Carbohydrate Research, 164 (1987) 277–296
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TOTAL SYNTHESIS OF CYCLOMALTOHEXAOSE*,†

YUKIO TAKAHASHI AND TOMOYA OGAWA**
RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama, 351-01 (Japan)
(Received September 4th, 1986; accepted for publication, January 26th, 1987)

ABSTRACT

Described for the first time is a total synthesis of cyclomaltohexaose, in 0.3% overall yield, in 21 steps starting from maltose. Maltose was transformed into allyl *O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**5**) and *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (**6**). Glycosylation of compound **5** with compound **6**, and partial deprotection of the product gave allyl *O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside, which was further glycosylated with the glycosyl donor **6**, and converted into the key intermediate *O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-tetrakis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (**3**). The crucial cyclization was achieved through intramolecular glycosylation of the key intermediate **3**, to afford a 21% yield of octadeca-*O*-benzylcyclomaltohexaose (**2**). Catalytic transfer hydrogenation of compound **2** yielded cyclomaltohexaose.

INTRODUCTION

Cyclomalto-oligosaccharides (cyclodextrins), degradation products of starch by an amylase (EC 2.4.1.19) of *Bacillus macerans*[2], have been the subjects of intense research in terms of chemical modifications[3] for the development of artificial functional molecules useful not only in fundamental research but also for industrial development. In spite of such broad interests, an approach to the total synthesis of cyclodextrins remained to be developed. We report here the first total synthesis of cyclomaltohexaose, starting from maltose.

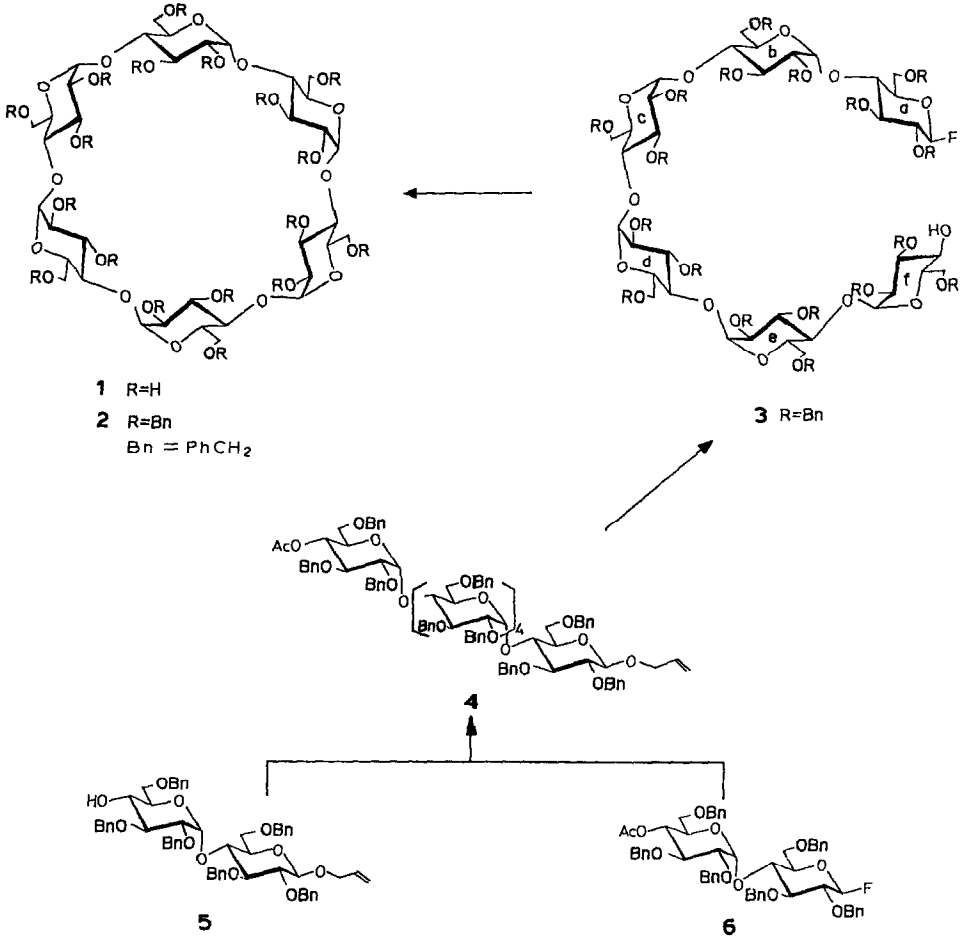
Retrosynthetic analysis of cyclomaltohexaose led us to design the D-glucohexaose derivative **3**, which may be suitable to examine for possible use in an intramolecular glycosylation to form octadeca-*O*-benzylcyclomaltohexaose (**2**).

*Dedicated to Burckhardt Helferich in commemoration of the hundredth anniversary of his birth.
†Glucan Synthesis, Part VI. For Part V (preliminary communication), see ref. 1.
**To whom enquiries should be addressed.

0008-6215/87/$ 03.50

Anomeric β-D-fluoride structure **3** was designed for intramolecular formation of an α-(1→4)-glycosidic linkage for the following reasons. First, selective cleavage of *O*-acyl groups in the presence of an anomeric C–F bond under mildly basic conditions had been observed in 1926 by Helferich and co-workers[4]. Therefore, introduction of an anomeric fluoride atom, and subsequent manipulation of a protecting group at OH-4f for the preparation of compound **3** should be possible. Second, an efficient method for activation of an anomeric β-D-fluoride to give an α-D-glucoside with reasonable selectivity had been developed by Mukaiyama and co-workers[5].

The anomeric fluoride **3** may be obtained from allyl glycoside **4**, which, in turn could be prepared by repeated glycosylation of glycosyl acceptor **5** with glycosyl donor **6**. A synthetic route to anomeric fluorides was first developed in



Scheme 1

	R¹	R²	R³	R⁴
5	$CH_2CH=CH_2$	Bn	H	Bn
7	Ac	Ac	Ac	Ac
8	$CH_2CH=CH_2$	Ac	Ac	Ac
9	$CH_2CH=CH_2$	H	H	H
10	$CH_2CH=CH_2$	H	CMe_2	
11	$CH_2CH=CH_2$	Bn	CMe_2	
12	$CH_2CH=CH_2$	Bn	H	H
13	$CH_2CH=CH_2$	Bn	Ac	Bn
14	H	Bn	Ac	Bn

	X	Y
6	F	H
15	H	Cl
16	H	F
17	$OC(=NH)CCl_3$	H
18	H	$OC(=NH)CCl_3$

	R¹	R²	R³
19	$CH_2CH=CH_2$	Bn	Ac
20	$CH_2CH=CH_2$	Bn	H
21	Pr	H	H

	R¹	R²	R³
22	$CH_2CH=CH_2$	Bn	Ac
23	$CH_2CH=CH_2$	Bn	H
24	Pr	H	H

	R¹	R²
25	Bn	Ac
26	H	H

Scheme 2

1923 by Brauns[6], using water-free hydrofluoric acid. A much milder and stereoselective approach to anomeric β-D-fluorides was reported in 1929 by Helferich and Gootz[7] through SN2 displacement of an anomeric α-D bromide by silver fluoride in acetonitrile.

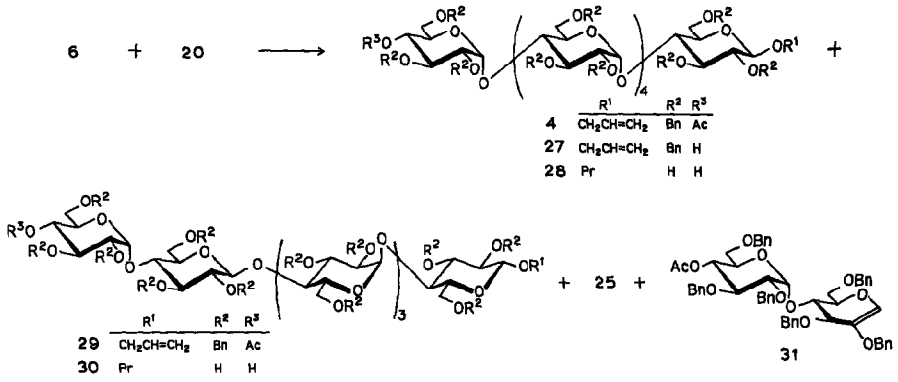
In spite of the availability of several recently developed procedures for the preparation of anomeric fluorides[8], we followed the Helferich and Gootz approach, in order to achieve highly stereoselective formation of a β-D-fluoride.

RESULTS AND DISCUSSION

Allyl glycoside **8**, obtainable from maltose octaacetate **7** by treatment with allyl tributyltin oxide[9], was converted into the penta-*O*-benzyl derivative **12** in 36% overall yield by sequential treatment with (*1*) sodium methoxide in methanol, (*2*) 2,2-dimethoxypropane and *p*-toluenesulfonic acid, (*3*) benzyl bromide and sodium hydride, and (*4*) 1:1 acetic acid–methanol. Selective benzylation at a primary hydroxyl group of compound **12** by the stannylation–alkylation method[10] afforded the desired glycosyl acceptor **5** in 95% yield.

Such glycosyl donors as chloride **15**, fluoride **6**, and imidate **17** or **18** were prepared from compound **5** in order to determine efficient conditions for the stereoselective synthesis of the D-glucotetraosyl derivative **19**. Acetylation of compound **5** gave acetate **13**, and *O*-deallylation of compound **13** with palladium(II) chloride–sodium acetate–aq. acetic acid[11] afforded a 93% yield of hemiacetal **14**. Treatment of compound **14** with thionyl chloride–*N*,*N*-dimethylformamide[12] afforded an 89% yield of α-D-chloride **15**, which was converted into β-D-fluoride **6** in 90% yield by treatment with silver fluoride in acetonitrile. The configuration at C-1a of compound **6** was assigned in harmony with the following ^{13}C-, ^{1}H-, and ^{19}F-n.m.r. data: signals for C-1a, H-1a, and C_{1a}–F appeared at δ_C 109.6 with $^{1}J_{CH}$ 172 and $^{1}J_{CF}$ 217 Hz (ref. 13), δ_H 5.378 with $^{3}J_{HH}$ 5.9 and $^{2}J_{HF}$ 54.1 Hz (ref. 14), and δ_F 133.7 with $^{2}J_{HF}$ 53.7 and $^{3}J_{HF}$ 10.4 Hz (ref. 14), respectively. A mixture of the β- and α-D-fluorides **6** and **16** was obtained in 75% yield, in the ratio of 3:2, when compound **14** was treated with diethylhexafluoropropylamine[15]. The configuration at C-1a of compound **16** was assignable according to ^{13}C- and ^{1}H-n.m.r. data, which included signals for C-1a and H-1a at δ_C 105.0 with $^{1}J_{CH}$ 180 and $^{1}J_{CF}$ 227 Hz (ref. 13), and at δ_H 5.540 with $^{3}J_{HH}$ 2.9 and $^{2}J_{HF}$ 52.6 Hz (ref. 14). The imidates **17** and **18** were readily obtained according to Schmidt and co-workers[16].

Glycosylations of glycosyl acceptor **5** with glycosyl donors were examined as follows. Silver triflate-promoted glycosylation with a slight excess of chloride **15** in dichloroethane gave a 63% yield of a mixture of glucotetraosyl derivatives **19** and **22** in the ratio of 1.74:1, as well as an 8% yield of the 1,6-anhydro derivative **25**. The structure of compound **25** was assigned from the ^{13}C- and ^{1}H-n.m.r. spectra, which contained signals for H-1a at δ_H 5.470 as a singlet, and C-1a at δ_C 100.7, and was further confirmed by transformation into deblocked product **26**. The ^{1}H- and ^{13}C-n.m.r. spectra of compound **26** showed signals for H-1a, H-1b, C-1a,



Scheme 3

and C-1b at δ_H 5.482 (singlet), δ_H 5.144 with $^3J_{HH}$ 3.7 Hz, δ_C 102.0 with $^1J_{CH}$ 177 Hz, and δ_C 98.5 with $^1J_{CH}$ 170 Hz, respectively. When mercuric bromide–mercuric cyanide was used instead of silver triflate, the 1,6-anhydro derivative **25** became the major product. Mukaiyama[5] glycosylation of **5** with 1.15 equivalents of β-fluoride **6** afforded an 80% yield of a 1.76:1 mixture of **19** and **22**, as well as a 15% yield of 1,6-anhydro derivative **25**. Addition of other Lewis acids, such as boron trifluoride etherate, or cesium fluoride, did not improve the ratio of **19** to **22** in favor of **19**. Trichloroacetimidates **17** and **18** were also separately examined as glycosyl donors in the presence of Me_3Si triflate, but only inferior results were obtained in our hands.

The structures of glucotetraosyl derivatives **19** and **22** were assigned from their ^{13}C-n.m.r. data. For compound **19**, one signal for a β-D-anomeric carbon atom was observed at δ 102.6, while for compound **22**, two signals, for two β-D-anomeric carbon atoms were observed at δ 102.5 and 102.2. These assignments were confirmed by transformation into deblocked propyl glucotetraosides **21** and **24**, respectively. The ^1H-n.m.r. spectra of compounds **21** and **24**, shown in Fig. 1, clearly showed the stereochemistry of these compounds. Judging from the results thus far obtained from glycosylation experiments for the synthesis of compound **19**, we decided to use glycosyl fluorides as the most efficient glycosyl donors for the extension of a glucan chain in an α-D-(1→4) fashion.

Having obtained glucotetraosyl intermediate **19**, two synthesis routes to glucohexaosyl derivative **4** were examined. The first approach utilized the glucotetraosyl glycosyl acceptor **20** and glycosyl donor **6**, and the second employed glucotetraosyl glycosyl donor **34** and glycosyl acceptor **5**.

Glycosylation of glucotetraosyl derivative **20** (obtained from compound **19** with 2 equivalents of glycosyl donor **6** in the presence of silver triflate and stannous(II) chloride[5], afforded a 65% yield of a 1.95:1 mixture of the desired product **4** and the β anomer **29**, as well as a 21% yield of recovered glycosyl

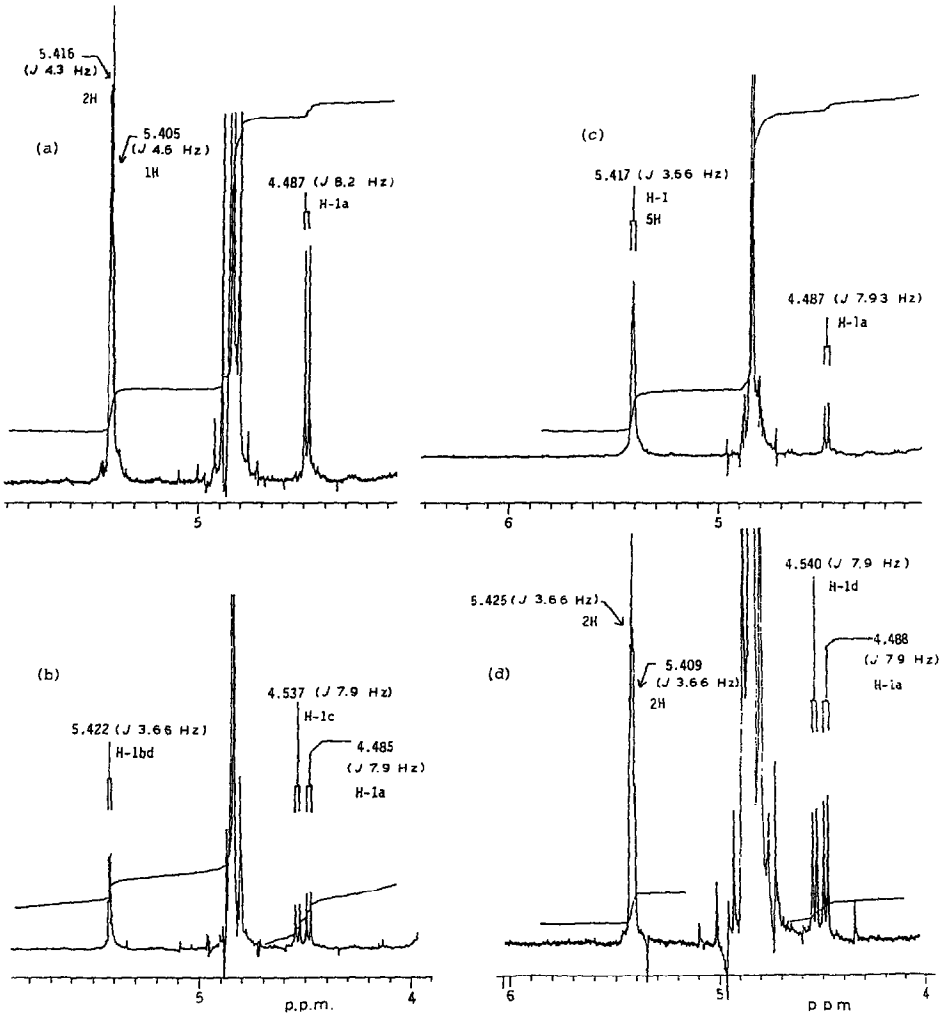
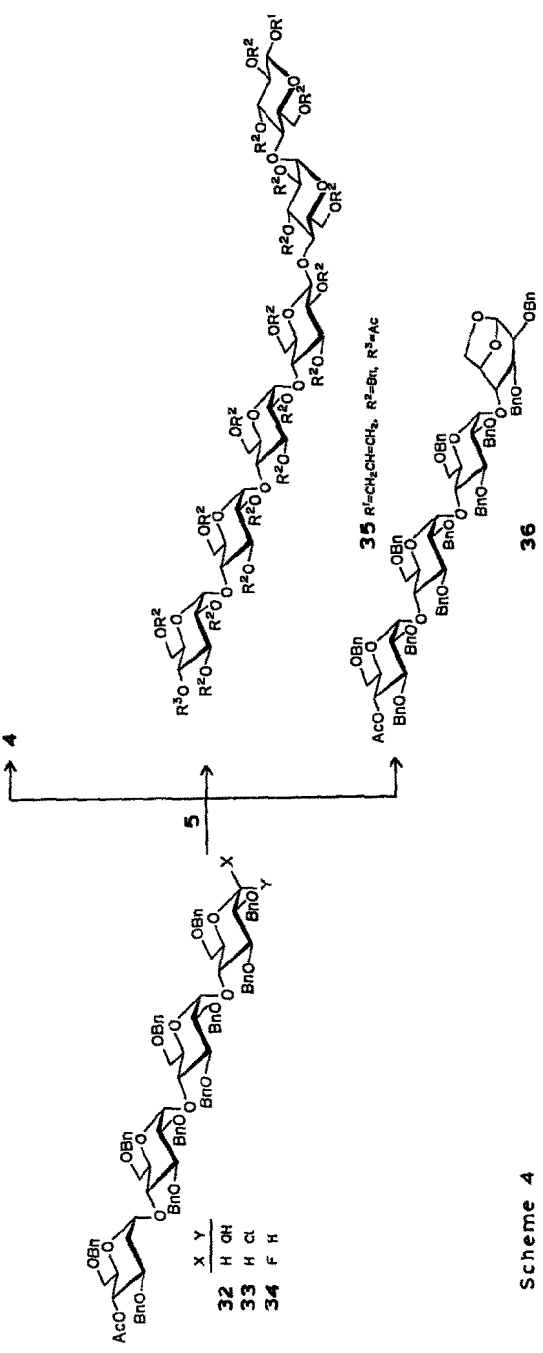


Fig. 1. 400-MHz, ^{1}H-n.m.r. spectra of synthetic propyl glycosides: (a) Glcα(→4Glcα)$_2$→Glcβ→OPr (**21**). (b) Glcα→4Glcβ→4Glcα→4Glcβ→OPr (**24**). (c) Glcα(→4Glcα)$_4$→Glcβ→OPr (**28**), and (d) Glcα→4Glcβ(→4Glcα)$_3$→Glcβ→OPr (**30**). The spectra were recorded in D_2O at 20°.

acceptor **20**. The excess of glycosyl donor **6** was converted into 1,6-anhydro derivative **25** and glycal derivative **31**, in 25 and 23% yield, respectively. The structures of **4** and **29** were assigned from ^{13}C-n.m.r. data. In the case of compound **4**, one signal for a β-D-anomeric carbon atom was observed at δ 102.7, along with five signals for α-D-anomeric carbon atoms at δ 96.9, 96.6, 96.4, and 96.2 in the ratios of 1:1:1:2, whereas, in the case of compound **29**, two signals for β-D-anomeric carbon atoms were observed, at δ 102.6 and 102.2, along with four signals for α-D-anomeric carbon atoms, at δ 96.9, 96.6, 96.5, and 96.2. These structural

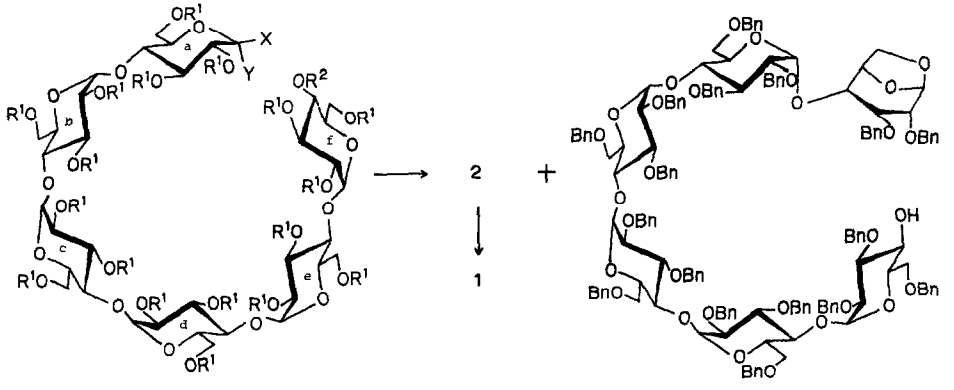


Scheme 4

assignments for compounds **4** and **29** were confirmed by their transformation into deblocked propyl glycosides **28** and **30**, respectively. The ^{1}H-n.m.r. spectra shown in Fig. 1 clearly proved their anomeric configurations.

An alternative route to glucohexaosyl derivative **4** was based on coupling of glucotetraosyl glycosyl donor **34** with glycosyl acceptor **5**. Synthesis of glycosyl donor **34** from compound **19** was straightforward. Three steps for the conversion of compound **19** into fluoride **34** were performed, *via* hemiacetal **32**, in 48% overall yield: (*1*) palladium(II) chloride–sodium acetate–aq. acetic acid, (*2*) thionyl chloride–*N*,*N*-dimethylformamide, and (*3*) silver fluoride–acetonitrile. The configuration at C-1a of compound **34** was again determined as β-D from ^{1}H-, ^{13}C-, and ^{19}F-n.m.r. data. Silver triflate and stannous chloride-promoted glycosylation[5] of glycosyl acceptor **5** with glycosyl donor **34** in diethyl ether was examined by using 14.5 equivalents of compound **5** in order to minimize side reactions of the glycosyl donor **34**, and a 1.74:1 mixture of compound **4** and isomer **35** were obtained in 55% yield, as well as a 33% yield of 1,6-anhydro derivative **36**. Compound **35** was not characterized by n.m.r. data, but was most probably the stereoisomer of compound **4**, as shown in Scheme 4. The structure of compound **36** was assigned from ^{1}H-n.m.r. data, which contained characteristic signals for H-1a and H-1b at δ 5.482 as a singlet and at δ 4.992 as a doublet, respectively. From the viewpoint of synthesis efficiency, the former route to compound **4** by use of glucotetraosyl glycosyl acceptor **20** and glucobiosyl glycosyl donor **6** was chosen, rather than the latter.

Having prepared the key glucohexaosyl derivative **4**, transformation of compound **4** into the key glycosyl fluoride **3** was studied. First, replacement of the *O*-acetyl group of compound **4** by an *O*-(monochloroacetyl) group was performed to give compound **37** in 86% overall yield in two steps. Palladium-catalyzed *O*-deallylation of compound **37** gave a 60% yield of hemiacetal **38**, which was stereoselectively converted into β-D-fluoride **39** in 73% yield. The configuration at C-1a



	X	Y	R¹	R²
3	F	H	Bn	H
37	$OCH_2CH=CH_2$	H	Bn	$COCH_2Cl$
38	OH	H	Bn	$COCH_2Cl$
39	F	H	Bn	$COCH_2Cl$
40	OH	H	Bn	H

Scheme 5

was assigned from the ^{13}C-n.m.r. spectrum of compound **39**, which contained a signal for C-1a at δ 109.2. Zemplén deacylation of compound **39** was readily achieved, in agreement with the observation of Helferich and co-workers[3] in 1926, to afford a 95% yield of the key glycosyl fluoride **3**. The ^{13}C- and ^{1}H-n.m.r. data for compound **3** were in agreement with the structure assigned. Crucial intramolecular glycosylation of compound **3** under the Mukaiyama conditions[5] furnished a 21% yield of the protected cyclomaltohexaose **2**, as well as a 20% yield of 1,6-anhydro derivative **41**. The structure of compound **41** was assigned from ^{1}H-n.m.r. data, which revealed four doublets with J 3.4 Hz at δ 5.682, 5.620, 5.594, and 5.560 for H-1c, H-1d, H-1e, and H-1f, as well as a characteristic singlet and a doublet, with J 3.4 Hz at δ 5.478 and 5.002 for H-1a and H-1b, respectively. Compound **2** was also obtainable by benzylation of commercially available cyclomaltohexaose. Comparison of the ^{1}H- and ^{13}C-n.m.r. data of the totally synthetic sample of **2** and the natural derivative proved their identity. *O*-Debenzylation of compound **2** under hydrogen-transfer conditions[17] afforded cyclomaltohexaose (**1**).

In conclusion, a total synthesis of cyclomaltohexaose (**1**) was excecuted in 21 steps from maltose in 0.3% overall yield. The crucial intramolecular glycosylation employing β-maltohexaosyl fluoride **3** was achieved in 21% yield.

EXPERIMENTAL

General. —Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Column chromatography was performed on columns of Silica Gel (Merck, 70–230 mesh). Flash chromatography was performed on columns of Wako gel C-300 (200–300 mesh). T.l.c. and high-performance t.l.c. was performed on Silica Gel 60 F_{254} (Merck, Darmstadt). Molecular sieves were purchased from Nakarai Chemicals, Ltd. I.r. spectra were recorded with an EPI-G2 Hitachi spectrophotometer, using KBr pellets for the crystalline samples, and films for the liquid samples. ^{1}H-N.m.r. spectra were recorded with either a JNM-GX400 or a JNM-FX90Q n.m.r. spectrometer. ^{13}C-N.m.r. spectra were recorded with a JNM-FX 100FT n.m.r. spectrometer operated at 25.05 MHz. The values of δ_C and δ_H are expressed in p.p.m. downwards from the signal for internal Me_4Si, for solutions in $CDCl_3$, unless noted otherwise. Values of δ_F, expressed in p.p.m. upfield from the signal for trichlorofluoromethane, were measured against an internal standard of hexafluorobenzene (163.0 p.p.m.). Values of δ_H (D_2O) and δ_C (D_2O) are expressed in p.p.m. downward from Me_4Si, by reference to internal standards of Me_2CO (2.225) or Me_3COH (1.230), and 1,4-dioxane (67.4) or MeOH (49.8), respectively.

Allyl O-*(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**8**). — To a solution of $Bu_3SnOCH_2CH{=}CH_2$ (6.0 g, 17 mmol) in $Cl(CH_2)_2Cl$ (80 mL) were added dropwise a solution of $SnCl_4$ (2.0 mL,

14.7 mmol) in $Cl(CH_2)_2Cl$ (40 mL) at −5°, and then, dropwise, a solution of compound **7** (10 g, 14.7 mmol) in $Cl(CH_2)_2Cl$ (40 mL) during 40 min at 20°. The mixture was stirred for 1.5 h at 20°, poured into aq. $NaHCO_3$, and extracted with EtOAc. The organic layer was vigorously stirred with aq. KF, filtered through Celite, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 6:1 toluene–THF afforded **8** (7.3 g, 73%); m.p. 106–107° (EtOAc–iPr_2O), $[\alpha]_D$ +50.4° (*c* 0.2); R_F 0.47 in 3:1 toluene–THF; n.m.r. data: δ_H 6.04–5.62 (m, 1 H, CH_2–C*H*=), 2.14, 2.10, 2.04 (3 s, 9 H, 3 CH_3CO), 2.02 (s, 6 H, 2 CH_3CO), and 2.00, and 1.99 (2 s, 6 H, 2 CH_3CO); δ_C 98.9 ($^1J_{CH}$ 160 Hz, C-1a) and 95.4 ($^1J_{CH}$ 177 Hz, C-1b).

Anal. Calc. for $C_{29}H_{40}O_{18}$: C, 51.5; H, 6.0. Found: C, 51.7; H, 6.0.

Allyl O-*(4,6-O-isopropylidene-α-D-glucopyranosyl)-(1→4)-β-D-glucopyranoside* (**10**). — A solution of compound **8** (5.8 g, 8.5 mmol) in 0.05M NaOMe–MeOH (30 mL) was stirred for 2 h at 20°, made neutral with Amberlyst 15, and the suspension filtered. The filtrate was evaporated, to give crude **9** (3.3 g). A mixture of crude **9** (3.3 g), $(MeO)_2CMe_2$ (4.8 mL, 39 mmol), and *p*TsOH·H_2O (5 mg) in DMF (20 mL) was stirred for 1 h at 20°, the acid neutralized with Et_3N, and the solution evaporated *in vacuo*. The residue was stirred in 20:1 MeOH–AcOH (20 mL) for 12 h at 20°, and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 90:9:1 CH_2Cl_2–MeOH–Et_3N afforded **10** (2.3 g, 63%).

Compound **9**: N.m.r. data: δ_H (D_2O) 5.42 (d, 1 H, *J* 4.2 Hz, H-1b) and 4.53 (d, 1 H, *J* 8.1 Hz, H-1a); δ_C (CD_3OD) 102.9, 102.3 (C-1a, C-1b), and 80.7 (C-4a).

Compound **10**: $[\alpha]_D$ +28.4° (*c* 0.2); R_F 0.60 in 5:1 $CHCl_3$–MeOH; n.m.r. data: δ_H 1.31 and 1.23 (2 s, 6 H, CCH_3); δ_C (CD_3OD) 103.4 (CMe_2 and C-1a), 100.9 (C-1b), and 81.6 (C-4a).

Anal. Calc. for $C_{18}H_{30}O_{11}$: C, 51.2; H, 7.2. Found: C, 50.9; H, 7.4.

Allyl O-*(2,3-di-O-benzyl-4,6-O-isopropylidene-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-O-benzyl-β-D-glucopyranoside)* (**11**). — To a solution of compound **10** (0.4 g, 1.0 mmol) in DMF (20 mL) was added NaH (0.27 g, 50% oil suspension, 5.6 mmol) at 0°, and the mixture was stirred for 30 min at 20°. To the mixture was added, dropwise, $C_6H_5CH_2Br$ (0.68 mL, 5.6 mmol) at −5°. The mixture was stirred for 1 h, and the excess of NaH was decomposed by adding MeOH. After evaporation *in vacuo*, a solution of the residue in EtOAc was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 100:3:1 toluene–EtOAc–Et_3N afforded **11** (0.68 g, 83%); $[\alpha]_D$ +19.8° (*c* 0.5); R_F 0.59 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 1.48 and 1.46 (2 s, 6 H, CCH_3); δ_C 102.6 ($^1J_{CH}$ 166 Hz, C-1a), 99.3 (CMe_2), 97.4 ($^1J_{CH}$ 177 Hz, C-1b), and, 29.3 and 19.3 (CCH_3).

Anal. Calc. for $C_{53}H_{60}O_{11}$: C, 72.9; H, 6.9. Found: C, 72.8; H, 6.9.

Allyl O-*(2,3-di-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside* (**12**). — A solution of compound **11** (0.42 g, 480 μmol) in 1:1 MeOH–AcOH (10 mL) was stirred for 1 h at 80°, cooled, concentrated *in vacuo*, and the concentrate dissolved in EtOAc. The organic layer was successively washed

with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–THF afforded **12** (277 mg, 70%); $[\alpha]_D$ +23.6°, m.p. 101–102° (EtOAc–iPr_2O); R_F 0.34 in 3:1 toluene–THF; n.m.r. data: δ_C 102.5 ($^1J_{CH}$ 160 Hz, C-1a), 96.4 ($^1J_{CH}$ 174 Hz, C-1b), 84.7 (C-3a), 82.1 (C-2a), 81.2 (C-3b), and 79.3 (C-4a).

Anal. Calc. for $C_{50}H_{56}O_{11}$: C, 72.1; H, 6.8. Found: C, 71.7; H, 6.8.

Allyl O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**5**). — A mixture of compound **12** (9.2 g, 11 mmol) and $(Bu_3Sn)_2O$ (4.73 g, 7.9 mmol) in toluene (200 mL) was stirred for 4 h under reflux with continuous azeotropic removal of water, and concentrated to ~100 mL. To this mixture were added Bu_4NBr (3.56 g, 11 mmol) and $C_6H_5CH_2Br$ (6.6 mL, 55 mmol). The mixture was stirred for 24 h at 80–85°, cooled, and evaporated *in vacuo*. A solution of the residue in EtOAc was washed successively with aq. $NaHCO_3$ and aq. KF, dried ($MgSO_4$), filtered, and the filtrate evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded **5** (9.66 g, 95%); $[\alpha]_D$ +21.6° (*c* 0.5); R_F 0.52 in 5:1 toluene–EtOAc; n.m.r. data: δ_C 102.6 ($^1J_{CH}$ 159 Hz, C-1a), 96.6 ($^1J_{CH}$ 172 Hz, C-1b), 84.8 (C-3a), 82.2 (C-2a), 81.3 (C-3b), 79.1 (C-4a), and 69.9 and 69.4 (C-6a and C-6b).

Anal. Calc. for $C_{57}H_{62}O_{11}$: C, 74.2; H, 6.8. Found: C, 74.3; H, 6.8.

O-(4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-D-glucopyranose (**14**). — A solution of compound **5** (1.73 g, 1.9 mmol) in 2:1 pyridine–Ac_2O (6 mL) was stirred for 4 h at 20° and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded allyl *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**13**; 1.8 g, quantitative); $[\alpha]_D$ +28.0° (*c* 0.6); R_F 0.61 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 1.80 (s, 3 H, Ac); δ_C 102.5 (C-1a), 96.7 (C-1b), 84.6 (C-3a), 82.1 (C-2a), 79.3 (C-3b), 79.2 (C-4a), and 20.8 ($COCH_3$).

A mixture of compound **13** (13.3 g, 13.8 mmol), $PdCl_2$ (5.3 g, 30 mmol), and AcONa (5.3 g. 65 mmol) in 9:1 AcOH–H_2O (50 mL) was stirred for 1 h at 70°, filtered through Celite, and the filtrate evaporated *in vacuo*. A solution of the residue in EtOAc was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 7:1 toluene–EtOAc afforded a 1:1 mixture of the α and β anomers of **14** (11.9 g, 93%); $[\alpha]_D$ +36.0° (*c* 0.7); R_F 0.37 and 0.26 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 1.80 (s, 3 H, CH_3CO); δ_C 97.4 (C-1aβ), 96.9 and 96.7 (C-1b), and 90.6 (C-1aα).

Anal. Calc. for $C_{56}H_{60}O_{12}$: C, 72.7; H, 6.5. Found: C, 73.1; H, 6.6.

O-(4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranosyl fluoride (**6**). — To a solution of compound **14** (4.45 g, 4.8 mmol) in $Cl(CH_2)_2Cl$ (20 mL) were added $SOCl_2$ (1.75 mL, 24 mmol) and DMF (0.3 mL, 4 mmol). The mixture was stirred for 2 days at 20°, filtered through SiO_2 gel, and the filtrate evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–EtOAc afforded *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride (**15**; 4.02 g,

89%); $[\alpha]_D$ +81.9° (*c* 0.1); R_F 0.70 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 6.06 (d, 1 H, *J* 3.7 Hz, H-1a), 5.57 (d, 1 H, *J* 3.3 Hz, H-1b), and 1.81 (s, 3 H, CH_3CO); δ_C 97.1 (C-1b), 93.2 (C-1a), and 20.8 ($COCH_3$).

[*A*]. A mixture of compound **15** (2.1 g, 2.2 mmol) and AgF (0.8 g, 6.3 mmol) in CH_3CN (20 mL) was stirred for 18 h at 20° with protection from light. After filtration through Celite, the filtrate was evaporated *in vacuo*. A solution of the residue in EtOAc was washed with aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–EtOAc afforded **6** (1.86 g, 90%); $[\alpha]_D$ +45.4° (*c* 0.2); R_F 0.48 in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.538 (d, 1 H, *J* 3.7 Hz, H-1b), 5.378 (dd, 1 H, *J* 5.9 and 54.1 Hz, H-1a), 5.050 (t, 1 H, *J* 9.3 Hz, H-4b), and 1.844 (s, 3 H, CH_3CO); δ_C 109.6 ($^1J_{CH}$ 172 Hz and $^1J_{CF}$ 217 Hz, C-1a), 97.0 ($^1J_{CH}$ 173 Hz, C-1b), 82.9 ($^3J_{CF}$ 8.5 Hz, C-3a), 80.5 ($^2J_{CF}$ 25.6 Hz, C-2a), 79.3 (C-3b), 79.2 (C-4a), and 20.9 ($COCH_3$); δ_F 133.7 (dd, $^2J_{HF}$ 53.7, $^3J_{HF}$ 10.4 Hz).

Anal. Calc. for $C_{56}H_{59}FO_{11}$: C, 72.6; H, 6.4. Found: C, 72.3; H, 6.4.

[*B*]. To a solution of compound **14** (50 mg, 50 μmol) in Et_2O (5 mL) was added a solution of diethyl-1,1,2,3,3,3-hexafluoropropylamine (15 mg, 70 μmol) in Et_2O (2 mL) at −5°. After stirring for 24 h at 20°, a solution of diethylhexafluoropropylamine (5 mg, 23 μmol) in Et_2O (1 mL) was added. The mixture was stirred for 4 h at 20°, and poured into aq. KF. The organic layer was dried ($MgSO_4$), and evaporated *in vacuo*. Purification of the residue on Lobar LiChroprep Si60 (size A) in 30:1 toluene–EtOAc gave a 2:3 mixture of **16** and **6** (37 mg, 75%).

Compound **16**: R_F 0.48 in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.586 (d, 1 H, *J* 3.5 Hz, H-1b), 5.538 (dd, 1 H, *J* 2.5, 53.8 Hz, H-1a), and 1.816 (s, 3 H, CH_3CO); δ_C 105.0 ($^1J_{CF}$ 227, $^1J_{CH}$ 180 Hz, C-1a) and 97.1 ($^1J_{CH}$ 172 Hz, C-1b).

O-(4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β- and α-D-glucopyranosyl trichloroacetimidate (**17** *and* **18**). — A mixture of compound **14** (500 mg, 540 μmol), Cl_3CCN (540 μL, 5.4 mmol) and NaH (50% oil dispersion, 30 mg, 630 μmol) in CH_2Cl_2 (2 mL) was stirred for 1 h at 0°. The mixture was filtered through Celite, and the filtrate was evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–EtOAc afforded **18** (370 mg, 65%) and **17** (170 mg, 30%).

Compound **17**: R_F 0.52 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 5.91 (d, 1 H, *J* 5.7 Hz, H-1a), 5.57 (d, 1 H, *J* 3.5 Hz, H-1b), and 1.81 (s, 3 H, CH_3CO).

Compound **18**: R_F 0.61 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 6.52 (d, 1 H, *J* 4.8 Hz, H-1a), 5.62 (d, 1 H, *J* 4.8 Hz, H-1b), and 1.81 (s, 3 H, CH_3CO); δ_C 169.4 ($COCH_3$), 161.3 (*C*=NH), 96.8 (C-1b), 94.1 (C-1a), and 20.8 ($COCH_3$).

Allyl O-(4-O-acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-bis[O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**19**), *allyl O-(4-O-acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl-(1→4)-O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside* (**22**), *and O-(4-O-acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-1,6-anhydro-2,3-di-O-benzyl-β-D-*

glucopyranose (**25**). — [*A*]. To a mixture of compound **5** (3.1 g, 3.3 mmol), $AgOSO_2CF_3$ (2.51 g, 9.8 mmol), and powdered molecular sieves 4A (9 g) in $Cl(CH_2)_2Cl$ (8 mL) was added dropwise a solution of compound **15** (3.12 g, 3.4 mmol) in $Cl(CH_2)_2Cl$ (10 mL). The mixture was stirred for 19 h at 20°, filtered through Celite, and the Celite washed with EtOAc. The filtrates were combined, successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded **19** (2.42 g, 40%), **22** (1.38 g, 23%), **25** (190 mg, 8%), and recovered **5** (640 mg, 21%).

[*B*]. To a mixture of compound **5** (3.1 g, 3.3 mmol), $AgOSO_2CF_3$ (1 g, 3.9 mmol), $SnCl_2$ (740 mg, 3.9 mmol), and powdered molecular sieves 4A (9 g) in Et_2O (15 mL) was added dropwise a solution of compound **6** (3.5 g, 3.8 mmol) in Et_2O (15 mL). After stirring for 20 h, more of the solution of compound **6** (200 mg, 220 μmol) was added. The mixture was stirred for 24 h at 20°, and filtered through Celite. The filtrate was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded **19** (3.0 g, 51%), **22** (1.7 g, 29%), **25** (460 mg, 15%), and recovered **5** (590 mg, 17%).

[*C*]. To a mixture of compounds **5** (100 mg, 110 μmol) and **17** (122 mg, 120 μmol), and powdered molecular sieves 4A (200 mg) in $Cl(CH_2)_2Cl$ (0.5 mL) was added $Me_3SiOSO_2CF_3$ (23 μL, 120 μmol) under Ar. The mixture was stirred for 1 h at 0°, diluted with EtOAc, and filtered through Celite. The filtrate was washed successively with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on Lobar LiChroprep Si60 (size A) in 20:1 toluene–EtOAc afforded **19** (42 mg, 21%), **22** (24 mg, 12%), and trimethylsilylated **5** (34 mg, 32%). The α-imidate **18** (130 mg) under the same conditions afforded **19** (54 mg, 27%), **22** (60 mg, 30%), and recovered **5** (45 mg).

Compound **19**: $[\alpha]_D$ +58.2° (*c* 0.2); R_F 0.65 (h.p.t.l.c.) in 5:1 toluene–EtOAc; n.m.r. data: δ_H 7.25–7.0 (m, 60 H, aromatic), 6.2–5.66 (m, 1 H, CH_2CH=), and 1.79 (s, 3 H, CH_3CO); δ_C 102.6 ($^1J_{CH}$ 155 Hz, C-1a), 96.9, 96.5, 96.3 ($^1J_{CH}$ 170–172 Hz, C-1b, C-1c, and C-1d), 84.7 (C-3a), 82.1 (C-2a), 81.4 (C-3b and C-3c), 79.6 (C-3d), 79.3 (C-4a, C-4b, C-4c), and 20.9 ($COCH_3$).

Anal. Calc. for $C_{113}H_{120}O_{22}$: C, 74.2; H, 6.6. Found: C, 74.1; H, 6.6.

Compound **22**: $[\alpha]_D$ +41.4° (*c* 0.2); R_F 0.59 (h.p.t.l.c.) in 5:1 toluene–EtOAc; n.m.r. data: δ_H 7.25–7.0 (m, 60 H, aromatic), 6.2–5.66 (m, 1 H, CH_2CH=), and 1.79 (s, 3 H, CH_3CO); δ_C 102.5 (C-1a), 102.2 (C-1c), 96.9 (C-1b and C-1d), 84.7, 84.6 (C-3a and C-3c), 82.5, 82.3 (C-2a and C-2c), and 20.8 ($COCH_3$).

Anal. Calc. for $C_{111}H_{120}O_{22}$: C, 74.2; H, 6.6. Found: C, 73.9; H, 6.6.

Compound **25**; m.p. 92–93° (EtOAc–iPr_2O), $[\alpha]_D$ +6.1° (*c* 0.3); R_F 0.29 (h.p.t.l.c.) in 5:1 toluene–EtOAc; n.m.r. data: δ_H 7.3–7.1 (m, 25 H, aromatic), 5.478 (s, 1 H, H-1a), 5.012 (t, 1 H, *J* 10.0 Hz, H-4b), 4.951 (d, 1 H, *J* 3.4 Hz, H-1b), and 1.855 (s, 3 H, CH_3CO); δ_C 169.3 ($COCH_3$), 100.7 (C-1a), 98.1 (C-1b), 65.6 (C-6a), and 20.6 ($COCH_3$).

Anal. Calc. for $C_{49}H_{52}O_{11}$: C, 72.0; H, 6.4. Found: C, 71.8; H, 6.4.

Allyl O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-bis[O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**20**) *and its deprotection product.* — To a solution of compound **19** (2.28 g, 1.25 mmol) in 1.1 MeOH–THF (40 mL) was added 0.5M NaOMe–MeOH (2.5 mL), and the mixture was stirred for 24 h at 20° and then for 2 h at 50°. Neutralization with Amberlyst 15, filtration, and evaporation of the filtrate *in vacuo* afforded a residue which was chromatographed on SiO_2 gel in 15:1 toluene–EtOAc, to give **20** (2.15 g, 97%); $[\alpha]_D$ +44.6° (*c* 0.3); R_F 0.50 in 9:1 toluene–EtOAc; n.m.r. data: δ_C 102.6 (C-1a), 96.7, 96.5, 96.3 (C-1b, C-1c, C-1d), 84.6 (C-3a), 82.0 (C-2a), 81.6 (C-3d), and 81.4 (C-3b, C-3c).

Anal. Calc. for $C_{111}H_{118}O_{21}\cdot 0.2\,H_2O$: C, 74.4; H, 6.7. Found: C, 74.1; H, 6.7.

A mixture of **20** (18.8 mg) and 10% Pd–C (19 mg) in AcOH (2 mL) was stirred for 1 h at 80° under H_2, cooled, and filtered through Celite. The filtrate was evaporated *in vacuo*, and the residue was purified by means of Sephadex G-25 in H_2O, to give propyl *O*-α-D-glucopyranosyl-(1→4)-bis[*O*-α-D-glucopyranosyl-(1→4)]-β-D-glucopyranoside (**21**; 6.6 mg, 96%); R_F 0.54 in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (D_2O) 5.416 (d, 2 H, *J* 4.3 Hz) and 5.405 (d, 1 H, *J* 4.6 Hz, H-1b, H-1c, H-1d), 4.487 (d, 1 H, *J* 8.2 Hz, H-1a), 3.298 (dd, 1 H, *J* 8.2 and 9.5 Hz, H-2a), and 3.428 (t, 1 H, *J* 9.5 Hz, H-3a); δ_C (D_2O) 102.8 (C-1a), 100.6, 100.5, 100.3 (C-1b, C-1c, C-1d), 78.0 (C-4a, C-4b, C-4c), 23.0 (CH_2CH_3), and 10.4 (CH_2CH_3).

Allyl O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**23**) *and its deprotected product.* — Compound **22** (220 mg, 120 μmol) was treated as for the preparation of **20**, to give **23** (quantitative); $[\alpha]_D$ +29.6° (*c* 0.4); R_F 0.24 in 7:1 toluene–EtOAc.

Anal. Calc. for $C_{111}H_{118}O_{21}$: C, 74.6; H, 6.7. Found: C, 74.6; H, 6.7.

A mixture of compound **23** (86 mg, 50 μmol) and 10% Pd–C (20 mg) in AcOH (2 mL) was stirred for 30 min at 80° under H_2. The usual work-up, and chromatography on Sephadex G-25 in H_2O, afforded propyl *O*-α-D-glucopyrano-syl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (**24**; 34 mg, quantitative); R_F 0.71 in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (D_2O) 5.422 (d, 2 H, *J* 3.7 Hz, H-1b and H-1d), 4.537 (d, 1 H, *J* 7.9 Hz, H-1c), 4.485 (d, 1 H, *J* 7.9 Hz, H-1a), 3.423 (t, 2 H, *J* 9.5 Hz, H-4a and H-4a), 3.357 (dd, 1 H, *J* 7.9 and 9.5 Hz, H-2c), and 3.297 (dd, 1 H, *J* 7.9 and 9.5 Hz, H-2a); δ_C (D_2O) 103.1, 102.8 (C-1a and C-1c), 100.2 and 99.9 (C-1b and C-1d), 22.9 (CH_2CH_3), and 10.4 (CH_2CH_3).

Deprotection of **25** *to give O-α-D-glucopyranosyl-(1→4)-1,6-anhydro-β-D-glucopyranose (1,6-anhydromaltose)* (**26**). — A solution of compound **25** (60 mg, 70 μmol) in 0.05M NaOMe–MeOH (2 mL) was stirred for 16 h at 20°, and worked up. Chromatography of the crude product on Lobar LiChroprep Si60 (size A) in 6:1 toluene–EtOAc gave the deacetylation product (40 mg, 69%); R_F 0.75 in 3:1 toluene–THF. A mixture of this compound (40 mg) and 10% Pd–C (42 mg) in AcOH

(1.5 mL) was stirred for 30 min at 80° under H_2. Work-up, and chromatography of the product on Sephadex G-25 in H_2O, afforded **26** (quantitative); R_F 0.63 in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (D_2O) 5.482 (s, 1 H, H-1a), 5.144 (d, 1 H, *J* 3.7 Hz, H-1b), 4.780 (d, 1 H, *J* 5.2 Hz, H-5a), and 4.148 (d, 1 H, *J* 7.9 Hz, H-6a); δ_C (D_2O) 102.0 ($^1J_{CH}$ 177 Hz, C-1a), 98.5 ($^1J_{CH}$ 170 Hz, C-1b), 66.0 (C-6a) and 61.4 (C-6b); lit.[18] δ_C (D_2O) 101.7 (C-1a), 98.3 (C-1b), 65.7 (C-6a), and 61.2 (C-6b).

Allyl O-*(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-tetrakis-*[O-*(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)*]-*2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**4**), *and allyl* O-*(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-*D*-glucopyranosyl)-(1→4)-tris-*[O-*(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)*]-*2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**29**). — To a stirred mixture of compound **20** (1.0 g, 560 μmol), $AgOSO_2CF_3$ (400 mg, 1.6 mmol), $SnCl_2$ (270 mg, 1.4 mmol), and powdered molecular sieves 4A (2.5 g) in Et_2O (4 mL) was added dropwise a solution of compound **6** (1.05 g, 1.1 mmol) in Et_2O (10 mL) during 3 h at −5 to 0°. The mixture was stirred for 16 h at 20°, filtered through Celite, and the Celite washed with EtOAc. The filtrate and washings were combined, successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc and then on Lobar LiChroprep Si60 (size C) in 17:1 toluene–EtOAc afforded **4** (650 mg, 43% based on **20**), **29** (330 mg, 22% based on **20**), **25** (230 mg, 25% based on **6**), the glycal **31** (230 mg, 23% based on **6**), and recovered **20** (220 mg, 21%).

Compound **4**: $[\alpha]_D$ +64.7° (*c* 0.3); R_F 0.32 (h.p.t.l.c.) in 9:1 toluene–EtOAc; n.m.r. data: δ_H 1.79 (s, 3 H, Ac); δ_C 134.3 (–*C*H=CH_2), 117.2 (CH=*C*H_2), 102.7 (C-1a), 96.9, 96.6, 96.4, and 96.2 (C-1b, C-1c, C-1d, C-1e, and C-1f in the ratios of 1:1:1:2), 84.7 (C-3a), 82.1 (C-2a), and 20.9 (CO*C*H_3).

Anal. Calc. for $C_{167}H_{176}O_{32}$: C, 74.4; H, 6.6. Found: C, 74.3; H, 6.6.

Compound **29**: $[\alpha]_D$ +57.6° (*c* 0.3); R_F 0.25 (h.p.t.l.c.) in 9:1 toluene–EtOAc; n.m.r. data: δ_C 134.2 (–*C*H=CH_2), 117.2 (–CH=*C*H_2), 102.6 (C-1a), 102.2 (C-1e), 96.9, 96.6, 96.5, 96.2 (C-1b, C-1c, C-1d, C-1f), 84.7 (C-3a, C-3e), and 20.8 (CO*C*H_3).

Anal. Calc. for $C_{167}H_{176}O_{32}$: C, 74.4; H, 6.6. Found: C, 74.6; H, 6.6.

Compound **31**: R_F 0.23 (h.p.t.l.c.) in 9:1 toluene–EtOAc; n.m.r. data: δ_H 6.334 (s, 1 H, H-1a), 5.135 (d, 1 H, *J* 3.7 Hz, H-1b), and 1.829 (s, 3 H, C*H*$_3$CO); δ_C 169.5 (*C*=O), 96.6 (C-1b), and 20.8 (CO*C*H_3).

Allyl O-*(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-tetrakis*[O-*(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)*]-*2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**27**) *and its deprotection product.* — A solution of compound **4** (500 mg, 190 μmol) in 1:1 MeOH–THF (4 mL) containing 0.5M NaOMe (0.1 mL) was stirred for 19 h at 20°. Work-up, and chromatography on Lobar LiChroprep (size B) in 15:1 toluene–EtOAc, afforded **27** (390 mg, 79%); $[\alpha]_D$ +64.7° (*c* 0.3); R_F 0.49 in 8:1 toluene–EtOAc; n.m.r. data: δ_C 134.2 (*C*H=CH_2), 117.1 (CH=*C*H_2), 102.6 (C-1a), 96.8, 96.6, 96.3 (five anomeric carbon atoms in the ratios of 1:1:3), 84.6 (C-3a), 82.0 (C-2a), and 81.4 (C-3b, C-3c, C-3d, C-3e, and C-3f).

Anal. Calc. for $C_{165}H_{173}O_{31}$: C, 74.7; H, 6.6. Found: C, 74.5; H, 6.6.

A mixture of compound **27** (19 mg, 7 μmol) and 10% Pd–C (19 mg) in AcOH (2 mL) was stirred for 1 h at 80° under H_2. Work-up, and purification through use of Sephadex G-25 in H_2O, gave propyl *O*-α-D-glucopyranosyl-(1→4)-tetrakis[α-D-glucopyranosyl-(1→4)]-β-D-glucopyranoside (**28**; 7 mg, 94%); R_F 0.56 in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (D_2O, 20°) 5.417 (d, 5 H, *J* 3.7 Hz, H-1b, H-1c, H-1d, H-1e, and H-1f), 4.487 (d, 1 H, *J* 7.9 Hz, H-1a), 3.428 (t, 1 H, *J* 9.5 Hz, H-4a), 3.298 (dd, 1 H, *J* 7.9 and 9.5 Hz, H-2a), and 0.924 (t, 3 H, *J* 7.3 Hz, CH_2CH_3).

Deprotection of **29**. — Compound **29** (31 mg, 12 μmol) was treated as for **27**, to give the deacetylation product (29 mg, 93%): $[\alpha]_D$ +55.1° (*c* 0.7); R_F 0.60 in 5:1 toluene–EtOAc. A mixture of the deacetylation product (10 mg, 4 μmol) and 10% Pd–C (20 mg) in 1:9 HCO_2H–MeOH (1 mL) was stirred for 1 h at 50°, cooled, and filtered through Celite. Evaporation of the filtrate *in vacuo*, and chromatography of the residue on Sephadex G-25 in H_2O, afforded propyl *O*-α-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-tris[*O*-α-D-glucopyranosyl-(1→4)]-β-D-glucopyranoside (**30**; 3.6 mg, 89% from **29**); R_F 0.59 in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (D_2O) 5.425 (d, 3 H, *J* 3.7 Hz), and 5.409 (d, 1 H, *J* 3.7 Hz, H-1b, H-1c, H-1d, and H-1f), 4.540 (d, 1 H, *J* 7.9 Hz, H-1e), 4.488 (d, 1 H, *J* 7.9 Hz, H-1a), 3.424 (t, 2 H, *J* 9.5 Hz, H-4a, H-4e), 3.358 (t, 1 H, *J* 9.2 Hz, H-2e), 3.298 (t, 1 H, *J* 8.9 Hz, H-2a), and 0.924 (t, 3 H, *J* 7.5 Hz, CH_2CH_3).

O-(4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)*]*-2,3,6-tri-O-benzyl-D-glucopyranose* (**32**) *and its conversion into the glycosyl fluoride.* — A mixture of compound **19** (320 mg, 170 μmol), $PdCl_2$ (40 mg, 230 μmol), and AcONa (40 mg, 500 μmol) in 9:1 AcOH–H_2O (10 mL) was stirred for 1 h at 70°, cooled, and filtered through Celite. The filtrate was evaporated *in vacuo*, and a solution of the residue in EtOAc was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–EtOAc afforded **32** (230 mg, 74%); $[\alpha]_D$ +61.5° (*c* 0.6); R_F 0.39 and 0.53 in 5:1 toluene–EtOAc; n.m.r. data: δ_H 1.79 (s, 3 H, CH_3CO); δ_C 96.8, 96.6, 96.2 (C-1b, C-1c, C-1d), 90.8 (C-1aα), and 20.8 ($COCH_3$).

Anal. Calc. for $C_{110}H_{115}O_{22}$: C, 73.2; H, 6.4. Found: C, 73.5; H, 6.5.

A mixture of compound **32** (230 mg, 130 μmol), $SOCl_2$ (50 μL, 700 μmol), and a trace of DMF in $Cl(CH_2)_2Cl$ (4 mL) was stirred for 16 h at 20°, filtered through SiO_2 gel, and the filtrate evaporated *in vacuo*. To a solution of the residue in CH_3CN (2 mL) was added AgF (40 mg, 320 μmol). The mixture was stirred for 16 h at 20° in the dark, filtered through Celite, the filtrate evaporated, and the residue dissolved in EtOAc. The solution was washed with aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 15:1 toluene–EtOAc afforded *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (**34**; 150 mg, 65%); R_F 0.38 (h.p.t.l.c.) in 9:1

toluene–EtOAc; n.m.r. data: δ_H 5.643 (d, 1 H, *J*3.6 Hz), 5.556 (d, 1 H, *J* 3.6 Hz), 5.472 (d, 1 H, *J* 3.6 Hz) (H-1b, H-1c, and H-1d), 5.363 (dd, 1 H, *J* 6.1 and 54.0 Hz, H-1a), 5.082 (t, 1 H, *J* 10.0 Hz, H-4d), and 1.790 (s, 3 H, CH_3CO); δ_C 169.4 ($COCH_3$), 109.6 ($^1J_{CF}$ 217 Hz, H-1a), 96.8 and 96.4 (C-1b, C-1c, and C-1d, in the ratio of 2:1), 82.9 ($^3J_{CF}$ 9.8 Hz, C-3a), 81.4 (C-3b, C-3c, C-3d), 80.5 ($^2J_{CF}$ 24.4 Hz, C-2a), 79.9 (C-3d), 79.4 (C-4a, C-4b, C-4c), and 20.8 ($COCH_3$); δ_F 134.2 ($^2J_{HF}$ 53.7 and $^3J_{HF}$ 11.0 Hz).

Coupling of **34** *to* **5**. — To a mixture of compound **5** (62 mg, 900 μmol), $AgOSO_2CF_3$ (24 mg, 900 μmol), $SnCl_2$ (17 mg, 900 μmol), and powdered molecular sieves 4A (200 mg) in Et_2O (2.5 mL) was added a solution of compound **34** (111 mg, 62 μmol) in Et_2O (2.5 mL) at 0°. The mixture was stirred for 24 h at 20°, filtered through Celite, and the Celite washed with EtOAc. The filtrate and washings were combined, successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on Lobar LiChroprep Si60 (size A) in 15:1 toluene–EtOAc afforded allyl *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-tetrakis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**4**; 59 mg, 35%), allyl *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-*O*-(2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**35**; 34 mg, 20%), and *O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**36**; 79 mg, 33%).

Compound **4**: R_F 0.40 (h.p.t.l.c.), *compound* **35**: R_F 0.35 (h.p.t.l.c.) in 8:1 toluene–EtOAc.

Compound **36**: R_F 0.18 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.590 (d, 1 H, *J* 3.4 Hz), 5.535 (d, 1 H, *J* 3.4 Hz, H-1c and H-1d), 5.482 (s, 1 H, H-1a), 5.061 (t, 1 H, *J* 9.8 Hz, H-4d), 4.992 (d, 1 H, *J* 3.4 Hz, H-1b), and 1.784 (s, 3 H, CH_3CO).

Allyl O-[*2,3,6-tri*-O-*benzyl-4*-O-*(monochloroacetyl)*-α-D-*glucopyranosyl*]-*(1→4)-tetrakis*[O-*(2,3,6-tri*-O-*benzyl*-α-D-*glucopyranosyl)-(1→4)*]-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**37**). — A mixture of compound **27** (390 mg, 150 μmol) and $(ClCH_2CO)_2O$ (50 mg, 290 μmol) in $Cl(CH_2)_2Cl$ (6 mL) containing pyridine (50 μL, 600 μmol) was stirred for 1.5 h at 20°, and evaporated *in vacuo*. A solution of the residue in EtOAc was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on Lobar LiChroprep (size B) in 10:1 toluene–EtOAc afforded **37** (350 mg, 88%); $[\alpha]_D$ +69.4° (*c* 0.2); R_F 0.52 in 8:1 toluene–EtOAc; n.m.r. data: δ_C 165.7 ($COCH_2Cl$), 134.2 ($CH{=}CH_2$), 117.1 ($CH{=}CH_2$), 102.6 (C-1a), 96.6, 96.4, 96.2 (in the ratios of 1:1:3, C-1b, C-1c, C-1d, C-1e, C-1f), 84.6 (C-3a), 82.0 (C-2a), 81.5 (C-3b, C-3c, C-3d, C-3e), 79.4 (C-3f, C-4a, C-4b, C-4c, C-4d, C-4e), and 40.5 ($COCH_2Cl$).

Anal. Calc. for $C_{167}H_{175}ClO_{32} \cdot C_6H_5CH_3$: C, 74.1; H, 6.5. Found: C, 74.0; H, 6.5.

O-[*2,3,6-Tri*-O-*benzyl-4*-O-*(monochloroacetyl)*-α-D-*glucopyranosyl*]-*(1→4)*-

tetrakis[2,3,6-tri-O-benzyl-α-D-glucopyranosyl-(1→4)]-2,3,6-tri-O-benzyl-D-glucopyranose (**38**). — A mixture of compound **37** (340 mg, 120 μmol), $PdCl_2$ (150 mg, 850 μmol), and NaOAc (150 mg, 1.8 mmol) in 9:1 AcOH–H_2O (10 mL) was sonicated with an ultrasonic cleaner (TOCHO) for 1 h at 20°, and then stirred for 16 h at 20°, filtered through Celite, and the filtrate evaporated *in vacuo*. A solution of the residue in EtOAc was successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 15:1 toluene–EtOAc afforded **38** (200 mg, 60%); $[\alpha]_D$ +93.8° (*c* 0.1); R_F 0.18 and 0.23 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_C 165.8 ($COCH_2Cl$), 96.7 and 96.2 (in the ratio of 2:3, C-1b, C-1c, C-1d, C-1e, and C-1f), 90.7 (C-1aα), and 40.6 ($COCH_2Cl$).

Anal. Calc. for $C_{164}H_{171}ClO_{32}$: C, 73.2; H, 6.4. Found: C, 73.5; H, 6.4.

O-*[2,3,6-Tri-O-benzyl-4-O-(monochloroacetyl)-α-D-glucopyranosyl]-(1→4)-tetrakis[O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-O-benzyl-β-D-glucopyranosyl fluoride* (**39**). — A mixture of compound **38** (177 mg, 70 μmol) and $SOCl_2$ (40 μL, 360 μmol) in $Cl(CH_2)_2Cl$ (2 mL) containing a trace of DMF was stirred for 24 h at 20° and then filtered through SiO_2 gel. The filtrate was evaporated *in vacuo*, to give crude α-chloride; R_F 0.59 (h.p.t.l.c.) in 8:1 toluene–EtOAc. A mixture of the crude chloride and AgF (20 mg, 160 μmol) in CH_3CN (1.5 mL) was stirred for 16 h at 20° in the dark, filtered through Celite, and the Celite washed with EtOAc. The filtrate and washings were combined, successively washed with aq. NaCl and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded **39** (129 mg, 73%); $[\alpha]_D$ +72.5° (*c* 0.1); R_F 0.57 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_C 165.8 ($COCH_2Cl$), 109.2 (d, $^1J_{CF}$ 217 Hz, C-1a), 96.7, 96.5, 96.2 (in the ratios of 2:1:2, C-1b, C-1c, C-1d, C-1e, C-1f), 82.9 (d, $^3J_{CF}$ 9.8 Hz, C-3a), 81.5 (C-3b, C-3c, C-3d, C-3e), 80.6 (d, $^2J_{CF}$ 24.4 Hz, C-2a), and 40.6 ($COCH_2Cl$).

Anal. Calc. for $C_{164}H_{170}ClFO_{31}$: C, 73.2; H, 6.3. Found: C, 73.2; H, 6.4.

O-*(2,3,6-Tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-tetrakis[O-(2,3,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→4)]-2,3,6-tri-O-benzyl-β-D-glucopyranosyl fluoride* (**3**). — A solution of compound **39** (40 mg, 15 μmol) in 1:1 MeOH–THF (dried over activated molecular sieves 4A) containing 0.5M NaOMe–MeOH (4 μL) was stirred for 2 h at 20°, and then evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 20:1 toluene–EtOAc afforded **3** (37 mg, 95%); $[\alpha]_D$ +56.2° (*c* 0.2); R_F 0.37 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.693, 5.653, 5.595, 5.560, 5.475 (5 d, 5 H, *J* 3.6 Hz, H-1b, H-1c, H-1d, H-1e, H-1f), and 5.358 (dd, 1 H, *J* 6.0 and 54.0 Hz, H-1a); δ_C 109.7 (d, $^1J_{CF}$ 217 Hz, C-1a), 96.8, 96.3 (in the ratio of 2:3, C-1b, C-1c, C-1d, C-1e, C-1f), 82.9 (d, $^3J_{CF}$ 9.8 Hz, C-3a), 81.4 (C-3b, C-3c, C-3d, C-3e), and 80.4 (d, $^2J_{CF}$ 24.5 Hz, C-2a).

Anal. Calc. for $C_{162}H_{169}FO_{30}$: C, 74.4; H, 6.4. Found: C, 74.6; H, 6.5.

Cyclization of **3**. — To a stirred mixture of $AgOSO_2CF_3$ (10 mg, 40 μmol), $SnCl_2$ (10 mg, 50 μmol), and powdered molecular sieves 4A (100 mg) in Et_2O (2 mL) was added dropwise a solution of compound **40** (35 mg, 14 μmol) in Et_2O (5

mL) during 20 min at −5 to 0° under Ar. The mixture was stirred for 16 h at 20°, filtered through Celite, and the Celite washed with EtOAc. The filtrate and washings were combined, successively washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 gel in 10:1 toluene–EtOAc afforded octadeca-*O*-benzylcyclomaltohexaose (**2**; 71 mg, 21%); *O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-tetrakis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**41**; 6.7 mg, 20%), and hydrolysis product **40** (5.1 mg, 14%).

Compound **2**: $[\alpha]_D$ +34.7° (*c* 0.2); R_F 0.74 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.163 (d, 1 H, *J* 10.7 Hz, C*H*$_2$Ph), 5.065 (d, 1 H, *J* 3.4 Hz, H-1), 4.852 (d, 1 H, *J* 10.9 Hz, C*H*$_2$Ph), 4.470 (d, 1 H, *J* 12.5 Hz, C*H*$_2$Ph), 4.423 (d, 1 H, *J* 12.7 Hz, C*H*$_2$Ph), 4.377 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.295 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.121 (t, 1 H, *J* 9.8 Hz, H-3), 4.018 (t, 1 H, *J* 9.5 Hz, H-4), 3.980 (dd, 1 H, *J* 2.8 and 10.4 Hz, H-6), 3.881 (bd, 1 H, *J* 9.5 Hz, H-5), 3.461 (d, 1 H, *J* 10.2 Hz, H-6′), and 3.445 (dd, 1 H, *J* 3.4 and 9.8 Hz, H-2); δ_C 98.7 (C-1), 81.1 (C-4), 79.3 (C-3), 79.2 (C-2), 75.7, 73.5, 72.9 (3*C*H$_2$Ph), 71.7 (C-5), and 69.2 (C-6).

Compound **41**: R_F 0.21 (h.p.t.l.c.) in 8:1 toluene–EtOAc; n.m.r. data: δ_H 5.682, 5.620, 5.594, 5.560 (4 d, 4 H, *J* 3.4 Hz, H-1c, H-1d, H-1e, H-1f), 5.478 (s, 1 H, H-1a), and 5.002 (d, 1 H, *J* 3.4 Hz, H-1b).

*Octadeca-*O*-benzylcyclomaltohexaose* (**2**) *by benzylation of the natural material.* — To a suspension of NaH (50%, 0.64 g, 11 mmol) in DMF (2 mL) was added cyclomaltohexaose (500 mg, 510 μmol), and the mixture was stirred for 20 min at 20°. To this mixture was added dropwise $C_6H_5CH_2Br$ (1.32 mL, 11 mmol) at −5°. The mixture was stirred for 1 h at 0°, and then for 2 h at 20°. The usual work-up, and chromatography on SiO_2 gel in 20:1 toluene–EtOAc afforded a quantitative yield of **2**; $[\alpha]_D$ +34.1° (*c* 0.7); n.m.r. data: δ_H 5.162 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 5.065 (d, 1 H, *J* 3.4 Hz, H-1), 4.851 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.470 (d, 1 H, *J* 12.7 Hz, C*H*$_2$Ph), 4.422 (d, 1 H, *J* 12.7 Hz, C*H*$_2$Ph), 4.377 (d, 1 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.294 (d, 1 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.120 (t, 1 H, *J* 9.8 Hz, H-3), 4.018 (t, 1 H, *J* 8.5 Hz, H-4), 3.970 (dd, 1 H, *J* 2.6 and 10.7 Hz, H-6), 3.880 (bd, 1 H, *J* 9.3 Hz, H-5), 3.460 (d, 1 H, *J* 10.4 Hz, H-6′), and 3.445 (dd, 1 H, *J* 3.4 and 9.8 Hz, H-2); δ_C 98.6 (C-1), 81.0 (C-4), 79.3 (C-3), 79.1 (C-2), 75.6, 73.4, 72.8 (3 *C*H$_2$Ph), 71.6 (C-5), and 69.1 (C-6).

Anal. Calc. for $C_{162}H_{168}O_{30}$: C, 75.0; H, 6.5. Found: C, 74.6; H, 6.4.

Cyclomaltohexaose (**1**). — A mixture of compound **2** (148 mg, 58 μmol) and 10% Pd–C (150 mg) in 2:2:1 THF–MeOH–H_2O (30 mL) containing HCO_2H (3 mL) was stirred for 3 h at 50°, filtered through Celite, and the filtrate evaporated *in vacuo*. A suspension of the residue in H_2O (10 mL) was filtered through a 0.5μm filter unit (MILEX-SR) to remove a trace of Pd–C, and the filtrate was evaporated *in vacuo*, to give **1** (quantitative); R_F 0.56 (h.p.t.l.c.) in 2:2:1 BuOH–MeOH–H_2O; n.m.r. data: δ_H (99:1 D_2O–HCO_2H) 4.76 (d, 1 H, *J* 3.1 Hz, H-1); δ_C (99:1 D_2O–HCO_2H) 102.2 (C-1), 82.0 (C-4), 74.1 (C-3), 72.8 (C-2), 72.5 (C-5), and 61.2 (C-6).

N.m.r. data for natural **1**: δ_H (99:1 D_2O–HCO_2H) 4.74 (d, 1 H, *J* 3.1 Hz,

H-1); δ_C (99:1 D_2O–HCO_2H) 102.4 (C-1), 82.1 (C-4), 74.2 (C-3), 72.8 (C-2), 72.6 (C-5), and 61.2 (C-6).

ACKNOWLEDGMENTS

We thank Dr. J. Uzawa and Mrs. T. Chijimatsu for recording and measuring the n.m.r. spectra, and Dr. H. Honma and his staff for the elemental analyses. We also thank A. Takahashi and K. Moriwaki for their technical assistance.

REFERENCES

1 T. OGAWA AND Y. TAKAHASHI, *Carbohydr. Res.*, 138 (1985) c5–c9.
2 D. FRENCH, *Adv. Carbohydr. Chem.*, 12 (1957) 189–210; W. SAENGER, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 344–362.
3 R. BRESLOW, *Science*, 218 (1982) 532–537; I. TABUSHI, *Acc. Chem. Res.*, 15 (1982) 66–72; A. P. CROFT AND R. A. BARTSCH, *Tetrahedron*, 39 (1983) 1417–1474.
4 B. HELFERICH, K. BÄUERLEIN, AND F. WIEGAND, *Ann.*, 447 (1926) 27–37.
5 T. MUKAIYAMA, Y. MURAI, AND S. SHODA, *Chem. Lett.*, (1981) 431–432.
6 D. H. BRAUNS, *J. Am. Chem. Soc.*, 45 (1923) 833–839.
7 B. HELFERICH AND R. GOOTZ, *Ber.*, 62 (1929) 2505–2507.
8 T. MUKAIYAMA, Y. HASHIMOTO, AND S. SHODA, *Chem. Lett.*, (1983) 935–983; Y. ARAKI, K. WATANABE, F.-H. KUAN, K. ITOH, N. KOBAYASHI, AND Y. ISHIDO, *Carbohydr. Res.*, 127 (1984) c5–c9; M. HAYASHI, S. HASHIMOTO, AND R. NOYORI, *Chem. Lett.*, (1984) 1747–1750; W. A. SZAREK, G. GRYNKIEWICZ, B. DOBOSZEWSKI, AND G. W. HAY, *ibid.*, (1984) 1751–1754; K. C. NICOLAOU, R. E. DOLLE, D. P. PAPAHATJIS, AND J. L. RANDALL, *J. Am. Chem. Soc.*, 106 (1984) 4189–4192; W. ROSENBROOK, JR., D. A. RILEY, AND P. A. LARTEY, *Tetrahedron Lett.*, (1985) 3–4; G. H. POSNER AND S. R. HAINES, *ibid.*, (1985) 5–8.
9 T. OGAWA AND M. MATSUI, *Carbohydr. Res.*, 51 (1976) c13–c18.
10 T. OGAWA AND M. MATSUI, *Carbohydr. Res.*, 56 (1977) c1–c6; 62 (1978) c1–c4; *Tetrahedron*, 37 (1981) 2362–2369; A. VEYRIÈRES, *J. Chem. Soc., Perkin Trans. 1*, (1981) 1626–1629.
11 T. OGAWA AND S. NAKABAYASHI, *Carbohydr. Res.*, 93 (1981) c1–c5; T. OGAWA, S. NAKABAYASHI, AND T. KITAJIMA, *ibid.*, 114 (1983) 225–236.
12 M. S. NEWMAN AND P. K. SUJEETH, *J. Org. Chem.*, 43 (1978) 4367–4369; see also ref. 11.
13 K. BOCK AND C. PEDERSEN, *Acta. Chem. Scand., Ser. B*, 29 (1975) 682–686; V. WRAY, *J. Chem. Soc., Perkin Trans. 2*, (1976) 1598–1605.
14 L. D. HALL, J. F. MANVILLE, AND N. S. BHACCA, *Can. J. Chem.*, 47 (1969) 1–17; L. PHILLIPS AND V. WRAY, *J. Chem. Soc. B*, (1971) 1618–1624.
15 A. TAKAOKA, H. IWAKIRI, AND N. ISHIKAWA, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3377–3380.
16 R. R. SCHMIDT AND J. MICHEL, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 731–732; 21 (1982) 77–78.
17 B. ELAMIN, G. M. ANANTHARAMAIAH, G. P. ROYER, AND G. E. MEANS, *J. Org. Chem.*, 44 (1979) 3442–3444; V. S. RAO AND A. S. PERLIN, *Carbohydr. Res.*, 83 (1980) 175–177.
18 P. KARRER AND L. KAMIENSKI, *Helv. Chim. Acta*, 15 (1932) 739–740; M. MORI, M. HAGA, AND S. TEJIMA, *Chem. Pharm. Bull.*, 22 (1974) 1331–1338; H. MATSUDA AND S. TEJIMA, *Yakugaku Zasshi*, 101 (1981) 814–821.