Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Research 340 (2005) 155–159
Carbohydrate RESEARCH

Note

An efficient and concise synthesis of a β-(1→6)-linked D-galactofuranosyl hexasaccharide

Guohua Zhang, Mingkun Fu and Jun Ning*

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

Received 16 September 2004; received in revised form 20 October 2004; accepted 1 November 2004
Available online 21 November 2004

Abstract—A β-(1→6)-linked D-galactofuranosyl hexasaccharide was synthesized efficiently in a block construction manner by the well-known Schmidt glycosylation method using 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate (**1**) and allyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (**3**) as the key synthons. Coupling of **3** with **1** gave β-(1→6)-linked disaccharide **4**. Subsequent selective deacetylation of **4** afforded the disaccharide acceptor **5**, while deallylation of **4** followed by trichloroacetimidate formation produced the disaccharide donor **6**. Condensation of **5** with **6** gave the tetrasaccharide **7**, and subsequent deacetylation afforded the tetrasaccharide acceptor **8**. Finally, coupling of **8** with **6** followed by deacylation yielded the target β-(1→6)-linked galactofuranose hexasaccharide **10**. All of the reactions in the synthesis were carried out smoothly and in high yield.

Keywords: Galactofuranosyl hexasaccharide; Trichloroacetimidate; Synthesis

Increased appreciation of the roles of carbohydrates in the biological and pharmaceutical sciences has led to increased interest in carbohydrate chemistry. However, compared with other biopolymers such as peptides and nucleic acids, the roles of oligosaccharides have been relatively neglected. This can be attributed, in part, to difficulties in oligosaccharide synthesis. The specific structural constraints in glycosidic bond-formation often lead to laborious synthetic transformations, complex protecting group manipulations, and tedious intermediate isolations, which complicate the overall synthetic process and decrease efficiency. In spite of the considerable progression oligosaccharide synthesis over the past few decades,[1,2] a general method for glycosylation has not yet appeared.[3] In our efforts dedicated to the synthesis of oligosaccharides, we have developed, in the last few years, highly efficient strategies for the construction of 3,6-branched gluco-oligosaccharides,[4,5] 2,6-branched manno-oligosaccharides,[6,7] 2,6-branched,[8] 3,6-branched, and 5,6-branched galacto-oligosaccharides,[9,10] respectively.

β-(1→6)-Linked galactofuranosyl oligosaccharides are present as constituents of the cell-wall polysaccharides from bacteria and fungi, including some clinically significant pathogens.[11–13] McNeil et al.[11] have demonstrated that the highly immunogenic arabinogalactans from *Mycobacterium leprae* and *Mycobacterium tuberculosis* contain, exclusively, arabinofuranosyl and galactofuranosyl moieties, and some β-(1→6)-linked galactofuranose residues. β-(1→6)-Linked galactofuranose oligomers are also found in the cell-wall polysaccharide of *Fusarium*.[13] The fungus *Fusarium* causes many physiological or genetic disorders, nutrient deficiencies, and environmental stress both in plants and in animals, including humans. Plants react to penetration by *Fusarium* by accumulation of callose or plant cell-wall components, by an increase of the steady-state mRNA level of phenylpropanoid pathway enzymes or pathogenesis-related like proteins.[10] Plants infested by the fungus also elicit chitinases and accumulate phytoalexins.[10] Research revealed that the β-(1→6)-linked galactofuranoside fraction of *Fusarium* origin exhibited elicitor activity, although its mechanism is still unclear.[12]

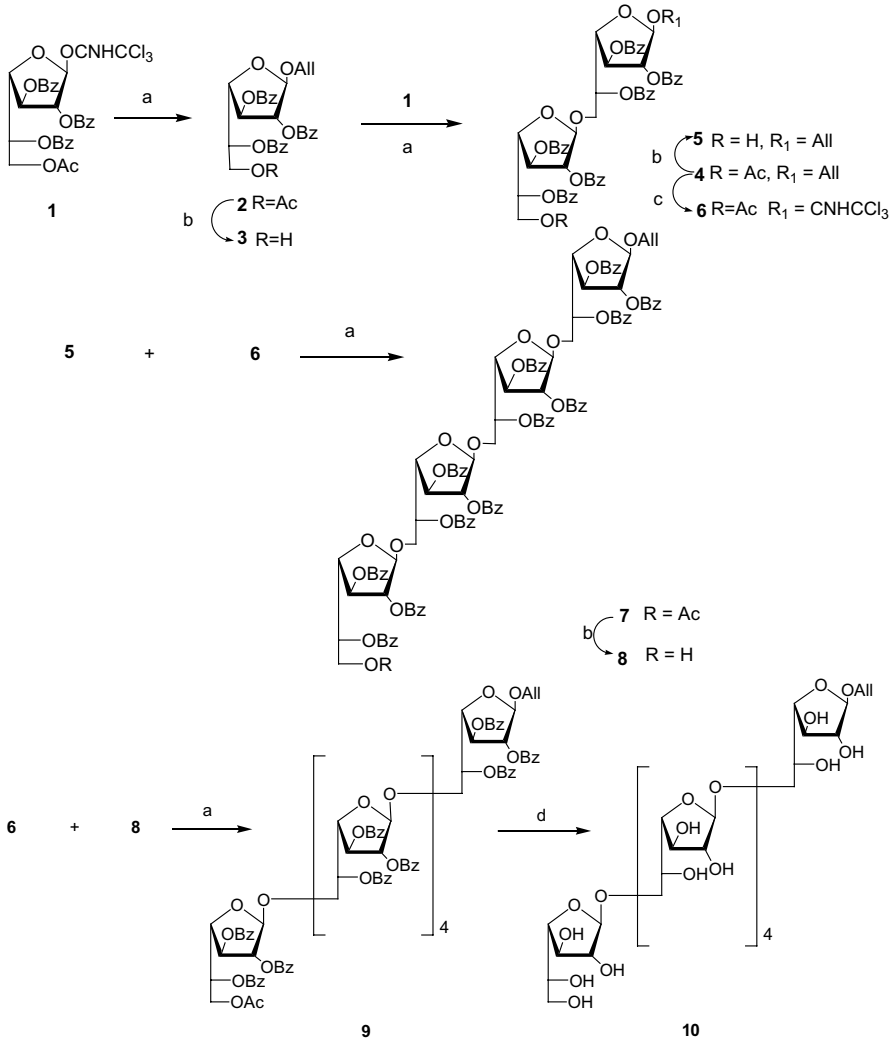
The synthesis of β-(1→6)-linked galactofuranose oligomers is therefore of interest. These oligosaccharides are

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

0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.11.001

expected to be can be valuable in immunological studies[14] and in fundamental biochemical studies that may lead to the isolation and purification of the appropriate biosynthetic enzymes. Previously, acquisition of these oligosaccharides has involved hydrolysis of polysaccharides and separation of the resulting oligomers.[11,13] Among the synthetic work done on the preparation of β-(1→6)-linked oligosaccharides is the work by de Lederkremer and co-workers, who prepared methyl β-galactofuranosyl-(1→6)-β-galactofuranoside with a benzoylated galactofuranosyl benzoate as the donor and $SnCl_4$ as the catalyst.[15] We describe here a strategy for the synthesis of β-(1→6)-linked galactofuranose oligomers using 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate[16] as the starting material. To demonstrate the use of the methodology, a β-(1→6)-linked galactofuranosyl hexasaccharide allyl glycoside was synthesized.

In our synthesis, the key starting material, 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate (**1**),[16] was obtained from methyl β-D-galactofuranoside.[17] As shown in Scheme 1, coupling of imidate **1** with allyl alcohol afforded allyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (**2**). Selective 6-*O*-deacetylation of **2** by methanolysis in acetyl chloride and methanol (0.5%, v/v) afforded the monosaccharide acceptor **3** in high yield (95%). The disaccharide **4** was obtained in 87% yield from condensation of **1** and **3** with TMSOTf as the catalyst in dichloromethane at room temperature. The ^{1}H NMR spectrum of **4** showed two singlets at δ 5.36 and 5.35, respectively, for the anomeric protons, indicating the β-configuration of the two galactofuranose units.[18] Under the same conditions as described for the preparation of **3**, selective removal of acetyl group of **4** afforded disaccharide acceptor **5**. Meanwhile, deallylation of **4** with $PdCl_2$ in methanol–



Scheme 1. Reagent and conditions: (a) allyl alcohol, TMSOTf (cat), CH_2Cl_2 (dry), 4 Å MS, rt, 2 h; (b) CH_2Cl_2–CH_3OH/0.6% acetyl chloride, rt, 12 h; (c) i. $PdCl_2$, CH_3OH, 40 °C, 4 h; ii. CCl_3CN, K_2CO_3, CH_2Cl_2 (dry), rt, overnight; (d) CH_3OH saturated with dry NH_3, rt, 24 h.

dichloromethane and subsequent trichloroacetimidate formation produced the disaccharide donor **6**.

Glycosylation of **5** with **6** under the promotion of TMSOTf at room temperature provided tetrasaccharide **7** in 90% yield. Serious overlap in the ^{1}H NMR spectrum of **7** made assignment difficult, however, the ^{13}C NMR spectrum of **7** showed four clear anomeric carbon signals (δ 106.8, 106.4, 106.3, 104.9) corresponding to four β-galactofuranosyl residues.

We were gratified to find that there was no difficulty in repeating the selective removal of acetyl group from **7**, and the tetrasaccharide acceptor **8** was obtained readily. Finally, the condensation of **8** with **6** yielded 90% of the protected hexasaccharide **9**, which was deprotected affording the target hexasaccharide **10** in 90% yield. The stereoselectivity of the glycosylation was confirmed in the ^{13}C NMR spectrum of **9**, which showed six β-Gal*f* anomeric carbons at δ 106.8, 106.7, 106.5, 106.3, 105.6, and 104.9, respectively.

In summary, an efficient synthesis of a β-(1→6) linked galactofuranosyl hexasaccharide was achieved in a block construction manner with TMSOTf as catalyst using the well-known Schmidt glycosylation method.[19]

1. Experimental

1.1. General methods

Optical rotations were determined at 20 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on 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. Chemical shifts are given in ppm downfield from internal $(CH_3)_4Si$ for spectra recorded in $CDCl_3$, or internal DSS (sodium 4,4-dimethyl-4-silapentane-sulfonate) for spectra recorded in D_2O. 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 by elution of a column (16 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) with mixtures of EtOAc and petroleum ether (60–90 °C) as the eluent. Solutions were concentrated at <60 °C under reduced pressure.

1.2. Allyl 6-*O*-acetyl-3,4,5-tri-*O*-benzoyl-β-D-galactofuranoside (2)

A solution of **1** (5.1 g, 7.5 mmol) and allyl alcohol (1.1 mL, 16 mmol) in dry CH_2Cl_2 (150 mL) was stirred with activated 4 Å molecular sieves (2 g) at rt for 20 min. To the solution was added TMSOTf (45 μL). The reaction mixture was stirred for 2 h, at which time TLC (4:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, filtered, and the filtrate was concentrated. Purification of the residue by chromatography (4:1, petroleum ether–EtOAc) afforded **2** (4.0 g, 92%). $[\alpha]_D$ −12.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–7.30 (m, 15H, 3Ph*H*), 5.98–5.95 (m, 1H, C*H*=CH_2), 5.92–5.88 (m, 1H, H-5), 5.57 (d, 1H, J = 9.2 Hz, H-3), 5.49 (s, 1H, H-2), 5.39 (dd, 1H, ^{2}J = 1.6 Hz, $^{3}J_{trans}$ = 17.2 Hz, CH=CH_2), 5.35 (s, 1H, H-1), 5.25 (dd, 1H, ^{2}J = 1.3 Hz, $^{3}J_{cis}$ = 10.4 Hz, CH=CH_2), 4.61–4.58 (m, 1H, H-4), 4.57–4.54 (dd, 1H, J = 4.5, 11.7 Hz, H-6a), 4.50–4.46 (dd, 1H, J = 6.0, 11.7 Hz, H-6b), 4.27–4.11 (m, 2H, CH_2CH=CH_2), 2.00 (s, 3H, CH_3CO). Anal. Calcd for $C_{32}H_{30}O_{10}$: C, 66.89; H, 5.26. Found: C, 66.75; H, 5.20.

1.3. Allyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (3)

To a solution of **2** (3.0 g, 5.2 mmol) in CH_2Cl_2 (5 mL) and CH_3OH (200 mL) was added acetyl chloride (1.2 mL). The mixture was stirred at rt for 12 h when TLC (4:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, concentrated under reduced pressure and purified by chromatography (4:1, petroleum ether–EtOAc) to give monosaccharide acceptor **3** (2.6 g, 95%). $[\alpha]_D$ −87.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–7.24 (m, 15H, 3Ph*H*), 5.98–5.95 (m, 1H, C*H*=CH_2), 5.63–5.59 (m, 2H, H-5, H-3), 5.49 (s, 1H, H-2), 5.38–5.33 (m, 3H, H-1, CH=CH_2), 4.67–4.65 (m, 1H, H-4), 4.30–4.10 (m, 2H, CH_2CH=CH_2), 4.05–4.04 (m, 2H, H-6a, H-6b). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 68.37; H, 5.32.

1.4. Allyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-3,4,5-tri-*O*-benzoyl-β-D-galactofuranoside (4)

A solution of **3** (1.8 g, 3.4 mmol) and **1** (2.5 g, 3.7 mmol) in dry CH_2Cl_2 (100 mL) was stirred with activated 4 Å molecular sieves (2 g) at rt for 20 min and then TMSOTf (50 μL) was added. The reaction mixture was stirred for 2 h, at which time TLC (4:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, filtered, and the filtrate was concentrated. Purification of the residue by chromatography (4:1, petroleum ether–EtOAc) afforded disaccharide **4** (3.1 g, 87%). $[\alpha]_D$ −16.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.24 (m, 30H, 6Ph*H*), 5.98–5.95 (m, 1H, C*H*=CH_2), 5.91–5.81 (m, 2H, H-5, H-5′), 5.62 (d, 1H, J = 4.8 Hz, H-3), 5.54 (d, 1H, J = 4.8 Hz, H-3′), 5.49 (s, 1H, H-2), 5.38 (s, 1H, H-2′), 5.36 (s, 1H, H-1), 5.35 (s, 1H, H-1′), 5.31–5.27 (dd, 1H, ^{2}J = 1.4 Hz, $^{3}J_{trans}$ = 18.5 Hz, CH=CH_2), 5.26–5.23 (dd, 1H, ^{2}J = 1.3 Hz, $^{3}J_{cis}$ = 10.4 Hz, CH=CH_2), 4.73–4.70 (m, 1H, J = 4.3 Hz, H-4),

4.62–4.67 (m, 1H, J = 4.3 Hz, H-4′), 4.57–4.46 (m, 2H, H-6a, 6b), 4.20–4.01 (m, 2H, H-6a′, 6b′), 4.29–4.10 (m, 2H, CH_2CH=CH$_2$), 2.0 (s, 3H, CH_3CO). Anal. Calcd for $C_{59}H_{52}O_{18}$: C, 67.55; H, 5.00. Found: C, 67.40; H, 5.10.

1.5. Allyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (5)

To a solution of **4** (1.5 g, 1.4 mmol) in CH_2Cl_2 (3 mL) and CH_3OH (100 mL) was added acetyl chloride (0.6 mL). The mixture was stirred at rt for 12 h, when TLC (3:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, concentrated under reduced pressure, and purified by chromatography (3:1, petroleum ether–EtOAc) to provide disaccharide **5** (1.3 g, 90%). $[\alpha]_D$ −19.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.26 (m, 30H, 6Ph*H*), 6.03–6.01 (m, 1H, H-5), 5.98–5.95 (m, 1H, C*H*=CH$_2$), 5.61–5.58 (m, 1H, H-5′), 5.57 (d, 1H, J = 4.8 Hz, H-3), 5.53 (d, 1H, J = 4.8 Hz, H-3′), 5.49 (s, 1H, H-2), 5.41 (s, 1H, H-2′), 5.40 (s, 1H, H-1), 5.37 (s, 1H, H-1′), 5.36–5.35 (dd, 1H, ^2J = 1.4 Hz, $^3J_{trans}$ = 18.5 Hz, CH=CH_2), 5.19–5.17 (dd, 1H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz, CH=CH_2), 4.84–4.82 (m, 1H, J = 4.3 Hz, H-4), 4.69–4.67 (m, 1H, J = 4.3 Hz, H-4′), 4.16–4.03 (m, 4H, H-6a, 6b, 6a′, 6b′, CH_2CH=CH$_2$), 2.86–2.81 (m, 1H, O*H*). Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 5.00. Found: C, 67.74; H, 4.95.

1.6. 6-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl trichloroacetimidate (6)

To a solution of **4** (2.0 g, 1.9 mmol) in anhydrous CH_3OH (150 mL) was added $PdCl_2$ (20 mg, 0.11 mmol), and the mixture was stirred at 40 °C for 4 h, at which time TLC (3:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness. The resulting residue was dissolved in dry CH_2Cl_2 (100 mL), and then CCl_3CN (2.0 mL) and K_2CO_3 (10.0 g) were added. The reaction mixture was stirred at rt overnight, when TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated. Purification of the residue by chromatography (3:1, petroleum ether–EtOAc) gave disaccharide **6** (1.4 g, 63%). $[\alpha]_D$ −12.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H, OC(N*H*)CCl_3), 8.05–6.68 (m, 30H, 6Ph*H*), 6.68 (s, 1H, H-1), 5.99–5.98 (m, 1H, H-5), 5.90–5.85 (m, 1H, H-5′), 5.74 (d, 1H, J = 4.8 Hz, H-3), 5.73 (s, 1H, H-2), 5.48 (d, 1H, J = 4.8 Hz, H-3′), 5.34 (s, 1H, H-1′), 5.33 (s, 1H, H-2′), 4.89–4.88 (m, 1H, H-4), 4.62–4.60 (m, 1H, H-4′), 4.58–4.43 (m, 2H, H-6a, H-6b), 4.23–4.01 (m, 2H, H-6a′, 6b′), 2.00 (s, 3H, CH_3CO). Anal. Calcd for $C_{58}H_{48}O_{18}NCl_3$: C, 60.40; H, 4.19. Found: C, 60.31; H, 4.22.

1.7. Allyl 6-*O*-acetyl-3,4,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (7)

A solution of **5** (1.0 g, 0.99 mmol) and **6** (1.4 g, 1.2 mmol) in dry CH_2Cl_2 (100 mL) was stirred with activated 4 Å molecular sieves (1.5 g) at rt for 20 min and then TMSOTf (20 μL) was added. The reaction mixture was stirred for 2 h, at which time TLC (3:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, filtered, and the filtrate was concentrated. Chromatography (3:1, petroleum ether–EtOAc) of the residue gave tetrasaccharide **7** (1.8 g, 90%). $[\alpha]_D$ −11.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09–7.26 (m, 60H, 12Ph*H*), 5.93–5.86 (m, 5H, 4H-5, C*H*=CH$_2$), 5.59–5.52 (m, 3H, 3H-3), 5.47–5.45 (d, 2H, H-3, H-2), 5.36–5.28 (m, 8H, 4H-1, 3H-2, CH=CH_2), 5.15–5.13 (dd, 1H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz, CH=CH_2), 4.74–4.65 (m, 4H, 4H-4), 4.48–4.45 (m, 2H, 2H-6), 4.25–4.04 (m, 8H, 6H-6, CH_2CH=CH$_2$), 2.00 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 166.0, 165.9, 165.8, 165.8, 165.7, 165.7, 165.6, 165.3, 165.2, 165.1, 133.7, 133.4, 133.3, 133.2, 133.1, 130.0–128.4, 117.6, 106.8, 106.4, 106.3, 104.9, 82.4, 82.3, 82.1, 82.0, 81.8, 81.4, 71.9, 71.7, 71.3, 70.4, 68.1, 67.4, 67.2, 62.9, 20.4. Anal. Calcd for $C_{113}H_{96}O_{34}$: C, 67.93; H, 4.84. Found: C, 67.84; H, 4.75.

1.8. Allyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (8)

To a solution of **7** (1.0 g, 0.50 mmol) in CH_2Cl_2 (3 mL) and CH_3OH (100 mL) was added acetyl chloride (0.6 mL). The mixture was stirred at rt for 12 h, at which point TLC (2:1 petroleum ether–EtOAc) indicated the reaction was complete. The reaction mixture was neutralized with Et_3N, and then concentrated to dryness. Purification of the residue by chromatography (2:1, petroleum ether–EtOAc) afforded tetrasaccharide **8** (0.88 g, 90%). $[\alpha]_D$ −17.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.16 (m, 60H, 12Ph*H*), 6.25–5.88 (m, 4H, C*H*=CH$_2$, 3H-5), 5.59–5.52 (m, 3H, 3H-3), 5.47–5.45 (m, 2H, H-3, H-2), 5.36–5.28 (m, 8H, 4H-1, 3H-2, CH=CH_2), 5.15–5.13 (dd, 1H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz, CH=CH_2), 4.80–4.69 (m, 4H, 4H-4), 4.25–4.00 (m, 10H, 8H-6, CH_2CH=CH$_2$), 3.16 (t, 1H, O*H*). Anal. Calcd for $C_{111}H_{94}O_{33}$: C, 68.16; H, 4.84. Found: C, 68.31; H, 4.79.

1.9. Allyl 6-*O*-acetyl-3,4,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside (9)

A solution of **8** (0.25 g, 0.13 mmol) and **6** (0.16 g, 0.14 mmol) in dry CH_2Cl_2 (50 mL) was stirred with activated 4 Å molecular sieves (1.0 g) at rt for 20 min and then TMSOTf (15 μL) was added. The reaction mixture was stirred for 2 h, at which time TLC (1:1, petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was neutralized with Et_3N, filtered, and the filtrate was concentrated. Chromatography (1:1, petroleum ether–EtOAc) of the residue afforded hexasaccharide **9** (90%, 0.34 g). $[\alpha]_D$ −27.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.13 (m, 90H, 18Ph*H*), 5.96–5.85 (m, 8H, C*H*=CH_2, 6H-5, H-3), 5.58–5.43 (m, 7H, 5H-3, 2H-2), 5.35–5.27 (m, 11H, 6H-1, 4H-2, C*H*=CH_2), 5.15–5.13 (dd, 1H, ^2J = 1.3 Hz, $^3J_{cis}$ = 10.4 Hz, CH=CH_2), 4.73–4.69 (m, 6H, 6H-4), 4.46–4.00 (m, 4H, 12H-6, CH_2CH=CH_2), 2.00 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 166.0–165.1, 133.7, 133.3, 133.0, 130.0, 117.6, 106.8, 106.7, 106.5, 106.3, 105.6, 104.9, 82.6, 82.4, 82.3, 82.1, 82.0, 81.8, 81.3, 72.0, 71.7, 71.3, 70.2, 68.1, 67.8, 67.4, 67.2, 66.2, 62.9, 20.4. Anal. Calcd for $C_{167}H_{140}O_{50}$: C, 68.07; H, 4.79. Found: C, 67.95; H, 4.83.

1.10. Allyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranoside (10)

Compound **9** (0.34 g, 0.12 mmol) was dissolved in CH_3OH saturated with ammonia (50 mL). After 24 h at rt, the reaction mixture was concentrated to about 10 mL, then CH_2Cl_2 (100 mL) was added. The resultant precipitate was filtered and washed four times with CH_2Cl_2 to afford **10** (0.11 g, 90%). $[\alpha]_D$ −11.6 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.96 (m, 1H), 5.33 (s, 1H), 5.28 (d, 1H), 5.25 (d, 1H), 5.03–4.78 (m, 5H), 4.22–3.63 (m, 52H); ^{13}C NMR (100 MHz, D_2O): δ 136.4, 121.1, 110.5 (5C-1), 109.2, 85.9, 83.6, 79.6, 73.6, 72.3, 71.8, 71.4, 65.5. Anal. Calcd for $C_{39}H_{66}O_{31}$: C, 45.44; H, 6.45. Found: C, 45.34; H, 6.58.

Acknowledgements

This work was supported by the National Key Project for Basic Research (2003CB114400), the Beijing Natural Science Foundation (6021004), and The Ministry of Science and Technology (2001AA246014).

References

1. Plante, O. J.; Palmacci, E. R.; Seeberger, P. H. *Science* **2001**, *291*, 1523.
2. Sears, P.; Wong, C. H. *Science* **2001**, *291*, 2344.
3. Davis, B. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2137.
4. Ning, J.; Yi, Y.; Kong, F. *Tetrahedron Lett.* **2002**, *43*, 5545.
5. Ning, J.; Zhang, W.; Yi, Y.; Yang, G.; Wu, Z.; Yi, Z.; Kong, F. *Bioorg. Med. Chem.* **2003**, *11*, 2193.
6. Xing, Y.; Ning, J. *Tetrahedron: Asymmetry* **2003**, *14*, 1275.
7. Ning, J.; Heng, L.; Kong, F. *Tetrahedron Lett.* **2002**, *43*, 673.
8. Ning, J.; Yi, Y.; Yao, Z. *Synlett* **2003**, *14*, 2208.
9. Ning, J.; Wang, H.; Yi, Y. *Tetrahedron Lett.* **2002**, *43*, 7349.
10. Wang, H.; Ning, J. *J. Org. Chem.* **2003**, *68*, 2521.
11. McNeil, M.; Wallner, S. J.; Hunter, S. W.; Brennan, P. J. *Carbohydr. Res.* **1987**, *166*, 299.
12. Nita-Lazar, M.; Chevolot, L.; Iwahara, S.; Takegawa, K.; Furmanek, A.; Lienart, Y. *Acta Biochim. Pol.* **2002**, *49*, 1019.
13. Ramli, N.; Shinohara, H.; Takegawa, K.; Iwahara, S. *J. Ferment. Bioeng.* **1994**, *78*, 341.
14. Suzuki, E.; Mortara, R. A.; Takahashi, H. K.; Straus, A. H. *Clin. Diagn. Lab. Immunol.* **2001**, *8*, 1031.
15. Marino, C.; Varela, O.; de Lederkremer, R. M. *Carbohydr. Res.* **1989**, *190*, 65.
16. Sarkar, S. K.; Roy, N. *J. Carbohydr. Chem.* **2003**, *22*, 285.
17. Sarkar, S. K.; Chouhury, A. K.; Mukhopadhyay, B.; Boy, N. *J. Carbohydr. Chem.* **1999**, *18*, 1121.
18. Mortier, C. D.; Varela, O.; de Lederkremer, R. M. *Carbohydr. Res.* **1989**, *189*, 79.
19. Schmidt, R. R.; Kinzy, W. *Carbohydr. Chem. Biochem.* **1994**, *50*, 21.