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Efficient regioselective chemical modifications of maltotriose: an easy access to oligosaccharidic scaffold

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ABSTRACT

Regioselective chlorination of fully unprotected maltotriose has given in high yield $1^{I},2^{I-III},3^{I-III},4^{III}$-octa-*O*-acetyl-$6^{I-III}$-trichloro-$6^{I-III}$-trideoxymaltotriose. Moreover, regioselective ditritylation of methyl β-maltotrioside has provided the two regioselectively C_6-disubstituted trisaccharides. Selective deprotection of these new compounds gives the corresponding diol and halogenated analogues, respectively, in good yield. All compounds have been completely characterized and the substitution pattern in the oligosaccharidic sequence has been elucidated. A new family of amphiphilic carbohydrates, namely the 6-deoxy-6-alkylthiomaltotriose derivatives, bearing either two or three thioalkyl hydrophobic chains, respectively, has been synthesized. Critical micellar concentration (CMC) values as well as the antimicrobial properties have been evaluated for amphiphilic compounds.

1. Introduction

Carbohydrates are polyfunctionalized compounds that contain primary and secondary hydroxyl groups differing in terms of reactivity. Nevertheless, some chemical transformations of these functions have been shown to proceed regioselectively. For example, it is well known that the primary hydroxyl groups of sugar derivatives are in many cases more reactive towards halogenations than are secondary groups.[1] A variety of reagents have been developed for the direct replacement of primary hydroxyl groups of unprotected (or protected only at the anomeric position) alditols,[2] monosaccharides[3–5] and few disaccharides[6–9] by halogeno substituents. Moreover, perhalogenations at primary positions on polysaccharides such as amylose,[10,11] chitin[12] and cellulose[13,14] has been well described.

To our knowledge, no direct halogenation of maltotriose or higher acyclic maltodextrins has been described in the literature. We report here a method for synthesis of 6-deoxy-6-trichloro- and triiodomaltotriose derivatives **1** and **2** by direct chlorination of totally unprotected maltotriose (Fig. 1). Per-6-O-substitution gives access to the corresponding modified oligosaccharides but a regioselective disubstitution of maltotriose would provide new oligosaccharidic scaffolds which could serve as precursors of complex branched oligosaccharides or new amphiphilic carbohydrates for examples. We report also the synthesis of 6-deoxy-6-dichloro and diiodomaltotriose derivatives **10–11** and **12–13**, respectively, and of the corresponding diols **8–9** using a new method for the regioselective ditritylation[15] of methyl β-maltotrioside (Fig. 1).

As an example of their potential, compounds **2**, **10** and **13** served as precursors to a new family of amphiphilic carbohydrates, namely, the 6-deoxy-6-alkylthiomaltotriose derivatives **19** to **23**, **26** and **27** (Fig. 2) with the aim to study the influence of the position of alkyl chains on their properties. Amphiphilic carbohydrates are well known to show interesting applications in multiple areas. They display various biological and physiological properties. Amongst these can be cited their use as model biomembranes[16] or their potential antitumour activities.[17] They can also form liquid crystals[18] and have found practical uses as surfactants and non-ionic detergents.[19] It was generally recognized that *n*-alkyl glycosides containing a C_8 and C_{12} alkyl chain showed a broad spectrum of antimicrobial activity. Amongst them, those with *n*-dodecyl groups were particularly effective against Gram-positive strains as well as fungal strains.[20] Preliminary physico-chemical and antimicrobial data generated for the disubstituted derivatives **26** and **27** correlate not only with the number and the length but also the location of the grafted alkyl chains.

2. Results and discussion

2.1. Synthesis of 6^{I-III}-deoxy-6^{I-III}-trichloromaltotriose and 6^{I-III}-deoxy-6^{I-III}-triiodomaltotriose derivatives 1 and 2

Direct halogenation of the 6^{I}, 6^{II} and 6^{III} positions of maltotriose was first studied as an alternative to the multistep method[21] previously described for the synthesis of the desired target **1**. As

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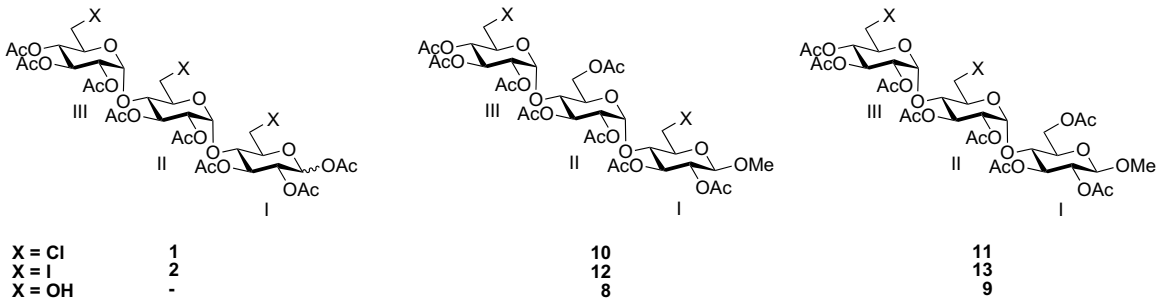


Figure 1. Structures of targets maltotriose derivatives **1**, **2**, **8**, **9** and **10** to **13** (roman numbers located below glucopyranosidic rings refer to each unit and are used to indicate their associated protons and carbons in the NMR data).

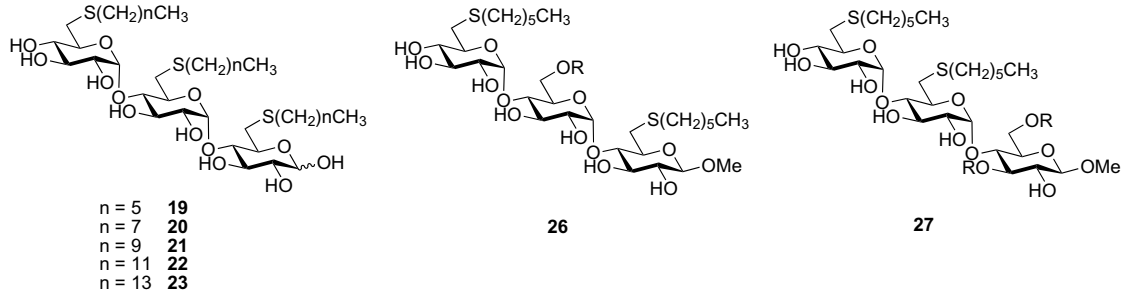
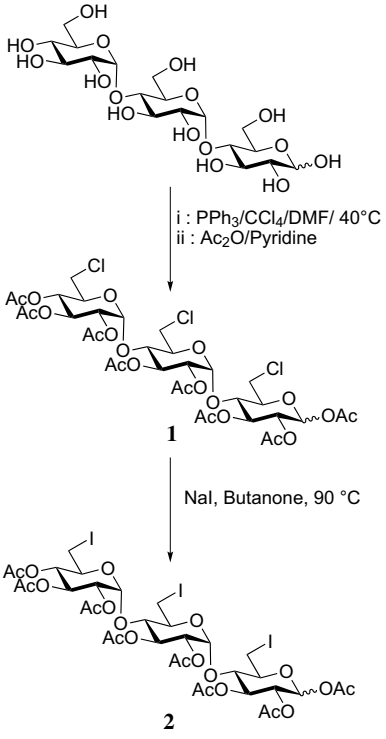


Figure 2. Structures of targets maltotriose derivatives **19** to **23**, **26** and **27**.

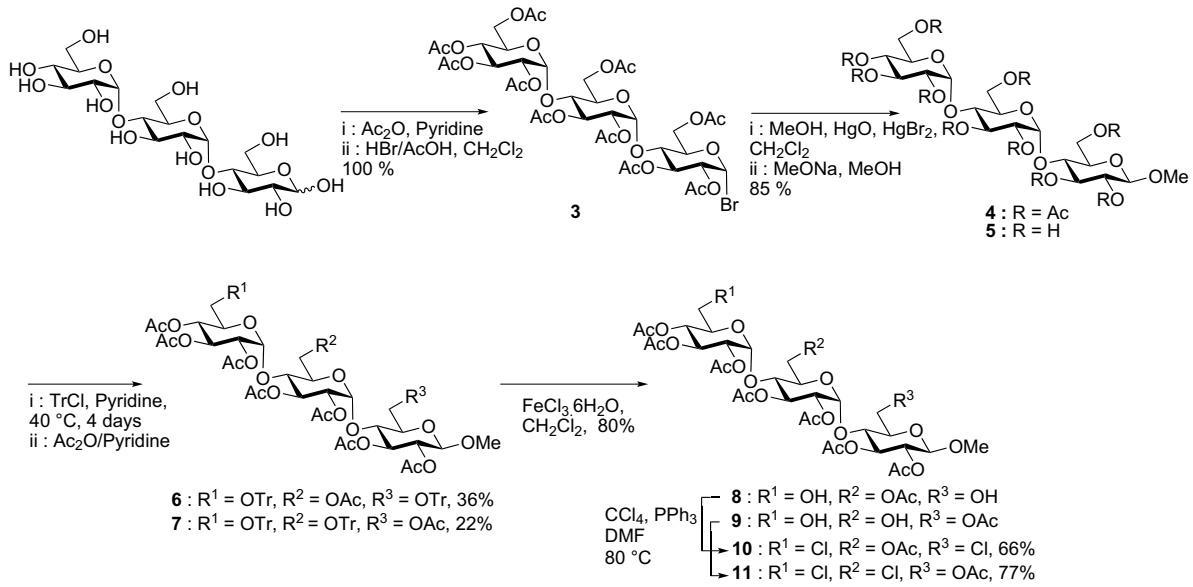
shown in Scheme 1, maltotriose was allowed to react with CCl_4 in presence of PPh_3 in DMF at 40 °C to give, after acetylation of the remaining free OH groups, the $1^{I},2^{I-III},3^{I-III},4^{III}$-octa-*O*-acetyl-$6^{I-III}$-trideoxy-$6^{I-III}$-trichloromaltotriose **1** in 95% yield. We found that ratio of PPh_3/maltotriose and CCl_4/maltotriose is crucial for the complete halogenation of all the primary positions. The use of less than 9 equivalents of each reagent leads to the mixtures of di- and trihalogenated maltotriose derivatives. Investigation of the direct bromination and iodination of fully unprotected maltotriose was also undertaken. Taking a lead from former work completed within our laboratory on monosaccharides,[5] a broad range of halogenous reagents were tested. Unfortunately, couples PPh_3/CBr_4, PPh_3/NBS, PPh_3/CI_4 or PPh_3/NIS under various conditions of temperature and time, gave only traces of a monohalogeno derivative as determined by mass spectroscopy. Consequently, the $1^{I},2^{I-III},3^{I-III},4^{III}$-octa-*O*-acetyl-$6^{I-III}$-trideoxy-$6^{I-III}$-triiodomaltotriose **2** was prepared from **1** which was allowed to react with sodium iodide in butanone. Using optimized conditions, compound **2** was obtained in the presence of an anhydro derivative which was readily separated by flash chromatography. The target product **2** was isolated in 85% yield (Scheme 1).



Scheme 1.

2.2. Synthesis of regioselectively difunctionalized methyl β-maltotrioside analogues 9 to 13

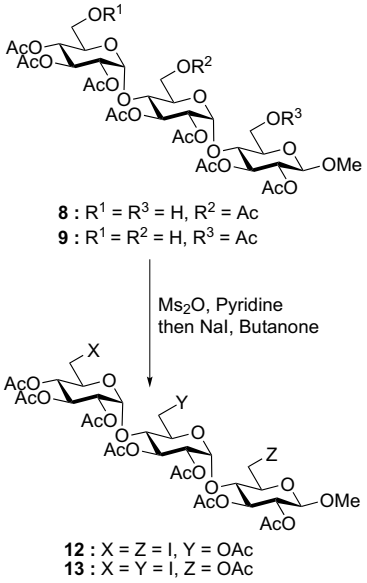
Methyl β-maltotrioside **5** was synthesized in 4 steps from maltotriose following the procedure reported by Takeo.[22] This latter route requires full acetylation of maltotriose, bromination of the anomeric position, Koenigs–Knorr condensation of the resulting 2^{I-III}, 3^{I-III}, 4^{III}, 6^{I-III}-deca-*O*-acetyl-α-maltotriosyl bromide **3** with methanol and, finally, deacetylation under Zemplén methanolysis (Scheme 2). The glycosylation step, slightly modified, was performed in the classical manner[23] using mercuric bromide and yellow mercuric oxide as promoters in dry dichloromethane to afford the desired methyl β-maltotrioside derivative **4** in 85% yield. Methyl β-maltotrioside **5** was allowed to react with 5 equivalents of trityl chloride at 40 °C for 4 days then treated with acetic anhydride. The ditritylated compounds **6** and **7** obtained were readily separated by column chromatography in 36% and 22% yields, respectively. Then, the ditritylated maltotrioside derivatives **6** and **7** were selectively deprotected using hydrated ferric chloride, which is known to prevent acetate migration,[24] to afford the corresponding diols **8** and **9** in 98% and 71% yields, respectively.



Scheme 2.

Unambiguous NMR assignment of each carbohydrate unit of compounds **6** to **9** and their structural elucidation revealed to be quite difficult. Since it is well known that chloro atoms induced strong chemical shifts, we chose to prepared their chlorinated analogues **10** and **11** (Scheme 2). Chlorination of the diol derivatives **8** and **9** was performed using CCl_4 and PPh_3 to afford the two dihalogenated derivatives **10** and **11** in 66% and 77% yields, respectively. The unequivocal structural elucidation of the two dichloro compounds **10** and **11** by NMR spectroscopy[25] demonstrates that chloro atoms are located at the primary position of the upstream (III) and the downstream ends (I) for **10**. In the case of **11**, the upstream end (III) and the middle unit (II) bear a chloride group at the primary carbon. This allowed the structural elucidation of compounds **6** to **9**.

Iodinated analogues **12** and **13** were prepared starting from diols **8** and **9**. Activation of the free OH groups of both diols was achieved under classical conditions through mesylate groups in quantitative yield. Then iodination step was performed in butanone in presence of sodium iodide to give methyl $6^{I,III}$-deoxy-$6^{I,III}$-diiodo-β-maltotrioside **12** and methyl $6^{II,III}$-deoxy-$6^{II,III}$-diiodo-β-maltotrioside **13** each in 95% yield (see Scheme 3).



Scheme 3.

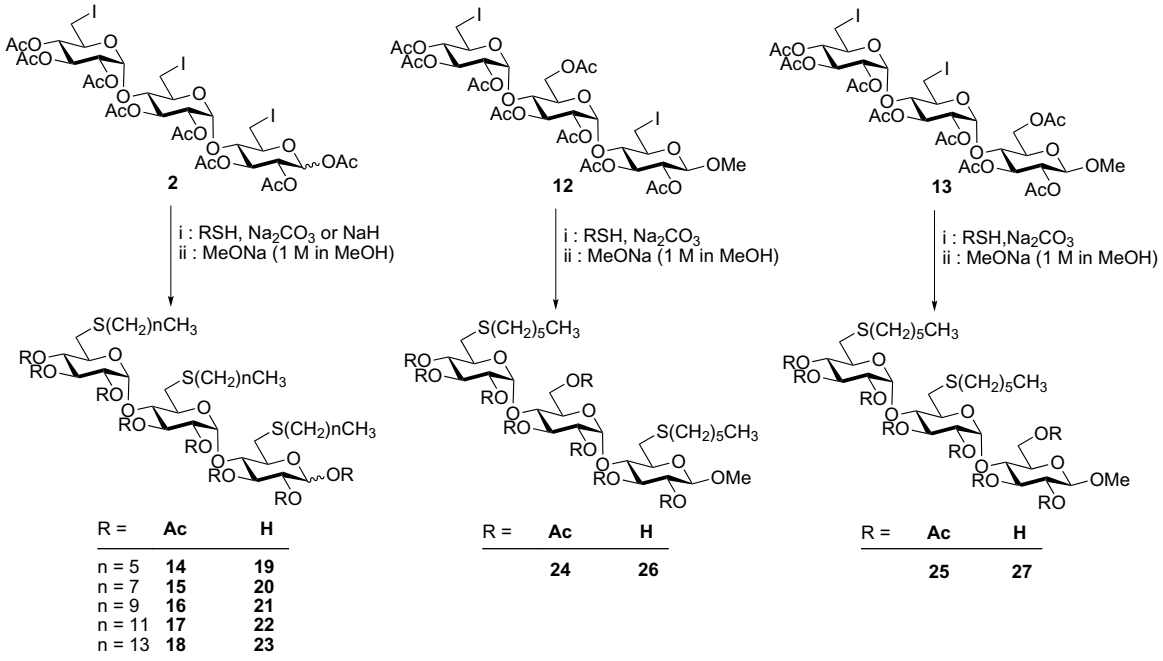
2.3. Synthesis of $6^{I–III}$-deoxy-$6^{I–III}$-trialkylthiomaltotriose 19 to 23, methyl $6^{I,III}$-deoxy-$6^{I,III}$-dihexylthio-β-maltotrioside 26 and methyl $6^{II,III}$-deoxy-$6^{II,III}$-dihexylthio-β-maltotrioside 27 derivatives

In our initial experiments, nucleophilic displacement of iodide groups of **2** with hexanethiol was performed at 0 °C using NaH in DMF to generate the thiolate ion. The desired $1^{I},2^{I–III},3^{I–III},4^{III}$-octa-*O*-acetyl-$6^{I–III}$-trideoxy-$6^{I–III}$-trihexylthiomaltotriose **14** was obtained in 90% yield. Repeating these conditions, *n*-octyl or *n*-decyl mercaptan led only to O-deacylation and anhydro formation. This was overcome by generating the thiolate ion alternatively using Na_2CO_3in DMF.[26] In this manner, *n*-octyl, *n*-decyl, *n*-dodecyl and *n*-tetradecyl mercaptan could be introduced in high yield. The $1^{I},2^{I–III},3^{I–III},4^{III}$-octa-*O*-acetyl-$6^{I–III}$-trideoxy-$6^{I–III}$-trialkylthiomaltotriose derivatives **15** to **18** were obtained in 89%, 85%, 85% and 70% yields, respectively. O-Deacylation of **14** to **18** gave the corresponding $6^{I–III}$-trideoxy-$6^{I–III}$-trialkylthiomaltotriose derivatives **19** to **23** (see Scheme 4).

Moreover, nucleophilic reaction of hexylthiolate with either the di-iodo derivatives **12** or **13** occurred at 80 °C in one day to give, after Zemplén methanolysis, the desired methyl $6^{I,III}$-deoxy-$6^{I,III}$-hexylthio-β-maltotrioside **26** and methyl $6^{II,III}$-deoxy-$6^{II,III}$-hexylthio-β-maltotrioside **27**, respectively.

2.4. Physical and biological properties of compounds 26 and 27

In a preliminary examination, critical micellar concentrations (CMCs) of compounds **19** to **23**, **26** and **27** were measured at 20 °C in water. Unfortunately, $6^{I–III}$-deoxy-$6^{I–III}$-trialkylthiomaltotriose derivatives **19** to **23** were insoluble in water whatever the length of the alkyl chain. On the other hand, compounds **26** and **27** have a CMC of 0.096 mM and 0.078 mM, respectively. The CMC was determined at the break of the slope in the surface tension (γ) versus log*C* plots (Fig. 3) as usual. It should be pointed out that both compounds bearing two small alkyl chains exhibit very low CMC values compared to more classical alkyl glycosides



R =	Ac	H
n = 5	**14**	**19**
n = 7	**15**	**20**
n = 9	**16**	**21**
n = 11	**17**	**22**
n = 13	**18**	**23**

R =	Ac	H
	24	**26**

R =	Ac	H
	25	**27**

Scheme 4.

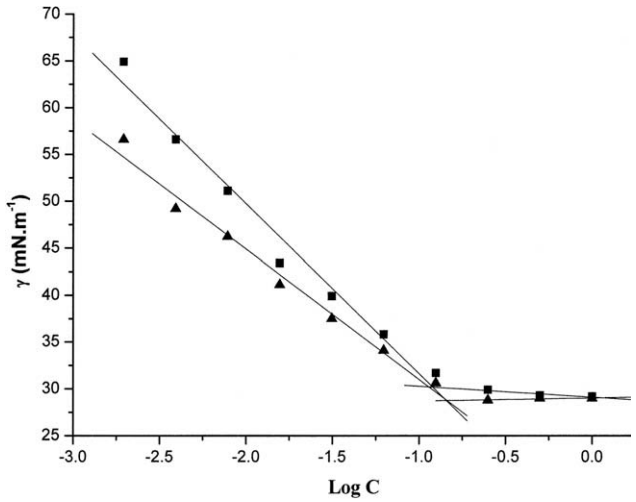


Figure 3. Surface tension of the compounds **26** (▲) and **27** (■)/water systems at 20 °C.

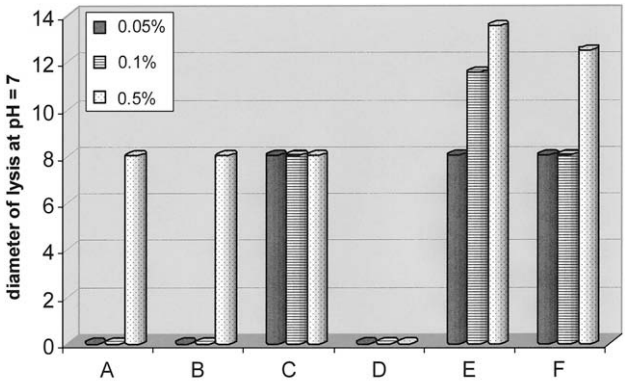


Figure 4. Inhibition (expressed by a diameter of lysis of the medium culture) of the growth of *Pseudomonas aeriginosa* (A), *Burkholderia cepacia* (B), *Enterococcus hirae* (C), *Staphylococcus aureus* (D), *Candida albicans* (E) and *Aspergillus niger* (F) by compound **27** (concentration: 0.05%, 0.1% and 0.5%) at pH 7. A diameter smaller than or identical to 8 mm was not considered as significant.

described in literature.[27] Taking into account the same polar head and the same number of carbon atoms of the hydrophobic part, a great difference of the CMC value can be observed between **26** and **27** (0.096 and 0.078 mM, respectively) and dodecyl β-maltotrioside (0.22 mM).[27] In our case, considering the amphiphilic properties, the presence of two short alkyl chains seems to be more effective than that of a single long alkyl chain.

The antimicrobial activity of derivatives **26** and **27** was evaluated against Gram-positive and Gram-negative strains and fungal strains using the diffusion method.[28] $6^{I,III}$-deoxy-$6^{I,III}$-dihexylthio-β-maltotrioside **26** did not exhibit any antimicrobial activity against any of the microorganisms tested. On the other hand, methyl $6^{II,III}$-deoxy-$6^{II,III}$-dihexylthio-β-maltotrioside **27** showed activity over *Candida albicans* and to a lesser extent against *Aspergilus niger* while it proved inactive against *Pseudomonas aeruginosa*, *Burkholderia cepacia*, *Enterococcus hirae* and *Staphylococcus aureus* (Fig. 4). Compound **27** exhibited an interesting selectivity against fungal species', and is especially active for *Candida ablicans* which is the most widespread asexual fungus of genus *Candida* causing candidiasis often observed in immunocompromised patients.

No antimicrobial activity of 6-alkyl-maltooligosaccharide derivatives had previously been reported. Then, activities of **27** were compared with that reported previously for other alkyl glycosides such as *n*-dodecyl galactosides, mannosides, glucosides and arabinosides.[20,29] The minimum inhibitory concentration (MIC) of these compounds is reported in Table 1 and compared to that of **27**. Since the sizes of the molecules are significantly different, the MICs are given both in $\mu g\ mL^{-1}$ and $\mu mol\ L^{-1}$.

Alkyl glycosides showed better antimicrobial activity against Gram-positive bacterial strains tested than Gram-negative bacterial strains. However, **27** showed better antimicrobial activity against fungal strains. It was well known that antimicrobial properties are influenced both by the length of the alkyl chain and the structure of the glycopyranosyl residue. This study reveals that the location of the grafted alkyl chains on the sugar skeleton is also important.

Table 1
Antimicrobial activity expressed as minimum inhibitory concentration (MIC) in $\mu g\,mL^{-1}$ and as $\mu mol\,L^{-1}$ in brackets

Miroorganism	$C_{12}\alpha$DGlc[20]	$C_{12}\beta$DGlc[20]	$C_{12}\alpha$Dman[20]	$C_{12}\alpha$Larab[29]	$C_{12}\beta$Larab[29]	Compound **27**
S. aureus	10 (29)	25 (72)	25 (72)	300 (903)	>300 (>903)	500 (>668)
P. aeruginosa	200 (547)	>400 (>1150)	>400 (>1150)	>300 (>903)	>300 (>903)	500 (>668)
C. albicans	400 (1150)	500 (1440)	200 (547)	>300 (>903)	>300 (>903)	50 (66)
C. aspergillus	200 (547)	200 (547)	400 (1150)	>300 (>903)	>300 (>903)	100 (133)

3. Experimental

3.1. General methods

Optical rotations were measured with a JASCO DIP-370 digital polarimeter, using a sodium lamp ($\lambda = 589$ nm) at 20 °C. All NMR experiments were performed at 300.13 MHz using a Bruker DMX300 spectrometer equipped with a *Z*-gradient unit for pulsed-field gradient spectroscopy. Chemical shifts are given relative to external tetramethylsilane (TMS) at 0 ppm with calibration having been done using the residual solvent signals. The length of the 90° pulse was approximately 7 μs (^{1}H NMR) and 10 μs (^{13}C NMR), respectively. Elemental analyses were performed at the Service de Microanalyse de l'Université de Champagne-Ardennes in Reims, France. Thin-layer chromatography was performed on E. Merck glass plates silica gel sheets (Silica Gel F_{254}) followed by charring with vanillin. Column chromatography was performed on Kieselgel (E. Merck 230–400 mesh). High-resolution electrospray mass spectra in the positive ion mode were obtained on Waters-Micromass Q-TOF *Ultima Global* hybrid quadrupole/time-of-flight instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Waters-Micromass, Manchester, UK). Surface tension (γ) was measured by use of the Wilhemly method (TD 2000 Prolabo tensiometer): for each compound, a primary solution S_0 was prepared in water at 20 °C. Several samples were obtained by dilution of S_0 in the range $S_0/2$, $S_0/4$, $S_0/8$, $S_0/16$, $S_0/32$, $S_0/64$ and $S_0/128$. γ was measured for each solution, after reaching thermal and area equilibrium. The critical micellar concentration value (CMC) was determined using graph $\gamma = f(\log c)$, in which c indicates molar concentration of the solution. Antimicrobial activity of compounds **26** and **27** was evaluated by A.C.M. Pharma (Bellegarde France) in solid medium by the diffusion method. The following bacteria and fungi were used in the tests: *Pseudomonas aeriginosa* (CIP 82.1118), *Burkholderia cepacia* (CIP 103924), *E. hirae* (CIP 58.55), *S. aureus* (CIP 4.83), *C. albicans* (IP 48.72) and *A. niger* (IP 1431.83). Each microorganism was cultured over gelose at 31 °C for 24 h (48 h at 24 °C in case of *C. albicans*). Then the culture media were put into a petri dish. After solidification, four cylinders of steel with a diameter of 8 mm were placed on the gelose and filled with a solution (100 μL) of each compound **26** and **27** (concentration of **14** or **15**: 0.05%, 0.1% and 0.5%) in methanol and water. Methanol was used as a negative control. Microorganisms were incubated at 37 °C for 24 h (48 h in case of *E. hirae*). After incubation and diffusion of **26** or **27** through the gelose, an inhibition zone appeared and its diameter was measured.

3.2. 2,3,4-Tri-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-chloro-6-deoxy-D-glucopyranose (1)

A solution of maltotriose (2 g, 3.9 mmol) in DMF (35 mL) was warmed up to 40 °C, then PPh_3 (9.4 g, 35.7 mmol) and CCl_4 (3.6 mL, 35.7 mmol) were added. The reaction mixture was stirred for 5 h, and then quenched by the addition of water (5 mL). After concentration under diminished pressure, the residue was diluted in water (30 mL). The aq layer was washed with EtOAc (30 mL) and evaporated under diminished pressure to afford crude trichloro-6^{I-III}-trideoxy-maltotriose which was diluted in pyridine (50 mL). Ac_2O (20 mL) was added and the solution was stirred at room temperature for 24 h. After concentration in vacuum, the residue was diluted in EtOAc (30 mL) and the organic solution was washed with water (30 mL). The aq solution was extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried (Na_2SO_4) and concentrated in vacuum to dryness. The residue was purified by flash chromatography (hexane/ethyl acetate, 7:3, v/v then 3:2, v/v) to afford **1** (3.4 g, 95%) as a white powder (66:34 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.9, 169.6, 169.3, 169.2, 168.9, 168.8 (CH_3CO), 95.4, 95.3 (C-1^{II-III}), 91.1 (C-1β^{I}), 88.9 (C-1α^{I}), 75.1, 73.0, 71.9, 71.6, 71.4, 71.1, 70.9, 70.3, 69.8, 69.6, 69.5, 69.2, 69.1 (C-2^{I-III}, C-3^{I-III}, C-4^{I-III}, C-5^{I-III}), 44.5, 44.4, 44.1, 43.3 (C-6^{I-III}), 20.8, 20.6, 20.4, 20.3 (CH_3CO); HRESIMS: calcd for $C_{34}H_{45}Cl_3NaO_{21}$ 917.1417, found *m/z* 917.1426 [M+Na]$^+$. Anal. Calcd for $C_{34}H_{45}Cl_3O_{21}$: C, 45.57; H, 5.06. Found C, 45.21; H, 5.07.

3.3. 2,3,4-Tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-deoxy-6-iodo-D-glucopyranose (2)

To a solution of **1** (1 g, 1.1 mmol) in butanone (30 mL) was added NaI (5 g, 33.5 mmol). The reaction mixture was stirred at 90 °C for 96 h. The solvent was removed by concentration under diminished pressure. The residue was diluted in EtOAc (20 mL) then washed with water (20 mL). The aq layer was extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried (Na_2SO_4) and concentrated in vacuum to dryness. The residue was purified by flash chromatography (hexane/ethyl acetate, 3:2, v/v then 1:1, v/v) to give **2** (1.1 g, 85%) as a white powder (45:55 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.3, 169.9, 169.8, 169.7, 169.6, 169.3, 169.2, 168.8, 168.1 (CH_3CO), 95.4, 95.3, 95.2, 95.1 (C-1^{II-III}), 90.7 (C-1β^{I}), 88.7 (C-1α^{I}), 76.4, 76.2, 76.1, 74.6, 72.2, 71.5, 70.8, 70.7, 70.5, 70.2, 70.1, 69.6, 69.4, 69.0, 68.9, 68.7 (C-2^{I-III}, C-3^{I-III}, C-4^{I-III}, C-5^{I-III}), 20.9, 20.8, 20.7, 20.6, 20.5, 20.3 (CH_3CO), 8.6, 8.5, 7.8, 6.9, 5.2, 5.0 (C-6^{I-III}); HRESIMS: calcd for $C_{34}H_{45}I_3NaO_{21}$ 1192.9485, found *m/z* 1192.9481 [M+Na]$^+$. Anal. Calcd for $C_{34}H_{45}I_3O_{21}$: C 34.89, H 3.88. Found C, 35.08; H, 3.76.

3.4. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (6) and methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (7)

A solution of methyl β-D-maltotrioside[22] (1 g, 1.93 mmol) and trityl chloride (2.69 g, 9.65 mmol) in pyridine (45 mL) was stirred at 40 °C for 4 days. Then, acetic anhydride (16 mL) was added. The reaction mixture was stirred for two additional days, then quenched by the addition of MeOH (16 mL) at 0 °C. After concentration under diminished pressure, the residue was diluted in EtOAc (40 mL) and the organic solution washed successively with 20% aq $KHSO_4$ (15 mL), satd aq $NaHCO_3$ (15 mL) and water (15 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated under diminished pressure. The residue was subjected to flash chromatography (hexane/ethyl acetate, 3:2, v/v) to give

first pure **6** (930 mg, 36%), then derivative **7** (570 mg, 22%). Data for **6** $[\alpha]_D$ +73 (*c* 0.11, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.24 (30H, $(C_6H_5)_3C$), 5.44 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1^{III}), 5.38 (m, 2H, H-3^{III}, H-4^{III}), 5.26 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.8 Hz, H-3^{II}), 5.22 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.1 Hz, H-3^{I}), 5.18 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{II}), 4.99 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2^{III}), 4.87 (dd, 1H, $J_{1,2}$ 8.1 Hz, H-2^{I}), 4.71 (dd, 1H, H-2^{II}), 4.43 (d, 1H, H-1^{I}), 3.93–3.80 (m, 3H, H-4^{I}, H-4^{II}, H-6a^{II}), 3.68 (dd, 1H, $J_{5,6}$ 3.4 Hz, $J_{6a,6b}$ 12.4 Hz, H-6b^{II}), 3.66–3.60 (m, 4H, H-5^{III}, OCH_3), 3.53–3.50 (m, 3H, H-5^{I}, H-6a^{I}, H-6b^{I}), 3.41 (m, 1H, H-5^{II}), 3.21 (d, 1H, $J_{6a,6b}$ 10.1 Hz, H-6a^{III}), 2.88 (dd, 1H, $J_{5,6}$ 2.7 Hz, H-6b^{III}), 2.12, 2.07, 2.06, 2.05, 2.00, 1.77, 1.68 (8s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.2, 168.8 (CH_3CO), 143.6–127.1 (C_6H_5), 101.0 (C-1^{I}), 95.7 (C-1^{III}), 95.3 (C-1^{II}), 86.9, 86.3 (($C_6H_5)_3C$), 75.5 (C-3^{I}), 74.2 (C-4^{I}), 73.9 (C-5^{I}), 72.3 (C-2^{I}), 71.9 (C-3^{II}), 71.7 (C-4^{I,II}), 70.4 (C-2^{II}), 70.1 (C-2^{III}, C-3^{III}), 69.6 (C-5^{III}), 68.6 (C-5^{II}), 68.1 (C-4^{III}), 63.7 (C-6^{I}), 62.3 (C-6^{II}), 60.5 (C-6^{III}), 56.7 (OCH_3), 20.7 (CH_3CO); HRESIMS calcd for $C_{73}H_{78}O_{24}Na$ 1361.4781, found *m/z* 1361.4738 $[MNa]^+$. Anal. Calcd for $C_{73}H_{78}O_{24}$: C, 65.46; H, 5.87. Found C, 65.36; H, 6.19. Data for **7** $[\alpha]_D$ +24 (*c* 0.14, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.01 (30H, $(C_6H_5)_3C$), 5.44 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{III}), 5.39–5.23 (m, 4H, H-1^{II}, H-3^{I},H-3^{II}, H-4^{III}), 5.02 (t, 1H, $J_{3,4}$ = $J_{2,3}$ 10.0 Hz, H-3^{III}), 4.90–4.82 (m, 3H, H-2^{I}, H-2^{II}, H-2^{III}), 4.45–4.43 (m, 2H, H-1^{I}, H-6a^{I}), 4.28 (dd, 1H, $J_{5,6}$ 3.6 Hz, $J_{6a,6b}$ 12.1 Hz, H-6b^{I}), 4.13–4.00 (m, 2H, H-4^{II}, H-5^{II}), 3.94 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.1 Hz, H-4^{I}), 3.66 (m, 1H, H-5^{I}), 3.53–3.46 (m, 4H, H-6a^{III}, OCH_3), 3.26–3.20 (m, 2H, H-5^{III}, H-6b^{III}), 3.12 (d, 1H, $J_{6a,6b}$ 10.1 Hz, H-6a^{II}), 2.43 (dd, 1H, $J_{5,6}$ 1.6 Hz, H-6b^{II}), 2.07, 2.05, 2.04, 2.02, 1.95, 1.85, 1.68 (8s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.0, 169.8, 169.7, 169.6, 168.3 (CH_3CO), 143.5–126.8 (C_6H_5), 101.0 (C-1^{I}), 95.4 (C-1^{II}), 94.8 (C-1^{III}), 86.7, 86.0 (($C_6H_5)_3C$), 74.8 (C-3^{I}), 74.1 (C-4^{I}), 72.3 (C-5^{I}), 72.2 (C-3^{II}), 71.9 (C-2^{II}), 71.2 (C-4^{II}), 70.9 (C-2^{I}), 70.4 (C-5^{II}), 70.1 (C-2^{III}), 69.8 (C-3^{III}), 69.0 (C-5^{III}), 67.4 (C-4^{III}), 62.7 (C-6^{I}), 62.4 (C-6^{III}), 60.6 (C-6^{II}), 56.7 (OCH_3), 20.9, 20.8, 20.6, 20.5, 20.4, 20.3 (CH_3CO); HRESIMS calcd for $C_{73}H_{78}O_{24}Na$ 1361.4781, found *m/z* 1361.4768 $[M+Na]^+$. Anal. Calcd for $C_{73}H_{78}O_{24}$: C, 65.46; H, 5.87. Found C, 64.87; H, 5.88.

3.5. Methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-β-D-glucopyranoside (8)

A mixture of compound **6** (80 mg, 0.06 mmol) and $FeCl_3{\cdot}6H_2O$ (70 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. Then, the solution was diluted with CH_2Cl_2 (20 mL) and washed with water (3 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under diminished pressure. The residue was subjected to flash chromatography (hexane/ethyl acetate, 1:4, v/v) to give **8** (50 mg, 98%). $[\alpha]_D$ +80 (*c* 0.15, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.39–5.29 (m, 3H, H-1^{III}, H-3^{II}, H-4^{III}), 5.27 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{II}), 5.23 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.5 Hz, H-3^{I}), 4.93 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.8 Hz, H-3^{III}), 4.77 (dd, 1H, $J_{1,2}$ 3.9 Hz, $J_{2,3}$ 10.2 Hz, H-2^{III}), 4.73 (dd, 1H, $J_{1,2}$ 7.8 Hz, H-2^{I}), 4.66 (dd, 1H, $J_{2,3}$ 10.2 Hz, H-2^{II}), 4.44 (dd, 1H, $J_{5,6}$ 1 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a^{II}), 4.41 (d, 1H, H-1^{I}), 4.18 (dd, 1H, $J_{5,6}$ 2.9 Hz, H-6b^{II}), 4.09 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4^{I}), 3.95–3.85 (m, 3H, H-4^{II}, H-5^{II}, H-6a^{III}), 3.81 (m, 1H, H-6b^{III}), 3.69 (m, 1H, H-5^{III}), 3.61–3.47 (m, 3H, H-5^{I}, H-6a^{I}, H-6b^{I}), 3.45 (s, 3H, OCH_3), 2.08, 2.00, 1.96, 1.95, 1.93 (5s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 170.7, 170.6, 170.5, 170.3, 170.1, 169.8, 169.6 ($COCH_3$), 101.3 (C-1^{I}), 95.7 (C-1^{III}), 95.2 (C-1^{II}), 75.2 (C-3^{I}), 74.4 (C-5^{I}), 72.3 (C-5^{II}), 72.1 (C-2^{I}), 71.8 (C-4^{III}), 71.3 (C-4^{I}), 70.6 (C-5^{III}), 70.5 (C-2^{II}), 70.1 (C-2^{III}), 69.0 (C-3^{III}), 68.6 (C-4^{II}), 68.6 (C-3^{III}), 62.7 (C-6^{II}), 61.0 (C-6^{III}), 60.8 (C-6^{I}), 56.9 (OCH_3), 20.7, 20.5, 20.4 ($COCH_3$); HRESIMS calcd for $C_{35}H_{50}O_{24}Na$ 877.2590, found *m/z* 877.2568 $[M+Na]^+$. Anal. Calcd for $C_{35}H_{50}O_{24}$: C, 49.18; H, 5.90; Found C, 48.81; H, 6.01.

3.6. Methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (9)

Compound **7** (110 mg, 0.08 mmol) was treated as described for the synthesis of **8** to afford the desired maltotrioside derivative **9** (50 mg, 71 %). $[\alpha]_D$ +34 (*c* 0.15, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.5 Hz, H-3^{II}), 5.32 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1^{III}), 5.29 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.9 Hz, H-4^{III}), 5.20 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1^{II}), 5.16 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.2 Hz, H-3^{I}), 4.83 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.9 Hz, H-3^{III}), 4.77–4.67 (m, 3H, H-2^{I}, H-2^{II}, H-2^{III}), 4.41 (dd, 1H, $J_{5,6}$ 2.5 Hz, $J_{6\ a,6b}$ 12.1 Hz, H-6a^{I}), 4.36 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^{I}), 4.12 (dd, 1H, $J_{5,6}$ 3.9 Hz, H-6b^{I}), 4.09 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4^{II}), 3.90 (t, 1H, $J_{4,5}$ 9.2 Hz, H-4^{I}), 3.82–3.58 (m, 5H, H-5^{I}, H-5^{II}, H-5^{III}, H-6a^{II}, H-6b^{II}), 3.54–3.44 (m, 2H, H-6a^{III}, H-6b^{III}), 3.39 (s, 3H, OCH_3), 2.06, 1.96, 1.95, 1.94, 1.92, 1.91, 1.89 (8s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.0, 169.9, 169.8, 169.7, 169.6 ($COCH_3$), 100.8 (C-1^{I}), 95.7 (C-1^{II}), 95.4 (C-1^{III}), 75.2 (C-3^{I}), 73.1 (C-4^{I}), 71.9 (C-2^{I}, C-3^{II}), 71.7 (C-5^{I}), 71.1 (C-5^{II}), 70.9 (C-5^{III}), 70.5 (C-4^{II}), 70.3 (C-2^{II}), 70.0 (C-2^{III}), 69.2 (C-4^{III}), 68.6 (C-3^{III}), 62.7 (C-6^{I}), 61.0 (C-6^{III}), 59.6 (C-6^{II}), 56.8 (OCH_3), 20.8, 20.7, 20.6, 20.5, 20.4, 20.3, 20.2 ($COCH_3$); HRESIMS calcd for $C_{35}H_{50}O_{24}Na$ 877.2590, found *m/z* 877.2603 $[M+Na]^+$. Anal. Calcd for $C_{35}H_{50}O_{24}$: C, 49.18; H, 5.90. Found C, 48.59; H, 5.76.

3.7. Methyl 2,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-chloro-6-deoxy-β-D-glucopyranoside (10)

A mixture of compound **8** (50 mg, 0.06 mmol), PPh_3 (100 mg, 0.36 mmol), CCl_4 (50 μL, 0.36 mmol) in DMF (30 mL) was stirred at 80 °C for 5 h. After concentration under diminished pressure, the residue was diluted in EtOAc (10 mL) and the organic solution washed with water (3 × 5 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated under diminished pressure. The residue was subjected to flash chromatography (hexane/ethyl acetate, 1:1, v/v) to afford **10** (34 mg, 66%). $[\alpha]_D$ +16 (*c* 0.11, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.44 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1^{III}), 5.41–5.34 (m, 2H, H-3^{II}, H-4^{III}), 5.33 (t, 1H, $J_{1,2}$ 4.1 Hz, H-1^{II}), 5.26 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.1 Hz, H-3^{I}), 5.06 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, H-3^{III}), 4.84 (dd, 1H, $J_{2,3}$ 10.5 Hz, H-2^{III}), 4.81 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.1 Hz, H-2^{I}), 4.74 (dd, 1H, $J_{2,3}$ 10.3 Hz, H-2^{II}), 4.49 (m, 2H, H-1^{I}, H-6a^{II}), 4.25 (dd, 1H, $J_{5,6b}$ 3.2 Hz, $J_{6a,6b}$ 12.3 Hz, H-6b^{II}), 4.11 (t, 1H, $J_{4,5}$ 9.1 Hz, H-4^{I}), 4.03–3.93(m, 4H, H-4^{II}, H-5^{II},H-5^{III}, H-6a^{I}), 3.87 (dd, 1H, $J_{5,6b}$ 3.6 Hz, $J_{6a,6b}$ 12.4 Hz, H-6b^{I}), 3.79 (m, 1H, H-5^{I}), 3.60–3.54 (m, 2H, H-6a^{III}, H-6b^{III}), 3.51 (s, 3H, OCH_3), 2.14, 2.05, 2.02, 2.01, 2.00, 1.98 (6s, 24H, $OCOCH_3$); ^{13}C NMR(75 MHz, $CDCl_3$): δ 170.5, 170.1 (CH_3CO), 100.9 (C-1^{I}), 95.5 (C-1^{III}), 95.3 (C-1^{II}), 75.1 (C-3^{I}), 72.9 (C-4^{I}), 72.7 (C-5^{I}), 72.3 (C-5^{III}), 72.0 (C-2^{I}), 71.7 (C-4^{III}), 70.3 (C-2^{II}), 69.9 (C-2^{III}), 69.5 (C-4^{II}), 69.3 (C-3^{II}), 69.1 (C-3^{III}), 68.9 (C-5^{II}), 62.7 (C-6^{II}), 57.0 (OCH_3), 44.2 (C-6^{I}), 43.2 (C-6^{III}), 20.9, 20.6 (CH_3CO); HRESIMS calcd for $C_{35}H_{48}Cl_2O_{22}Na$ 913.1912, found *m/z* 913.1906 $[M+Na]^+$. Anal. Calcd for $C_{35}H_{48}Cl_2O_{22}$: C, 47.15; H, 5.43. Found C, 47.74; H, 5.76.

3.8. Methyl 2,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (11)

Compound **9** (50 mg, 0.06 mmol) was treated as described for the synthesis of **10** to afford **11** (40 mg, 77%). $[\alpha]_D$ +36 (*c* 0.22, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.45 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1^{III}), 5.43–5.34 (m, 2H, H-3^{II}, H-4^{III}), 5.31 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1^{II}), 5.23 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.0 Hz, H-3^{I}), 5.11 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.7 Hz, H-3^{III}), 4.83 (dd, 1H, H-2^{III}), 4.78 (dd, 1H, $J_{1,2}$ 7.7 Hz, H-2^{I}),

4.73 (dd, 1H, $J_{2,3}$ 10.3 Hz, H-2^{II}), 4.48–4.41 (m, 2H, H-6a^{I}, H-1^{I}), 4.24 (dd, 1H, $J_{5,6b}$ 4.2 Hz, $J_{6a,6b}$ 12.1 Hz, H-6b^{I}), 4.06–4.04 (m, 2H, H-4^{II}, H-5^{II}), 4.01 (t, 1H, H-5^{III}), 3.95 (t, 1H, $J_{4,5}$ 9.0 Hz, H-4^{I}), 3.89 (dd, 1H, $J_{5,6}$< 1 Hz,$J_{6a,6b}$ 11.9 Hz, H-6a^{II}), 3.80 (dd, 1H, $J_{5,6}$< 1 Hz, H-6b^{II}), 3.74 (dd, 1H, $J_{5,6}$ 2.7 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a^{III}), 3.67 (m, 1H, H-5^{I}), 3.58 (dd, 1H, $J_{5,6}$ 3.8 Hz, H-6b^{III}), 3.47 (s, 3H, OCH_3), 2.14, 2.05, 2.03, 2.00, 1.99, 1.98, 1.97 (7s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.1, 169.9, 169.7, 169.2 (CH_3CO), 100.9 (C-1^{I}), 95.8 (C-1^{II}), 95.3 (C-1^{III}), 75.3 (C-3^{I}), 73.8 (C-4^{I}), 72.1, 72.0, 71.9 (C-2^{I}, C-4^{II}, C-5^{I}), 71.3 (C-3^{II}), 70.3 (C-2^{II}), 69.9 (C-2^{III}), 69.4 (C-5^{III}), 69.2 (C-4^{III}, C-5^{II}), 69.1 (C-3^{III}), 62.9 (C-6^{I}), 57.0 (OCH_3), 44.3 (C-6^{II}), 43.3 (C-6^{III}), 20.9, 20.6, 20.5, 20.4 (CH_3CO); HRESIMS calcd for $C_{35}H_{48}Cl_2O_{22}Na$ 913.1912, found *m*/z 913.1926 [M+Na]$^+$. Anal. Calcd for $C_{35}H_{48}Cl_2O_{22}$: C, 47.15; H, 5.43. Found C, 46.69; H, 5.44.

3.9. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranoside (12)

A solution of compound **8** (100 mg, 0.12 mmol) and methanesulfonic anhydride (204 mg, 1.17 mmol) in pyridine (3 mL) was stirred overnight at room temperature. The excess of methanesulfonic anhydride was destroyed by addition of methanol (3 mL), and solvents were removed under diminished pressure. The residue was diluted in EtOAc (20 mL) and the organic solution washed successively with 20% aq $KHSO_4$ (10 mL), satd aq $NaHCO_3$ (10 mL) and water (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was then evaporated and replaced by butanone (10 mL). NaI (350 mg, 2.34 mmol) was added and the reaction mixture was stirred at reflux overnight. After concentration under reduced pressure, the residue was diluted in EtOAc (20 mL) and the organic solution washed with water (3 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The resulting crude product was purified on silica gel (hexane/ethyl acetate, 1:1, v/v) to afford **12** (117 mg, 93%). $[\alpha]_D$ +29 (*c* 0.21, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38–5.30 (m, 3H, H-1^{III}, H-3^{II}, H-4^{III}), 5.27 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{II}), 5.25 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.0 Hz, H-3^{I}), 4.86 (t, 1H, $J_{2,3}$ 9.6 Hz, H-3^{III}), 4.82–4.72 (m, 3H, H-2^{I}, H-2^{II}, H-2^{III}), 4.54 (dd, 1H, $J_{5,6}$ 2.3 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a^{II}), 4.49 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{I}), 4.34 (dd, 1H, $J_{5,6}$ 4.0 Hz, H-6b^{II}), 3.93 (m, 1H, H-5^{II}), 3.89 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.7 Hz, H-4^{I}), 3.81 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.0 Hz, H-4^{I}), 3.70–3.65 (m, 2H, H-5^{III}, H-6a^{I}), 3.51 (s, 3H, OCH_3), 3.37–3.35 (m, 2H, H-5^{I}, H-6b^{I}), 3.28 (dd, 1H, $J_{5,6}$ 2.6 Hz,$J_{6a,6b}$ 11.2 Hz, H-6a^{III}), 3.11 (dd, 1H, $J_{5,6}$ 6.4 Hz, H-6b^{III}), 2.14, 2.04, 2.03, 2.01, 1.99, 1.97, 1.96 (7s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 170.1, 169.9, 169.8, 169.7, 169.4 ($COCH_3$), 100.7 (C-1^{I}), 95.6 (C-1^{II}), 95.4 (C-1^{III}), 77.6 (C-4^{I}), 74.9 (C-3^{I}), 73.3 (C-4^{II}), 72.3 (C-5^{I}), 72.2 (C-3^{III}), 72.1 (C-2^{III}), 71.3 (C-3^{II}), 70.4 (C-2^{I}), 70.2 (C-2^{II}), 69.4 (C-5^{II}), 69.2 (C-5^{III}), 68.9 (C-4^{III}), 63.3 (C-6^{II}), 57.1 (OCH_3), 21.1, 21.0, 20.9, 20.8, 20.7, 20.6 ($COCH_3$), 6.2 (C-6^{I}), 4.2 (C-6^{III}); HRESIMS calcd for $C_{35}H_{48}I_2O_{22}Na$ 1097.0624, found *m*/z 1097.0584 [M+Na]$^+$. Anal. Calcd for $C_{35}H_{48}I_2O_{22}$: C, 39.12; H, 4.50. Found C, 38.86; H, 4.24.

3.10. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (13)

Compound **9** (425 mg, 0.49 mmol) was treated as described for the synthesis of **12** to afford the desired maltotrioside derivative **13** (507 mg, 95 %). $[\alpha]_D$ +38 (*c* 0.11, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 8.9 Hz, H-3^{II}), 5.39 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1^{III}), 5.32 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.5 Hz, H-4^{III}), 5.26 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{II}), 5.21 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.1 Hz, H-3^{I}), 4.90 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.5 Hz, H-3^{III}), 4.81 (dd, 1H, H-2^{III}), 4.76 (dd, 1H, $J_{1,2}$ 7.7 Hz, H-2^{I}), 4.69 (dd, 1H, $J_{2,3}$ 10.4 Hz, H-2^{II}), 4.46 (dd, 1H, $J_{5,6}$ 3.5 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a^{I}), 4.41 (d, 1H, H-1^{I}), 4.32 (dd, 1H, $J_{5,6}$ 4.4 Hz, H-6b^{I}), 3.94 (t, 1H, $J_{3,4}$ = $J_{4,5}$ 9.1 Hz, H-4^{I}), 3.79 (t, 1H, $J_{4,5}$ 8.9 Hz, H-4^{II}), 3.68 (m, 1H, H-5^{I}), 3.62 (m, 1H, H-5^{III}), 3.56 (m, 1H, H-5^{II}), 3.51–3.43 (m, 6H, H-6a^{II}, H-6b^{II}, H-6a^{III}, OCH_3), 3.16 (dd, 1H, $J_{5,6}$ 5.4 Hz, $J_{6a,6b}$ 11.3 Hz, H-6b^{III}), 2.12, 2.03, 2.01, 1.98, 1.96 (5s, 24H, $OCOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.3, 170.1, 169.8, 169.6, 169.2 ($COCH_3$), 100.9 (C-1^{I}), 95.6 (C-1^{II}), 95.3 (C-1^{III}), 76.1 (C-4^{II}), 75.1 (C-3^{I}), 74.0 (C-4^{I}), 72.3 (C-5^{I}), 72.2 (C-3^{III}), 72.0 (C-2^{I}, C-5^{I}), 70.8 (C-3^{II}), 70.4 (C-2^{III}), 70.0 (C-2^{II}), 68.7 (C-4^{III}, C-5^{III}), 68.5 (C-5^{II}), 63.1 (C-6^{I}), 56.9 (OCH_3), 20.8, 20.6, 20.5 ($COCH_3$), 7.4 (C-6^{II}), 4.9 (C-6^{III}); HRESIMS calcd for $C_{35}H_{48}I_2O_{22}Na$ 1097.0624, found *m*/z 1097.0637 [M+Na]$^+$. Anal. Calcd for $C_{35}H_{48}I_2O_{22}$: C, 39.12; H, 4.50. Found C, 39.85; H, 4.85.

3.11. 2,3,4-Tri-*O*-acetyl-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-deoxy-6-hexylthio-D-glucopyranose (14)

A solution of 1^{I},2$^{I–III}$,3$^{I–III}$,4^{III}-octa-*O*-acetyl-6$^{I–III}$-trideoxy-6$^{I–III}$-triiodo-maltotriose **2** (460 mg, 0.39 mmol), 1-hexanethiol (1.65 mL, 11.8 mmol) and Na_2CO_3 (1.15 g, 11.8 mmol) in DMF (10 mL) was stirred at 40 °C for 36 h. After concentration in vacuum, the residue was diluted in EtOAc (20 mL) and the organic solution was washed with water. The aq layer was extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried (Na_2SO_4) and evaporated under diminished pressure to afford crude 21 which was subjected to flash chromatography (hexane/ethyl acetate, 2:1, v/v then 3:2, v/v) to give pure **14** (400 mg, 90%) as a white powder (53:47 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 169.9, 169.8, 169.7, 169.6, 169.4, 169.0, 168.7 (CH_3CO), 95.6, 95.4, 95.1, 95.0 (C-1$^{II–III}$), 91.3 (C-1β^{I}), 88.7 (C-1α^{I}), 75.7, 75.0, 74.7, 74.6, 74.1, 73.9, 72.7, 72.0, 71.8, 71.6, 71.0, 70.9, 70.8, 70.7, 70.1, 70.1, 69.8, 69.3 (C-2$^{I–III}$, 3$^{I–III}$, 4$^{I–III}$, 5$^{I–III}$), 34.0, 33.8, 33.7, 33.5, 33.4, 33.3 (C-6$^{I–III}$), 31.4, 31.3, 29.6, 29.4, 29.3, 28.5, 28.3, 22.4 (3 × S(CH_2)$_5$$CH_3$), 20.9, 20.8, 20.6, 20.5, 20.3 (CH_3CO), 13.9 (3 × S(CH_2)$_5$$CH_3$); HRESIMS calcd for $C_{52}H_{84}NaO_{21}S_3$ 1163.4565, found *m*/z 1163.4546 [M+Na]$^+$. Anal. Calcd for $C_{52}H_{84}O_{21}S_3$: C, 54.72; H, 7.42. Found C, 54.13; H, 7.61.

3.12. 2,3,4-Tri-*O*-acetyl-6-deoxy-6-octylthio-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-octylthio-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-deoxy-6-octylthio-D-glucopyranose (15)

This was obtained from **2** and octanethiol as described for the synthesis of **14** in 89% yield as a white powder (35:65 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.0, 169.9, 169.8, 169.6, 169.5, 169.1, 168.8 (CH_3CO), 95.7, 95.6, 95.2 (C-1$^{II–III}$), 91.4 (C-1β^{I}), 88.8 (C-1α^{I}), 75.9, 75.1, 74.8, 74.7, 74.1, 74.0, 72.8, 72.1, 71.8, 71.1, 71.0, 70.7, 70.3, 70.2, 69.8, 69.4 (C-2$^{I–III}$, 3$^{I–III}$, 4$^{I–III}$, 5$^{I–III}$), 34.1, 33.9, 33.8, 33.6, 33.4 (C-6$^{I–III}$), 31.8, 29.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.9, 28.8, 22.6 (3 × S(CH_2)$_7$$CH_3$), 21.0, 20.9, 20.8, 20.7, 20.7, 20.6, 20.4 (CH_3CO), 14.0 (3 × S(CH_2)$_7$$CH_3$); HRESIMS calcd for $C_{58}H_{96}NaO_{21}S_3$ 1247.5504, found *m*/z 1247.5494 [M+Na]$^+$. Anal. Calcd for $C_{58}H_{96}O_{21}S_3$: C, 56.84; H, 7.90. Found C, 56.54; H, 8.18.

3.13. 2,3,4-Tri-*O*-acetyl-6-decylthio-6-deoxy-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-decylthio-6-deoxy-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-decylthio-6-deoxy-D-glucopyranose (16)

This was obtained from **2** and decanethiol as described for the synthesis of **14** in 85% yield as a white powder (45:55 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.0, 169.8, 169.7, 169.5,

169.1, 168.7 (CH_3CO), 95.7, 95.6, 95.2 (C-1^{II-III}), 91.4 (C-$1\beta^{I}$), 88.8 (C-$1\alpha^{I}$), 75.8, 75.1, 74.8, 74.7, 74.2, 74.0, 73.1, 72.8, 72.1, 71.9, 71.8, 79.2, 71.0, 70.7, 70.3, 70.2, 69.9, 69.4 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 34.1, 34.0, 33.2, 33.8, 33.6, 33.4 (C-6^{I-III}), 31.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.0, 28.9, 28.8, 22.6 ($3 \times S(CH_2)_9CH_3$), 21.0, 20.9, 20.8, 20.7, 20.6, 20.57, 20.4 (CH_3CO), 14.0 ($3 \times S(CH_2)_9CH_3$); HRESIMS calcd for $C_{64}H_{108}NaO_{21}S_3$ 1331.6443, found *m/z* 1331.6454 $[M+Na]^+$. Anal. Calcd for $C_{64}H_{108}O_{21}S_3$: C, 58.69; H, 8.31. Found C, 58.37; H, 8.63.

3.14. 2,3,4-Tri-*O*-acetyl-6-deoxy-6-dodecylthio-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-dodecylthio-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-deoxy-6-dodecylthio-D-glucopyranose (17)

This was obtained from **2** and dodecanethiol as described for the synthesis of **14** in 85% yield as a white powder (65:35 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.9, 169.8, 169.7, 169.6, 169.5, 169.4, 169.0, 168.7 (CH_3CO), 95.6, 95.5, 95.1 (C-1^{II-III}), 91.3 (C-$1\beta^{I}$), 88.7 (C-$1\alpha^{I}$), 75.7, 75.0, 74.7, 74.6, 74.1, 73.9, 72.7, 72.0, 71.8, 71.7, 71.0, 70.9, 70.8, 70.7, 70.1, 70.0, 69.8, 69.4 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 34.0, 33.9, 33.8, 33.7, 33.49, 33.3 (C-6^{I-III}), 31.8, 29.5, 29.2, 29.1, 28.9, 28.7, 28.4, 22.5 ($3 \times S(CH_2)_{11}CH_3$), 20.9, 20.8, 20.6, 20.5, 20.3 (CH_3CO), 14.0 ($3 \times S(CH_2)_{11}CH_3$); HRESIMS calcd for $C_{70}H_{120}NaO_{21}S_3$ 1415.7382, found *m/z* 1415.7426 $[M+Na]^+$. Anal. Calcd for $C_{70}H_{120}O_{21}S_3$: C, 60.32; H, 8.68. Found C, 59.83; H, 9.10.

3.15. 2,3,4-Tri-*O*-acetyl-6-deoxy-6-tetradecylthio-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-tetradecylthio-α-D-glucopyranosyl-(1→4)-1,2,3-tri-*O*-acetyl-6-deoxy-6-tetradecylthio-D-glucopyranose (18)

This was obtained from **2** and tetradecanethiol as described for the synthesis of **14** in 70% yield as a white powder (60:40 α/β mixture). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.2, 170.0, 169.7, 169.5, 169.4, 169.3, 168.9, 168.6 (CH_3CO), 95.6, 95.5, 95.0 (C-1^{II-III}), 91.2 (C-$1\beta^{I}$), 88.7 (C-$1\alpha^{I}$), 75.7, 74.9, 74.7, 74.1, 73.2, 72.7, 72.0, 71.7, 71.6, 71.0, 70.9, 70.8, 70.6, 70.3, 70.0, 69.8, 69.3 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 33.9, 33.8, 33.6, 33.4, 33.2 (C-6^{I-III}), 31.7, 29.5, 29.2, 28.9, 28.8, 28.7, 28.3, 28.2, 22.5 ($3 \times S(CH_2)_{13}CH_3$), 20.7, 20.5, 20.4, 20.2 (CH_3CO), 13.9 ($3 \times S(CH_2)_{13}CH_3$); HRESIMS calcd for $C_{76}H_{132}NaO_{21}S_3$ 1499.8321, found *m/z* 1499.8251 $[M+Na]^+$. Anal. Calcd for $C_{76}H_{132}O_{21}S_3$: C, 61.76; H, 9.00. Found C, 62.08; H, 9.19.

3.16. 6-Deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-hexylthio-D-glucopyranose (19)

To a solution of 6^{I-III}-trideoxy-6^{I-III}-trihexylthio-D-maltotriose **14** (130 mg, 0.11 mmol) in dry MeOH (8 mL) was added sodium methoxide (1 N in MeOH, 120 μL). The reaction mixture was stirred for 20 min, then neutralized with acidic resin (Amberlite IR 120) and filtered. Solvent was removed in vacuum to afford **19** (90 mg, 99%) as a white powder. ^{13}C NMR (75 MHz, CD_3OD): δ 103.2, 102.9 (C-1^{II-III}), 98.1(C-$1\beta^{I}$), 93.6 (C-$1\alpha^{I}$), 85.6, 85.2, 77.6, 76.8, 75.8, 75.1, 74.7, 74.4, 73.4, 71.3 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 34.9, 34.5, 34.0 (C-6^{I-III}), 32.7, 30.9, 30.8, 29.7, 23.7 ($3 \times S(CH_2)_5CH_3$), 14.5 ($3 \times S(CH_2)_5CH_3$); HRESIMS calcd for $C_{36}H_{68}NaO_{13}S_3$ 827.3720, found *m/z* 827.3683 $[M+Na]^+$.

3.17. 6-Deoxy-6-octylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-octylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-octylthio-D-glucopyranose (20)

To a solution of $1^{I},2^{I-III},3^{I-III},4^{III}$-octa-*O*-acetyl-$6^{I-III}$-trideoxy-$6^{I-III}$-trioctylthio-D-maltotriose **15** (160 mg, 0.13 mmol) in a mixture of dry MeOH (5 mL) and DMSO (5 mL) was added sodium methoxide (1 N in MeOH, 120 μL). The reaction mixture was stirred for 20 min, then neutralized with acidic resin (Amberlite IR 120) and filtered. Solvents were removed in vacuum and the residue was precipitated in diethyl ether. The suspension was centrifuged to afford, after centrifugation, the compound **20** (110 mg, 99%) as a white powder. ^{13}C NMR (75 MHz, CD_3OD): δ 103.3, 103.0 (C-1^{II-III}), 98.1 (C-$1\beta^{I}$), 93.6 (C-$1\alpha^{I}$), 85.7, 85.3, 77.6, 76.8, 75.8, 75.1, 74.8, 74.4, 74.0, 73.8, 73.4, 71.3 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 35.1, 34.5, 34.2 (C-6^{I-III}), 33.1, 31.0, 30.9, 30.5, 30.1, 30.0, 23.8 ($3 \times S(CH_2)_7CH_3$), 14.5 ($3 \times S(CH_2)_7CH_3$); HRESIMS calcd for $C_{42}H_{80}NaO_{13}S_3$ 911.4659, found *m/z* 911.4625 $[M+Na]^+$.

3.18. 6-Decylthio-6-deoxy-α-D-glucopyranosyl-(1→4)-6-decylthio-6-deoxy-α-D-glucopyranosyl-(1→4)-6-decylthio-6-deoxy-D-glucopyranose (21)

This was obtained from **16** as described for the synthesis of **20** in 99% yield. ^{13}C NMR (75 MHz, DMSO-d_6): δ 101.9, 101.3 (C-1^{II-III}), 96.8 (C-$1\beta^{I}$), 92.1 (C-$1\alpha^{I}$), 84.7, 84.1, 83.9, 76.0, 74.4, 74.3, 73.5, 72.9, 72.7, 72.0, 71.7, 69.4 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 33.8, 33.6, 33.5 (C-6^{I-III}), 32.8, 32.4, 31.5, 29.5, 29.2, 28.9, 28.5, 28.4, 22.2 ($3 \times S(CH_2)_9CH_3$), 14.0 ($3 \times S(CH_2)_9CH_3$); HRESIMS calcd for $C_{48}H_{92}NaO_{13}S_3$ 995.5598, found *m/z* 995.5588 $[M+Na]^+$.

3.19. 6-Deoxy-6-dodecylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-dodecylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-dodecylthio-D-glucopyranose (22)

This was obtained from **17** as described for the synthesis of **20** in 99% yield. ^{13}C NMR (75 MHz, DMSO-d_6): δ 101.6, 101.0 (C-1^{II-III}), 96.5(C-$1\beta^{I}$), 91.8 (C-$1\alpha^{I}$), 84.3, 83.7, 83.5, 75.8, 74.0, 73.1, 72.6, 72.4, 71.8, 71.5, 71.3, 69.1 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 33.6, 33.3, 33.0 (C-6^{I-III}), 32.5, 32.0, 31.1, 29.1, 28.9, 28.6, 28.1, 21.9 ($3 \times S(CH_2)_{11}CH_3$), 13.7 ($3 \times S(CH_2)_{11}CH_3$); HRESIMS calcd for $C_{54}H_{104}NaO_{13}S_3$ 1079.6537, found *m/z* 1079.6570 $[M+Na]^+$.

3.20. 6-Deoxy-6-tetradecylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-tetradecylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-tetradecylthio-D-glucopyranose (23)

This was obtained from **18** as described for the synthesis of **20** in 99% yield. A mixture of DMF/MeOH (1:2 v/v) as solvent was used instead of DMSO/MeOH. ^{13}C NMR (75 MHz, DMSO-d_6, 70 °C): δ 101.3, 100.8 (C-1^{II-III}), 96.6 (C-$1\beta^{I}$), 91.8 (C-$1\alpha^{I}$), 83.9, 83.4, 83.2, 75.9, 74.3, 73.0, 72.8, 72.4, 71.8, 71.7, 71.2, 69.3 (C-2^{I-III}, 3^{I-III}, 4^{I-III}, 5^{I-III}), 33.7, 33.6, 33.2 (C-6^{I-III}), 32.5, 32.1, 30.9, 29.1, 29.0, 28.6, 28.3, 28.3, 27.9, 21.6 ($3 \times S(CH_2)_{13}CH_3$), 13.3 ($3 \times S(CH_2)_{13}CH_3$); HRESIMS calcd for $C_{60}H_{116}NaO_{13}S_3$ 1163.7476, found *m/z* 1163.7445 $[M+Na]^+$.

3.21. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-hexyltio-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-hexylthio-β-D-glucopyranoside (24)

A solution of the diiodo derivative **12** (645 mg, 0.6 mmol), 1-hexanethiol (1.69 mL, 12 mmol) and Na_2CO_3 (1.27 g, 12 mmol) in DMF (20 mL) was stirred at 80 °C for 24 h. After concentration in vacuum, the residue was diluted in EtOAc (20 mL) and the organic solution was washed with water (3 × 10 mL). The aq layer was extracted with EtOAc (3 × 10 mL). The organic layers were

combined, dried over Na_2SO_4 and evaporated under diminished pressure to afford crude **24** which was subjected to flash chromatography (hexane/ethyl acetate, 3:2, v/v) to give pure **24** (280 mg, 44%). $[\alpha]_D$ +56 (*c* 0.13, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.36–5.32 (m, 3H, H-1^{III}, H-3^{II}, H-4^{III}), 5.28 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1^{II}), 5.24 (t, 1H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3^{I}), 5.02 (t, 1H, $J_{2,3} = J_{3,4}$ 9.6 Hz, H-3^{III}), 4.83–4.77 (m, 2H, H-2^{I}, H-2^{III}), 4.74 (dd, 1H, $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 10.3 Hz, H-2^{II}), 4.50 (dd, 1H, $J_{5,6}$ < 1 Hz, $J_{6a,6\ b}$ 12.3 Hz, H-6a^{II}), 4.42 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{I}), 4.30 (dd, 1H, $J_{5,6}$ 2.9 Hz, H-6b^{II}), 4.02 (t, 1H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4^{I}), 3.97–3.91 (m, 3H, H-4^{II}, H-5^{II}, H-5^{III}), 3.71 (ddd, 1H, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 6.0 Hz, $J_{6a,6b}$ 14.4 Hz, H-5^{I}), 3.48 (s, 3H, OCH_3), 3.01 (dd, 1H, H-6a^{I}), 2.83 (dd, 1H, H-6b^{I}), 2.68 (t, 2H, $J_{H,H}$ 6.8 Hz, S*CH*$_2$(CH$_2$)$_4$CH$_3$), 2.61 (m, 2H, H-6^{III}), 2.53 (t, 2H, $J_{H,H}$ 7.4 Hz, S*CH*$_2$(CH$_2$)$_4$CH$_3$), 2.16, 2.05, 2.02, 2.01, 1.99, 1.98, 1.97 (7s, 24H, $OCOCH_3$), 1.31 (m, 16H, 2 × SCH$_2$(*CH*$_2$)$_4$CH$_3$), 0.87 (t, 6H, $J_{H,H}$ 3.0 Hz, 2 × SCH$_2$(CH$_2$)$_4$*CH*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 170.2, 169.9, 169.8, 169.7, 169.6 (*C*OCH$_3$), 101.0 (C-1^{I}), 95.5 (C-1^{II}), 95.2 (C-1^{III}), 75.3 (C-3^{I},C-4^{I}), 75.1 (C-5^{I}), 72.7 (C-5^{II}), 72.2 (C-2^{I}), 71.8 (C-3^{II}), 71.0 (C-3^{III}), 70.5 (C-2^{III}), 70.4 (C-2^{II}), 70.2 (C-5^{III}), 69.3 (C-4^{III}), 69.1 (C-4^{II}), 63.2 (C-6^{II}), 56.7 (OCH_3), 33.8, 33.7 (2 × SCH$_2$(CH$_2$)$_4$CH$_3$), 33.6 (C-6^{III}), 33.5 (C-6^{I}), 31.4, 29.6, 29.5, 28.5, 28.4, 22.5 (2 × SCH$_2$(*CH*$_2$)$_4$CH$_3$), 21.0, 20.9, 20.8, 20.6, 20.5 (CO*CH*$_3$), 14.0 (2 × S(CH$_2$)$_5$*CH*$_3$); HRESIMS calcd for $C_{47}H_{74}O_{22}Na_{32}S_2$ 1077.4011, found *m/z* 1077.4023 $[M+Na]^+$. Anal. Calcd for $C_{47}H_{74}O_{22}S_2$: C, 53.50; H, 7.07. Found C, 53.40; H, 7.50.

3.22. Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (25)

This was obtained from **13** as described for the synthesis of **24** in 37% yield. A mixture hexane/ethyl acetate (1:4, v/v) was used for flash chromatography. $[\alpha]_D$ +40 (*c* 0.11, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.30–5.11 (m, 5H, H-1^{II}, H-1^{III}, H-3^{I}, H-3^{II}, H-4^{III}), 4.91 (t, 1H, $J_{2,3} = J_{3,4}$ 9.7 Hz, H-3^{III}), 4.73–4.68 (m, 2H, H-2^{I}, H-2^{III}), 4.59 (m, 1H, H-2^{II}), 4.42 (dd, 1H, $J_{5,6}$ 2.6 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a^{I}), 4.34 (d, 1H, $J_{1,2}$ 6.7 Hz, H-1^{I}), 4.32 (dd, 1H, H-6b^{II}), 3.98–3.77 (m, 4H, H-4^{I}, H-4^{II}, H-5^{II}, H-5^{III}), 3.61 (m, 1H, H-5^{I}), 3.38 (s, 3H, OCH_3), 2.82–2.42 (m, 8H, H-6a^{II}, H-6b^{II}, H-6a^{III}, H-6b^{III}, 2 × S*CH*$_2$(CH$_2$)$_4$CH$_3$), 2.05 (s, 3H, $OCOCH_3$), 1.92–1.88 (m, 21H, $OCOCH_3$), 1.52–1.19 (m, 16H, 2 × SCH$_2$(*CH*$_2$)$_4$CH$_3$), 0.78 (m, 6H, 2 × S(CH$_2$)$_5$*CH*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 170.2, 170.0, 169.8, 169.5, 169.4, 169.2 (*C*OCH$_3$), 100.8 (C-1^{I}), 95.1 (C-1^{II}), 95.0 (C-1^{III}), 74.9 (C-3^{I}), 74.3 (C-4^{II}), 73.8 (C-4^{II}), 71.9 (C-5^{I}, C-2^{I}), 71.4 (C-4^{III}), 70.9 (C-5^{II}), 70.7 (C-3^{III}), 70.6 (C-2^{II}), 70.2 (C-5^{III}), 69.9 (C-2^{III}), 69.1 (C-3^{II}), 63.1 (C-6^{I}), 56.6 (OCH_3), 34.0 (C-6^{II}), 33.7, 33.5 (2 × SCH$_2$(CH$_2$)$_4$CH$_3$), 33.1 (C-6^{III}), 31.2, 29.4, 29.3, 28.3, 28.2, 22.2 (2 × SCH$_2$(*CH*$_2$)$_4$CH$_3$), 20.6, 20.4, 20.3 (CO*CH*$_3$), 13.8 (2 × S(CH$_2$)$_5$*CH*$_3$); HRESIMS calcd for $C_{47}H_{74}O_{22}Na_{32}S_2$ 1077.4011, found *m/z* 1077.4053 $[M+Na]^+$. Anal. Calcd for $C_{47}H_{74}O_{22}S_2$: C, 53.50; H, 7.07. Found C, 53.15; H, 6.87.

3.23. Methyl 6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl-(1→4)-6-deoxy-6-hexylthio-β-D-glucopyranoside (26)

To a solution of compound **24** (166 mg, 0.15 mmol) in dry MeOH (10 mL) was added sodium methoxide (1 N in MeOH, 300 μL). The reaction mixture was stirred for 12 h, then neutralized with acidic resin (Amberlite IR 120) and filtered. Solvent was removed in vacuum to afford **26** (112 mg, 99%) as a white powder. $[\alpha]_D$ +64 (*c* 0.16, MeOH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 103.7 (C-1^{I}), 101.1, 101.0 (C-1^{II}, C-1^{III}), 83.6, 79.7, 75.8, 74.9, 72.9, 72.7, 72.6, 72.1, 71.9 (C-2$^{I–III}$, C-3$^{I–III}$,C-4$^{I–III}$, C-5$^{I–III}$), 60.1 (C-6^{II}), 56.0 (OCH_3), 33.6, 33.1 (C-6^{I}, C-6^{III}), 32.4, 30.9, 29.2, 27.0, 22.1 (2 × S(CH$_2$)$_5$CH$_3$), 14.0 (2 × S(CH$_2$)$_5$CH$_3$); HRESIMS calcd for $C_{31}H_{58}O_{14}Na_{32}S_2$ 741.3166, found *m/z* 741.3184 $[M+Na]^+$.

3.24. Methyl 6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-6-deoxy-6-hexylthio-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (27)

This was obtained from **25** as described for the synthesis of **26** in 99% yield. $[\alpha]_D$ +47 (*c* 0.1, MeOH); ^{13}C NMR (75 MHz, DMSO-d_6): δ 103.6 (C-1^{I}), 101.4, 100.1 (C-1^{II}, C-1^{III}), 83.4, 79.4, 76.1, 75.2, 73.2, 72.9, 72.8, 72.7, 72.6, 72.4, 71.9, 71.2 (C-2$^{I–III}$, C-3$^{I–III}$, C-4$^{I–III}$, C-5$^{I–III}$), 60.6 (C-6^{I}), 56.0 (OCH_3), 33.7, 33.4 (C-6^{II}, C-6^{III}), 32.6, 32.3, 30.8, 29.2, 29.0, 27.9, 27.8, 21.9 (2 × S(CH$_2$)$_5$CH$_3$), 13.8 (2 × S(CH$_2$)$_5$CH$_3$); HRESIMS calcd for $C_{31}H_{58}O_{14}Na_{32}S_2$ 741.3166, found *m/z* 741.3185 $[M+Na]^+$.

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