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Synthesis of a pentasaccharide fragment of Polysaccharide II of *Mycobacterium tuberculosis*

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Abstract

Stereocontrolled, stepwise synthesis of decyl glycosides of α-(1 → 2)-linked di- to pentaglucosides (**1–5**) is described; these constitute fragments of Polysaccharide II of *Mycobacterium tuberculosis*. Phenyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-1-thio-α-D-glucopyranoside (**7**) was used as the single key intermediate, obtained from 1,3,4,6-tetra-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranose (**6**) and $PhSSiMe_3$. Halogenolysis of **7** afforded the isolated β bromide (**10**) and β chloride (**13**). Solvolysis of **10** with decanol without heavy metal salts gave decyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranoside (**14**) in a highly stereoselective reaction, in high yield. Subsequent, iterative hydrogenolytic removal of the *O*-benzyl group and glycosylation with the β-chloride **13** under catalysis by silver salts afforded the protected di- to penta-saccharide glycosides **16**, **19**, **21**, and **23**, which were conventionally deblocked.

Keywords: Pentasaccharide; Polysaccharide II; *Mycobacterium tuberculosis*

1. Introduction

Tuberculosis caused by *Mycobacterium tuberculosis* is a major public health problem worldwide, causing the deaths of 3 million people annually [1]; this exceeds the death toll of any other communicable disease [2]. Following infection, *M. tuberculosis* survives predominantly in macrophages and remains asymptomatic over long periods. In contrast to previous decades when ~90% of tuberculosis cases were caused by reactivation of latent infection [3], about one third of new cases result from direct transmission [4]. In the United States this trend is attributed to the appearance of

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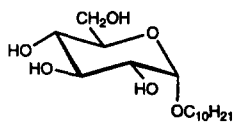
multiple drug-resistant strains in patients infected by the human immunodeficiency virus which appears to facilitate direct transmission of *M. tuberculosis* [4]. As part of the effort to define the molecular basis of the virulence of this pathogen, the structure of the cell-wall of *M. tuberculosis* has been the subject of intense research. The discovery of an electron-translucent zone around virulent mycobacteria suggests that these organisms are surrounded by a capsule that may be part of the defense mechanism [5]. Several complex, cell-wall-associated and secreted polysaccharides have been identified which can be important in the pathogenesis of tuberculosis and may function as protective antigens [6]. These include multiply branched lipoarabinomannan [7], arabinogalactan, a glycogen-like branched glucan [8], and a linear glucan termed "Polysaccharide II" [9]. Kent proposed that, in the latter polysaccharide, D-glucose residues are connected by α-(1 → 2) interglucosidic linkages [9c]. This linkage has rarely been found in natural products (as reviewed by Takeo and Suzuki [10]) and may confer unique specificity to Polysaccharide II. In order to provide molecular tools available for the serodiagnosis of mycobacteria and to explore the possible role of mycobacterial polysaccharides as protective antigens, considerable synthetic work has been devoted to the preparation of well-defined fragments of the polysaccharide components of various *Mycobacterium* strains, as reviewed by Lipták et al. [11]. The targets of earlier synthetic work related to carbohydrate antigens of *M. tuberculosis* were di- and tri-saccharide fragments of glycolipid fractions [12]. Here we describe a stepwise approach to a pentasaccharide fragment of Polysaccharide II and its lower homologues linked to a lipid anchor as the aglycon (**1–5**). The aglycon enables reversible absorption of the target saccharides to hydrophobic surfaces, such as plastic wells, Sep-Pak C_{18} particles [13], and attachment to red blood cells [14].

Syntheses of gluco-oligosaccharides having α-(1 → 2) interglycosidic linkages, such as koji-biose [15], -triose [10,16], -tetraose [10], and -pentaose [10] utilized several building blocks for each target. Retrosynthetic analysis of the target pentasaccharide **5** suggests that a single building block, equipped with a temporary, nonparticipating group [17] at O-2, may be sufficient for its construction, thereby significantly reducing the synthetic work in comparison with the previous studies [10,15,16]. Much of our current knowledge about the factors that govern the formation of α-D-glucopyranosyl bonds [18] is based on the work of Lemieux, who showed in 1968 that tetra-*O*-benzyl-β-D-glucopyranosyl bromide, generated in situ from the synthetically accessible α-bromide under bromide-ion catalysis, reacts spontaneously with alcohols to give α-glycosides, whereas the corresponding α anomer is unreactive under such conditions [19]. Because of the low concentration of the β bromide in equilibrium, the reaction rates and the yields of halide ion-catalyzed glycosylations are generally low. Ishikawa and Fletcher found that methanolysis of isolated 2-*O*- and 2,3-di-*O*-benzylated β-D-glucopyranosyl bromides having 4-nitrobenzoyl groups at the other positions proceeded with an impressive 94:6 α/β stereoselectivity [20]. Although the precursors to these bromides are readily accessible, their conversion into the reactive β-bromides is characterized by low yields, and this may explain the limited attention received by this approach [21]. Since a stable, isolated β-glycopyranosyl bromide may hold the potential as a useful α-D-glucopyranosyl donor, we explored a practical route to such a compound.



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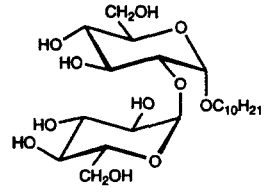

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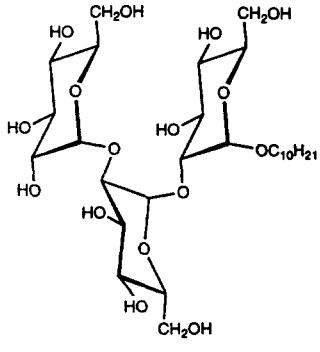

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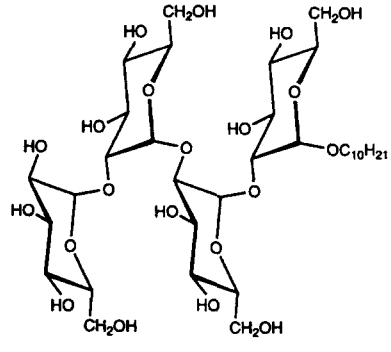

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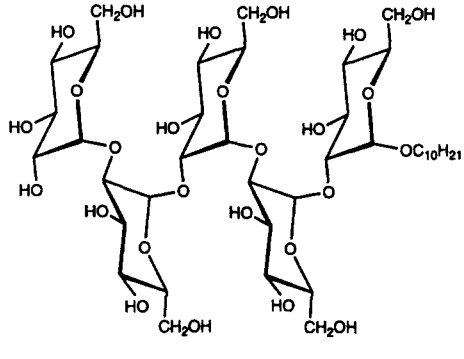
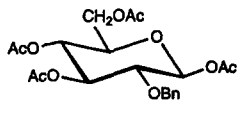


5

2. Results and discussion

Limited evidence, based on polarimetric measurements by Weygand and Ziemann, indicates that reaction of *O*-benzyl-protected 1-thio-α-glucosides with bromine leads to β-glucosyl bromides as the initial products [22]. Thus, a high-yielding synthesis of 1-thio-α-glucosides would be tantamount to a high-yielding synthesis of β-D-glucosyl bromides, provided that auto-anomerization of the latter is not significant. The known

tetraacetate **6** [23] was selected as the precursor in which the anomeric acetoxy group was replaced by the phenylthio group using $PhSSiMe_3$–Me_3SiOTf in $ClCH_2CH_2Cl$, according to a well-documented method [24]. The reaction proceeded under a high degree of stereocontrol and gave the 1-thio-α-glucoside **7** in 90% yield. A small amount ($\sim 2\%$) of a byproduct was detected by ^1H NMR spectroscopy and was tentatively identified as the β anomer of **7**. The byproduct could be removed by crystallization. Treatment of the phenylthio glucoside **7** with 2 equimolar amounts of bromine in $CDCl_3$ at 22°C in a 5 mm NMR tube led to its complete disappearance and conversion within 1 min to the β-bromide **10** as indicated by the doublet at 5.508 ppm (J 8.8 Hz) in the ^1H NMR spectrum of the reaction mixture. The α anomer **11** [23] ($\delta_{H\text{-}1} = 6.336$ ppm, J 3.8 Hz) was also present in 3–5%. The anomerization of **10** was promoted by Hünig's base and 2,6-di-*tert*-butyl-4-methylpyridine and was slightly suppressed by Me_3SiOTf.



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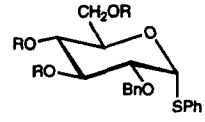
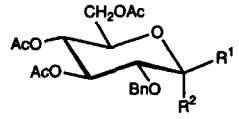
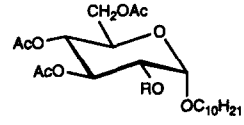


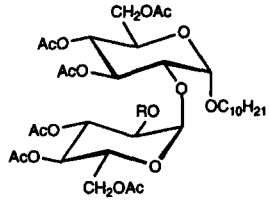
7 R=Ac
8 R=H
9 R=Bz



	R^1	R^2
10	Br	H
11	H	Br
12	H	OEt
13	Cl	H



14 R=Bn
15 R=H

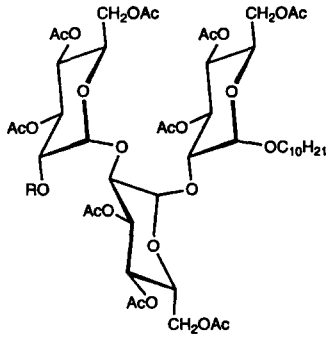


16 R=Bn
17 R=H
18 Ac

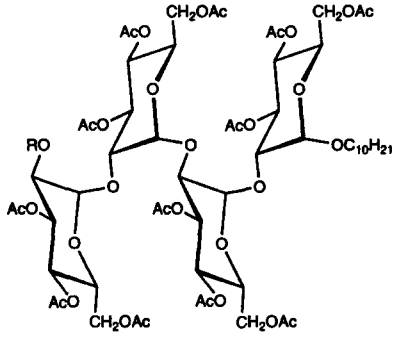
Crystalline **10** could be isolated in 90–95% yields. In a model experiment, condensation of **10** with EtOH in CH_2Cl_2 quickly afforded the α-glycoside **12** as the main product, together with the α-bromide **11**. The ratio of **12** to **11** was $\sim$ 2:1 after 12 h at 22°C. The intermediacy of **11** indicates an α-attack of the bromide ion generated in the reaction of **10** and EtOH. The α-bromide **11** was slowly converted to the α-glycoside **12**, presumably by bromide ion-catalyzed regeneration of **10**. Thus, while in the initial phase

of the reaction much of the starting β-glucosyl bromide **10** reacted directly with the alcohol to provide the α-glycoside **12**, the subsequent events resemble Lemieux's halide-ion catalysis without, however, added halide ions. Reaction of the β-bromide **10** with MeOH-d_4 without additional solvent afforded the corresponding α-glycoside and the α-bromide **11** in 95:5 ratio within 2 min. Similar to the previous experiments, β-glycoside could be observed in trace amounts only in the ^{1}H NMR spectrum of the reaction mixture recorded at 300 MHz. Compound **7** and by analogy the corresponding benzoate **9**, which was obtained from **7** in a two-step conversion [(i) NaOMe, MeOH → **8**, (ii) BzCl, C_5H_5N], are thus promising precursors for stereocontrolled synthesis of α-glucopyranosides. Indeed, reaction of **10** with 1-decanol in CH_2Cl_2 in the presence of Hünig's base afforded the α-glucoside **14** in 91% isolated yield. The reported example is based on the in situ procedure, whereby the generation of the bromide **10** from the precursor **7** and its reaction with the aglycon take place in the same flask [22,25]. The corresponding β-glycoside could not be detected (TLC and ^{1}H NMR). In order to compare the solvolytic synthesis of α-glucopyranosides with the traditional, Koenigs–Knorr approach, we also studied the reactions of **10** and the analogous β-glucosyl chloride **13** with the same alcohol, under promotion by silver salts. Chloride **13** was previously prepared by Igarashi et al. [26] from the tetraacetate **6** in a two-step conversion in 35% overall yield. We found that compound **13** can be conveniently prepared from the known α-bromide **11** [23] by anomerization with Et_4NCl in MeCN, according to a well-known protocol [10,27]. Such reactions may be monitored by polarimetry, and can be terminated by precipitation of the ammonium salts by benzene. Examination of this reaction by ^{1}H NMR spectroscopy indicated that, in addition to the expected β-product **13**, the corresponding α-chloride was also formed prior to complete conversion of the starting bromide **11**. Polarimetry should therefore be used with caution when examining anomerization by halide ions, and unless the desired glycosyl halide can be isolated in a crystalline form [28] or is suitable for chromatographic purification, products of such reactions should be considered as mixtures. Fortunately, the β-chloride **13** could be purified by column chromatography and obtained in a crystalline form in 50% yield. Alternatively, crystalline **13** was obtained from the 1-thioglycoside **7** by treatment with chlorine in CCl_4 [29] in 76% yield. Reaction of the β-bromide **10** with decanol under promotion by $AgClO_4$–Ag_2CO_3 afforded a 4:1 mixture (^{1}H NMR) of the α-glycoside **14** and the corresponding β anomer (^{1}H NMR). Under similar conditions reaction of the β-chloride **13** with decanol afforded a 5:1 mixture (^{1}H NMR) of **14** and its β anomer, from which the required α-glycoside **14** was isolated in 72% yield. These observations demonstrate that solvolysis of the β-glucosyl bromide **10** as already described, rather than its Koenigs–Knorr-type application, is the method of choice for stereoselective α-glucosylation of highly reactive, primary alcohols. Removal of the benzyl group from **14** (H_2–Pd/C) afforded the alcohol **15** (92%). Attempted coupling of **15** with the β-bromide **10** without silver salts proceeded unacceptably slowly and this approach was abandoned. Subsequent glycosylation reactions utilized the β chloride **13** instead of the β-bromide **10** because of the higher α-anomeric selectivity obtained with **13** under promotion by silver salts. Thus, $AgClO_4$–Ag_2CO_3-assisted reaction of the β-chloride **13** with the acceptor **15** afforded the disaccharide **16** in 95% yield. Iteration of the deblocking (→ **17**, 85%) and the glucosylation steps afforded the trisaccharide **19**

(65%). In this reaction ~ 22% of the starting disaccharide was also recovered as its acetate **18**.

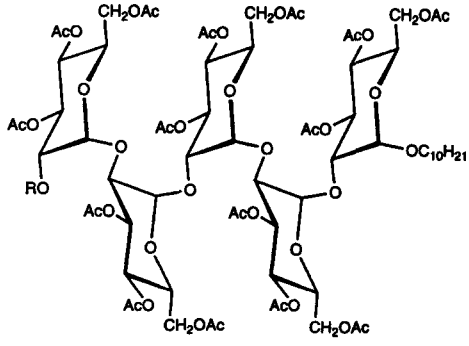


19 R=Bn
20 R=H



21 R=Bn
22 R=H

Subsequent iterations of the hydrogenolytic removal of the benzyl protecting group (→ **20**, 93%) and glucosylation with the β-chloride **13** as just described afforded the fully protected tetrasaccharide **21** (63%). The pentasaccharide **23** was obtained in a similar manner through the intermediacy of the tetrasaccharide alcohol **22** in 65% combined yield. Conventional deprotection of compounds **15**, **17**, **20**, **22** (NaOMe, MeOH) and **23** [(i) H_2–Pd/C, EtOH → **24**; (ii) NaOMe, MeOH] afforded the lipid-anchored mono- to penta-saccharide glycosides **1–5**.



23 R=Bn
24 R=H

The mono- and di-saccharides **1** and **2** are crystalline compounds characterized by two melting-point ranges, which correspond to transitions to an anisotropic phase and to an isotropic liquid phase, respectively [30]. The structures of the intermediates and the targets **1–5** were verified by combined use of ^1H and ^{13}C NMR spectroscopy and by chemical-ionization and fast-atom-bombardment mass spectroscopy and fully support

the proposed structures (see Experimental). Interestingly, two discrete sets of signals can be observed in the anomeric region of the tri- to penta-saccharides **3–5**. In each of these compounds two signals appear in the 96–97 ppm region and correspond to the terminal residues. Those appearing in the 92–94 ppm region show a characteristic broadening and are assigned to interchain residues. It is likely that the significant changes in the ^{13}C NMR spectral parameters (see Experimental) reflect major conformational changes as a function of the chain length of compounds **3–5**. Similar dependence of the NMR parameters has previously been observed for α-(2 → 8)-linked oligomers of *N*-acetylneuraminic acid [31], but not for O-polysaccharides of Gram-negative bacteria [32,33]. The lack of coalescence within the interresidual group indicates that further residues are necessary to attain the internal conformation of an extended α-(1 → 2)-linked D-glucan. It has been hypothesized that ordered conformations for this chain type are difficult to achieve because of "extensive clashes between non-consecutive units" [34]. The convergence of the anomeric resonances of the internal residues in **4** and **5** appears to question this assumption. Ongoing work in this laboratory is aimed at synthesizing extended fragments of Polysaccharide II [9] for immunochemical and conformational studies. The synthetic work described in this paper implies that monomer-based, linear synthesis of these saccharides is not practicable beyond the pentasaccharide level. We are currently exploring routes to a multifunctional disaccharide donor–acceptor intermediate for the construction of extended glucans containing all-α-(1 → 2) interglycosidic linkages.

3. Experimental

General methods.—Melting points were taken on a Meltemp capillary melting-point apparatus and are uncorrected. All chemicals were commercial grade and were used without purification. Anhydrous solvents were obtained from Aldrich. Optical rotations were measured at 22°C with a Perkin–Elmer Type 241MC or 341 polarimeter for $CHCl_3$ solutions, except where indicated otherwise. Column chromatography was performed on silica gel 60 (0.040–0.063 mm). The NMR spectra were measured at 296 K, using a Varian XL-300 or a Gemini 300 spectrometer operating at 300 MHz for ^1H, and at 75.5 MHz for ^{13}C. Internal references: Me_4Si (0.000 ppm for ^1H and for ^{13}C for solutions in organic solvents), acetone (2.225 ppm for ^1H and 31.00 ppm for ^{13}C for solutions in D_2O), and $CDCl_3$ (77.00 ppm for ^{13}C for solutions in $CDCl_3$). The methylene carbon resonances were identified by a DEPT-135 experiment. Subscripts A–E refer to the individual sugar residues, with A being for the reducing-end unit. The fast-atom-bombardment mass spectra were run on a JEOL SX102 mass spectrometer using 6 keV xenon atoms to ionize the samples which were desorbed from a mixture of dithiothreitol and dithioerythritol, from glycerol or from 3-nitrobenzyl alcohol as the matrix. Chemical-ionization mass spectra (CI-MS) were obtained by using NH_3 as the ionizing gas. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

*Phenyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-1-thio-*α*-*D*-glucopyranoside* (**7**).—A solution of **6** [23] (9.5 g, 22 mmol), (phenylthio)trimethylsilane (7 mL, 37 mmol), and trimethylsilyl

trifluoromethanesulfonate (1.3 mL) in CH_2Cl_2 (60 mL) was stirred under reflux for 64 h. The volatiles were removed under vacuum. Toluene (50 mL) was added to and evaporated from the residue thrice. The semisolid was triturated with hexane. Filtration afforded **7** (9.5 g, 90%). A portion was recrystallized from MeOH; mp 95–98°C; $[\alpha]_D$ +208° (*c* 0.5). NMR ($CDCl_3$): ^{1}H, δ 7.5–7.3 (aromatic), 5.635 (d, 1 H, $J_{1,2}$ 5.7 Hz, H-1), 5.378 (dd, 1 H, $J_{2,3} + J_{3,4} = 19.1$ Hz, H-3), 4.988 (dd, 1 H, $J_{3,4} + J_{4,5} = 19.7$ Hz, H-4), 4.716 and 4.602 (2 d, 2 H, $J \sim 12.3$ Hz for each, CH_2 of Bn), 4.547 (ddd, 1 H, H-5), 4.283 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6'}$ 12.3 Hz, H-6), 3.969 (dd, 1 H, $J_{5,6'}$ 2.2 Hz, H-6'), 3.892 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 2.070, 2.035, and 2.003 (3 s, 9 H, CH_3CO); ^{13}C, δ 131.7–127.5 (aromatic), 86.3 (C-1), 76.2, 72.2, 68.6, and 68.1 (C-2,3,4,5), 72.4 (*C*H_2 of Bn), 62.0 (C-6), and 20.7 (*C*H_3CO). CI-MS: *m/z* 506 [$(M + NH_4)^+$]. Anal. Calcd for $C_{25}H_{28}O_8S$: C, 61.46; H, 5.78; S, 6.56. Found: C, 61.56; H, 5.75; S, 6.62.

*Phenyl 2-*O*-benzyl-1-thio-α-*D*-glucopyranoside* (**8**).—A solution of **7** (5.0 g) in anhydrous MeOH (20 mL) was treated with a catalytic amount of NaOMe for 48 h at 22°C. The solution was treated with Dowex 50 × 2 (H^+), filtered, and concentrated to afford a solid which was recrystallized from diisopropyl ether–hexane to afford **8** (3.55 g, 96%); mp 98–100°C; $[\alpha]_D$ + 181° (*c* 1.5, MeOH). NMR (MeOH-d_4): ^{1}H, δ 7.5–7.17 (aromatic), 5.603 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 4.740 and 4.663 (2 d, 2 H, $J \sim 12.5$ Hz for each, CH_2 of Bn), 4.078 (ddd, 1 H, $J_{5,6}$ 3.5 Hz, $J_{6,6'}$ 7.0 Hz, H-5), 3.78–3.62 (m, 4 H, H-2,3,6,6'), and 3.421 (dd, 1 H, $J_{3,4}$ 8.6 Hz, $J_{4,5}$ 9.9 Hz, H-4); ^{13}C, δ 139.3–128.2 (aromatic), 86.5 (C-1), 80.5 (C-2), 74.9, 74.2, and 71.3 (C-3,4,5), 73.2 (CH_2 of Bn), and 62.0 (C-6). CI-MS: *m/z* 380 [$(M + NH_4)^+$]. Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.96; H, 6.12; S, 8.85. Found: C, 62.76; H, 6.19; S, 8.67.

*Phenyl 3,4,6-tri-*O*-benzoyl-2-*O*-benzyl-1-thio-α-*D*-glucopyranoside* (**9**).—To a stirred solution of **8** (5.0 g, 13.8 mmol) in pyridine (60 mL) were added a catalytic amount of 4-dimethylaminopyridine and BzCl (9.6 mL, 83 mmol) at 0°C. The mixture was allowed to reach 22°C in 3 h, then was recooled to 0°C and was treated with MeOH (10 mL). The volatiles were removed under vacuum. Extractive work-up ($CHCl_3$–H_2O) afforded a solid that was recrystallized from EtOH to give **9** (7.7 g, 83%); mp 150–152°C; $[\alpha]_D$ + 146° (*c* 2). NMR ($CDCl_3$): ^{1}H, δ 5.909 (dd, 1 H, $J_{2,3} + J_{3,4} = 19.3$ Hz, H-3), 5.766 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.483 (dd, 1 H, $J_{3,4} + J_{4,5} = 19.7$ Hz, H-4), 4.943 (m, 1 H, H-5), 4.724 and 4.595 (2 d, 2 H, $J \sim 12.4$ Hz for each, CH_2 of Bn), 4.476 and 4.460 (2 br s, 2 H, H-6,6'), and 4.100 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2); ^{13}C, δ 166.0, 165.5, and 165.4 (*C*=O), 133.3–127.3 (aromatic), 86.5 (C-1), 76.3 (C-2), 72.2 (*C*H_2 of Bn), 72.2, 69.7, and 68.7 (C-3,4,5), and 63.3 (C-6). CI-MS: *m/z* 692 [$(M + NH_4)^+$]. Anal. Calcd for $C_{40}H_{34}O_8S$: C, 71.20; H, 5.08; S, 4.75. Found: C, 71.38; H, 5.20; S, 4.96.

*3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-β-*D*-glucopyranosyl bromide* (**10**).—Bromine (420 μL, 8.2 mmol) was added to a solution of **7** (4.0 g, 8.2 mmol) in CH_2Cl_2 at 0°C. After 1 min the solution was treated with 1-hexene (1 mL) and concentrated. Trituration of the solid residue with hexane followed by filtration afforded **10** (3.54 g, 94%); $[\alpha]_D$ + 23° (*c* 0.8, CH_2Cl_2). NMR ($CDCl_3$): ^{1}H, δ, 5.504 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 5.195–5.094 (m, 2 H, H-3,4), 4.923 and 4.676 (2 d, 2 H, $J \sim 11$ Hz for each, CH_2 of Bn), 4.267 (dd, 1 H, $J_{5,6}$ 4.8 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 4.139 (dd, 1 H, $J_{5,6'}$ 3.2 Hz, H-6'), 3.83-3.78 (m, 2 H, H-2,5), 2.096, 2.015, and 1.981 (3 s, 9 H, CH_3CO).

*Ethyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-*D*-glucopyranoside* (**12**).—A solution of 1-

thioglucoside **7** (1.0 g) was treated with bromine as described for the preparation of **10**. After the addition of 1-hexene, the mixture was treated with EtOH (1 mL) and *N*-ethyldiisopropylamine (1 mL) at 22°C. After 80 h at this temperature the solution was concentrated. Column chromatographic purification of the residue (3:1 hexane–EtOAc) afforded **12** as a colorless syrup containing traces (< 1%) of a co-chromatographing by-product (730 mg, 84%); $[\alpha]_D + 82°$ (*c* 1.8). NMR ($CDCl_3$): ^1H, δ 5.453 (dd, 1 H, $J_{2,3} + J_{3,4} = 19.2$ Hz, H-3), 4.962 (dd, 1 H, $J_{3,4} + J_{4,5} = 19.8$ Hz, H-4), 4.780 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.663 and 4.577 (2 d, 2 H, $J \sim 12.5$ Hz for each, CH_2 of Bn), 4.262 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 4.05–3.95 (m, 2 H, H-5,6'), 3.706 and 3.504 (2 m, 2 H, H_2CCH_3), 3.558 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 2.067, 2.016, and 2.003 (3 s, 9 H, CH_3CO); ^{13}C, δ 137.7–127.8 (aromatic), 96.5 (C-1), 76.8 (C-2), 72.9 (CH_2 of Bn), 71.9, 68.8, and 67.1 (C-3,4,5), 64.0 (CH_2CH_3), 62.0 (C-6), 20.8 and 20.7 (2C) (CH_3CO), and 14.9 (CH_3CH_2). CI-MS: m/z 442 $[(M + NH_4)^+]$. Anal. Calcd for $C_{21}H_{28}O$: C, 59.43; H, 6.65. Found: C, 59.36; H, 6.66.

*3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-β-*D*-glucopyranosyl chloride* (**13**).—(*a*) A solution of Et_4NCl (1.0 g, 6.0 mmol) in MeCN (20 mL) was added to a solution of compound **11** [23] (1.0 g, 2.1 mmol) in MeCN (20 mL) at 22°C. The optical rotation of an aliquot of the mixture was followed in a polarimeter. After ~ 20 min the rotation reached a minimum. At this point benzene (300 mL) was added then the mixture was extracted with H_2O (3 × 100 mL). The organic phase was dried (Na_2SO_4), and concentrated. Column-chromatographic purification (4:1 hexane–EtOAc) of the residue followed by crystallization (diisopropyl ether–hexane) afforded **13** (450 mg, 50%); mp 119–121°C; $[\alpha]_D + 57°$ (*c* 0.3); lit. [26] mp 127.5–128.5°C, $[\alpha]_D + 51.4°$ (*c* 1, $CHCl_3$). NMR ($CDCl_3$): ^1H, δ 7.38–7.26 (aromatic), 5.266 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 5.175 (dd, 1 H, $J_{2,3} + J_{3,4} = 18.2$ Hz, H-3), 5.076 (dd, 1 H, $J_{3,4} + J_{4,5} = 19.3$ Hz, H-4), 4.907 and 4.666 (2 d, 2 H, $J \sim 11.2$ Hz for each, CH_2 of Bn), 4.271 (dd, 1 H, $J_{6,6}$ 4.9 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 4.139 (dd, 1 H, $J_{5,6}$ 2.2 Hz, H-6'), 3.780 (ddd, 1 H, H-5), 3.669 (dd, 1 H, H-2), 2.095, 2.014, and 1.908 (3 s, 9 H, CH_3CO). Anal. Calcd for $C_{19}H_{23}ClO_8$: C, 55.01; H, 5.59; Cl, 8.55. Found: C, 54.91; H, 5.63; Cl, 8.47.

(*b*) To a solution of **7** (512 mg, 0.95 mmol) in dry CH_2Cl_2 (10 mL) was added a solution of Cl_2 in CCl_4 (~ 2 equiv) at 0°C. The solution was kept for 15 min at 22°C and then was treated with 1-hexene (excess). The colorless solution was concentrated under diminished pressure. Trituration of the residue in diethyl ether–diisopropyl ether afforded crystalline **13** (330 mg, 76%), having physical properties identical to those of the product in experiment (a).

*Decyl 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-*D*-glucopyranoside* (**14**).—(*a*) A solution of **13** (4.4 g, 10.6 mmol) in dry CH_2Cl_2 (50 mL) was added to stirred mixture of decyl alcohol (2.2 mL, 11.5 mmol), Ag_2CO_3 (4.5 g, 16.3 mmol), $AgClO_4$ (~ 200 mg, 1 mmol), and 4 Å molecular sieves (2 g) in dry CH_2Cl_2 (60 mL) at 0°C. The mixture was allowed to reach 22°C. After 4 h the mixture was recooled to 0°C and was treated with aq $NaHCO_3$. Filtration followed by extractive work-up and column chromatographic purification (5:1 hexane–EtOAc) afforded **14** as a syrup (4.0 g, 72%); $[\alpha]_D + 76°$ (*c* 0.4). NMR ($CDCl_3$): ^1H, δ 7.37–7.28 (aromatic), 5.440 (dd, H, $J_{2,3} + J_{3,4} = 19.3$ Hz, H-3), 4.958 (d, 1 H, $J_{3,4} + J_{4,5} = 19.7$ Hz, H-4), 4.766 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.653 and 4.573 (2 d, 2 H, $J \sim 12.5$ Hz for each, CH_2 of Bn), 4.260 (dd, 1 H, $J_{5,6}$ 4.9 Hz,

$J_{6,6'}$ 12.5 Hz, H-6), 4.020 (dd, 1 H, $J_{5,6'}$ 2.5 Hz, H-6), 3.981 (ddd, 1 H, H-5), 3.629 and 3.401 (2 m, 2 H, H_2CO of decyl), 3.557 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 2.069, 2.017, and 2.005 (3 s, 9 H, CH_3CO), 1.67–1.58 and 1.39–1.22 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 170.6, 170.1, and 169.8 (C=O), 137.8 and 128.4–127.8 (aromatic), 96.7 (C-1), 76.8 (C-2), 72.8 (CH_2 of Bn), 71.9 (C-3), 69.8 (CH_2O of the decyl), 69.8 and 67.1 (C-4,5), 62.1 (C-6), 31.9, 29.6 (2C), 29.4, 29.3 (2C), 26.1, and 22.7 (CH_2 of decyl), 20.8, 20.72, and 20.68 (CH_3CO), and 14.1 (CH_3 of decyl). FABMS: m/z 537 $[(M + H)^+]$, 535 $[(M + H - H_2)^+]$, 379 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{29}H_{44}O_9$: C, 64.90; H, 8.26. Found: C, 64.94; H, 8.25.

(*b*) Bromine (320 μL, 6.2 mmol) was added to a solution of 1-thioglucoside **7** (3.0 g, 6.1 mmol) in CH_2Cl_2 (15 mL) at 0°C. The solution was allowed to reach 22°C during 5 min. 1-Hexene (1 mL), decanol (10 mL, 52 mmol), and *N*-ethyldiisopropylamine (1.5 mL, 8.6 mmol) were added and the mixture was carefully concentrated in a rotary evaporator to remove most of the CH_2Cl_2. After 36 h the mixture was applied to a column of silica gel prepared in 20:1 hexane–EtOAc. Elution with 20:1 → 6:1 hexane–EtOAc afforded **14** (3.0 g, 91%), having physical properties identical to those of the product in experiment (a).

*Decyl 3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside* (**15**).—A mixture of **14** (2.4 g), 10% Pd-C (~ 200 mg), EtOH (40 mL), and AcOH (2 mL) was stirred under hydrogen at 22°C at 345 kPa for 14 h. Removal of the catalyst by filtration and the volatiles under vacuum followed by column chromatographic purification (5:1 → 3:1 hexane–EtOAc) afforded **15** as a syrup (1.83 g, 92%); $[\alpha]_D$ + 117° (*c* 0.4). NMR ($CDCl_3$): ^1H, δ 5.228 (dd, 1 H, $J_{2,3} + J_{3,4}$ = 19.3 Hz, H-3), 5.007 (dd, 1 H, $J_{3,4} + J_{4,5}$ = 19.7 Hz, H-4), 4.913 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.273 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6'}$ 12.3 Hz, H-6), 4.072 (dd, 1 H, $J_{5,6'}$ 2.3 Hz, H-6'), 3.963 (ddd, 1 H, H-5), 3.733 and 3.498 (2 m, 2 H, H_2CO of decyl), 3.675 (ddd, 1 H, H-2), 2.089, 2.081, and 2.034 (3 s, 9 H, CH_3CO), 1.68–1.58 and 1.40–1.22 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 98.2 (C-1), 73.6 (C-3), 70.9 (C-2), 68.9 (CH_2O of decyl), 68.0 (C-4), 67.6 (C-5), 62.0 (C-6), 31.8, 29.5 (2C), 29.4, 29.3 (2C), 26.0, and 22.6 (CH_2 of decyl), 20.9, 20.7, and 20.6 (CH_3CO), and 14.1 (CH_3 of decyl). FABMS: m/z 447 $[(M + H)^+]$, 445 $[(M + H - H_2)^+]$, 289 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{23}H_{38}O_9$: C, 59.18; H, 8.58. Found: C, 59.66; H, 8.65.

*Decyl O-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside* (**16**).—A mixture of **15** (2.9 g, 6.5 mmol), **13** (4.1 g, 9.7 mmol), Ag_2CO_3 (3.5 g, 12.7 mmol), and 4 Å molecular sieves (3 g) in dry CH_2Cl_2 (50 mL) was stirred for 2 h at 22°C, then $AgClO_4$ (~ 200 mg, 1 mmol) was added. After 48 h the mixture was processed conventionally, followed by column-chromatographic purification (3:1 hexane–EtOAc) to afford **16** as a syrup (5.1 g, 95%); $[\alpha]_D$ + 125° (*c* 0.5). NMR ($CDCl_3$): ^1H, δ 7.39–7.21 (aromatic), 5.457 (dd, 1 H, $J_{2,3} + J_{3,4}$ = 19.1 Hz, $H\text{-}3_B$), 5.397 (dd, 1 H, $J_{3,4} + J_{4,5}$ = 19.3 Hz, $H\text{-}3_A$), 5.000 (d, 1 H, $J_{1,2}$ ~ 3 Hz, $H\text{-}1_B$), 4.964 (t, 2 H, $H\text{-}4_A,4_B$), 4.900 (d, 1 H, $J_{1,2}$ 3.3 Hz, $H\text{-}1_A$), 4.596 (s, 2 H, CH_2 of Bn), 4.274 and 4.216 (2 dd, 2 H, $H\text{-}6_A,6_B$), 4.13–4.02 (m, 4 H, $H\text{-}5_A,5_B6'_A,6'_B$), 3.680 (dd, 1 H, $H\text{-}2_B$), 3.558 (dd, 1 H, $H\text{-}2_A$), 2.086–1.978 (6 s, 18 H, 6 CH_3CO), 1.68–1.57 and 1.40–1.22 (CH_2 of decyl), and 0.92–0.85 (Me of decyl); ^{13}C, δ 170.7–169.9 ($C = O$), 137.6 and 128.6–127.7 (aromatic), 97.7 and 96.7 ($C\text{-}1_A,1_B$), 77.1 and 76.7 ($C\text{-}2_A,2_B$),

73.0 (CH_2 of Bn), 71.8 (2C), (C-3_A,3_B), 69.4 (CH_2O of decyl), 68.7, 68.4, 68.2, and 67.2 (C-4_A,4_B5_A,5_B), 62.0 and 61.5 (C-6_A,6_B), 31.8, 29.5, 29.4, 29.3, 26.2, and 22.6 (CH_2 of decyl) 20.7 and 20.6 (CH_3CO), and 14.0 (CH_3 of decyl). FABMS: m/z 823 $[(M + H - H_2)^+]$, 667 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{41}H_{60}O_{17}$: C, 59.70; H, 7.33. Found: C, 59.72; H, 7.26.

Decyl O-*(3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl)-(1 → 2)-3,4,6-tri*-O-*acetyl*-α-D-*glucopyranoside (***17***).*—Hydrogenolysis of disaccharide **16** under conditions described for the preparation of **15** followed by column chromatographic purification (2:1 hexane–EtOAc) afforded crystalline **17** (85%); mp 103–106°C; $[\alpha]_D$ + 163° (*c* 0.4). NMR ($CDCl_3$): ^{1}H, δ 5.438 and 5.119 (2 dd, 2 H, H-3_A,3_B), 5.047–4.930 (m, 4 H, H-1_A,1_B,4_A,4_B), 4.292 and 4.259 (2 dd, 2 H, H-6_A,6_B), 4.11–4.05 (m, 2 H, H-$6'_A$,$6'_B$), 4.03–3.83 (m, 2 H, H-5_A,5_B), 3.910 (dd, 1 H, $J_{1,2}$ 3.8 Hz, $J_{2,3}$ 10.0 Hz, H-2_A), 3.703 and 3.450 (2 m, 2 H, H_2CO of decyl), 3.655 (ddd, 1 H, H-2_B), 2.400 (d, 1 H, J ~ 12 Hz, *HO*), 2.102–2.018 (6 s, 18 H, 6 CH_3CO), 1.68–1.57 and 1.40–1.22 (CH_2 of decyl), and 0.92–0.85 (Me of decyl); ^{13}C, δ 170.7–169.6 (*C* = O), 98.8 and 95.3 (C-1_A,1_B), 74.5 (C-2_A), 73.1 (C-3_B), 71.0 (C-3_A), 70.4 (C-2_B), 68.8 (CH_2O of decyl), 68.45, 68.38, 67.6, and 67.2 (C-4_A,4_B,5_A,5_B), 61.8 and 61.5 (C-6_A,6_B), 31.7, 29.4, 29.3, 29.2 (3C), 25.9, and 22.5 (CH_2 of decyl), 20.6–20.4 (CH_3CO), and 13.9 (CH_3 of decyl). FABMS: m/z 735 $[(M + H)^+]$, 733 $[(M + H - H_2)^+]$, 577 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{34}H_{54}O_{17}$: C, 55.58; H, 7.41. Found: C, 55.57; H, 7.43.

Decyl O-*(3,4,6-tri*-O-*acetyl-2*-O-*benzyl*-α-D-*glucopyranosyl)-(1 → 2)*-O-*(3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl)-(1 → 2)-3,4,6-tri*-O-*acetyl*-α-D-*glucopyranoside (***19***).*—A mixture of **13** (1.17 g, 2.82 mmol), **17** (1.38 g, 1.878 mmol), Ag_2CO_3 (2 g, 7.2 mmol), and 4 Å molecular sieves (2 g) in dry CH_2Cl_2 (20 mL) was stirred at 22°C for 1 h and was then treated with $AgClO_4$ (~ 100 mg, 0.5 mmol). After 36 h the mixture was processed as described for the preparation of compound **16** followed by acetylation [Ac_2O (5 mL), pyridine (5 mL), 4-dimethylaminopyridine (cat), 22°C, 24 h], and chromatographic purification (2:1 hexane–EtOAc) to afford a syrup containing mainly (> 95%) compound **18** {320 mg, ~ 22%, NMR ($CDCl_3$): ^{1}H, δ 5.455 (dd, 1 H, $J_{2,3} + J_{3,4}$ = 20 Hz, H-3_A), 5.386 (dd, 1 H, $J_{2,3} + J_{3,4}$ = 19.8 Hz, H-3_B), 5.215 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1_B), 5.047 (dd, 1 H, $J_{3,4} + J_{4,5}$ = 19.6 Hz, H-4_B), 4.965 (dd, 1 H, $J_{3,4} + J_{4,5}$ = 19.3 Hz, H-4_A), 4.947 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1_A), 4.786 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2_B), 2.11–2.00 (CH_3CO), 1.69–1.57 and 1.41–1.19 (CH_2 of decyl), and 0.94–0.82 (Me of decyl); ^{13}C, δ 170.5–169.5 (*C* = O), 95.7 and 94.4 (C-1_A,1_B), 74.7 (C-2_A), 71.3 and 70.9 (C-3_A,2_B), 69.7 (C-3_B), 69.0 (CH_2O of decyl), 68.6 (C-4_B), 68.0 (2C) and 67.2 (C-4_A,5_A,5_B), 61.8 and 61.2 (C-6_A,6_B), 31.7, 29.4, 29.3, 29.2, 29.1, 25.9, and 22.4 (CH_2 of decyl), 20.4 and 20.3 (CH_3CO), and 13.9 (CH_3 of decyl). FABMS: m/z 777 $[(M + H)^+]$, 717 $[(M + H - AcOH)^+]$, 619 $[(M + H - C_{10}H_{21}OH)^+]$}, followed by **19** obtained as a syrup (1.35 g, 65%); $[\alpha]_D$ + 138° (*c* 0.7). NMR ($CDCl_3$): ^{1}H, δ 7.44–7.24 (aromatic), 5.410, 5.397, and 5.320 (3 dd, 3 H, H-3_A, 3_B, 3_C), 5.115, 4.935, and 4.855 (3 d, 3 H, $J_{1,2}$ ~ 3.5 Hz, H-1_A,1_B,1_C), 4.987, 4.974, and 4.900 (3 dd, 3 H, H-4_A,4_B,4_C), 4.640 and 4.580 (2 d, 2 H, CH_2 of Bn), 2.08–1.98 (CH_3CO), 1.72–1.61 and 1.44–1.24 (CH_2 of decyl), and 0.92–0.82 (Me of decyl); ^{13}C, δ 170.6–169.8 (*C* = O), 137.3 and 128.9–128.2 (aromatic), 98.5 (2C) and 97.1 (C-1_A,1_B,1_C), 78.8, 78.0, and 76.9 (C-2_A,2_B,2_C), 74.0 (CH_2 of Bn), 72.5, 71.8, and 71.1

(C-3_A,3_B,3_C), 69.3 (*C*H_2O of decyl), 68.9, 68.6, 68.5, 68.1 (2C), and 66.9 (C-4_A,4_B,4_C,5_A,5_B,5_C), 62.4, 61.4, and 61.2 (C-6_A,6_B,6_C), 31.9, 29.6 (2C), 29.5 (2C), 29.3, 26.1, and 22.6 (CH_2 of decyl), 20.8–20.5 (*C*H_3CO), and 14.0 (CH_3 of decyl). FABMS: *m/z* 1111 $[(M + H - H_2)^+]$, 955 $[(M + H - C_{10}H_{21}OH)^+]$.

Decyl O-*(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside (**20**).*—Hydrogenolysis of trisaccharide **19** under conditions described for the preparation of **15** followed by column-chromatographic purification (1:1 hexane–EtOAc) afforded **20** as an amorphous solid (93%); $[\alpha]_D$ + 165° (*c* 0.7). NMR ($CDCl_3$): ^{1}H, δ 5.496, 5.354, and 5.110 (3 dd, 3 H, $J_{2,3} + J_{3,4}$ = 19.3 Hz, H-3_A,3_B,3_C), 5.196, 5.091, and 4.991 (3 d, 3 H, $J_{1,2}$ ~ 3.4 Hz, H-1_A,1_B,1_C), 5.018, 5.013, and 4.997 (3 dd, 3 H, H-4_A,4_B,4_C), 3.863 and 3.825 (2 dd, 2 H, H-2_A,2_B), 2.74 (d, *J* ~ 10.6 Hz, *HO*), 2.11–2.02 (CH_3CO), 1.69–1.58 and 1.43–1.24 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 171.3–170.1 (*C* = O), 96.3, 95.5, and 93.1 (C-1_A,1_B,1_C), 74.2 and 73.4 (C-2_A,2_B), 73.1 (C-3_C), 71.4 and 70.5 (C-3_A,3_B), 70.4 (C-2_C), 68.8 (*C*H_2O of decyl), 68.6, 68.4, 68.3, 68.0, 67.8, and 67.5 (C-4_A,4_B,4_C,5_A,5_B,5_C), 62.0, 61.7, and 61.4 (C-6_A,6_B,6_C), 31.8, 29.6 (2C), 29.3 (3C), 26.0, and 22.6 (CH_2 of decyl), 21.0–20.4 (*C*H_3CO), and 14.0 (*C*H_3 of decyl). FABMS: *m/z* 865 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{46}H_{70}O_{25}$: C, 54.01; H, 6.90. Found: C, 53.96; H, 6.87.

Decyl O-*(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside (**21**).*—A mixture of **20** (1.00 g, 0.978 mmol), **13** (1.01 g, 2.440 mmol), Ag_2CO_3 (5.8 g, 21 mmol), and 4 Å molecular sieves (4 g) in dry CH_2Cl_2 (20 mL) was stirred at 22°C for 1 h, then was treated with $AgClO_4$ (~ 100 mg, 0.5 mmol). After 20 h the mixture was processed as described for the preparation of compound **16**. Column-chromatographic purification (7:5 hexane–EtOAc) afforded **21** as a syrup (865 mg, 63%); $[\alpha]_D$ + 157° (*c* 0.6). NMR ($CDCl_3$): ^{1}H, δ 7.46–7.26 (aromatic), 5.501, 5.337, 5.305, and 5.284 (4 dd, 4 H, H-3_A,3_B,3_C,3_D), 5.214, 5.144, 4.930, and 4.810 (4 d, 4 H, $J_{1,2}$ ~ 3.5 Hz, H-1_A,1_B,1_C,1_D), 5.004 (3 H) and 4.929 (4 H, H-4_A,4_B,4_C,4_D), 4.660 and 4.587 (2 d, 2 H, *J* ~ 11.8 Hz, CH_2 of Bn), 2.09–1.97 (CH_3CO), 1.72–1.61 and 1.44–1.24 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 170.7–169.6 (*C* = O), 137.1 and 128.9–128.2 (aromatic), 99.1 98.9, 97.4, and 96.6 (C-1_A,1_B,$1_C$$1_D$), 79.5, 78.3, 76.8, and 76.2 (C-2_A,2_B,2_C,2_D), 74.1 (*C*H_2 of Bn), 72.1, 72.0, 71.6, and 71.2 (C-3_A,3_B,3_C,3_D), 69.3 (*C*H_2O of decyl), 69.2, 68.7 (2C), 68.4, 67.9, 67.7 (2C), and 67.1 (C-4_A,4_B,4_C,4_D,5_A,5_B,5_C,5_D), 62.4, 61.7, 61.3, and 61.0 (C-6_A,6_B,6_C,6_D), 31.7, 29.5 (2C), 29.4, 29.3, 29.2, 26.1, and 22.5 (CH_2 of decyl), 20.6–20.4 (*C*H_3CO), and 13.9 (CH_3 of decyl). FABMS: *m/z* 1399 $[(M + H - H_2)^+]$, 1243 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{65}H_{92}O_{33}$: C, 55.71; H, 6.62. Found: C, 55.60; H, 6.56.

Decyl O-*(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside (**22**).*—Hydrogenolysis of tetrasaccharide **21** under conditions described for the preparation of **15** followed by column-chromatographic purification (2:1 hexane–EtOAc) afforded **21** as an amorphous solid (90%); $[\alpha]_D$ + 191° (*c* 0.4). NMR ($CDCl_3$): ^{13}C, δ 170.9–169.7 (*C*=O), 95.9, 95.3, 93.3, and 92.9 (C-

1_A,1_B,1_C,1_D), 74.4, 73.2, and 73.1 (C-2_A,2_B,2_C), 72.5 (C-3_D), 71.15 and 71.12 (C-3_B,3_C), 70.5 (C-3_A), 70.0 (C-2_D), 68.9 (2C), 68.5, 68.3, 68.0 (2C), and 67.5 (2C) (C-4_A,4_B,4_C,4_D,5_A,5_B,5_C,5_D), 62.0, 61.8, and 61.5 (C-6_A,6_B,6_C,6_D), 31.8, 29.6 (2C), 29.3 (3C), 26.1, and 22.6 (CH_2 of decyl), 20.6 (CH_3CO), and 14.0 ($CH_3$of decyl). FABMS: m/z 1333 $[(M + Na)^+]$, 1311 $[(M + H)^+]$, 1153 $[(M + H - C_{10}H_{21}OH)^+]$. Anal. Calcd for $C_{58}H_{86}O_{33}$: C, 53.13; H, 6.61. Found: C, 53.16; H, 6.64.

Decyl O-*(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside (**23**).*—A mixture of **22** (490 mg, 0.374 mmol), **13** (500 mg, 1.208 mmol), Ag_2CO_3 (2.1 g, 7.6 mmol), and 4 Å molecular sieves (1.3 g) in dry CH_2Cl_2 (10 mL) was stirred at 22°C for 1 h and then treated with $AgClO_4$ (~ 50 mg, 0.25 mmol). The mixture was stirred for 48 h during which time additional amounts of **13** (1.1 g, 2.657 mmol) and $AgClO_4$ (~ 100 mg) were added. The usual processing and column chromatographic purification (1:1 hexane–EtOAc) afforded **23** as an amorphous solid (457 mg, 72%); $[\alpha]_D$ + 162° (*c* 0.7). NMR ($CDCl_3$): ^{1}H, δ 7.46–7.26 (aromatic), 5.509, 5.400, 5.304, 5.301, and 5.286 (5 dd, 5 H, H-3_A,3_B,3_C,3_D,3_E), 5.293, 5.205, 5.156, 4.93, and 4.764 (5 d, 5 H, $J_{1,2}$ ~ 3.5 Hz, H-1_A,1_B,1_C,1_D,1_E), 5.057, 5.045, 5.025, 4.985, and 4.962 (5 dd, 5 H, H-4_A,4_B,4_C,4_D,4_E), 4.682 and 4.587 (2 d, 2 H, *J* ~ 12 Hz, CH_2 of Bn), 2.09–1.97 (CH_3CO), 1.72–1.61 and 1.44–1.24 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 170.7–169.5 (*C* = O), 137.0 and 128.9–128.2 (aromatic), 100.0, 99.7, 99.4 (2C), and 96.8 (C-1_A,1_B,1_C,1_D,1_E), 80.6, 79.8, 77.4, 77.1, and 76.3 (C-2_A,2_B,2_C,2_D,2_E), 73.9 (*C*H_2 of Bn), 72.3 (2C), 72.1, 71.5, and 70.6 (C-3_A,3_B,3_C,3_D,3_E), 69.3 (*C*H_2O of decyl), 69.3, 69.2, 68.8 (2C), 68.4, 68.1, 68.0, 67.9, 67.7, and 67.0 (C-4_A,4_B,4_C,4_D,4_E,5_A,5_B,5_C,5_D,5_E), 62.4, 62.0, 61.33, 61.25, and 61.0 (C-6_A,6_B,6_C,6_D,6_E), 31.8, 29.6 (3C), 29.5, 29.3, 26.3, and 22.6 (CH_2 of decyl), 20.9–20.4 (*C*H_3CO), and 14.0 (CH_3 of decyl). FABMS: m/z 1727 $[(M + K)^+]$, 1712 $[(M + Na)^+]$, 1687 $[(M + H - H_2)^+]$, 1629 $[(M + H - AcOH)^+]$. Anal. Calcd for $C_{77}H_{108}O_{41}$: C, 54.74; H, 6.44. Found: C, 54.84; H, 6.50.

Decyl O-*(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 2)-3,4,6-tri-*O*-acetyl-α-*D*-glucopyranoside (**24**).*—Hydrogenolysis of pentasaccharide **23** under conditions described for the preparation of **15** followed by column-chromatographic purification (1:1 hexane–EtOAc) afforded **24** as an amorphous solid (80%); $[\alpha]_D$ +187° (*c* 0.4). NMR ($CDCl_3$): ^{1}H, δ 5.487, 5.338, 5.313, 5.298, 5.105, 5.079, 5.050, 5.019, 4.986, and 4.981 (10 dd, 10 H, H-3_A,3_B,3_C,3_D,3_E,4_A,4_B,4_C,4_D,4_E), 5.418, 5.280, 5.223, 5.148, and 4.898 (5 d, 5 H, $J_{1,2}$ ~ 3.5 Hz, H-1_A,1_B,1_C,1_D,1_E), 2.115–2.002 (CH_3CO), 1.72–1.60 and 1.41–1.22 (CH_2 of decyl), and 0.92–0.84 (Me of decyl); ^{13}C, δ 170.8–169.5 (*C* = O), 95.9, 95.6, ~ 94.7 (broad, 2C) and 93.8 (broad) (C-1_A,1_B,1_C,1_D,1_E), 69.0 (*C*H_2O of decyl), 62.1, 62.0, 61.6, 61.4, and 61.3 (C-6_A,6_B,6_C,6_D,6_E), 31.8, 29.64, 29.58, 29.5, 29.4, 29.3, 26.0, and 22.6 (CH_2 of decyl), 20.8–20.6 (*C*H_3CO), and 14.0 (CH_3 of decyl). FABMS: m/z 1621 $[(M + Na)^+]$, 1599 $[(M + H)^+]$, 1441 $[(M + H - AcOH)^+]$. Anal. Calcd for $C_{70}H_{102}O_{41}$: C, 52.55; H, 6.43. Found: C, 52.35; H, 6.38.

Decyl α-*D*-*glucopyranoside* (**1**).*—A solution of **15** (340 mg) in anhydrous MeOH

(20 mL) was treated with a catalytic amount of NaOMe for 24 h at 22°C. The solution was treated with Dowex 50x2 (H^+), filtered, and concentrated to afford crystalline **1** (234 mg, 93%); mp: 70–74°C (anisotropic), 134–136°C (isotropic); $[\alpha]_D$ +106° (*c* 0.3, MeOH). NMR (MeOH-d_4): ^{1}H, δ 4.761 (d, H, $J_{1,2}$ 3.8 Hz, H-1), 3.790 (dd, 1 H, $J_{5,6}$ 2.4 Hz, $J_{6,6'}$ 11.8 Hz, H-6), 3.703 and 3.448 (2 m, 2 H, H_2CO of decyl), 3.686 (dd, 1 H, H-6'), 3.637 (dd, 1 H, H-3), 3.564 (dd, 1 H, $J_{5,6'}$ 5.6 Hz, H-6'), 3.388 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.296 (dd, 1 H, H-4), 1.71–1.59 (2 H, CH_2CH$_2$O of decyl), 1.44–1.24 (CH_2 of decyl), and 0.92–0.82 (Me of decyl); ^{13}C, δ 100.1 (C-1), 75.2 (C-3), 73.6 [(2C) C-2,5)], 71.9 (C-4), 69.2 (*C*H$_2$O of decyl), 62.7 (C-6), 33.1, 30.8 (2C), 30.7 (2C), 30.5, 27.4, and 23.8 (CH_2 of decyl), and 14.5 (CH$_3$ of decyl). CI-MS: *m/z* 338 [(M + NH$_4$)$^+$]. Anal. Calcd for $C_{16}H_{32}O_6 \cdot 1/2\ H_2O$: C, 58.34; H, 10.10. Found: C, 58.81; H, 9.95.

Decyl O-α-D-*glucopyranosyl-(1 → 2)-α-D-glucopyranoside* (**2**).—Deacetylation of **17** as described for the preparation of **1** afforded crystalline **2** (89%); mp 98–102°C (anisotropic), 114–118°C (isotropic); $[\alpha]_D$ + 138° (*c* 0.5, MeOH). NMR (MeOH-d_4): ^{1}H, δ 5.014 ($J_{1,2}$ 3.5 Hz), 4.980 ($J_{1,2}$ 3.8 Hz) (2 d, 2 H, H-1$_A$,1$_B$), 3.576 and 3.373 (2 dd, 2 H, $J_{2,3}$ 9.8, H-2$_A$,2$_B$), 1.68–1.58 and 1.44–1.25 (CH_2 of decyl), and 0.93–0.87 (Me of decyl); ^{13}C, δ 97.9 and 97.2 (C-1$_A$,1$_B$), 77.3 (C-2$_A$), 75.1 (C-3$_B$), 73.72, 73.70, 73.6, and 73.5 (C-2$_B$,3$_A$,5$_A$,5$_B$), 71.7 and 71.6 (C-4$_A$,4$_B$), 69.1 (*C*H$_2$O of decyl), 62.7, and 62.6 (C-6$_A$,6$_B$), 33.1, 30.79, 30.77, 30.7, 30.6, 30.5, 27.4, and 23.8 (CH_2 of decyl), and 14.5 (CH$_3$ of decyl). FABMS: *m/z* 505 [(M + Na)$^+$]. Anal. Calcd for $C_{22}H_{42}O_{11} \cdot H_2O$: C, 52.79; H, 8.86. Found: C, 52.88; H, 8.73.

Decyl O-α-D-*glucopyranosyl-(1 → 2)*-O-α-D-*glucopyranosyl-(1 → 2)*-α-D-*glucopyranoside* (**3**).—Deacetylation of **20** as described for the preparation of **1** afforded **3** as an amorphous solid (93%); $[\alpha]_D$ + 155° (*c* 0.4, H$_2$O). NMR (7.5:1 MeOH-d_4–D$_2$O): ^{1}H, δ 5.276 ($J_{1,2}$ 3.5 Hz), 5.122 ($J_{1,2}$ ~ 2.8 Hz), and 5.111 ($J_{1,2}$ 3.5 Hz) (3 d, 3 H, H-1$_A$,1$_B$,1$_C$), 1.72–1.58 and 1.42–1.25 (CH_2 of decyl), and 0.94–0.86 (Me of decyl); ^{13}C, δ 97.0, 96.9, and 94.6 (C-1$_A$,1$_B$,1$_C$), 77.4 and 76.5 (C-2$_A$,2$_B$), 74.9 (C-3$_C$), 73.7, 73.5, 73.4 (2C), 73.3, and 73.0 (C-2$_C$,3$_A$,3$_B$,5$_A$,5$_B$,5$_C$), 71.5 and 71.3 (2C) (C-4$_A$,4$_B$,4$_C$), 69.0 (*C*H$_2$O of decyl), 62.5, and 61.3 (C-6$_A$,6$_B$,6$_C$), 32.9, 30.6 (2C), 30.5 (2C), 30.3, 27.2, and 23.6 (CH_2 of decyl), and 14.4 (CH$_3$ of decyl). Anal. Calcd for $C_{28}H_{52}O_{16}$: C, 52.16; H, 8.13. Found: C, 52.02; H, 8.08.

Decyl O-α-D-*glucopyranosyl-(1 → 2)*-O-α-D-*glucopyranosyl)-(1 → 2)*-O-α-D-*glucopyranosyl-(1 → 2)*-α-D-*glucopyranoside* (**4**).—Deacetylation of **22** as described for the preparation of **1** afforded **4** as an amorphous solid; $[\alpha]_D$ + 129° (*c* 0.4, H$_2$O). NMR (5:1 MeOH-d_4–D$_2$O): ^{1}H, δ 5.454 ($J_{1,2}$ 3.6 Hz), 5.368 ($J_{1,2}$ 3.7 Hz), 5.199 ($J_{1,2}$ 4.2 Hz), and 5.195 ($J_{1,2}$ ~ 3.3 Hz) (4 d, 4 H, H-1$_A$,1$_B$,1$_C$,1$_D$), 1.72–1.58 and 1.40–1.23 (CH_2 of decyl), and 0.93–0.86 (Me of decyl); ^{13}C, δ 96.6 and 96.5 (C-1$_A$,1$_D$), 93.2 and 93.1 (C-1$_B$,1$_C$), 76.1, 76.0, and 75.6 (C-2$_A$,2$_B$,2$_C$), 74.6 (C-3$_D$), 73.8, 73.7, 73.4, 73.3 (3C), 73.25, and 73.1 (C-2$_D$,3$_A$,3$_B$,3$_C$,5$_A$,5$_B$,5$_C$,5$_D$), 71.6, 71.4, 70.8, and 70.7 (C-4$_A$,4$_B$,4$_C$,4$_D$), 69.1 (*C*H$_2$O of decyl), 62.6, 62.5, and 62.1 (2C) (C-6$_A$,6$_B$,6$_C$,6$_D$), 32.9, 30.6 (3C), 30.5, 30.3, 27.2, and 23.6 (CH_2 of decyl), and 14.4 (CH$_3$ of decyl). FABMS: *m/z* 829 [(M + Na)$^+$], 807 [(M + H)$^+$].

Decyl O-α-D-*glucopyranosyl-(1 → 2)*-O-α-D-*glucopyranosyl)-(1 → 2)*-O-α-D-*glucopyranosyl-(1 → 2)*-O-α-D-*glucopyranosyl)-(1 → 2)*-α-D-*glucopyranoside* (**5**).—

Deacetylation of **24** as described for the preparation of **1** afforded **5** (98%) as an amorphous solid; $[\alpha]_D$ + 161° (*c* 0.4, H_2O). NMR (5:1 MeOH-d_4–D_2O): ^1H, δ 5.566 ($J_{1,2}$ 3.6 Hz), 5.490 ($J_{1,2}$ 3.6 Hz), 5.380 (2H) ($J_{1,2}$ 3.5 Hz), and 5.173 ($J_{1,2}$ 3.2 Hz) H-1_A,1_B,1_C,1_D,1_E), 1.78–1.61 (CH_2CH$_2$O of decyl), 1.38–1.25 (CH_2 of decyl), and 0.93–0.87 (Me of decyl); ^{13}C, δ 95.9 and 95.7 (C-1_A,1_E), 92.4, 92.3, and 92.0 (C-1_B,1_C,1_D), 75.5, 74.9, 74.8, 74.5 (2C), 74.0, 73.7 (2C), 73.4 (3C), 73.25, 73.17, 73.05, and 72.99 (C-2_A,2_B,2_C,2_D,2_E,3_A,3_B,3_C,3_D,3_E,5_A,5_B,5_C,5_D,5_E), 71.4, 71.3, 71.1 (2C), and 70.7 (C-4_A,4_B,4_C,4_D,4_E), 69.2 (CH_2O of decyl), 62.7, 62.5, 62.2 (2C), and 61.9 (C-6_A,6_B,6_C,6_D,6_E), 33.0, 30.7, 30.6, 30.5, 30.4, 30.2, 27.0, and 23.6 (CH_2 of decyl), and 14.4 (CH_3 of decyl). FABMS: *m/z* 991 [(M + Na)$^+$], 811 [(M + H − $C_{10}H_{21}OH$)$^+$]. Anal. Calcd for $C_{40}H_{72}O_{26} \cdot 4\ H_2O$: C, 46.13; H, 7.75. Found: C, 46.05; H, 7.78.

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References

[1] (a) D.E. Snider, *Rev. Infect. Dis.*, 11, Suppl. 2 (1989) S336–S337; (b) A. Kochi, *Tubercle*, 72 (1991) 1–11; (c) *Bull. W.H.O.*, 70 (1992) 17–21.
[2] B.R. Bloom and C.J.L. Murray, *Science*, 257 (1992) 1055–1064.
[3] *Morb. Mortal. Wkly. Rep.*, 39 (1990) 9–12.
[4] M.A. Hamburg and T.R. Frieden, *N. Engl. J. Med.*, 330 (1994) 1750–1751.
[5] P. Draper and R.J.W. Rees, *Nature (London)*, 228 (1970) 860–861.
[6] P.J. Brennan, S.W. Hunter, M. McNeil, and M. Daffé, in E.M. Ayoub, G.H. Cassel, W.C. Branche, and T.J. Henry (Eds.), *Microbial Determinants of Virulence and Host Response*, American Society for Microbiology, Washington, DC, 1990, pp 55–74.
[7] D. Chatterjee, K.-H. Khoo, M.R. McNeil, A. Dell, H.R. Morris, and P.J. Brennan, *Glycobiology*, 3 (1993) 497–506.
[8] A. Lemassu and M. Daffé, *Biochem. J.*, 297 (1994) 351–357.
[9] (a) S.R. Coates, D. Hansen, G. Schecter, G. Slutkin, P. Hopewell, L. Affronti, and D.F. Echenberg, *J. Clin. Microbiol.*, 24 (1986) 126–130; (b) F.B. Seibert, M. Stacey, and P.W. Kent, *Biochim. Biophys. Acta*, 3 (1949) 632–640; (c) P.W. Kent, *J. Chem. Soc.*, (1951) 364–368.
[10] K. Takeo and Y. Suzuki, *Carbohydr. Res.*, 162 (1987) 95–109.
[11] A. Lipták, A. Borbás, and I. Bajza, *Med. Res. Rev.*, 14 (1994) 307–352.
[12] (a) G.H. Veeneman, S.H. van Leeuwen, H. Zuurmond, and J.H. van Boom, *J. Carbohydr. Chem.*, 9 (1990) 783–796; (b) M.K. Gurjar and G. Viswanadham, *J. Carbohydr. Chem.*, 10 (1991) 481–485; (c) M. Daffé, S.-N. Cho, D. Chatterjee, and P.J. Brennan, *J. Infect. Dis.*, 163 (1991) 161–168; (d) H.H. Baer and X. Wu, *Carbohydr. Res.*, 238 (1993) 215–230; (e) P.A. Wallace and D.E. Minnikin, *Carbohydr. Res.*, 263 (1994) 43–59.
[13] T.L. Lowary, S.J. Swiedler, and O. Hindsgaul, *Carbohydr. Res.*, 256 (1994) 257–273, and references cited therein.
[14] N. Grossman, S.B. Svenson, L. Leive, and A.A. Lindberg, *Mol. Immunol.*, 27 (1990) 859–865.
[15] (a) K. Matsuda, *Nature (London)*, (1957) 985; (b) B. Helferich and J. Zirner, *Chem. Ber.*, 95 (1962) 2604–2611; (c) M.L. Wolfrom, A. Thompson, and D.R. Lineback, *J. Org. Chem.*, 28 (1963) 860–861; (d) W.E. Dick, Jr, J.E. Hodge, and G.E. Inglett, *Carbohydr. Res.*, 36 (1974) 319–329; (e) K. Igarashi, J.

Irisawa, and T. Honma, *Carbohydr. Res.*, 39 (1975) 341–343; (f) R.R. Schmidt and J. Michel, *Angew. Chem. Int. Ed. Engl.*, 19 (1980) 731–732; (g) G.O. Aspinall and M.K. Gurjar, *Carbohydr. Res.*, 143 (1985) 266–270.

[16] K. Takeo, *Carbohydr. Res.*, 88 (1981) 158–161.

[17] H. Paulsen, *Angew. Chem. Int. Ed. Engl.*, 21 (1982) 155–173.

[18] (a) G.H. Veeneman and J.H. van Boom, *Tetrahedron Lett.*, 31 (1990) 275–278; (b) H.P. Wessel, *Tetrahedron Lett.*, 31 (1990) 6863–6866; (c) M. Bols, *Acta Chem. Scand.*, 47 (1994) 829–834.

[19] Ref. 4 in R.U. Lemieux, K.B. Hendricks, R.V. Stick, and K. James, *J. Am. Chem. Soc.*, 97 (1975) 4056–4062.

[20] T. Ishikawa and H.G. Fletcher, Jr, *J. Org. Chem.*, 34 (1969) 563–571.

[21] (a) H.M. Flowers, *Carbohydr. Res.*, 18 (1971) 211–218; (b) U. Zehavi and A. Patchornik, *J. Am. Chem. Soc.*, 95 (1973) 5673–5677; (c) J.M. Berry and G.G.S. Dutton, *Can. J. Chem.*, 52 (1974) 681–683; (d) J.M. Berry and G.G.S. Dutton, *Carbohydr. Res.*, 38 (1974) 339–345.

[22] F. Weygand and H. Ziemann, *Justus Liebigs Ann. Chem.*, 657 (1962) 179–198.

[23] S. Brennan and P.A. Finan, *J. Chem. Soc. (C)*, (1970) 1742–1744.

[24] (a) V. Pozsgay and H.J. Jennings, *Tetrahedron Lett.*, 28 (1987) 1375–1376; (b) V. Pozsgay and H.J. Jennings, *J. Org. Chem.*, 53 (1988) 4042–4052; (c) V. Pozsgay and H.J. Jennings, *Carbohydr. Res.*, 179 (1988) 61–75; (d) S. Nambiar, J.F. Deauble, R.J. Doyle, and K. Grant Taylor, *Tetrahedron Lett.*, 30 (1989) 2179–2182; (e) A. Kameyama, H. Ishida, M. Kiso, and A. Hasegawa, *Carbohydr. Res.*, 193 (1989) c1–c5; (f) A. Kameyama, H. Ishida, M. Kiso, and A. Hasegawa, *Carbohydr. Res.*, 200 (1990) 269–285; (g) S. Knapp and P.J. Kukkola, *J. Org. Chem.*, 55 (1990) 1632–1636; (h) N. Sakairi, L.-X. Wang, and H. Kuzuhara, *J. Chem Soc., Chem Commun.*, (1991) 289–290; (i) R.K. Jain, A.K. Sarkar, and K.L. Matta, *Carbohydr. Res.*, 220 (1991) c1–c4; (j) A. Hasegawa, K. Hotta, A. Kameyama, H. Ishida, and M. Kiso, *J. Carbohydr. Chem.*, 10 (1991) 439–459; (k) A. Hasegawa, H. Ohki, T. Nagahama, H. Ishida, and M. Kiso, *Carbohydr. Res.*, 212 (1991) 277–281; (l) R.K. Jain and K.L. Matta, *Carbohydr. Res.*, 226 (1992) 91–100; (m) R.K. Jain, C.F. Piskorz, R.D. Locke, and K.L. Matta, *Carbohydr. Res.*, 236 (1992) 327–334; (n) V. Pozsgay, C.P.J. Glaudemans, J.B. Robbins, and R. Schneerson, *Tetrahedron*, 48 (1992) 10249–10264; (o) S.H. Khan and K.L. Matta, *J. Carbohydr. Chem.*, 12 (1993) 335–348; (p) R.K. Jain, C.F. Piskorz, and K.L. Matta, *Carbohydr. Res.*, 243 (1993) 385–391; (q) V. Pozsgay and B. Coxon, *Carbohydr. Res.*, 257 (1994) 189–215; (r) A. Hasegawa, T. Ando, M. Kato, H. Ishida, and M. Kiso, *Carbohydr. Res.*, 257 (1994) 55–65; (s) N. Hada, T. Takeda, and Y. Ogihara, *Carbohydr. Res.*, 258 (1994) 93–104; (t) W. Stahl, U. Sprengard, G. Kretzschmar, and H. Kunz, *Angew. Chem., Int. Ed. Engl.*, 33 (1994) 2096–2098.

[25] (a) D. Horton and D.H. Hutson, *Adv. Carbohydr. Chem.*, 18 (1963) 123–199; (b) F. Andersson, P. Fügedi, P.J. Garegg, and M. Nashed, *Tetrahedron Lett.*, 27 (1986) 3919–3922; (c) J. Kihlberg, D.A. Leigh, and D.R. Bundle, *J. Org. Chem.*, 55 (1990) 2860–2863.

[26] K. Igarashi, T. Honma, T. Mori, and J. Irisawa, *Carbohydr. Res.*, 38 (1974) 312–315.

[27] (a) R.U. Lemieux and J. Hayami, *Can. J. Chem.*, 43 (1965) 2162–2173; (b) B. Helferich, W.N. Müller, and S. Karbach, *Justus Liebigs Ann. Chem.*, (1974) 1514–1521; (c) H. Paulsen and W. Stenzel, *Chem. Ber.*, 111 (1978) 2334–2347; (d) H. Paulsen and W. Stenzel, *Chem. Ber.*, 111 (1978) 2348–2357; (e) H. Paulsen, C. Kolar, and W. Stenzel, *Chem. Ber.*, 111 (1978) 2358–2369.

[28] H. Paulsen and M. Paal, *Carbohydr. Res.*, 135 (1984) 71–84.

[29] M.L. Wolfrom and W. Groebke, *J. Org. Chem.*, 28 (1963) 2986–2988.

[30] H.A. van Doren, R. van der Geest, F. van Bolhuis, R.M. Kellog, and H. Wynberg, *Carbohydr. Res.*, 194 (1989) 79–86.

[31] F. Michon, J.-R. Brisson, and H.J. Jennings, *Biochemistry*, 26 (1987) 8399–8405.

[32] K. Bock, M. Meldal, D.R. Bundle, T. Iversen, B.M. Pinto, P.J. Garegg, I. Kvanström, T. Norberg, A.A. Lindberg, and S.B. Svenson, *Carbohydr. Res.*, 130 (1984) 35–53.

[33] (a) V. Pozsgay, C.P.J. Glaudemans, J.B. Robbins, and R. Schneerson, *Bioorg. Med. Chem. Lett.*, 2 (1992) 255–260; (b) V. Pozsgay, *J. Am. Chem. Soc.*, 117 (1995) 6673–6681.

[34] D.A. Powell, in R.C.W. Berkeley, G.W. Gooday, and D.C. Ellwood (Eds.), *Microbial Polysaccharides and Polysaccharases*, Academic Press, London, 1979, pp 117–160.