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Synthesis of oligosaccharide derivatives related to those from sanqi, a Chinese herbal medicine from *Panax notoginseng*

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Abstract

Oligosaccharide derivatives from sanqi, a Chinese herbal medicine derived from *Panax notoginseng*, methyl β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranoside, diosgenyl β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranoside, and methyl β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranoside, were synthesized under standard glycosylation conditions. An unexpected α-(1→4) linkage was formed predominantly in the presence of neighboring participation group during regioselective synthesis of hexasaccharide via 3 + 3 strategy.

Keywords: Natural products; Neighboring-group effects; Stereoselectivity; Glycosylations; Oligosaccharide

1. Introduction

Panax notoginseng (Burk.) F.H. Chen. (sanqi) is widely used in China as a medicine to promote the circulation of blood.[1] It is very effective in treating coronary heart diseases and angina pectoris. The active components in sanqi are believed to be carbohydrates and their saponins.[2] Structural analysis shows that β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-D-galactopyranose is the major fraction in active sanqi oligosaccharides.[3] In stereocontrolled glycosylation, the best-established method is based on the participation of a group at C-2 of the glycosyl donor to direct 1,2-trans glycosidic bond formation.[4] Although the experimental conditions for this procedure have been modified case by case, the basic principle of neighboring-group participation has not been obliterated.[5] We herein present the synthesis of sanqi oligosacchride derivatives and an unexpected result in regio- and stereoselective synthesis of a hexasaccharide in the presence of neighboring-group participation during a 3 + 3 glycosylation.

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2. Results and discussion

Regioselective glycosylation of 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl trichloroacetimidate[6] (**1**) and methyl 3,4-*O*-isopropylidene-α-D-galactopyranoside[7] (**2**) in dry CH_2Cl_2 with TMSOTf as a promoter afforded methyl 2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→6)-3,4-*O*-isopropylidene-α-D-galactopyranoside (**3**, 76%). Acetylation of **3** with acetic anhydride in pyridine (→**4**), followed by cleavage of acetonide in 90% TFA (→**5**, 92%) and regioselective condensation with 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranose trichloroacetimidate (**6**) furnished trisaccharide **7**. Deacylation of **7** in ammonia-saturated methanol furnished the methyl glycoside of sanqi oligosaccharide repeating unit **8** in 61% yield (from **5**, Scheme 1).

To further study structure–activity relationships, we turned our attention to the synthesis of sanqi oligosaccharide analogues. Thus, 6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-ethylidene-α-D-galactopyranose[8] (**9**) was glycosylated with **6** in the presence of TMSOTf to give the (1→3)-linked disaccharide **10** (94%) which was subsequently desilylated with TBAF[9] in THF to give the 4,6-diol **11**. Coupling of **11** with donor **1** under standard glycosylation conditions gave trisaccharide **12** (54%). Trisaccharide imidate **15** was prepared in 64%

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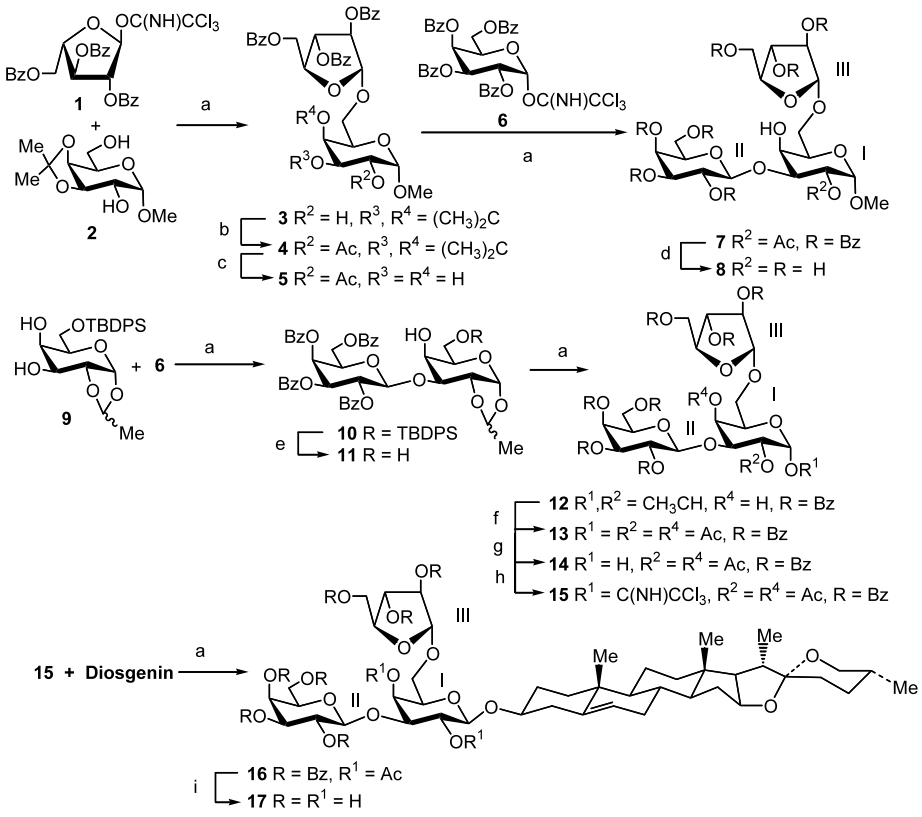
overall yield via protection group manipulation of **12**, i.e., de-ethylidenation,[8] acetylation (→**13**), deacetylation[10] on the anomeric carbon (→**14**) and finally Schmidt activation.[11] Condensation of **15** and diosgenin furnished saponin derivative **16** that was treated with aqueous 1 N NaOH in methanol (pH 9) to give the completed sanqi saponin analogue **17** (60% for two steps).

With the aim to synthesize the dimerized sanqi oligosaccharide, disaccharide **5** was coupled with phenyl 2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-1-thio-β-D-galactopyranoside[7] (**18**) to yield methyl 2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(1→3)-[2,3,5-tri-*O*-benzoyl-α-L-arabinofuranosyl-(1→6)]-2-*O*-acetyl-α-D-galactopyranoside (**19**), which was then acetylated in pyridine with acetic anhydride to give **20**. Removal of the acetonide group in 90% TFA then afforded the trisaccharide 3,4-diol **21** in a total yield of 42% from **5** (Scheme 2).

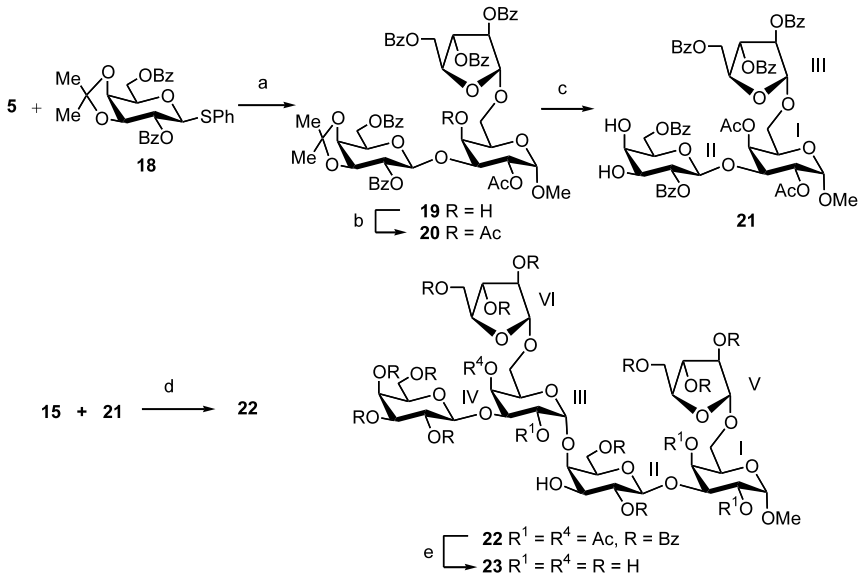
The coupling reaction of **15** and **21** was carried out in anhydrous CH_2Cl_2 in the presence of TMSOTf at 0 °C. Surprisingly, a 41% yield of the α-(1→4)-linked dimer **22** was isolated from the reaction mixture. To determine the correct assignments of this intriguing structure, we have run ^1H NMR, coupled ^{13}C NMR and ^1H–^1H, ^1H–^{13}C COSY experiments. The H-1 of sugar residue III appears at δ 5.21 ppm ($J_{1,2}$ 3.6 Hz) in the ^1H NMR, while the corresponding C-1^{III} at δ 98.5 ppm ($J_{C\text{-}1,H\text{-}1}$ 171 Hz) in ^{13}C NMR spectroscopy, indicating an α linkage between carbohydrate units II and III in **22**. Compared to acceptor **21**, the chemical shift of C-4^{II} in **22** moved downfield to δ 78.6 ppm from δ 68.8 ppm, while the C-3^{II}s of **21** and **22** appear at δ 72.2 and δ 71.9 ppm in ^{13}C NMR spectra, respectively, which confirms the C-4 glycosylation of unit II. Furthermore, acetylated **22** gave H-3^{II} at δ 5.08 ppm, further confirming this assignment. Decreasing the reaction temperature (-40 °C) and/or adding more TMSOTf (up to 0.4 equiv) did not improve the yield of this coupling reaction. The major byproducts showed ^1H NMR spectra that could not be identified and gave smaller masses compared to that of **22**. Full deprotection of **22** in ammonia-saturated methanol gave the α-(1→4)-linked sanqi dimer **23** in 93% yield. The potential bioactivity of compounds **8**, **17** and **23** is currently under investigation.

3. Experimental

General methods.—Optical rotations were determined at 25 °C with a Perkin–Elmer model 241 MC



Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2; 76% for **3**; 82% for **7**; 94% for **10**; 61% for **16**; (b) Ac_2O, Pyr; (c) 90% TFA; 92%; (d) NH_3, MeOH; 74%; (e) TBAF, THF; 77%; (f) 90% TFA; Ac_2O, Pyr; (g) NH_3, THF–MeOH (7:3); 69% from **12**; (h) Cl_3CCN, DBU; 93%; (i) 1 N NaOH, MeOH; 99%.



Scheme 2. (a) NIS, TMSOTf; 45%; (b) Ac_2O, Pyr; (c) 90% TFA; 94%; (d) TMSOTf, CH_2Cl_2; 41%; (e) NH_3, MeOH; 93%.

automatic polarimeter. ^1H NMR, ^{13}C NMR and ^1H–^1H, ^1H–^{13}C COSY spectra were recorded with ARX 400 spectrometers for solutions in $CDCl_3$, CD_3OD and D_2O. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectra were measured using MALDITOF-MS with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix, or recorded with a VG PLATFORM mass spectrometer using the electrospray ionization (ESI) technique to introduce the sample. High-resolution thin-layer chromatography (HRTLC) 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 UV detection. 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 EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Solutions were concentrated at < 60 °C under diminished pressure.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-*2*-O-*acetyl*-*3,4*-O-*isopropylidene*-α-D-*galacto*-*pyranoside* (**4**).—To a mixture of **1** (11.16 g, 18.4 mmol) and **2** (3.52 g, 15 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C was added TMSOTf (85 μL, 0.47 mmol). The mixture was stirred at this temperature for 2.5 h, then neutralized with Et_3N and concentrated. The residue was subjected to column chromatography on silica gel with 2:1 petroleum ether–EtOAc as the eluent to give **3** (7.7 g, 76%). To a mixture of **3** (7.15 g, 10.5 mmol) in pyridine (15 mL) was added Ac_2O (2.5 mL). The mixture was stirred at rt for 10 h, then co-evaporated with toluene to dryness. The residue was subjected to silica gel column chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **4** as a syrup (6.7 g, 88%): $[\alpha]_D$ +78° (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): 1.24, 1.52 (2 s, 6 H, 2 CH_3), 2.13 (s, 3 H, $COCH_3$), 3.38 (s, 3 H, OCH_3), 3.85 (dd, 1 H, $J_{6a,6b}$ 10.3, $J_{6a,5}$ 7.1 Hz, H-6a), 4.10 (dd, 1 H, $J_{6b,5}$ 5.4 Hz, H-6b), 4.26 (ddd, 1 H, $J_{5,4}$ 2.4 Hz, H-5), 4.27 (dd, 1 H, $J_{4,3}$ 5.3 Hz, H-4), 4.31 (dd, 1 H, $J_{3,2}$ 8.0 Hz, H-3), 4.60–4.62 (m, 1 H, H-4′), 4.70 (dd, 1 H, $J_{5a',5b'}$ 11.9, $J_{5a',4'}$ 4.9 Hz, H-5a′), 4.84 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.87 (dd, 1 H, $J_{5b',4'}$ 3.4 Hz, H-5b′), 4.97 (dd, 1 H, H-2), 5.41 (s, 1 H, H-1′), 5.56 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3′), 5.63 (s, 1 H, H-2′), 7.27–8.06 (m, 15 H, Ph); Anal. Calcd for $C_{38}H_{40}O_{14}$: C, 63.33; H, 5.55. Found: C, 63.60; H, 5.48.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-*2*-O-*acetyl*-α-D-*galactopyranoside* (**5**).—A solution of **4** (5 g, 6.93 mmol) in CH_2Cl_2 (2 mL) and 90% TFA was stirred at rt for about 10 min at which time TLC indicated the reaction was complete. The mixture was neutralized with aq $NaHCO_3$, then extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel with 2:1 petroleum ether–EtOAc as the eluent to give **5** as a syrup (4.34 g, 92%): $[\alpha]_D$ +52° (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): 2.06 (s, 3 H, $COCH_3$), 3.29 (s, 3 H, OCH_3), 3.75–3.78 (m, 1 H, H-6a), 3.91–4.01 (m, 3 H, H-3, H-5 and H-6b), 4.04 (d, 1 H, $J_{4,3}$ 3.3 Hz, H-4), 4.58–4.63 (m, 2 H, H-4′ and H-5a′), 4.70–4.80 (m, 1 H, H-5b′), 4.82 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.96 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2), 5.30 (s, 1 H, H-2′), 5.46 (s, 1 H, H-1′), 5.51 (d, 1 H, *J* 3.0 Hz, H-3′), 7.19–8.00 (m, 15 H, Ph); Anal. Calcd for $C_{35}H_{36}O_{14}$: C, 61.76; H, 5.33. Found: C, 61.55; H, 5.42.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-[*2,3,4,6-tetra*-O-*benzoyl*-β-D-*galactopyranosyl*-(1→3)]-*2*-O-*acetyl*-α-D-*galactopyranoside* (**7**).—To a solution of **5** (0.8 g, 1.17 mmol) and **6** (1.023 g, 1.38 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C was added TMS-

OTf (23 μL, 0.13 mmol). The mixture was stirred at this temperature for 2 h, then neutralized with Et_3N, and the solvents were evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel with 1.5:1 to 1:1 petroleum ether–EtOAc as the eluent to give **7** as a foam (1.215 g, 82%): $[\alpha]_D$ +95° (*c* 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): 1.53 (s, 3 H, $COCH_3$), 3.32 (s, 3 H, OCH_3), 3.46 (dd, 1 H, $J_{6a,6b}$ 11.2, $J_{6a,5}$ 3.1 Hz, H-6a^I), 3.90 (dd, 1 H, $J_{6b,5}$ 8.0 Hz, H-6b^I), 3.98 (dd, 1 H, H-5^I), 4.10 (dd, 1 H, $J_{3,2}$ 10.2, $J_{3,4}$ 3.2 Hz, H-3^I), 4.22 (d, 1 H, H-4^I), 4.32 (br t, 1 H, H-5^{II}), 4.46 (dd, 1 H, $J_{6a,6b}$ 11.0, $J_{6a,5}$ 5.3 Hz, H-6a^{II}), 4.57–4.61 (m, 2 H, H-6b^{II} and H-4^{III}), 4.72 (dd, 1 H, $J_{5a,5b}$ 12.1, $J_{5a,4}$ 4.8 Hz, H-5a^{III}), 4.86 (dd, 1 H, $J_{5b,4}$ 3.7 Hz H-5b^{III}), 4.90 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1^I), 5.00 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{II}), 5.15 (dd, 1 H, H-2^I), 5.38 (s, 1 H, H-2^{III}), 5.57 (s, 1 H, H-1^{III}), 5.59 (d, 1 H, $J_{3,4}$ 3.0 Hz, H-3^{III}), 5.62 (dd, 1 H, $J_{3,2}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3^{II}), 5.83 (dd, 1 H, H-2^{II}), 5.98 (d, 1 H, H-4^{II}), 7.21–8.08 (m, 35 H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): 20.00 ($CO\mathit{C}H_3$), 54.96 ($O\mathit{C}H_3$), 62.01 (C-6^{II}), 63.70 (C-5^{III}), 67.04 (C-6^I), 67.93 (C-4^{II}), 68.63 (C-2^{II}), 69.11 (C-2^I), 69.31 (C-3^{II}), 69.35 (C-5^{II}), 71.33 (C-5^I), 71.68 (C-4^I), 77.79 (C-3^I), 77.94 (C-3^{III}), 81.19 (C-4^{III}), 81.91 (C-2^{III}), 96.76 (C-1^I), 101.90 (C-1^{II}), 106.05 (C-1^{III}), 128.24, 128.37, 128.43, 128.46, 128.63, 128.66, 129.76, 129.78, 129.94, 132.99, 133.34, 133.36, 133.45, 133.52, 164.87, 165.26, 165.44, 165.51, 165.61, 165.82, 166.14, 169.92; Anal. Calcd for $C_{69}H_{62}O_{23}$: C, 65.81; H, 4.96. Found: C, 65.60; H, 5.09.

Methyl α-L-*arabinofuranosyl-(1→6)-[*β-D-*galactopyranosyl-(1→3)]-*α-D-*galactopyranoside* (**8**).—A solution of **7** (0.7 g, 0.556 mmol) in ammonia-saturated MeOH (100 mL) was stirred at rt for 7 days. The solvents were evaporated, and the residue was purified on a Sephadex LH-20 column with MeOH as the eluent to give **8** as solid (0.2 g, 74%): $[\alpha]_D$ +23° (*c* 1, CH_3OH); ^1H NMR (400 MHz, CD_3OD): 3.41 (s, 3 H, OCH_3), 3.56 (m, 2 H), 3.66–3.79 (m, 6 H), 3.88–3.93 (m, 4 H), 3.99–4.05 (m, 4 H), 4.22 (d, 1 H, $J_{4,3}$ 2.4 Hz, H-4^I), 4.52 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.77 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1^I), 5.00 (s, 1 H, H-1^{III}); ^{13}C NMR (100 MHz, CD_3OD): 55.61 (OCH_3), 62.46, 62.88, 68.22, 70.00, 70.13, 70.52, 70.62, 72.88, 74.45, 76.52, 78.65, 81.52, 83.40, 85.43, 100.99, 106.34, 109.72; ESIMS: Calcd for $C_{18}H_{32}O_{15}$, 488.17 [M]; Found, 487 $[M-H]^+$.

*2,3,4,6-Tetra-*O-*benzoyl-*β-D-*galactopyranosyl-(1→3)-6-*O-tert-*butyldiphenylsilyl-1,2-*O-*ethylidene-*α-D-*galactopyranose* (**10**).—To a solution of **9** (5.3 g, 11.9 mmol) and **6** (9.34 g, 12.6 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added TMSOTf (90 μL, 0.5 mmol) under an N_2 atmosphere. The mixture was stirred at this temperature for 1.5 h at which time TLC indicated the reaction was complete. It was then neutralized with Et_3N and concentrated. The residue was subjected to column chromatography on silica gel with 4:1 petroleum ether–EtOAc as the eluent to give **10** (R, S mixture) as a syrup (11.46 g, 94%): ^1H NMR (300 MHz, $CDCl_3$): 1.04 (s, 9 H, $C(CH_3)_3$), 1.24, 1.40 (2 d, 3 H, $CHCH_3$, the ratio of the isomers is about 1.7:1.3), 3.76–3.94 (m, 4 H), 4.09–4.15 (m, 1 H, H-5), 4.32–4.47 (m, 3 H, H-4, H-5′ and H-6a′), 4.56–4.64 (m, 1 H, H-6b′), 5.20–5.26 (m, 2 H), 5.45 (br d, 1 H, H-1), 5.60–5.80 (m, 2 H), 6.00 (d, 1 H, $J_{4',3'}$ 3 Hz, H-4′), 7.20–8.12 (m, 30 H, Ph); Anal. Calcd for $C_{58}H_{58}O_{15}Si$: C, 68.09; H, 5.71. Found: C, 68.37; H, 5.69.

*2,3,4,6-Tetra-*O-*benzoyl-*β-D-*galactopyranosyl-(1→3)-1,2-*O-*ethylidene-*α-D-*galactopyranose* (**11**).—To a solution of **10** (10.5 g, 10.3 mmol) in THF (100 mL) was added TBAF (7.048 g, 23.7 mmol). The mixture was stirred at rt for 2.5 h at which time TLC indicated the reaction was complete. The solvents were evaporated, and the residue was subjected to column chromatography on silica gel with 1:1 petroleum ether–EtOAc as the eluent to give **11** (6.2 g, 77%) as a syrup; MALDITOF-MS: Calcd for $C_{42}H_{40}O_{15}$, 784.24 [M]; Found, 807.30 $[M+Na]^+$. Treatment of **11** (20 mg) with Ac_2O in pyridine gave 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-4,6-di-*O*-acetyl-1,2-*O*-ethylidene-α-D-galactopyranose as a syrup: ^1H NMR (400 MHz, $CDCl_3$): 1.23 (d, 1.7 H, *J* 3.6 Hz, $CHCH_3$), 1.34 (d, 1.3 H, *J* 3.6 Hz, $CHCH_3$), 1.85 (s, 1.7 H, $COCH_3$), 1.89 (s, 1.3 H, $COCH_3$), 2.05, 2.06 (br s, 3 H, $COCH_3$), 3.90 (t, 0.43 H, $J_{3,4}$ 4.0 Hz, H-3), 4.06–4.19 (m, 4 H), 4.24 (t, 0.57 H), 4.34 (t, 1 H), 4.40–4.47 (m, 1 H), 4.63–4.69 (m, 1 H), 5.11 (q, 0.43 H, *J* 4.8 Hz, $CHCH_3$), 5.22–5.30 (m, 1.57 H), 5.39 (d, 0.43 H, $J_{1',2'}$ 4.8 Hz), 5.49 (d, 1 H), 5.54 (br s, 0.57 H), 5.62–5.65 (br d, 1 H), 5.71–5.77 (m, 1 H), 5.99 (br s, 1 H, H-4′), 7.24–8.12 (m, 20 H, Ph).

*2,3,5-Tri-*O-*benzoyl-*α-L-*arabinofuranosyl-(1→6)-[2,3,4,6-tetra-*O-*benzoyl-*β-D-*galactopyranosyl-(1→3)]-1,2-*O-*ethylidene-*α-D-*galactopyranose* (**12**).—To a solution of **11** (2.4 g, 3.06 mmol) and **1** (1.89 g, 3.11 mmol) in CH_2Cl_2 (20 mL) at 0 °C were added TMSOTf (40 μL, 0.22 mmol). The mixture was stirred at this temperature for 1 h at which time TLC indicated the reaction was complete. It was then neutralized with Et_3N and concentrated. The residue was subjected to column chromatography on silica gel with 2:1 petroleum ether–EtOAc as the eluent to give **12** as a syrup (2.03 g, 54%). One isomer gave ^1H NMR (300 MHz, $CDCl_3$) as follows: 1.17 (d, 3 H, *J* 4.8 Hz, $CHCH_3$), 1.18 (s, 3 H, $COCH_3$), 3.59 (dd, 1 H, $J_{6a,6b}$ 10.2, $J_{6a,5}$ 6.3 Hz, H-6a^I), 3.79 (dd, 1 H, $J_{6b,5}$ 5.4 Hz H-6b^I), 4.07–4.14 (m, 3 H), 4.26 (m, 1 H), 4.41 (dd, 1 H, *J* 11.4, 6.0 Hz), 4.57–4.64 (m, 3 H), 4.79 (m, 1 H), 5.20–5.26 (m, 3 H), 5.48–5.63 (m, 5 H), 5.75 (dd, 1 H, *J* 10.5, 7.6 Hz), 5.96 (d, 1 H, $J_{4,3}$ 3.3 Hz, H-4^{II}), 7.23–8.12 (m, 35 H, Ph); MALDITOF-MS: Calcd for $C_{68}H_{60}O_{22}$, 1228.36 [M]; Found, 1251 $[M+Na]^+$.

*2,3,5-Tri-*O-*benzoyl-*α-L-*arabinofuranosyl-(1→6)-[2,3,4,6-tetra-*O-*benzoyl-*β-D-*galactopyranosyl-(1→3)]-*

2,4-di-O-*acetyl*-α-D-*galactopyranosyl trichloroacetimidate* (**15**).—To a solution of **12** (1.52 g, 1.24 mmol) in CH_2Cl_2 (2 mL) was added aq 90% TFA (15 mL). The mixture was stirred at rt for 2 h, then co-evaporated with toluene under reduced pressure. The residue was dissolved in pyridine (10 mL) and Ac_2O (5 mL), and stirred at rt for 6 h, then concentrated to dryness to give crude **13**. Crude **13** dissolved in 7:3 ammonia-saturated THF–MeOH (100 mL) was stirred at rt for 30 min, and the solvents were then evaporated at 35 °C. The residue was subjected to column chromatography on silica gel with 1.5:1 petroleum ether–EtOAc as the eluent to give **14** as a syrup (1.1 g, 69% from **12**). Compound **14** (0.73 g, 0.567 mmol) was dissolved in CH_2Cl_2 (6 mL), then CCl_3CN (0.5 mL, 0.5 mmol) and DBU (50 μL) were added at 0 °C. The mixture was stirred at rt for 2 h, then concentrated. The residue was subjected to column chromatography on silica gel with 1.5:1 petroleum ether–EtOAc as eluent to give **15** as a syrup (0.749 g, 93%): $[\alpha]_D$ +59° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 1.51 (s, 3 H, $COCH_3$), 2.23 (s, 3 H, $COCH_3$), 3.68 (dd, 1 H, $J_{6a,6b}$ 11.0, $J_{6a,5}$ 4.3 Hz, H-6a^I), 3.82 (dd, 1 H, $J_{6b,5}$ 4.8 Hz, H-6b^I), 4.18 (dd, 1 H, H-5^{II}), 4.27 (dd, 1 H, $J_{3,2}$ 10.2, $J_{3,4}$ 3.2 Hz, H-3^I), 4.29–4.36 (m, 2 H, H-5^I and H-6a^{II}), 4.59–4.69 (m, 3 H, H-6b^{II}, H-4^{III} and H-5a^{III}), 4.85 (dd, 1 H, $J_{5b,5a}$ 11.9, $J_{5b,4}$ 3.1 Hz, H-5b^{III}), 4.97 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^{II}), 5.23 (dd, 1 H, $J_{2,1}$ 3.6 Hz, H-2^I), 5.53–5.58 (m, 3 H, H-3^{II}, H-3^{III} and H-2^{III}), 5.72 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2^{II}), 5.83 (d, 1 H, H-4^I), 5.91 (d, 1 H, $J_{4,3}$ 3.2 Hz, H-4^{II}), 6.46 (d, 1 H, H-1^I), 7.25–8.11 (m, 35 H, Ph), 8.49 (s, 1 H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 19.72 ($CO\underline{C}H_3$), 20.72 ($CO\underline{C}H_3$), 61.63 (C-6^{II}), 63.52 (C-5^{III}), 65.82 (C-6^I), 67.66 (C-4^{II}), 68.64 (C-2^I), 69.26 (C-4^I), 69.93 (C-2^{II}), 71.17 (C-5^{II}), 71.31 (C-5^I), 71.31 (C-3^{II}), 73.84 (C-3^I), 77.95 (C-3^{III}), 81.16 (C-4^{III}), 82.12 (C-2^{III}), 93.56 (C-1^I), 101.16 (C-1^{II}), 106.03 (C-1^{III}), 128.17, 128.25, 128.43, 128.48, 128.61, 128.95, 128.99, 129.12, 129.18, 129.31, 129.57, 129.69, 129.72, 129.81, 129.88, 130.06, 132.97, 133.32, 133.46, 133.61, 160.53, 164.69, 165.26, 165.39, 165.51, 165.74, 165.85, 166.16, 169.64, 169.73; MALDITOF-MS: Calcd for $C_{72}H_{62}Cl_3NO_{24}$, 1429.27 [M]; Found, 1452.17 $[M+Na]^+$. Anal. Calcd for $C_{72}H_{62}Cl_3NO_{24}$: C, 60.41; H, 4.37. Found: C, 60.68; H, 4.29.

Diosgenyl 2,3,4,6-tetra-O-*benzoyl*-β-D-*galactopyranosyl-(1→3)-[2,3,5-tri*-O-*benzoyl*-α-L-*arabinofuranosyl-(1→6)]-2,4-di*-O-*acetyl*-β-D-*galactopyranoside* (**16**).—To a solution of **15** (0.53 g, 0.37 mmol) and diosgenin (0.185 g, 0.45 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added TMSOTf (25 μL, 0.14 mmol). The mixture was stirred at this temperature for about 1 h, then neutralized with Et_3N and concentrated. The residue was subjected to column chromatography on silica gel with 1.5:1 petroleum ether–EtOAc as the eluent to give **16** (0.38 g, 61%) as a foam: $[\alpha]_D$ +30° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 0.71 (s, 3 H, CH_3), 0.79 (d, 3 H, *J* 6.4 Hz, CH_3), 0.81 (s, 3 H, CH_3), 0.84–0.87 (m, 2 H), 0.97 (d, 3 H, *J* 6.8 Hz, CH_3), 1.01–1.15 (m, 2 H), 1.21–1.30 (m, 5 H), 1.42–2.09 (m, 24 H), 1.55 (s, 3 H, $COCH_3$), 2.17 (s, 3 H, $COCH_3$), 3.34 (m, 1 H, 3α-H), 3.37 (t, 1 H, *J* 10.9 Hz, H-26a), 3.47 (dd, 1 H, $J_{26b,25}$ 4.1 Hz, H-26b), 3.72 (dd, 1 H, $J_{6a,6b}$ 12.1, $J_{6a,5}$ 8.4 Hz, H-6a^I), 3.79–3.83 (m 2 H, H-5^I and H-6b^I), 3.87 (dd, 1 H, $J_{3,2}$ 10.0, $J_{3,4}$ 3.6 Hz, H-3^I), 4.17 (t, 1 H, H-5^{II}), 4.29 (dd, $J_{6a,6b}$ 11.2, $J_{6a,5}$ 7.0 Hz, H-6a^{II}), 4.38 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1^I), 4.29 (t, 1 H, *J* 6.8 Hz, H-16), 4.58 (m, 3 H, H-6a^{II}, H-4^{III} and H-5a^{III}), 4.82 (dd, 1 H, $J_{5b,5a}$ 11.9, $J_{5b,4}$ 3.3 Hz, H-5b^{III}), 4.88 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{II}), 5.11 (dd, 1 H, H-2^I), 5.24 (d, $J_{6,7a}$ 4 Hz, H-6 of diosgenyl), 5.34 (s, 1 H, H-1^{III}), 5.51–5.56 (m, 3 H, H-3^{II}, H-3^{III} and H-2^{III}), 5.60 (d, 1 H, H-4^I), 5.69 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2^{II}), 5.90 (d, 1 H, $J_{4,3}$ 4 Hz, H-4^{II}), 7.23–8.09 (m, 35 H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): 14.57 (C-21), 16.25 (C-18), 17.17 (C-27), 19.15 (C-19), 20.22 ($COCH_3$), 20.68 (C-11), 20.85 ($CO\underline{C}H_3$), 26.93 (C-24), 29.44 (C-2), 30.31 (C-25), 31.32 (C-23), 31.40 (C-8), 31.84 (C-15), 31.98 (C-7), 36.69 (C-10), 36.84 (C-1), 38.95 (C-4), 39.71 (C-12), 40.23 (C-13), 41.61 (C-20), 49.75 (C-9), 56.38 (C-14), 61.65 (C-6^{II}), 62.12 (C-17), 63.68 (C-5^{III}), 66.60 (C-6^I), 66.86 (C-26), 67.73 (C-4^{II}), 69.36 (C-4^I), 69.93 (C-2^{II}), 70.62 (C-2^I), 71.19 (C-5^{II}), 71.47 (C-3^{II}), 73.22 (C-5^I), 77.76 (C-3^I), 77.92 (C-3^{III}), 80.10 (C-3), 80.81 (C-16), 80.92 (C-4^{III}), 82.23 (C-2^{III}), 100.40 (C-1^I), 101.43 (C-1^{II}), 106.38 (C-1^{III}), 109.29 (C-22), 121.553 (C-6), 128.24, 128.33, 128.51, 128.54, 128.68, 129.02, 129.19, 129.38, 129.45, 129.77, 129.88, 129.95, 130.10, 133.05, 133.24, 133.34, 133.55, 133.66, 140.45 (C-5), 164.74, 165.32, 165.46, 165.61, 165.73, 165.91, 166.17, 168.66, 170.11; MALDITOF-MS: Calcd for $C_{97}H_{102}O_{26}$, 1682.67 [M]; Found, 1705.31 $[M+Na]^+$. Anal. Calcd for $C_{97}H_{102}O_{26}$: C, 69.19; H, 6.11. Found: C, 69.51; H, 5.93.

Diosgenyl β-D-*galactopyranosyl-(1→3)-[*α-L-*arabinofuranosyl-(1→6)]-*β-D-*galactopyranoside* (**17**).—To a solution of **16** (0.32 g, 0.19 mmol) in MeOH (100 mL) was added aq 1 N NaOH until pH 9–10 was attained. The mixture was stirred at rt overnight, then neutralized with Amberlite IR-120 (H^+). The solvents were evaporated, and the residue was subjected to column chromatography on Sephadex LH-20 with MeOH as the eluent to give **17** as an amorphous solid (0.16 g, 99%): $[\alpha]_D$ −51° (*c* 1, CH_3OH); ^{1}H NMR (400 MHz, CD_3OD): 0.81 (d, 3 H, *J* 6.4 Hz, CH_3), 0.83 (s, 3 H, CH_3), 0.98 (d, 3 H, *J* 6.8 Hz, CH_3), 1.07 (s, 3 H, CH_3), 0.97–1.0 (m, 1 H), 1.09–2.04 (m, 25 H), 2.29 (t, 1 H, *J* 12.0 Hz), 2.45 (d, 1 H, *J* 10.8 Hz), 3.32–4.13 (m, 27 H), 4.41 (t, 1 H, *J* 7.6 Hz, H-16), 4.42 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1^I), 4.44 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.95 (s, 1 H, H-1^{III}), 5.41 (br s, 1 H, H-6 of diosgenyl); ^{13}C NMR (100 MHz, $DOCD_3$): 14.90 (C-21), 16.79 (C-18), 17.50 (C-27), 19.87 (C-19), 21.99 (C-11), 29.88 (C-24), 30.76

(C-25), 31.43 (C-23), 32.42 (C-15), 32.74 (C-7), 32.79 (C-2), 33.17 (C-8), 37.99 (C-10), 38.48 (C-1), 39.75 (C-12), 40.92 (C-13), 41.41 (C-20), 42.89 (C-4), 51.61 (C-9), 57.80 (C-14), 62.56 (C-17), 63.02 (C-6^{II}), 63.74 (C-5^{III}), 67.84 (C-26), 67.96 (C-6^{I}), 69.85 (C-4^{II}), 70.24 (C-4^{I}), 71.51 (C-2^{II}), 71.56 (C-2^{I}), 74.60 (C-5^{II}), 74.63 (C-3^{II}), 76.72 (C-5^{I}), 78.88 (C-3), 80.04 (C-16), 82.19 (C-3^{I}), 83.43 (C-3^{III}), 84.73 (C-4^{III}), 85.70 (C-2^{III}), 102.63 (C-1^{I}), 106.27 (C-1^{II}), 109.29 (C-22), 110.55 (C-1^{III}), 122.50 (C-6), 142.04 (C-5); MALDITOF-MS: Calcd for $C_{44}H_{70}O_{17}$, 870.46 [M]; Found 893.39 $[M + Na]^+$.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-*[2,6-di*-O-*benzoyl*-*3,4*-O-*isopropylidene*-β-D-*galactopyranosyl*-(1→3)]-*2*-O-*acetyl*-α-D-*galactopyranoside* (**19**).—To a mixture of **5** (1.22 g, 1.76 mmol) and **18** (1.2 g, 2.3 mmol) in dry CH_2Cl_2 (10 mL) at −20 °C were added *N*-iodosuccinimide (NIS, 0.8 g, 3.57 mmol) and TMSOTf (22 μL, 0.12 mmol). The mixture was stirred at this temperature for 80 min, at which time TLC indicated the reaction was complete. The mixture was neutralized with Et_3N, and concentrated. The residue was subjected to column chromatography on silica gel with 1.5:1 petroleum ether–EtOAc as the eluent to give syrupy **19** (0.87 g, 45%): $[\alpha]_D$ +28° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 1.26, 1.58 (s, 6 H, 2 CH_3), 1.64 (s, 3 H, COCH_3), 3.28 (s, 3 H, OCH_3), 3.64 (d, 1 H, *J* 9.2 Hz, H-6a^{I}), 3.83–3.88 (m, 2 H, H-4^{I}, H-6b^{I}), 3.96 (d, 1 H, *J* 9.6 Hz, H-5^{I}), 4.26 (s, 1 H, $J_{4,3}$ 4.1 Hz, H-4^{II}), 4.26 (br s, 1 H, H-3^{I}), 4.32 (br s, 1 H, H-3^{II}), 4.40 (br s, 1 H, H-5^{II}), 4.54 (d, 1 H, H-4^{III}), 4.58–4.73 (m, 4 H, H-5a^{III}, H-5b^{III}, H-1^{II}, H-6a^{II}), 4.81 (d, 1 H, *J* 10.8 Hz, H-6b^{II}), 4.85 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-1^{I}), 5.07 (dd, 1 H, $J_{2,3}$ 6.8 Hz, H-2^{I}), 5.25 (br s, 1 H, H-2^{II}), 5.45 (s, 1 H, H-1^{III}), 5.53 (s, 1 H, H-2^{III}), 5.55 (d, 1 H, $J_{3,4}$ 4.0 Hz, H-3^{III}), 7.27–8.04; MALDITOF-MS: Calcd for $C_{58}H_{58}O_{21}$, 1090.35 [M]; Found, 1113 $[M + Na]^+$. Anal. Calcd for $C_{58}H_{58}O_{21}$: C, 63.85; H, 5.36. Found: C, 64.04; H, 5.19.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-*[2,6-di*-O-*benzoyl*-*3,4*-O-*isopropylidene*-β-D-*galactopyranosyl*-(1→3)]–*2,4-di*-O-*acetyl*-α-D-*galactopyranoside* (**20**).—Compound **19** (1.85 g, 1.69 mmol) and Ac_2O (1 mL) were dissolved in pyridine (5 mL) at rt. The mixture was stirred at rt for 10 h, then co-evaporated with toluene. The residue was subjected to column chromatography on silica gel with 3:1 petroleum ether–EtOAc as the eluent to give quantitative **20** as a syrup: $[\alpha]_D$ +11° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 1.35, 1.61 (2 s, 6 H, CH_3), 1.73, 2.10 (2 s, 6 H, COCH_3), 3.27 (s, 3 H, OCH_3), 3.56 (dd, 1 H, $J_{6a,6b}$ 10.9, $J_{6a,5}$ 3.2 Hz, H-6a^{I}), 3.91 (dd, 1 H, $J_{6b,5}$ 4.0 Hz, H-6b^{I}), 4.00–4.03 (m, 1 H, H-5^{I}), 4.09–4.11 (m, 1 H, H-4^{II}), 4.13 (dd, 1 H, $J_{3,2}$ 10.2, $J_{3,4}$ 3.4 Hz, H-3^{I}), 4.32 (dd, 1 H, H-3^{II}), 4.38–4.42 (m, 1 H, H-5^{II}), 4.59–4.62 (m, 2 H, H-5a^{III} and H-4^{III}), 4.66–4.73 (m, 3 H, H-5b^{III}, H-1^{II}, H-6a^{II}), 4.81 (dd, 1 H, $J_{6b,5}$ 3.2 Hz, H-6b^{II}), 4.87 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.95 (dd, 1 H, H-2^{I}), 5.25 (t, 1 H, $J_{1,2}$ 7.3 Hz, H-2^{II}), 5.33 (s, 1 H, H-1^{III}), 5.52 (s, 1 H, H-2^{III}), 5.53 (d, 1 H, H-4^{I}), 5.56 (d, 1 H, $J_{3,4}$ 4.8 Hz, H-3^{III}), 7.26–8.10 (m, 25 H, Ph); MALDITOF-MS: Calcd for $C_{60}H_{60}O_{22}$, 1132.36 [M]; Found, 1155.4 $[M + Na]^+$.

Methyl 2,3,5-tri-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)-*[2,6-di*-O-*benzoyl*-β-D-*galactopyranosyl*-(1→3)]-*2,4-di*-O-*acetyl*-α-D-*galactopyranoside* (**21**).—A solution of **20** (1.00 g, 1.13 mmol) in CH_2Cl_2 (2 mL) and 90% TFA were stirred at rt for about 10 min, at which time TLC indicated the reaction was complete. The mixture was neutralized with aq $NaHCO_3$, then extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography on silica gel with 1:1 petroleum ether–EtOAc as the eluent to give **21** as a syrup (0.915 g, 94%): $[\alpha]_D$ +38° (*c* 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 1.68, 2.11 (2 s, 6 H, 2 COCH_3), 3.28 (s, 3 H, OCH_3), 3.60 (dd, 1 H, $J_{6a,6b}$ 10.9, $J_{6a,5}$ 3.1 Hz, H-6a^{I}), 3.76–3.84 (m, 3 H, H-3^{II}, H-5^{II} and H-6b^{I}), 4.01 (br s, 1 H, H-5^{I} and H-4^{II}), 4.16 (dd, 1 H, $J_{3,2}$ 10.4, $J_{3,4}$ 3.2 Hz, H-3^{I}), 4.58–4.62 (m, 3 H, H-4^{III}, H-5a^{III} and H-5b^{III}), 4.68 (dd, 1 H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 4.4 Hz, H-6a^{II}), 4.69 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1^{II}), 4.83 (dd, 1 H, $J_{6b,5}$ 3.2 Hz, H-6b^{II}), 4.87 (4 H, d, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.94 (dd, 1 H, H-2^{I}), 5.18 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2^{II}), 5.33 (s, 1 H, H-1^{III}), 5.54 (s, 1 H, H-2^{III}), 5.55 (d, 1 H, H-4^{I}), 5.56 (d, $J_{3,4}$ 5.2 Hz, H-3^{III}), 7.26–8.08 (m, 25 H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): 20.28, 27.77, 55.14, 62.51 (C-5^{III}), 63.55 (C-6^{II}), 66.32 (C-6^{I}), 68.41 (C-5^{I}), 68.77 (C-4^{II}), 70.22 (C-2^{I}), 70.80 (C-4^{I}), 72.26 (C-3^{II}), 72.46 (C-5^{II}), 72.60 (C-3^{I}), 73.68 (C-2^{II}), 77.85 (C-3^{III}), 81.00 (C-4^{III}), 82.04 (C-2^{III}), 96.75 (C-1^{I}), 101.26 (C-1^{II}), 106.17 (C-1^{III}), 128.28, 128.42, 128.47, 128.96, 129.08, 129.58, 129.64, 129.68, 129.72, 129.87, 133.012 133.22, 133.27, 133.46, 133.50, 165.30, 165.75, 166.17, 166.33, 169.83, 170.76; MALDITOF-MS: Calcd for $C_{57}H_{56}O_{22}$, 1092.33 [M]; Found, 1115.17 $[M + Na]^+$. Anal. Calcd for $C_{57}H_{56}O_{22}$: C, 62.63; H, 5.16. Found: C, 62.88; H, 5.02.

Methyl 2,3,4,6-tetra-O-*benzoyl*-β-D-*galactopyranosyl*-(1→3)-*[2,3,5-tri*-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)]-*2*-O-*acetyl*-α-D-*galactopyranosyl*-(1→4)-*2,6-di*-O-*benzoyl*-β-D-*galactopyranosyl*-(1→3)-*[2,3,5-tri*-O-*benzoyl*-α-L-*arabinofuranosyl*-(1→6)]-*2,4-di*-O-*acetyl*-α-D-*galactopyranoside* (**22**).—To a solution of **15** (0.794 g, 0.56 mmol) and **21** (0.519 g, 0.47 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C was added TMSOTf (10 μL, 0.06 mmol). The mixture was stirred at this temperature for 2 h, then neutralized with Et_3N, and the solvents were evaporated. The residue was subjected to column chromatography on silica gel with 1.5:1 petroleum ether–EtOAc as the eluent to give **22** as an amorphous solid (0.46 g, 41%): $[\alpha]_D$ +91° (*c* 1, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$): 1.51 (s, 3 H, $COCH_3$), 1.60 (s, 6 H, 2 $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 3.31 (s, 3 H, OCH_3), 3.63–3.66 (m, 2 H, H-6a^{I} and H-6a^{III}), 3.72 (dd, 1 H, $J_{6b,6a}$ 11.3, $J_{6b,5}$ 4.3 Hz, H-6b^{III}), 3.83–3.86 (m, 3 H, H-3^{II}, H-6b^{I} and H-5^{II}), 4.03 (d, 1 H, $J_{4,3}$ 2.4 Hz, H-4^{II}), 4.10 (m, 2 H, H-6a^{II} and H-5^{I}), 4.20 (dd, 1 H, $J_{3,2}$ 10.4, $J_{3,4}$ 3.5 Hz, H-3^{I}), 4.25–4.35 (m, 2 H, H-6a^{IV} and H-5^{IV}), 4.51–4.60 (m, 5 H, H-3^{III}, H-4^{VI}, H-5a^{V}, H-4^{V} and H-6b^{II}), 4.65–4.73 (m, 4 H, H-6b^{IV}, H-5b^{V}, H-5a^{VI}, H-1^{II}), 4.80 (dd, 1 H, $J_{5b,5a}$ 11.8, $J_{5b,4}$ 3.2 Hz, H-5b^{VI}), 4.85 (m, 1 H, H-5^{III}), 4.92 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 5.03 (dd, 1 H, H-2^{I}), 5.16 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1^{IV}), 5.21 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{III}), 5.22 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2^{III}), 5.32 (dd, 1 H, $J_{2,3}$ 10.4, $J_{2,1}$ 7.6 Hz, H-2^{II}), 5.34 (s, 1 H, H-1^{V}), 5.36 (s, 1 H, H-1^{VI}), 5.42 (d, 1 H, $J_{2,3}$ 1.6 Hz, H-2^{VI}), 5.54–5.62 (m, 4 H, H-2^{V}, H-3^{V}, H-4^{I}, H-3^{VI}), 5.63 (dd, 1 H, $J_{3,2}$ 10.4, $J_{3,4}$ 3.3 Hz, H-3^{IV}), 5.77 (dd, 1 H, H-2^{IV}), 5.81 (d, 1 H, $J_{4,3}$ 3.1 Hz, H-4^{III}), 5.96 (d, 1 H, H-4^{IV}), 7.25–8.10 (m, 60 H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): 19.83, 20.17, 20.81, 20.95 (4 $COCH_3$), 55.20 (OCH_3), 61.39 (C-6^{IV}), 61.46 (C-6^{II}), 63.31 (C-5^{V}), 63.52 (C-5^{VI}), 65.68 (C-6^{III}), 66.81 (C-6^{I}), 67.75 (C-4^{IV}), 68.88 (C-5^{I}), 69.40 (C-5^{III}), 69.76 (C-2^{III}), 69.91 (C-2^{IV}), 70.05 (C-2^{I}), 70.17 (C-4^{III}), 70.52 (C-4^{I}), 70.95 (C-5^{IV}), 71.60 (C-3^{IV}), 71.73 (C-5^{II}), 71.92 (C-3^{II}), 72.51 (C-2^{II}), 73.55 (C-3^{I}), 73.90 (C-3^{III}), 77.51 (C-3^{V}), 77.89 (C-3^{VI}), 78.64 (C-4^{II}), 80.30 (C-4^{V}), 81.24 (C-4^{VI}), 81.84 (C-2^{V}), 82.67 (C-2^{VI}), 96.79 (C-1^{I}), 98.50 (C-1^{III}), 101.51 (C-1^{IV}), 101.67 (C-1^{II}), 106.06 (C-1^{V}), 106.21 (C-1^{VI}), 128.18, 128.21, 128.26, 128.35, 128.39, 128.44, 128.47, 128.54, 129.51, 129.67, 129.72, 129.78, 129.84, 129.92, 130.01, 133.45, 165.36, 165.49, 165.52, 165.66, 165.69, 165.74, 166.15, 169.74, 169.91, 170.14, 170.32; MALDITOF-MS: Calcd for $C_{127}H_{116}O_{45}$, 2360.68 [M]; Found, 2383.32 $[M + Na]^+$. Anal. Calcd for $C_{127}H_{116}O_{45}$: C, 64.57; H, 4.95. Found: C, 64.81; H, 5.06.

Methyl β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranosyl-(1→4)-β-D-galactopyranosyl-(1→3)-[α-L-arabinofuranosyl-(1→6)]-α-D-galactopyranoside (**23**).—A solution of **22** (0.27 g, 0.114 mmol) in ammonia-saturated MeOH (100 mL) was stirred at rt for 7 days. The solvents were evaporated, and the residue was purified on a Sephadex LH-20 column with MeOH as the eluent to give **23** as an amorphous solid (0.10 g, 93%): $[\alpha]_D$ +7° (*c* 1, CH_3OH); ^{1}H NMR (400 MHz, D_2O): 3.38 (s, 3 H, OCH_3), 3.61–4.10 (m, 32 H), 4.18 (d, 1 H, *J* 2.8 Hz), 4.26 (d, 1 H, *J* 2.4 Hz), 4.60 (d, 1 H, $J_{1,2}$ 7.6 Hz), 4.62 (d, 1 H, $J_{1,2}$ 8.0 Hz), 4.81 (1 H, overlapped by D_2O), 4.96 (d, 1 H, $J_{1,2}$ 3.6 Hz), 4.20 (s, 1 H), 5.20 (d, 1 H, $J_{1,2}$ 1.1 Hz); ^{13}C NMR (100 MHz, D_2O): 56.03 (OCH_3), 58.42, 61.07, 61.80, 62.01, 67.20, 68.06, 68.21, 68.43, 69.42, 69.84, 70.02, 70.08, 71.91 (3 C), 71.96, 72.67, 73.04, 73.37, 75.69, 75.86, 77.23, 77.34, 78.62, 79.74, 80.20, 81.64, 81.90, 84.62, 84.67, 100.16 (C-1^{I}, $J_{C\text{-}1,H\text{-}1}$ 173 Hz), 101.10 (C-1^{III}, $J_{C\text{-}1,H\text{-}1}$ 171 Hz), 105.22 (C-1^{IV}, $J_{C\text{-}1,H\text{-}1}$ 164 Hz), 105.39 (C-1^{II}, $J_{C\text{-}1,H\text{-}1}$ 165 Hz), 108.24 (C-1^{V}, $J_{C\text{-}1,H\text{-}1}$ 173 Hz), 108.72 (C-1^{VI}, 174 Hz); ESI-MS Calcd for $C_{83}H_{72}O_{23}S$, 944.3 [M]; Found, 962.6 $[M + NH_4]^+$.

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