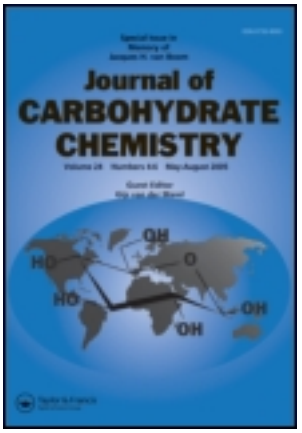

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Synthesis of Two Tetrasaccharides Related to the O-Antigen from *Azospirillum brasilense* S17 and *Azospirillum lipoferum* SR65

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Synthesis of two isomeric tetrasaccharides, β-D-Glu*p*-(1→2)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-L-Rha*p* (I) and β-D-Glu*p*-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p* (II), the repeating units from the lipopolysaccharides of the nitrogen-fixing bacterium *Azospirillum brasilense* S17 and *Azospirillum lipoferum* SR65, was achieved via assembly of the building blocks 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate (**2**), *p*-methoxyphenyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**3**), 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**6**), 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (**8**), and *p*-methoxy phenyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**14**). Condensation of **3** with **6** or **8** provided the disaccharides **9** or **11,** respectively. Deallyloxycarbonylation of **11** gave the disaccharide aceptor **12**, while removal of the *p*-methoxyphenyl group in **9** followed by trichloroacetimidation of the anomeric hydroxyl group afforded the disaccharide donor **10**. Meanwhile, disaccharide donor **16** and acceptor **18** were prepared from **6**, **8,** and **14** similarly. Finally, condensation of **10** with **12** or **16** with **18**, followed by deprotection, gave the target tetrasaccharides **I** or **II,** respectively.

Keywords Synthesis; D-Glucose; L-Rhamnose; Oligosaccharides; Nitrogen fixing

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INTRODUCTION

Azospirilla species are gram-negative bacteria widely distributed in soils. They colonize the rhizosphere and have a positive effect on plant growth and development by excreting phytohormones, vitamins, and other biologically active substances into the rhizosphere.[1] Very recently, it was reported that the antigenic lipopolysaccharides from the nitrogen-fixing bacteria *Azospirillum brasilense* S17 and *Azospirillum lipoferum* SR65 are made up of linear repeating units with (1→2)- and (1→3)-linked rhamnan backbone and D-glucose in the side chains as shown in Figure 1A, B.[2,3]

The lipopolysaccharide (LPS) is the major antigen of the bacterial outer membrane of the *Azospirillum* cell envelope. Together with other cell surface carbohydrate polymers such as the exopolysaccharide (EPS) and the capsular polysaccharide (CPS), they play important roles for the survival of the bacteria in adverse environmental conditions as well as regulate the interaction with the roots of plants.[1] The LPS is thought to play an important role in the molecular mechanism of symbiotic infections, and the involvement of the carbohydrate-rich molecules in establishing the interaction between the nitrogen-fixing bacterium and the host has been reported.[4,5] It was also revealed that the LPSs of the *Azospirillum* outer membrane play an important

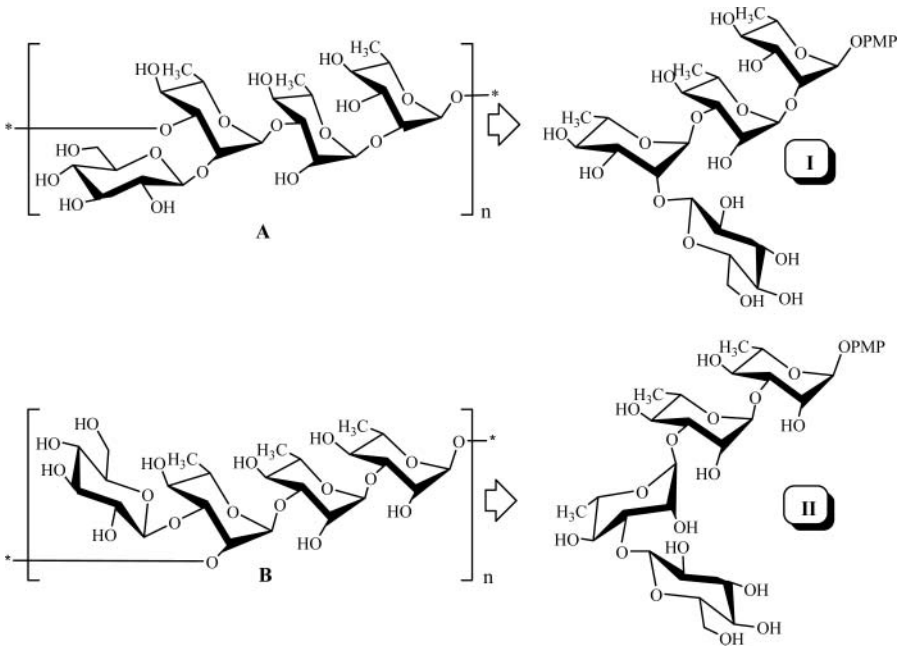
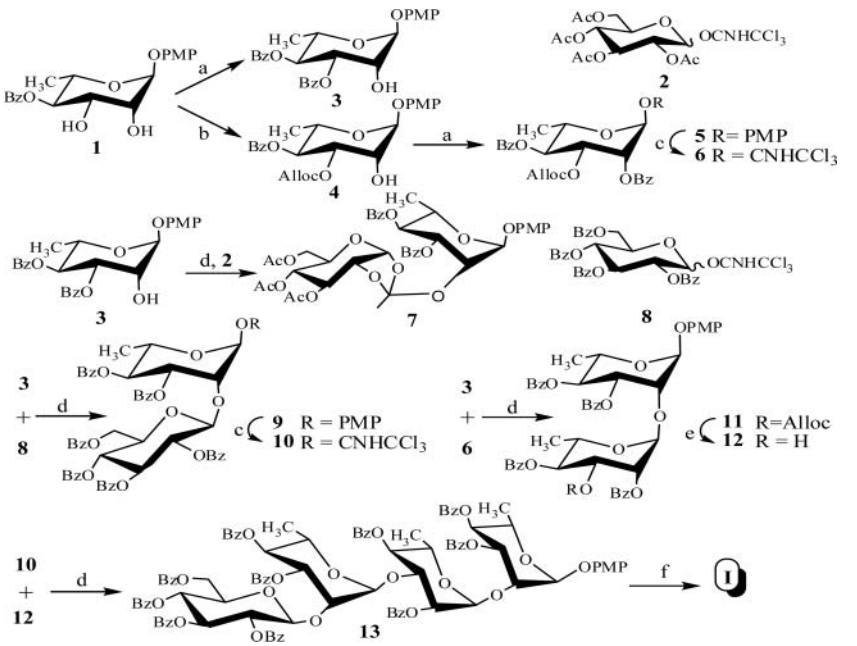


Figure 1: Structure of the lipopolysaccharides of *A. brasilense* **S17** (**A**), *A. lipoferum* **SR65** (**B**), and the synthesized tetrasaccharides **I** and **II**.

role in the formation of bacterial association with the roots of cereals; for example, mutants defective in LPS synthesis are worse colonizers to wheat root[6] and worse absorbers to maize root[7] compared to their nondefective counterparts. These facts are of particular interest from the viewpoint of the biological roles of carbohydrates. For a better understanding of the role the LPSs play in the symbiotic infections of the bacterium with the host, considerable interest has been paid to the synthesis of these antigenic repeating units.[8–10] Here we report the efficient synthesis of the tetrasaccharide repeating units (Fig. 1A, B) of the LPS from *A. brasilense* S17 and *A. lipoferum* SR65 in the form of their *p*-methoxyphenyl glycosides.

RESULTS AND DISCUSSION

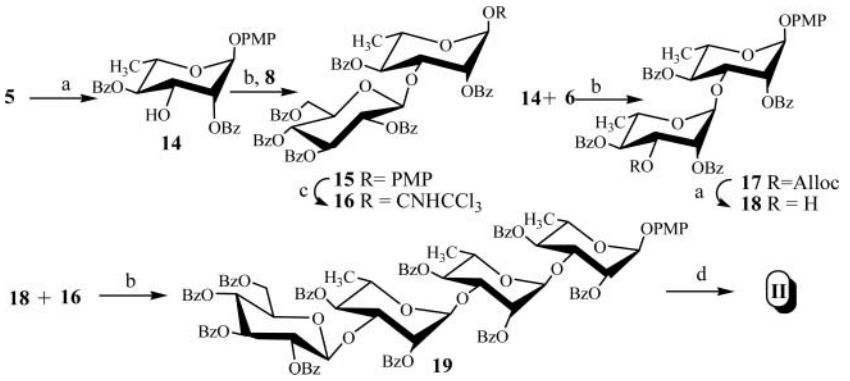
As shown in Scheme 1, synthesis of the tetrasaccharide **I** was commenced with the synthesis of suitably protected L-rhamnose and D-glucose synthons followed by stepwise glycosylation and deprotection. Therefore, known *p*-methoxyphenyl 4-*O*-benzoyl-α-L-rhamnopyranoside (**1**)[11] was treated with benzoyl chloride (or allyl chloroformate) in dichloromethane at –10°C in the



Scheme 1: Synthesis of the target tetrasaccharide **I. Reagents and conditions:** (a) Benzoyl chloride, CH_2Cl_2, pyridine, 92% for **3**; 98% for **5**; (b) AllocCl, Py, CH_2Cl_2, –10°C, 93%; (c) 80% MeCN, CAN, then Cl_3CCN, DBU, CH_2Cl_2, 0°C, 68% for **6** (two steps); 61% for **10** (two steps); (d) TMSOTf, CH_2Cl_2, –10°C to rt, 2 h, 81% for **7**; 88% for **9**; 89% for **11**; 78% for **13**; (e) MeOH-THF = 1:1, $NaBH_4$, $Pd(P(C_6H_5)_3)_4$, 90%; (f) satd NH_3–MeOH, rt, 96 h, 92%.

presence of 4 equiv. of pyridine, and the C-3 hydroxyl group was selectively blocked, giving acceptor **3** or compound **4** in 92% or 93%, respectively, yield.[12,13] Low temperature and slow addition of the chlorides were necessary for ensuring the regioselectivity. The regioselectivity of the process was established by ^{1}H NMR spectroscopy, and the characteristic C-3 proton moved downfield upon acylation ($\delta_{\text{H-3}} = 4.20$ ppm in **1**, $\delta_{\text{H-3}} = 5.80$ ppm in **3,** and $\delta_{\text{H-3}} = 5.50$ ppm in **4**). Benzoylation of **4** in pyridine with benzoyl chloride provided *p*-methoxyphenyl 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**5**) in 98% yield. Cleavage of the *p*-methoxyphenyl group of **5** with ceric ammonium nitrate (CAN), followed by trichloroacetimidation,[14] provided 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate **6**. At the beginning, we tried to synthesize the (1→2)-linked glucose-containing disaccharide by the condensation of the 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate **2**[15] with acceptor **3**. However, instead of getting the desired compound, (1→2)-linked orthoester **7** was obtained as the main product. The formation of the orthoester was confirmed from the ^{1}H NMR spectrum, showing the characteristic signals at δ 1.64 for C$\underline{\text{H}}_3$O$_3$.[16] Later on, benzoylated glucose trichloroacetimidate **8**[17] was used as the glycosyl donor and the (1→2)-linked disaccharide **9** was obtained without detecting the orthoester formation. Cleavage of the *p*-methoxyphenyl group of **9** with CAN followed by trichloroacetimidation with CCl_3CN in the presence of DBU or K_2CO_3 gave the disaccharide donor **10**. At the same time, condensation of the donor **6** with the acceptor **3** in the presence of catalytic TMSOTf furnished the (1→2)-linked disaccharide **11**. The allyloxycarbonyl group of **11** was successfully removed in MeOH-THF[18] in the presence of CH_3COONH_4, $Pd[P(C_6H_5)_3]_4$, and $NaBH_4$ within 5 min without affecting any of the benzoyl groups, giving the desired disaccharide acceptor **12** in 90% yield. Condensation of the disaccharide acceptor **12** and donor **10** proceeded smoothly in dichloromethane in the presence of TMSOTf, giving the tetrasaccharide **13** in 78% yields. Deacylation of **13** in ammonium-saturated methanol afforded the target tetrasaccharide **I**. The structure of **I** was confirmed from its ^{1}H NMR and ^{13}C NMR spectra and HSQC, showing the characteristic signals such as δ 5.45, 5.39, and 4.98 ppm for three H-1 (α) of rhamnose, and δ 4.56 ppm ($J_{1,2} = 7.9$ Hz) for H-1 (β) of glucose, and δ 98.1, 100.8, 101.9, and 104.2 ppm for the anomeric C-1 signals.

Meanwhile, tetrasaccharide **II** was prepared in a similar way (Sch. 2). At the beginning, the allyloxycarbonyl group of **5** was successfully removed in MeOH-THF[18] with $Pd[P(C_6H_5)_3]_4$ to provide the monosaccharide acceptor **14** (95%), then condensation of donor **8** or **6** with C-3-OH acceptor **14** in the presence of TMSOTf gave the (1→3)-linked disaccharide **15** or **17**, respectively. Removal of the *p*-methoxyphenyl group of **15** followed by trichloroacetimidation provided the disaccharide donor **16**, and condensation of the **16** with acceptor **18**, which was prepared from **17** through deallyloxycarbonylation, furnished



Scheme 2: Synthesis of the target tetrasaccharide **II. Reagents and conditions:** (a) MeOH-THF = 1:1, $NaBH_4$, $Pd(P(C_6H_5)_3)_4$, 95% for **14**; 90% for **18**; (b) TMSOTf, CH_2Cl_2, –10°C to rt, 2 h, 83% for **15**; 86% for **17**; 75% for **19**; (c) 80% MeCN, CAN, then Cl_3CCN, DBU, CH_2Cl_2, 0°C, 68% for two steps; (d) satd NH_3–MeOH, rt, 96 h, 89%.

the tetrasaccharide **19** in 75% yield. Finally, deacylation of **19** in ammonium-saturated methanol gave the target tetrasaccharide **II**. The ^1H NMR and ^{13}C NMR spectra of **II** were in accordance with the recently reported data by Prashant et al., and they synthesized this tetrasaccharide in different way.[9]

In summary, an efficient synthesis of *p*-methoxyphenyl β-D-glucopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside **I** and its isomer **II** were achieved through a [2 + 2] strategy. Compared to Prashant's synthesis of **II**, the procedure was more simple owing to the use of only acyl groups in the syntheses. In terms of efficiency, the method can be used for construction of higher oligosaccharides with similar structures. The biological experiments of the synthetic tetrasaccharides are currently under way in our research group and will be reported in due course.

EXPERIMENTAL

General Methods

Solvents were purified in the usual way. All commercially available reagents were used as received. All reactions were monitored by TLC analysis and TLC was performed on silica gel HF with detection by charring with 30% (v/v) H_2SO_4 in CH_3OH or by UV detection. Column chromatography was conducted by elution of a column (8 × 100, 16 × 240, 18 × 300, 35 × 400mm) of silica gel (200–300 mesh) with EtOAc-PE (b.p. 60–90°C) as the eluent. Air- and moisture-sensitive reactions were performed under dry N_2 atmosphere. Optical rotations were recorded using a Perkin-Elmer 241 polarimeter. ^1H and ^{13}C NMR spectra were recorded with Varian XL-300 spectrometers in $CDCl_3$ or

D_2O solutions. Internal references: TMS (δ 0.000 ppm for ^1H), $CDCl_3$ (δ 77.00 ppm for ^{13}C), HOD (δ 4.700 for ^1H). ^1H NMR and ^{13}C NMR signals of some compounds were assigned with the aid of COSY and HSQC. Elemental analysis was performed on a Yanaco CHN Corder MF-3 automatic elemental analyzer. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the electronspray ionization (ESI) mode. Solutions were concentrated at a temperature less than 60°C under diminished pressure.

p-Methoxyphenyl 3,4-di-*O*-benzoyl-6-deoxy-α-L-rhamnopyranoside (3)

Benzoyl chloride (0.55 mL, 4.80 mmol) in dry dichloromethane (1.7 mL) was added dropwise to the solution of compound **1**[11] (1.7 g, 4.5 mmol) and dry pyridine (1.8 mL) in dry dichloromethane (10 mL) over 30 min under nitrogen atmosphere, which was cooled in an ice-salt bath. The reaction mixture was slowly raised to rt and stirred for 12 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with ice water and 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and the residue was subjected to column chromatography (4:1 petroleum ether-EtOAc) to give the desired product **3** (2.0 g, 92%) as a foamy solid. $R_f = 0.23$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ –42.1 (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.99–7.32 (m, 10 H, Bz-H), 7.11–6.85 (m, 4 H, $MeOC_6H_4$), 5.80 (dd, $J = 2.9$, 10.0 Hz, 1 H, H-3), 5.68 (dd, $J = 10.0$, 9.9 Hz, 1 H, H-4), 5.51 (d, $J = 1.8$ Hz, 1 H, H-1), 4.49 (dd, $J = 1.8$, 2.9 Hz, 1 H, H-2), 4.28–4.19 (m, 1 H, H-5), 3.78 (s, 3 H, OCH_3), 2.72 (s, 1 H, OH), 1.29 (d, $J = 6.3$ Hz, 3 H, H-6); Anal. Calcd for $C_{27}H_{26}O_8$: C, 67.77; H, 5.48. Found: C, 67.81; H, 5.50.

p-Methoxyphenyl 3-*O*-allyloxycarbonyl-4-*O*-benzoyl-α-L-rhamnopyranoside (4)

Compound **1**[11] (3.7 g, 10 mmol) was dissolved in dry dichloromethane (40 mL) containing pyridine (8.1 mL, 100 mmol); then under N_2 atmosphere, allyl chloroformate (1.2 mL, 11 mmol) in anhydrous dichloromethane (10 mL) was added dropwise to the solution over 30 min at 0°C. The reaction mixture was slowly raised to rt and stirred for 2 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with dichloromethane (100 mL), washed with water and 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and purification of the residue by column chromatography on silica gel (3:1 petroleum ether-EtOAc) gave compound **4** (4.2 g, 93%) as a syrup. $R_f = 0.4$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ –50.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.05–7.41 (m, 5 H,

Bz-H), 7.07–6.83 (m, 4 H, $MeOC_6H_4$), 5.76–5.67 (m, 1 H, CH_2=CH-CH_2OCO), 5.54–5.47 (m, 3 H, H-1, H-3, H-4), 5.21–5.04 (m, 2 H, CH_2=CH-CH_2OCO), 4.51–4.48 (m, 2 H, CH_2 = CH-CH_2OCO), 4.38 (dd, J = 0.5, 2.7 Hz, 1 H, H-2), 4.16–4.11 (m, 1 H, H-5), 3.77 (s, 3 H, OCH_3), 2.85 (s, 1 H, OH), 1.25 (d, J = 6.3 Hz, 3 H, H-6); Anal. Calcd for $C_{24}H_{26}O_9$: C, 62.88; H, 5.72. Found: C, 62.71; H, 5.89.

p-Methoxyphenyl 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (5)

Compound **4** (4.0 g, 8.7 mmol) was benzoylated under the same conditions as that used for the preparation of **3** from **1**,[11] giving **5** (4.8 g, 98%) as a foamy solid. R_f = 0.7 (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +36.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.14–7.43 (m, 10 H, Bz-H), 7.09–6.84 (m, 4 H, $MeOC_6H_4$), 5.79–5.58 (m, 5 H), 5.18–5.02 (m, 2 H, CH_2=CH-CH_2OCO), 4.51–4.49 (m, 2 H, CH_2=CH-CH_2OCO), 4.26–4.21 (m, 1 H, H-5), 3.77 (s, 3 H, OCH_3), 1.29 (d, J = 6.3 Hz, 3 H, H-6). Anal. Calcd for $C_{31}H_{30}O_{10}$: C, 66.18; H, 5.38. Found: C, 66.03; H, 5.77.

3-*O*-Allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (6)

To a solution of **5** (3.0 g, 5.3 mmol) in 80% MeCN (100 mL) was added ceric ammonium nitrate (11.7 g, 21.3 mmol). The mixture was stirred for 20 min at 35°C, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solvents were evaporated in vacuo at 50°C to give a residue, which was dissolved in CH_2Cl_2, and washed with water. The organic phase was dried (Na_2SO_4) and concentrated. Purification by silica gel chromatography with 3:1 petroleum ether-EtOAc as the eluent afforded a foamy residue. The residue was dried under high vacuum for 2 h, then was dissolved in dry CH_2Cl_2 (50 mL) and trichloroacetonitrile (2 mL, 19.4 mmol) and 1,8-diazabicyclo[5.4.0] undecene (DBU) (0.2 mL, 20 mmol) were added. The mixture was aged under the nitrogen atmosphere until completion (TLC, 3:1 petroleum ether-EtOAc). Concentration of the reaction mixture and purification of the residue by column chromatography (4:1 petroleum ether-EtOAc) gave **6** (2.2 g, 68%) as a white foamy solid. R_f = 0.65 (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +98.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.81 (s, 1 H, C=NH), 8.14–7.44 (m, 10 H, Bz-H), 6.45 (d, J = 1.8 Hz, 1 H, H-1), 5.82 (dd, J = 1.8, 3.2 Hz, 1 H, H-2), 5.72–5.51 (m, 3 H, CH_2=CH-CH_2OCO, H-3, H-4), 5.18–5.03 (m, 2 H, CH_2=CH-CH_2OCO), 4.51–4.49 (m, 2 H, CH_2=CH-CH_2OCO), 4.35–4.26 (m, 1 H, H-5), 1.39 (d, J = 6.3 Hz, 3 H, H-6). Anal. Calcd for $C_{26}H_{24}Cl_3NO_9$: C, 51.97; H, 4.03; N, 2.33. Found: C, 52.30; H, 3.91; N, 2.59.

p-Methoxyphenyl 3′,4′,6′-tri-*O*-acetyl-α-D-glucopyranose-1′,2′-(3,4-di-*O*-benzoyl-α-L- rhamnopyranoside 2-yl) Orthoacetate (7)

Compound **3** (0.56 g, 1.2 mmol) and **2**[15] (0.62 g, 1.3 mmol) and 4 Å molecular sieves (1.0 g) were dried together under high vacuum for 2 h, then dissolved in anhydrous redistilled CH_2Cl_2 (50 mL). TMSOTf (18 uL, 0.10 mmol) was added dropwise at –10°C with nitrogen protection. The reaction mixture was allowed to rise to rt and was stirred for 2 h, and then was quenched with Et_3N (2 drops). Filtration of the reaction mixture and concentration of the filtrate, followed by purification of the residue by column chromatography (5:1 petroleum ether-EtOAc), provided the orthoester **7** (0.87 g, 81%). $R_f = 0.30$ (3:1 petroleum ether-EtOAc). $[\alpha]_D^{25}$ +5.26 (c 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$): δ 7.98–7.34 (m, 10 H, Bz-H), 7.11–6.86 (m, 4 H, $MeOC_6H_4$), 5.71 (d, $J = 4.9$ Hz, 1 H, H-1′), 5.69 (dd, $J = 3.2$, 9.5 Hz, 1 H, H-3), 5.60 (dd, $J = 9.5$, 10.2 Hz, 1 H, H-4), 5.38 (d, $J = 1.8$ Hz, 1 H, H-1), 4.95 (dd, $J = 2.8$, 3.0 Hz, 1 H, H-3′), 4.81 (dd, $J = 2.8$, 9.3 Hz, 1 H, H-4′), 4.51 (dd, $J = 1.8$, 3.2 Hz, 1 H, H-2), 4.39 (dd, $J = 4.9$, 3.0 Hz, 1 H, H-2′), 4.12–4.10 (m, 3 H), 3.83–3.75 (m, 4 H), 2.05–2.04 (m, 9 H, 3 × CH_3CO), 1.64 (s, 3 H, CH_3CO_3), 1.30 (d, $J = 6.2$ Hz, 3 H, H-6). ^{13}C NMR ($CDCl_3$): δ 170.4, 169.3, 168.6, 165.9, 165.5, (5 C=O), 155.1, 150.0, 133.2, 133.1, 129.5, 129.3, 129.2, 129.2, 128.3, 128.3, 121.9, 117.7, 114.6, 98.2 (C-1), 97.0 (C-1), 77.2, 73.3, 71.1, 71.1, 70.3, 69.7, 67.6, 67.3, 67.1, 62.9, 55.5 (OCH_3), 21.5 (CH_3CO_3), 20.6, 20.6, 20.5 (3 CH_3CO), 17.4 (C-6). Anal. Calcd for $C_{41}H_{44}O_{17}$: C, 60.89; H, 5.48. Found: C, 60.95; H, 5.21.

p-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranose-(1→2)-3,4-di-*O*-benzoyl -α-L-rhamnopyranoside (9)

Compound **3** (1.0 g, 2.1 mmol) and **8**[17] (1.8 g, 2.4 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **9** (1.9 g, 88%) as a foamy solid. $R_f = 0.17$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +0.65 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.97–7.08 (m, 30 H, Bz-H), 7.06–7.78 (m, 4 H, $MeOC_6H_4$), 5.86–5.51 (m, 6 H), 5.0 (d, $J = 7.7$ Hz, 1 H, H-1′), 4.61–4.38 (m, 3 H), 4.41 (dd, $J = 5.6$, 12.2 Hz, 1 H, H-3), 4.14–4.01 (m, 2 H, H-5, H-5′), 3.77 (s, 3 H, OCH_3), 1.24 (d, $J = 6.2$ Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 166.0, 165.9, 165.7, 165.1, 165.0, 164.9 (6 C=O), 154.9, 149.9, 133.4, 133.2, 133.0, 132.9, 132.8, 130.0, 129.8, 129.7, 129.6, 129.6, 129.5, 129.4, 129.2, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 117.3, 114.5, 101.9 (C-1), 97.6 (C-1), 76.4, 72.5, 72.3, 72.0, 71.6, 71.3, 69.3, 67.3, 62.6, 55.5 (OCH_3), 17.5 (C-6). Anal. Calcd for $C_{61}H_{52}O_{17}$: C, 69.31; H, 4.96. Found: C, 69.19; H, 4.90.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranose-(1$\rightarrow$2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (10)

Compound **9** (1.7 g, 1.6 mmol) was trichloroacetimidated under the same conditions as that used for the preparation of **6** from **5**, giving **10** (1.1 g, 61%) as a foamy solid. $R_f = 0.20$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +14.7 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.5 (s, 1 H, C=NH), 8.01–7.00 (m, 30 H, Bz-H), 6.59 (d, $J = 1.8$ Hz, 1 H, H-1), 5.86–5.58 (m, 5 H), 5.01 (d, $J = 7.7$ Hz, 1 H, H-1′), 4.62–4.48 (m, 3 H), 4.33–4.07 (m, 2 H), 1.33 (d, $J = 6.2$ Hz, 3 H, H-6). Anal. Calcd for $C_{56}H_{46}Cl_3NO_{16}$: C, 61.41; H, 4.23; N, 1.28. Found: C, 61.53; H, 4.54; N, 1.65.

p-Methoxyphenyl 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1$\rightarrow$2) -3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (11)

Compound **3** (0.47 g, 0.97 mmol) and **6** (0.64 g, 1.1 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **11** (0.79 g, 89%) as a foamy solid. $R_f = 0.31$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +57.5 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10–7.34 (m, 20 H, Bz-H), 7.13–6.87 (m, 4 H, $MeOC_6H_4$), 5.98 (dd, $J = 3.3$, 10.0 Hz, 1 H, H-3), 5.82–5.50 (m, 6 H), 5.20–5.02 (m, 3 H), 4.54–4.51 (m, 2 H, CH_2=CH-CH_2), 4.48 (dd, $J = 2.0$, 3.3 Hz, 1 H, H-2), 4.28–4.23 (m, 2 H), 3.79 (s, 3 H, OCH_3), 1.37 (d, $J = 6.3$ Hz, 3 H, H-6), 1.31 (d, $J = 6.3$ Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 165.7, 165.6, 165.1, 163.6, 155.2, 153.9, 150.1, 133.4, 133.4, 133.2, 133.2, 131.1, 130.0, 129.9, 129.7, 129.3, 129.1, 129.0, 128.9, 128.4, 128.3, 118.8, 117.6, 114.7, 99.2 (C-1), 97.7 (C-1), 72.8, 71.8, 71.5, 70.9, 70.1, 68.8, 67.7, 67.5, 55.6 (OCH_3), 17.6 (C-6), 17.5 (C-6). Anal. Calcd for $C_{51}H_{48}O_{16}$: C, 66.80; H, 5.28. Found: C, 66.86; H, 5.13.

p-Methoxyphenyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1$\rightarrow$2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (12)

To a cooled (–5°C) solution of **11** (0.60 g, 0.69 mmol) and CH_3COONH_4 (0.50 g, 6.9 mmol) in 1:1 MeOH-THF (50 mL) in a 150-mL flask were added $NaBH_4$ (0.02 g, 0.46 mmol), $Pd[P(C_6H_5)_3]_4$ (0.03 g, 0.02 mmol), and $NaBH_4$ (0.06 mg, 1.5 mmol) in three portions immediately one after another. The mixture was vigorously stirred until TLC (3:1 petroleum ether-EtOAc) indicated completion of the reaction. The reaction mixture was concentrated under vacuum, the residue was dissolved in CH_2Cl_2 (100 mL) and washed with water (20 mL), and then the organic phase was dried over Na_2SO_4. Evaporation and purification by flash column chromatography (4:1 petroleum ether-EtOAc) afforded compound **12** as a foamy solid (0.52 g, 90%). $R_f = 0.24$ (3:1 petroleum

ether-EtOAc); $[\alpha]_D^{25}$ +14.7 (c 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.13–7.36 (m, 20 H, Bz-H), 7.13–6.87 (m, 4 H, $MeOC_6H_4$), 5.97 (dd, J = 3.2, 10.0 Hz, 1 H, H-3), 5.69–5.57 (m, 3 H), 5.31 (dd, J = 9.8, 9.4 Hz, 1 H, H-4), 5.18 (d, J = 1.5 Hz, 1 H, H-1), 4.47–4.45 (m, 2 H), 4.30–4.21 (m, 2 H), 3.79 (s, 3 H, OCH_3), 2.47 (d, J = 7.1 Hz, 1 H, OH), 1.35 (d, J = 6.3 Hz, 3 H, H-6), 1.31 (d, J = 6.3 Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 166.8, 165.7, 165.5, 165.4 (4 C=O), 155.2, 150.1, 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.3, 129.2, 128.9, 128.4, 128.2, 117.6, 114.7, 99.5 (C-1), 97.8 (C-1), 76.7, 75.0, 72.8, 71.8, 70.7, 68.7, 67.5, 67.2, 55.5 (OCH_3), 17.7 (C-6), 17.5 (C-6). Anal. Calcd for $C_{47}H_{44}O_{14}$: C, 67.78; H, 5.33. Found: C, 67.91; H, 5.38.

p-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranose-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (13)

Compound **12** (0.50 g, 0.60 mmol) and **10** (0.90 g, 0.80 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **13** (0.83 g, 78%) as a foamy solid. R_f = 0.31 (2:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +73.7 (c 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$): δ 8.12–7.26 (m, 50 H, Bz-H), 7.12–6.85 (m, 4 H, $MeOC_6H_4$), 5.97 (dd, J = 3.2, 10.1 Hz, 1 H, H-3), 5.74 (dd, J = 1.8, 3.2 Hz, 1 H, H-2′), 5.70 (dd, J = 9.8, 10.1 Hz, 1 H, H-4), 5.63 (dd, J = 9.7, 9.9 Hz, 1 H), 5.61 (d, J = 1.8 Hz, 1 H, H-1), 5.56 (dd, J = 9.5, 9.7 Hz, 1 H), 5.48–5.40 (m, 3 H), 5.33 (d, J = 1.8 Hz, 1 H, H-1′), 5.30 (dd, J = 9.6, 9.9 Hz, 1 H, H-4″), 5.26 (d, J = 1.7 Hz, 1 H, H-1″), 4.77 (d, J = 7.6 Hz, 1 H, H-1‴), 4.67 (dd, J = 3.2, 9.4 Hz, 1 H, H-3′), 4.50 (dd, J = 1.8, 3.2 Hz, 1 H, H-2), 4.33–3.97 (m, 6 H), 3.79 (s, 3 H, OCH_3), 3.51–3.45 (m, 1 H), 1.32 (d, J = 6.2 Hz, 3 H, H-6), 1.30 (d, J = 6.2 Hz, 3 H, H-6), 1.04 (d, J = 6.2 Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 165.8, 165.7, 165.5, 165.5, 165.3, 165.0, 165.0, 165.0, 164.8, 164.9 (10 C=O), 155.2, 150.3, 133.2, 133.2, 133.1, 133.0, 132.9, 132.7, 132.7, 130.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 129.1, 129.1, 128.9, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.1, 117.7, 114.8, 100.9 (C-1), 100.4 (C-1), 99.5 (C-1), 97.9 (C-1), 76.7, 75.5, 74.6, 73.3, 72.7, 72.1, 72.0, 72.0, 71.8, 71.6, 71.4, 71.0, 69.7, 67.8, 67.7, 67.6, 62.8, 55.7 (OCH_3), 17.7 (C-6), 17.3 (C-6). Anal. Calcd for $C_{101}H_{88}O_{29}$: C, 68.70; H, 5.02. Found: C, 68.88; H, 5.10.

p-Methoxyphenyl β-D-glucopyranose-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (I)

Tetrasaccharide **13** (400 mg, 0.23 mmol) was dissolved in satd NH_3-MeOH (30 mL). After 96 h at rt, the reaction mixture was concentrated, and the

residue was puried by chromatography on Sephadex LH-20 (MeOH) to afford **I** (153 mg, 92%) as a foamy solid. $[\alpha]_D^{25}$ +23.0 (c 0.5, water); ^{1}H NMR (D_2O): δ 7.07–6.93 (m, 4 H, $MeOC_6\underline{H}_4$), 5.45 (s, 1 H, H-1), 5.39 (s, 1 H, H-1), 4.98 (s, 1 H, H-1), 4.56 (d, J = 7.9 Hz, 1 H, H-1‴), 4.15–4.03 (m, 3 H), 3.93–3.66 (m, 11 H), 3.55–3.29 (m, 7 H), 1.28 (d, J = 6.2 Hz, H-6), 1.22 (d, J = 6.1 Hz, H-6), 1.22 (d, J = 6.1 Hz, H-6); ^{13}C NMR (D_2O): δ 154.6, 149.3, 118.9, 118.9, 115.0, 115.0 ($\underline{C}_6H_4$), 104.2 (C-1), 101.9 (C-1), 100.8 (C-1), 98.1 (C-1), 80.1, 78.3, 77.8, 75.6, 75.3, 73.1, 72.0, 72.0, 71.2, 69.7, 69.7, 69.6, 69.4, 69.1, 69.1, 68.8, 60.3, 55.7 ($O\underline{C}H_3$), 16.5 (C-6), 16.5 (C-6). ESIHRMS: m/z calcd for $C_{31}H_{48}O_{19}Na[M+Na^+]$: 747.2687; $C_{31}H_{48}O_{19}K[M+K^+]$: 763.2427. Found: m/z 747.2673; 763.2413.

p-Methoxyphenyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (14)

Compound **5** (2.8 g, 4.9 mmol) was deallyloxycarbonylated under the same conditions as that used for the preparation of **12** from **11**, giving **14** (2.2 g, 95%) as a foamy solid. R_f = 0.23 (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ –17.5 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.15–7.44 (m, 10 H, Bz-$\underline{H}$), 7.07–6.83 (m, 4 H, $MeOC_6\underline{H}_4$), 5.59–5.56 (m, 2 H, H-1, H-2), 5.35 (dd, J = 9.8, 9.9 Hz, 1 H, H-4), 4.52 (dd, J = 3.3, 9.9 Hz, 1 H, H-3), 4.27–4.20 (m, 1 H, H-5), 3.78 (s, 3 H, $OC\underline{H}_3$), 2.57 (s, 1 H, O$\underline{H}$), 1.31 (d, J = 6.3 Hz, 3 H, H-6). Anal. Calcd for $C_{27}H_{26}O_8$: C, 67.77; H, 5.48. Found: C, 67.67; H, 5.30.

p-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranose-(1→3)-2,4-di-*O*-benzoyl -α-L-rhamnopyranoside (15)

Compound **14** (0.60 g, 1.3 mmol) and **8**[17] (1.1 g, 1.4 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **15** (1.1 g, 83%) as a foamy solid. R_f = 0.15 (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +12.9 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.17 (m, 30 H, Bz-H), 7.00–6.80 (m, 4 H, $MeOC_6\underline{H}_4$), 5.78–5.46 (m, 6 H), 5.1 (d, J = 7.8 Hz, 1 H, H-1′), 4.63–4.39 (m, 3 H), 4.42–4.10 (m, 2 H), 3.78 (s, 3 H, $OC\underline{H}_3$), 1.16 (d, J = 6.2 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$): δ 166.0, 165.9, 165.6, 165.0, 164.9, 164.4 (6 $\underline{C}$=O), 155.2, 150.0, 133.2, 133.0, 133.0, 132.9, 132.7, 132.5, 129.9, 129.8, 129.6, 129.6, 129.5, 129.4, 129.3, 129.1, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 117.9, 114.5, 101.5, (C-1), 96.4 (C-1), 75.9, 72.8, 72.5, 72.1, 72.0, 71.8, 69.1, 67.0, 62.7, 55.5 ($O\underline{C}H_3$), 17.5 (C-6). Anal. Calcd for $C_{61}H_{52}O_{17}$: C, 69.31; H, 4.96. Found: C, 69.52; H, 4.81.

2,3,4,6-Tetra–*O*-benzoyl-β-D-glucopyranose-(1→3)-2, 4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (16)

Compound **15** (1.0 g, 1.0 mmol) was trichloroacetimidated under the same conditions as that used for the preparation of **6** from **5**, giving **16** (0.7 g, 68%) as a foamy solid. $R_f = 0.17$ (3:1 petroleum ether-EtOAc). $[\alpha]_D^{25}$ +20.0 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.8 (s, 1 H, C=NH), 8.09–7.10 (m, 30 H, Bz-H), 6.45 (d, $J = 2.0$ Hz, 1 H, H-1), 5.80–5.41 (m, 5 H), 5.1 (d, $J = 7.8$ Hz, 1 H, H-1′), 4.53–4.37 (m, 3 H), 4.20–4.10 (m, 2 H), 1.22 (d, $J = 6.2$ Hz, 3 H, H-6). Anal. Calcd for $C_{56}H_{46}Cl_3NO_{16}$: C, 61.41; H, 4.23; N, 1.28. Found: C, 61.27; H, 4.22; N, 1.54.

p-Methoxyphenyl 3-*O*-allyloxycarbonyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3) -2,4-di-*O*-benzoyl-α -L-rhamnopyranoside (17)

Compound **14** (0.40 g, 0.80 mmol) and **6** (0.60 g, 0.90 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **17** (0.7 g, 86%) as a foamy solid. $R_f = 0.31$ (3:1 petroleum ether-EtOAc). $[\alpha]_D^{25}$ +28.3 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.10–7.38 (m, 20 H, Bz-H), 7.07–6.84 (m, 4 H, $MeOC_6H_4$), 5.68–5.54 (m, 4 H), 5.37–5.22 (m, 4 H), 5.08–4.95 (m, 2 H), 4.66 (dd, $J = 3.5$, 9.8 Hz, 1 H, H-3), 4.35–4.33 (m, 2 H), 4.23–4.05 (m, 2 H), 3.78 (s, 3 H, OCH_3), 1.33 (d, $J = 6.2$ Hz, 3 H, H-6), 1.14 (d, $J = 6.3$ Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 166.0, 165.8, 165.3, 165.1, 155.3, 153.5, 150.0, 133.6, 133.5, 133.3, 133.2, 133.2, 131.1, 130.0, 130.0, 129.9, 129.9, 129.8, 129.7, 129.6, 129.4, 129.4, 129.3, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 118.6, 117.7, 117.7, 114.7, 99.2 (C-1), 96.4 (C-1), 72.9, 72.5, 72.1, 71.4, 70.4, 68.5, 67.6, 67.4, 55.6 (OCH_3), 17.7 (C-6), 17.3 (C-6). Anal. Calcd for $C_{51}H_{48}O_{16}$: C, 66.80; H, 5.28. Found: C, 66.63; H, 5.49.

p-Methoxyphenyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl -α-L-rhamnopyranoside (18)

Compound **17** (0.60 g, 0.70 mmol) was deallyloxycarbonylated under the same conditions as that used for the preparation of **12** from **11**, giving **18** (0.50 g, 90%) as a foamy solid. $R_f = 0.24$ (3:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +28.9 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.24–7.38 (m, 20 H, Bz-H), 7.08–6.84 (m, 4 H, $MeOC_6H_4$), 5.70–5.58 (m, 3 H), 5.27 (d, $J = 1.5$ Hz, 1 H, H-1), 5.1 (dd, $J = 9.7$, 9.7 Hz, 1 H, H-4), 5.0 (dd, $J = 1.5$, 3.3 Hz, 1 H, H-2), 4.6 (dd, $J = 3.4$, 9.8 Hz, 1 H, H-3), 4.25–3.98 (m, 3 H), 3.78 (s, 3 H, OCH_3), 2.27 (d, $J = 5.6$ Hz, 1 H, OH), 1.33 (d, $J = 6.2$ Hz, 3 H, H-6), 1.15 (d, $J = 6.2$ Hz, 3 H, H-6); ^{13}C

NMR ($CDCl_3$): δ 166.6, 165.9, 165.8, 165.4 (4 C=O), 155.2, 149.9, 133.5, 133.3, 133.2, 129.9, 129.8, 129.6, 129.3, 129.2, 129.1, 128.7, 128.5, 128.3, 128.2, 117.6, 114.6, 99.3 (C-1), 96.3 (C-1), 76.3, 75.0, 72.9, 72.9, 72.2, 68.4, 67.3, 67.0, 55.5 (OCH_3), 17.7 (C-6), 17.3 (C-6). Anal. Calcd for $C_{47}H_{44}O_{14}$: C, 67.78; H, 5.33. Found: C, 67.72; H, 5.14.

2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranose-(1→3)-2,4-di-O-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-O-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-O-benzoyl-α-L-rhamnopyranoside (19)

Compound **18** (0.37 g, 0.44 mmol) and **16** (0.53 g, 0.48 mmol) were coupled under the same conditions as that used for the preparation of **7** from **3** and **2**, giving **19** (0.58 mg, 75%) as a foamy solid. $R_f = 0.29$ (2:1 petroleum ether-EtOAc); $[\alpha]_D^{25}$ +208.8 (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.04–7.08 (m, 50 H, Bz-H), 7.07–6.83 (m, 4 H, $MeOC_6H_4$), 5.71 (dd, $J = 1.8$, 3.4 Hz, 1 H, H-2), 5.61 (dd, $J = 9.8$, 9.8 Hz, 1 H, H-4), 5.60 (dd, $J = 1.8$ Hz, 1 H, H-1), 5.51 (dd, $J = 9.7$, 9.7 Hz, 1 H), 5.44 (dd, $J = 7.8$, 9.7 Hz, 1 H), 5.34 (dd, $J = 9.7$, 9.7 Hz, 1 H), 5.28–5.22 (m, 2 H, H-1′, H-4′), 5.19 (dd, $J = 9.8$, 9.9 Hz, 1 H, H-4″), 5.13 (dd, $J = 1.8$, 3.2 Hz, 1 H, H-2′), 5.02 (dd, $J = 1.9$, 3.2 Hz, 1 H, H-2″), 4.68 (d, $J = 1.9$ Hz, 1 H, H-1″), 4.63 (dd, $J = 3.4$, 9.7 Hz, 1 H, H-3), 4.36 (d, $J = 7.8$ Hz, 1 H, H-1‴), 4.23–4.00 (m, 6 H), 3.81–3.76 (m, 4 H), 3.61–3.56 (m, 1 H), 1.32 (d, $J = 6.2$ Hz, 3 H, H-6), 1.11 (d, $J = 6.2$ Hz, 3 H, H-6), 0.52 (d, $J = 6.2$ Hz, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 166.0, 165.9, 165.9, 165.8, 165.7, 165.3, 165.2, 164.8, 164.5, 164.3 (10 C=O), 155.3, 150.1, 133.7, 133.3, 133.2, 133.0, 132.5, 130.0, 129.7, 129.7, 129.6, 129.6, 129.5, 129.5, 129.4, 129.3, 129.4, 129.2, 129.0, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 117.7, 114.7, 101.1 (C-1), 98.9 (C-1), 98.6 (C-1), 96.4 (C-1), 77.2, 77.2, 76.8, 76.8, 72.9, 72.8, 72.4, 72.2, 71.9, 71.7, 71.3, 70.8, 68.3, 67.6, 67.4, 67.1, 61.3, 55.6 (OCH_3), 17.7 (C-6), 17.3 (C-6), 16.7 (C-6). Anal. Calcd for $C_{101}H_{88}O_{29}$: C, 68.70; H, 5.02. Found: C, 68.90; H, 4.81.

p-Methoxyphenyl β-D-glucopyranose-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L- rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (II)

Compound **19** (400 mg, 0.23 mmol) was deblocked under the same conditions as that used for the preparation of **I** from **13**, giving **II** (146 mg, 89%) as a foamy solid. $[\alpha]_D^{25}$ +64.3 (c 0.5, water), ^{1}H NMR (D_2O): δ 7.06–6.90 (m, 4 H, $MeOC_6H_4$), 5.35 (s, 1 H, H-1), 5.01 (s, 2 H, H-1′, H-1″), 4.65 (d, $J = 7.8$ Hz, 1 H, H-1‴), 4.27 (bs, 1 H, H-2), 4.18 (bs, 1 H, H-2′), 4.13 (bs, 1 H, H-2″), 3.98–3.95 (m, 2 H), 3.90–3.78 (m, 5 H), 3.74 (s, 3 H, OCH_3), 3.67–3.51 (m, 4 H), 3.48–3.28

(m, 4 H); ^{13}C NMR (D_2O): δ 154.5, 149.2, 118.6, 118.6, 114.9, 114.9 ($\underline{C}_6H_4$), 103.4 (C-1), 102.0 (C-1), 101.8 (C-1), 98.8 (C-1), 79.7, 78.1, 77.6, 75.5, 75.3, 73.1, 71.1, 71.1, 70.8, 69.7, 69.6, 69.5, 69.3, 69.3, 69.0, 68.8, 60.4, 55.6 ($O\underline{C}H_3$), 16.4 (C-6), 16.4 (C-6), 16.4 (C-6). ESIHRMS: m/z calcd for $C_{31}H_{48}O_{19}Na[M+Na^+]$: 747.2687. Found: m/z 747.2674.

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