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Synthesis of octopus glycosides: core molecules for the construction of glycoclusters and carbohydrate-centered dendrimers

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Abstract

Allyl α-D-glucopyranoside was perallylated to allyl 2,3,4,6-tetra-*O*-allyl-α-D-glucopyranoside and this was converted into an array of uniformly functionalized spacer glycosides of an ''octopus'' type, taking advantage of the rich chemistry of the allyl ether function. Thus, carbohydrate-derived pentaaldehydes, pentaalcohols and pentaamines with different spacer lengths were obtained by ozonolysis, reductive amination, hydroboration or photoaddition of cysteamine hydrochloride, respectively. The new octopus glycosides are useful core molecules for the synthesis of glycoclusters and for the construction of carbohydrate-centered dendrimers.

Keywords: Multivalent glycomimetics; Glycoclusters; Multivalency; Spacer glycosides; Allyl ether modifications

1. Introduction

Carbohydrates have been extensively used as chiral pool starting materials for enantioselective synthesis in numerous reports [1]. Usually the number of functionalities is reduced during these modifications to remove an ''overload'' of chiral centers as well as hydroxyl groups. Conversely, carbohydrates can be of great use as polyfunctional molecules for the design of multivalent core molecules. These are of interest for the synthesis of carbohydrate-centered multivalent glycomimetics, such as glycoclusters and glycodendrimers [2], which have recently been shown to serve as high affinity ligands in many carbohydrate-protein interactions due to the ''multivalency effect'' [3] operating in such interactions. Furthermore, multivalent carbohydrate derivatives are of interest as initiator cores for the synthesis of carbohydrate-centered dendrimers in order to obtain chiral dendrimers (Fig. 1), an area of research only recently explored [4].

To turn carbohydrates into suitable cores for glycocluster and dendrimer synthesis, the uniform derivatization of all hydroxyl groups of the sugar ring is desirable. At the same time, the hydroxyl functions should be equipped with spacers of various chain lengths and different functionalities attached at the ω-position. Allyl ethers offer a great

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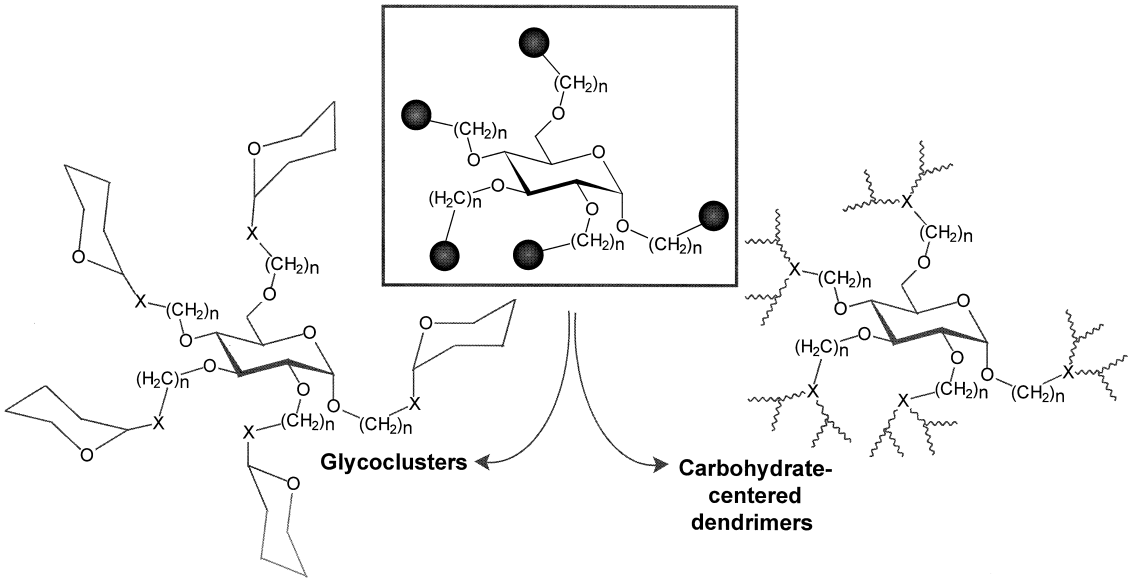


Fig. 1. Glycosides, uniformly modified at all hydroxyl groups of the sugar ring have been designed to serve as core molecules for the construction of glycoclusters or carbohydrate-centered dendrimers.

potential for the generation of diverse spacers with different functionalities [5] under conditions that do not harm glycosidic linkages as exemplified in Fig. 2. As such, per-allylated glycosides appear to be suitable precursors for the synthesis of the desired polyfunctional carbohydrate cores. The functionalities resulting from the allyl ether modifications can be used as tethers for the attachment of other glycosides leading to glycoclusters [6] or for the multiplication of functional groups in a dendritic manner in order to form carbohydrate-centered hyperbranched molecules for the synthesis of chiral hybrid dendrimers.

The chemistry of carbohydrate *O*-allyl ethers has been employed in many cases [7] and is well described. However, the complete conversion of all allyl functions of a per-allylated glycoside to uniformly functionalized octopus-like derivatives has not yet been investigated. To outline this chemistry, the synthesis and characterization of various octopus glycosides from the per-*O*-allylated allyl glucoside **2** is described in this paper.

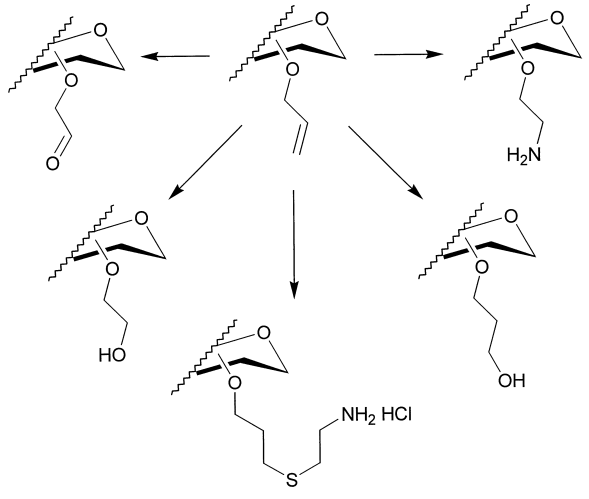


Fig. 2. Versatile transformations of the allyl ether function.

2. Results and discussion

For the synthesis of a per-*O*-allylated glucoside, the anomerically pure allyl α-D-glucopyranoside **1** was used as inexpensive starting material (Scheme 1). Allylation of **1** was carried out under phase transfer conditions with allyl chloride as the organic phase. Under these conditions the reaction rate increases with the extent of allylation and thus side products which are only partially allylated are not obtained [8]. Purification on silica gel is not necessary for further derivatizations of **2**. Thus, the perallylated glucoside **2** served directly as starting material for exhaustive ozonolysis, photoaddition of cysteamine hydrochloride as well as for hydroboration.

Initially, ozonolysis of **2** was carried out to form the pentaaldehyde derivative **3**. The reaction yielded different products, depending on the applied solvent mixture in accordance with the Criegee mechanism for the ozonolysis reaction (Fig. 3). When **2** was treated with ozone in an aprotic solvent such as dichloromethane, a pentacarbonyl

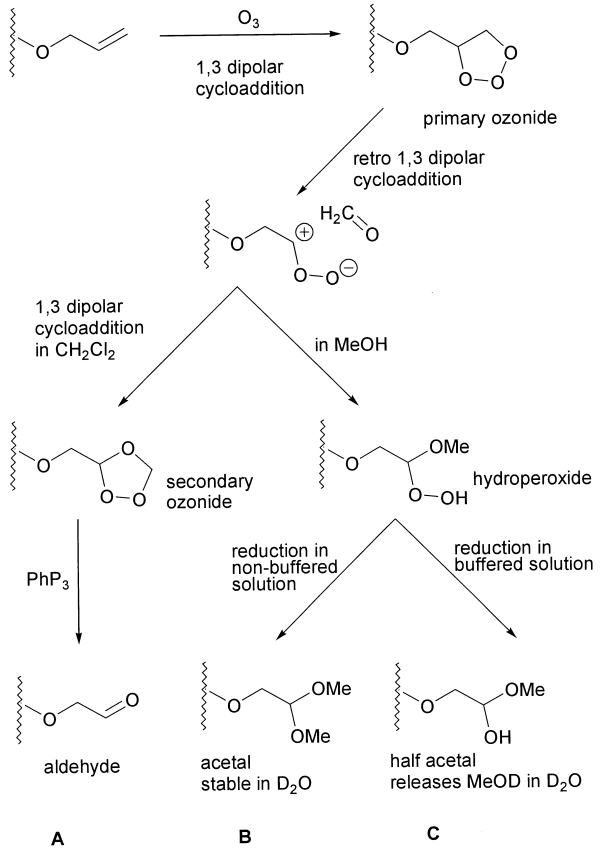
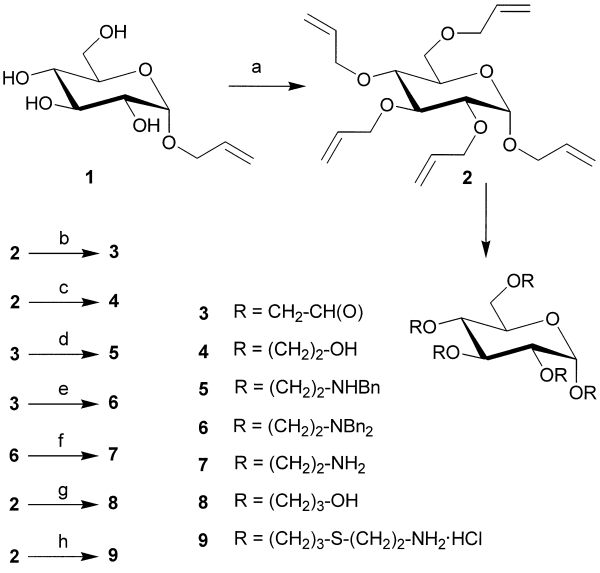


Fig. 3. Schematic representation of the Criegee mechanism of



Scheme 1. Reagents and conditions: (a) allyl chloride (5 equiv), aq 40% NaOH, TBABr (1 equiv), 35 °C, 16 h; (b) O_3, $NaHCO_3$ (>5 equiv), 6:1 CH_2Cl_2–MeOH, PPh_3; (c), O_3, $NaHCO_3$ (>5 equiv), 5:1 CH_2Cl_2–MeOH, $NaBH_4$; (d) $BnNH_2$, $NaHB(OAc)_3$, HOAc, THF, −10 °C; (e) Bn_2NH, $NaHB(OAc)_3$, HOAc, THF, −10 °C; (f) Pd-C, NH_4HCO_2, MeOH, Δ; (g) 9-BBN, THF, Δ; (h) cysteamine hydrochloride (25 equiv) in MeOH (1 g/mL), 254 nm.

product of type **A** (Fig. 3) was expected. However, only an insoluble polymeric mixture was obtained. The same reaction in methanol was expected to give the corresponding acetal derivative (type **B**), however, the product could not be characterized by NMR. Finally, ozonolysis in buffered dichloromethane–methanol [9] afforded the desired product mainly as the hemiacetal (type **C**). Upon reaction with ozone at −78 °C and using one equivalent of sodium hydrogencarbonate per allyl group to buffer the reaction mixture, complete conversion of all allyl groups of **2** was achieved with no side product formation or decomposition observed. The yield of this reaction can only be estimated to be at least 75% as the hemiacetal-type product also contained traces of the corresponding carbonyl and hydrate derivatives. The ^1H NMR spectrum of the ozonolysis product **3** in deuterium oxide displays the expected peaks for the pentahydrate and for released methanol.

The ozonolysis product **3** could be reduced to the pentaalcohol **4**. However, it was more feasible to treat the hydroperoxide, formed during the ozonolysis reaction, with sodium borohydride on aluminium oxide to give the penta-(2-hydroxyethyl) derivative **4** directly from **2** in 85% overall yield.

For further derivatization the ozonolysis product **3** was treated with benzylamine under reductive conditions to effect reductive amination to **5**. After extensive optimization studies, treatment of **3** with sodium triacetoxyborohydride [10] as the reducing agent in tetrahydrofuran and acetic acid, at low temperature, was selected as an effective procedure. The reductive amination product was purified by size-exclusion chromatography on Sephadex LH-20 with 1:1 methanol–dichloromethane as eluent. Dichloromethane was an important component, because it increased the solubility of the product and eliminated adsorption at the LH-20 gel, which otherwise led to low yields. However, careful MS analysis of the purified material clearly revealed ill-defined compounds in addition to the desired product **5**, due to intramolecular ring closure reactions to cyclic amines. This problem was overcome by application of dibenzylamine instead of benzylamine under the afore-mentioned optimized reaction conditions, which led to pure **6** in 74% yield. NMR and MS analyses proved the uniform functionalisation to the dibenzylamine cluster **6**. Debenzylation of **6** to the free amine **7** was achieved by transfer hydrogenation [11] with ammonium formate and Pd-C in methanol in 89% yield.

Regioselective hydroboration of allyl groups is described in the literature using 9-borabicyclo[3.3.1]nonane or disiamylborane [12]. For the conversion of the allyl groups of glucoside **2** into 3-hydroxy-propyl spacers, 9-borabicyclo-[3.3.1]nonane was used in refluxing tetrahydrofuran [13]. This afforded the pentaalcohol **8** nearly quantitatively, which could be purified on silica gel. Even though **8** carries five hydroxyl groups, it is readily solubilized in chloroform due to the lipophilic spacers.

The functionalization of allyl groups by photoaddition reaction of cysteamine hydrochloride has been described in water [14] and is typically performed with a large excess of cysteamine hydrochloride. As the pentaallyl derivative **2** is not water-soluble, another solvent is required for the photoaddition reaction, which can also dissolve high concentrations of cysteamine hydrochloride. Thus, methanol was used to convert the allyl glycoside **2** into the amino-terminated core molecule **9** by photoaddition. The large excess of cysteamine hydrochloride could be removed by gel permeation chromatography on Sephadex LH-20. Unfortunately, our attempts to apply this procedure to derivatives, insoluble in methanol or water, were not successful.

NMR spectra of the described octopus glycosides are characterized by a number of overlapping peaks due to several magnetically similar OCH_2 groups on each molecule. The assignments are facilitated by ^1H-^{13}C HMBC NMR, which frequently allows the assignment of all peaks for each individual spacer. Interestingly, in the ^{13}C NMR spectra the anomeric OCH_2 group is the most high field shifted of all OCH_2 groups bound to the sugar ring. Additionally it is at higher field also when compared to the C-6 methylene group, in many cases.

3. Conclusions

The methodology presented in this paper allows the transformation of all hydroxyl groups of a sugar ring into the corresponding hydroxy ethyl, hydroxy propyl, amino ethyl and amino-3-thiahexyl derivatives with great ease. It is expected that the approach shown in this paper can be extended to more complex systems such as disaccharides and oligosaccharides. The resulting homologous functionalized octopus glycosides are currently being evaluated for the synthesis of glycoclusters and carbohydrate-centered dendrimers. Furthermore, the presented octopus glycosides and hyperbranched derivatives thereof imply the possibility of combinatorial approaches for future developments.

4. Experimental

General methods.—Optical rotations were determined with a Perkin–Elmer 241 polarimeter (10 cm cells, Na-D-line: 589 nm). NMR spectra were recorded at 400 or 500 MHz on Bruker AMX-400 and Bruker DRX-500 instruments with Me_4Si (δ 0) as the internal standard. All reactions were monitored by TLC on silica gel FG_{254} (Merck) with detection by UV light, by charring with 10% ethanolic sulphuric acid or by a hydroperoxide specific reagent [15]. Flash column chromatography was performed on silica gel 60 (200–400 mesh, Macherey Nagel & Co). Gel permeation chromatography was carried out on Sephadex G-15 (Pharmacia). Photochemical irradiations were carried out under N_2. The degassed solutions were placed in quartz glass tubes and irradiated at 254 nm in a RPR-100 reactor from Rayonet. Lyophilisation was performed with a Leybold–Heraeus Lyovac GT 2 apparatus. Elemental analyses were determined by the Microanalytical Laboratory of the Department of Organic Chemistry at the University of Hamburg.

Allyl 2,3,4,6-tetra-O-*allyl*-α-D-*glucopyranoside* (**2**).—To a solution of **1** (2.08 g, 9.4 mmol) [16] in aq 33% NaOH (140 mL) the phase transfer catalyst tetrabutylammonium bromide (TBABr, 2.3 g) was added. Then, allyl chloride (4.6 mL, 56.5 mmol) was added dropwise at 30 °C over 1 h. The mixture was stirred for 12 h, additional allyl chloride (1.2 mL) was added and the mixture was stirred for another 6 h. When the reaction was complete, toluene (100 mL) was added, the organic layer was separated and washed five times with water. The neutral organic phase was dried ($MgSO_4$), filtered, and concentrated to yield **2** (2.57 g, 72%) as a colourless oil; $[\alpha]^{19}_D$ +105.3° (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 5.85–6.02 (dddd ≈ m, 5 H, 5 OCH_2CHCH_2), 5.23–5.34 (ddd, 5 H, 5 OCH_2CHCHH), 5.12–5.22 (ddd, 5 H, 5 OCH_2CHCHH), 4.93 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.37, 4.32, and 4.25 (3 dddd, each 1 H, 3 $OCHHCHCH_2$), 4.20–4.02 (m, 6 H, 6 $OCHHCHCH_2$), 3.99 (dddd, 1 H, $OCHHCHCH_2$), 3.74

(dd ≈ t, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 3.71 (ddd, 1 H, H-5), 3.65 (dd, 1 H, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 10.2 Hz, H-6a), 3.61 (dd, 1 H, $J_{5,6b}$ 2.6 Hz, H-6b), 3.43 (dd ≈ t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 3.40 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 135.0, 134.6, 134.5, 134.2, and 133.4 (allyl-C-2), 117.5, 116.9, 116.7, 116.3, and 115.9 (allyl-C-3), 95.3 (C-1), 81.1 (C-3), 79.0 (C-2), 77.0 (C-4), 73.8, 73.4, 72.0, and 71.8 (allyl-C-1), 69.7 (C-5), 68.1 (C-6), 67.6 (allyl-C-1). Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.28; H, 8.48. Found: C, 66.09; H, 8.48.

(2-Oxo-ethyl) 2,3,4,6-tetra-O-*(2-oxo-ethyl)*-α-D-*glucopyranoside* (**3**).—A solution of **2** (200 mg, 0.53 mmol) and $NaHCO_3$ (340 mg, 4.0 mmol) in 6:1 CH_2Cl_2–MeOH (70 mL) was treated with ozone at −78 °C until the colour of the solution turned blue. N_2 was bubbled through the solution until the blue colour had disappeared and then triphenylphoshine (790 mg, 3.0 mmol) was added. When the reduction of the hydroperoxide was complete, the solution was purified by flash chromatography (6:1→5:1 CH_2Cl_2–MeOH) to yield **3** (210 mg); ^{1}H NMR (500 MHz, D_2O, MeOH 3.35 ppm): δ 9.64, 9.61, 9.61, 9.60, and 9.56 (5 s, traces of C*H*O), 5.23–5.10 (m, 6 H, H-1, 5 C*H*$(OH)_2$), 3.85–3.74, 3.69–3.63, and 3.59–3.49 (each m, 7 H, 4 H, 5 H, H-2,3,4,5,6a,6b, 10 OC*H*HCH$(OH)_2$); ^{13}C NMR (100.62 MHz, D_2O, MeOH 50.2 ppm): δ 97.9 (C-1), 89.8, 89.7, 89.7, 89.7, and 89.6 (5 *C*H$(OH)_2$), 82.8 (C-3), 81.4 (C-2), 79.0 (C-4), 77.0, 76.6, 75.0, 74.9, and 72.0 (5 CH_2*C*H$(OH)_2$), 71.0 (C-5), 70.6 (C-6); ^{1}H-^{13}C HMQC: δ 5.13 (H-1), 3.84 (H-5), 3.76 (H-3), 3.55 (H-2), 3.48 (H-4); ^{1}H-^{13}C HMBC: δ 3.83 (H-6a), 3.80 (H-6b).

(2-Hydroxy-ethyl) 2,3,4,6-tetra-O-*(2-hydroxy-ethyl)*-α-D-*glucopyranoside* (**4**).—A solution of **2** (210 mg, 0.55 mmol) and $NaHCO_3$ (570 mg, 6.8 mmol) in 5:1 CH_2Cl_2–MeOH (60 mL) was treated with ozone at −78 °C until the colour of the reaction mixture turned blue. After decolourisation by a N_2 stream, $NaBH_4$ on Al_2O_3 (1.18 g, 2.95 mmol) was added. After the reduction was complete, the mixture was purified by flash chromatography (5:1→4:1 CH_2Cl_2–MeOH) to yield **4** (190 mg, 85%) as a colourless oil; $[\alpha]^{26}_D$ +90.2° (*c* 0.95, MeOH); ^{1}H NMR (400 MHz, MeOH-d_4 3.35 ppm): δ 5.03 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.98–3.88 (m, 3 H, 3 OC*H*HCH$_2$OH), 3.83–3.56 (m, 21 H, 7 OC*H*HCH$_2$OH, 10 OCH$_2$C*H*HOH, H-6a, 5,3,6b), 3.42 (dd ≈ t, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.41 (dd∼t, 1 H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4); ^{13}C NMR (100.62 MHz, MeOH-d_4 50.2 ppm): δ 99.4 (C-1), 84.0 (C-3), 83.2 (C-2), 80.6 (C-4), 76.9, 76.5, 75.2, and 74.9 (4 OCH_2CH_2OH), 73.0 (C-5), 72.0 and 71.8 (C-6, OCH_2CH_2OH), 63.9, 63.9, 63.6, 63.4, and 63.3 (5 OCH$_2$CH_2OH); ^{1}H-^{13}C HMQC: δ 3.735 (H-5), 3.685 (H-3); ^{1}H-^{13}C HMBC: δ 3.76 (H-6a), 3.68 (H-6b).

(2-N,N-Dibenzyl-amino-ethyl) 2,3,4,6-tetra-O-*(2-N,N-dibenzyl-amino-ethyl)*-α-D-*glucopyranoside* (**6**).—The perallylated allyl glucoside **2** (340 mg, 0.894 mmol) was transformed to **3** as described above and dissolved in THF (20 mL). Dibenzylamine (0.39 mL, 6.8 mmol), HOAc (0.39 mL, 6.8 mmol) and sodium triacetoxyborohydride (2.3 g, 10.8 mmol) were added and the mixture was stirred for 3 h at −10 °C. When the reaction was complete, CH_2Cl_2 (100 mL) was added, the organic layer was washed three times with 1 M aq NaOH (100 mL) and five times with water. The neutral organic phase was dried ($MgSO_4$), filtered, and concentrated. After purification on Sephadex LH-20 (1:1 CH_2Cl_2–MeOH) **6** was obtained as a colourless oil (854 mg, 74%); $[\alpha]^{27}_D$ +35.2° (*c* 1.175, $CDCl_3$); M_r (FAB): 1297.2 $(M+1)^+$-ion; MALDI-TOF: 1299.7 $(M+1)^+$-ion; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.13 (m, 50 H, arom H), 4.72 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.85 (m, 1 H, OC*H*HCH$_2$N), 3.75 (m, 1 H, OCH*H*CH$_2$N), 3.71–3.36 (m, 32 H, H-3,5,6a,6b, 8 OC*H*HCH$_2$N, 10 NCH_2C$_6$H$_5$), 3.13 (dd, 1 H, H-4), 3.10 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 2.71–2.46 (m, 10 H, 5 OCH$_2$CH_2N); ^{13}C NMR (125.83 MHz, $CDCl_3$): δ 139.0, 128.1, 128.0, 127.6, 127.5, 126.2, and 126.1 (60 arom C), 96.2 (C-1), 81.3 (C-3), 80.1 (C-2), 77.5 (C-4), 69.7 (C-5), 71.0, 70.9, 69.7, 69.2, and 65.6 (5 OCH_2CH_2N), 69.0 (C-6), 58.3, 58.3, 58.1, 58.1, and 57.9 (5 NCH_2C$_6$H$_5$), 52.6 (3×), 52.1, and 51.7 (5 OCH$_2$CH_2N); ^{1}H-^{1}H COSY: δ 3.43 (H-3), 3.50 (H-5); ^{1}H-^{13}C HMBC: δ 3.46 (H-6a), 3.40 (H-6b).

(2-Amino-ethyl) 2,3,4,6-tetra-O-*(2-amino-ethyl)*-α-D-*glucopyranoside* (**7**).—To a solution of **6** (181 mg, 0.14 mmol) in dry MeOH (50 mL), Pd (10% on charcoal, 240 mg) and ammonium formate (2.5 g, 39.6 mmol) were added under N_2 and the suspension was stirred under reflux for 2 h. Then additional ammonium formate (2.5 g, 39.6 mmol) was added and stirring at reflux temperature was continued for 1 h. When the reduction was complete, the solution was filtered through Celite, and concentrated to yield **7** (49 mg, 89%) as a colourless oil; $[\alpha]^{28}_D$ +76.8° (*c* 0.6, MeOH); ^{1}H NMR (500 MHz, MeOH-d_4 3.35 ppm): δ 5.02 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.93–3.51 (m, 14

H, 5 OCH_2CH$_2$NH$_2$, H-3,5,6a,6b), 3.41 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.40 (dd ≈ t, 1 H, H-4), 2.96–2.79 (m, 10 H, 5 OCH$_2$CH_2NH$_2$); ^{13}C NMR (125.83 MHz, MeOH-d_4 50.2 ppm): δ 99.2 (C-1), 83.9 (C-3), 83.0 (C-2), 80.7 (C-4), 76.1, 76.0, 74.0, 74.7, 71.9, and 71.8 (C-6, 5 OCH_2CH$_2$NH$_2$), 73.1 (C-5), 43.9, 43.9, 43.5, 43.2, and 43.2 (5 OCH$_2$CH_2NH$_2$); ^{1}H-^{13}C HMQC: δ 3.74 (H-5), 3.70 (H-3), 71.9 or 71.8 (C-6); ^{1}H-^{13}C HMBC: δ 3.77 (H-6a), 3.70 (H-6b).

(3-Hydroxy-propyl) 2,3,4,6-tetra-O-*(3-hydroxy-propyl)*-α-D-*glucopyranoside* (**8**).—To a solution of **2** (300 mg, 0.79 mmol) in dry THF (8 mL), 9-BBN (0.5 M solution in THF; 23.5 mL, 11.75 mmol) was added under N_2 atmosphere, and the solution was stirred at reflux temperature for 6 h. Then the excess of 9-BBN was destroyed by dropwise addition of water at 0 °C. The hydroboration mixture was oxidized by adding 3 M aq NaOH (11.75 mL) and 30% H_2O_2 (11.75 mL) at 0 °C, followed by stirring at room temperature overnight. The aq phase was saturated with K_2CO_3 and the THF phase was separated. The aq phase was extracted twice with THF (40 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated to afford **8** (360 mg, 97%) as a colourless oil; $[\alpha]^{19}_D$ +87.7° (*c* 1.08, $CHCl_3$); M_r (FAB): 493.5 $(M + Na)^+$; ^{1}H NMR (500 MHz, MeOH-d_4): δ 4.96 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.94–3.82 (m, 4 H, 2 OCH_2CH$_2$CH$_2$OH), 3.78–3.55 (m, 19 H, 3 OCH_2-CH$_2$CH$_2$OH, 5 OCH$_2$CH$_2$–CH_2OH, H-5,6a,6b), 3.54 (dd ≈ t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.29 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 3.26 (dd ≈ t, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 1.91–1.79 (m, 10 H, 5 OCH$_2$CH_2CH$_2$OH); ^{13}C NMR (125.77 MHz, MeOH-d_4): δ 99.1 (C-1), 84.1 (C-3), 83.0 (C-2), 80.6 (C-4), 72.9 (C-5), 72.6, 72.1, 71.9, 70.7, 70.2, and 67.4 (5 OCH_2CH$_2$CH$_2$OH, C-6), 61.6, 61.4, 61.4, 61.4, and 61.2 (5 OCH$_2$CH$_2$-CH_2OH), 35.7, 35.5, 35.2, 34.8, and 34.5 (5 OCH$_2$CH_2CH$_2$OH); ^{1}H-^{1}H COSY: δ 3.66 (H-5).

(Amino-3-thia-hexyl) 2,3,4,6-tetra-O-*(amino-3-thia-hexyl)*-α-D-*glucopyranoside pentahydrochloride* (**9**).—To a solution of **2** (230 mg, 0.60 mmol) in degassed MeOH (1 mL), cysteamine hydrochloride (1.1 g, 9.7 mmol) was added and the resulting suspension was irradiated at 254 nm for 2 h. Additional cysteamine hydrochloride (1.1 g, 9.7 mmol) was added and the suspension was irridated at 254 nm for another 2 h. It was purified by gel filtration chromatography on Sephadex G-15 using water as eluent. After lyophilisation **9** was isolated as an almost colourless glass (550 mg, 97%); $[\alpha]^{25}_D$ +45.1° (*c* 1.04, H_2O); M_r (FAB): 766.5 $(M + 1)^+$-ion without hydrochlorine; ^{1}H NMR (500 MHz, D_2O, acetone 2.22 ppm): δ 5.07 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 3.61–3.91 (m, 13 H, 5 OCH_2CH$_2$CH$_2$S, H-6a,6b,5), 3.57 (dd ≈ t, 1 H, H-3), 3.32–3.42 (m, 2 H, H-2,4), 3.23 (m ≈ t, 5 H, SCH$_2$CH_2NH$_2$HCl), 2.84–2.90 (m, 5 H, SCH_2CH$_2$NH$_2$HCl), 2.65–2.72 (m, 5 H, OCH$_2$CH$_2$CH$_2$S), 1.84–1.98 (m, 5 H, OCH$_2$ CH_2CH$_2$S); ^{13}C NMR (100.61 MHz, D_2O): δ 96.4 (C-1), 81.5 (C-3), 79.9 (C-2), 78.0 (C-4), 72.5, 70.1, 69.8, 69.1, and 66.8 (5 OCH_2CH$_2$CH$_2$S), 72.1 (C-6), 70.0 (C-5), 38.8 (5 SCH$_2$CH_2NH$_2$ HCl), 29.7, 29.5, 29.3, 28.9, and 28.7 (5 OCH$_2$CH_2CH$_2$S), 28.6 (3×) and 28.5 (2×) (5 SCH_2CH$_2$NH$_2$ HCl), 27.8 (2×), 27.8, and 27.7 (2×) (5 OCH$_2$CH$_2$CH_2S); ^{1}H-^{1}H COSY: δ 3.72 (H-5), 3.40 (H-2), 3.37 (H-4); ^{1}H-^{13}C HMQC: δ 3.91 (H-6a), 3.76 (H-6b).

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