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Carbohydrate Research 339 (2004) 43–49
Carbohydrate RESEARCH

A concise synthesis of two isomeric pentasaccharides, the O repeat units from the lipopolysaccharides of *P. syringae* pv. porri NCPPB 3364^T and NCPPB 3365

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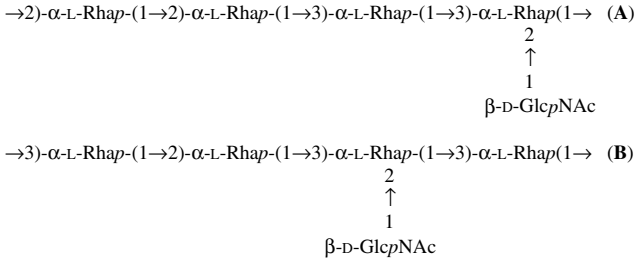
Received 3 September 2003; accepted 10 September 2003

Abstract—A concise synthesis of two isomeric pentasaccharides, α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→3)-[β-D-Glc*p*NAc-(1→2)]-α-L-Rha*p* (**A**) and α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-[β-D-Glc*p*NAc-(1→2)]-α-L-Rha*p*-(1→3)-α-L-Rha*p* (**B**), the O repeats from the lipopolysaccharides of *Pseudonomonas syringae* pv. porri NCPPB 3364^T and 3365 was achieved via assembly of the building blocks, allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**1**), 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (**2**), allyl 4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (**6**), 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**7**), and allyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**10**). Coupling of **1** with **2** followed by deallylation and trichloroacetimidate formation gave the disaccharide donor **5**, while condensation of **6** with **7**, followed by dechloroacetylation, offered the disaccharide acceptor **9**. Then, **5** was coupled with **10** to obtain the trisaccharide **11**, and subsequent deallylation and trichloroacetimidate formation furnished the trisaccharide donor **13**. Coupling of **9** with **13**, followed by deprotection, afforded pentasaccharide **19**, while condensation of **9** with **5**, followed by deallylation and trichloroacetimidate formation, gave the tetrasaccharide donor **16**, whose coupling with **10** and subsequent deprotection yielded another pentasaccharide **22**.

Keywords: Oligosaccharide; Rhamnose; Glucosamine

1. Introduction

The lipopolysaccharides (LPS) of strains of *Pseudonomonas syringae*, a phytopathogenic bacterium, was reported as the causative agent of the bacterial blight of leek (*Allium porrum*).[1,2] The O polysaccharides (OPS) obtained from the LPS of *P. syringae* pv. porri NCPPB 3364^T and 3365 possess multiple oligosaccharide O repeats, some of which are linear and composed of L-rhamnose in the main chain and GlcNAc in the side chains. Both branched O repeats, which differ in the position of substitution of one of the rhamnose residues and in the site of attachment of GlcNAc, were found in the two strains, O repeat **A** being the major in strain NCPPB 3364^T and **B** in strain NCPPB 3365:[3]



Synthetic samples of rhamnan structures with GlcNAc side chains would be very valuable in research on plant pathology and in the design of immunodiagnostic

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doi:10.1016/j.carres.2003.09.014

reagents. The syntheses of several similar structures occurring in the cell-wall polysaccharide with alternate (1 → 2)- and (1 → 3)-linked rhamnan backbone and 3-*O*-GlcNAc side chains on the →2)-rhamnose residues have been reported by Pinto's group.[4–7] A general and convergent method for the synthesis of (1 → 2)- and (1 → 3)-linked rhamnans with arbitrary sugar side chains on the 3-OH of the rhamnose residues has been reported by our group.[8] We present herein a facile synthesis of two isomeric pentasaccharides consisting of (1 → 2)- and (1 → 3)-linked rhamnan backbone with 2-*O*-GlcNAc side chain on the rhamnose residues.

2. Results and discussion

As outlined in Scheme 1, condensation of allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside[8] (**1**) with 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate[8] (**2**) in the presence of a catalytic amount of TMSOTf gave allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**3**) in satisfactory yield (84%). Deallylation of **3** with $PdCl_2$ in methanol,[9] followed by trichloroacetimidate formation[10] with trichloroacetonitrile in the presence of DBU, produced the disaccharide donor **5** (67% for two steps). Coupling of allyl 4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (**6**)[8] with 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**7**) furnished disaccharide **8**. Subsequent dechloroacetylation with thiourea gave a co-used disaccharide acceptor **9** (75%) for further couplings. Glycosylation of the acceptor allyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside[8] (**10**) with donor **5** afforded trisaccharide **11** in high yield (79%), which was activated by deallylation and trichloroacetimidate formation to furnish the trisaccharide donor **13** (72%, for two steps). Condensation of donor **5** and acceptor **9** gave tetrasaccharide **14** in acceptable yield (63%), and consecutive deallylation and trichloroacetimidate formation offered tetrasaccharide donor **16** (67%, for two steps). Condensation of the disaccharide acceptor **9** with the trisaccharide donor **13** yielded pentasaccharide **17** (60%), while coupling of the monosaccharide acceptor **10** with the tetrasaccharide donor **16** furnished another pentasaccharide **20** (73%).

Hydrazinolysis to remove the phthalimido group from **17** or **20** was carried out in 10% hydrazine hydrate–EtOH under reflux, and it was accompanied by reduction of the allyl group and debenzoylation.[8] Subsequent acetylation of the resultant product with acetic anhydride in pyridine readily gave acetylated pentasaccharide **18** or **21**. Finally deacetylation of **18** or **21** in ammonia–methanol gave the target pentasaccharide **19** and **22**.

In summary, a concise synthesis of two branched pentasaccharides, consisting of α-(1 → 2)- and (1 → 3)-linked rhamnan backbone with 2-branched D-Glc*p*NAc was achieved. In terms of simplicity and efficiency, this method can be used for construction of higher oligosaccharides with similar structures.

3. Experimental

3.1. General methods

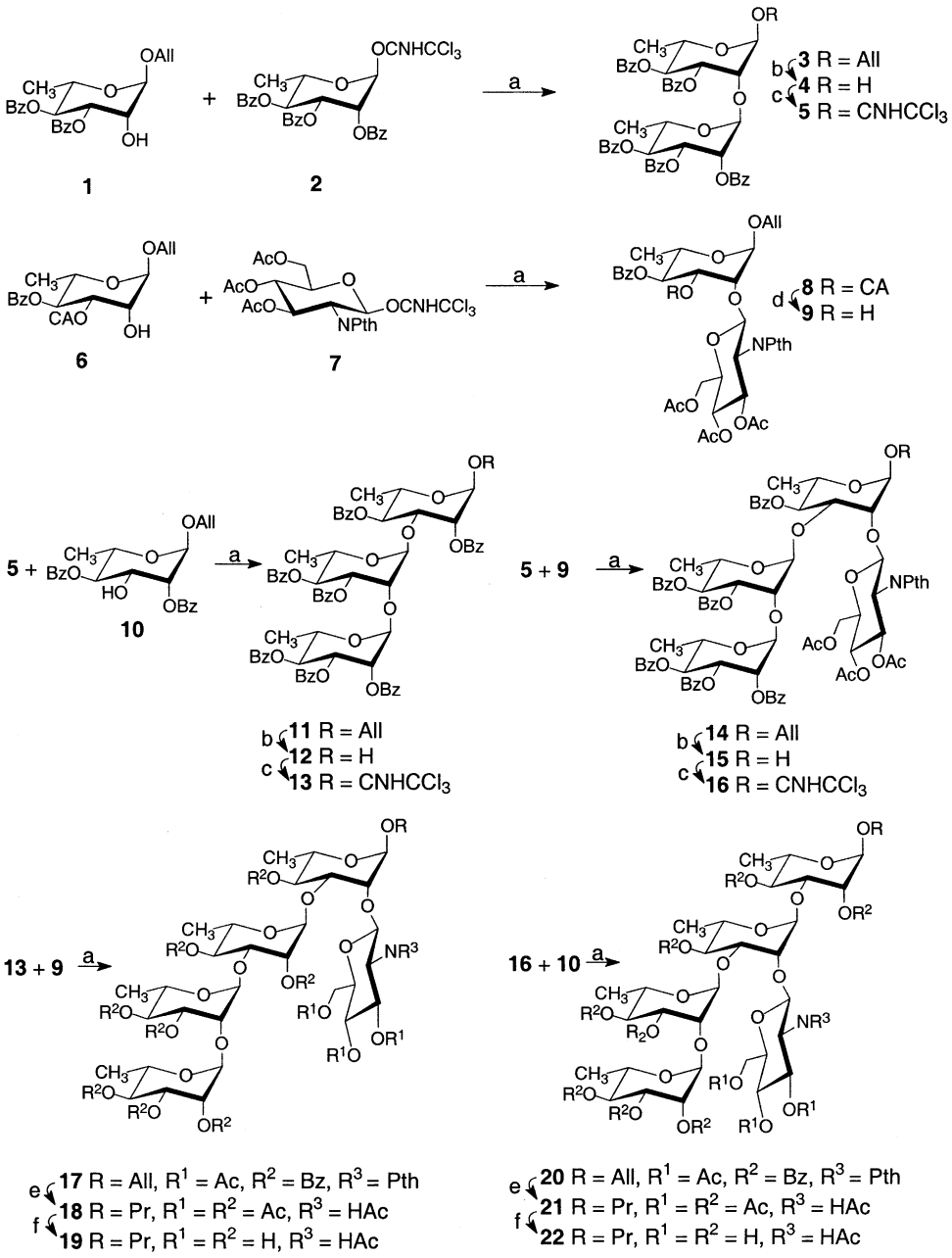
Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^{1}H, 100 MHz for ^{13}C) at 25 °C for solutions in $CDCl_3$ or D_2O as indicated. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} plates with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV lamp. 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 (60–90 °C) as the eluent. Solutions were concentrated at <60 °C under reduced pressure.

3.2. General procedure for the glycosylations

A mixture of donor and acceptor was dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2. TMSOTf (0.05 equiv) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column, gave the desired products.

3.3. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (3)

As described in the general procedure, **1** (0.82 g, 1.98 mmol) and **2** (1.49 g, 2.40 mmol) were coupled, and the product was purified by silica gel column chromatography with 4:1 petroleum ether–EtOAc as the eluent to give **3** (1.46 g, 84%) as a foamy solid: $[\alpha]_D$ +80.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.25 (m, 25H, 5*Ph*), 6.02–5.85 (m, 2H, H-3′, CH_2–C*H*=CH_2), 5.87 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.3 Hz, H-2′), 5.83 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.67 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4′), 5.66 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.42–5.37 (m, 1H, CH_2–CH=CH_{trans}), 5.30–5.27 (m, 1H, CH_2–CH=CH_{cis}), 5.15 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1′), 5.06 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.37–4.29 (m, 2H, H-2, CH_2–CH=CH_2), 4.18–4.12 (m, 2H, H-5, H-5′), 1.41, 1.35 (2d, 6H, $J_{5,6}$ 6.3 Hz, 2CH_3). Anal. calcd for $C_{50}H_{46}O_{14}$: C, 68.96; H, 5.32. Found: C, 68.79; H, 5.29.



Scheme 1. Reagents and conditions: (a) TMSOTf (0.01 equiv), CH_2Cl_2, −20–0 °C, 2–4 h; 84% for **3**, 71% for **8**, 79% for **11**, 63% for **14**, 60% for **17**, and 73% for **20**, respectively; (b) $PdCl_2$, MeOH, rt, 2 h; 78%, 83%, 80% for **4**, **12**, and **15**, respectively; (c) Cl_3CN, DBU, CH_2Cl_2, rt, 3 h; 86%, 86%, 84% for **5**, **13**, and **16**, respectively; (d) thiourea in EtOH–CH_2Cl_2 (1:4), reflux, 16 h; 75%; (e) i: EtOH–10% hydrazine hydrate, reflux, 48 h; ii: Ac_2O–pyridine (dry), rt, 12 h; 83% for **18**, 80% for **21**; (f) satd NH_3–MeOH, rt, 72 h; 89% for **19**, 88% for **22**.

3.4. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (5)

To a solution of **3** (1.16 g, 1.33 mmol) in anhyd MeOH (13 mL) was added $PdCl_2$ (30 mg). After stirring the mixture at rt for 2 h, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give **4** (864 mg, 78%) as a white foam. A mixture of **4** (851 mg, 1.02 mmol), trichloroacetonitrile (204 μL, 2.04 mmol) and 1,8-diazabicyclo[5.4.0]-undecene (DBU) (55 μL) in dry CH_2Cl_2 (10 mL) was stirred under nitrogen for 3 h and then concentrated. The residue was purified by flash chromatography (4:1 petroleum ether–EtOAc) to give **5** (856 mg, 86%) as a foamy solid: $[\alpha]_D$ +160.5 (*c* 1.0,

$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H, CN*H*CCl_3), 8.04–7.26 (m, 25H, 5*Ph*), 6.50 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 5.97 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.1 Hz, H-3′), 5.87–5.84 (m, 2H, H-2′, H-3), 5.78 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4′), 5.70 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.22 (dd, 1H, $J_{1,2}$ 1.3 Hz, H-1′), 4.58 (m, 1H, H-2), 4.43–4.34 (m, 2H, H-5, H-5′), 1.46 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.40 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{49}H_{42}Cl_3NO_{14}$: C, 60.35; H, 4.34. Found: C, 60.08; H, 4.46.

3.5. Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)-4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (8)

Donor **7** (878 mg, 1.5 mmol) was coupled with acceptor **6** (486 mg, 1.26 mmol) as described in the general procedure, and the product was purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **8** (714 mg, 71%) as a foamy solid: $[\alpha]_D$ −5.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.27 (m, 9H, *Ph*, *Pth*), 5.94–5.83 (m, 2H, H-3′, CH_2–C*H*=CH_2), 5.42–5.37 (m, 2H, H-1′, H-3), 5.34–5.29 (m, 1H, CH_2–CH=CH_{trans}), 5.23–5.20 (m, 1H, CH_2–CH=CH_{cis}), 5.16 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 4.95 (d, 1H, $J_{1,2}$ 2.0 Hz, H-1), 4.90 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4′), 4.45 (dd, 1H, $J_{1,2}$ 8.1 Hz, $J_{2,3}$ 10.8 Hz, H-2′), 4.29 (dd, 1H, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 12.3 Hz, H-6′b), 4.22–4.17 (m, 2H, H-5, H-6′a), 4.08 (dd, 1H, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 2.7 Hz, H-2), 4.06–4.07 (m, 1H, H-5′), 3.88, 3.52 (ABq, 2H, *J* 14.9 Hz, CH_2ClCO), 3.88–3.83 (m, 2H, CH_2–CH=CH_2), 2.12, 2.04, 1.89 (3s, 3H, 3CH_3CO), 1.14 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{38}H_{40}ClNO_{16}$: C, 56.90; H, 5.03. Found: C, 57.12; H, 5.09.

3.6. Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)-4-*O*-benzoyl-α-L-rhamnopyranoside (9)

To a solution of **8** (695 g, 0.87 mmol) in EtOH (5 mL)–CH_2Cl_2 (20 mL) was added thiourea (0.33 g), and the mixture was refluxed for 16 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated. The residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **9** (473 mg, 75%) as a foamy solid: $[\alpha]_D$ −36.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.84–7.27 (m, 9H, *Ph*, *Pth*), 5.91–5.86 (m, 2H, H-3′, CH_2–C*H*=CH_2), 5.56 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1′), 5.34–5.29 (m, 1H, CH_2–CH=CH_{trans}), 5.32–5.15 (m, 3H, H-4, CH_2–CH=CH_{cis}), 4.95 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1), 4.65 (dd, 1H, $J_{3,4} = J_{4,5} =$ 9.7 Hz, H-4′), 4.46 (dd, 1H, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 10.7 Hz, H-2′), 4.31 (dd, 1H, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 12.2 Hz, H-6′b), 4.21–4.15 (m, 2H, H-5′, H-6′a), 4.02–3.85 (m, 5H, H-2, H-3, H-5, CH_2–CH=CH_2), 2.12, 2.04, 1.90 (3s, 3H, 3CH_3CO), 1.17 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{36}H_{39}NO_{15}$: C, 59.58; H, 5.42. Found: C, 59.48; H, 5.40.

3.7. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (11)

Donor **5** (355 mg, 0.36 mmol) was coupled with acceptor **10** (150 mg, 0.36 mmol) as described in the general procedure, and the product was purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **11** (352 mg, 79%) as a foamy solid: $[\alpha]_D$ +140.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.24–7.24 (m, 35H, 7*Ph*), 6.03–5.96 (m, 1H, CH_2–C*H*=CH_2), 5.81 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.2 Hz, H-3″), 5.63 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.4 Hz, H-2″), 5.57–5.47 (m, 5H, H-2, H-3′, H-4, H-4′, H-4″), 5.38 (m, 1H, CH_2–CH=CH_{trans}), 5.30 (m, 1H, CH_2–CH=CH_{cis}), 5.24 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1″), 5.08 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 4.66 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.49 (dd, 1H, $J_{2,3}$ 3.6 Hz, $J_{3,4}$ 9.7 Hz, H-3), 4.30–4.25 (m, 1H, H-5″), 4.14–4.08 (m, 4H, H-5, H-5′, CH_2–CH=CH_2), 3.97 (dd, 1H, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 2.8 Hz, H-2′), 1.33, 1.26, 1.08 (3d, 9H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6); ^{13}C NMR (100 MHz, $CDCl_3$), δ 166.4, 166.0, 165.7, 165.5, 165.4, 165.3, 165.0 (Ph*C*O), 133.7–128.4 (*Ph*CO, –CH_2–*C*H=CH_2), 118.2 (–CH_2–CH=*C*H_2), 100.7, 99.2, 96.8 (C-1), 76.0, 75.3, 73.8, 72.6, 71.7, 70.7, 70.5, 69.8, 68.8, 68.2, 67.8, 67.6, 66.9 (C-2–5, –*C*H_2–CH=CH_2), 17.8–17.6 (Rha*p* C-6). Anal. Calcd for $C_{70}H_{64}O_{20}$: C, 68.62; H, 5.26. Found: C, 68.83; H, 5.37.

3.8. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (13)

Compound **11** (340 mg, 0.8 mmol) was deallylated and subsequently trichloroacetimidated under the same conditions as those used for the preparation of **5** from **3**, giving **13** (265 mg, 72% for two steps) as a foamy solid: $[\alpha]_D$ +126.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H, CN*H*CCl_3), 6.38 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 5.82 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4} = 10.1$ Hz, H-3″), 5.76 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.4 Hz, H-2″), 5.66–5.48 (m, 5H, H-2, H-3′, H-4, H-4′, H-4″), 5.26 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1″), 4.75 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 4.59 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.7 Hz, H-3), 4.31–4.26 (m, 1H, H-5″), 4.22–4.18 (m, 1H, H-5′), 4.07–3.99 (m, 2H, H-2′, H-5), 1.37, 1.26, 0.96 (3d, 9H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6). Anal. Calcd for $C_{69}H_{60}Cl_3NO_{20}$: C, 62.33; H, 4.55. Found: C, 62.56; H, 4.64.

3.9. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranoside (14)

Compound **5** (472 mg, 0.48 mmol) and **9** (293 mg, 0.37 mmol) were coupled under the same conditions as described in the general procedure. Purification of the product by chromatography with 1:1 petroleum ether–EtOAc as the eluent afforded **14** (392 g, 63%) as a foamy solid: $[\alpha]_D$ +76.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–7.17 (m, 34H, 6*Ph*, *Pth*), 6.14 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 9.4 Hz, Glc*p* H-3′), 6.01–5.86 (m, 4H, Glc*p* H-1, 2Rha*p* H-3, CH_2–C*H*=CH_2), 5.82 (dd, 1H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.3 Hz, Rha*p* H-2″), 5.58 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, Rha*p* H-4′), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, Rha*p* H-4), 5.36–5.32 (m, 1H, CH_2–CH=CH_{trans}), 5.28 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, Rha*p* H-4), 5.25–5.22 (dq, 1H, CH_2–CH=CH_{cis}), 5.04 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1), 4.95 (d, 2H, $J_{1,2}$ 1.4 Hz, 2Rha*p* H-1), 4.87 (dd, 1H, $J_{3,4} = J_{4,5} = 9.4$ Hz, Glc*p* H-4′), 4.51–3.71 (m, 12H, Glc*p* H-2, H-5, H-6, Rha*p* 2H-2, H-3, 3H-5, CH_2–CH=CH_2), 2.11, 2.10, 1.90 (3s, 3H, 3CH_3CO), 1.48, 1.01, 0.77 (d, 9H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.0, 169.8 (CH_3*C*O), 167.9 (Pth*C*O), 165.9, 165.7, 165.3, 165.2, 165.0, 164.5 (Ph*C*O), 134.1–128.2 (*Ph*, –CH_2–*C*H=CH_2), 117.1 (–CH_2–CH=*C*H_2), 99.6, 99.2, 98.4, 98.3 (C-1), 76.6, 74.2, 72.8, 72.6, 71.9, 70.5, 70.4, 69.8, 69.6, 68.5, 68.3, 68.1, 67.5, 67.3, 62.2, 61.7, 54.9, 52.2 (C-2–6, –*C*H_2–CH=CH_2), 20.8–20.7 (*C*H_3CO), 17.8, 17.6 17.5 (Rha*p* C-6). Anal. Calcd for $C_{83}H_{79}NO_{28}$: C, 64.80; H, 5.18. Found: C, 65.05; H, 5.23.

3.10. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (16)

Compound **14** (305 mg, 0.8 mmol) was deallylated and subsequently trichloroacetimidated under the same conditions as those used for the preparation of **5** from **3**, giving **16** (218 mg, 67% for two steps) as a foamy solid: $[\alpha]_D$ +84.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H, CN*H*CCl_3), 8.02–7.25 (m, 34H, 6*Ph*, *Pth*), 6.37 (d, 1H, Rha*p* H-1), 6.08 (dd, 1H, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 9.0 Hz, Glc*p* H-3′), 6.02 (d, 1H, $J_{1,2}$ 8.4 Hz, Glc*p* H-1′), 5.87–5.79 (m, 3H, Rha*p* H-2″, 2H-3), 5.56 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, Rha*p* H-4″), 5.45 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, Rha*p* H-4′), 5.29 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, Rha*p* H-4), 5.05 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1″), 5.00 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, Glc*p* H-4), 4.95 (d, 2H, $J_{1,2}$ 1.3 Hz, 2Rha*p* H-1′), 4.51–3.93 (m, 10H, Glc*p* H-2′, H-5, Rha*p* 2H-2, H-3, 3H-5, Glc*p* H-6), 2.07, 2.06, 1.87 (3s, 3H, 3CH_3CO), 1.40, 1.04, 0.70 (d, 9H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6). Anal. Calcd for $C_{82}H_{75}Cl_3N_2O_{28}$: C, 59.95; H, 4.60. Found: C, 59.77; H, 4.49.

3.11. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranoside (17)

As described in the general procedure, **9** (164 mg, 0.23 mmol) and **13** (250 mg, 0.19 mmol) were coupled, and the product was purified by silica gel column chromatography with 1:1 petroleum ether–EtOAc as the eluent to give **17** (214 g, 60%) as a foamy solid: $[\alpha]_D$ +64.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): 8.25–7.21 (m, 44H, 8*Ph*, *Pth*), 6.02 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 9.1 Hz, Glc*p* H-3′), 5.95–5.87 (m, 4H, Glc*p* H-1′, Rha*p* H-3‴, H-3″, CH_2–C*H*=CH_2), 5.77 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.2 Hz, Rha*p* H-2″), 5.58–5.44 (m, 4H), 5.32–5.27 (m, 1H, CH_2–CH=CH_{trans}), 5.21–5.18 (m, 1H, CH_2–CH=CH_{cis}), 5.10 (dd, 1H, $J_{3,4} = J_{4,5} = 9.4$ Hz, Rha*p* H-4), 5.08 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1), 5.01 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.2 Hz, Rha*p* H-2′), 4.44 (dd, 1H, $J_{1,2}$ 8.3 Hz, $J_{2,3}$ 10.6 Hz, Glc*p* H-3′), 4.36–3.69 (m, 12H, Glc*p* H-5, H-6, Rha*p* 2H-2, H-3, 4H-5, CH_2–CH=CH_2), 1.98, 1.94, 1.28 (3s, 3H, 3CH_3CO), 1.38, 1.21, 1.07, 0.74 (d, 12H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 169.5, 169.4 (CH_3*C*O), 165.6, 165.3, 165.2, 165.1, 165.0, 164.9, 164.8, 163.7 (Pth*C*O, Ph*C*O), 133.7–128.0 (*Ph*, –CH_2–*C*H=CH_2), 117.3 (–CH_2–CH=*C*H_2), 100.3, 100.2, 98.8, 98.4, 97.6 (C-1), 75.7, 75.4, 73.5, 72.4, 72.2, 71.8, 71.6, 71.0, 70.4, 69.9, 69.6, 69.5, 68.2, 67.8, 67.7, 67.4, 67.2, 62.1, 54.9 (C-2–6, –*C*H_2–CH=CH_2), 20.8, 20.6, 20.5 (*C*H_3CO), 17.9, 17.7, 17.6, 17.5 (Rha*p* C-6). Anal. Calcd for $C_{103}H_{97}NO_{34}$: C, 65.36; H, 5.17. Found: C, 65.55; H, 5.20.

3.12. Propyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)]-4-*O*-acetyl-α-L-rhamnopyranoside (18)

Pentasaccharide **17** (166 mg, 0.09 mmol) was dissolved in EtOH (20 mL) to which was added 100% hydrazine hydrate (4 mL), and the solution was refluxed for 48 h. The solution was then concentrated, and the residue was co-evaporated several times with toluene. The residue was dissolved in pyridine (5 mL) to which was added Ac_2O (3 mL). The solution was stirred for 12 h at rt and then evaporated to dryness. Purification of the residue by column chromatography (EtOAc) gave **18** (95 mg, 83% for two steps) as a foamy solid: $[\alpha]_D$ −21.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 6.14 (d, 1H, $J_{1,2}$ 8.0 Hz, N*H*Ac), 5.56 (dd, 1H, $J_{2,3} = J_{3,4} = 9.4$ Hz, Glc*p*

H-3′), 5.34 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, Rha*p* H-3‴), 5.30–5.28 (m, 2H, Rha*p* H-2‴, H-3″), 5.22 (d, 1H, $J_{1,2}$ 1.6 Hz, Rha*p* H-1‴), 5.11–4.92 (m, 7H), 4.84 (d, 1H, $J_{1,2}$ 2.5 Hz, Rha*p* H-1‴), 4.80 (d, 1H, $J_{1,2}$ 1.6 Hz, Rha*p* H-1′), 4.74 (d, 1H, $J_{1,2}$ 1.8 Hz, Rha*p* H-1), 4.31 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 8.5 Hz, Rha*p* H-3), 4.25 (dd, 1H, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 12.2 Hz, Glc*p* H-6b), 4.11 (dd, 1H, $J_{5,6a}$ 2.5 Hz, $J_{6a,6b}$ 12.2 Hz, Glc*p* H-6a), 4.05–3.37 (m, 9H), 2.18, 2.17, 2.16, 2.15, 2.13, 2.07, 2.06, 2.04, 2.03, 2.00, 1.99, 1.98 (12s, 36H, 12CH_3CO), 1.59 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.27, 1.23, 1.16, 1.15 (d, 12H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6), 0.92 (t, 3H, *J* 7.4 Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$), δ 171.7, 171.3, 170.7, 170.6, 170.5, 170.4, 170.2, 170.1, 170.0, 169.8, 169.7, 169.5 (CH_3CO), 99.5, 99.4, 99.3, 99.1, 99.0 (C-1), 75.7, 74.1, 73.0, 72.6, 71.8, 71.5, 71.2, 70.1, 70.9, 70.3, 69.9, 69.4, 68.8, 67.3, 67.7, 67.0, 66.9, 62.2, 55.8 (C-2–6, $OCH_2CH_2CH_3$), 24.9, 23.1, 22.7, 21.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6 (CH_3CO), 17.6, 17.3, 17.2, 17.2 (Rha*p* C-6), 10.5 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{57}H_{83}NO_{33}$: C, 52.25; H, 6.38. Found: C, 52.04; H, 6.50.

3.13. Propyl α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)]-α-L-rhamnopyranoside (19)

Pentasaccharide **18** (84 mg, 0.06 mmol) was dissolved in satd NH_3–MeOH (20 mL). After 96 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **19** (48 mg, 89%) as a foamy solid: $[\alpha]_D$ −17.6 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.21 (s, 1H, Rha*p* H-1‴), 5.00 (s, 1H, Rha*p* H-1″), 4.98 (d, 1H, $J_{1,2}$ 1.5 Hz, Rha*p* H-1′), 4.95 (s, 1H, Rha*p* H-1), 4.58 (d, 1H, $J_{1,2}$ 8.3 Hz, Glc*p* H-1′), 1.99 (s, 3H, CH_3CONH), 1.60 (m, 2H, $OCH_2CH_2CH_3$), 1.33–1.27 (m, 12H, Rha*p* H-6), 0.92 (t, 3H, *J* 7.4 Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (100 MHz, D_2O): δ 173.0 (CH_3CONH), 102.9, 102.1, 101.8, 100.5, 98.6 (C-1), 55.5 ($OCH_2CH_2CH_3$), 16.5, 16.4, 16.3, 16.2 (Rha*p* C-6), 9.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{35}H_{61}NO_{22}$: C, 49.58; H, 7.25. Found: C, 49.69; H, 7.24.

3.14. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (20)

Donor **16** (206 mg, 0.13 mmol) was coupled with acceptor **10** (103 mg, 0.25 mmol) as described in the general procedure, and the product was purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to give **20** (173 mg, 73%) as a foamy solid: $[\alpha]_D$ +104.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 8.13–7.25 (m, 44H, 8*Ph*, *Pth*), 6.02–5.90 (m, 2H, Glc*p* H-3″, CH_2–C*H*=CH_2), 5.81 (dd, 1H, $J_{2,3}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz, Rha*p* H-3‴), 5.78–5.73 (m, 2H, Rha*p* H-2‴, H-3″), 5.65 (d, 1H, $J_{1,2}$ 8.4 Hz, Glc*p* H-1″), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, Rha*p* H-4‴), 5.46 (dd, 1H, $J_{3,4} = J_{4,5} = 10.2$ Hz, Rha*p* H-4″), 5.41 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, Rha*p* H-4′), 5.40–5.25 (m, 2H, Rha*p* H-2′, CH_2–CH=CH_{trans}), 5.28–5.25 (m, 1H, CH_2–CH=CH_{cis}), 5.07 (dd, 1H, $J_{3,4} = J_{4,5} = 9.5$ Hz, Rha*p* H-4), 5.04 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1‴), 5.02 (d, 1H, $J_{1,2}$ 1.5 Hz, Rha*p* H-1″), 4.85 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1′), 4.79 (d, 1H, $J_{1,2}$ 1.2 Hz, Rha*p* H-1), 4.68 (dd, 1H, $J_{2,3} = J_{3,4} = 9.8$ Hz, Glc*p* H-4″), 4.39 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, Rha*p* H-3), 4.29 (dd, 1H, $J_{1,2}$ 8.4 Hz, $J_{2,3}$ 10.8 Hz, Glc*p* H-2″), 4.26–3.53 (m, 12H), 2.06, 2.03, 1.83 (3s, 3H, 3CH_3CO), 1.28, 1.26, 0.82, 0.69 (d, 12H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6); ^{13}C NMR (100 MHz, $CDCl_3$), δ 170.5, 169.6, 169.5 (CH_3CO), 167.5 (Pth*C*O), 165.8, 165.6, 165.4, 165.1, 165.0, 164.9, 164.8, 164.0 (Ph*C*O), 133.9–128.0 (*Ph*, –CH_2–*C*H=CH_2), 117.8 (–CH_2–CH=*C*H_2), 100.9, 98.8, 98.7, 98.0, 96.2 (C-1), 76.2, 76.1, 73.6, 72.9, 72.7, 72.3, 71.6, 71.1, 70.2, 70.1, 70.0, 69.3, 68.9, 68.4, 68.1, 67.7, 67.1, 66.4, 61.4, 54.4 (C-2–6, –*C*H_2–CH=CH_2), 20.6, 20.5, 20.3 (*C*H_3CO), 17.4, 17.3, 17.2, 17.0 (Rha*p* C-6). Anal. Calcd for $C_{103}H_{97}NO_{34}$: C, 65.36; H, 5.17. Found: C, 65.63; H, 5.13.

3.15. Propyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-[3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)]-4-*O*-acetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-acetyl-α-L-rhamnopyranoside (21)

Pentasaccharide **20** (164 mg, 0.09 mmol) was dissolved in EtOH (20 mL) to which was added 100% hydrazine hydrate (4 mL), and the solution was refluxed for 48 h. The solution was then concentrated, and the residue was co-evaporated several times with toluene. The residue was taken up in pyridine (5 mL) to which was added Ac_2O (3 mL). The solution was stirred for 12 h at rt and then evaporated to dryness. Purification of the residue by column chromatography (EtOAc) gave **21** (91 mg, 80% for two steps) as a foamy solid: $[\alpha]_D$ −36.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (d, 1H, $J_{1,2}$ 9.8 Hz, N*H*Ac), 5.30 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.8 Hz, Rha*p* H-3), 5.29 (d, 1H, $J_{1,2}$ 1.4 Hz, Rha*p* H-1‴), 5.22 (dd, 1H, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 10.5 Hz, Rha*p* H-3), 5.16 (dd, 1H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.5 Hz, Rha*p* H-2), 5.09–5.01 (m, 5H), 4.93 (d, 1H, $J_{1,2}$ 1.6 Hz, Rha*p* H-1″), 4.89 (d, 1H, $J_{1,2}$ 8.5 Hz, Glc*p* H-1″), 4.77 (d, 1H, $J_{1,2}$ 1.2 Hz, Rha*p* H-1′), 4.69 (d, 1H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1), 2.17, 2.15, 2.15, 2.10, 2.09, 2.09, 2.07, 2.06, 2.05, 2.02, 2.02, 1.97 (12s, 36H, 12CH_3CO), 1.60 (m, 2H, $OCH_2CH_2CH_3$), 1.32, 1.21, 1.19, 1.14 (d, 12H, $J_{5,6}$ 6.2 Hz, Rha*p* H-6), 0.94 (t, 3H, *J* 7.4 Hz, $OCH_2CH_2CH_3$);

^{13}C NMR (100 MHz, $CDCl_3$), δ 171.4, 171.0, 170.7, 170.4, 170.3, 170.1, 170.0, 170.0, 169.9, 169.8, 169.4, 169.3 (CH_3CO), 101.7, 99.9, 99.7, 99.4, 97.3 (C-1), 75.2, 74.9, 73.6, 73.4, 72.5, 72.4, 71.9, 71.6, 71.4, 70.8, 69.8, 69.8, 69.6, 69.0, 68.6, 67.8, 67.4, 67.3, 66.2, 62.2, 55.9 (C-2–6, $OCH_2CH_2CH_3$), 17.8, 17.3, 17.2, 17.1 (Rha*p* C-6), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{57}H_{83}NO_{33}$: C, 52.25; H, 6.38. Found: C, 52.14; H, 6.43.

3.16. Propyl α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 2)]-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranoside (22)

Pentasaccharide **21** (88 mg, 0.07 mmol) was dissolved in satd NH_3–MeOH (20 mL). After 96 h at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **22** (50 mg, 88%) as a foamy solid: $[\alpha]_D$ −42.1 (*c* 1.0, H_2O); ^{1}H NMR (D_2O): δ 5.25 (s, 1H, Rha*p* H-1‴), 5.24 (s, 1H, Rha*p* H-1″), 5.06 (s, 1H, Rha*p* H-1′), 4.98 (s, 1H, Rha*p* H-1), 4.55 (d, 1H, $J_{1,2}$ 8.5 Hz, Glc*p* H-1″), 1.99 (s, 3H, CH_3CONH), 1.61 (m, 2H, $OCH_2CH_2CH_3$), 1.33–1.24 (m, 12H, Rha*p* H-6), 0.92 (t, 3H, *J* 7.4 Hz, $OCH_2CH_2CH_3$); ^{13}C NMR (100 MHz, D_2O): δ 173.2 (CH_3CONH), 102.7, 101.9, 101.1, 100.3, 99.3 (C-1), 55.5 ($OCH_2CH_2CH_3$), 16.5, 16.4, 16.3, 16.2 (Rha*p* C-6), 9.7 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{35}H_{61}NO_{22}$: C, 49.58; H, 7.25. Found: C, 49.72; H, 7.28.

Acknowledgements

This work was supported by The National Natural Science Foundation of China (Projects 39970864 and 30070815).

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