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Synthesis of a hexasaccharide fragment of group E streptococci polysaccharide and the tetrasaccharide repeating unit of *E. coli* O7:K98:H6

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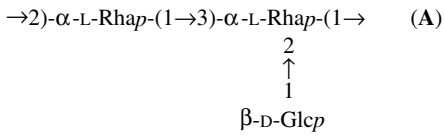
Abstract—Syntheses of a hexasaccharide, the dimer of the repeating unit of the group E streptococci polysaccharide, and a tetrasaccharide, the repeating unit of the *E. coli* O7:K98:H6, were achieved by constructing alternate α-L-(1→2)- and α-L-(1→3)-linked L-rhamnopyranose backbones and substituting with β-linked D-glucopyranose side chains for the former, and a D-glucopyranosyluronate branch for the latter, respectively, at O-2 of the L-rhamnose ring.

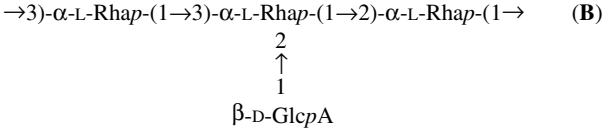
Keywords: Rhamnose oligosaccharides; Trichloroacetimidates

1. Introduction

The cell-wall polysaccharides of streptococci are composed primarily of a peptidoglycan lattice and one or more secondary polymers. These accessory wall polymers can include teichoic or teichuronic acids as well as neutral or acidic polysaccharides that contain L-rhamnose, such as group-specific polysaccharides of group A streptococci[1a,b] and group E streptococci (**A**).[2] Group A streptococci express a variety of both cell-surface and extracellular virulence factors that are responsible for a variety of human diseases, and are defined by the presence of a cell-wall-associated polysaccharide composed of *N*-acetyl-D-glucosamine and L-rhamnose. However, group E streptococci are defined by the presence of a polysaccharide consisting of D-glucose and L-rhamnose (**A**) and *E. coli* O7:K98:H6 by a capsular polysaccharides (K98 antigen) composed of L-rhamnopyranose and D-glucopyranosyluronate (**B**).[3] These polysaccharides consist of an alternating α-(1→2)- and -(1→3)-linked L-rhamnopyranose backbone with branching *N*-acetyl-D-glucosamine residue, a D-glucopyranose residue or D-glucopyranosyluronate linked β-(1→2) or β-(1→3) to an L-rhamnose ring. The syntheses of several structures corresponding to fragments of the group A streptococci polysaccharides have been reported.[4–7] We present herein a facile synthesis of two oligosaccharides consisting of (1→2)- and (1→3)-linked rhamnan backbone with a 2-*O*-D-Glc*p* side chain (**A**) or a 2-*O*-D-Glc*p*A side chain (**B**) on the rhamnose residues.



(**A**)



(**B**)

2. Results and discussion

Syntheses of the hexasaccharide consisting of two trisaccharide repeating units of the group E streptococci polysaccharide and the tetrasaccharide repeating unit of

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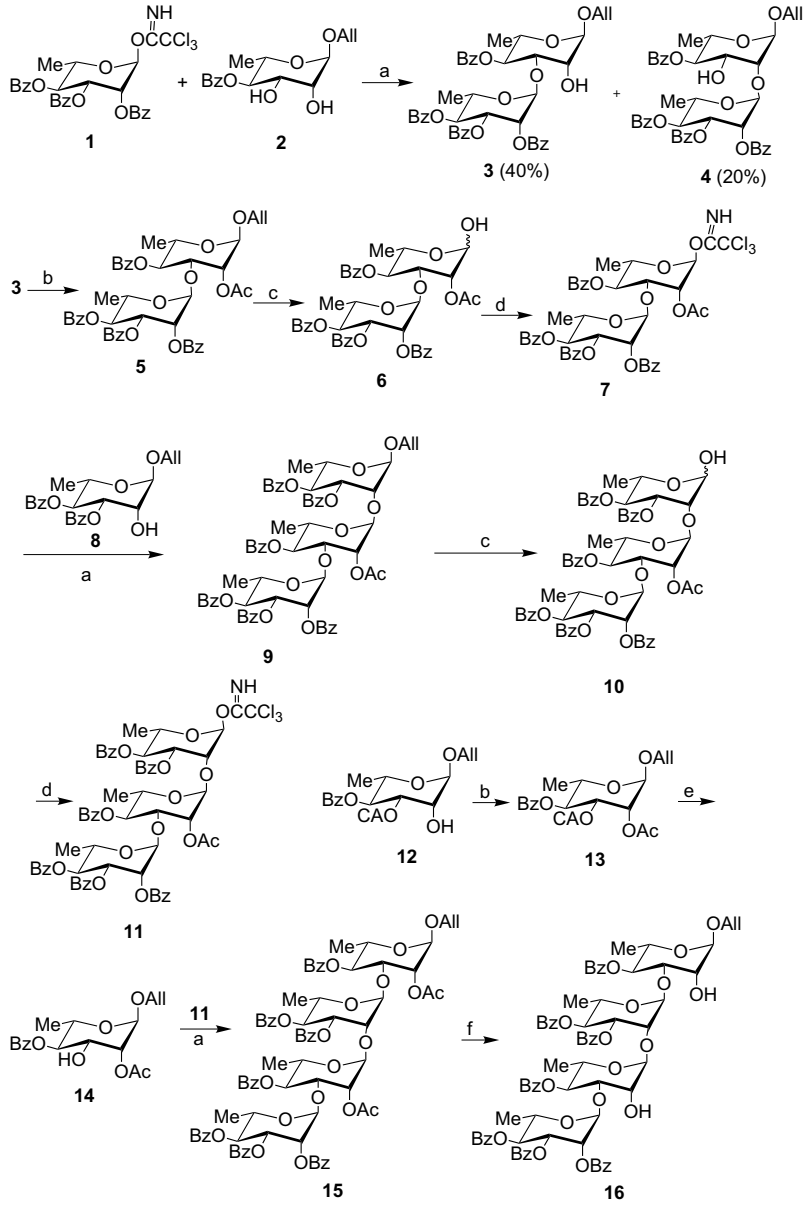
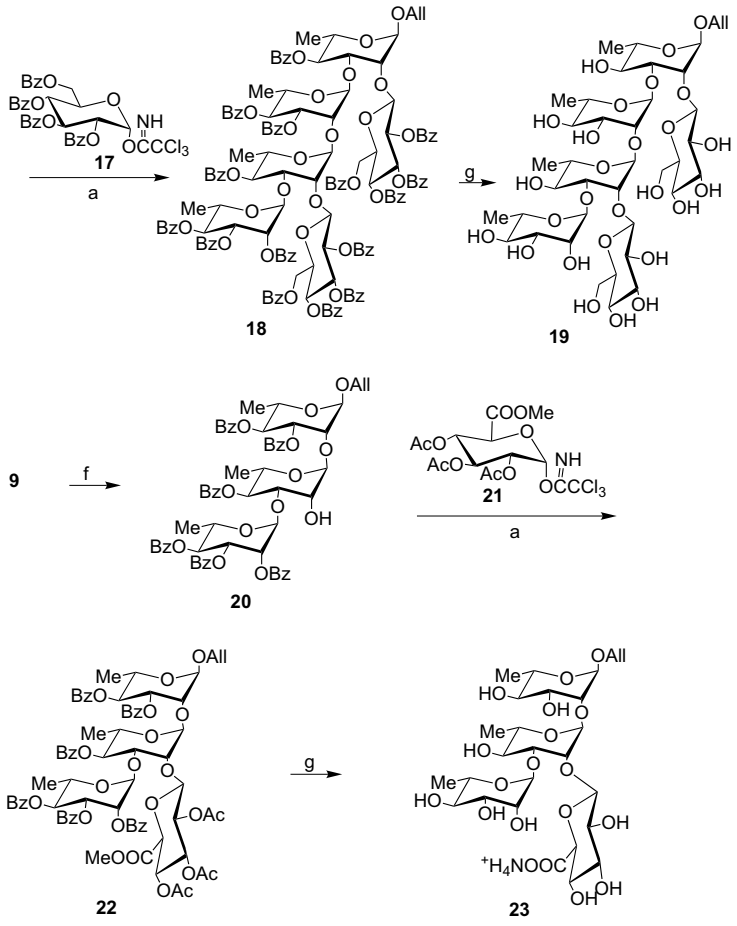
the *E. coli* O7:K98:H6 are outlined in Scheme 1. A strategy that first constructed the rhamnan backbone, then attached the side chains was used. Thus, allyl 4-*O*-benzoyl-α-L-rhamnopyranoside (**2**) was used as the starting material, since its 3-*O*-rhamnosylation with perbenzoylated rhamnosyl donor, followed by acetylation, produced a key building block with a potential free hydroxyl group at C-2. It has been reported[8] that condensation of the donor 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate[9] (**1**) with the unprotected acceptor, allyl α-L-rhamnopyranoside, selectively gave allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranoside in satisfactory yield (63.2%). In the present research, selective glycosylation of **2** with **1** similarly gave the α-(1 → 3)-linked disaccharide **3** (40%) as the major product, together with the α-(1 → 2)-linked disaccharide **4** (20%) and a small amount of allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-[2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)]-4-*O*-benzoyl-α-L-rhamnopyranoside. Since the unreacted **2** (21%) was recoverable and the disaccharides **3** and **4** were readily separated on a gram scale, owing to their relatively large difference in polarity, the selective rhamnosylation of **2** is an acceptable procedure in practical preparations. The regioselectivity was confirmed by benzoylation of **4**, and the ^{1}H NMR spectrum



Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, 0 °C to rt; (b) Ac_2O–pyridine (dry), rt, 12 h; (c) $PdCl_2$, MeOH–CH_2Cl_2, rt, 5 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt; (e) thiourea in 1:4 EtOH–CH_2Cl_2, reflux, 16 h; (f) 7% CH_3COCl–CH_3OH–CH_2Cl_2, rt; (g) satd NH_3–MeOH, rt, 2 weeks.



Scheme 1 *(continued)*

of the product showed the same data as that reported in the literature.[10] Acetylation of **3** gave **5**, whose H-2 at δ 5.34 ppm with $J_{1,2} = 1.8$ Hz and $J_{2,3} = 3.5$ Hz, also verified the 3-*O*-glycosylation. The donor **7** was obtained from disaccharide **5** by deallylation with $PdCl_2$,[11] and then by trichloroacetimidate formation with trichloroacetonitrile.[9] Coupling of **7** with allyl 3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**8**)[12] gave trisaccharide **9** in high yield (85%). Deallylation of **9**, followed by trichloroacetimidate formation, furnished trisaccharide donor **11**. Allyl 4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (**12**)[12] was converted to allyl 2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (**14**) by acetylation and dechloroacetylation. Compound **14** was also a key component since it contains another potential hydroxyl group at C-2 after its condensation with the trisaccharide donor **11**. The tetrasaccharide acceptor **16** with two free hydroxyl groups at C-2 and C-2″ was obtained by coupling of **14** with **11**, followed by 2-*O*-selective deacetylation by methanolysis.[13a] Due to the relatively large steric hindrance at 2- and 2″-OAc, 7% acetyl chloride in 1:2 methanol–dichloromethane (v/v) was used instead of the usual 2–3% concentration of reagent.[13b,c,d] Attachment of the side chains was carried out by coupling of **16** with perbenzoylated glucosyl trichloroacetimidate **17**, giving hexasaccharide **18** (52%). Deacylation of the protective hydroxyl groups with ammonia–saturated methanol gave the unprotected hexasaccharide **19** (94%) that was characterized by ^{13}C NMR and ^{1}H NMR spectroscopy. The signals at δ 5.25, 5.21, 5.09, 5.06 (4H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1), 4.84 (1H, $J_{1,2}$ 8.0 Hz, Glc*p* H-1), 4.80 (1H, $J_{1,2}$ 7.8 Hz, Glc*p* H-1), 103.9, 103.9 (2C, 2Glc*p* C-1), 102.0, 100.7, 100.4, 97.4 (4C, 4Rha*p* C-1) correspond with the designated structure.

2-*O*-Selective deacetylation of **9** gave the trisaccharide acceptor **20** (80%). Condensation of **20** with **21** yielded tetrasaccharide **22** (62%). Deacylation of **22** with ammonia–saturated methanol gave the unprotected tetrasaccharide **23** (95%) that showed characteristic NMR signals at δ 5.22, 5.04, 4.91 (3H, $J_{1,2}$ 1.3 Hz, Rha*p* H-1), 4.63 (1H, $J_{1,2}$ 7.6 Hz, Glc*p*A H-1), 103.9 (Glc*p*A C-1), 102.0, 100.7, and 96.9 (3C, 3Rha*p* C-1).

In summary, we have presented herein a convergent method that can be applied to the synthesis of (1 → 2)- and (1 → 3)-linked rhamnans with β-linked GlcA and Glc side chains at O-2 of the rhamnose residue.

3. Experimental

3.1. General methods

Melting points were determined using a 'Mel-Temp' apparatus. Optical rotations were determined using a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm jacketed cell. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker ARX 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13} C) at 25 °C for solutions in $CDCl_3$ or D_2O as indicated, and individual resonances could not be identified with the specific sugar residues. Chemical shifts are expressed in ppm downfield from the Me_4Si absorption. Mass spectra were recorded on a VG Platform mass spectrometer in the electrospray-ionization (ESI) mode. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) sulfuric acid in MeOH or by UV detection. Column chromatography was conducted by the elution of columns (8×100 mm, 16×240 mm, 18×300 mm, 35×400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless-steel column packed with silica gel (Spherisorb SiO_2, 10 300 mm or 4.6×250 mm), differential refractometer (132-RI Detector), and a UV–vis detector (model 118). EtOAc–petroleum ether (bp 60–90 °C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature <560 °C under reduced pressure.

3.2. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (5)

To a cooled solution (0 °C) of **1** (3.10 g, 5.0 mmol) and **2** (1.54 g, 5.0 mmol) in anhyd CH_2Cl_2 (50 mL) was added TMSOTf (20 μL, 0.12 mmol). The mixture was stirred for 2 h, during which time the temperature was gradually raised to ambient temperature. The mixture was quenched with Et_3N (four drops) and then evaporated to give a residue that was purified by silica gel column chromatography with 4:1 petroleum ether–EtOAc as the eluent to give disaccharide **3** (1.53 g, 40%), disaccharide **4** (0.76 g, 20%), unreacted **2** (0.32 g, 21%), and a small mount of trisaccharide. To a solution of **3** (1.46 g, 1.9 mmol) in pyridine (10 mL) was added Ac_2O (5 mL). The mixture was stirred for 2 h at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicted that the reaction was complete. The mixture was dried and co-vaporized with toluene (5 mL) three times. The residue was purified by chromatography with 4:1 petroleum ether–EtOAc as the eluent to give disaccharide **5** (1.41 g, 92%) as a foamy solid. $[\alpha]_D^{25}$ +141.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.18 (m, 20H, Bz-*H*), 5.95 (m, 1H, $CH_2CH{=}CH_2$), 5.65 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.9 Hz, H-3′), 5.54 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4′), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.39 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.4 Hz, H-2′), 5.53 (d, 1H, *J* 1.5 Hz, *J* 17.2 Hz, CH_2–$CH{=}CH_2$), 5.34 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.25 (d, 1H, *J* 1.3 Hz, *J* 10.4 Hz, CH_2–$CH{=}CH_2$), 5.16 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1′), 4.88 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.44 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.26–4.00 (m, 4H, H-5′, H-5, $2CH_2CH{=}CH_2$), 2.33 (s, 3H, CH_3CO), 1.33 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6′), 1.30 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6). Anal. Calcd for $C_{45}H_{44}O_{14}$: C, 66.82; H, 5.48. Found: C, 66.69; H, 5.42.

3.3. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (7)

To a solution of compound **5** (3.4 g, 4.2 mmol) in MeOH (100 mL) was added $PdCl_2$ (50 mg, 0.28 mmol), and the mixture was stirred at rt for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the filter cake was washed with CH_2Cl_2, and the combined filtrate and washings were concentrated. Purification by column chromatography with 4:1 petroleum ether–EtOAc as the eluent afforded compound **6**. A mixture of **6**, trichloroacetonitrile (2.1 mL, 10 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU, 0.20 mL, 1.6 mmol) in dry CH_2Cl_2 (50 mL) was stirred for 3 h and then concentrated. The residue was purified by flash chromatography with 4:1 petroleum ether–EtOAc as the eluent to give **7** (3.1 g, 81% for two steps) as a white foam. $[\alpha]_D^{25}$ +186.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H, $CNHCCl_3$), 8.08–7.21 (m, 20H, Bz-*H*), 6.31 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 5.67 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.1 Hz, H-3′), 5.61–5.51 (m, 3H, H-2′, H-4, H-4′), 5.36 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.19 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1′), 4.51 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.9 Hz, H-3), 4.28 (ddd, 1H, $J_{4,5}$ 9.9 Hz, $J_{5,6}$ 6.2 Hz, H-5′), 4.17 (ddd, 1H, $J_{4,5}$ 9.9 Hz, $J_{5,6}$ 6.3 Hz, H-5), 2.38 (s, 3H, CH_3CO), 1.35 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6′), 1.31 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6). Anal. Calcd for $C_{44}H_{40}Cl_3NO_{14}$: C, 57.87; H, 4.42. Found: C, 57.62; H, 4.39.

3.4. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (9)

Donor **7** (3.0 g, 3.28 mmol) and acceptor **8** (1.18 g, 2.86 mmol) were coupled in the presence of a catalytic amount of TMSOTf (20 μL, 0.11 mmol) under the same conditions as described for the coupling of **2** with **1**. Purification by chromatography with 3:1 petroleum ether–EtOAc as the eluent gave triasaccharide **9** (2.83 g, 85%) as a foamy solid. $[\alpha]_D^{25}$ +129.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–7.15 (m, 30H, Bz-*H*), 6.02–5.89 (m, 3H, H-2″, H-3″, $CH_2CH{=}CH_2$), 5.85 (dd,

1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.76 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4″), 5.63 (dd, 1H, $J_{3,4} = J_{4,5} =$ 9.9 Hz, H-4′), 5.61 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.48 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1″), 5.45 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1′), 5.34 (d, 1H, J 1.4 Hz, J 17.2 Hz, CH_2–C*H*=CH_2), 5.27 (dd, 1H, $J_{1,2}$ 1.7 Hz,$J_{2,3}$ 3.5 Hz, H-2′), 5.26 (d, 1H, J 1.4 Hz, J 10.4 Hz, CH_2–CH=C*H*$_2$), 5.09 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 4.47–4.00 (m, 7H, H-2, H-3′, H-5″, H-5′, H-5, 2C*H*$_2$CH=CH_2), 2.04 (s, 3H, C*H*$_3$CO), 1.39 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6″), 1.38 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6′), 1.30 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{65}H_{62}O_{20}$: C, 67.12; H, 5.37. Found: C, 66.89; H, 5.46.

3.5. 2,3,4-Tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl trichloroacetimidate (11)

To a solution of **9** (2.8 g, 2.4 mmol) in MeOH (100 mL) was added $PdCl_2$ (30 mg, 0.17 mmol), and the mixture was stirred at rt for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the filter cake was washed with CH_2Cl_2, and the combined filtrate and washings were concentrated. Purification by column chromatography with 3:1 petroleum ether–EtOAc as the eluent afforded compound **10**. A mixture of **10**, trichloroacetonitrile (1.1 mL, 5 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.10 mL, 0.8 mmol) in dry CH_2Cl_2 (50 mL) was stirred for 3 h and then concentrated. The residue was purified by chromatography with 4:1 petroleum ether–EtOAc as the eluent to give **11** (2.4 g, 79% for two steps) as a white foam. $[\alpha]_D^{25}$ +93.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H, CN*H*CCl_3), 8.10–7.22 (m, 30H, Bz-*H*), 6.43 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 5.78 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3″), 5.69 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4″), 5.67 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.2 Hz, H-3), 5.59 (dd, 1H, $J_{3,4} = J_{4,5} =$ 9.8 Hz, H-4′), 5.57 (dd, 1H, $J_{1,2}$ 1.4 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.52 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.38 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.2 Hz, H-2′), 5.24 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1″), 5.03 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1′), 4.58 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3′), 4.51 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.2 Hz, H-2), 4.39–4.30 (m, 2H, H-5″, H-5′), 4.18 (ddd, 1H, $J_{4,5}$ 10.0 Hz, $J_{5,6}$ 6.2 Hz, H-5), 2.24 (s, 3H, C*H*$_3$CO), 1.41 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6″), 1.39 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6′), 1.33 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{64}H_{58}Cl_3NO_{20}$: C, 60.65; H, 4.61. Found: C, 60.41; H, 4.74.

3.6. Allyl 2-*O*-acetyl-4-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (13)

To a solution of **12** (3.84 g, 10 mmol) in pyridine (30 mL) was added Ac_2O (10 mL). The mixture was stirred for 2 h at rt, at the end of which time TLC (4:1 petroleum ether–EtOAc) indicted that the reaction was complete. The mixture was dried and co-vaporized with toluene (10 mL) three times. The residue was purified by chromatography with 4:1 petroleum ether–EtOAc as the eluent to give **13** (3.88 g, 91%) as a foamy solid. $[\alpha]_D^{25}$ +152.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.43 (m, 5H, Bz-*H*), 5.95 (m, 1H, CH_2C*H*=CH_2), 5.65 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.1 Hz, H-3), 5.38 (dd, 1H, $J_{3,4} = J_{4,5} = 10.1$ Hz, H-4), 5.36 (d, 1H, J 1.5 Hz, J 17.2 Hz, CH_2–C*H*=C*H*$_2$), 5.33 (dd, 1H, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.53 (d, 1H, J 1.5 Hz, J 10.4 Hz, CH_2–CH=C*H*$_2$), 5.16 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 4.26–4.00 (m, 3H, H-5, 2C*H*$_2$CH=C*H*$_2$), 3.89, 3.88 (ABq, 2H, J 18.2 Hz, ClC*H*$_2$CO), 2.18 (s, 3H, C*H*$_3$CO), 1.28 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{20}H_{23}ClO_8$: C, 56.28; H, 5.43. Found: C, 56.11; H, 5.38.

3.7. Allyl 2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (14)

Thiourea (1.6 g, 20.9 mmol) was added to a solution (100 mL) of **13** (1.63 g, 3.81 mmol) in MeOH and CH_2Cl_2 (v/v, 1:2), then the reaction mixture was refluxed for 17 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to 1/5 of the original volume, diluted with CH_2Cl_2, and washed with satd aq $NaHCO_3$ and water, and the organic phase was dried and concentrated. Purification by silica gel chromatography with 3:1 petroleum ether–EtOAc as the eluent afforded **14** (1.16 g, 87 %). $[\alpha]_D^{25}$ +154.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.43 (m, 5H, Bz-*H*), 5.89 (m, 1H, CH_2C*H*=CH_2), 5.31 (d, 1H, J 1.5 Hz, J 17.2 Hz, CH_2–C*H*=CH_2), 5.22 (d, 1H, J 1.5 Hz, J 10.4 Hz, CH_2–CH=C*H*$_2$), 5.13–5.06 (m, 2H, H-2, H-4), 4.86 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 4.22–3.94 (m, 4H, H-3, H-5, C*H*$_2$CH=CH_2), 2.16 (s, 3H, C*H*$_3$CO), 1.24 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.42; H, 6.39.

3.8. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-2-*O*-acetyl-4-*O*-benzoyl-α-L-rhamnopyranoside (15)

Compound **11** (1.52 g, 1.2 mmol) and **14** (351 mg, 1.0 mmol) were coupled in the presence of catalytic TMSOTf (20 μL, 0.11 mmol) under the same conditions as described for the coupling of **2** with **1**. Purification by silica gel chromatography with 3:1 petroleum ether–EtOAc as the eluent gave tetrasaccharide **15** (1.31 g, 90%) as a foamy solid. $[\alpha]_D^{25}$ +208.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.15 (m, 35H, Bz-*H*), 5.93 (m, 1H, CH_2C*H*=CH_2), 5.65–5.52 (m, 3H, 2H-3, H-4), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.42–5.29 (m, 6H, 3H-2, CH_2–CH=C*H*$_2$, 2H-4), 5.26 (d, 1H, J 1.4 Hz, J 10.4 Hz, CH_2–CH=C*H*$_2$), 5.18 (d, 1H, $J_{1,2}$

1.4 Hz, H-1), 5.12 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.86 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.54 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.46 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.40 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.7 Hz, H-3), 4.35–3.78 (m, 7H, H-2, 4H-5, CH_2CH=CH_2), 2.33 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 1.36 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.29 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 0.92 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 169.8 (2C, 2CH_3CO), 165.7, 165.6, 165.5, 165.4, 165.1, 165.1, 164.6 (7C, 7Ph*C*O), 133.4–128.6 (*Ph*CO, –CH_2–*C*H=CH_2), 117.9 (1C, –CH_2–CH=*C*H_2), 100.0, 99.3, 98.5, 96.6 (4C, 4C-1), 73.8, 73.7, 73.4, 72.5, 71.6, 71.4, 71.3, 70.8, 70.4, 70.3, 69.2, 68.4, 67.6, 67.5, 67.4, 66.7 (C-2–5, –*C*H_2–CH=CH_2), 20.9, 20.8 (2C, 2*C*H_3CO), 17.5, 17.4, 17.4, 17.1 (4C, 4C-6). Anal. Calcd for $C_{80}H_{78}O_{26}$: C, 66.02; H, 5.40. Found: C, 65.93; H, 5.52.

3.9. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-benzoyl-α-L-rhamnopyranoside (16)

To a solution of **15** (1.1 mg, 0.74 mmol) in mixed solvents of MeOH (33 mL) and CH_2Cl_2 (67 mL) was added AcCl (7 mL). The mixture was stirred at rt until the TLC (2:1 petroleum ether–EtOAc) suggested that the reaction was complete. The mixture was dried, and purified by silica gel chromatography with 2:1 petroleum ether–EtOAc as the eluent to give **16** (612 mg, 62%) as a foamy solid. $[\alpha]_D^{25}$ +155.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.19 (m, 35H, Bz-*H*), 5.93 (m, 1H, CH_2C*H*=CH_2), 5.81–5.17 (m, 10H, 1H-1, 1H-2, 2H-3, 4H-4, CH_2–CH=CH_2), 5.14 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.96 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1), 4.36–3.78 (m, 11H, 3H-2, 2H-3, 4H-5, CH_2CH=CH_2), 1.36 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.29 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 0.99 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6).^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 165.7, 165.7, 165.5, 165.2, 165.1, 164.6 (7C, 7Ph*C*O), 133.6–128.1 (*Ph*CO, –CH_2–*C*H=CH_2), 117.7 (1C, –CH_2–CH=*C*H_2), 100.1, 100.4, 98.8, 98.4 (4C, 4C-1), 75.8, 73.3, 72.9, 71.8, 71.5, 71.3, 71.0, 70.4, 69.4, 68.3, 67.6, 67.5, 67.4, 66.6, 60.4 (C-2–5, –*C*H_2–CH=CH_2), 17.6, 17.5, 17.5, 17.3 (4C, 4C-6). Anal. Calcd for $C_{76}H_{74}O_{24}$: C, 66.56; H, 5.44. Found: C, 66.37; H, 5.37.

3.10. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranoside (18)

Compound **16** (345 mg, 0.25 mmol) and **17** (555 mg, 0.75 mmol) were coupled in the presence of a catalytic amount of TMSOTf (10 μL, 0.06 mmol) under the same conditions as described for the coupling of **2** with **1**. Purification by a chromatography with 3:1 petroleum ether–EtOAc as the eluent gave hexasaccharide **18** (331 mg, 52%) as a foamy solid. $[\alpha]_D^{25}$ +100.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–7.11 (m, 75H, Bz-*H*), 6.22 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 6.14 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.95 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.87–5.16 (m, 14H, 1H-1, 3H-2, 3H-3, 4H-4, CH_2–C*H*=CH_2, CH_2–CH=CH_2), 4.97 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.94 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.94 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.69–3.54 (m, 17H, 3H-2, 2H-3, 6H-5, 4H-6, CH_2CH=CH_2), 1.52 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.35 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 0.99 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.9, 165.9, 165.6, 165.5, 165.5, 165.5, 165.5, 165.4, 165.2, 165.2, 165.0, 164.9, 164.8, 164.4 (15C, 15Ph*C*O), 133.76–128.1 (*Ph*CO, –CH_2–*C*H=CH_2), 117.1 (1C, –CH_2–CH=*C*H_2), 101.0 ($J_{C\text{-}1,H\text{-}1}$ 162.1 Hz, β-C-1), 100.4 ($J_{C\text{-}1,H\text{-}1}$ 167.6 Hz, β-C-1), 99.2 ($J_{C\text{-}1,H\text{-}1}$ 177.6 Hz, α-C-1), 98.4 ($J_{C\text{-}1,H\text{-}1}$ 172.3 Hz, α-C-1), 98.3 ($J_{C\text{-}1,H\text{-}1}$ 172.3 Hz, α-C-1), 98.3 ($J_{C\text{-}1,H\text{-}1}$ 172.3 Hz, α-C-1), 77.4, 76.2, 74.1, 73.8, 73.7, 73.6, 72.9, 72.2, 72.1, 72.0, 71.9, 71.6, 70.6, 70.1, 69.7, 69.3, 69.1, 68.4, 68.3, 68.1, 67.3, 62.7, 62.4, 60.4 (27C, C-2–5, C-6, –*C*H_2–CH=CH_2), 17.8, 17.7, 17.2, 16.6 (4C, 4C-6). Anal. Calcd for $C_{144}H_{126}O_{42}$: C, 68.40; H, 5.02. Found: C, 68.20; H, 4.93.

3.11. Allyl α-L-rhamnopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-α-L-rhamnopyranoside (19)

Compound **18** (301 mg, 0.12 mmol) was dissolved in satd ammonia–MeOH (10 mL). After 2 weeks at rt, the reaction mixture was concentrated, and the residue was purified on a BioGel P2 column with MeOH–water as the eluent to afford **19** (105 mg, 93%) as an amorphous solid. $[\alpha]_D^{25}$ −153.5 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.93 (m, 1H, OCH_2C*H*=CH_2), 5.33 (dd, 1H, *J* 1.4 Hz, *J* 17.2 Hz, CH_2–CH=CH_2), 5.28 (dd, 1H, *J* 1.4 Hz, *J* 10.2 Hz, CH_2–CH=CH_2), 5.25 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 5.21 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 5.09 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 5.06 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.84 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.80 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.58–3.31 (m, 30H, H-2–5, 4H-6, CH_2CH=CH_2), 1.32 (d, 3H, $J_{5,6}$ 5.6 Hz, H-6), 1.30 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6), 1.28 (d, 3H, $J_{5,6}$ 5.8 Hz, H-6), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, D_2O): δ 134.0 (1C, –CH_2–*C*H=CH_2), 118.1 (1C, –CH_2–CH=*C*$_2$), 103.9, 103.9, 102.0, 100.7, 100.4, 97.4 (6C, 6C-1), 78.9, 77.6, 76.3, 75.9, 75.5, 75.3, 73.0, 72.1, 71.9, 71.8, 71.6, 70.4, 69.9, 69.8, 69.7, 69.2, 68.9, 68.5, 67.9, 60.3 (27C, C-2–5, 2C-6, –*C*H_2–CH=CH_2), 16.5, 16.4, 16.3, 16.2 (4C, 4C-6). Anal. Calcd for $C_{39}H_{66}O_{27}$: C, 48.44; H, 6.88. Found: C, 48.29; H, 6.90.

3.12. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (20)

To a solution of **9** (512 mg, 0.44 mmol) in mixed solvents of MeOH (33 mL) and CH_2Cl_2 (67 mL) was added AcCl (5 mL). The mixture was stirred at rt until the TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was dried and purified by chromatography with 2:1 petroleum ether–EtOAc as the eluent to give **20** (395 mg, 80%) as a foamy solid. $[\alpha]_D^{25}$ +127.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.23 (m, 30H, Bz-*H*), 5.97 (m, 1H, OCH_2-C*H*=CH_2), 5.76 (dd, 1H, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.9 Hz, H-3″), 5.69 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.9 Hz, H-3), 5.63 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4″), 5.58 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4′), 5.49 (dd, 1H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4), 5.44 (dd, 1H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.5 Hz, H-2″), 5.37 (dd, 1H,*J* 1.4 Hz, *J* 17.2 Hz, CH_2–CH=CH_2), 5.29 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1″), 5.27 (dd, 1H, *J* 1.4 Hz, *J* 10.4 Hz, CH_2–CH=CH_2), 5.03 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1′), 5.02 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.45 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3′), 4.35 (dd, 1H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.2 Hz, H-2), 4.35–4.26 (m, 4H, 2H-2′, H-5″, 1CH_2CH=CH_2), 4.15–4.07 (m, 3H, H-5′, H-5, 1CH_2CH=CH_2), 1.39 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6″), 1.34 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6′), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 165.6, 165.5, 165.5, 165.1, 164.6 (6C, 6Ph*C*O), 133.4–128.1 (*Ph*CO, –CH_2–*C*H=CH_2), 117.8 (1C, –CH_2–CH=*C*H_2), 101.5, 98.9, 97.7 (3C, 3C-1), 77.2, 76.0, 76.5, 72.9, 71.8, 71.7, 71.1, 70.4, 69.3, 68.3, 67.6, 67.5, 66.8 (13C, C-2–5, –*C*H_2–CH=CH_2), 17.6, 17.5, 17.4 (3C, 3C-6). Anal. Calcd for $C_{63}H_{60}O_{19}$: C, 67.49; H, 5.39. Found: C, 67.42; H, 5.46.

3.13. Allyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-[methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-uronate-(1 → 2)]-4-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzoyl-α-L-rhamnopyranoside (22)

Donor **21** (109 mg, 0.23 mmol) and acceptor **20** (214 mg, 0.19 mmol) were coupled in the presence of a catalytic amount of TMSOTf (3 μL, 0.02 mmol) under the same conditions as described for the coupling of **2** with **1**. Purification by a chromatography with 2:1 petroleum ether–EtOAc as the eluent gave tetrasaccharide **22** (169 mg, 62%) as a foamy solid. $[\alpha]_D^{25}$ +134.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–7.23 (m, 30H, Bz-*H*), 5.95 (m, 1H, OCH_2C*H*=CH_2), 5.81 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.67 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.64 (dd, 1H, $J_{3,4} = J_{4,5} =$ 10.0 Hz, H-4), 5.57 (dd, 1H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.45–5.23 (m, 7H, H-1, H-2, H-3, 2H-4, $2CH_2$–CH=CH_2), 5.21 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 5.15 (d, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.6 Hz, H-2), 5.06 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 5.02 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.55 (d, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.0 Hz, H-3), 4.38–4.04 (m, 8H, 2H-2, H-3, 3H-5, 2CH_2CH=CH_2), 3.83 (d, 1H, $J_{5,6}$ 10.0 Hz, H-5), 3.46 (s, 3H, COOCH_3), 2.32 (s, 3H, CH_3CO), 2.04 (s, 3H, CH_3CO), 2.01 (s, 3H, CH_3CO),1.50 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6), 1.34 (d, 3H, 6.2 Hz, H-6), 1.23 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.9, 169.4, 166.8 (4C, 3CH_3CO, *C*OOCH_3), 165.8, 165.4, 165.3, 165.3, 164.9, 164.7 (6C, 6Ph*C*O), 133.4–128.1 (*Ph*CO, –CH_2–*C*H=CH_2), 117.9 (1C, –CH_2–CH=*C*H_2), 101.1, 100.9, 98.5, 97.8, (4C, J_{C1-H1} 174.4, 165.0, 171.2, 170.2 Hz, 4C-1), 76.8, 74.7, 73.1, 72.0, 71.9, 71.8, 71.7, 71.3, 70.9, 70.5, 69.4, 68.9, 68.3, 68.1, 67.9, 66.8, 52.5 (17C, C-2–5, –*C*H_2–CH=CH_2), 29.6 (C, COO*C*H_3), 22.6, 20.6, 20.5 (3C, 3*C*H_3CO), 17.7, 17.5, 17.5 (3C, 3C-6). Anal. Calcd for $C_{76}H_{76}O_{28}$: C, 63.50; H, 5.33. Found: C, 63.31; H, 5.28.

3.14. Allyl α-L-rhamnopyranosyl-(1 → 3)-[β-D-glucopyranosyluronic acid-(1 → 2)]-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside, ammonium salt (23)

Compound **22** (142 mg, 0.10 mmol) was dissolved in a satd ammonia–MeOH (10 mL). After 2 weeks at rt, the reaction mixture was concentrated, and the residue was purified on a BioGel P2 column with MeOH–water as the eluent to afford **23** (64 mg, 95%) as an amorphous solid. $[\alpha]_D^{25}$ +180.3 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.94 (m, 1H, OCH_2C*H*=CH_2), 5.34 (dd, 1H, *J* 1.4, *J* 17.2 Hz, CH_2–CH=CH_2), 5.29 (dd, 1H, *J* 1.4 Hz, *J* 10.2 Hz, CH_2–CH=CH_2), 5.22 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 5.04 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.91 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.63 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.23–3.37 (m, 18H, H-2–5, 2CH_2CH=CH_2), 1. 32 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6), 1.29 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (100 MHz, D_2O): δ 172.9 (C, *C*OONH_4^+), 134.2 (1C, –CH_2–*C*H=CH_2), 118.4 (1C, –CH_2–CH=*C*H_2), 103.9, 102.0, 100.7, 96.9 (4C, 4C-1), 79.2, 78.2, 76.2, 74.7, 74.6, 74.5, 72.5, 71.9, 71.6, 71.1, 69.8, 69.7, 69.1, 68.6, 67.9 (18C, C-2–5, C-6, –*C*H_2–CH=CH_2), 16.5, 16.3, 16.1 (3C, 3C-6). MALDI-TOF MS: Calcd for the ammonium salt of **23**, C_{27} H_{47} NO_{19}: 689.6 [M]. Found: 689.3; 694.3 ($M-NH_4^+ + Na^+$).

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