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Synthesis of galactose-containing analogues of (1→6)-branched (1→3)-glucohexaose and its lauryl glycoside

Guohua Zhang, Mingkun Fu and Jun Ning*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, China

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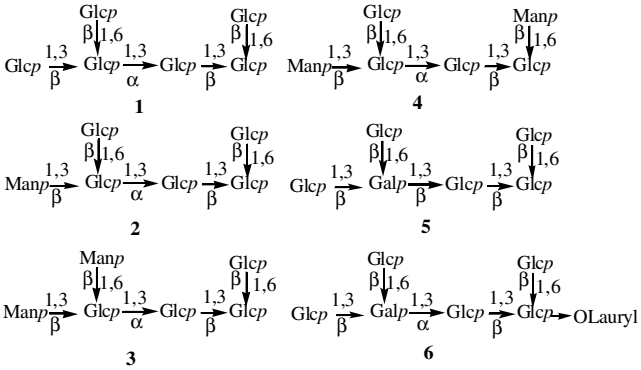
Abstract—Coupling of the trisaccharide acceptor either 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**13**) or lauryl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,5-di-*O*-acetyl-α-D-glucopyranoside (**15**) with the trisaccharide donor 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**12**) gave α-linked hexasaccharides **14** and **16**, respectively, while coupling of either **13** or **15** with trisaccharide donor 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate **17** did not afford any hexasaccarides. The analogues of the immunomodulator β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-β-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**1**) was obtained by deprotection of **14** and **16**.

Keywords: Glucohexaose; Galactoglucan; Oligosaccharide; Synthesis

1. Introduction

Unlike most of chemotherapeutic antitumor agents that have severe side effects due to their cytotoxicity against healthy cells, some glucans coming from fungi such as *Ganoderma lucidum*, *Schizophyllum commune*, and *Lentinus edodes*[1] exert their antitumor function through stimulating the host immunopotentiation, which is associated with macrophage activation, the promotion of T cell differentiation, and the augmentation of NK-activity,[2] rather than the direct inhibition of tumor cell growth.[3] Early, some physicochemical and immunopharmacological investigations showed that the antitumor activity of these glucans may be closely related to their triple-helix[4] structures with certain molecular weights (MW > 16,000).[5] However, we hypothesized that the activity of lentinan might be dependent upon its basic structure—the oligosacharide unit—rather than its macroscopic morphology, and this hypothesis was proved by our research results.[6] During our study, an interesting and surprising result was found in that a β-(1→6)-branched, α-D-(1→3)-linked glucohexaose, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-D-Glc*p* (**1**), had similar or even better activity compared to that of lentinan.[7] Moreover, compound **1** was more easily obtained than



* Corresponding author. Tel.: +86 10 62849157; fax: +86 10 62923563; e-mail: jning@mail.rcees.ac.cn

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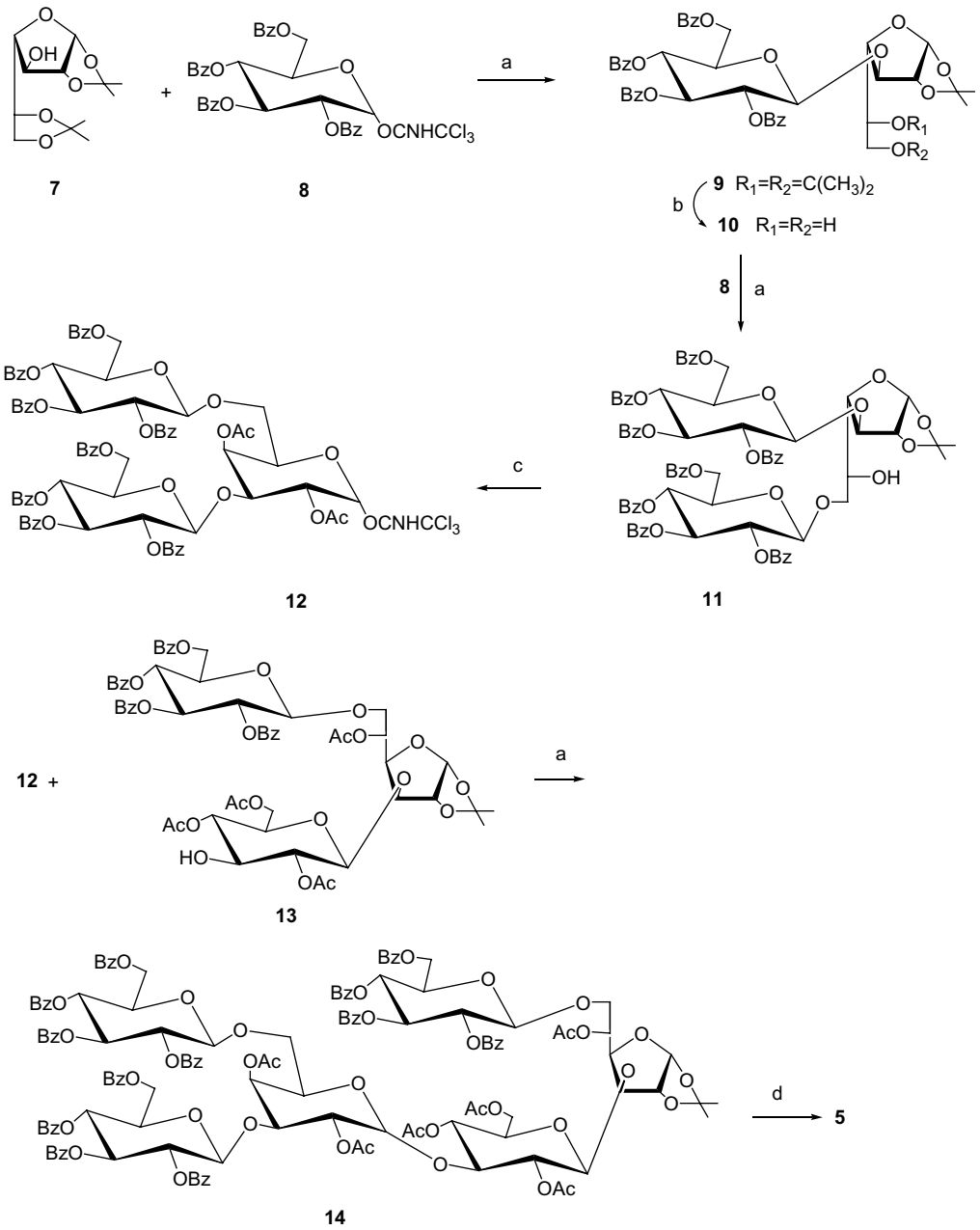
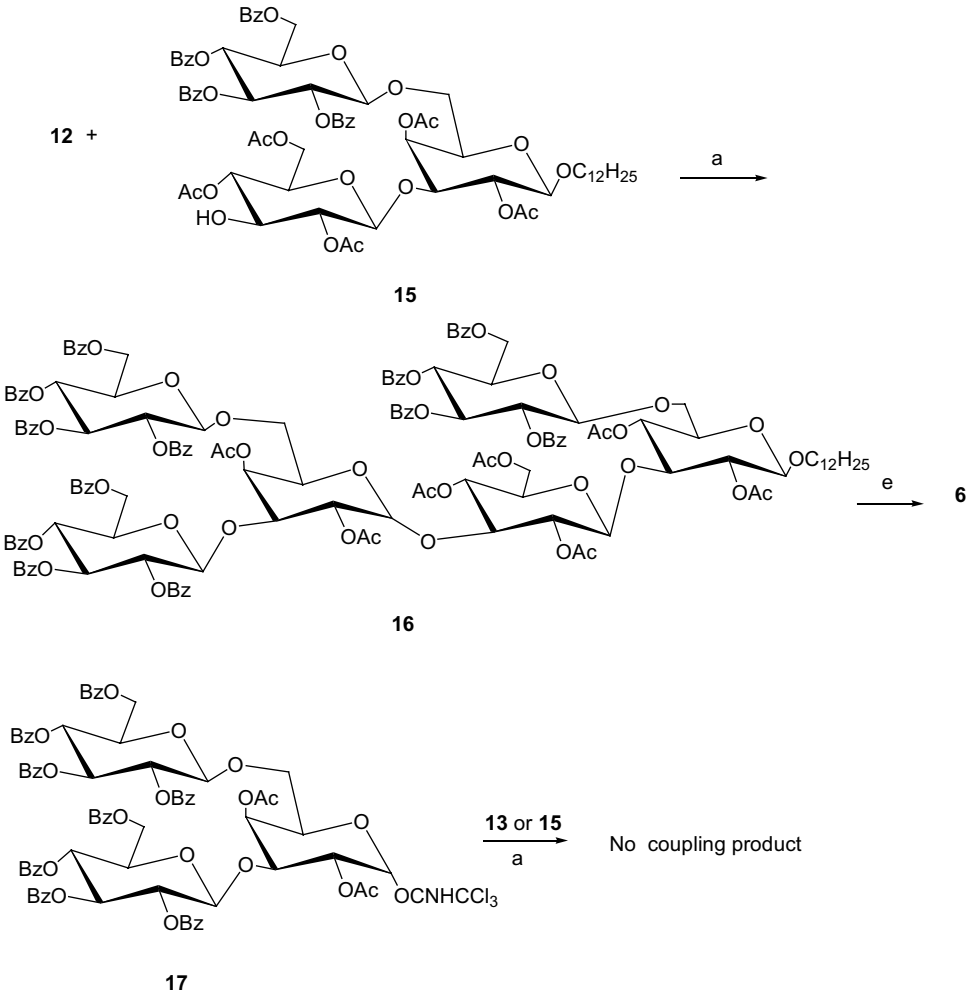
its corresponding β-(1→6)-branched β-D-(1→3)-linked glucohexaose isomer by a synthetic route.[6] Encouraged by this discovery, many analogues of **1**, such as α-D-Man*p*-(1→3)-[β-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**2**), α-D-Man*p*-(1→3)-[α-D-Man*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**3**), and α-D-Man*p*-(1→3)-[α-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Man*p*-(1→6)]-β-D-Glc*p* (**4**) were synthesized in our lab to develop new immunopotentiating reagents.[8,9] For furthering the study of structure–activity relationships of this kind of antitumor oligosaccharide, we present herein the synthesis of a galactose-containing hexasaccharide **5** and its lauryl glycoside **6**.

2. Results and discussion

As shown in Scheme 1, coupling of acceptor **7**[10] with donor **8**[11] in the presence of TMSOTf as the catalyst,



Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, rt, 3 h, 90% for **11**, 30% for **14**, 25% for **16**; (b) 90% HOAc, 40 °C, 24 h, 81% for **10** (for two steps); (c) (i) 80% HOAc, reflux, 5 h; (ii) Ac_2O–pyridine, rt, 3 h; (iii) THF–CH_3OH–1.5 N NH_3, rt, 3 h; (iv) CH_2Cl_2, CCl_3CN, K_2CO_3, rt, 12 h, 71% (for four steps); (d) (i) 80% HOAC, reflux, 4 h; (ii) CH_2Cl_2–CH_3OH satd with NH_3, rt, 24 h, 85% (for two steps); (e) CH_2Cl_2–CH_3OH sat. with NH_3, rt, 24 h, 90%.



Scheme 1 (*continued*)

followed by selective 5,6-*O*-deacetonation, afforded 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1,2-*O*-isopropylidene-α-D-galactofuranose (**10**) in a high yield (81% over two steps). Condensation of β-(1→3)-linked disaccharide **10** with **8** catalyzed by TMSOTf regio- and stereoselectively gave 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-1,2-*O*-isopropylidene-α-D-galactofuranose (**11**) in excellent yield (90%). Removal of the 1,2-*O*-isopropylidene group of **11** in 80% HOAc, followed by acetylation with acetic anhydride in pyridine, selective 1-*O*-deacetylation with $PhCH_2NH_2$ in THF, and subsequent treatment with trichloroacetonitrile in the presence of K_2CO_3, afforded the 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**12**) in good yield (71% over four steps).

Coupling of the trisaccharide glycosyl donor **12** with either trisaccharide glycosyl acceptor **13**[6] or **15**,[6] catalyzed by TMSOTf in CH_2Cl_2, didn't afford the expected β-linked hexasaccharides, but stereoselectively gave the α-linked hexasaccharides, 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**14**) and lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,5-di-*O*-acetyl-α-D-glucopyranoside (**16**) in low yields. The structures of **14** and **16** were unambiguously confirmed by ^{13}C NMR data. The ^{13}C NMR spectra of **14** showed that characteristic signals at δ 95.56 with $J_{C\text{-}1\text{–}H\text{-}1}$ 175 Hz for α-C-1 of Gal*p*, and correspondingly the ^{13}C NMR spectrum of **16** showed a signal (δ 93.93 ppm) in the anomeric region, which was in accordance with the α-configuration at C-1. Deprotection of α-linked hexasaccharides **14** and **16** gave the target compounds **5** and **6**, respectively.

In order to obtain more analogues, coupling of trisaccharide glycosyl donor **17**[12] with **13** or **15** was carried

out. But we found that no expected coupling product was obtained, and only the decomposed byproducts of the donor were detected. A similar result also occurred in our previous work.[13] These results indicate that glycosidic bond formation is strongly dependent on the properties of both the glycosyl donor and acceptor.[14] Now in our laboratory, a number of derivatives of (1→6) branched (1→3)-linked glucohexaoses are in preparation, and interesting results about the structure–activity relationship of the newly discovered biologically active oligosaccharides will be reported in the due course.

3. Experimental

3.1. General methods

Optical rotations were determined at 25 °C with a digital polarimeter. The NMR spectra were recorded with a Bruker ARX 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) for solutions in $CDCl_3$ or D_2O as indicated. Mass spectra were recorded on an Autospec mass spectrometer using the ESI technique to introduce the sample. Elemental analyses were done on an elemental analyzer, model 1108 EA. Thin-layer chromatography (TLC) was performed on silica gel HF_{254}, with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV detector. Column chromatography was conducted on a column (10 × 240 mm, or 18 × 300 mm, or 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether bp 60–90 °C as eluent. Solutions were concentrated at <60 °C under reduced pressure. Dry solvents were distilled over CaH_2 and stored over molecular sieves.

3.2. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1,2-*O*-isopropylidene-α-D-galactofuranose (10)

To a stirred solution of 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose (**7**) (10 g, 0.038 mol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**8**) (26 g, 0.035 mol) in dry CH_2Cl_2 (600 mL) was added TMSOTf (70 μL) at room temperature. After 3 h, Et_3N was added to the solution to quench the reaction. The solution was concentrated, and the resulting residue was directly dissolved in 90% aq HOAc (500 mL). The mixture was kept at 40 °C for 24 h, and then concentrated to a residue under reduced pressure. The resulting residue was subjected to a short silica-gel column (3:1 petroleum ether–EtOAc) to give compound **10** (22.6 g, 81% for two steps): $[\alpha]_D$ +18.5 (*c* 2.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.26 (m, 20H, 4Bz*H*), 5.90 (t, 1H, *J* 9.7 Hz, H-3), 5.71–5.66 (m, 2H, H-1′, H-4), 5.49 (dd, 1H, *J* 7.9 Hz, 9.7 Hz, H-2), 5.03 (d, 1H, *J* 7.9 Hz, H-1), 4.81 (dd, 1H, *J* 3.7 Hz, *J* 11.9 Hz, H-6a), 4.45–4.40 (m, 3H, H-2′, H-3′, H-6b), 4.19–4.16 (m, 1H, H-5), 4.08 (dd, 1H, *J* 4.9 Hz, H-4′), 3.88 (m, 1H, H-5), 3.68 (m, 2H, 2H-6′), 1.47 (s, 3H, C(C*H*$_3$)), 1.25 (s, 3H, C(C*H*$_3$)). Anal. Calcd for $C_{43}H_{42}O_{15}$: C, 64.66; H, 5.30. Found: C, 64.79; H, 5.25.

3.3. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-1,2-*O*-isopropylidene-α-D-galactofuranose (11)

To a stirred solution of **10** (8.0 g, 0.010 mol) and **8** (8.0 g, 0.011 mol) in dry CH_2Cl_2 (400 mL) was added TMSOTf (40 μL) at room temperature. After 3 h, Et_3N was added to the solution to quench the reaction. The solution was concentrated, and the residue was subjected to column chromatography with 2:1 petroleum ether–EtOAc as the eluent to give the trisaccharide **11** (12.4 g, 90%): $[\alpha]_D$ +13.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.18 (m, 40H, 8Bz*H*), 5.86 (t, 1H, *J* 9.7 Hz, H-4), 5.81 (t, 1H, *J* 9.7 Hz, H-4), 5.63 (t, 1H, *J* 9.7 Hz, H-3), 5.56 (t, 1H, *J* 9.7 Hz, H-3), 5.62 (dd, 1H, *J* 9.7 Hz, H-2), 5.53–5.45 (m, 2H, H-1′, H-2), 5.35 (dd, 1H, *J* 7.9 Hz, *J* 9.7 Hz, H-2), 4.90 (d, 1H, *J* 7.9 Hz, H-1), 4.89 (d, 1H, *J* 7.9 Hz, H-1), 4.66 (dd, 1H, *J* 3.4 Hz, *J* 12.3 Hz, H-6), 4.58 (dd, 1H, *J* 4.9 Hz, *J* 12.2 Hz, H-6), 4.40 (dd, 1H, *J* 3.4 Hz, *J* 12.2 Hz, H-6), 4.34–4.30 (m, 2H, H-6, H-3′), 4.22 (d, 1H, *J* 4.2 Hz, H-2′), 4.11–4.07 (m, 2H, 2H-5), 3.91–3.88 (m, 2H, H-5′, H-6a′), 3.65 (dd, 1H, *J* 6.0, 11.7 Hz, H-6b′), 1.36, 1.30 (2s, 6H, 2 CC*H*$_3$). Anal. Calcd for $C_{77}H_{68}O_{24}$: C, 67.15; H, 4.98. Found: C, 67.29; H, 5.02.

3.4. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (12)

Compound **11** (10 g, 7.3 mmol) was added to 80% aq HOAc (50 mL), and the mixture was heated under reflux for 5 h. Then the mixture was concentrated, and the residue was acetylated with AC_2O (50 mL) in pyridine (56 mL) for 3 h at rt. The resultant trisaccharide was dissolved in a 1.5 N NH_3 solution of 3:1 THF–CH_3OH (200 mL), and the solution was stirred at rt for 3 h. The solution was concentrated, and the residue was dissolved in CH_2Cl_2 (400 mL). To the solution were added K_2CO_3 (20 g), CCl_3CN (3.2 mL), and the mixture was stirred at rt for 12 h. Filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography (2:1 petroleum ether–EtOAc) giving the trisaccharide donor **12** (8.1 g, 71% for four steps): $[\alpha]_D$ +23.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H, N*H*), 7.90–7.26 (m, 40H, 8Bz*H*), 6.29 (d, 1H, *J* 3.6 Hz, H-1′), 5.88–5.80 (m, 2H, 2H-4), 5.67–5.60 (m, 3H, 2H-3, H-4′), 5.49–5.43 (m, 2H, 2H-2), 5.11 (dd, 1H, *J* 3.6, 10.4 Hz, H-2′), 4.94 (dd, 1H, *J* 7.9 Hz, H-1), 4.93 (dd,

1H, *J* 7.9 Hz, H-1), 4.66–4.58 (m, 2H, 2H-6), 4.50–4.44 (m, 2H, H-6, H-5′), 4.15–4.13 (m, 4H, H-3′, 2H-5, H-6a′), 3.92 (dd, 1H, *J* 2.8 Hz, *J* 11.3 Hz, H-6), 3.64 (dd, 1H, *J* 6.0, 11.7 Hz, H-6b′), 2.05 (s, 3H, C*H*$_3$CO), 1.58 (s, 3H, C*H*$_3$CO). Anal. Calcd for $C_{80}H_{68}Cl_3NO_{26}$: C, 61.37; H, 4.38. Found: C, 61.53; H, 4.41.

3.5. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (14)

To a stirred solution of **12** (6.7 g, 4.3 mmol) and **13** (4.5 g, 4.0 mmol) in dry CH_2Cl_2 (80 mL) was added TMSOTf (40 μL) at rt. After 3 h, Et_3N was added to the solution to quench the reaction, and the solution was concentrated to dryness. The residue was purified by column chromatography (1.5:1 petroleum ether–EtOAc) to afford the hexasaccharide **14** (3.0 g, 30%): $[\alpha]_D$ +23.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.99 (d,1H, α-H-1, *J* 3.9 Hz), 4.96 (d, 1H, β-H-1, *J* 8.0 Hz), 4.92 (β-H-1, *J* 8.0 Hz), 4.82 (d, 1H, α-H-1, *J* 3.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.45, 171.36, 170.20, 170.03, 170.03, 170.02 (6 *C*OCH$_3$), 167.01, 167.01, 166.87, 166.67, 166.65, 166.40, 166.15, 165.99, 165.97, 165.94, 165.78, 165.78 (12 *C*OPh), 112.9 (*C*(CH$_3$)$_2$, 105.78 ($J_{C\text{-}1\text{-}H\text{-}1}$ 181 Hz, α-C-1), 101.85 ($J_{C\text{-}1\text{-}H\text{-}1}$ 164 Hz, β-C-1), 100.60 ($J_{C\text{-}1\text{-}H\text{-}1}$ 165 Hz, β-C-1), 100.59 ($J_{C\text{-}1\text{-}H\text{-}1}$ 165 Hz, β-C-1), 98.75 ($J_{C\text{-}1\text{-}H\text{-}1}$ 158 Hz, β-C-1), 95.56 ($J_{C\text{-}1\text{-}H\text{-}1}$ 175 Hz, α-C-1). Anal. Calcd for $C_{135}H_{126}O_{49}$: C, 64.03; H, 5.01. Found: C, 64.43; H, 4.97.

3.6. Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,5-di-*O*-acetyl-α-D-glucopyranoside (16)

To a stirred solution of **12** (4.5 g, 2.9 mmol) and **15** (3.5 g, 2.7 mmol) in dry CH_2Cl_2 (80 mL) was added TMSOTf (40 μL) at rt. After 3 h, Et_3N was added to the solution to quench the reaction, and the solution was concentrated to dryness. The residue was purified by column chromatography (1.5:1 petroleum ether–EtOAc) to afford the hexasaccharide **16** (1.8 g, 25%): $[\alpha]_D$ +23.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (d, 1H, *J* 9.7 Hz, β-H-1), 4.92 (d, 1 H, *J* 9.5 Hz, β-H-1), 4.86 (d, 1H, *J* 3.6 Hz, α-H-1). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.73, 170.43, 169.98, 169.87, 169.48, 169.28, 168.72 (7 CH$_3$*C*O), 166.05, 165.94, 165.66, 165.60, 165.51, 165.47, 165.14, 165.13, 165.06, 165.03, 165.02, 164.72 (12 Ph*C*O), 101.67, 101.42, 101.21, 100.49, 100.37 (5 β-C-1), 93.93 (α-C-1). Anal. Calcd for $C_{146}H_{148}O_{50}$: C, 64.88; H, 5.52. Found: C, 64.56; H, 5.67.

3.7. β-D-Glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-galactopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranose (5)

Compound **14** (1.0 g, 0.40 mmol) was dissolved in 80% aq HOAc (60 mL), and the mixture was heated under reflux for 4 h. Concentration of the mixture, followed by deacylation in a solution of CH_2Cl_2 (10 mL) and CH_3OH (90 mL) saturated with ammonia at rt for 24 h, gave **5** (333 mg, 85%): $[\alpha]_D$ +5.7 (*c* 1.0, D_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (m, 2H, 2H-1), 4.52–4.45 (m, 4H, 4H-1). ^{13}C NMR (100 MHz, D_2O): δ 103.86, 102.92, 102.81, 102.74, 102.67 (5 β-C-1), 99.28 (1 α-C-1). Anal. Calcd for $C_{36}H_{62}O_{31}$: C, 43.64; H, 6.30. Found: C, 43.56; H, 6.65. MALDI-TOFMS: Calcd for $C_{36}H_{62}O_{31}$, 990.86 [M]. Found: 1013.92 $(M+Na)^+$.

3.8. Lauryl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-galactopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranose (6)

Compound **16** (1.0 g, 0.37 mmol) was dissolved in an ammonia-saturated solution of 1:9 CH_2Cl_2–MeOH (100 mL) at rt. After 24 h, the mixture was concentrated to about 10 mL, and then CH_2Cl_2 (100 mL) was added. The mixture was filtered and washed with CH_2Cl_2 (4 × 50 mL) to afford **6** (386 mg, 90%) as a white solid: $[\alpha]_D$ −18.6 (*c* 1.0, D_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.56 (d, 1H, *J* 4.1 Hz, α-H-1), 4.39–4.20 (m, 5H, 5H-1), 1.53–1.19 (m, 23H, $CH_2C_{11}H_{23}$). ^{13}C NMR (100 MHz, D_2O): δ 103.91, 103.11, 102.80, 102.69, 102.26 (5 β-C-1), 99.28 (1 α-C-1). Anal. Calcd for $C_{48}H_{86}O_{31}$: C, 49.74; H, 7.48. Found: C, 49.65; H, 7.60. MALDI-TOFMS: Calcd for $C_{48}H_{86}O_{31}$, 1159.18 [M]. Found: 1182.30 $(M+Na)^+$.

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References

1. Sasaki, T.; Takasuka, N. *Carbohydr. Res.* **1976**, *47*, 99–105.

2. (a) Goro, C.; Juji, H.; Yukiko, Y. M. *Cancer Res.* **1970**, *30*, 2776; (b) Misaki, A.; Kakuta, M. Fungal (1→3)-β-D-Glucans: Chemistry and Antitumor Activity. *Carbohydrates in Drug Design*; Dekker: New York, 1997.
3. (a) Jun, Y.; Hongliang, Z.; Aiguo, S. *Int. Immunopharmacol.* **2003**, *3*, 1861–1871; (b) Maeda, Y.; Chihara, G. *Nature* **1971**, *229*, 634; (c) Chihara, G.; Hamuro, J.; Maeda, Y.; Arai, Y. *Cancer Res.* **1970**, *30*, 2776–2781.
4. (a) Yanaki, T.; Ito, W.; Tabata, K.; Norisuye, T.; Takano, T.; Fujita, H. *Biophys. Chem.* **1983**, *17*, 337–342; (b) Norisue, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci. Polym. Phys. Edit.* **1980**, *18*, 547–558.
5. Sasaki, T.; Takasuka, N.; Chilhara, G.; Maeda, Y. Y. *Gann* **1976**, *67*, 191–195.
6. Ning, J.; Zhang, W.; Yi, Y.; Yang, G.; Wu, Z. *Bioorg. Med. Chem.* **2003**, *11*, 2193–2203.
7. Yan, J.; Zong, H.; Shen, A.; Chen, S.; Yin, X.; Shen, X.; Liu, W.; Gu, X.; Gu, J. *Int. Immunopharmacol.* **2003**, *3*, 1851–1861.
8. Wu, Z.; Kong, F. *Carbohydr. Res.* **2003**, *338*, 1727–1735.
9. Wu, Z.; Kong, F. *Carbohydr. Res.* **2004**, *339*, 377–384.
10. Wang, H.; Zhang, G.; Ning, J. *Carbohydr. Res.* **2003**, *338*, 1033–1037.
11. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123.
12. Jun, N.; Hairong, W.; Yuetao, Y. *Tetrahedron Lett.* **2002**, *43*, 7349–7352.
13. Zicheng, W.; Jun, N.; Fanzuo, K. *Carbohydr. Res.* **2003**, *338*, 2203–2212.
14. Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503–1531.