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Note

Concise synthesis of the trisaccharide repeating unit of the O-polysaccharide from *Aeromonas hydrophila* A19 (O:14)

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ABSTRACT

Chemical synthesis of the trisaccharide repeating unit of the O-polysaccharide from *Aeromonas hydrophila* A19 (O:14) is reported in the form of its *p*-methoxyphenyl glycosides. Suitably protected monosaccharide synthons were prepared either by literature procedure or by strategies developed in house. Stereoselective glycosylations were accomplished by the activation of thioglycosides using N-iodosuccinimide in conjunction with H_2SO_4–silica in good to excellent yields.

Bacterial O-polysaccharide (O-antigen) is important for various host–pathogen interaction mechanisms such as adhesion to the epithelial cells, resistance to the antimicrobial compounds and immunostimulatory activities. Thus, the repeating unit of the O-polysaccharide is of particular interest to elucidate the exact biological activities they are involved in. *Aeromonas hydrophila* is a Gram-negative mesophilic motile bacterium of the family *Aeromonadaceae*.[1] Initial understanding indicated that they are important pathogens for fish and other cold-blooded species.[2] However, in recent times it has been established that the genus *Aeromonas* is also responsible for various human infections in both immuno-competent like gastroenteritis and wound infection and immuno-compromised patients. It can lead to grave diseases like septicemia.[3–5] Out of the 24 species belonging to the genus *Aeromonadaceae*, only three (*A. hydrophila, A. caviae* and *A. veronii* bv. *Sobria*) are found in 85% of human infections and clinical isolates.[6] Recently, Corsaro et al.[7] reported the structure of the O-polysaccharide isolated from *A. hydrophila* A19 (O:14) that has a trisaccharide repeating unit containing two α-D-glucose and one α-L-rhamnose moieties. In this communication we report the chemical synthesis of the trisaccharide repeating unit in the form of its *p*-methoxyphenyl glycoside (**1**, Fig. 1).

The known *p*-tolyl 2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (**3**)[8] was acetylated using Ac_2O in pyridine to afford the corresponding diacetate compound **4** in 93% yield. It was then glycosylated with the known acceptor **2** using NIS in the presence of H_2SO_4–silica[9–13] at −40 °C to furnish the 1,2-*cis* disaccharide **5** in 89% isolated yield. The particular donor having 6-*O*-acetyl group is suitable for the α-glycosylation due to remote participation.[14] The use of H_2SO_4–silica as an alternative to the traditional Lewis acid promoters like TfOH[15] or TMSOTf[16] was found to be beneficial. The similar glycosylation reactions promoted by TfOH and TMSOTf afforded the desired disaccharide in 75% and 81% yields respectively. The solid promoter is easy to handle and can be weighed directly as required. It is devoid of toxic fumes associated with TfOH or TMSOTf and very stable at room temperature. The desiccant property of silica gel is also advantageous to maintain the dry condition in a glycosylation reaction. Further, regioselective opening of the benzylidene acetal of the disaccharide **5** using Et_3SiH in the presence of $BF_3{\cdot}Et_2O$[17] at 0 °C furnished the disaccharide acceptor **6** in 83% yield. Then, the disaccharide acceptor **6** was glycosylated with the known *p*-tolyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (**7**)[18] using NIS in the presence of H_2SO_4–silica afforded the trisaccharide **8** in 84% yield. Hydrogenolysis of the benzyl groups using H_2 in the presence of Pd–C as catalyst using the flow hydrogenation assembly (H-Cube®, ThalesNano, Hungary) afforded the trisaccharide triol **9** in 81% yield. Finally, Zemplén de-O-acetylation using NaOMe in MeOH furnished the target trisaccharide, *p*-methoxyphenyl 4-*O*-(α-L-rhamnopyranosyl)-α-D-glucopyranosyl-(1→2)-β-D-glucopyranoside (**1**) in 78% yield over two steps (Scheme 1).

In conclusion, we have developed a concise strategy for the synthesis of the trisaccharide repeating unit of the O-polysaccharide isolated from *Aeromonas hydrophila* A19 (O:14) in the form of its *p*-methoxyphenyl glycoside. Required glycosylations were accomplished by the activation of thioglycosides using N-iodosuccinimide in conjunction with H_2SO_4–silica in good to excellent yields with absolute stereoselectivity. The strategy developed is capable to achieve the target oligosaccharide in good quantity that leaves

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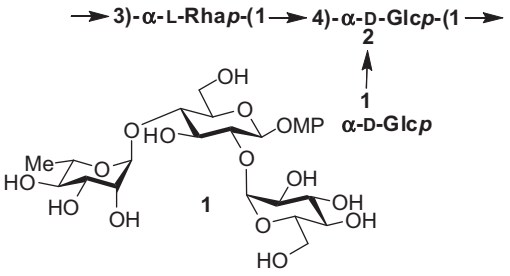


Figure 1. Structure of the repeating unit and the target trisaccharide **1**.

the scope for further utilization of the molecule in vaccine designing.

1. Experimental

1.1. General methods

All solvents and reagents were dried prior to use according to literature methods.[19] The commercially purchased reagents were used without any further purification unless mentioned otherwise. Dichloromethane wad dried and distilled over P_2O_5 to make it anhydrous and moisture-free. All reactions were monitored by Thin Layer Chromatography (TLC) on Silica Gel 60-F_{254} with detection by fluorescence followed by charring after immersion in 10% ethanolic solution of H_2SO_4. Flash chromatography was performed with Silica Gel 230–400 mesh. Optical rotations were measured on sodium D-line at ambient temperature. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE 500 MHz spectrometer.

1.2. Preparation of H_2SO_4–silica

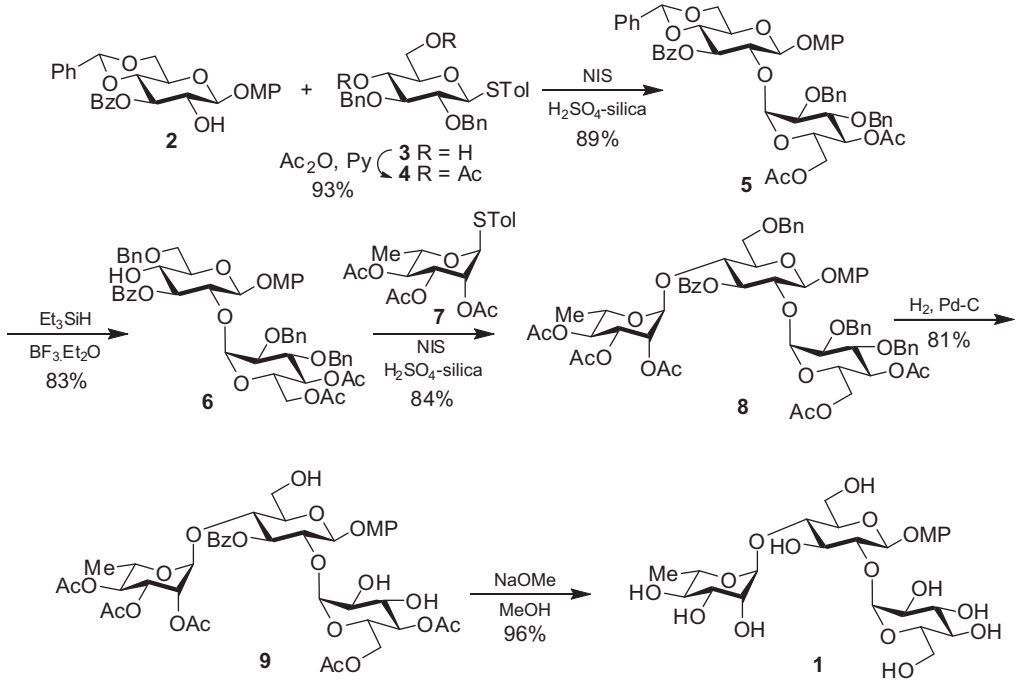
To slurry of silica gel (10 g, 200–400 mesh) in dry diethyl ether (50 mL) was added commercially available concentrated H_2SO_4 (1 mL) and the slurry shaken for 5 min. The solvent was evaporated under reduced pressure resulting in free flowing H_2SO_4–silica that was dried at 110 °C for 3 h and used for the reactions.

1.3. *p*-Tolyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (4)

To a solution of *p*-tolyl 2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (**3**) (3.0 g, 6.4 mmol) in dry pyridine (20 mL), Ac_2O (15 mL) was added and the solution was stirred at room temperature for 2 h when TLC (*n*-hexane–EtOAc; 2:1) showed complete conversion of the starting material to a faster moving compound. Then the solvents were evaporated in vacuo and co-evaporated with toluene. The residue was purified by flash chromatography using *n*-hexane–EtOAc (2:1) as eluent to afford pure compound **4** (3.3 g, 93%) as amorphous white mass. $[\alpha]_D^{25}$ +128 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.33–7.12 (m, 14H, Ar*H*), 5.04 (t, 1H, $J_{3,4}$, $J_{4,5}$ 10.0 Hz, H-4), 4.92, 4.83, 4.72, 4.65 (4d, 4H, AB system, *J* 11.0 Hz, CH_2Ph), 4.61 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1), 4.23 (dd, 1H, $J_{5,6a}$ 5.5 Hz, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.13 (dd, 1H, $J_{5,6b}$ 2.0 Hz, $J_{6a,6b}$ 12.0 Hz, H-6_b), 3.68 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 3.58 (m, 1H, H-5), 3.54 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-2), 2.36 (s, 3H, $SC_6H_4CH_3$), 2.09, 1.93 (2s, 6H, 2 × $COCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 170.6, 169.5 (2 × $COCH_3$), 138.0, 137.9, 137.8, 132.9(3), 129.6(2), 129.2, 128.4(3), 128.2(2), 127.9, 127.7(3) (ArC), 87.7 (C-1), 83.8, 80.5, 75.8, 75.4, 75.3, 69.7, 62.6 (C-6), 21.04, 20.7 (2 × $COCH_3$), 20.7 ($SC_6H_4CH_3$). HRMS calcd for $C_{31}H_{34}O_7SNa$ $(M+Na)^+$: 573.1923, found: 573.1919.

1.4. *p*-Methoxyphenyl-4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranosyl-(1→2)-4,6-*O*-benzylidene-3-*O*-benzoyl-β-D-glucopyranoside (5)

A mixture of acceptor **2** (1.0 g, 2.1 mmol), donor **4** (1.5 g, 2.7 mmol) and MS 4 Å (2.0 g) in dry CH_2Cl_2 (20 mL) was stirred under nitrogen atmosphere for 30 min at −40 °C. Then NIS (790 mg, 3.5 mmol) was added followed by H_2SO_4–silica (100 mg) and the mixture was stirred at −40 °C for another 30 min when TLC (*n*-hexane–EtOAc; 2:1) showed complete consumption of the acceptor.



Scheme 1. Synthesis of the trisaccharide **1**.

The mixture was filtered through a pad of Celite® and the filtrate was washed successively with aq $Na_2S_2O_3$ (2 × 30 mL), saturated $NaHCO_3$ (2 × 30 mL) and H_2O (30 mL). The organic layer was collected, dried (Na_2SO_4) and filtered. The solvent was evaporated in vacuo and the residue was purified by flash chromatography using *n*-hexane–EtOAc (2.5:1) as eluent to afford pure disaccharide **5** (1.7 g, 89%) as white amorphous mass. $[\alpha]_D^{25}$ +103 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.04–6.80 (m, 24H, Ar*H*), 5.84 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 5.72 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.54 (s, 1H, C*H*Ph), 5.38 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.85 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 9.5 Hz, H-4′), 4.83, 4.57, 4.54, 4.49 (4d, 4H, *J* 11.5 Hz, 2 × CH_2Ph), 4.40 (m, 1H, H-5), 4.22 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.5 Hz, H-2), 3.88 (t, 1H, $J_{3,4}$, $J_{4,5}$ 9.5 Hz, H-4), 3.86–3.78 (m, 3H, H-3′, H-6a, H-6b), 3.77 (s, 3H, $OC_6H_4OCH_3$), 3.72 (m, 1H, H-5′), 3.67 (dd, 1H, $J_{5',6a'}$ 2.0 Hz, $J_{6a',6b'}$ 12.5 Hz, H-6′$_a$), 3.58 (dd, 1H, $J_{5',6b'}$ 3.5 Hz, $J_{6a',6b'}$ 12.5 Hz, H-6′$_b$), 3.54 (dd, 1H, $J_{1',2'}$ 3.5 Hz, $J_{3',4'}$ 9.5 Hz, H-2′), 2.02, 1.52 (s, 6H, 2 × COCH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 169.3 (2 × *C*OCH$_3$), 165.1 (*C*OPh), 155.6, 149.9, 138.4, 137.5, 136.7, 133.5, 129.8(2), 128.6(2), 128.5(2), 128.4(3), 128.3(2), 128.2(3), 128.1(3), 126.1(3), 117.5(2), 114.8(2) (ArC), 101.7 (C-1), 101.4 (*C*HPh), 95.5 (C-1′), 79.0, 78.6, 78.1, 75.2, 74.6, 73.0, 72.3, 68.8, 68.5, 67.7, 66.3, 61.4, 55.6 ($C_6H_4OCH_3$), 20.7, 20.4 (2 × COCH_3). HRMS calcd for $C_{51}H_{52}O_{15}Na$ (M+Na)$^+$: 927.3204, found: 927.3207.

1.5. *p*-Methoxyphenyl-4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-3-*O*-benzoyl-β-D-glucopyranoside (6)

To a stirred solution of compound **5** (1.5 g, 1.65 mmol) and Et_3SiH (3.2 mL, 19.8 mmol) in dry CH_2Cl_2 (20 mL), $BF_3.Et_2O$ (420 μL, 3.3 mmol) was added at 0 °C and the mixture was allowed to stir for 2 min when TLC (*n*-hexane–EtOAc; 2:1) showed complete conversion of the starting material to a slower moving spot. The mixture was washed successively with H_2O (2 × 30 mL), saturated $NaHCO_3$ (2 × 30 mL) and brine (30 mL). The organic layer was collected, dried (Na_2SO_4) and filtered. The solvent was evaporated in vacuo and the residue was purified by flash chromatography using *n*-hexane–EtOAc (2:1) as eluent to afford pure disaccharide acceptor **6** (1.25 g, 83%) as colourless foam. $[\alpha]_D^{25}$ +117 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.07–6.77 (m, 24H, Ar*H*), 5.77 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.59 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5, H-3), 5.26 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 5.85 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 10.0 Hz, H-4′), 4.80 (d, 1H, *J* 11.5 Hz, CH_2Ph), 5.54 (m, 5H, CH_2Ph), 4.16 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.5 Hz, H-2), 3.99 (t, 1H, $J_{3,4}$, $J_{4,5}$ 9 Hz, H-4), 3.95–3.70 (m, 6H, H-3′, H-5, H-5′, H-6$_a$, H-6′$_a$, H-6′$_b$), 3.76 (s, 3H, $OC_6H_4OCH_3$), 3.63 (dd, 1H, $J_{5,6b}$ 4.0 Hz, $J_{6a,6b}$ 12.5 Hz, H-6$_b$), 3.54 (dd, 1H, $J_{1',2'}$ 3.5 Hz, $J_{2',3'}$ 10.0 Hz, H-2′), 2.98 (br s, 1H, O*H*), 2.04 (s, 3H, COCH_3), 1.48 (s, 3H, COCH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 169.2 (2 × *C*OCH$_3$), 166.1 (*C*OPh), 155.3, 150.1, 138.3, 137.4, 133.3, 129.8(2), 129.4, 128.4(3), 128.3(2), 128.1(2), 127.9(3), 127.8, 127.7(3), 127.5(3), 127.4, 117.5(2), 114.7(2) (ArC), 101.2 (C-1), 95.3 (C-1′), 79.0, 78.11, 76.1, 75.2, 74.2, 73.7, 73.4, 72.8, 71.0, 69.8, 68.8, 67.6, 61.5, 55.6 (O*C*H$_3$), 20.6, 20.3 (2 × *C*OCH$_3$). HRMS calcd for $C_{51}H_{54}O_{15}Na$ (M+Na)$^+$: 929.3360, found: 929.3356.

1.6. *p*-Methoxyphenyl-4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranosyl-(1→2)-6-*O*-benzyl-3-*O*-benzoyl-4-O-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside (8)

A mixture of acceptor **6** (1.0 g, 1.1 mmol), donor **7** (570 mg, 1.4 mmol) and MS 4 Å (1.5 g) in dry CH_2Cl_2 (15 mL) was stirred under nitrogen atmosphere for 30 min at 0 °C. Then, NIS (410 mg, 1.8 mmol) was added followed by H_2SO_4–silica (75 mg) and the mixture was stirred for another 30 min when TLC (*n*-hexane–EtOAc; 3:1) showed complete consumption of the acceptor. The mixture was filtered through a pad of Celite® and the filtrate was washed successively with aq $Na_2S_2O_3$ (2 × 30 mL), saturated $NaHCO_3$ (2 × 30 mL) and H_2O (30 mL). The organic layer was collected, dried (Na_2SO_4) and filtered. The solvent was evaporated in vacuo and the crude residue thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (2:1) as eluent to afford pure trisaccharide **7** (1.1 g, 84%) as white foam. $[\alpha]_D^{25}$ +97 (*c* 0.9, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.07–6.78 (m, 24H, Ar*H*), 5.76 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.74 (t, 1H, $J_{2,3}$, $J_{3,4}$ 10.5 Hz, H-3), 5.20 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 5.18 (dd, 1H, $J_{1'',2''}$ 1.5 Hz, $J_{2'',3''}$ 3.0 Hz, H-2″), 5.14 (dd, 1H, $J_{2'',3''}$ 3.0 Hz, $J_{3'',4''}$ 10.0 z, H-3″), 4.92 (d, 1H, $J_{1'',2''}$ 1.5 Hz, H-1″), 4.89 (t, 1H, $J_{3'',4''}$, $J_{4'',5''}$ 10.0 Hz, H-4″), 4.80 (d, 1H, *J* 11.0 Hz, $CH_2C_6H_5$), 4.79 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 9.0 Hz, H-4′), 4.54 (m, 5H, C$H_2C_6H_5$), 4.21 (t, 1H, $J_{3,4}$, $J_{4,5}$ 9.5 Hz, H-4), 4.13 (t, 1H, $J_{1,2}$, $J_{2,3}$ 7.5 Hz, H-2), 3.87 (dd, 1H, $J_{5',6a'}$ 3.5 Hz, $J_{6a',6b'}$ 11.5 Hz, H-6′$_a$), 3.81 (dd, 1H, $J_{5',6b'}$ 1.0 Hz, $J_{6a',6b'}$ 11.5 Hz, H-6′$_b$), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.77–3.68 (m, 3H, H-3′, H-5, H-5′), 3.61 (m, 2H, H-5″, H-6$_a$), 3.56 (dd, 1H, $J_{5,6b}$ 4.5 Hz, $J_{6a,6b}$ 13.0 Hz, H-6$_b$), 3.52 (dd, 1H, $J_{1',2'}$ 3.5 Hz, $J_{2',3'}$ 9.5 Hz, H-2′), 2.03, 2.01, 1.96, 1.93, 1.47 (5*s*, 15H, 5 × COCH_3). ^{13}C NMR ($CDCl_3$) δ: 171.0, 170.1, 170.0, 169.8, 169.2 (5 × *C*OCH$_3$), 165.1 (*C*OPh), 155.4, 150.2, 138.5, 137.9, 137.6, 133.5, 129.9(2), 129.8, 128.4(2), 128.3(3), 128.2(3), 128.0(3), 127.5(2), 127.4(4), 117.6(2), 114.7(2) (ArC), 101.3 (C-1), 99.2 (C-1″), 95.1 (C-1′), 79.0, 78.0, 77.2, 75.1, 74.5, 74.3, 73.9, 73.1, 72.8, 70.5, 69.8, 68.8, 68.6, 68.1, 67.7, 67.4, 61.3, 55.6 ($C_6H_4OCH_3$), 20.8, 20.7, 20.6(2), 20.4 (5 × *C*OCH$_3$), 16.9 (C-*C*H$_3$). HRMS calcd for $C_{63}H_{70}O_{22}Na$ (M+Na)$^+$: 1201.4256, found: 1201.4253.

1.7. *p*-Methoxyphenyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzoyl-4-O-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranoside (9)

A dilute solution of the protected trisaccharide **8** (1.0 g, 0.8 mmol) in MeOH (100 mL) containing AcOH (0.5 mL) was passed through the 10% Pd–C cartridge of a flow hydrogenation assembly (H-cube®, Thales Nano, Hungary) and the process was repeated three times for complete removal of the benzyl ethers. The solvents were evaporated in vacuo and the residue was purified by flash chromatography using CH_2Cl_2–MeOH (8:1) as eluent to afford pure compound **9** (620 mg, 81%) as white foam. $[\alpha]_D^{25}$ +123 (*c* 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.10–6.82 (m, 9H, Ar*H*), 5.60 (t, 1H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 5.51 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.13 (dd, 1H, $J_{1'',2''}$ 2.0 Hz, $J_{2'',3''}$ 3.5 Hz, H-2″), 5.10 (dd, 1H, $J_{2'',3''}$ 3.5 Hz, $J_{3'',4''}$ 10.0 Hz, H-3″), 5.07 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.95 (d, 1H, $J_{1'',2''}$ 1.5 Hz, H-1″), 4.88 (t, 1H, $J_{3'',4''}$, $J_{4'',5''}$ 10.0 Hz, H-4″), 4.73 (t, 1H, $J_{3',4'}$, $J_{4',5'}$ 9.5 Hz, H-4′), 4.16 (t, 1H, $J_{3,4}$, $J_{4,5}$ 9.5 Hz, H-4), 4.01 (t, 1H, $J_{1,2}$, $J_{2,3}$ 9.5 Hz, H-2), 4.00 (m, 1H, H-6′$_a$), 3.89 (dd, 1H, $J_{5',6b'}$ 3.0 Hz, $J_{6a',6b'}$ 12.0 Hz, H-6′$_b$), 3.77 (s, 3H, $C_6H_4OCH_3$), 3.69 (dd, 1H, $J_{5,6a}$ 3.5 Hz, $J_{6a,6b}$ 12.5 Hz, H-6$_a$), 3.62 (m, 5H, H-3′, H-5, H-5′, H-5″, H-6$_b$), 3.49 (dd, 1H, $J_{1',2'}$ 3.5 Hz, $J_{2',3'}$ 9.5 Hz, H-2′), 2.09, 1.99, 1.96, 1.90, 1.81 (s, 15H, 5 × COCH_3), 0.61 (d, 3H, J 6.5 Hz, –CH_3). ^{13}C NMR ($CDCl_3$) δ: 170.6, 170.5, 170.1(2), 169.7 (5 × *C*OCH$_3$), 165.7 (*C*OPh), 155.9, 150.3, 133.7, 129.9(2), 129.5, 128.6(2), 118.7(2), 114.8(2) (ArC), 101.9 (C-1), 98.7 (C-1″), 98.2 (C-1′), 76.4, 75.7, 75.3, 75.3, 72.5, 72.1, 70.4, 70.0, 69.4, 68.6, 68.1, 67.4, 61.2, 60.8, 55.6 ($C_6H_4OCH_3$), 20.9, 20.7(3), 20.6 (5 × *C*OCH$_3$), 16.8 (*C*H$_3$). HRMS calcd for $C_{42}H_{52}O_{22}Na$ (M+Na)$^+$: 931.2848, found: 931.2844.

1.8. *p*-Methoxyphenyl β-D-glucopyranosyl-(1→2)-4-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside (1)

To a solution of compound **9** (600 mg, 0.66 mmol) in MeOH (10 mL), NaOMe (1 mL, 0.5 M in MeOH) was added and the solution was stirred at room temperature for 12 h. The solution was neutralized by DOWEX 50 W H^+ resin, filtered through a cotton plug and the solvents were evaporated in vacuo to afford pure tar-

get trisaccharide **1** (375 mg, 96%) as white amorphous mass. $[\alpha]_D^{25}$ +78 (*c* 0.7, MeOH). ^{1}H NMR (CD_3OD, 500 MHz) δ: 7.05–6.77 (Ar*H*), 5.42 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.95 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.86 (s, 1H, H-1″), 4.08 (m, 1H, H-5), 3.95 (m, 1H, H-5″), 3.86–3.74 (m, 4H, H-2″, H-5′, H-6$_a$, H-6′$_a$), 3.71–3.60 (m, 8H, H-2, H-2′, H-3, H-3′, H-3″, H-4′, H-6$_b$, H-6′$_b$), 3.40–3.26 (m, 5H, H-4, H-4″, $C_6H_4OCH_3$), 1.23 (d, 3H, *J* 6.0 Hz, H-6″). ^{13}C NMR (CD_3OD, 125 MHz) δ: 156.8, 152.6, 119.8(2), 115.3(2) (Ar*C*), 103.5 (C-1), 102.8 (C-1″), 99.5 (C-1′), 79.5, 79.0, 76.7, 75.3, 74.9, 73.7, 73.6, 73.2, 72.3, 72.1, 71.5, 70.5, 62.3 (C-6), 61.6 (C-6′), 56.0 ($C_6H_4OCH_3$), 17.9 (C-6″).

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