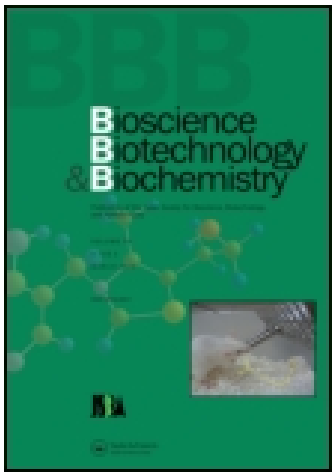

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Yi Qiu[a], Yoshiaki Nakahara[a] & Tomoya Ogawa[ab]
[a] The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01, Japan
[b] Graduate School for Agriculture and Life Sciences, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113, Japan
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Design and Synthesis of Gentiohexaosyl Derivatives for an ANP Receptor Antagonist, HS-142-1†

Yi QIU,* Yoshiaki NAKAHARA,*,†† and Tomoya OGAWA*,**,††

* *The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01, Japan*
** *Graduate School for Agriculture and Life Sciences, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113, Japan*
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A hexaosyl fragment of the major component of lipooligosaccharide HS-142-1, *O*-(3-*O*-caproyl-β-D-glucopyranosyl)-(1→6)-[*O*-(β-D-glucopyranosyl)-(1→6)-*O*-(3-*O*-caproyl-β-D-glucopyranosyl)-(1→6)]$_2$-D-glucopyranose (1), was efficiently synthesized by block synthesis. More stable analogs, *O*-(3-*O*-hexyl-β-D-glucopyranosyl)-(1→6)-[*O*-(β-D-glucopyranosyl)-(1→6)-*O*-(3-*O*-hexyl-β-D-glucopyranosyl)-(1→6)]$_2$-D-glucopyranose (4) and *O*-(3-*O*-caproyl-2,4,6-tri-*O*-methyl-β-D-glucopyranosyl)-(1→6)-[*O*-(2,3,4-tri-*O*-methyl-β-D-glucopyranosyl)-(1→6)-*O*-(3-*O*-caproyl-2,4-di-*O*-methyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-*O*-methyl-D-glucopyranose (2), were also designed and synthesized in a similar manner.

Key words: gentiohexaose; β1→6-glycosylation; ANP antagonist; HS-142-1

The lipo-oligosaccharide HS-142-1 was isolated from the culture broth of *Aureobasidium pullulans* var. *melanigenum* and known as a specific nonpeptide antagonist for the functional receptors (A and B) of atrial natriuretic peptide (ANP), a circulating hormone that regulates body fluid volume and blood pressure. This unique lipo-oligosaccharide may be regarded as a lead for a novel drug and a useful probe for further research on ANP receptor-ligand binding mechanisms, due to its remarkable biological activity and low toxicity.[1]

HS-142-1 is a mixture of β-1→6 oligoglucosides (DP: 10–30) partly acylated with caproyl ($C_5H_{11}CO$) groups (5–15 in number). Comparison of the NMR data with those of di-*O*-caproyl gentiobioses synthesized in this laboratory[3] showed that the major components of HS-142-1 are caproylated at the O-3 position of the glucose residues. For further studies on the structure–activity relationship of HS-142-1, especially in connection with a question concerning the minimum molecular size of the active component, we planned to synthesize a gentiohexaosyl fragment **1**, with caproyl groups at the O-3 position on every other glucose residue from the non-reducing terminal as shown in Fig. 1. During the course of investigation, we became aware of the instability of 3-*O*-caproylated gentiooligosaccharides. Therefore a more stable 3-*O*-hexyl derivative **4** and a 3-*O*-caproyl-2,4-di-*O*-methylated congener **2** were also designed and synthesized from the standpoint of interest in the antagonist activity of those modified oligosaccharides. In connection with compound **2**, it is to be noted that *O*-methyl and *O*-ethyl analogs of heparin fragments were shown to be as biologically active as their natural counterparts.[4] In this paper we describe stereo- and regio-controlled syntheses of the gentiohexaose fragment and the relating derivatives.

Results and Discussion

A block synthesis strategy for the target compounds **1**–**5** is shown in Fig. 2. We designed an appropriately protected disaccharide **9** as the key intermediate. The 2-(trimethylsilyl)ethyl (SE) glycoside[5] would readily be converted into a glycosyl donor **7** *via* hemiacetal, while selective cleavage of the levulinoyl (Lev) group[6] would provide a glycosyl acceptor **8**. Glycosylation would proceed in favor of β-glycoside formation by the help of neighboring-participation of the toluoyl (T) group[7] at the O-2 position. An allyl (All)[8] group was used for the temporary protection of the 3′-hydroxy group, which could be transformed further by acylation or alkylation in a later stage after completion of the sugar chain elongation.

First we describe the syntheses of monosaccharide synthons as shown in Scheme 1. The known 2-(trimethylsilyl)-ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside **12**[5] was toluoylated with toluoyl chloride in the presence of 4-dimethylamino-pyridine (DMAP) in a mixture of pyridine and 1,2-dichloroethane to give **13** in 97% yield. After removal

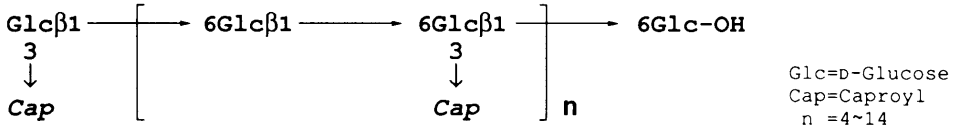


Fig. 1. Putative Structure of HS-142-1.

† Synthetic Studies on the Lipo-oligosaccharide HS-142-1, a Novel Nonpeptide Antagonist for the Atrial Natriuretic Peptide Receptor. Part 2.
†† Corresponding author.

Abbreviations: All, allyl; ANP, atrial natriuretic peptide; Bn, benzyl; Cap, caproyl; CMPI, 2-chloro-1-methylpyridinium iodide; DABCO, 1,4-diazabicyclo[2.2.2]octane; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMAP, 4-dimethylaminopyridine; DMF, *N*,*N*-dimethylformamide; DP, degree of polymerization; FAB-MS, fast atom bombardment mass spectrometry; Lev, levulinoyl; 4-Me-DTBP, 2,6-di-*tert*-butyl-4-methylpyridine; NBA, 3-nitrobenzyl alcohol; SE, 2-(trimethylsilyl)ethyl; T, toluoyl; TFA, trifluoroacetic acid.

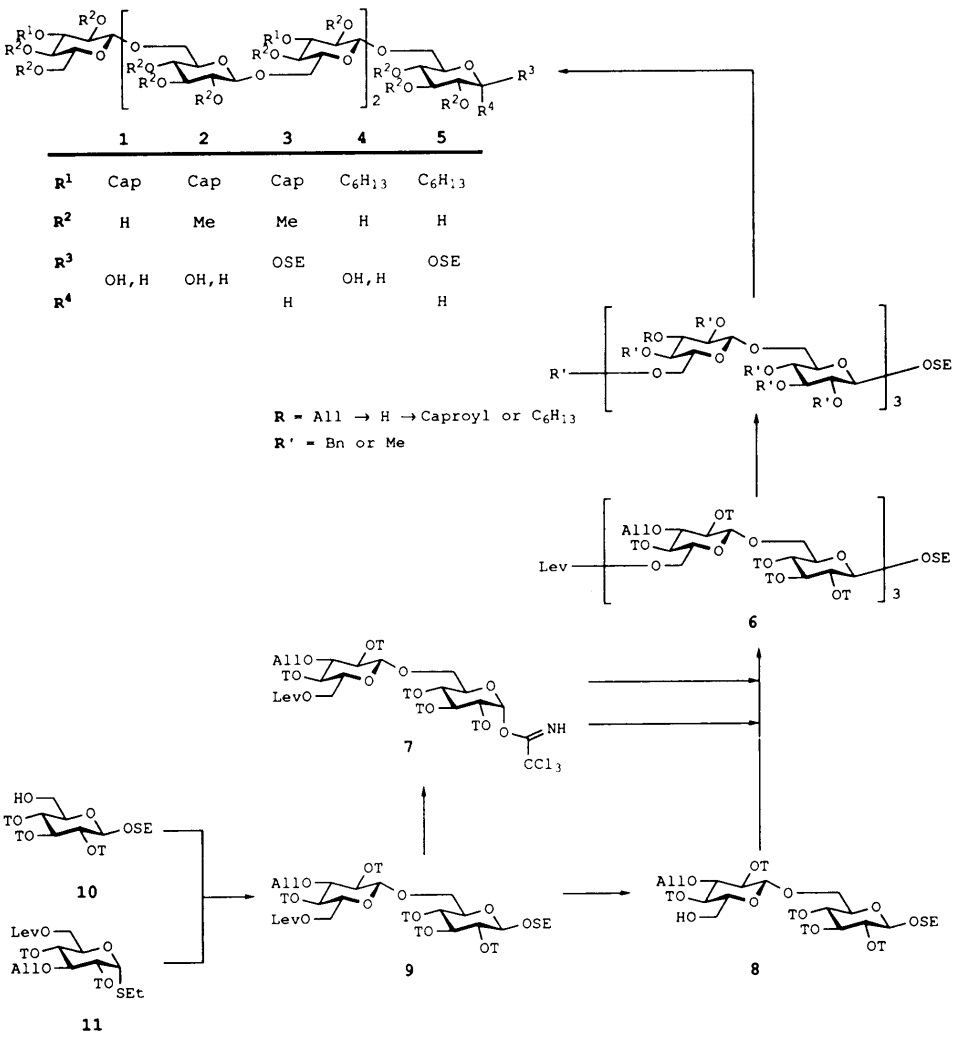
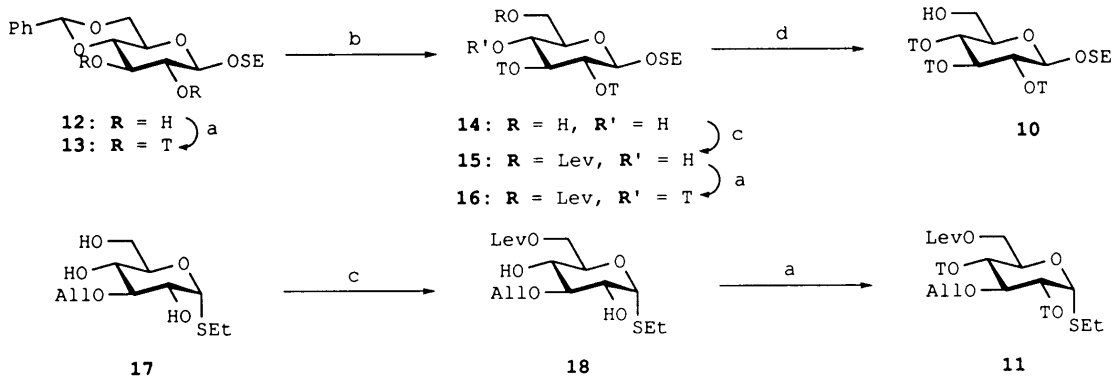


Fig. 2. Synthetic Strategy.



Scheme 1. Preparation of Monosaccharide Synthons.

a) TCl, DMAP (*Cat.*), pyridine; b) 90% TFA*aq*; c) LevOH, CMPI, DABCO; d) $NH_2NH_2 \cdot AcOH$.

of the benzylidene group with 90% trifluoroacetic acid (TFA), the resulting diol **14** (88%) was selectively 6-*O*-levulinoylated and then 4-*O*-toluoylated to give **16** in 99% yield (2 steps). De-leuvlinoylation of **16** with methylhydrazine acetate in a 2:25 mixture of acetic acid[3] and toluene furnished the glycosyl acceptor **10**. Monosaccharide donor **11** was obtained from known ethyl 3-*O*-allyl-1-thio-α-D-glucopyranoside **17**[9] *via* selective 6-*O*-levulinoylation and toluoylation in 81% yield (2 steps).

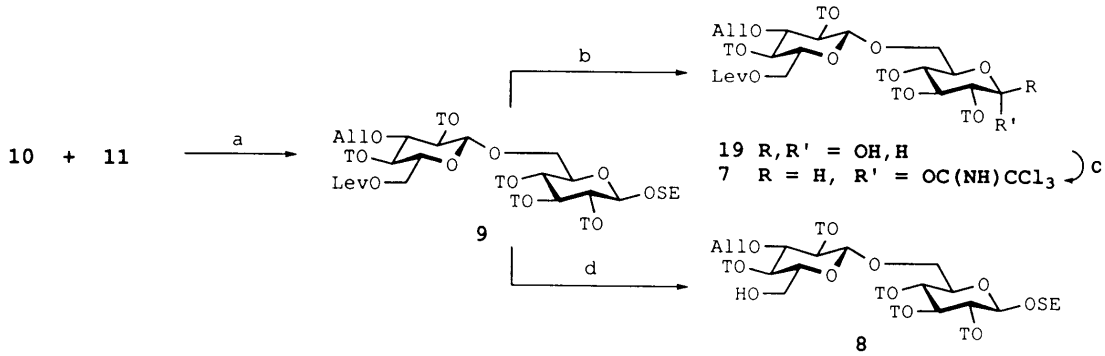
Having prepared suitably protected monosaccharide synthons, glycosylation of **10** with **11** (1.2 equivalent) was done in the presence of methyl trifluoromethanesulfonate (1 equivalent to **11**) and a catalytic amount of silver trifluoromethanesulfonate (0.2 equivalent to **11**) to afford the key gentiobiose intermediate **9** in 97% yield. In the absence of added silver trifluoromethanesulfonate, 6-*O*-methylation of **11** was observed in a noticeable amount because an excess of methyl trifluoromethanesulfonate (5 equivalent to **11**) was required to complete the glycosylation. SE group of **9** was removed *via* hydrolysis with

TFA[5] to give a hemiacetal **19** which was transformed [Cl_3CCN, DBU (*Cat.*)][3] to the gentiobiosyl trichloroacetimidate **7** in 94% (2 steps) yield. On the other hand, the Lev group of **9** was removed with methylhydrazine acetate to give a disaccharide acceptor **8** in 87% yield.

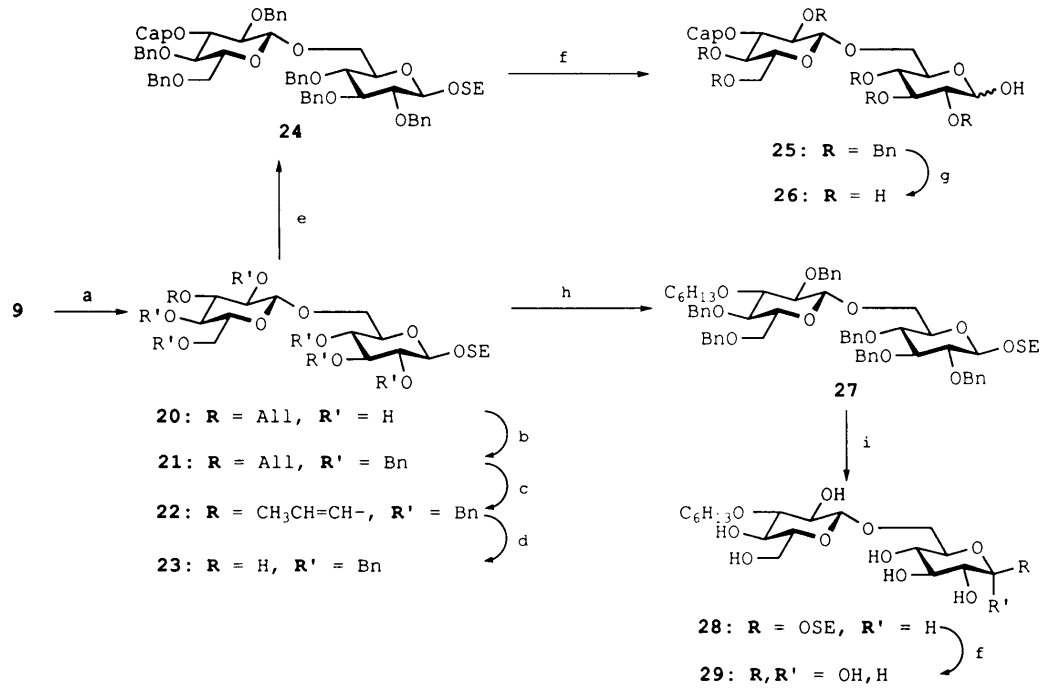
Before further elongating the sugar chain, the model studies of protecting group manipulation and side-chain introduction were examined using disaccharide derivatives as shown in Scheme 3. Hydrolysis of **9** with a catalytic amount of methanoic sodium methoxide afforded hexaol **20**, which was benzylated (NaH, BnBr) in DMF to give per-benzylated gentiobiose derivative **21** (98%, 2 steps). Two-step deallylation involving the cationic-iridium-complex-catalyzed isomerization[10] of **21** gave 3'-hydroxy compound **23** quantitatively. Caproylation of **23** with caproyl chloride afforded 3'-*O*-caproyl-gentiobioside derivative **24** in 92% yield. Hydrolysis of SE glycoside with TFA followed by catalytic hydrogenolysis of benzyl ethers with palladium on carbon to give 3'-*O*-caproyl-gentiobiose **26**, though in an unsatisfactory yield (21%, 2 steps) partly due to de-acylation during the last purification.[11] On the other hand, 3'-*O*-hexyl-gentiobioside derivative **27** was obtained by alkylation of **23** with NaH/hexyl bromide in 71% yield, which was de-protected *via* catalytic hydrogenolysis of benzyl ethers with palladium hydroxide on carbon[12] and hydrolysis of SE glycoside with TFA to give 3'-*O*-hexyl-gentiobiose **29** in 98% (2 steps) yield.

Gentiohexaose was constructed as shown in Scheme 4. Silver trifluoromethanesulfonate-promoted[13] glycosylation of **8** with **7** (1.3 equivalent) afforded a gentiotetraose **30** in 89% yield, which was de-levulinoylated with methylhydrazine acetate to give a gentiotetraose acceptor **31** in 66% yield. Glycosylation of **31** with **7** (1.3 equivalent) afforded a desired gentiohexaosyl intermediate **6** in 82% yield.

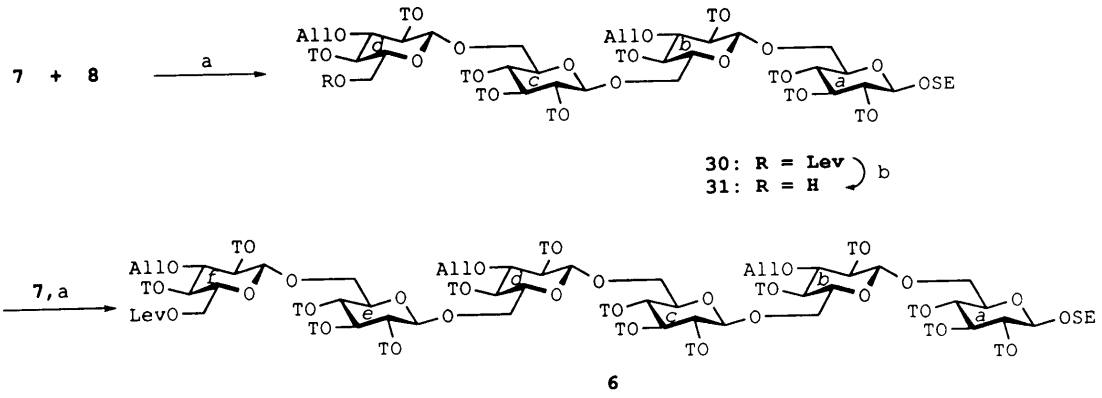
Having prepared the gentiohexaose derivative, caproylation and hexylation were now examined through the manipulation of protecting groups as described for the disaccharide model. Compound **6** was converted into the tri-*O*-allyl-per-benzylated gentiohexaose derivative **33** *via* the hexadecaol **32** in 61% yield (2 steps). Deallylation of **33** with iridium complex followed by hydrolysis afforded a triol **35** in 92% yield. Caproylation of **35** with caproyl



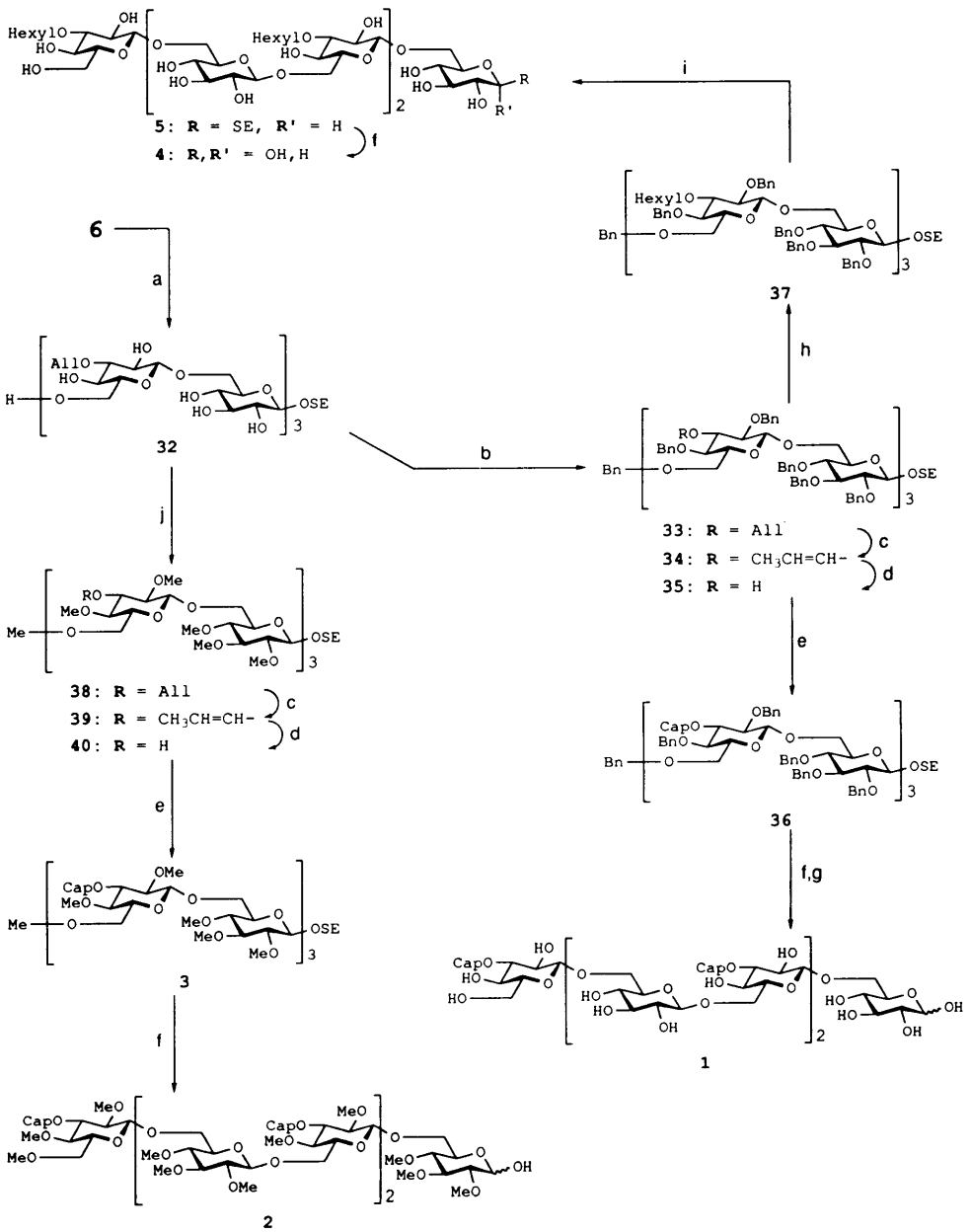
Scheme 2. Preparation of Disaccharide Synthons.
a) MeOTf, AgOTf, MS 4A; b) TFA; c) CCl_3CN, DBU (*Cat.*); d) $NH_2NH_2 \cdot AcOH$.



Scheme 3. Syntheses of Gentiobiose Derivatives.
a) MeONa, MeOH; b) NaH, BnBr; c) $\{Ir(COD)[P(Me)Ph_2]_2\}PF_6$; d) $HgCl_2$, HgO; e) CapCl, pyridine; f) TFA; g) [H_2], Pd/C; h) NaH, $C_6H_{13}Br$; i) [H_2], $Pd(OH)_2$/C.



Scheme 4. Syntheses of Gentiotetra- and hexaoses.
a) AgOTf, MS AW-300; b) $NH_2NH_2 \cdot AcOH$.



Scheme 5. Syntheses of Gentiohexaose Derivatives.
a) MeONa, MeOH; b) NaH, BnBr; c) $[Ir(COD)[P(Me)Ph_2]_2]PF_6$; d) $HgCl_2$, HgO; e) CapCl, pyridine; f) TFA; g) $[H_2]$, Pd/C; h) NaH, $C_6H_{13}Br$; i) $[H_2]$, $Pd(OH)_2/C$; j) NaH, MeI.

chloride afforded a tri-*O*-caproyl gentiohexaose derivative **36** in 41% yield, while hexylation of **35** with hexyl bromide afforded at tri-*O*-hexyl gentiohexaose derivative **37** in 85% yield. Hydrolysis of SE glycoside (**36**) with TFA followed by catalytic hydrogenolysis of benzyl ethers with palladium on carbon gave the target molecule, tri-*O*-caproyl gentiohexaose **1**. However, its mass spectral data and the insufficient integration of the signals of caproyl groups in the NMR spectrum indicated that the product was obtained as a mixture contaminated with di-*O*-caproyl gentiohexaose and mono-*O*-caproyl gentiohexaose derivatives. Most probably de-acylation[11] might take place partly during hydrogenation and/or purification by gel filtration chromatography on LH-20 with methanol. In contrast, deprotection of the tri-*O*-hexyl gentiohexaose derivative **37** was done without difficulty as in the case of the disaccharide model to give de-benzylated derivative **5** in 84% yield, which was quantitatively transformed into the tri-*O*-hexyl gentiohexaose **4** as a white powder after gel filtration chromatographic purification (Sephadex LH-20, MeOH) and lyophilization.

Since the loss of 3-*O*-caproyl groups from **1** was assumed to occur *via* intra- and/or inter-molecular acyl-migration processes in aqueous or alcoholic media, we next synthesized tri-*O*-caproyl-hexadecamethyl gentiohexaoside **2** in which all adjacent hydroxy groups were masked as methyl ethers, since there are some examples in which permethylation of bio-active oligosaccharides did not decrease their activities.[4] The hexadecaol **32** was methylated with methyl iodide and NaH, then deallylated and caproylated to give **3** (23%, 3 steps). Finally hydrolysis of the SE glycoside **3** quantitatively afforded the desired compound **2**, which is immiscible with water and methanol but stable in organic solvents such as chloroform and ethyl acetate.

In summary, we synthesized a possible hexaosyl fragment of lipo-oligosaccharide HS-142-1. However, the desired tri-*O*-caproylated compound was too unstable to isolate, and was obtained as a mixture contaminated with di- and mono-*O*-caproyl congeners. On the other hand, tri-*O*-hexyl and tri-*O*-caproyl-per-methyl analogs were obtained as stable compounds by a regio- and stereo-controlled synthetic sequence. Biotesting of these synthetic compounds is being done.

Experimental

General methods. Melting points (mp) were measured with a Yanagimoto micro-melting-point apparatus and are uncorrected. Concentration of the organic solvents was done under reduced pressure at a <40 C bath temperature. Optical rotation was measured with a JASCO DIP 370 polarimeter at 25±5 C for a solution in $CHCl_3$, unless otherwise stated. NMR spectra were recorded with a JEOL JNM-EX270 spectrometer or a Bruker AM400 spectrometer, chemical shifts being given in ppm relative to internal standards. The following reference signals were used: $(CH_3)_4Si$, δ 0.00 (^{1}H in $CDCl_3$); $CHCl_3$, δ 7.26 (^{1}H in $CDCl_3$) and δ 77.0 (^{13}C in $CDCl_3$); $(CH_3)_2CO$, δ 2.00 (^{1}H in $CDCl_3$); CD_3OD, δ 49.8 (^{13}C in CD_3OD); and HDO, δ 4.70 (^{1}H in D_2O). The signals were assigned based on 2D H-H, C-H COSY and DEPT data. FAB-MS spectra were measured with a JEOL JMS-HX110 mass spectrometer. TLC was done on silica gel F254 (Merck, Darmstadt, Germany) with detection by UV light and/or by charring with 10% sulfuric acid in ethanol. Flash chromatography was done on silica gel [silica gel C-60 (230–400 mesh)]. Powdered molecular sieves were desiccated at 180 C under a vacuum overnight immediately before use.

2-(Trimethylsilyl)ethyl 4,6-O-benzylidene-2,3-di-O-toluoyl-β-D-glucopyranoside (**13**). Toluoyl chloride (15 ml, 110 mmol) was added dropwise to a mixture of **12** (18 g, 50 mmol), DMAP (1 g, 10 mmol) and pyridine (50 ml) in 1,2-dichloroethane (100 ml) at 0 C under an argon atmosphere. The reaction mixture was stirred at room temperature overnight, and quenched with water (25 ml) at 0 C. The reaction mixture was concentrated and dissolved in EtOAc (300 ml), washed with water, saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Purification of the crude product by flash chromatography on silica gel with toluene–$CHCl_3$ (1:1) afforded **13** (30 g, 97%) as a white solid. R_f 0.34 (EtOAc/hexane = 1/9). mp 98–99 C. $[\alpha]_D$ +39° (*c* 1.0). ^{1}H-NMR ($CDCl_3$): δ 7.85 [d, 4H, *J* = 8.2 Hz, aromatic (T)], 7.37 (m, 5H, Ph), 7.17 [d, 2H, *J* = 6.9 Hz, aromatic (T)], 7.15 [d, 2H, *J* = 7.9 Hz, aromatic (T)], 5.75 (t, 1H, *J* = 9.6 Hz, H-3), 5.54 (s, 1H, PhCH), 5.45 (dd, 1H, *J* = 7.9 Hz, 9.6 Hz, H-2), 4.80 (d, 1H, *J* = 7.9 Hz, H-1), 4.44 (dd, 1H, *J* = 4.9 Hz, 10.6 Hz, H-6), 4.01–3.85 [m, 3H, H-4, 6, OCH_2 (SE)], 3.54 [m, 2H, H-5, OCH_2 (SE)], 2.36, 2.34 [2 × s, 2 × 3H, CH_3 (T)], 0.89 [m, 2H, $SiCH_2$ (SE)], −0.07 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 166.1, 165.7 [C=O (T)], 144.2–126.6 (aromatic), 101.9, 101.8 (C-1, PhCH), 79.4, 72.8, 72.5, 69.2, 68.2, 68.4, 67.1 [C-2, 3, 4, 5, 6, OCH_2 (SE)], 22.1 [CH_3 (T)], 18.5 [$SiCH_2$ (SE)], −1.04 [CH_3 (SE)]. Positive FAB-MS (matrix = NBA) *m/z*: 603.2 $(M+H)^+$.

Anal. Found: C, 67.28; H, 6.62. Calcd. for $C_{34}H_{40}O_8Si$: C, 67.52; H, 6.67%.

2-(Trimethylsilyl)ethyl 2,3-di-O-toluoyl-β-D-glucopyranoside (**14**). To a solution of **13** (5 g, 8.2 mmol) in 1,2-dichloroethane (100 ml) was added aqueous TFA (90%, 10 ml). The mixture was stirred for 1.5 h at 0 C, then diluted with $CHCl_3$ (250 ml), and worked up as described for **13**. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (3:7) afforded **14** (4 g, 88%) as a colorless syrup. R_f 0.37 (EtOAc/$CHCl_3$ = 2/3). $[\alpha]_D$ +97° (*c* 1.0). ^{1}H-NMR ($CDCl_3$): δ: 5.37 (m, 2H, H-2, 3), 4.73 (d, 1H, *J* = 7.9 Hz, H-1), 4.05–3.87 (m, 4H, H-4, 6, OCH_2 (SE)], 3.59 [m, 2H, H-5, OCH_2 (SE)], 2.354, 2.346 [2 × s, 2 × 3H, CH_3 (T)], −0.08 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 100.6 (C-1), 77.2, 75.7, 71.4, 69.9, 67.7 [C-2, 3, 4, 5, OCH_2 (SE)], 62.2 (C-6), 21.6, 21.5 [CH_3 (T)], −1.54 [CH_3 (SE)]. Positive FAB-MS (matrix = NBA) *m/z*: 539.1 $(M+Na)^+$, 517.1 $(M+H)^+$.

Anal. Found: C, 63.30; H, 6.98. Calcd. for $C_{27}H_{36}O_8Si \cdot 0.1$ toluene: C, 63.26; H, 7.05%.

2-(Trimethylsilyl)ethyl 6-O-levulinoyl-2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**16**). A solution of DABCO (10 g, 78 mmol) in THF (100 ml) was added to a mixture of **14** (9 g, 17 mmol), levulinic acid (7 ml, 68 mmol) and CMPI (9 g, 35 mmol) in THF/MeCN (80 ml/30 ml) during 15 min at 0 C, and stirred at 0 C for 1.5 h. The mixture was filtered and the filtrate was concentrated to give **15** [R_f 0.29 (EtOAc/toluene = 1/3)] which was used for the next reaction without purification. Toluoylation of **15** was done as described for **13**. Purification of the crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1:9) afforded **16** (12 g, 99%, 2 steps) as a colorless syrup. R_f 0.55 (EtOAc/toluene = 1/4). $[\alpha]_D$ −0.5° (*c* 1.0). ^{1}H-NMR ($CDCl_3$): δ 7.83, 7.79, 7.70, 7.16, 7.157, 7.06 [6 × d, 6 × 2H, *J* = 8.2 Hz, aromatic (T)], 5.81 (t, 1H, *J* = 9.6 Hz, H-3), 5.50 (t, 1H, *J* = 9.9 Hz, H-4), 5.45 (dd, 1H, *J* = 7.9 Hz, 9.6 Hz, H-2), 4.80 (d, 1H, *J* = 7.9 Hz, H-1), 4.30 (d, 2H, *J* = 4.3 Hz, H-6), 4.00 [m, 2H, H-5, OCH_2 (SE)], 3.63 [dt, 1H, *J* = 6.6 Hz, 9.2 Hz, OCH_2 (SE)], 2.72, 2.57 [2 × m, 2 × 2H, CH_2 (Lev)], 2.36, 2.35, 2.28 [3 × s, 3 × 3H, CH_3 (T)], 2.17 [s, 3H, CH_3 (Lev)], −0.06 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 206.3 [C=O (Lev)], 172.3 [OC=O (Lev)], 165.7, 165.2, 165.0 [C=O (T)], 100.6 (C-1), 72.8, 72.0, 71.7, 69.4, 67.6 [C-2, 3, 4, 5, OCH_2 (SE)], 62.9 (C-6), 37.8, 27.8 [CH_2 (Lev)], 29.7 [CH_3 (Lev)], −1.51 [CH_3 (SE)]. Positive FAB-MS (matrix = NBA) *m/z*: 771.0 $(M+K)^+$, 755.1 $(M+Na)^+$.

Anal. Found: C, 65.51; H, 6.61. Calcd. for $C_{40}H_{48}O_{11}Si$: C, 65.55; H, 6.61%.

2-(Trimethylsilyl)ethyl 2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**10**). Methylhydrazine acetate (3.5 g, 33 mmol) in AcOH (20 ml) was added to a solution of **16** (12.0 g, 16 mmol) in toluene (250 ml) at room temperature for 2 h. The reaction mixture was diluted with EtOAc (300 ml), washed with water, saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Purification of the crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1:9) afforded **10** (10.0 g, 98%) as a white solid. R_f 0.52 (EtOAc/toluene = 1/4). mp 64–65 C. $[\alpha]_D$ −4° (*c* 0.8). ^{1}H-NMR ($CDCl_3$): δ 5.89 (t, 1H, *J* = 9.6 Hz, H-3), 5.46 (dd, 1H, *J* = 7.9 Hz, 9.6 Hz, H-2), 5.43 (t, 1H, *J* = 9.2 Hz, H-4), 4.87 (d, 1H, *J* = 7.9 Hz, H-1), 4.04, 3.60 [2 × dt, 2 × 1H, *J* = 5.9 Hz, 10.2 Hz, OCH_2 (OSE)], 3.80 (m,

3H, H-5, 6), 2.36 [s, 6H, CH_3 (T)], 2.28 [s, 3H, CH_3 (T)]. ^{13}C-NMR ($CDCl_3$): δ 165.9, 165.7, 164.9 [C=O (T)], 100.6 (C-1), 74.5 (C-5), 72.6 (C-3), 71.7 (C-2), 69.4 (C-4), 67.4 [OCH_2 (SE)], 61.2 (C-6). Positive FAB-MS (matrix = NBA) *m/z*: 673.0 $(M+K)^+$, 634.9 $(M+H)^+$.

Anal. Found: C, 66.11; H, 6.64. Calcd. for $C_{35}H_{42}O_9Si$: C, 66.22; H, 6.67%.

Ethyl 3-O-allyl-6-O-levulinoyl-2,4-di-O-toluoyl-1-thio-α-D-glucopyranoside (**11**). This was obtained from **17** (3.2 g, 8.2 mmol) *via* **18** [R_f 0.27 (EtOAc/toluene = 1/3)] according to the procedure described for **16**. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 3) afforded **11** (4.0 g, 81% 2 steps) as a white solid. R_f 0.60 (EtOAc/$CHCl_3$ = 1/4). mp 78–79°C. $[\alpha]_D$ +70° (*c* 1.0). ^{1}H-NMR ($CDCl_3$): δ 7.60, 7.95 [2 × d, 2 × 2H, *J* = 8.2 Hz, aromatic (T)], 7.26 [m, 4H, aromatic (T)], 5.80 (d, 1H, *J* = 5.6 Hz, H-1), 5.62 [m, 1H, =CH (All)], 5.31 (m, 2H, H-2, 4), 5.10–4.94 [m, 2H, CH_2=(All)], 4.54 (m, 1H, H-5), 4.31–4.02 [m, 5H, H-3, 6, OCH_2 (All)], 2.78–2.53 [m, 6H, CH_2 (Lev), SCH_2], 2.43 [s, 6H, CH_3 (T)], 2.18 [s, 3H, CH_3 (Lev)], 1.26 (t, 3H, *J* = 7.3 Hz, SCH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 206.5 [C=O (Lev)], 172.3 [OC=O (Lev)], 165.3, 165.1 [C=O (T)], 144.1–126.5 [aromatic, =CH (All)], 117.2 [CH_2=(All)], 81.9 (C-1), 77.2 (C03), 73.8, 72.9, 70.3, 68.1 [C-2, 4, 5, OCH_2 (All)], 62.7 (C-6), 37.7, 27.7 [CH_2 (Lev)], 29.7 (CH_3 (Lev)], 24.1 (SCH_2), 21.63, 21.6 [CH_3 (T)], 14.6 (SCH_2CH_3). Positive FAB-MS (matrix = NBA) *m/z*: 621.0 $(M+Na)^+$, 599.1 $(M+H)^+$, 537.1 $(M+H-SEt)^+$.

Anal. Found: C, 64.43; H, 6.46; S, 5.17. Calcd. for $C_{32}H_{38}O_9S$: C, 64.19; H, 6.40; S, 5.36%.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-6-O-levulinoyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**9**). Methyl trifluoromethanesulfonate (0.22 ml, 1.9 mmol) and silver trifluoromethanesulfonate (50 mg, 0.2 mmol) were added to a stirred mixture of **10** (1.0 g, 1.6 mmol), **11** (1.1 g, 1.9 mmol), and powder MS 4A (3.5 g) in 1,2-dichloroethane (35 ml) at room temperature under an argon atmosphere. Triethylamine (2 ml) was added after 24 h, the mixture was stirred for an additional 0.5 h, filtered through Celite, and concentrated. Purification of the crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1 : 19) afforded **9** (1.8 g, 97%) as a white solid. R_f 0.19 (EtOAc/hexane = 3/7). mp 181–182°C. $[\alpha]_D$ −5° (*c* = 0.8). ^{1}H-NMR ($CDCl_3$): δ 7.95, 7.90, 7.79, 7.77, 7.65 [5 × d, 5 × 2H, *J* = 8.2 Hz, aromatic (T)], 7.14 [m, 10H, aromatic (T)], 5.72 (t, 1H, *J* = 9.9 Hz, H-3), 5.52 [m, 1H, =CH (All)], 5.35 (dd, 1H, *J* = 7.9 Hz, 9.9 Hz, H-2), 5.25 (m, 3H, H-2', 4, 4'), 5.01–4.87 [m, 2H, CH_2=(All)], 4.77 (d, 1H, *J* = 7.9 Hz, H-1), 4.63 (d, 1H, *J* = 7.9 Hz, H-1'), 4.16 (d, 2H, *J* = 4.6 Hz, H-6'), 3.95 [m, 4H, H-6, OCH_2 (All)], 3.82 [m, 4H, H-3', 5, 5', OCH_2 (SE)], 3.37 [q, 1H, *J* = 7.9 Hz, OCH_2 (SE)], 2.68, 2.48 [2 × m, 2 × 2H, CH_2 (Lev)], 2.41, 2.35 [2 × s, 2 × 6H, CH_3 (T)], 2.27 [s, 3H, CH_3 (T)], 2.16 [s, 3H, CH_3 (Lev)], 0.67 [m, 2H, $SiCH_2$ (SE)], −0.12 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 206.3 [C=O (Lev)], 172.2 [OC=O (Lev)], 165.6, 165.4, 165.0, 164.9, 164.8 [C=O (T)], 144.2–126.0 [aromatic, =CH (All)], 117.3 [CH_2=(All)], 101.2, 100.3 (C-1, 1'), 79.4 (C-3'), 74.0–67.1 [C-2, 2', 3, 4, 4', 5, 5', 6, OCH_2 (All, SE)], 62.9 (C-6'), 37.8, 27.8 [CH_2 (Lev)], 29.7 [CH_3 (Lev)], −1.44 [CH_3 (SE)].

Anal. Found: C, 66.80; H, 6.40. Calcd. for $C_{65}H_{74}O_{18}Si$: C, 66.65; H, 6.37%.

O-[(3-O-Allyl-6-O-levulinoyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-toluoyl-α-D-glucopyranosyl)] trichloroacetimidate (**7**). To a stirred solution of **9** (1.6 g, 1.3 mmol) in 1,2-dichloroethane (10 ml) was added TFA (10 ml) at room temperature. The mixture was stirred for 0.5 h and concentrated to give hemiacetal **19** [R_f 0.17 (EtOAc/toluene = 1/3)], which was used for the next reaction without further purification. A catalytic amount of DBU (50 μl, 0.3 mmol) was added at 0°C to a mixture of **19** and trichloroacetonitrile (1.5 ml, 15 mmol) in 1,2-dichloroethane (15 ml), and the mixture was stirred at room temperature for 24 h. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 3) afforded **7** (1.5 g, 94%, 2 steps) as a white solid. R_f 0.51 (EtOAc/toluene = 1/4). mp 89–90°C. $[\alpha]_D$ +10° (*c* 1.3). ^{1}H-NMR ($CDCl_3$): δ 8.28 (s, 1H, NH), 6.67 (d, 1H, *J* = 3.6 Hz, H-1), 6.13 (t, 1H, *J* = 9.9 Hz, H-3), 5.58–5.44 [m, 2H, H-4, =CH (All)], 5.41 (dd, 1H, *J* = 3.6 Hz, 9.9 Hz, H-2), 5.27 (m, 2H, H-2', 4'), 4.95 [m, 2H, CH_2=(All)], 4.77 (d, 1H, *J* = 7.9 Hz, H-1'), 4.44 (m, 1H, H-5), 4.18 (d, 2H, *J* = 4.3 Hz, H-6'), 4.06 (dd, 1H, *J* = 9.9 Hz, H-6), 4.00 [dd, 2H, *J* = 1.3 Hz, 5.9 Hz, OCH_2 (All)], 3.90 (t, 1H, *J* = 8.9 Hz, H-3'), 3.79 (m, 2H, H-5', 6), 2.70, 2.49 [2 × m, 2 × 2H, CH_2 (Lev)], 2.40, 2.38, 2.35, 2.32, 2.28 [5 × s, 5 × 3H, CH_3 (T)], 2.16 [s, 3H, CH_3 (Lev)]. ^{13}C-NMR ($CDCl_3$): δ 206.2 [C=O (Lev)], 172.0 [OC=O (Lev)], 160.0 (C=NH), 134.0 [=CH (All)], 101.8 (C-1'), 92.8 (Cl_3C), 90.5 (C-1), 79.2 (C-3'), 72.8 [OCH_2 (All)], 72.4 (C-4'), 71.9 (C-5), 70.4 (C-2), 70.3 (C-2'), 69.7 (C-3), 68.4 (C-4), 67.2 (C-6), 62.7 (C-6'), 37.6, 27.7 [CH_2 (Lev)], 29.5 [CH_3 (Lev)].

Anal. Found: C, 60.96; H, 5.14; N, 1.16. Calcd. for $C_{62}H_{62}O_{18}NCl_3$: C, 61.26; H, 5.14; N, 1.15.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**8**). This was obtained from **9** (1.85 g, 1.6 mmol) according to the procedure described for **10**. Purification of crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1 : 9) afforded **8** (1.48 g, 87%) as a white solid. R_f 0.44 (EtOAc/$CHCl_3$ = 1/9). mp 198–199°C. $[\alpha]_D$ −33° (*c* 0.9). ^{1}H-NMR ($CDCl_3$): δ 5.73 (t, 1H, *J* = 9.6 Hz, H-3), 5.53 [m, 1H, =CH (All)], 5.37 (m, 2H, H-2', 4), 5.19 (dd, 1H, *J* = 7.9 Hz, 9.6 Hz, H-2), 5.09 (t, 1H, *J* = 9.2 Hz, H-4'), 4.77 (d, 1H, *J* = 7.9 Hz, H-1), 4.65 (d, 1H, *J* = 7.9 Hz, H-1'), 4.06–3.79 [m, 7H, H-3', 6, 6', OCH_2 (All)], 3.69–3.35 [m, 4H, H-5, 5', OCH_2 (SE)], 2.42 [s, 6H, CH_3 (T)], 2.36, 2.35, 2.27 [3 × s, 3 × 3H, CH_3 (T)]. ^{13}C-NMR ($CDCl_3$): δ 134.1 [=CH (All)], 100.5, 100.3 (C-1, 1'), 79.4 (C-3'), 74.7–69.9 [C-2, 2', 3, 4, 4', 5, 5', OCH_2 (All)], 67.6, 67.1 [C-6, OCH_2 (SE)], 61.2 (C-6'), −1.56 [CH_3 (SE)].

Anal. Found: C, 66.83; H, 6.40. Calcd. for $C_{60}H_{68}O_{16}Si \cdot 0.25H_2O$: C, 66.86; H, 6.40%.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**21**). To a solution of **9** (700 mg, 0.6 mmol) in MeOH/THF (15 ml/15 ml) was added 0.1 N methanoic sodium methoxide (3 ml). The mixture was stirred at room temperature for 24 h, neutralized with Amberlyst 15 resin, and concentrated. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH afforded **20** [R_f 0.29 (MeOH/$CHCl_3$ = 1/4). $[\alpha]_D$ −39° (*c* 1.0, MeOH)] which was used for the next reaction without purification. To a solution of **20** in DMF (10 ml) was added NaH (60% in mineral oil, 300 mg, 7.5 mmol) portionwise under an argon atmosphere at 0°C and this was stirred for 0.5 h. Benzyl bromide (0.8 ml, 6.7 mmol) was added at 0°C, and the reaction mixture was stirred at room temperature overnight. Excess reagents were destroyed by careful addition of ice water, and the volatiles were removed under vacuum. The residue was dissolved in EtOAc, washed with water, and dried (Na_2SO_4), and concentrated. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 19) afforded **21** (593 mg, 98%, 2 steps) as a white solid. R_f 0.59 (EtOAc/$CHCl_3$ = 1/19). mp 126–127°C. $[\alpha]_D$ +9° (*c* 0.9). ^{1}H-NMR ($CDCl_3$): δ 7.25 [m, 30H, aromatic (Bn)], 5.91 [m, 1H, =CH (All)], 5.25–5.09 [m, 2H, CH_2=(All)], 4.93 [m, 18H, H-1, 6, OCH_2 (All, Bn, SE)], 3.69–3.31 (m, 12H, H-2, 3, 4, 5, 6), 0.91 [t, 2H, *J* = 8.3 Hz, $SiCH_2$ (SE)], −0.12 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 138.6–127.5 [aromatic, =CH (All)], 116.6 [CH_2=(All)], 103.8, 103.1 (C-1, 1'), 84.7–79.4 [C-2, 2', 3, 3', 4, 4', 5, 5', OCH_2 (All, Bn)], 68.8, 68.5, 67.5 [C-6, 6', OCH_2 (SE)].

Anal. Found: C, 72.41; H, 7.40. Calcd. for $C_{62}H_{74}O_{11}Si \cdot 0.25H_2O$: C, 72.44; H, 7.31%.

2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**23**). A solution of 1,5-cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (1 mg) in THF (1 ml) was degassed, stirred under a hydrogen atmosphere for activation (red→colorless), and then degassed completely. A solution of **21** (57 mg, 56 μmol) in THF (3 × 1 ml) was added to the solution of activated catalyst at room temperature under an argon atmosphere. The mixture was stirred for 2 h, and concentrated to give 1-propenyl product **22** [R_f 0.42 (EtOAc/toluene = 1/19)], which was treated with HgO (18 mg, 83 μmol) and $HgCl_2$ (22 mg, 54 μmol) in acetone/water (1.5 ml/0.1 ml) for 24 h at room temperature and then filtered through Celite. The filtrate was diluted with EtOAc (25 ml) and successively washed with 1 M KI, water, dried (Na_2SO_4), and concentrated. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 9) afforded **23** (55 mg, 100%) as a white solid. R_f 0.26 (EtOAc/toluene = 1/9). mp 120–121°C. $[\alpha]_D$ +14° (*c* 0.3). ^{1}H-NMR ($CDCl_3$): δ: 4.98–4.38 [m, 14H, H-1, OCH_2 (Bn)], 4.21 (d, 1H, *J* = 9.6 Hz, H-6), 3.72–3.37 [m, 11H, H-2, 2', 3, 4, 4', 5, 5', 6, 6', OCH_2 (SE)], 3.26 (dd, 1H, *J* = 7.9 Hz, 8.9 Hz, H-3'), 0.95 [t, 2H, *J* = 8.6 Hz, $SiCH_2$ (SE)], −0.07 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 138.6–127.6 (aromatic), 103.5, 103.1 (C-1, 1'), 84.7–74.4 (C-2, 2', 3, 3', 4, 4', 5, 5'), 75.6, 75.0, 74.8, 74.2, 73.5 [OCH_2 (Bn)], 68.9, 68.6, 67.6 [C-6, 6', OCH_2 (SE)].

Anal. Found: C, 71.82; H, 7.19. Calcd. for $C_{59}H_{70}O_{11}Si$: C, 72.07; H, 7.18%.

2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-benzyl-3-O-caproyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**24**). Caproyl chloride (50 μl, 0.35 mmol) was added dropwise to a mixture of **23** (33 mg, 33 μmol) and pyridine (1.5 ml) in 1,2-dichloroethane (1.5 ml) at 0°C under an argon atmosphere. The reaction mixture was stirred at room temperature overnight, and quenched with water at 0°C. The reaction mixture was worked up as described for **13**. Purification of the crude product by gel permeation chromatography on Bio-beads S-X1 with toluene afforded **24** (33 mg, 92%) as a colorless syrup. R_f 0.52 (EtOAc/toluene = 1/9). $[\alpha]_D$ +8° (*c* 0.7). ^{1}H-NMR ($CDCl_3$): δ 5.22 (t, 1H, *J* = 9.6 Hz, H-3'), 4.98–4.43 [m, 13H, H-1', OCH_2 (Bn)], 4.38 (d, 1H, *J* = 7.9 Hz, H-1), 4.19 (d, 1H, *J* = 10.89 Hz, H-6), 3.69–3.33 [m, 11H, H-2, 2', 3, 4, 4', 5, 5', 6, OCH_2 (SE)], 2.09 [t, 2H, *J* = 7.3 Hz, α-CH_2 (Cap)], 1.55 [m, 2H, β-CH_2 (Cap)], 1.23 [m, 4H, CH_2 (Cap)], 0.83 [t, 3H, *J* = 6.9 Hz, CH_3 (Cap)], −0.07 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 172.5 [C=O (Cap)], 103.9 (C-1'), 103.1 (C-1), 84.7–74.5 (C-2, 2', 3, 4, 4', 5, 5'), 75.3 (C-3'), 75.6, 74.9, 74.7, 74.2, 73.9, 73.5 [OCH_2 (Bn)], 68.7, 68.3 (C-6, 6'), 67.6 [OCH_2 (SE)], 34.2, 31.3, 24.4, 22.3 [CH_2 (Cap)], 13.8 [CH_3 (Cap)], −1.47 [CH_3 (SE)].

Anal. Found: C, 70.89; H, 7.32. Calcd. for $C_{65}H_{80}O_{12}Si \cdot H_2O$: C, 71.01; H, 7.51%.

O-(3-O-Caproyl-β-D-glucopyranosyl)-(1→6)-D-glucopyranose (**26**). The hemiacetal **25** [R_f 0.63 (EtOAc/toluene = 3/7)] was obtained from **24** (20 mg, 18 μmol) according to the procedure described for **19**, and used for the next reaction without purification. To a solution of **25** in MeOH (1 ml) was added 10% Pd/C (10 mg), then the mixture was stirred under a hydrogen atmosphere at room temperature for 7 days. The catalyst was removed by filtration and the filtrate was concentrated. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH afforded **26** (5 mg, 21%, 2 steps) as a colorless syrup. R_f 0.29 ($MeOH/H_2O/CHCl_3$ = 7/1/12). $[\alpha]_D$ −9° (*c* 0.9, MeOH). ^{1}H-NMR (D_2O): δ 5.42 [m, 0.3H, H-1 (α)], 5.20 (m, 1H, H-3'), 4.46 [m, 1.7H, H-1', 1 (β)], 4.17 (m, 4H, H-6), 4.00–3.20 (m, 7H, H-2, 2', 3, 4, 4', 5, 5'), 2.43 [m, 2H, α-CH_2 (Cap)], 1.59 [m, 2H, β-CH_2 (Cap)], 1.27 [m, 4H, CH_2 (Cap)], 0.85 [m, 3H, CH_3 (Cap)]. Positive FAB-MS (matrix = glycerol) *m/z*: 462.9 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-benzyl-3-O-hexyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**27**). To a solution of **23** (60 mg, 61 μmol) in DMF (1 ml) was added NaH (60% in mineral oil, 13 mg, 0.32 mmol) portionwise under an argon atmosphere at 0°C and stirred for 0.5 h. *n*-Hexyl bromide (43 μl, 0.12 mmol) was added at 0°C, and after 24 h, excess reagents was destroyed by careful addition of ice water, and worked up as described for **21**. Purificarion of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 9) afforded **27** (46 mg, 71%) as a white solid. R_f 0.50 (EtOAc/toluene = 1/9). mp 113–114°C. $[\alpha]_D$ +5° (*c* 0.9). ^{1}H-NMR ($CDCl_3$): δ 4.38, 4.34 (2 × d, 2 × 1H, *J* = 7.3 Hz, 7.6 Hz, H-1, 1'), 4.15 (d, 1H, *J* = 9.9 Hz, H-6), 3.80 [m, 1H, OCH_2 (Hexyl)], 3.69–3.58 [m, 5H, H-3', 6, OCH_2 (Hexyl)], 3.54–3.31 [m, 8H, H-2, 2', 3, 4, 4', 5, 5', OCH_2 (SE)], 1.54 [m, 2H, β-CH_2 (Hexyl)], 1.22 [m, 4H, CH_2 (Hexyl)], 0.82 [t, 3H, *J* = 6.6 Hz, CH_3 (Hexyl)], −0.12 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 103.9 (C-1'), 103.1 (C-1), 84.8, 84.7 (C-3, 3'), 82.4–74.8 (C-2, 2', 4, 4', 5, 5'), 75.6, 74.9, 74.88, 73.5 [OCH_2 (Bn)], 74.0 [OCH_2 (Hexyl)], 68.9, 68.5 (C-6, 6'), 31.8, 25.9, 22.6 [CH_2 (Hexyl)], 30.5 [β-CH_2 (Hexyl)], 14.0 [CH_3 (Hexyl)], −1.47 [CH_3 (SE)].

Anal. Found: C, 73.44; H, 7.87. Calcd. for $C_{65}H_{82}O_{11}Si$: C, 73.14; H, 7.74%.

O-(3-O-Hexyl-β-D-glucopyranosyl)-(1→6)-D-glucopyranose (**29**). A mixture of **27** (45 mg, 42 μmol) and 20% $Pd(OH)_2$/C (5 mg) in THF/MeOH (1.5 ml/1.5 ml) was stirred under a hydrogen atmosphere at room temperature overnight, then the catalyst was removed by filtration. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH afforded **28** (15 mg, 68%) [R_f 0.31 ($MeOH/CHCl_3$ = 1/4)] as a syrup, which was used for the next reaction without purification. To a stirred solution of **28** (12 mg, 23 μmol) in 1,2-dichloroethane (0.5 ml) was added TFA (0.5 ml) at room temperature. The mixture was stirred for 0.5 h and concentrated. Purification of the crude product by reverse-phase chromatography on Boud-Elut C8 with H_2O and lyophilization afforded **28** (10 mg, 98%) as a white powder. R_f 0.13 ($MeOH/CHCl_3$ = 1/3). ^{1}H-NMR (D_2O): δ 5.11 [d, 0.4H, *J* = 3.63 Hz, H-1 (α)], 4.53 [d, 0.6H, *J* = 7.91 Hz, H-1 (β)], 4.38 (m, 1H, H-1'), 4.06 [m, 1.4H, H-5 (α), OCH_2 (Hexyl)], 3.82–3.10 [m, 12.6H, H-2, 2', 3, 3', 4, 4', 5, 5', 6, 6', OCH_2 (Hexyl)], 1.48 [m, 2H, β-CH_2 (Hexyl)], 1.19 [m, 6H, CH_2 (Hexyl)], 0.75 [t, 3H, *J* = 6.6 Hz, CH_3 (Hexyl)]. ^{13}C-NMR (D_2O): δ 105.5 (C-1'), 99.1 [C-1 (β)], 94.8 [C-1 (α)], 87.1–70.9 [C-2, 2', 3, 3', 4, 4', 5, 5', 6, OCH_2 (Hexyl)], 63.5 (C-6'), 33.7, 32.1, 27.6, 24.5 [CH_2 (Hexyl)], 15.2 [CH_3 (Hexyl)]. Positive FAB-MS (matrix = glycerol) *m/z*: 449.4 $(M+Na)^+$, 427.3 $(M+H)^+$.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-6-O-levulinoyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-toluoyl-β-D-glucopyraoside (**30**). Silver trifluoromethanesulfonate (33 mg, 0.13 mmol) was added to a stirred mixture of **7** (152 mg, 0.12 mmol), **8** (103 mg, 0.15 mmol) and powdered MS AW-300 (200 mg) in dichloromethane (4 ml) at room temperature under an argon atmosphere. The mixture was stirred in the dark for 48 h, filtered through Celite, and concentrated. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 4) and gel permeation chromatography on Bio-beads S-X1 with toluene afforded **30** (181 mg, 89%) as a white solid. R_f 0.52 (EtOAc/toluene = 1/4). mp 134–135°C. $[\alpha]_D$ −45° (*c* 0.8). ^{1}H-NMR ($CDCl_3$): δ 5.71 [m, 4H, H-3a, 3c, =CH (All)], 5.54–5.20 (m, 6H, H-2, 4), 5.07–4.68 [m, 8H, H-1, H-1, 2, CH_2=(All)], 4.75, 4.39 (2 × d, 2 × 1H, *J* = 7.9 Hz, H-1), 4.24 (d, 2H, *J* = 4.0 Hz, H-6d), 4.16–4.02 [m, 6H, H-6, OCH_2 (All)], 3.94–3.61 [m, 10H, H-3b, 3d, 5, 6, OCH_2 (SE)], 3.48 (m, 1H, H-5), 2.50, 2.43, 2.39, 2.35, 2.32, 2.31, 2.28, 2.25 [8 × s, 8 × 3H, CH_3 (T)], 2.40 [s, 6H, CH_3 (T)], 2.15 [s, 3H, CH_3 (Lev)], −0.11 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 206.3 [C=O (Lev)], 172.2 [OC=O (Lev)], 117.2, 117.1 [CH_2=(All)], 101.2, 101.1, 100.4, 100.1 (C-1), 79.4 (C-3b, 3d), 74.6–67.0 [C-2, 3a, 3c, 4, 5, 6, OCH_2 (All, SE)], 62.9 (C-6d). Positive FAB-MS (matrix = NBA) *m/z*: 2165.1 $(M+K)^+$, 2148.8 $(M+Na)^+$.

Anal. Found: C, 67.98; H, 6.12. Calcd. for $C_{120}H_{128}O_{33}Si$: C, 67.78; H, 6.07%.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**31**). This was obtained from **30** (670 mg, 0.3 mmol) according to the procedure described for **10**. Purification of the crude product by fiash chromatography on silica gel with EtOAc–$CHCl_3$ (1 : 9) afforded **31** (420 mg, 66%) as a white solid. R_f 0.38 (EtOAc/$CHCl_3$ = 1/9). mp 124–125°C. $[\alpha]_D$ −31° (*c* 1.1). ^{1}H-NMR ($CDCl_3$): δ 5.75–5.48 [m, 4H, H-3a, 3c, =CH (All)], 5.37–4.78 [m, 13H, H-1, 2, 4, CH_2=(All)], 4.64, 4.58, 4.47 (3 × d, 3 × 1H, *J* = 7.9 Hz, H-1), 4.15–3.32 [m, 20H, H-3b, 3d, 5, 6, 6, OCH_2 (All, SE)], −0.12 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 134.3, 134.2 [=CH (All)], 101.2, 100.8, 100.4, 100.2 (C-1), 79.4, 79.3 (C-3b, 3d), 74.3–67.0 [C-2, 3a, 3c, 4, 5, 6, OCH_2 (All, SE)], 61.4 (C-6d).

Anal. Found: C, 66.83; H, 6.03. Calcd. for $C_{115}H_{122}O_{31}Si \cdot 2H_2O$: C, 66.91; H, 6.15%.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-6-O-levulinoyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-toluoyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-2,4-di-O-toluoyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-toluoyl-β-D-glucopyranoside (**6**). This was obtained from **31** (206 mg, 100 μmol) and **7** (162 mg, 132 μmol) according to the procedure described for **30**. Purification of the crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1 : 9) and gel permeation chromatography on Bio-beads S-X1 with toluene afforded **6** (236 mg, 82%) as a white solid. R_f 0.37 (acetone/hexane = 3/7). mp 134–135°C. $[\alpha]_D$ −45° (*c* 0.7). ^{1}H-NMR ($CDCl_3$): δ 5.78–5.47 [m, 6H, H-3a, 3c, 3e, =CH (All)], 5.38–4.72 [m, 20H, H-1, 2, 4, CH_2=(All)], 4.57 (m, 3H, H-1), 4.43 (d, 1H, *J* = 7.9 Hz, H-1), 4.25 (d, 2H, *J* = 4.0 Hz, H-6b), 3.99–3.44 (m, 19H, H-3b, 3d, 3f, 5, 6), 2.74, 2.60 [2 × m, 2 × 2H, CH_2 (Lev)], 2.49, 2.44, 2.443, 2.42, 2.36, 2.33, 2.22, 2.27, 2.22 [9 × s, 9 × 3H, CH_3 (T)], 2.39, 2.29, 2.25 [3 × s, 3 × 6H, CH_3 (T)], 2.15 [s, 3H, CH_3 (Lev)], −0.12 [s, 9H, CH_3 (SE)]. ^{13}C-NMR ($CDCl_3$): δ 206.5 [C=O (Lev)], 117.3, 117.2, 117.1 [CH_2=(All)], 101.3, 101.2, 101.1, 100.7, 100.5, 100.2 (C-1), 79.4, 79.3 (C-3b, 3d, 3f), 74.7–67.0 [C-2, 3a, 3c, 3e, 4, 5, 6, OCH_2 (All, SE)], 63.0 (C-6f), 37.9, 28.0 [CH_2 (Lev)], 29.7 [CH_3 (Lev)], −1.34 [CH_3 (SE)].

Anal. Found: C, 68.20; H, 5.96. Calcd. for $C_{175}H_{182}O_{48}Si$: C, 68.21; H, 5.95%.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-β-D-glucopyranosyl)-(1→6)-[O-(β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-β-D-glucopyranosyl)-(1→6)]$_2$-β-D-

glucopyranoside (**32**). To a solution of **6** (330 mg, 0.1 mmol) in MeOH/THF (3 ml/3 ml) was added 0.1 N methanoic sodium methoxide (1 ml). The mixture was stirred at room temperature for 24 h, neutralized with Amberlyst 15 resin, and concentrated. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH afforded **32** (118 mg, 91%) as a white powder. R_f 0.39 (MeOH/$CHCl_3$ = 2/3). mp 140–141°C. $[\alpha]_D$ −47° (*c* = 0.3, MeOH). ^{1}H-NMR (CD_3OD): δ 5.98 [m, 3H, =C<u>H</u> (All)], 5.29–5.08 [m, 6H, C<u>H</u>$_2$=(All)], 4.40–4.27 [m, 12H, H-1, OC<u>H</u>$_2$ (All)], 4.14 (m, 5H, H-6), 3.87–3.13 [m, 32H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE)], 0.99 [m, 2H, SiC<u>H</u>$_2$ (SE)], 0.03 [s, 9H, C<u>H</u>$_3$ (SE)]. Positive FAB-MS (matrix = glycerol) *m/z*: 1249.5 $(M+K)^+$, 1233.5 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-2,4-di-O-benzyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**33**). To a solution of **32** (88 mg, 72 μmol) in THF (6 ml) was added NaH (60% in mineral oil, 300 mg, 7.5 mmol) portionwise at room temperature under an argon atmosphere and reaction mixture was heated at 60°C then stirred for 1 h. Benzyl bromide (0.8 ml, 7 mmol) was added. After stirring for 24 h at 60°C, the mixture was cooled and worked up as described fo **21**. Purification of the crude product by flash chromatography on silica gel with EtOAc–toluene (1 : 9) and gel permeation chromatography on Bio-beads S-X1 with toluene afforded **33** (129 mg, 67%) as a syrup. R_f 0.44 (EtOAc/toluene = 1/9). $[\alpha]_D$ +13° (*c* 1.0). ^{1}H-NMR ($CDCl_3$): δ 7.45–7.12 [m, 80H, aromatic (Bn)], 6.02–5.85 [m, 3H, =C<u>H</u> (All)], 5.32–5.14 [m, 6H, C<u>H</u>$_2$=(All)], 5.03 [m, 50H, H-1, 6, OC<u>H</u>$_2$ (All, Bn, SE)], 3.74–3.31 [m, 32H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE)], 1.00[t, 2H, *J* = 8.6 Hz, SiC<u>H</u>$_2$ (SE)], 0.06 [s, 9H, C<u>H</u>$_3$ (SE)]. ^{13}C-NMR ($CDCl_3$): δ 135.2, 135.1, 135.0 [=C<u>H</u> (All)], 116.5, 116.3, 116.2 [C<u>H</u>$_2$=(All)], 104.1, 103.9, 102.9 (C-1), 84.8–67.5 [C-2, 3, 4, 5, 6, O<u>C</u>H$_2$ (All, Bn, SE)], −1.38 [<u>C</u>H$_3$ (SE)]. Positive FAB-MS (matrix = NBA) *m/z*: 2653.4 $(M+Na)^+$.

2-(Trimethylsilyl)-ethyl O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-O-(2,4-di-O-benzyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**35**). This was obtained from **33** (52 mg, 19 μmol) *via* **34** according to the procedure described for **23**. Purification of the crude product by gel permeation chromatography on Bio-beads S-X1 with toluene afforded **35** (44 mg, 92%) as a syrup, which was used for the next reaction without further purification. R_f 0.40 (EtOAc/toluene = 1/4). $[\alpha]_D$ +13° (*c* 0.8). ^{1}H-NMR ($CDCl_3$): δ 5.01 4.33 [m, 38H, H-1, OC<u>H</u>$_2$ (Bn)], 4.12 (m, 5H, H-6), 3.99 [m, 1H, OC<u>H</u>$_2$ (SE)], 366 3.14 [m, 32H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE)], 2.32, 2.28, 2.20 (3 × d, 3 × 1H, *J* = 1.98 Hz, O<u>H</u>). ^{13}C-NMR ($CDCl_3$): δ 104.1 103.1 (C-1), 84.6 67.6 [C-2, 3, 4, 5, 5, O<u>C</u>H$_2$ (SE, Bn)], −1.44 [<u>C</u>H$_3$ (SE)].

Intermediate **34**: R_f 0.39 (EtOAc/toluene = 1/9). ^{1}H-NMR ($CDCl_3$): δ 6.39–6.21 (m, 3H, OC<u>H</u>=CH–CH$_3$), 1.70–1.48 (m, 9H, OCH=CH–C<u>H</u>$_3$).

*2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-benzyl-3-O-*caproyl*-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-O-(2,4-di-O-benzyl-3-O-caproyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-benzyl-β-D-glucopyranoside* (**36**). This was obtained from **35** (12 mg, 4.7 μmol) according to the procedure described for **24**. Purification of the crude product by preparative thin-layer chromatography on silica gel with EtOAc–toluene (1 : 9) afforded **36** (6 mg, 41%) as a syrup, which was used for the next reaction without further purification. R_f 0.54 (EtOAc/toluene = 1/19). $[\alpha]_D$ +14° (*c* 0.4). ^{1}H-NMR ($CDCl_3$): δ 5.21 (m, 3H, H-3b, 3d, 3f), 4.97–4.04 [m, 44H, H-1, 6, OC<u>H</u>$_2$ (Bn, SE)], 3.67–3.26 [m, 29H, H-2, 3a, 3c, 3e, 4, 5, 6, OC<u>H</u>$_2$ (SE)], 2.06 [m, 6H, α-C<u>H</u>$_2$ (Cap)], 1.48 [m, 6H, β-C<u>H</u>$_2$ (Cap)], 1.22 [m, 12H, C<u>H</u>$_2$ (Cap)], 0.80 [m, 9H, C<u>H</u>$_3$ (Cap)].

2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-benzyl-3-O-hexyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-benzyl-β-D-glucopyranosyl)-(1→6)-O-(2,4-di-O-benzyl-3-O-hexyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-benzyl-β-D-glucopyranoside (**37**). This was obtained from **35** (44 mg, 17 μmol) according to the procedure described for **27**. Purification of the crude product by gel permeation chromatography on Bio-beads S-X1 with EtOAc–toluene (1 : 1) afforded **37** (40 mg, 85%) as a syrup, which was used for the next reaction without further purification. R_f 0.55 (EtOAc/toluene = 1/9). $[\alpha]_D$ +9° (*c* 1.3). ^{1}H-NMR ($CDCl_3$): δ 5.01–4.33 [m, 38H, H-1, OC<u>H</u>$_2$ (Bn)], 4.09 [m, 6H, H-6, OC<u>H</u>$_2$ (SE)], 3.80 [m, 3H, OC<u>H</u>$_2$ (Hexyl)], 3.63–3.26 [m, 35H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE, Hexyl)], 1.53 [m, 6H, β-C<u>H</u>$_2$ (Hexyl)], 1.25 [m, 18H, C<u>H</u>$_2$ (Hexyl)], 0.97 [t, 2H, *J* = 8.3 Hz, SiC<u>H</u>$_2$ (SE)], 0.86 [m, 9H, C<u>H</u>$_3$ (Hexyl)]. ^{13}C-NMR ($CDCl_3$): δ 105.8–104.1 (C-1), 86.5–69.1 [C-2, 3, 4, 5, 6, O<u>C</u>H$_2$ (Bn, SE, Hexyl)], 33.4, 32.2, 27.5, 24.2 [<u>C</u>H$_2$ (Hexyl)], 20.1 [Si<u>C</u>H$_2$ (SE)], 15.7 [<u>C</u>H$_3$ (Hexyl)], 0.31 [<u>C</u>H$_3$ (SE)].

2-(Trimethylsilyl)ethyl O-(3-O-hexyl-β-D-glucopyranosyl)-[(1→6)-O-(β-D-glucopyranosyl)-(1→6)-O-(3-O-hexyl-β-D-glucopyranosyl)]$_2$-(1→6)-β-D-glucopyranoside (**5**). A mixture of **37** (33 mg, 12 μmol) and 20% $Pd(OH)_2$/C (10 mg) in THF/MeOH (1 ml/1 ml) was stirred under a hydrogen atmosphere at 50°C for 48 h, then the catalyst was removed by filtration, and the filtrate was concentrated. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH afforded **5** (14 mg, 84%) as a syrup. R_f 0.53 (MeOH/H_2O/$CHCl_3$ = 4/1/5). $[\alpha]_D$ −36° (*c* 0.5, MeOH). ^{1}H-NMR (CD_3OD): δ 4.37 (M, 5H, H-1), 4.29 (d, 1H, *J* = 7.6 Hz, H-1), 4.14 (m, 5H, H-6), 3.87–3.12 [m, 38H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE, Hexyl)], 1.60 [m, 6H, β-C<u>H</u>$_2$ (Hexyl)], 1.34 [m, 18H, C<u>H</u>$_2$ (Hexyl)], 1.00 [m, 2H, SiCH$_2$ (OSE)], 0.89 [t, 9H, *J* = 6.6 Hz, C<u>H</u>$_3$ (Hexyl)], 0.03 [s, 9H, C<u>H</u>$_3$ (SE)]. ^{13}C-NMR (CD_3OD): δ 105.8, 105.77, 105.72, 104.6 (C-1), 87.1–63.5 [C-2, 3, 4, 5, 6, O<u>C</u>H$_2$ (SE, Hexyl)], 33.8, 32.2, 27.7, 24.5 [<u>C</u>H$_2$ (Hexyl)], 20.0 [Si<u>C</u>H$_2$ (SE)], 15.2 (<u>C</u>H$_3$ (Hexyl)], −0.42 [<u>C</u>H$_3$ (SE)]. Positive FAB-MS (matrix = glycerol) *m/z*: 1265.9 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl O-(3-O-allyl-2,4,6-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-allyl-2,4-di-O-methyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-methyl-β-D-glucopyranoside (**38**). This was obtained from **32** (29 mg, 23 μmol) according to the procedure for **21**, using iodomethane (0.5 ml, 8 mmol) instead of benzyl bromide. Purification of the crude product by flash chromatography on silica gel with EtOAc–$CHCl_3$ (1 : 1) and gel permeation chromatography on Bio-beads S-X1 with EtOAc–toluene (1 : 1) afforded **38** (22 mg, 68%) as a syrup. R_f 0.73 (acetone/$CHCl_3$ = 1/1). $[\alpha]_D$ −33° (*c* 0.9). ^{1}H-NMR ($CDCl_3$): δ 5.95 [m, 3H, =C<u>H</u> (All)], 5.30–5.12 [m, 6H, C<u>H</u>$_2$=(All)], 4.32–4.11 [m, 17H, H-1, 6, OC<u>H</u>$_2$ (All)], 3.63–2.92 [m, 80H, H-2, 3, 4, 5, 6, OC<u>H</u>$_2$ (SE), OC<u>H</u>$_3$], 0.99 [m, 2H, SiC<u>H</u>$_2$ (SE)]. ^{13}C-NMR ($CDCl_3$): δ 135.4 [=C<u>H</u> (All)], 103.9, 102.8 (C-1), 88.6–67.3 [C-2, 3, 4, 5, 6, O<u>C</u>H$_2$ (All, SE)], 60.8–59.3 (O<u>C</u>H$_3$).

2-(Trimethylsilyl)ethyl O-(2,4,6-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-O-(2,4-di-O-methyl-β-D-glucopyraosyl)-(1→6)]$_2$-2,3,4-tri-O-methyl-β-D-glucopyranoside (**40**). This was obtained from **38** (22 mg, 15 μmol) *via* **39** according to the procedure described for **23**. Purification of the crude product by flash chromatography on silica gel with EtOH–$CHCl_3$ (1 : 1) afforded **40** (13 mg, 63%) as a syrup, which was used for the next reaction without furthr purification. R_f 0.12 (EtOH/acetone/$CHCl_3$ = 1/1/18). $[\alpha]_D$ −35° (*c* 0.5). ^{1}H-NMR ($CDCl_3$): δ 4.38, 4.36, 4.35, 4.29, 4.28, 4.22 (6 × d, 6 × 1H, *J* = 7.59 Hz, H-1), 4.16 (m, 5H, H-6), 3.64–2.91 [m, 80H, H-2, 3, 4, 5, 6, OC<u>H</u>$_3$, OC<u>H</u>$_2$ (SE)].

Intermediate **39**: R_f 0.76 (acetone/$CHCl_3$ = 1/1). ^{1}H-NMR ($CDCl_3$): δ 6.27 (m, 3H, OC<u>H</u>=CH–CH$_3$), 5.04 (m, 3H, OCH=C<u>H</u>–CH$_3$), 1.60 (m, 9H, OCH=CH–C<u>H</u>$_3$), 0.09 [s, 9H, C<u>H</u>$_3$ (SE)].

2-(Trimethylsilyl)ethyl O-(3-O-caproyl-2,4,6-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-[O-(2,3,4-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-caproyl-2,4-di-O-methyl-β-D-glucopyranoyl)-(1→6)]$_2$-2,3,4-tri-O-methyl-β-D-glucopyranoside (**3**). This was obtained from **40** (12 mg, 9 μmol) according to the procedure described for **24**. Purification of the crude product by gel permeation chromatography on Bio-beads S-X1 with EtOAc–toluene (1 : 1) afforded **3** (8 mg, 53%) as a syrup. R_f 0.77 (acetone/$CHCl_3$ = 1/1). $[\alpha]_D$ −24° (*c* 0.4). ^{1}H-NMR ($CDCl_3$): δ 5.04 (m, 3H, H-3b, 3d, 3f), 4.40 (m, 3H, H-1), 4.28, 4.27, 4.21 (3 × d, 3 × 1H, *J* = 7.6 Hz, H-1), 4.15 (m, 5H, H-6), 3.67–2.92 [m, 77H, H-2, 3a, 3c, 3e, 4, 5, 6, OC<u>H</u>$_2$ (SE), OC<u>H</u>$_3$], 2.35 [t, 6H, *J* = 7.3 Hz, α-C<u>H</u>$_2$ (Cap)], 1.66 [m, 6H, β-C<u>H</u>$_2$ (Cap)], 1.30 [m, 12H, C<u>H</u>$_2$ (Cap)], 0.89 [m, 9H, C<u>H</u>$_3$ (Cap)]. ^{13}C-NMR ($CDCl_3$): δ 172.8, 172.7 [<u>C</u>=O (Cap)], 103.9, 103.8, 102.8 (C-1), 86.7–67.3 [C-2, 3, 4, 5, 6, O<u>C</u>H$_2$ (SE)], 60.8–59.3 (O<u>C</u>H$_3$), 34.5, 31.2, 24.7, 22.3 [<u>C</u>H$_2$ (Cap)], 13.9 [<u>C</u>H$_3$ (Cap)]. Positive FAB-MS (matrix = NBA) *m/z*: 1631.9 $(M+H+Na)^+$, 1607.8 $(M+H)^+$.

O-(3-O-Caproyl-β-D-glucopyranosyl)-(1→6)-[O-(β-D-glucopyranosyl)-(1→6)-O-(3-O-caproyl-β-D-glucopyranosyl)-(1→6)]$_2$-D-glucopyranose (**1**). This was obtained from **36** (5.5 mg, 1.9 μmol) according to the procedure described for **26**. Purification of the crude product by gel filtration chro-

matography on Sephadex LH-20 with MeOH and lyophilization afforded a white powder (1.5 mg) as a mixture of **1** and the partly decaproylated gentiohexaosides. Because of the instability of the caproyl substituent, isolation of **1** was unsuccessful. Negative FAB-MS (matrix = glycerol) *m/z*: 1283.6 $(M-H)^-$, 1185.5 $(M-H-Cap)^-$, 1087.4 $(M-H-2\times Cap)^-$, 989.3 $(M-H-3\times Cap)^-$.

O-(3-O-Hexyl-β-D-glucopyranosyl)-[(1→6)-O-(β-D-glucopyranosyl)-(1→6)-O-(3-O-hexyl-β-D-glucopyranosyl)]$_2$-(1→6)-D-glucopyranose (**4**). To a stirred solution of **5** (10 mg, 7.5 μmol) in 1,2-dichloroethane (0.5 ml) was added TFA (0.5 ml) at room tempeature. The mixture was stirred for 0.5 h and concentrated. Purification of the crude product by gel filtration chromatography on Sephadex LH-20 with MeOH and lyophilization afforded **4** (9 mg, 99%) as a white powder. R_f 0.53 ($MeOH/H_2O/CHCl_3$ = 4/1/5). $[\alpha]_D$ −11.8° (*c* 0.4, MeOH). ^{1}H-NMR (CD_3OD): δ 5.13 [d, 0.5H, *J* = 3.4 Hz, H-1a (α)], 4.51 [d, 0.5H, *J* = 7.8 Hz, H-1a (β)], 4.47–4.33 (m, 5H, H-1), 4.15 (m, 5H, H-6), 3.89–3.15 [m, 37H, H-2, 3, 4, 5, 6, OCH_2 (Hexyl)], 1.61 [m, 6H, β-CH_2 (Hexyl)], 1.35 [m, 18H, CH_2 (Hexyl)], 0.90 [t, 9H, *J* = 6.8 Hz, CH_3 (Hexyl)]. ^{13}C-NMR (CD_3OD): δ 105.8, 105.7, 105.5 (C-1), 99.0 [C-1a (β)], 94.8 [C-1a (α)], 87.0–70.9 [C-2, 3, 4, 5, 6, OCH_2 (Hexyl)], 63.5 (C-6d), 33.8, 32.2, 27.7, 24.5 [CH_2 (Hexyl)], 15.2 [CH_3 (Hexyl)]. Positive FAB-MS (matrix = glycerol) *m/z*: 1281.2 $(M+K)^+$, 1265.4 $(M+Na)^+$.

O-(3-O-Caproyl-2,4,6-tri-O-methyl-β-D-glucopyranosyl-(1→6)-[O-(2,3,4-tri-O-methyl-β-D-glucopyranosyl)-(1→6)-O-(3-O-caproyl-2,4-di-O-methyl-β-D-glucopyranosyl)-(1→6)]$_2$-2,3,4-tri-O-methyl-D-glucopyranose (**2**). This was obtained from **3** (6.5 mg, 4 μmol) according to the procedure described for **4**. Purification of the crude product by gel permeation chromatography on Bio-beads S-X1 with THF–$CHCl_3$ (5:2) afforded **2** (6 mg, 99%) as a syrup. R_f 0.34 (acetone/$CHCl_3$ = 1/3). $[\alpha]_D$ −9.8° (*c* 0.2). ^{1}H-NMR ($CDCl_3$): δ 5.30 [m, 0.6H, H-1a (α)], 5.07 (m, 3H, H-3b, 3d, 3f), 4.75 [d, 0.4H, *J* = 7.8 Hz, H-1a (β)], 4.48–3.88 (m, 10H, H-1, 6), 3.76 [m, 0.6H, H-5a (α)], 3.67–2.93 (m, 75.4H, H-2, 3a, 3c, 3e, 4, 5, 6, OCH_3), 2.36 [m, 6H, α-CH_2 (Cap)], 1.66 [m, 6H, β-CH_2 (Cap)], 1.31 [m, 12H, CH_2 (Cap)], 0.91 [m, 9H, CH_3 (Cap)]. ^{13}C-NMR ($CDCl_3$): δ 172.84, 172.8, 172.7 [C=O (Cap)], 103.9, 103.8 C-1), 97.4 [C-1a (β)], 90.6 [C-1a (α)], 83.6–67.4 (C-2, 3, 4, 5, 6), 60.9–58.9 (OCH_3), 34.5, 31.2, 24.7, 22.3 [CH_2 (Cap)], 13.9 [CH_3 (Cap)]. Positive FAB-MS (matrix = glycerol) *m/z*: 1602.7 $(M+H+glycerol)^+$, 1587.8 $(M+2+K)^{++}$.

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