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Note

Improved preparation of hexakis(6-deoxy)cyclomaltohexaose and heptakis(6-deoxy)cyclomaltoheptaose*

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As structurally modified cyclodextrins, per(6-deoxy)cyclomaltooligosaccharides command interest in view of possible changes in solubility and inclusion complex-forming characteristics. Hexakis(6-deoxy)cyclomaltohexaose (**6**) and heptakis(6-deoxy)cyclomaltoheptaose (**13**) were first prepared by Takeo *et al.*[1] from cyclomaltohexaose (alpha-cyclodextrin, **1**) and cyclomaltoheptaose (beta-cyclodextrin, **7**), respectively, by sequential bromination with methanesulfonyl bromide and *N,N*-dimethylformamide, to give the hexakis- and heptakis-(6-bromo-6-deoxy) derivatives **2** and **8**, followed by per-*O*-acetylation (giving **4** and **10**), reductive debromination with sodium borohydride in dimethyl sulfoxide (giving **5** and **12**), and final *O*-deacetylation. Although high yields were reported for each individual step, the degree of bromination was recognized to be slightly less than 100%, as indicated by the microanalytical data for the products and by g.l.c. analysis of methanolyzed **6** and **13**. More-recent approaches to **6** and **13** led[2,3] to their per-*O*-acetyl derivatives **5** and **12** in six steps from **1** and **7**, respectively, with 25 and 28% overall yields. They involved per(6-*O*-*tert*-butyldimethylsilyl)ation, followed by per-*O*-acetylation and desilylation, and subsequent methanesulfonylation, nucleophilic exchange by iodide, and catalytic hydrogenolysis (over Pd–C) at the 6-positions. Several efficient, alternative procedures for the preparation of **6** and **13** have now been developed in our laboratories.

It was found that unprotected cyclodextrins can be directly halogenated in the 6-positions, with high yields, by Vilsmeier-type reagents arising from interaction of bromine or iodine with triphenylphosphine and *N,N*-dimethylformamide, used *in situ*[4]. Thus, direct bromination of **1** at 80° during 15 h gave, in 93% yield, crystalline,

* Dedicated to Professor Serge David on the occasion of his 70th birthday.

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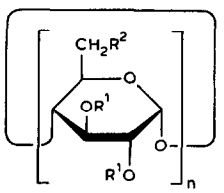

n = 6	n = 7
1 R^1 = H, R^2 = OH	**7** R^1 = H, R^2 = OH
2 R^1 = H, R^2 = Br	**8** R^1 = H, R^2 = Br
3 R^1 = H, R^2 = I	**9** R^1 = H, R^2 = I
4 R^1 = Ac, R^2 = Br	**10** R^1 = Ac, R^2 = Br
5 R^1 = Ac, R^2 = H	**11** R^1 = Ac, R^2 = I
6 R^1 = R^2 = H	**12** R^1 = Ac, R^2 = H
	13 R^1 = R^2 = H
	14 R^1 = H, R^2 = SPh
	15 R^1 = Ac, R^2 = SPh

analytically pure hexakis(6-bromo-6-deoxy)cyclomaltohexaose (**2**). The same procedure applied to **7** gave the heptakis(6-bromo-6-deoxy) analog **8** in the same yield, and the corresponding hexakis- and heptakis-(6-deoxy-6-iodo) derivatives **3** and **9** were obtained in yields of 80 and 89%, respectively, by use of iodine instead of bromine*. The products were characterized by microanalysis, f.a.b. mass spectra (in which they showed the expected molecular-ion peaks), and ^{13}C-n.m.r. spectra in which each displayed only one set of signals for C-1–C-6, as required by the six- and seven-fold symmetries of uniformly hexa- and hepta-substituted alpha- and beta-cyclodextrins.

In attempts to effect reductive debromination in **2** and **8** by means[5] of sodium borohydride in dimethyl sulfoxide, Takeo *et al.*[1] reported to have encountered practical difficulties; therefore, they performed the reductions on the per-*O*-acetylated bromides, which necessitated subsequent deacetylation of the 6-deoxy products. In our hands, the direct reductive dehalogenation of both the bromides **2** and **8**, and the iodides **3** and **9**, by treatment with the aforementioned reductant proceeded very well (24 h at 100°), furnishing the target compounds **6** and **13** in yields of 86–92%.

In an alternative approach, the heptakis(6-deoxy-6-iodo) compound **9** was conventionally acetylated to give the previously described[3,6], crystalline peracetate **11** in 84% yield. This had been converted[3] into **12** by overnight catalytic hydrogenation (83%). We performed its reduction with tributyltin hydride in refluxing toluene, which was complete within 45 min and, after chromatographic purification, afforded similar yields (81–89%) of **12**, suitable for conversion into **13** (see a subsequent paragraph).

A further route to **13** was elaborated by application of a method recently used successfully in monosaccharide chemistry[7], namely, the selective phenylthio substitu-

* The preparation of **3**, **8**, and **9** was reported in ref. 4.

tion of primary hydroxyl groups achievable with diphenyl disulfide in the presence of tributylphosphine and pyridine[8]. Treatment of **7** with this reagent at room temperature for 48 h gave heptakis(6-deoxy-6-*S*-phenyl-6-thio)cyclomaltoheptaose (**14**), isolated in 92% yield as its crystalline per-*O*-acetyl derivative **15**. A sample of **15** was deacetylated (Zemplén) to furnish crystalline **14** for analytical characterization. The ^{13}C-n.m.r. spectra of both **14** and **15** gave no evidence of nonuniformity with respect to substitution; each showed only one set of glucopyranoside and substituent signals, in line with a seven-fold molecular symmetry. Compound **15** was then desulfurized by reduction with Raney nickel. The process was slow (3–4 days at 30 kPa of H_2 pressure, or 8–9 days at ordinary pressure), but it did afford **12** in 88% yield after reacetylation of the crude product (that had suffered some loss of acetyl groups), and chromatographic purification. Compound **12** was thus obtained from **7** in 81% overall yield.

When a solution of **12** in methanol was treated with sodium methoxide for deacetylation, part of produced **13** appeared rapidly as a precipitate, and part of it was obtained after de-ionization by cation exchange and evaporation of the supernatant. Whereas the latter part was analytically pure, the former contained sodium as evidenced by microanalysis and mass spectrometry. (Similar observations were made in the aforementioned deacetylation of **15**.) However, the sodium was readily removed by reprecipitation of the material from dimethyl sulfoxide solution with aqueous hydrochloric acid, or by de-ionization of such a solution, followed by reprecipitation with water.

In summary, cyclomaltohexaose (**1**) and cyclomaltoheptaose (**7**) were converted into the respective per(6-deoxy) derivatives **6** and **13**, with 69–80 and 81–86% yields over two steps involving a Vilsmeier-type bromination or iodination at the 6-positions, followed by reductive dehalogenation with sodium borohydride. Known heptakis(2,3-di-*O*-acetyl-6-deoxy-6-iodo)cyclomaltoheptaose (**11**) and the corresponding, newly prepared 6-deoxy-6-*S*-phenyl-6-thio derivative **15**, both obtainable in high yields from **7**, were converted into **13** by reduction with tributyltin hydride and Raney nickel, respectively, followed by deacetylation.

EXPERIMENTAL

Methods. — For general preparative and instrumental techniques, see previous publications from these laboratories[7,9]. The $[\alpha]_D$ values refer to room temperature.

Hexakis(6-bromo-6-deoxy)cyclomaltohexaose) (**2**). — To a stirred solution of Ph_3P (21 g, 80 mmol; dried *in vacuo*) and Br_2 (4.1 mL, 80 mmol) in dry *N,N*-dimethylformamide (DMF, 80 mL) was added cyclomaltohexaose (**1**; 4.32 g, 4.44 mmol, 26.7 mequivs.; dried to constant weight *in vacuo* at 100° over P_2O_5). The mixture was stirred for 15 h at 80°, concentrated at reduced pressure to half its volume, and its pH was adjusted to 9–10 by the addition of 3M NaOMe in MeOH (30 mL), with external cooling. The solution was then stirred for 30 min at room temperature, in order to decompose the formate esters formed in the reaction, after which it was poured into ice–water (1.5 L). The precipitate was collected by filtration, washed with water (0.5 L), followed by

CH_2Cl_2 (1 L), redissolved in DMF, reprecipitated by addition of MeOH, collected, and washed with MeOH, to give pure **2** (5.60 g, 93.3%), m.p. 222°, $[\alpha]_D$ +124° (*c* 1.5, DMF) {lit.[1] m.p. 195–196°, $[\alpha]_D$ +91° (*c* 1, pyridine)}; ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 102.2 (C-1), 85.1 (C-4), 72.9, 72.0, 71.3 (C-2,3,5), and 34.9 (C-6); f.a.b. m.s. (glycerol–thioglycerol–NaI): *m/z* 1373.1 (100, $[M + Na]^+$), 1351.1 (40, $[M + H]^+$), 1293.2 (90, $[M + Na - HBr]^+$), and 1213.2 (60, $[M + Na - 2\,HBr]^+$) (values are for the strongest peaks in isotope clusters).

Anal. Calc. for $C_{36}H_{54}Br_6O_{24}$ (1350.2): C, 32.02; H, 4.03; Br, 35.51. Found: C, 32.08; H, 4.22; Br, 35.39.

Heptakis(6-bromo-6-deoxy)cyclomaltoheptaose (**8**). — Bromination of cyclomaltoheptaose (**7**; 4.32 g, 3.81 mmol, 26.7 mequivs.; dried *in vacuo* at 100° over P_2O_5), as just described for **1**, gave **8** (5.57 g, 92.8%)[4], m.p. 214° (dec.), $[\alpha]_D$ +78° (*c* 1.8, DMF) {lit.[1] m.p. 205–206° (dec.), $[\alpha]_D$ +98° (*c* 1, pyridine)}; ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 102.3 (C-1), 84.8 (C-4), 72.4, 72.2, 71.2 (C-2,3,5), and 33.5 (C-6); f.a.b. m.s. (glycerol–thioglycerol–NaI): *m/z* 1598.7, 1596.7 (87, 100, most abundant peaks of isotope cluster, $[M + Na]^+$), 1518.8, 1516.8 (59, 58, $[M + Na - HBr]^+$, 1438.9, and 1436.9 (37, 33, $[M + Na - 2\,HBr]^+$).

Anal. Calc. for $C_{42}H_{63}Br_7O_{28}$ (1575.3): C, 32.02; H, 4.03; Br, 35.51. Found: C, 32.03; H, 3.93; Br, 35.71.

Hexakis(6-deoxy-6-iodo)cyclomaltohexaose (**3**). — Compound **3** was prepared[4] from **1** (4.32 g), as subsequently detailed for **9**, the procedure being analogous to that for the preparation of **2**. The yield of **3** was 5.80 g (80%), m.p. 227° (dec.), $[\alpha]_D$ +95° (*c* 1.3, DMF); ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 101.8 (C-1), 86.3 (C-4), 72.3 (C-5), 71.8 (C-3), 70.8 (C-2), and 9.3 (C-6); f.a.b. m.s. [1:4 dithioerythritol–dithiothreitol, plus KI): *m/z* 1671.5 (90, $[M + K]^+$), 1633.6 (24, $[M + H]^+$, 1545.6 (100, $[M + K + H - I]^+$), 1418.7 (95, $[M + K + 2\,H - 2\,I]^+$, and 1292.8 (76, $[M + K + 3\,H - 3\,I]^+$).

Anal. Calc. for $C_{36}H_{54}I_6O_{24}$ (1632.2): C, 26.49; H, 3.33; I, 46.65. Found: C, 26.31; H, 3.45; I, 45.83.

Heptakis(6-deoxy-6-iodo)cyclomaltoheptaose (**9**). — To a stirred solution of desiccator-dried Ph_3P (21 g) in dry *N,N*-dimethylformamide (80 mL) was added I_2 (20.5 g) in small portions, followed after 30 min by **7** (4.32 g, dried *in vacuo* at 100° over P_2O_5). The mixture was stirred for 18 h at 80° under exclusion of atmospheric moisture, and then concentrated at reduced pressure to half its volume, cooled to 5°, made alkaline with 3M NaOMe in MeOH to pH 9–10, and kept at room temperature for 30 min for formate ester solvolysis. The solution was then poured into vigorously stirred ice–water (1.5 L), and the beige-colored precipitate was collected by filtration, if necessary after adding a liberal quantity of NaH_2PO_3 to partially coagulate the fine suspension. The product was washed well with water, dried in the air, and suspended in CH_2Cl_2 (or $CHCl_3$, 1 L). After thorough agitation of the suspension, the undissolved material (**9**) was filtered off, washed several times with CH_2Cl_2, dissolved in DMF (100 mL), and reprecipitated by pouring the solution into stirred ice–water. The dried product was freed from some remnant, discoloring impurity by trituration with a small amount of MeOH, to give colorless **9** (6.49 g, 89.5%), m.p. 224–224.5° (dec.), $[\alpha]_D$ +73° (*c* 1,

pyridine) and +79.5° (*c* 1, DMF) {a different sample showed[4] m.p. 235° (dec.), $[\alpha]_D$ +66° (*c* 1.15, DMF)}; ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 102.5 (C-1), 86.3 (C-4), 72.5, 72.3, 71.4 (C-2,3,5), and 9.8 (C-6); f.a.b. m.s. (glycerol–thioglycerol–NaI): *m/z* 1926.7 (100, $[M + Na]^+$), 1904.7 (21, $[M + H]^+$), and 1800.9 (71, $[M + H + Na - I]^+$).

Anal. Calc. for $C_{42}H_{63}I_7O_{28}$ (1904.3): C, 26.49; H, 3.33; I, 46.65. Found: C, 26.68; H, 3.48; I, 46.55.

Heptakis(2,3-di-O-acetyl-6-deoxy-6-iodo)cyclomaltoheptaose (**11**). — A solution of **9** (2.0 g) in Ac_2O (15 mL) and pyridine (10 mL) containing a catalytic amount of 4-dimethylaminopyridine was kept for 48 h at room temperature. The mixture was processed by addition of MeOH (30 mL), and coevaporation of the solvent with additional MeOH and several portions of toluene. The crude product was purified by passage through a column of SiO_2, with 1:1 EtOAc–hexane as the eluent, to give **11** (2.2 g, 84%) that crystallized on trituration with ether, m.p. 176–178° (dec.), raised to 180° (dec.) by recrystallization from Me_2CO–EtOH, $[\alpha]_D$ +82.5° (*c* 1, $CHCl_3$) {lit.[6] m.p. 172–177°, $[\alpha]_D$ +84° ± 2° (MeOH); lit.[3] amorphous, $[\alpha]_D$ +78° ($CHCl_3$)}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.31 (dd, $J_{3,4}$ 8.3, $J_{2,3}$ 9.9 Hz, H-3), 5.17 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.80 (dd, *J* 3.8, 9.9 Hz, H-2), 3.8–3.5 (complex m, 4 H, H-4,5,6a,6b), 2.06 and 2.03 (2 s, 3 H each, 2 OAc); ^{13}C-n.m.r. (50 MHz, $CDCl_3$): δ 170.7, 169.5 (2 CO), 96.4 (C-1), 80.4 (C-4), 70.3, 70.1, 69.9 (C-2,3,5), 20.5 (2 CO*C*H$_3$), and 7.7 (C-6); these values are in fair agreement with the reported[3] 90-MHz ^{1}H-n.m.r. and 22.6-MHz ^{13}C-n.m.r. data.

Anal. Calc. for $C_{70}H_{91}I_7O_{42}$ (2493.4): C, 33.72; H, 3.68; I, 35.65. Found: C, 33.87; H, 3.87; I, 35.49.

Heptakis(6-deoxy-6-S-phenyl-6-thio)cyclomaltoheptaose (**14**) *and heptakis-(2,3-di-O-acetyl-6-deoxy-6-S-phenyl-6-thio)cyclomaltoheptaose* (**15**). — A mixture of **7** (dried at 100° over P_2O_5), diphenyl disulfide (16.2 g), and Bu_3P (19 mL) in dry pyridine (60 mL) was stirred for 48 h at room temperature, after which Ac_2O (35 mL) and a catalytic amount of 4-dimethylaminopyridine were added. After a further 6 h, the mixture was diluted with $CHCl_3$ (100 mL), extracted with 5% HCl (3 × 100 mL), aq. $NaHCO_3$ (3 × 100 mL), and water (100 mL), then dried (Na_2SO_4), and evaporated. The syrupy residue was introduced dropwise by pipet into stirred ether (400 mL), whereby it solidified. The solid **15** was collected, washed with ether, and dried *in vacuo*; yield, 7.8 g (92.5%). It showed R_F 0.6 (t.l.c., EtOAc), and although a trace of slower-moving impurity was present (not observable in the ^{1}H-n.m.r. spectrum), it was sufficiently pure for further use. An analytical sample was purified by chromatography (SiO_2 column, 3:1 EtOAc–hexane) and crystallized from EtOH or ether, m.p. 123–125°, $[\alpha]_D$ +147° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.3–7.05 (m, 5 H, Ph), 5.30 (dd, $J_{3,4}$ 8.0, $J_{2,3}$ 9.6 Hz, H-3), 5.05 (d, $J_{1,2}$ 3.9 Hz, H-1), 4.78 (dd, *J* 3.9, 9.6 Hz, H-2), 4.15 (m, H-5), 3.80 (~ t, $J_{3,4}$ 8.6, $J_{4,5}$ 9.2 Hz, H-4), 3.31 (AB-m, 2 H, H-6a,6b), 2.05 and 2.03 (2 s, 3 H each, 2 OAc); ^{13}C-n.m.r. (75.4 MHz, $CDCl_3$): δ 170.6, 169.4 (2 CO), 155.1, 129.6, 129.1, 126.4 (Ph), 96.9 (C-1), 78.9 (C-4), 70.9, 70.8, 70.3 (C-2,3,5), 36.2 (C-6), 20.84 and 20.80 (2 CO*C*H$_3$).

Anal. Calc. for $C_{112}H_{126}O_{42}S_7$ (2368.6): C, 56.79; H, 5.36; S, 9.47. Found: C, 56.50; H, 5.47; S, 9.32.

A solution of **15** (0.50 g) in MeOH (15 mL) and $CHCl_3$ (5 mL) was made alkaline

to pH 8–9 (moist indicator paper) with NaOMe solution. A white precipitate of **14** appeared within minutes. Isolated after 30 min by filtration and washing with MeOH, the air-dried product (0.36 g) decomposed >230° and had $[\alpha]_D$ + 162° (*c* 1.6, pyridine). Although its n.m.r. spectra conformed to structure **14**, the microanalytical data suggested the presence of 1 equiv. of Na (presumably as Na_2CO_3) per molecule. Sodium-free **14** was obtained by dissolving the product in a minimum amount of Me_2SO and reprecipitating it with a large volume of 1M HCl, or alternatively by evaporating the alkaline reaction mixture to dryness, de-ionizing the residue dissolved in 1:1 Me_2SO–H_2O (20 mL) with Amberlite IR-120 (H^+) cation-exchange resin, and precipitating **14** with H_2O (250 mL); yield, 0.35 g (93%), m.p. 253–255° (dec.), $[\alpha]_D$ + 164° (*c* 1.5, pyridine); ^{1}H-n.m.r. (300 MHz, Me_2SO-d_6): δ 7.3–7.0 (m, 5 H, Ph), 4.95 (d, $J_{1,2}$ 2.8 Hz, H-1), 3.87 (t), 3.63 (t), and 3.4 (complex m) for the remaining protons; ^{13}C-n.m.r. (75.4 MHz, Me_2SO-d_6): δ 136.6, 128.5, 128.1, 125.3 (Ph), 101.9 (C-1), 84.6 (C-4), 72.5, 72.1, 70.0 (C-2,3,5), and 34.8 (C-6).

Anal. Calc. for $C_{84}H_{98}O_{28}S_7$ (1780.0): C, 56.68; H, 5.55; S, 12.61. Found: C, 56.51; H, 5.81; S, 12.44.

Hexakis(6-deoxy)cyclomaltohexaose (**6**). — Sodium borohydride (1.0 g, 26 mmol) was added portionwise to a solution of **2** (4.5 g, 3.33 mmol, 20 mequivs.) in Me_2SO (200 mL) at 100°, and the mixture was stirred for 24 h. After being cooled to 0°, it was diluted with MeOH (2 x 50 mL), and the solvents were evaporated under reduced pressure. The solid residue was dissolved in H_2O (100 mL), and 2% aq. AcOH was carefully added to obtain pH 7 of the solution, which was then demineralized by ultrafiltration against H_2O for 48 h using an Amicon 3200 device fitted with an Amicon Diaflo YC05 membrane, and freeze-dried to give **6** (2.50 g, 86%), m.p. 245°, $[\alpha]_D$ + 107° (*c* 1.1, pyridine) {lit.[1] $[\alpha]_D$ + 103° (pyridine)}; ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 102.1 (C-1), 88.8 (C-4), 73.3 (C-3), 72.4 (C-2), 66.8 (C-5), and 17.9 (C-6); f.a.b. m.s. (thioglycerol–NaI): *m/z* 899.7 (100, $[M + Na]^+$).

Anal. Calc. for $C_{36}H_{60}O_{24}\cdot 6H_2O$ (984.9): C, 43.90; H, 7.37. Found: C, 43.76; H, 7.47.

Dehalogenation of **3** by the same procedure gave **6** in similar yield.

Heptakis(6-deoxy)cyclomaltoheptaose (**13**). — (*a*) *From* **8** *or* **9**. The bromo compound **8** (4.5 g, 2.85 mmol, 20 mequivs.) was treated with $NaBH_4$, as described for **2**, to give **13** (2.70 g, 92.5%), m.p. 269.5–271° (dec.), $[\alpha]_D$ + 112° (*c* 0.9, pyridine) {lit.[1] $[\alpha]_D$ + 112° (pyridine)}; ^{13}C-n.m.r. (50 MHz, Me_2SO-d_6): δ 102.3 (C-1), 88.1 (C-4), 73.2 (C-3), 72.6 (C-2), 66.7 (C-5), and 17.4 (C-6); f.a.b. m.s. (thioglycerol–NaI): *m/z* 1045.3 (42, $[M + Na]^+$).

Dehalogenation of **9** by the same procedure gave **13** in similar yield.

(*b*) *From* **12**. A solution of **12** (4.80 g) in dry MeOH (300 mL) was made alkaline to pH 8–9 (indicator paper) with NaOMe solution. The white precipitate, isolated after 15 min, was washed with MeOH, and dried (1.61 g); it contained 1.5% of Na (determined as Na_2SO_4 ash in microanalysis); $[\alpha]_D$ + 110° (*c* 1, pyridine); f.a.b. m.s. (glycerol, without addition of Na^+): *m/z* 1045 (49, $[M + Na]^+$), 1046 (21, $[M + Na]^+$, isotope peak), 1023 (3, $[M + H]^+$), and 1024 (1.6, $[M + H]^+$, isotope peak); the ^{13}C-n.m.r. data were identical with those given in section (*a*).

The methanolic mother liquor was de-ionized with Amberlite IR-120 (H^+) cation-exchange resin, and evaporated to give sodium-free **13** (1.07 g), m.p. 270° (dec.), $[\alpha]_D$ +116° (*c* 1, pyridine), also obtained by precipitation of the Na-containing product from a concentrated solution in Me_2SO with aq. M HCl; ^{1}H-n.m.r. (300 MHz, Me_2SO-d_6): δ 5.7 (br, 2 OH), 4.80 (d, $J_{1,2}$ 3.5 Hz, H-1), 3.71 (dq, $J_{4,5}$ 9.4, $J_{5,Me}$ 6.2 Hz, H-5), 3.55 (t, $J_{2,3} + J_{3,4}$ 18.3 Hz, H-3), 3.22 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 2.99 (t, $J_{3,4} + J_{4,5}$ 18.3 Hz, H-4), and 1.18 (d, 3 H, *J* 6.2 Hz, CH_3); f.a.b. m.s. (glycerol): *m/z* 1023 (5, $[M + H]^+$), 585 (10, $[M + H - 3\,C_6H_{10}O_4]^+$), 439 (40, $[M + H - 4\,C_6H_{10}O_4]^+$), 295 (51, $[M + H - 5\,C_6H_{10}O_4]^+$) and 147 (70, $[M^+ + H - 6\,C_6H_{10}O_4]^+$); each peak was accompanied by an isotope peak at *m/z* + 1, with a relative intensity close to that calculated.

Anal. Calc. for $C_{42}H_{70}O_{28}$ (1022.98): C, 49.31; H, 6.90. Found: C, 49.20; H, 6.82.

Heptakis(2,3-di-O-acetyl-6-deoxy)cyclomaltoheptaose (**12**). — (*a*) *From* **11**. A solution of **11** (2.29 g), Bu_3SnH (6 mL), and a catalytic amount of 2,2′-azobis(2-methylpropionitrile) in toluene (100 mL) was boiled under reflux for 45 min in an N_2 atmosphere. The solvent was evaporated, and the residue, dissolved in CH_2Cl_2 (100 mL), was washed with H_2O (2 x 60 mL). The dried (Na_2SO_4) organic phase was concentrated and the product purified by column chromatography on SiO_2 with ether (200 mL), followed by 3:1 EtOAc–hexane as eluents, to give **12** (1.20 g, 81%), m.p. 168–170° (2-propanol). An experiment performed on a 120-mg scale gave an 89% yield. The ^{1}H- and ^{13}C-n.m.r. spectra were identical with those recorded in (*b*).

(*b*) *From* **15**. A solution of **15** (8.0 g) in oxolane (200 mL) and freshly prepared Raney nickel W-4 (~ 40 g, administered as a slurry in EtOH) was shaken for several days under H_2, with fresh portions of Ni being added daily. Progress of the reaction was monitored by t.l.c. (EtOAc), which indicated the transformation of **15** (R_F 0.5, u.v.-active) into **12** (R_F 0.4, u.v.-inactive). The reaction normally required 8–9 days at ordinary pressure, or 3–4 days at 25–30 kPa. The mixture was filtered, the filter residue washed well with oxolane, and the filtrate evaporated to dryness. The crude product was treated overnight at room temperature with Ac_2O (15 mL), dry pyridine (8 mL), and a catalytic amount of 4-dimethylaminopyridine. Conventional processing involving distribution of the mixture between H_2O and $CHCl_3$ gave **12** that was purified by chromatography (SiO_2, 4:1 EtOAc–hexane) to give pure **12** (4.80 g, 88%), m.p. 169–170° (2-propanol), $[\alpha]_D$ +109° (*c* 1, $CHCl_3$) {lit.[3] m.p. 162–165°, $[\alpha]_D$ +111° ($CHCl_3$)}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.25 (dd, $J_{3,4}$ 8.4, $J_{2,3}$ 9.7 Hz, H-3), 4.96 (d, $J_{1,2}$ 3.9 Hz, H-1), 4.74 (dd, $J_{1,2}$ 3.9, $J_{2,3}$ 9.9 Hz, H-2), 4.04 (m, H-5), 3.31 (~ t, $J_{3,4} \approx 8.4$, $J_{4,5} \approx 9.3$ Hz, H-4), 2.04, 2.01 (2 s, 3 H each, 2 OAc), and 1.35 (d, 3 H, *J* 6.2 Hz, CH_3); ^{13}C-n.m.r. (75.4 MHz, $CDCl_3$): δ 170.7, 169.3 (2 CO), 96.4 (C-1), 82.4 (C-4), 71.01, 70.97 (C-2,3), 67.0 (C-5), 20.7 (2 $COCH_3$), and 17.8 (C-6), in excellent agreement with reported[3] 22.6-MHz n.m.r. data.

Anal. Calc. for $C_{70}H_{98}O_{42}$ (1611.5): C, 52.17; H, 6.13. Found: C, 51.75; H, 6.18.

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