R^1 = R^2 = Ac
4 R^1 = Ac, R^2 = H
7 R^1 = Ac, R^2 = 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl
9 R^1 = Ac, R^2 = α-D-glucopyranosyl
10 R^1 = Ac, R^2 = β-D-glucopyranosyl



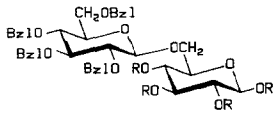
5 R^1 = H, R^2 = Br
6 R^1 = SMe, R^2 = H
8 R^1 = H, R^2 = OC(=NH)CCl$_3$



11 R = Ac
14 R = Bzl



12 R = Ac
15 R = Bzl



13 R = Ac
16 R = Bzl

cient for the glycosylation of unreactive hydroxyl groups[28], so that the resistance of a primary hydroxyl group is unexpected, especially since effective halide-ion catalysed glucosylation at O-6 of an acetylated maltose derivative has been reported[29]. Steric hindrance by the neighbouring substituted glucose residues may be the cause of the resistance of HO-6 in **4** to glycosylation and also the low rate in the final stage of the above acetylation reaction and the resistance of a primary hydroxyl to benzoylation of a tritylated derivative[15].

Glucosylation of **4** was achieved satisfactorily by using the trichloroacetimidate procedure[30,31]. Reaction of the benzylated imidate[30] **8** with **4** in dichloromethane at −20°, using trifluoromethanesulfonic acid as catalyst[32], gave 80% of the glucosylated derivative **7**, which seemed to be homogeneous in t.l.c.. After catalytic debenzylation (Pd/C), t.l.c. revealed an ~8:1 mixture of two components (**9** and **10**), which were isolated in yields of 75% and 10%, respectively. In the ^{13}C-n.m.r. spectrum of the major product **9**, a signal at 98.8 p.p.m. was separated from the bulk of the other signals of anomeric carbons (97.1–96.5 p.p.m.), whereas, in the spectrum of the minor product **10**, this signal was found at 102.5 p.p.m.. These chemical shifts are in the range expected for an α- and β-D-glucopyranoside, hence **9** and **10** are the 6-*O*-α- and -β-D-glucopyranosyl derivatives, respectively.

The stereoselective formation of the 1,2-*cis*-glycoside **9** using the imidate **8** is

worthy of comment since this compound has been used to obtain β-D-glucopyranosides under boron trifluoride etherate catalysis[30,31]. Retention of the anomeric configuration, however, was found with other trichloroacetimidates[32,33], and **8** gives α,β-mixtures having low stereoselectivity with other catalysts[34]. The preferential formation of an α-D-glucopyranoside (α,β-ratio 4:1) was observed in the reaction with the poorly nucleophilic hydroxyl group of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, although the yield was modest[34].

The reaction of **8** with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[35] (**11**) under trifluoromethanesulfonic acid catalysis gave a ~1:1 mixture of the disaccharide derivatives **12** and **13**. Comparable results were obtained in the glycosylation of benzyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside[36] (**14**) to give **15** and **16**. The difference in the stereoselectivity of these reactions and that in the glycosylation of **4** is due to the decreased reactivity of the primary hydroxyl of the cyclomaltoheptaose derivative.

Different physical constants have been reported[37-39] for the disaccharide **12**. Our data for **12** and **13** were at variance with the originally published values[37], but the optical rotation and ^{13}C-n.m.r. data of **12** agreed well with those reported recently[39]. In the ^{13}C-n.m.r. spectra of the disaccharides (Table I), there were characteristic differences in the glycosylation shifts, depending on the anomeric configuration of the glycosylating unit. The C-6 signal of the reducing D-glucose residue was found at ~66 p.p.m. in the α-D-glucopyranosylated derivatives **12** and **15**, but a glycosylation shift of ~3 p.p.m. larger was observed for the C-6 resonance (~69 p.p.m.) in the β-D-glucopyranosylated derivatives **13** and **16**.

Deacetylation of **9** with methanolic sodium methoxide and then with aqueous sodium hydroxide, followed by gel chromatography on Sephadex G-15, gave the target compound **1** in almost quantitative yield. In agreement with previous findings[4], the compound was far more retarded on the Sephadex gel than expected on the basis of its molecular weight.

In the ^{13}C-n.m.r. spectrum of **1** (Fig. 1.), the intense signals at 102.3, 81.6, 73.6, 72.6, 72.4, and 60.8 p.p.m. were readily assigned to C-1, C-4, C-3, C-2, C-5, and C-6, respectively, of the glucosyl residues. The asymmetry of the molecule is

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS (P.P.M.) OF MONO- AND DI-SACCHARIDES[a]

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
11	91.6	70.6	72.8	68.4	75.1	61.0						
12	91.6	70.4[b]	73.0	68.9	73.4	65.9	96.9	79.9	81.6	77.6	70.3[b]	68.5
13	91.5	70.4	73.0	68.9	73.4	68.9	103.8	82.0	84.4	77.6	74.9	68.4
14	103.0	82.6	84.8	77.4	75.4	62.2						
15	102.3	82.4	84.7	77.9[b]	74.8	65.8	97.0	80.1	81.8	77.8[b]	70.2	68.7
16	102.5	82.2[b]	84.7	78.2[c]	74.9[d]	69.0	103.9	82.1[b]	84.7	77.8[c]	75.1[d]	68.6

[a]For solutions in $CDCl_3$. [b,c,d]Assignments marked with identical letters may be interchanged.

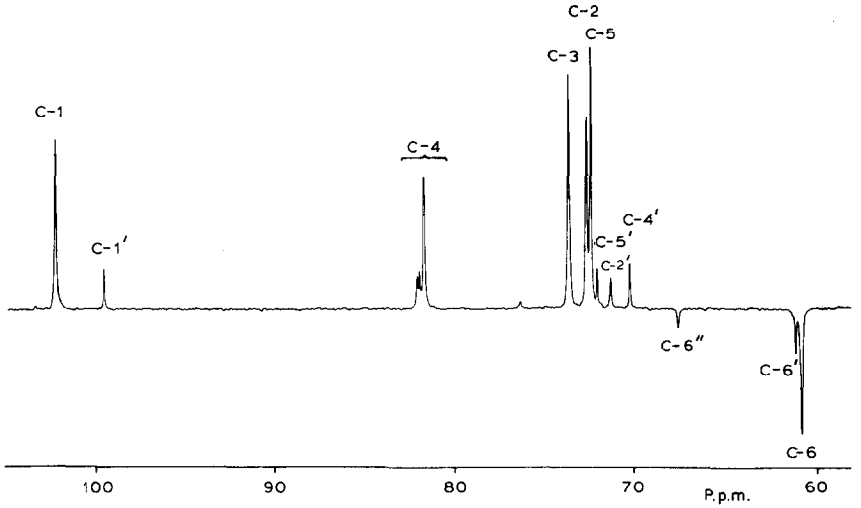


Fig. 1. 50-MHz ^{13}C-n.m.r. spectrum of 6-*O*-α-D-glucopyranosylcyclomaltoheptaose. Primed numbers refer to the carbons of the side chain, and double-primed numbers to the glucosyl residue bearing the side chain.

manifested in less intense signals at 82.0 and 81.9 p.p.m. for C-4, and 73.5 p.p.m. for C-3. The signal for C-6 of the glucosyl residue bearing the side chain was at 67.6 p.p.m., thereby proving the site of the side chain. Among the signals of the side chain, that at 99.6 p.p.m. of C-1 indicated an α linkage, the C-6 signal was found at 61.2 p.p.m., and the signals at 70.2, 71.3, and 72.0 p.p.m. are tentatively assigned to C-4, C-2, and C-5, respectively, of the side chain. These data, as well as the optical rotation of the compound, were in agreement with those reported[7,10,11] for the natural compound.

The synthesis strategy used in this work should be applicable for the preparation of other glycosylated cyclomalto-oligosaccharides.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined with a Kofler apparatus. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. N.m.r. spectra were recorded with a Bruker WP 200 SY spectrometer. Chemical shifts are given relative to that of internal Me_4Si for solutions in $CDCl_3$, and ^{13}C-n.m.r. chemical shifts for solutions in D_2O are relative to that of internal 1,4-dioxane (67.4 p.p.m.). Reactions were monitored by t.l.c. on Kieselgel 60 F_{254} (Merck) with detection by u.v. light and/or by charring with sulfuric acid. Solutions in organic solvents were dried with sodium sulfate. No correct analytical data were obtained for the cyclomaltoheptaose derivatives, probably as a result of complexation with solvents; the purity of these compounds, however, was carefully checked by t.l.c. and by n.m.r. spectroscopy.

tert-*Butyldimethylsilylation of cyclomaltoheptaose.* — To a solution of cyclomaltoheptaose (5.675 g, dried *in vacuo* over P_4O_{10} at 80°) in dry pyridine (80 mL) at −20° was added dropwise a solution of *tert*-butyldimethylsilyl chloride (0.942 g) in dry pyridine (20 mL) during 30 min with stirring. The reaction was followed by t.l.c. (1-butanol–ethanol–water, 5:4:3) and, when the formation of the mono(*tert*-butyldimethylsilyl) derivative was judged to be optimal (4 h), 4-dimethylaminopyridine (0.061 g) and acetic anhydride (50 mL) were added. The mixture was kept for 1 day at room temperature, then for 1 day at 60°, and concentrated to small volume, and ice was added followed by dichloromethane (1 L). The organic layer was washed with M sulfuric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Column chromatography (hexane–acetone, 3:2) of the residue gave, after a mixture, tris(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)tetrakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (0.545 g, 4.9%), $[\alpha]_D$ +105° (*c* 0.8, chloroform), R_F 0.48. N.m.r. data ($CDCl_3$): ^1H, δ 2.18–2.01 (54 H, 18 Ac), 0.90 and 0.87 (27 H, 3 CMe_3), 0.07–0.04 (18 H, 3 $SiMe_2$); ^{13}C, δ 96.8–95.8 (C-1), 62.9, 62.8, 62.6, 61.6, 61.4 (C-6), 25.9, 25.8 (CMe_3), 20.9, 20.7 (acetyl Me), −5.2, −5.5 (SiMe).

Eluted next was a bis(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)pentakis-(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (1.994 g, 18.4%), $[\alpha]_D$ +102° (*c* 1.2, chloroform), R_F 0.42. N.m.r. data ($CDCl_3$): ^1H, δ 2.17–1.97 (57 H, 19 Ac), 0.87 (s, 18 H, 2 CMe_3), 0.05 (s, 12 H, 2 $SiMe_2$); ^{13}C, δ 97.5–95.8 (C-1), 62.8, 62.4, 62.3, 61.2 (C-6), 25.7 (CMe_3), 20.7, 20.6 (acetyl Me), −5.4, −5.7 (SiMe).

Eluted next was bis(2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)pentakis-(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (0.532 g, 4.9%), $[\alpha]_D$ +103° (*c* 0.9, chloroform), R_F 0.36. N.m.r. data ($CDCl_3$): ^1H, δ 2.18–2.01 (57 H, 19 Ac), 0.89 and 0.88 (18 H, 2 CMe_3), 0.06 and 0.05 (12 H, 2 $SiMe_2$); ^{13}C, δ 96.8–96.1 (C-1), 62.6, 62.3, 61.3, 61.1 (C-6), 25.6 (CMe_3), 20.4 (acetyl Me), −5.4, −5.5, −5.7 (SiMe).

Eluted next was (2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl)hexakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (**2**; 4.210 g, 40.3%), $[\alpha]_D$ +109° (*c* 1.4, chloroform), R_F 0.29. N.m.r. data ($CDCl_3$): ^1H, δ 2.18–2.0 (60 H, 20 Ac), 0.87 (s, 9 H, CMe_3), 0.06 (s, 6 H, $SiMe_2$); ^{13}C, δ 97.3–95.8 (C-1), 62.7, 62.5, 62.3, 61.0 (C-6), 25.6 (CMe_3), 20.5 (acetyl Me), −5.4, −5.7 (SiMe).

Eluted last, with acetone–hexane (3:1), was heptakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (**3**; 2.037 g, 20.2%), m.p. 198–200° (from methanol), $[\alpha]_D$ +116° (*c* 1.3, chloroform), R_F 0.14; lit.[24] $[\alpha]_D$ +122° (chloroform); lit.[40] m.p. 195°, $[\alpha]_D$ +125° (methanol). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.4, 170.2, 169.2 (acetyl C=O), 96.7 (C-1), 76.8 (C-4), 70.8 (C-3), 70.4 (C-2), 69.6 (C-5), 62.5 (C-6), 20.5 (acetyl Me).

*(2,3-Di-*O*-acetyl)hexakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose* (**4**). — Compound **2** (2 g) was stirred in aqueous 70% acetic acid (50 mL) at 80° for 1.5 h, and the mixture was then concentrated. Column chromatography (hexane–acetone, 1:1) of the residue afforded amorphous **4** (1.081 g, 57.2%), $[\alpha]_D$ +107° (*c* 0.5, chloroform), R_F 0.25 (hexane–acetone, 1:1). N.m.r. data ($CDCl_3$): ^1H, δ 2.60 (s, 1 H, exchangeable with D_2O, OH), 2.15–2.0 (60 H, 20 Ac); ^{13}C, δ 96.8–96.1 (C-1), 62.7, 62.4, 61.0 (C-6), 20.3 (acetyl Me).

Glycosylation of **4**. — (*a*) A mixture of **4** (0.988 g) and powdered 4 Å molecular sieves (4 g) in dry dichloromethane (10 mL) was stirred under argon at −20°. A solution of **8** (0.685 g) in dichloromethane (10 mL) was added, followed, after 30 min, by a solution of trifluoromethanesulfonic acid (22 μL) in dichloromethane (2 mL). After 30 min, triethylamine (1 mL) was added, and the mixture was filtered through Celite, washed with M sulfuric acid, saturated aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Column chromatography (hexane–acetone, 1:1) of the residue gave amorphous [2,3-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)]hexakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose (**7**; 1.003 g, 80.3%), $[\alpha]_D$ +106° (*c* 0.9, chloroform), R_F 0.63 (hexane–acetone, 1:1). N.m.r. data ($CDCl_3$): ^1H, δ 7.35–7.1 (20 H, 4 Ph), 2.15–1.95 (60 H, 20 Ac); ^{13}C, δ 128.2–127.2 (Ph), 97.4, 97.0, 96.9, 96.7, 96.3, 96.2, 95.6 (C-1), 64.0, 62.6, 62.4, 62.3, 62.1 (C-6), 20.5, 20.2 (acetyl Me).

(*b*) A mixture of **4** (0.198 g), tetraethylammonium bromide (0.063 g), and 4 Å molecular sieves (2 g) in dichloromethane (10 mL) was stirred at room temperature. A solution of **5**, prepared by treatment of **6** (0.171 g) in dichloromethane (5 mL) with a solution of bromine (23 μL) in dichloromethane (2 mL) for 30 min followed by concentration and drying *in vacuo*, was added. After stirring the mixture for 5 days, the same amounts of **5** and tetraethylammonium bromide were added. After 4 days, the mixture was filtered, washed with aqueous sodium hydrogencarbonate and then water, dried, and concentrated. Column chromatography of the residue gave **7** (0.008 g, 3.2%) and **4** (0.120 g, 60.6%).

*[2,3-Di-*O*-acetyl-6-*O*-(α- and -β-*D*-glucopyranosyl)]hexakis(2,3,6-tri-*O*-acetyl)cyclomaltoheptaose* (**9** *and* **10**). — Compound **7** (0.769 g) (obtained by method *a*) was hydrogenated in acetic acid over 10% Pd/C (0.5 g) at atmospheric pressure overnight. Subsequent filtration, concentration, and column chromatography (acetone–hexane, 19:1) gave, first, **10** (0.067 g, 10.2%), $[\alpha]_D$ +103° (*c* 0.4, chloroform), R_F 0.61 (acetone). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.5 (C-1′), 97.6, 96.9, 96.8, 96.6, 96.2 (C-1), 62.7, 62.4 (C-6), 20.7 (acetyl Me).

Eluted next was **9** (0.490 g, 74.5%), $[\alpha]_D$ +123° (*c* 1, chloroform), R_F 0.54. ^{13}C-N.m.r. data ($CDCl_3$): δ 98.8 (C-1′), 97.1, 96.9, 96.7, 96.5 (C-1), 65.9 (C-6″), 62.9, 62.5 (C-6), 20.7 (acetyl Me).

*6-*O*-α-D-Glucopyranosylcyclomaltoheptaose* (**1**). — A solution of **9** (0.137 g) in methanol (10 mL) was treated with a catalytic amount of sodium methoxide. After 2 h, the deposited solid was dissolved by the addition of water (10 mL) and then M sodium hydroxide (1 mL) was added. The mixture was stored overnight at room temperature, deionised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Elution of the residue from a column (50 × 2.5 cm) of Sephadex G-15 with water, followed by freeze-drying, gave amorphous **1** (0.080 g, 97.6%), $[\alpha]_D$ +172° (*c* 0.6, water), R_F 0.29, $R_{CYCLOMALTOHEPTAOSE}$ 0.73 (1-butanol–ethanol–water, 5:4:3); lit.[7] $[\alpha]_D$ +178° (water); lit.[10] $[\alpha]_D$ +164° (water). ^{13}C-N.m.r. data (D_2O): δ 102.3 (C-1), 99.6 (C-1′), 82.0, 81.9, 81.6 (C-4), 73.6, 73.5 (C-3), 72.6 (C-2), 72.4 (C-5), 72.0 (C-5′), 71.3 (C-2′), 70.2 (C-4′), 67.6 (C-6″), 61.2 (C-6′), 60.8 (C-6).

1,2,3,4-Tetra-O-acetyl-6-O-(2,3,4,6-tetra-O-benzyl-α- and -β-D-glucopyranosyl)-β-D-glucopyranose (**12** *and* **13**). — A mixture of **11** (0.35 g) and 4 Å molecular sieves (3 g) in dichloromethane (10 mL) was stirred under argon and cooled to −20°. A solution of **8** (1.028 g) in dichloromethane (5 mL) was added, and, after 30 min, a solution of trifluoromethanesulfonic acid (36 μL) in dichloromethane (5 mL) was added dropwise during 10 min. After 1 h, triethylamine was added and the mixture was worked-up as described for **7**. Column chromatography (dichloromethane–methanol, 99:1) afforded **12** (0.434 g, 49.9%), as a syrup, $[\alpha]_D$ +45° (*c* 1.3, chloroform), R_F 0.47 (dichloromethane–methanol, 99:1); lit.[37] m.p. 80°, $[\alpha]_D$ +35° (chloroform); lit.[38] $[\alpha]_D$ +32° (chloroform); lit.[39] $[\alpha]_D$ +47° (chloroform).

Eluted next was **13** (0.329 g, 37.8%), m.p. 158–159° (from ethyl acetate–hexane), $[\alpha]_D$ +10° (*c* 1, chloroform), R_F 0.37; lit.[37] m.p. 145°, $[\alpha]_D$ +14° (chloroform).

Benzyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α- and -β-D-glucopyranosyl)-β-D-glucopyranoside (**15** *and* **16**). — Compound **14** (0.540 g) was glycosylated with **8** (1.028 g) and trifluoromethanesulfonic acid (9 μL) as described above. Column chromatography (dichloromethane–ethyl acetate, 49:1) of the product gave **15** (0.505 g, 47.5%), m.p. 129–130° (from ethyl acetate–hexane), $[\alpha]_D$ +26° (*c* 0.8, chloroform), R_F 0.46 (dichloromethane–ethyl acetate, 49:1).

Anal. Calc. for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64. Found: C, 76.72; H, 6.67.

Eluted next was **16** (0.406 g, 38.2%), m.p. 166–168° (from ethyl acetate–hexane), $[\alpha]_D$ +3° (*c* 1.2, chloroform), R_F 0.21.

Anal. Found: C, 76.88; H, 6.68.

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