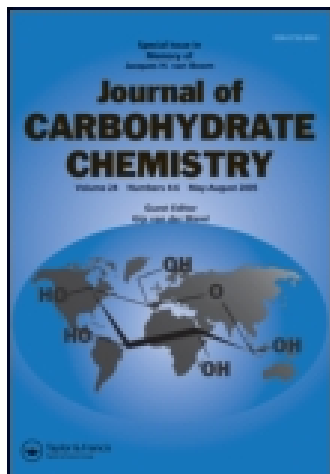




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SYNTHESIS OF A XYLOSYLATED RHAMNOSE PENTASACCHARIDE—THE REPEATING UNIT OF THE O-SPECIFIC SIDE CHAIN OF LIPOPOLYSACCHARIDES FROM THE REFERENCE STRAINS FOR *Stenotrophomonas maltophilia* SEROGROUP O18

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REFERENCE STRAINS FOR
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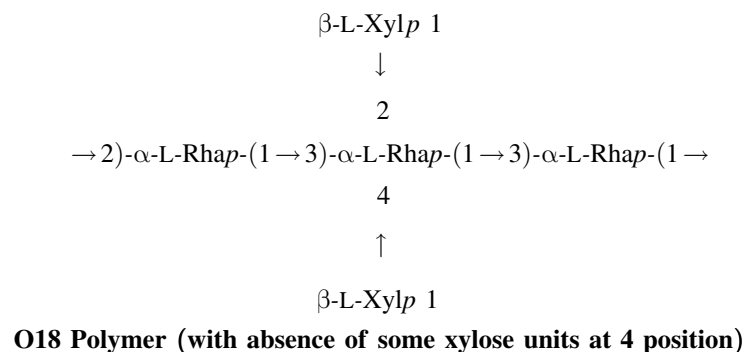
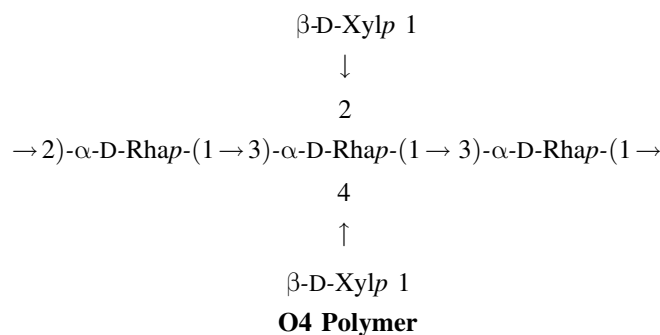
ABSTRACT

A xylosylated rhamnose pentasaccharide, α -L-Rhap-(1 $\rightarrow$ 3)-[β -L-Xylp-(1 $\rightarrow$ 2)-] [β -L-Xylp-(1 $\rightarrow$ 4)-] α -L-Rhap-(1 $\rightarrow$ 3)-L-Rhap, the repeating unit of the O-specific side chain of the lipopolysaccharides from the reference strains for *Stenotrophomonas maltophilia* serogroup O18, was synthesized by a highly regio- and stereoselective procedure. Thus coupling of methyl rhamnopyranoside (**9**) with 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl trichloroacetimidate (**8**) gave the (1 $\rightarrow$ 3)-linked disaccharide (**10**), and subsequent benzylation and deacetylation afforded the disaccharide acceptor **12**. Condensation of **12** with **8** yielded methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (**13**). Coupling of **13** with 2,3,4-tri-*O*-benzoyl- α -L-xylopyranosyl trichloroacetimidate (**4**) followed by deprotection gave the target pentasaccharide (**15**).

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INTRODUCTION

It was reported^[1] very recently that the O-specific side chains of lipopolysaccharides from the reference strains for *Stenotrophomonas maltophilia* serogroups O4 and O18 are both xylosylated rhamnans consisting of D- and L-form doubly branched pentasaccharide repeating units, respectively. The O4 polymer has a D-form, and the O18 polymer has an L-form as shown below.



It is known that *S. maltophilia* species has potential for bioremediation and the biological control of plant pathogens,^[2,3] and has emerged as a multi-drug-resistant opportunistic pathogen responsible for nosocomial infections.^[4] For investigation of the structure–bioactivity relationship of the oligosaccharide of O18 polymer, we report herewith a concise and efficient synthesis of the O18 pentasaccharide repeating unit.

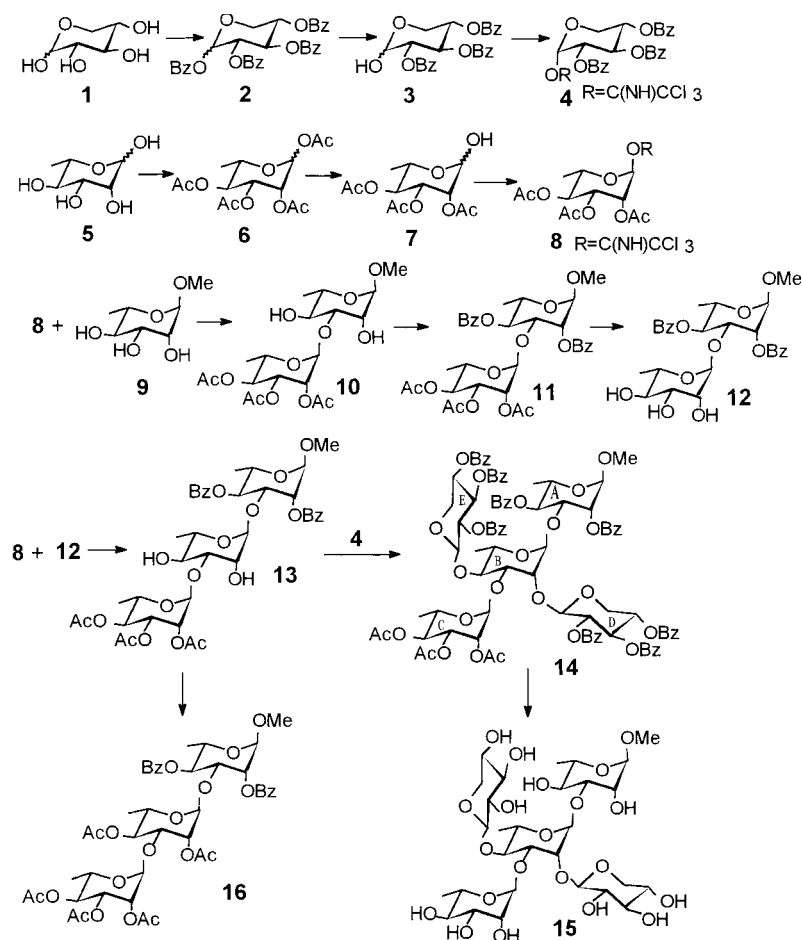
Although the pentasaccharide repeating unit is not very complex, its synthesis will need orthogonal masking groups and multi-protection–deprotection steps if a traditional stepwise method is used. Our previous work described highly regio- and stereoselective syntheses of oligosaccharides using unprotected sugars via an orthoester formation–rearrangement strategy.^[5–7] Later on we found that high regio- and stereoselectivity were achieved in a one-pot manner using glycosyl trichloroimidates as the donors and unprotected sugars as the acceptors.^[8,9] Based on these new findings we readily accomplished the synthesis of the title pentasaccharide.

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RESULTS AND DISCUSSION

As outlined in the Scheme 1, L-xylose (**1**) was converted to perbenzoylated xylopyranosyl trichloroacetimidate (**4**) through benzoylation with benzoyl chloride in pyridine, selective 1-*O*-debenzoylation in ammonia-methanol, and subsequent trichloroacetimidation with trichloroacetonitrile in the presence of DBU or potassium carbonate. 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl trichloroacetimidate (**8**) was obtained by acetylation of L-rhamnose (**5**), selective 1-*O*-deacetylation and trichloroacetimidation. Coupling of the rhamnose donor **8** with the acceptor methyl α -L-rhamnopyranoside (**9**) in the presence of catalytic TMSOTf selectively gave the (1 $\rightarrow$ 3)-linked disaccharide **10**. Its structure was confirmed by benzoylation to give methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (**11**, 66.2% for 2 steps) showing characteristic signals at δ 5.49 ppm (dd, $J_{3,4}=J_{4,5}=9.6$ Hz) and δ 5.42 ppm (dd, $J_{1,2}=1.8$ Hz, $J_{2,3}=3.4$ Hz) in its ^1H NMR spectrum for H-4 and H-2, respectively. It was



Scheme 1. Synthesis of xylosylated rhamnose pentasaccharide.

noted that the temperature during addition of TMSOTf had to be maintained below -20°C to ensure formation of the orthoester intermediate, otherwise, for example at room temperature, the regioselectivity was poor. Benzoylation with benzoyl chloride in pyridine followed by deacetylation^[10] furnished the disaccharide acceptor **12**. Condensation of the rhamnose donor **8** with the acceptor **12** promoted by catalytic TMSOTf selectively gave the 3-linked trisaccharide **13**. Acetylation of **13** gave **16**, as confirmed from the ^1H NMR spectrum of **16**. Coupling of the trisaccharide acceptor **13** with the xylose donor **4** gave the pentasaccharide **14** and subsequent deacylation in ammonia–methanol gave the target pentasaccharide **15**. The bioassay of the resultant pentasaccharide is in progress.

In summary, a branched xylosylated rhamnan pentasaccharide was synthesized in a highly regioselective way with a straightforward procedure. It should be possible to carry out large scale preparations of **15** employing this method.

EXPERIMENTAL

General Methods. Optical rotations were determined at 25°C with a Perkin–Elmer Model 241-Mc automatic polarimeter. Melting points were determined with a “Mel-Temp” apparatus. ^1H NMR, ^{13}C NMR, and ^1H NMR HOMO COSY spectra were recorded with Bruker ARX 400 spectrometers for solutions in CDCl_3 . Chemical shifts are given in parts per million (ppm) downfield from internal Me_4Si . Mass spectra were recorded with a JMS-D300S mass spectrometer using a direct sample introduction technique. 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 UV detection. Column chromatography was conducted by elution of a column (16×240 , 18×300 , 35×400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether ($60\text{--}90^{\circ}\text{C}$) as the eluent. Solutions were concentrated at $<60^{\circ}\text{C}$ under diminished pressure. L-Xylose and L-rhamnose were commercial products from Acros Organics.

2,3,4-Tri-*O*-benzoyl- α -L-xylopyranosyl trichloroacetimidate (4). To a solution of L-xylose **1** (7.50 g, 50 mmol) in pyridine (100 mL) was added benzoyl chloride (35 mL, 300 mmol) at 0°C . The reaction mixture was slowly warmed to room temperature and stirred for 12 h, at the end of which time TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (300 mL) was added to the reaction mixture, and stirring was continued for 30 min. The aq solution was extracted with CH_2Cl_2 (3×100 mL), the extract was washed with M HCl and saturated aq sodium bicarbonate, dried (Na_2SO_4) and concentrated to give **2** (27.5 g, 97.2%) as a white solid. Compound **2** (17.0 g, 30.0 mmol) was dissolved in a 2 M solution of ammonia–methanol (200 mL) and stirred for 14 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated, and purification of the residue by flash column chromatography on a silica gel column (3:1 petroleum ether–EtOAc) gave compound **3** (12.1 g, 87.3%) as a syrup. A mixture of **3** (9.2 g, 20 mmol), trichloroacetonitrile (6.3 mL, 30 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.50 mL, 4.04 mmol) in dry dichloromethane (50 mL) was stirred under nitrogen for 5 h and then concentrated in vacuo. The residue was purified by flash chromatography (4:1

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petroleum ether-EtOAc) to give **4** (10.8 g, 89.1%); $[\alpha]_D + 31.3^\circ$ (c 1.5, CHCl_3); lit.^[11] $[\alpha]_D + 33.1^\circ$ (c 1.3, CHCl_3).

2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl trichloroacetimidate (8**).** To a solution of rhamnose **5** (8.2 g, 50 mmol) in pyridine (100 mL) was added Ac_2O (28.3 mL, 300 mmol) at 0°C . The reaction mixture was slowly warmed to room temperature and stirred for 12 h. TLC (4:1 petroleum ether-EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated to dryness, and the residue was dissolved in CH_2Cl_2 (300 mL), washed with water and saturated aq sodium bicarbonate, dried (Na_2SO_4) and concentrated to give **6** (16.1 g, 97.0%). Compound **6** (10.0 g, 30.0 mmol) was dissolved in 1 M solution of ammonia-methanol (200 mL) and stirred for 6 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated, and purification of the residue by flash column chromatography on a silica gel column (3:1 petroleum ether-EtOAc) gave compound **7** (8.10 g, 93.1%) as a syrup. A mixture of **7** (5.80 g, 20.0 mmol), trichloroacetonitrile (6.3 mL, 30 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.50 mL, 4.04 mmol) in dry dichloromethane (50 mL) was stirred under nitrogen for 5 h and then concentrated in vacuo. The residue was purified by flash chromatography (4:1 petroleum ether-EtOAc) to give **8** (7.60 g, 87.5%) as a yellow syrup; $[\alpha]_D - 54.5^\circ$ (c 1.1, CHCl_3); lit.^[12] $[\alpha]_D - 52^\circ$ (c 1.0, CHCl_3).

Methyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (11**).** 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl trichloroacetimidate^[8] (4.35 g, 10.0 mmol) and methyl α -L-rhamnopyranoside (**9**) (1.78 g, 10.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhydrous CH_2Cl_2 (40 mL). TMSOTf (30 μL , 0.1 equiv) was added dropwise at -25°C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness to afford the crude methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranoside (**10**). To the solution of crude **10** in pyridine (20 mL), benzoyl chloride (3.5 mL, 30 mmol) was added dropwise, and the mixture was stirred overnight at room temperature. TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. Ice water was added, and the mixture was diluted with dichloromethane, washed with M HCl, water, and saturated aq sodium bicarbonate subsequently. The organic layer was combined, dried, and concentrated. Purification by column chromatography (3:1 petroleum ether-EtOAc) gave **11** (4.29 g, 66.2% for 2 steps) as a syrup. $[\alpha]_D + 37.1^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.15–7.43 (m, 10 H, 2 PhH), 5.49 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4_A), 5.42 (dd, 1 H, $J_{1,2}=1.8$ Hz, $J_{2,3}=3.4$ Hz, H-2_A), 5.05 (dd, 1 H, $J_{2,3}=3.2$ Hz, $J_{3,4}=9.8$ Hz, H-3_B), 4.89–4.81 (m, 4 H, H-1_A, H-1_B, H-2_B, H-4_B), 4.37 (dd, 1 H, $J_{2,3}=3.4$ Hz, $J_{3,4}=9.6$ Hz, H-3_A), 4.03–3.82 (m, 2 H, H-5_A, 5_B), 3.45 (s, 3 H, OCH_3), 1.89 (s, 3 H, COCH_3), 1.88 (s, 3 H, COCH_3), 1.82 (s, 3 H, COCH_3), 1.32 (d, 3 H, $J_{5,6}=6.3$ Hz, H-6_A/H-6_B), 1.05 (d, 3 H, $J_{5,6}=6.3$ Hz, H-6_A/H-6_B); ^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 168.9, 168.7 (3 C, 3 COCH_3), 165.7, 165.0 (2 C, 2 COPh), 98.7, 97.8 (2 C, C-1_A, 1_B), 72.9, 71.7, 70.5, 69.3, 68.0, 66.7, 66.1 54.8 (9 C, C-2_A, 2_B, 3_A, 3_B, 4_A, 4_B, 5_A, 5_B, OCH_3), 20.2, 20.1, 20.0, 17.2, 16.7 (5 C, C-6_A, 6_B, 3 COCH_3).

Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{O}_{14}$: C, 60.17; H, 5.82. Found: C, 60.24; H, 6.01.

Methyl α -L-Rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (12). To a solution of **11** (658 mg, 1.00 mmol) in anhydrous MeOH (50 mL) was added acetyl chloride (1.5 mL) at 0 °C. The solution was sealed in a flask and stirred at room temperature until TLC (3:1 petroleum ether-EtOAc) showed that the starting material disappeared. The solution was neutralized with Et₃N, then concentrated to dryness. The residue was passed through a short silica gel column to give **12** (510 mg, 95.9%) as a white solid; $[\alpha]_D + 42.1^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.11–7.44 (m, 10 H, 2 PhH), 5.47–5.42 (m, 2 H, H-4_A, H-2_A), 4.89 (d, 1 H, *J*_{1,2} = 1.6 Hz, H-1_B), 4.81 (d, 1 H, *J*_{1,2} = 1.5 Hz, H-1_A), 4.36 (dd, 1 H, *J*_{2,3} = 3.3 Hz, *J*_{3,4} = 9.7 Hz, H-3_A), 4.14–3.65 (m, 2 H, H-5_A, 5_B), 3.57 (dd, *J*_{1,2} = 1.6 Hz, *J*_{2,3} = 3.2 Hz, H-2_B), 3.48 (dd, 1 H, *J*_{2,3} = 3.2 Hz, *J*_{3,4} = 9.8 Hz, H-3_B), 3.45 (s, 3 H, OCH₃), 3.28 (dd, *J*_{3,4} = *J*_{4,5} = 9.8 Hz, H-4_B), 2.00–1.90 (br, 3 H, 3OH), 1.29 (d, 3 H, *J*_{5,6} = 6.3 Hz, H-6_A/H-6_B), 1.21 (d, 3 H, *J*_{5,6} = 6.3 Hz, H-6_A/H-6_B); ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 165.4 (2 C, 2 CPh), 101.2, 98.0 (2 C, C-1_A, 1_B), 74.3, 73.3, 72.3, 71.8, 70.7, 70.2, 68.5, 66.1, 54.8 (9 C, C-2_A, 2_B, 3_A, 3_B, 4_A, 4_B, 5_A, 5_B, OCH₃), 17.1, 16.7 (2 C, C-6_A, 6_B).

Anal. Calcd for C₂₇H₃₂O₁₁: C, 60.89; H, 6.06. Found: C, 60.77; H, 6.12.

Methyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (13). 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl trichloroacetimidate (**8**) (435 mg, 1.00 mmol) and methyl α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (**12**) (532 mg, 1.00 mmol) were dried together under high vacuum for 2 h, then dissolved in anhydrous CH₂Cl₂ (40 mL). TMSOTf (18 μ L, 0.10 mmol) was added dropwise at –25 °C with N₂ protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness. Purification of the residue by column chromatography (1:1 petroleum ether-EtOAc) gave **13** (547 mg, 68.0%) as a foamy solid. $[\alpha]_D + 11.5^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.12–7.44 (m, 10 H, 2 PhH), 5.48–5.43 (m, 2 H, H-4_A, H-2_A), 5.20 (dd, 1 H, *J*_{1,2} = 1.5 Hz, *J*_{2,3} = 3.4 Hz, H-2_C), 5.11 (dd, 1 H, *J*_{2,3} = 3.4 Hz, *J*_{3,4} = 9.7 Hz, H-3_C), 4.93 (dd, 1 H, *J*_{3,4} = *J*_{4,5} = 9.7 Hz, H-4_C), 4.91–4.83 (m, 3 H, H-1_A, 1_B, 1_C), 5.37 (dd, 1 H, *J*_{2,3} = 3.2 Hz, *J*_{3,4} = 9.8 Hz, H-3_A), 4.02–3.67 (m, 3 H, H-5_A, 5_B, 5_C), 3.60–3.55 (m, 2 H, H-2_B, 3_B), 3.48 (dd, 1 H, *J*_{3,4} = *J*_{4,5} = 9.7 Hz, H-4_B), 3.45 (s, 3 H, OCH₃), 2.10 (s, 3 H, COCH₃), 2.00 (s, 3 H, COCH₃), 1.94 (s, 3 H, COCH₃), 1.30 (d, 3 H, *J*_{5,6} = 6.3 Hz, H-6_A/H-6_B/6_C), 1.22 (d, 3 H, *J*_{5,6} = 6.1 Hz, H-6_A/H-6_B/6_C), 0.85 (d, 3 H, *J*_{5,6} = 6.2 Hz, H-6_A/H-6_B/6_C); ¹³C NMR (100 MHz, CDCl₃): δ 169.7, 169.6, 169.5 (3 C, 3 COCH₃), 165.5, 165.1 (2 C, 2 CPh), 100.9, 98.2, 98.0 (3 C, C-1_A, 1_B, 1_C), 77.9, 74.5, 73.2, 71.8, 71.5, 70.3, 70.3, 69.0, 68.7, 68.6, 66.4, 66.1, 54.8 (13 C, C-2_A, 2_B, 2_C, 3_A, 3_B, 3_C, 4_A, 4_B, 4_C, 5_A, 5_B, 5_C, OCH₃), 20.4, 20.3, 20.2, 17.2, 16.9, 16.5 (6 C, C-6_A, 6_B, 6_C, COCH₃, COCH₃, COCH₃).

Anal. Calcd for C₃₉H₄₈O₁₈: C, 58.20; H, 6.01. Found: C, 58.03; H, 6.08.

Methyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-[2,3,4-tri-*O*-benzoyl- β -L-xylopyranosyl-(1 $\rightarrow$ 2)][2,3,4-tri-*O*-benzoyl- β -L-xylopyranosyl-(1 $\rightarrow$ 4)]- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (14). 2,3,4-Tri-*O*-benzoyl- α -L-xylopyranosyl trichloroacetimidate (**4**) (606 mg, 1.00 mmol) and methyl 2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (**13**) (402 mg, 0.50 mmol) were dried together under high

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vacuum for 2 h, then dissolved in anhydrous CH_2Cl_2 (10 mL). TMSOTf (9.0 μL , 0.05 mmol) was added dropwise at -20°C with N_2 protection. The reaction mixture was stirred for 2 h, during which time the temperature was gradually warmed to ambient temperature. Then the mixture was neutralized with triethylamine and concentrated to dryness. Purification of the residue by column chromatography (3:1 petroleum ether–ethyl acetate) gave **14** (520 mg, 82.3%) as a syrup; $[\alpha]_{\text{D}} + 44.5^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.13–7.35 (m, 40 H, 8 PhH), 5.67 (dd, 1 H, $J_{2,3}=J_{3,4}=9.9$ Hz, H-3_D/H-3_E), 5.47 (dd, 1 H, $J_{1,2}=1.7$ Hz, $J_{2,3}=3.1$ Hz, H-2_C), 5.40–5.21 (m, 7 H, H-2_D, H-2_E, H-3_C, H-3_D/H-3_E, H-4_A, H-4_D, H-4_E), 5.14 (dd, 1 H, $J_{1,2}=1.6$ Hz, $J_{2,3}=3.3$ Hz, H-2_A), 4.99 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4_C), 4.98 (d, 1 H, $J_{1,2}=1.7$ Hz, H-1_C), 4.73 (d, 1 H, $J_{1,2}=1.6$ Hz, H-1_A), 4.67 (d, 1 H, $J_{1,2}=1.7$ Hz, H-1_B), 4.65 (d, 1 H, $J_{1,2}=6.0$ Hz, H-1_D/H-1_E), 4.13–4.06 (m, 2H, 1 H-5_D, 1 H-5_E), 4.08 (dd, 1 H, $J_{2,3}=3.3$ Hz, $J_{3,4}=9.8$ Hz, H-3_A), 4.00–3.85 (m, 2 H, H-5_A, H-5_C), 3.81 (d, 1 H, $J_{1,2}=5.9$ Hz, H-1_D/H-1_E), 3.62 (dd, 1 H, $J_{2,3}=3.1$ Hz, $J_{3,4}=9.6$ Hz, H-3_B), 3.49–3.39 (m, 7 H, H-2_B, H-4_B, H-5_B, 1 H-5_D/H-5_E, OCH₃), 2.91 (q, 1 H, $J=7.8$ Hz, H-5_D/H-5_E), 2.16 (s, 3 H, COCH₃), 2.03 (s, 3 H, COCH₃), 1.94 (s, 3 H, COCH₃), 1.26 (d, 3 H, $J_{5,6}=6.1$ Hz, H-6_A), 0.90 (d, 3 H, $J_{5,6}=6.3$ Hz, H-6_C), 0.80 (d, 3 H, $J_{5,6}=6.4$ Hz, H-6_B); ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 169.3, 169.2 (3 C, 3 COCH₃), 165.2, 164.8, 164.5, 164.4, 164.3 (8 C, some signals overlapped 8 CPh), 101.3, 99.2, 99.0, 98.7, 98.1 (5 C, C-1_A, 1_B, 1_C, 1_D, 1_E), 80.4, 77.6 (2 C, C-3_A, C-3_B), 74.3, 73.7, 73.6, 72.0, 71.5, 71.2, 71.1, 70.5, 70.0, 69.2, 68.9, 68.8, 67.9, 65.9, 65.8, 62.0, 60.9, 59.9 (18 C, C-2_{A–E}, 3_{C–E}, 4_{A–E}, 5_{A–E}), 54.7 (1 C, OCH₃), 20.5, 20.4, 20.3, 17.1, 16.6, 16.5 (6 C, C-6_A, 6_B, 6_C, 3 COCH₃).

Anal. Calcd for $\text{C}_{91}\text{H}_{88}\text{O}_{32}$: C, 64.53; H, 5.24. Found: C, 64.70; H, 5.15.

Methyl α -L-Rhamnopyranosyl-(1 $\rightarrow$ 3)-[β -L-xylopyranosyl-(1 $\rightarrow$ 2)][β -L-xylopyranosyl-(1 $\rightarrow$ 4)]- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranoside (15). Pentasaccharide **14** (500 mg, 0.30 mmol) was dissolved in a saturated solution of ammonia in MeOH (10 mL). After 96 h at room temperature, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **15** as a foamy solid (190 mg, 86.3%); $[\alpha]_{\text{D}} - 18.2^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 5.15 (d, 1 H, $J_{1,2}=1.5$ Hz, H-1), 5.08 (d, 1 H, $J_{1,2}=1.6$ Hz, H-1), 4.60 (d, 1 H, $J_{1,2}=1.5$ Hz, H-1), 4.38 (d, 1 H, $J_{1,2}=6.1$ Hz, H-1), 4.32 (d, 1 H, $J_{1,2}=6.0$ Hz, H-1), 3.44 (s, 3 H, OCH₃), 1.41 (d, 3 H, $J_{5,6}=6.1$ Hz, H-6), 1.32 (d, 3 H, $J_{5,6}=6.2$ Hz, H-6), 1.28 (d, 3 H, $J_{5,6}=6.0$ Hz, H-6); ^{13}C NMR (100 MHz, CDCl_3): δ 104.7, 103.3, 101.2, 101.2, 100.3 (5C, C-1), 81.2, 78.6, 77.3, 76.8, 76.5, 74.2, 73.2, 72.7, 71.9, 70.9, 70.7, 70.6, 69.9, 68.7, 68.6, 68.4, 65.6, 65.5 (some signals overlapped), 53.8 (1 C, OCH₃), 16.9, 16.6, 16.5 (3 C, C-6_{A–C}); MS (m/z) Calcd for $\text{C}_{29}\text{H}_{50}\text{O}_{21}$: 734.69 $[\text{M}]^+$. Found: 757.71 $[\text{M}+\text{Na}]^+$.

Methyl 2,3,4-Tri-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-acetyl- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-2,4-di-*O*-benzoyl- α -L-rhamnopyranoside (16). Acetylation of **13** (80 mg, 0.5 mmol) with acetic anhydride (1 mL) in pyridine (5 mL) at room temperature for 10 h gave compound **15** in a quantitative yield as a foamy solid; $[\alpha]_{\text{D}} + 23.6^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.10–7.45 (m, 10 H, 2 PhH), 5.47 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4_A), 5.43 (dd, 1 H, $J_{1,2}=1.8$ Hz, $J_{2,3}=3.4$ Hz, H-2_A), 5.00 (dd, 1 H, $J_{2,3}=3.3$ Hz, $J_{3,4}=9.9$ Hz, H-3_C), 4.93 (dd, 1 H, $J_{1,2}=1.6$ Hz, $J_{2,3}=3.3$ Hz, H-2_C), 4.91 (dd, 1 H, $J_{3,4}=J_{4,5}=9.9$ Hz, H-4_C), 4.90 (d, $J_{1,2}=1.5$ Hz, H-1_B), 4.88 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4_B), 4.85 (d, $J_{1,2}=1.6$ Hz, H-1_C), 4.82 (dd, 1 H, $J_{1,2}=1.5$ Hz,

$J_{2,3}=3.1$ Hz, H-2_B), 4.60 (d, $J_{1,2}=1.8$ Hz, H-1_A), 4.35 (dd, 1 H, $J_{2,3}=3.4$ Hz, $J_{3,4}=9.8$ Hz, H-3_A), 3.99 (m, 1 H, H-5_A), 3.84 (dd, 1 H, $J_{2,3}=3.1$ Hz, $J_{3,4}=9.7$ Hz, H-3_B), 3.71 (m, 1 H, 5_C), 3.57 (m, 1 H, H-5_B), 3.44 (s, 3 H, OCH₃), 2.11 (s, 3 H, COCH₃), 1.99 (s, 3 H, COCH₃), 1.98 (s, 3 H, COCH₃), 1.96 (s, 3 H, COCH₃), 1.92 (s, 3 H, COCH₃), 1.30 (d, 3 H, $J_{5,6}=6.2$ Hz, 6_C), 1.00 (d, 3 H, $J_{5,6}=6.1$ Hz, H-6_A), 0.75 (d, 3 H, $J_{5,6}=6.4$ Hz, 6_C); ¹³C NMR (100 MHz, CDCl₃): δ 169.6, 169.5, 169.4, 169.3, 169.1 (5 C, 5 COCH₃), 165.5, 165.3 (2 C, 2 CPh), 98.6, 98.0, 97.8 (3 C, C-1_A, 1_B, 1_C), 75.4, 73.6, 72.7, 71.6, 71.6, 70.7, 70.3, 69.6, 68.0, 67.1, 66.4, 66.1, 54.8 (13 C, C-2_A, 2_B, 2_C, 3_A, 3_B, 3_C, 4_A, 4_B, 4_C, 5_A, 5_B, 5_C, OCH₃), 20.4, 20.3, 20.2, 17.2, 16.8, 16.3 (8 C, some signals overlapped C-6_A, 6_B, 6_C, 5 COCH₃).

Anal. Calcd for C₄₃H₅₂O₂₀: C, 58.10; H, 5.90. Found: C, 57.96; H, 6.11.

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