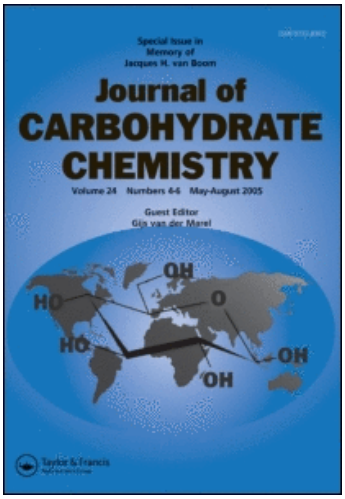


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# SYNTHESIS OF A XYLOSYLATED RHAMNOSE PENTASACCHARIDE—THE REPEATING UNIT OF THE O-SPECIFIC SIDE CHAIN OF LIPOPOLYSACCHARIDES FROM THE REFERENCE STRAINS FOR *STENOTROPHOMONAS MALTOPHILIA* SEROGROUP O18

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## ABSTRACT

A xylosylated rhamnose pentasaccharide, α-L-Rha*p*-(1→3)-[β-L-Xyl*p*-(1→2)-] [β-L-Xyl*p*-(1→4)-]α-L-Rha*p*-(1→3)-L-Rha*p*, 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→3)-linked disaccharide (**10**), and subsequent benzoylation and deacetylation afforded the disaccharide acceptor **12**. Condensation of **12** with **8** yielded methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→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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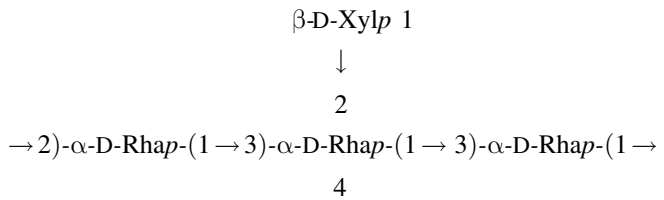
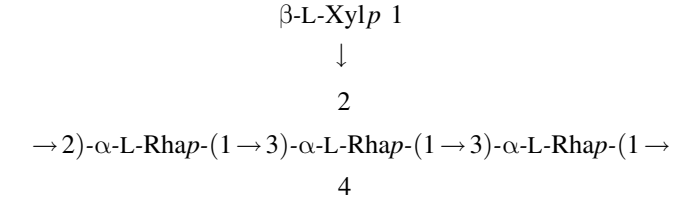
## INTRODUCTION

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.




**O4 Polymer**



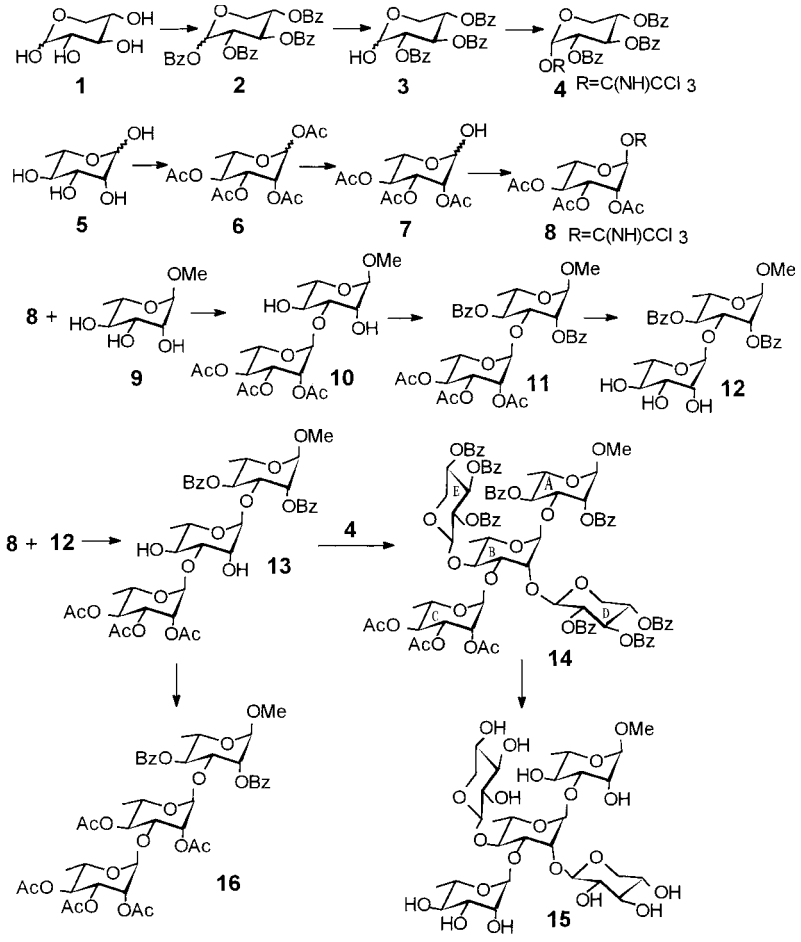

**O18 Polymer (with absence of some xylose units at 4 position)**

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.

## 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 trichloroactonitrile 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→3)-linked disaccharide **10**. Its structure was confirmed by benzoylation to give methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→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 $^1$H 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 $^1$H 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. $^1$H NMR, $^{13}$C NMR, and $^1$H 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 (60–90 °C) as the eluent. Solutions were concentrated at <60 °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

petroleum ether-EtOAc) to give **4** (10.8 g, 89.1%); $[\alpha]_D$ +31.3° (*c* 1.5, $CHCl_3$); lit.[11] $[\alpha]_D$ +33.1° (*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° (*c* 1.1, $CHCl_3$); lit.[12] $[\alpha]_D$ −52° (*c* 1.0, $CHCl_3$).

**Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→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→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° (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.15–7.43 (m, 10 H, 2 Ph*H*), 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, OC$H_3$), 1.89 (s, 3 H, CO$CH_3$), 1.88 (s, 3 H, CO$CH_3$), 1.82 (s, 3 H, CO$CH_3$), 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 *C*O$CH_3$), 165.7, 165.0 (2 C, 2 *C*OPh), 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-$2_A$, $2_B$, $3_A$, $3_B$, $4_A$, $4_B$, $5_A$, $5_B$, O$CH_3$), 20.2, 20.1, 20.0, 17.2, 16.7 (5 C, C-$6_A$, $6_B$, 3 CO$CH_3$).

Anal. Calcd for $C_{33}H_{38}O_{14}$: C, 60.17; H, 5.82. Found: C, 60.24; H, 6.01.

**Methyl α-L-Rhamnopyranosyl-(1→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 $Et_3N$, 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° (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.11−7.44 (m, 10 H, 2 Ph*H*), 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, OC*H*$_3$), 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-$6_B$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.5, 165.4 (2 C, 2 *C*OPh), 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-$2_A$, $2_B$, $3_A$, $3_B$, $4_A$, $4_B$, $5_A$, $5_B$, O*C*H$_3$), 17.1, 16.7 (2 C, C-$6_A$, $6_B$).

Anal. Calcd for $C_{27}H_{32}O_{11}$: C, 60.89; H, 6.06. Found: C, 60.77; H, 6.12.

**Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→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→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 $CH_2Cl_2$ (40 mL). TMSOTf (18 μL, 0.10 mmol) 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. 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° (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.12−7.44 (m, 10 H, 2 Ph*H*), 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, OC*H*$_3$), 2.10 (s, 3 H, COC*H*$_3$), 2.00 (s, 3 H, COC*H*$_3$), 1.94 (s, 3 H, COC*H*$_3$), 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-$6_B$/$6_C$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.7, 169.6, 169.5 (3 C, 3 *C*OCH$_3$), 165.5, 165.1 (2 C, 2 *C*OPh), 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-$2_A$, $2_B$, $2_C$ $3_A$, $3_B$, $3_C$, $4_A$, $4_B$, $4_C$, $5_A$, $5_B$, $5_C$, OCH$_3$), 20.4, 20.3, 20.2, 17.2, 16.9, 16.5 (6 C, C-$6_A$, $6_B$, $6_C$, COC*H*$_3$, COCH$_3$, COC*H*$_3$).

Anal. Calcd for $C_{39}H_{48}O_{18}$: C, 58.20; H, 6.01. Found: C, 58.03; H, 6.08.

**Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-[2,3,4-tri-*O*-benzoyl-β-L-xylopyranosyl-(1→2)][2,3,4-tri-*O*-benzoyl-β-L-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→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→3)-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**13**) (402 mg, 0.50 mmol) were dried together under high

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; $[\alpha]_D$ +44.5° (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.13−7.35 (m, 40 H, 8 Ph*H*), 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-$5_E$, $OCH_3$), 2.91 (q, 1 H, J=7.8 Hz, H-$5_D$/H-$5_E$), 2.16 (s, 3 H, CO*C*$H_3$), 2.03 (s, 3 H, CO*C*$H_3$), 1.94 (s, 3 H, CO*C*$H_3$), 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 *C*$OCH_3$), 165.2, 164.8, 164.5, 164.4, 164.3 (8 C, some signals overlapped 8 *C*OPh), 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, O*C*$H_3$), 20.5, 20.4, 20.3, 17.1, 16.6, 16.5 (6 C, C-$6_A$, $6_B$, $6_C$, 3 CO*C*$H_3$).

Anal. Calcd for $C_{91}H_{88}O_{32}$: C, 64.53; H, 5.24. Found: C, 64.70; H, 5.15.

**Methyl α-L-Rhamnopyranosyl-(1→3)-[β-L-xylopyranosyl-(1→2)][β-L-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (15).** Pentaasaccharide **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%); $[\alpha]_D$ −18.2° (*c* 1.0, $CHCl_3$); $^1$H 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, $OCH_3$), 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, $OCH_3$), 16.9, 16.6, 16.5 (3 C, C-$6_{A-C}$); MS (*m*/*z*) Calcd for $C_{29}H_{50}O_{21}$: 734.69 $[M]^+$. Found: 757.71 $[M+Na]^+$.

**Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→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; $[\alpha]_D$ + 23.6° (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.10−7.45 (m, 10 H, 2 Ph*H*), 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, O*C*$H_3$), 2.11 (s, 3 H, CO*C*$H_3$), 1.99 (s, 3 H, CO*C*$H_3$), 1.98 (s, 3 H, CO*C*$H_3$), 1.96 (s, 3 H, CO*C*$H_3$), 1.92 (s, 3 H, CO*C*$H_3$), 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, $6_C$); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.6, 169.5, 169.4, 169.3, 169.1 (5 C, 5 *C*OCH$_3$), 165.5, 165.3 (2 C, 2 *C*OPh), 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-$2_A$, $2_B$, $2_C$ $3_A$, $3_B$, $3_C$, $4_A$, $4_B$, $4_C$, $5_A$, $5_B$, $5_C$, O*C*H$_3$), 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 CO*C*H$_3$).

Anal. Calcd for $C_{43}H_{52}O_{20}$: C, 58.10; H, 5.90. Found: C, 57.96; H, 6.11.

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