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BRANCHED THIOCYCLOMALTO-OLIGOSACCHARIDES: SYNTHESIS AND PROPERTIES OF 6-*S*-α- AND 6-*S*-β-D-GLUCOPYRANOSYL-6-THIOCYCLOMALTOHEPTAOSE*†‡

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ABSTRACT

6-*S*-α- (**2**) and 6-*S*-β-D-glucopyranosyl-6-thiocyclomaltoheptaose (**3**) have been prepared by treatment of 6-*O*-*p*-tolylsulphonylcyclomaltoheptaose (**1**) with the sodium salts of 1-thio-α- and -β-D-glucopyranose, respectively, in 1,3-dimethyl-2-oxohexahydropyrimidine. Compounds **2** and **3**, which were characterised by f.a.b.-m.s. and ^{1}H- and ^{13}C-n.m.r. spectroscopy, are more soluble in water than cyclomaltoheptaose, and enhance the solubility of hydrophobic compounds by inclusion.

INTRODUCTION

Branched cyclomalto-oligosaccharides (cyclodextrins, CDs) bear one or more α-D-glucopyranosyl, α-maltosyl, and sometimes higher maltosyl oligomers as side chains at positions 6. These compounds have attracted much interest in connection with their enhanced solubility in water, their ability to increase the solubility of included hydrophobic compounds in hydroxylic solvents[3–6], and their increased stability towards alpha-amylase[3,4], as compared with the parent cyclomalto-oligosaccharides. There is some evidence that the side chain can be involved in host–guest interactions[7].

Branched CDs have been produced by the action of cyclomaltodextrin glucanotransferase on starch or amylopectin[3,8,9] or by transfer of maltose or maltotriose to CDs catalysed by pullulanase[10] or a bacterial isoamylase[11], and these methods have been described in patents[12]. Glucosyl fluoride has been proposed as

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†Stereoselective Thioglycoside Synthesis, Part X. For Part IX, see ref. 1.
‡For a preliminary report, see ref. 2.

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glycosyl donor in an effort to improve the yields and specificity of the latter enzymic synthesis[13,14]. Although improved procedures have been reported[11,15], the isolation and purification of these glycosylated CDs remain tedious[9,16].

Chemical syntheses have been proposed in order to overcome these problems. Partially protected CDs and appropriately activated glycoses have been used to prepare 6-*O*-α-D-glucopyranosyl-cyclomaltohexaose[17] and -cyclomaltoheptaose[18] by multi-step processes.

Thio sugars have been used to prepare analogues of oligosaccharide substrates for glycosidases, using the concept of nucleophilic enhancement of thiolate in polar aprotic solvents[19]. We now report the application of this approach in the synthesis of 6-*S*-α- (**2**) and 6-*S*-β-D-glucopyranosyl-6-thiocyclomaltoheptaose (**3**).

RESULTS AND DISCUSSION

Thioglycosides can be synthesised by reaction of non-anomeric thiolates with glycosyl halides or by nucleophilic displacement reactions of, for example, sulphonates[20] with glycose 1-thiolate in hexamethylphosphoric triamide.

6-*O*-*p*-Tolylsulphonylcyclomaltoheptaose (**1**), readily prepared from cyclomaltoheptaose[21–23], was treated with 2 mol of the sodium salt of either 1-thio-α-D-glucopyranose[20] or 1-thio-β-D-glucopyranose[24] at 70° in 1,3-dimethyl-2-oxohexahydropyrimidine[25] (less toxic than hexamethylphosphoric triamide). After 3–5 h, t.l.c. revealed the complete disappearance of **1** and each crude product contained a main component together with three unidentified faster-moving impurities. The main component of each crude product was isolated by chromatography in yields of 66% (**2**) and 60% (**3**).

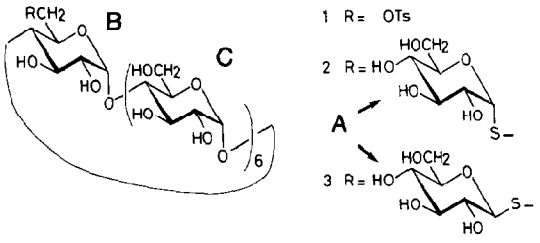
Positive ion f.a.b.-m.s. of **2** and **3** gave prominent signals at *m/z* 1313 for $[M + H]^+$, which were shifted to *m/z* 1335 upon addition of sodium iodide to the

TABLE I

^{13}C-N.M.R. DATA[a,b] (δ) FOR COMPOUNDS **2** AND **3**, AND FOR 6-*O*-α-D-GLUCOPYRANOSYLCYCLOMALTOHEPTAOSE[18] (IN PARENTHESES)

Compound	*Structural unit*[c]	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
2	A	85.9 (99.6)	71.3 (71.3)	73.7	69.8 (70.2)	72.5 (72.0)	60.6 (61.2)
	B	102	72.2	73.2	84.2	70.7	31 (67.6)
	C	102 (102.3)	72.2 (72.6)	73.2	81.4	71.9 (72.4)	60.5 (60.8)
3	A	87.1	72.1	79.8	69.7	77.4	61.2
	B	102	72.1	73	84.9	71.9	32.8
	C	102	72.1	73	81.2	71.9	60.4

[a]In D_2O (external CD_3OD). [b]These data correct tentative assignments made in a preliminary communication[2]. [c]See formulae.



Scheme 1. A, B, and C refer to the ^{13}C-n.m.r. assignments in Table I.

1-thioglycerol matrix. Weak ions at *m/z* 1173 and 1140, corresponding to loss of hexosyl and thiohexosyl fragments, respectively, were also observed under the latter conditions.

The ^{13}C-n.m.r. spectra of **2** and **3** contained intense signals at ~102, 81.3, 73.1, 72.2, 71.9, and 60.5 p.p.m. assigned (Table I) to C-1/6 of the unsubstituted 4-linked α-D-glucopyranosyl residues by reference to literature data[9,11,26–28]. The C-1 signal for the 1-thioglucosyl substituent (A in **2** and **3**), which was expected to be shielded by the sulphur atom, was found at 85.9 p.p.m. for the α anomer **2** and at 87.1 p.p.m. for the β anomer. These assignments were confirmed by a 2D heteronuclear correlation shown in Fig. 1 for **2**, where the resonance for C-1 is correlated with a doublet ($J_{1,2}$ 5.4 Hz) for H-1 indicating residue A to be α. The corresponding doublet ($J_{1,2}$ 10.2 Hz) for **3** was found at 4.6 p.p.m., indicating residue A to be β. The strong shielding effect of the sulphur atom allowed unambiguous assignment of the CH_2S carbon of ring B at 31 and 32.8 p.p.m., respectively, in **2** and **3** (*cf.* 67.6 p.p.m. for the corresponding C-6 in 6-*O*-α-D-glucopyranosylcyclomaltoheptaose[18]). A long-range effect of the sulphur atom was seen in the chemical shifts of the resonances for C-3 and C-5 in ring A of **2** at 73.7 and 72.5 p.p.m., respectively. The corresponding signals were at 79.8 and 77.4 p.p.m. for **3**, reflecting the 1,3-*syn*-diaxial deshielding[27]. The C-4 signal in residue B for **2** and **3** was assigned by considering the probable difference in molecular motion between the 4-linked α-D-glucopyranosyl rings of the toroidal structure (B and C), and the more mobile 1-thioglucosyl branch (A). Application of an inversion recovery pulse sequence [180°–τ–90°–acquisition] with a τ value of 0.1099 s to **2** led to a ^{13}C-n.m.r. spectrum where signals at 85.9, 73.7, 72.5, 71.3, and 69.8 (Table I) could no longer be seen. Consequently, these signals were assigned to C-1/5 of residue A. A further correlation with data in Fig. 1 led to the assignment of the signal at 84.2 p.p.m. for **2** and that at 84.9 p.p.m. for **3** to C-4 of residue B.

The enhancement of the solubilities and solubilisation abilities of cyclomaltoheptaoses by branching has been demonstrated[5–7]. Although the solubility in water of **2** (430 mg/mL at 25°) was less than that[5] (970 mg/mL) for 6-*O*-α-D-glucopyranosylcyclomaltoheptaose, probably because of the smaller tendency of sulphur to act as a hydrogen bond acceptor, it is much greater than that of cyclomaltoheptaose[5] (19 mg/mL). Increased solubility has been reported on 6-substitution of

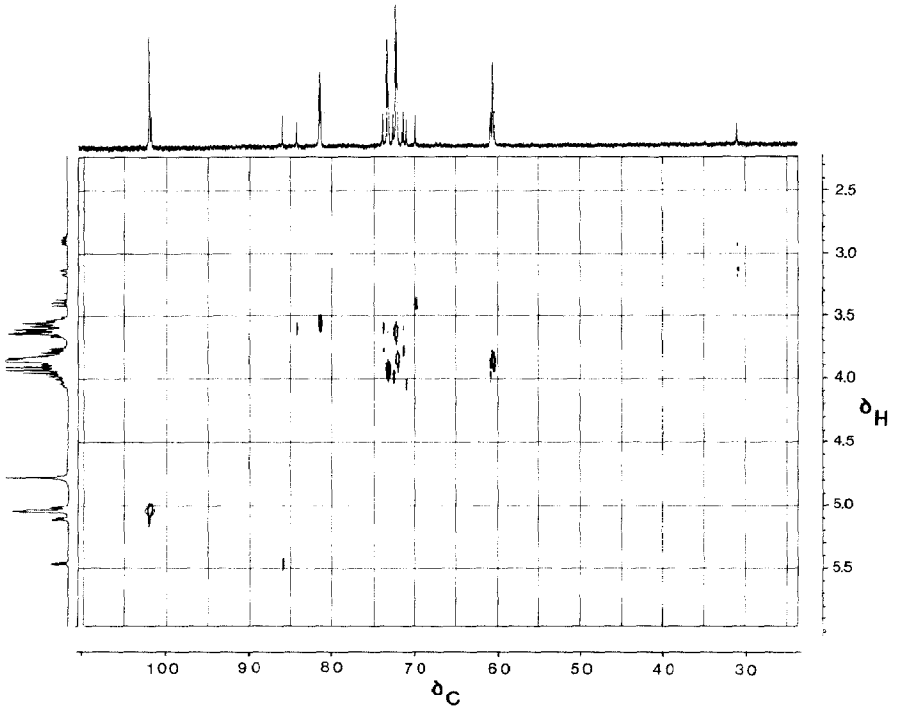


Fig. 1. 2D C–H Correlation contour plot for 6-*S*-α-D-glucopyranosyl-6-thiocyclomaltoheptaose (**2**) (100.616 MHz for ^{13}C; 400 MHz for ^{1}H, in D_2O).

cyclomalto-oligosaccharides by glycosyl[3–6] and hydroxyalkyl[29] residues. Interestingly, **3** is much less soluble in water (30 mg/mL at 25°) than **2**, and therefore the stereochemistry of the side chain in branched cyclomalto-oligosaccharides is important for solubility enhancement.

TABLE II

APPARENT STABILITY CONSTANTS (K, M^{-1}) OF COMPLEXES OF CYCLOMALTOHEPTAOSE, **2**, AND **3**; AND SOLUBILITY ENHANCEMENTS (C/C_o)[a] OF GUEST MOLECULES, IN WATER AT 25°

Host	*Guest*					
	2-Naphthol		*Hydrocortisone*		*Tolnaftate*[b]	
	K	C/C_o	K	C/C_o	K	C/C_o
Cyclomaltoheptaose	30	1.1	3720	4.6	1330	7.3
2	44	1.2	1660	3.9	34320	74.3
3	44	1.2	2790	4.4	17320	52.6

[a] C, water solubility of guest; C_o, solubility in a 5×10^{-3} M solution of the host. [b] *O*-2-Naphthyl methyl(3-methylphenyl)carbamothioate.

The apparent stability constants and solubility enhancements for some typical included molecules are shown in Table II. When 2-naphthol or hydrocortisone is the included molecule, similar stability constants are obtained with cyclomaltoheptaose, **2**, and **3**, in agreement with the general observation[5] that, for a given guest molecule, stability constants of branched and unbranched cyclomalto-oligosaccharides do not vary greatly. The concentrations chosen were below the precipitation points for the cyclomaltoheptaose complexes, and therefore the solubility enhancements parallel the stability constants. Tolnaftate shows exceptionally high stability constants and solubility enhancements with **2** and **3**, an effect which has also been observed with 2,6-di-*O*-methylcyclomaltoheptaose[30]. The new thiocyclomaltoheptaose derivatives **2** and **3**, particularly the very soluble α-anomer **2**, may have the same potential for use in the complexation of drugs and other substrates as previously reported for cyclomalto-oligosaccharides.

The synthesis strategy used in this work allows simple regio- and stereospecific glycosylation of cyclomalto-oligosaccharides and should be applicable to the preparation of other glycosylated and oligoglycosylated cyclic oligosaccharides. Work along these lines is in progress.

EXPERIMENTAL

Materials. — Cyclomaltoheptaose (>98%) was a commercial product and was freeze-dried at −40°/4 Pa for 20 h.

General methods. — Solutions were concentrated with a Büchi rotary evaporator at ≯45° except where stated otherwise. Melting points were determined in capillary tubes with a Büchi 535 apparatus and are corrected. Optical rotations were measured with a Jobin–Yvon (Paris) Digital Micropolarimeter. H.p.l.c. was carried out with a PREP LC/500 chromatograph (Waters Associates), equipped with a refractometric detector and a Prep Pak 500/C_{18}-bonded silica column, by elution with methanol–water (9:91) at 1.52 × 10^3 kPa and 100 mL/min. The retention parameter is expressed as the capacity factor k' where $k' = (t_R - t_o)/t_o$.

^{1}H-N.m.r. (400 MHz) and ^{13}C-n.m.r. spectra (100.616 MHz) were recorded with a Bruker AM 400 instrument for solutions in D_2O [external Me_4Si for ^{1}H, internal CD_3OD (49.0 p.p.m.) for ^{13}C, except where stated otherwise]. The ^{1}H signals were assigned using 2D C–H heteronuclear correlation, and the COSY technique with three-step relayed coherence transfer obtained by using the pulse sequence: RD–90°–D_ϕ–90°–D_2–180°–D_2–90°–D_3–180°–D_3–90°–FID. The delay times D_2 and D_3 were set to 35 ms; 128 experiments of 128 transients were accumulated for each value of D_ϕ with a relaxation delay of 0.3 s and a size of 2k. The initial data matrix of 2k × 128 was apodised with a sine-bell function and zero-filled for a final matrix size of 2k × 1k (spectral value of 2000 Hz). The 2D C–H heteronuclear correlation was recorded by using the Bruker programme XHCORR, with ^{1}H decoupling. The delay times D_3 and D_4 were set to 3.3 and 2 ms. The relaxation time D_1 was set to 2.5 s; 128 experiments of 400 transients with

a size of 2k were accumulated. Spectral values were 8771 Hz for the ^{13}C domain and 1271 Hz for the ^{1}H domain. The final data matrix was zero-filled at 2k × 1k and apodised with a sine-bell function in f_1 and a square function in f_2. For the assignment of carbon signals, DEPT and inversion recovery T_1 techniques, using the sequence $[\pi°-\tau-\pi/2-T]$ where $\tau = 0.1099$ s, were used.

Positive ion f.a.b-mass spectra were recorded (Xe, thioglycerol matrix, accelerating potential 7–8 keV) with an AEI-Kratos MS-50 mass spectrometer, fitted with a f.a.b. 11NV Ion Tech atom-gun and a Mat SS-200 Finnigan (DEC-PDP 11-34) computer. Solutions of the samples in *N,N*-dimethylformamide were added to the matrix.

Microanalyses were obtained from the Service Central de Microanalyse du C.N.R.S. (Lyon) from samples that had been freeze-dried, then dried at 110°/1.33 Pa. Apparent stability constants were measured by the method of Higuchi and Connors[5,31].

6-O-p-*Tolylsulphonylcyclomaltoheptaose* (**1**). — A solution of *p*-toluenesulphonyl chloride (3.15 g, 17 mmol) in dry pyridine (50 mL) was added at 0° to a solution of cyclomaltoheptaose (23 g, 20 mmol) in dry pyridine (300 mL). After stirring for 2 h at 0°, then 20 h at room temperature, the solvent was evaporated *in vacuo* at 40°. The residue was stirred with ether (300 mL) for 15 h at room temperature, and the solid (25 g) was collected and crystallised from water to give **1** (6.6 g, 26% after 3 recrystallisations), m.p. 160–162° (dec.), $[\alpha]_D^{20}$ +118° (*c* 4, methyl sulphoxide); lit.[22] m.p. 160–162° (dec.). ^{13}C-N.m.r. data [$(CD_3)_2SO$]: δ 130 and 127 (*C*Ar), 102.1 (C-1C), 81.7 (C-4C), 73.25 (C-3C), 72.6 (C-2C), 72.2 (C-5C), 69.9 (C-6B), 69.1 (C-5B), 60.1 (C-6C), 21.4 (CH_3, Ts). Mass spectrum: *m/z* 1289 (100%, $[M + H]^+$).

Anal. Calc. for $C_{49}H_{76}O_{37}S$: C, 45.65; H, 5.90; S, 2.48. Found: C, 45.42; H, 5.81; S, 2.77.

6-S-α-D-*Glucopyranosyl-6-thiocyclomaltoheptaose* (**2**). — To a suspension of 2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-D-glucopyranose[20] (1.3 g, 3.2 mmol) in methanol (27 mL) was added methanolic M sodium methoxide (3.9 mL). The solution was kept at room temperature for 12 h, then the solvent was removed under reduced pressure. A solution of the residue in 1,3-dimethyl-2-oxohexahydropyrimidine (8 mL) was stirred with powdered 6-*O*-*p*-tolylsulphonylcyclomaltoheptaose (2.08 g, 1.6 mmol) for 3 h at 70° under nitrogen. The solvent was evaporated at 54°/6 Pa, and a solution of the brown residue in water (20 mL) was passed through a bed of Amberlite MB-13. The colourless solution was extracted with dichloromethane (20 mL), then freeze-dried to give a solid residue (1.9 g) which showed a main component in h.p.l.c. with *k'* 12. Preparative h.p.l.c. and freeze-drying gave **2** (1.4 g, 66%), as a white powder, m.p. 282–284° (dec.), $[\alpha]_D^{20}$ +172° (*c* 0.6, water). ^{1}H-N.m.r. data: δ 5.45 (d, 1 H, $J_{1,2}$ 5.4 Hz, H-1A), 5.09 (d, 1 H, $J_{1,2}$ 4 Hz, H-1B or H-1C), 5.03 (m, 5 H, H-1C), 4.99 (d, 1 H, $J_{1,2}$ 4 Hz, H-1B or H-1C), 4.07–3.78 (m, H-5A,5B,5C,6A,6C), 3.76 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2A), 3.66–3.47 (m, H-2C,3A,4C), 3.88 (dd, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ <1 Hz, H-4A), 3.14 (dd, 1 H, $J_{5,6a}$

2.6, $J_{6a,6b}$ 12.5 Hz, H-6aB), 3.13 (dd, 1 H, $J_{5,6b}$ 5 Hz, H-6bB). Mass spectrum: *m/z* 1313 (100%, $[M + H]^+$); with NaI, *m/z* 1335 (100%, $[M + Na]^+$), 1173 (8%, $[M + Na - 162]^+$), 1140 (8%, $[M + Na - 195]^+$).

Anal. Calc. for $C_{48}H_{80}O_{39}S$: C, 43.88; H, 6.14; S, 2.44. Found: C, 44.62; H, 6.27; S, 2.54.

6-S-β-D-Glucopyranosyl-6-thiocyclomaltoheptaose (**3**). — A solution of **1** (0.33 g, 0.26 mmol) in 1,3-dimethyl-2-oxohexahydropyrimidine (1.5 mL) was stirred with dry powdered 1-thio-β-D-glucopyranose sodium salt[24] (67 mg, 0.31 mmol) at 70° for 5 h under nitrogen, then worked-up as described for **2**. The crude product (0.305 g), which contained a main component with *k'* 11, was purified by preparative h.p.l.c. to give **3** (0.2 g, 60%). The freeze-dried material, after recrystallisation from methanol, had m.p. 268–270° (dec.), $[\alpha]_D^{20}$ +116° (*c* 1, water). ^{1}H-N.m.r. data: δ 5.09 (d, 1 H, *J* 4 Hz, H-1B or H-1C), 5.03 (m, 6 H, H-1C or H-1B, 5 H-1C), 4.60 (d, 1 H, $J_{1,2}$ 10.2 Hz, H-1A), 4.12–3.75 (m, H-5A,5B,5C,6A,6C), 3.7–3 (m, H-2A,2C,3C,4A,4B,4C,5A,6aB), 2.95 (m, 1 H, H-6bB). Mass spectra: *m/z* 1313 (100%, $[M + H]^+$); with NaI, *m/z* 1335 (100%, $[M + Na]^+$), 1173 (12%, $[M + Na - 162]^+$), 1140 (10%, $[M + Na - 195]^+$).

Anal. Calc. for $C_{48}H_{80}O_{39}S$: C, 43.88; H, 6.14; S, 2.44. Found: C, 43.62; H, 5.83; S, 2.39.

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