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Concise synthesis of two trisaccharides related to the saponin isolated from *Centratherum anthelminticum*☆

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Dedicated to Dr. C. M. Gupta, Director, CDRI on the occasion of his superannuation

Abstract—Chemical synthesis of two trisaccharides related to the saponin isolated from *Centratherum anthelminticum* is reported. Stereoselective, high-yielding glycosylation strategies were developed using H_2SO_4 immobilized on silica for activation of trichloroacetimidate donors, or in conjunction with *N*-iodosuccinimide for activation of a thioglycoside. A late stage TEMPO-mediated oxidation was performed for the formation of the required uronic acid moiety.

1. Introduction

Saponins, the glycosylated secondary metabolites in plants, are important for growth and development.[1] Besides their roles in the plant kingdom, they often possess important biological activities that make them attractive medicinal targets for drug discovery against various diseases, for example, ginseng and liquorice.[2] As the saponins possess antifungal properties, they occur in high concentration in healthy plants acting as a preformed chemical barrier for fungal infections.[3] Although saponins earned a great deal of attraction for their biological properties with many of them in use commercially, detailed genetic machinery behind their formation in plants is not clearly understood. One common feature of all saponins is the presence of a sugar chain at 3-*O*-position mainly consisting of glucose, arabinose, glucuronic acid, xylose and rhamnose.[4] The glycosylation on the 3-*O*-position of the saponin aglycone, believed to be the terminal stage of its formation, is important for saponin bioactivities.[5] Therefore, in order to establish the order of events in saponin biosynthesis and elucidate the roles of glycosyltransferases involved, synthesis of the saccharide fragments becomes a useful target. Moreover, a synthetic route will in turn provide an alternative way to get hold of the biologically potent saponins, which require a rigorous exercise of isolation and chromatographic purification to obtain from natural sources. Therefore, chemical synthesis of such structures offers the scope of their use as medicines in future.

The plant, *Centratherum anthelminticum*, known as 'Somraj' and the seeds as 'kalijiri' in India, is a medicinally important plant.[6] It is well known as an ingredient of various folk medicines for the treatment of fever, cough, diarrhoea or used as general tonic. Medicinally attractive properties it possesses include anthelminthic, antiphlegmatic, cardiac, diuretic, febrifugal, alterative and digestive.[7] Recently, Mehta et al.[8] reported the isolation and structure elucidation of a new acetylated saponin from the methanol extract of the plant *C. anthelminticum*. In continuation to our effort towards the synthesis of various carbohydrate-based biodynamic molecules, here we report convergent chemical synthesis of two trisaccharides (**1** and **2**, Fig. 1) from commercially available monosaccharides through rational protecting group manipulations and sequential glycosylations.

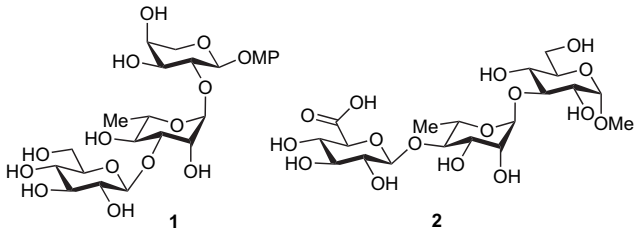

Figure 1. Target structure of the trisaccharides related to the saponin isolated from *C. anthelminticum*.

2. Results and discussion

2.1. Synthesis of the trisaccharide 1

Synthesis of the trisaccharide **1** was planned through the synthesis of Rha–Glc disaccharide from suitably protected

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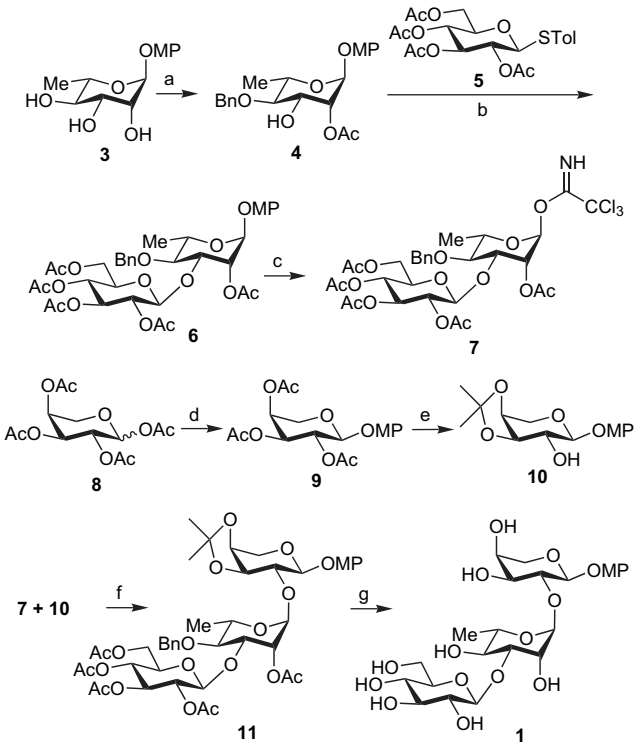
monosaccharide building blocks and final glycosylation with a suitable arabinopyranosyl acceptor. Thus, known *p*-methoxyphenyl α-L-rhamnopyranoside (**3**)[9] was subjected to sequential one-pot *ortho*-esterification–benzylation–*ortho*-ester rearrangement[10] to afford suitably protected acceptor **4** in 85% yield. Glycosylation of acceptor **4** with the known *p*-tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**5**)[11] donor was achieved by *N*-iodosuccinimide in the presence of H_2SO_4 immobilized on silica to afford the protected disaccharide (**6**) in 91% isolated yield on the basis of the acceptor used. Use of H_2SO_4–silica[12] instead of classical Lewis acid catalysts such as TfOH or TMSOTf proved to be advantageous as this solid acid source is much easier to handle and can be weighed neatly as required. Next, removal of the *p*-methoxyphenyl group using CAN in CH_3CN–H_2O (9:1)[13] followed by DBU catalyzed trichloroacetimidate formation[14] furnished the activated disaccharide donor **7** in 79% overall yield. For the preparation of the arabinose acceptor, known per-*O*-acetylated L-arabinopyranose (**8**)[11] was converted to the corresponding *p*-methoxyphenyl glycoside (**9**) through $BF_3{\cdot}Et_2O$ catalyzed glycosylation with *p*-cresol in 87% yield. Zemplén de-O-acetylation[15] followed by acid catalyzed acetonation using 2,2-DMP[16] afforded the required acceptor **10** in 83% yield over two steps. For the final glycosylation through trichloroacetimidate activation of the disaccharide donor **7**, H_2SO_4–silica has been used successfully to afford the protected trisaccharide **11** in 89% yield. Global deprotection of **11**, Pd–C catalyzed hydrogenation followed by opening of isopropylidene acetal using 80% AcOH at 80 °C[17] and de-O-acylation, furnished the target trisaccharide **1** in 78% yield over three steps (Scheme 1).



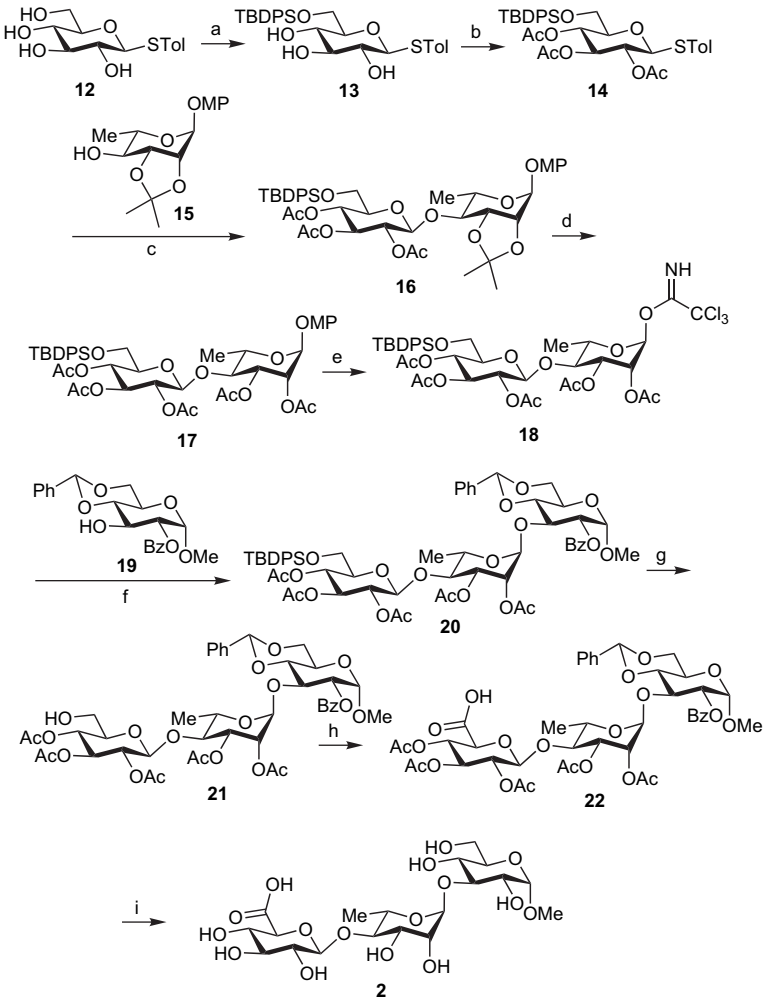
Scheme 1. Synthesis of trisaccharide **1**. Reagents and conditions: (a) (i) trimethyl *ortho*-acetate, CSA, CH_3CN, rt, 45 min; (ii) BnBr, NaH, rt, 45 min; (iii) 80% AcOH, rt, 1 h; (b) NIS, H_2SO_4–silica, CH_2Cl_2, MS 4 Å, 10 °C, 45 min; (c) (i) CAN, CH_3CN–H_2O, rt, 30 min; (ii) CCl_3CN, DBU, CH_2Cl_2, rt, 1 h; (d) *p*-cresol, $BF_3{\cdot}Et_2O$, CH_2Cl_2, rt, 3 h; (e) (i) NaOMe, MeOH; (ii) 2,2-DMP, CSA, acetone, rt, 30 min; (f) H_2SO_4–silica, CH_2Cl_2, −40 °C, 5 h; (g) (i) H_2, Pd–C, MeOH, rt, 6 h; (ii) 80% AcOH, 80 °C, 2 h; (iii) NaOMe, MeOH, rt, 3 h.

One can argue with the fact that the best possible way to make the trisaccharide **1** would be to prepare the Ara–Rha disaccharide followed by glycosylation with a suitable Glc donor. Initially we tried that route but found it to be unsuccessful with the choice of a suitable temporary protection at 3-OH of rhamnose moiety. Although chloroacetyl and *p*-methoxybenzyl groups are found to be suitable for making the Ara–Rha disaccharide, their selective deprotection was not compatible with the isopropylidene moiety on arabinose. Protection of the arabinose moiety with groups other than isopropylidene means increase in total number of steps. Therefore, we discarded that route.

2.2. Synthesis of the trisaccharide 2

In a similar fashion as for the synthesis of trisaccharide **1**, synthesis of trisaccharide **2** was planned through the formation of non-reducing end Rha–Glc disaccharide and final glycosylation with a suitably protected glucosyl acceptor to furnish the targeted scaffold. Thus, known *p*-tolyl 1-thio-β-D-glucopyranoside (**12**) was converted to the corresponding 6-*O*-*tert*-butyldiphenylsilyl derivative (**13**) using TBDPS-Cl in pyridine.[18] Per-O-acetylation of **13** with Ac_2O–pyridine afforded the protected donor **14** in 89% yield. Glycosylation of **14** with known *p*-methoxyphenyl 2,3-isopropylidene-α-L-rhamnopyranoside (**15**)[9] using NIS in the presence of H_2SO_4–silica furnished the protected disaccharide **16** in 86% yield.

At this point the isopropylidene group was deprotected using 80% AcOH at 80 °C followed by acetylation with Ac_2O–pyridine to afford the disaccharide **17** in 85% yield over two steps. Removal of the isopropylidene protection was necessary to avoid loss of compounds during later acid catalyzed transformations. CAN-mediated removal of the *p*-methoxyphenyl group[13] followed by DBU catalyzed trichloroacetimidate formation[14] led to the disaccharide donor **18** in 81% yield. Glycosylation of disaccharide donor **18** with known methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**19**) in the presence of H_2SO_4–silica afforded the trisaccharide **20** in 84% yield. Selective removal of the TBDPS group using Bu_4NF in THF produced the required trisaccharide **21** that is ready for oxidation to furnish the uronic acid moiety of the target molecule. At this stage, TEMPO-mediated oxidation of the primary hydroxyl to uronic acid was the target. Among different TEMPO-mediated[19] protocols available in the literature including the late stage oxidation approach by Nepogodiev et al.,[20] the procedure developed by Huang et al.[21] was particularly attractive for us as this protocol uses phase-transfer conditions suitable for protected oligosaccharides. Therefore, oxidation of compound **21** using similar conditions afforded the required uronic acid derivative **22** in 78% yield. Removal of the benzylidene acetal using 80% AcOH at 80 °C followed by de-O-acylation gave the target trisaccharide **2** as its methyl ester form in 81% yield (Scheme 2).



Scheme 2. Synthesis of trisaccharide **2**. Reagents and conditions: (a) TBDPS-Cl, Py, rt, 6 h; (b) Ac_2O, Py, rt, 2 h; (c) NIS, H_2SO_4–silica, CH_2Cl_2, MS 4 Å, 10 °C, 45 min; (d) (i) 80% AcOH, 80 °C, 2 h; (ii) Ac_2O, Py, rt, 2 h; (e) (i) CAN, CH_3CN–H_2O, rt, 30 min; (ii) CCl_3CN, DBU, CH_2Cl_2, rt, 1 h; (f) H_2SO_4–silica, CH_2Cl_2, −40 °C, 6 h; (g) Bu_4NF–THF, rt, 12 h; (h) TEMPO, NaOCl, $NaOCl_2$, CH_2Cl_2–H_2O, rt, 6 h; (i) (i) 80% AcOH, 80 °C, 2 h; (ii) NaOMe, MeOH, rt, 3 h.

3. Conclusion

We have developed convergent and efficient synthetic strategies for two trisaccharide fragments related to the saponin isolated from the methanol extract of the plant *C. anthelminticum*. H_2SO_4–silica has been used for the activation of glycosyl trichloroacetimidate and in conjunction with NIS for thioglycoside activation. This has proved to be an efficient and useful alternative to the classical Lewis acid catalysts that are corrosive and difficult to handle. The trisaccharides produced will be evaluated for their biological activities in due course.

4. Experimental

4.1. General methods

All reagents and solvents were dried prior to use according to standard methods.[22] Commercial reagents were used without further purification unless otherwise stated. Analytical TLC was performed on silica gel 60-F_{254} (Merck or Whatman) with detection by fluorescence and/or by charring following immersion in a 10% ethanolic solution of sulfuric acid. An orcinol dip, prepared by the careful addition of concentrated sulfuric acid (20 cm^3) to an ice-cold solution of 3,5-dihydroxytoluene (360 mg) in EtOH (150 cm^3) and water (10 cm^3), was used to detect deprotected compounds by charring. Flash chromatography was performed with silica gel 60 (Qualigens). Optical rotations were measured at the sodium D-line at ambient temperature, with a Perkin Elmer 141 polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 300 and 75 MHz, respectively, using Me_4Si or CH_3OH as internal standard, as appropriate.

Preparation of H_2SO_4–silica: To a slurry of silica gel (10 g, 200–400 mesh) in dry diethyl ether (50 mL) was added commercially available concd H_2SO_4 (1 mL) and shaken for 5 min. Solvents were evaporated under reduced pressure resulting in free flowing H_2SO_4–silica. It was then dried at 110 °C for 3 h and used for the reaction.

4.1.1. *p*-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (4). To a solution of **3** (3 g, 11 mmol) in dry CH_3CN (20 mL), trimethyl *ortho*-acetate (2.1 mL,

16.5 mmol) was added followed by CSA (20 mg). The mixture was stirred at room temperature until complete conversion of the starting material to a faster moving spot on TLC (~45 min). Then the solution was cooled on an ice-bath. NaH (790 mg, 60% in mineral wax) was added followed by slow addition of BnBr (1.6 mL, 13.2 mmol) and the mixture was allowed to stir at room temperature for another 45 min. Excess NaH was neutralized by MeOH (1 mL) and the solvents were evaporated in vacuo. The residue was dissolved in AcOH–H_2O (9:1, 30 mL) and stirred at room temperature for 1 h. Next, the solvents were evaporated in vacuo and the residue was purified by flash chromatography using *n*-hexane–EtOAc (3:1) as eluent to get pure compound **4** (3.8 g, 85%) as a colourless gel. $[\alpha]_D^{25}$ +39 (*c* 1.0, $CHCl_3$). IR (neat): 2943, 2371, 1693, 1589, 1281, 1097, 1012, 708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33–7.24 (m, 5H, ArH), 6.91, 6.77 (2d, 4H, $C_6H_4OCH_3$), 5.29 (s, 1H, H-1), 5.24 (br s, 1H, H-2), 4.85, 4.70 (2d, 2H, AB system, CH_2Ph), 4.26 (dd, 1H, *J* 3.3 Hz, 9.3 Hz, H-3), 3.88 (m, 1H, H-5), 3.73 (s, 3H, $C_6H_4OCH_3$), 3.38 (t, 1H, *J* 9.3 Hz, H-4), 2.48 (br s, 1H, O*H*), 2.17 (s, 3H, $OCOCH_3$), 1.30 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.5 ($COCH_3$), 155.1, 150.1, 138.3, 128.5, 127.8, 117.7, 114.6 (ArC), 96.4 (C-1), 81.5, 75.2, 72.6, 70.0, 68.1, 55.5 ($C_6H_4OCH_3$), 21.0 ($COCH_3$), 18.1 (C–CH_3). HRMS calcd for $C_{22}H_{30}O_7N$ (M+NH_4): 420.2022; found 420.2024.

4.1.2. *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (6). A mixture of compound **4** (2 g, 5.0 mmol), compound **5** (2.9 g, 6.5 mmol) and MS 4 Å (2 g) in dry CH_2Cl_2 (30 mL) was stirred under nitrogen for 1 h. NIS (1.75 g, 7.8 mmol) was added and the mixture was cooled to 10 °C using ice-water bath. After stirring for 15 min, H_2SO_4–silica (25 mg) was added and the mixture was allowed to stir at 10 °C until complete consumption of the acceptor **4** was evident by TLC (45 min). The mixture was immediately filtered through a pad of Celite and the filtrate was washed successively with $Na_2S_2O_3$ (2×30 mL), $NaHCO_3$ (2×30 mL) and brine (30 mL). Organic phase was collected, dried (Na_2SO_4) and evaporated to syrup. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (3:1) to afford pure compound **6** (3.3 g, 91%) as white foam. $[\alpha]_D^{25}$ +62 (*c* 1.1, $CHCl_3$). IR (neat): 2934, 2367, 1751, 1597, 1376, 1227, 1049 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.33–7.26 (m, 5H, ArH), 6.94, 6.78 (2d, 4H, $C_6H_4OCH_3$), 5.30 (dd, 1H, *J* 1.8 Hz, 3.3 Hz, H-2), 5.27 (d, 1H, *J* 1.8 Hz, H-1), 5.14 (t, 1H, *J* 9.6 Hz, H-4′), 5.09 (t, 1H, *J* 9.6 Hz, H-3′), 5.03 (dd, 1H, *J* 7.5 Hz, 9.6 Hz, H-2′), 4.81 (d, 1H, *J* 7.5 Hz, H-1′), 4.79, 4.54 (2d, 2H, *J* 11.4 Hz, AB system, CH_2Ph), 4.24 (m, 2H, H-3, H-6a′), 4.07 (dd, 1H, *J* 2.1 Hz, 12.3 Hz, H-6b′), 3.85 (m, 1H, H-5), 3.75 (s, 3H, $C_6H_4OCH_3$), 3.68 (m, 1H, H-5′), 3.48 (t, 1H, *J* 9.6 Hz, H-4), 2.15, 2.07, 2.04, 1.98, 1.70 (5s, 15H, 5×$COCH_3$), 1.24 (d, 3H, *J* 6.3 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.9, 169.8, 169.7, 169.0(2) (5×$COCH_3$), 155.0, 149.8, 138.1, 128.3, 127.6, 127.5, 127.2, 117.7, 114.5 (ArC), 100.9 (C-1′), 96.0 (C-1), 79.2, 78.8, 74.8, 73.0, 71.7, 71.5, 71.4, 68.0, 61.4 (C-6′), 55.3 ($C_6H_4OCH_3$), 20.9, 20.7, 20.5(2), 20.4 (5×$COCH_3$), 17.9 (C–CH_3). HRMS calcd for $C_{36}H_{48}O_{16}N$ (M+NH_4): 750.2973; found 750.2971.

4.1.3. *p*-Methoxyphenyl 3,4-isopropylidene-α-L-arabinopyranoside (10). To a solution of **8** (3 g, 9.4 mmol) and *p*-cresol (1.75 g, 14.1 mmol) in dry CH_2Cl_2 (30 mL), $BF_3 \cdot Et_2O$ (2.3 mL, 18.8 mmol) was added dropwise at 0 °C. After complete addition, the solution was stirred at the same temperature for 2 h. Then the solution was diluted with CH_2Cl_2 (20 mL) and washed successively with H_2O (2×50 mL), $NaHCO_3$ (2×50 mL) and brine (50 mL). The organic layer was separated, dried (Na_2SO_4) and evaporated to afford **9** (3.1 g, 87%) as light yellow syrup which was pure enough to proceed with. After dissolving the syrup in dry MeOH (40 mL), NaOMe (0.5 M in MeOH, 400 μL) was added and the solution was stirred at room temperature for 2 h. After complete conversion of the starting material, the solution was neutralized with DOWEX 50W H^+ resin, filtered and evaporated to an amorphous mass. It was suspended in acetone (30 mL), 2,2-DMP (1.2 mL, 9.7 mmol) was added followed by CSA (20 mg) and the mixture was stirred at room temperature for 30 min until the starting material was completely disappeared (TLC). The solution was neutralized with Et_3N and the solvents were evaporated to give the crude product as light brown syrup. It was purified by flash chromatography using *n*-hexane–EtOAc (4:1) to afford pure **10** (2 g, 83%) a colourless glass. $[\alpha]_D^{25}$ +103 (*c* 1.0, $CHCl_3$). IR (neat): 2360, 1598, 1373, 1226, 1075 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.94, 6.76 (2d, 4H, $C_6H_4OCH_3$), 4.73 (d, 1H, *J* 7.2 Hz, H-1), 4.27 (m, 1H, H-4), 4.10 (dd, 1H, *J* 2.4 Hz, 7.8 Hz, H-3), 4.08 (dd, 1H, *J* 7.2 Hz, 7.8 Hz, H-2), 3.86 (dd, 1H, *J* 2.1, 12.9 Hz, H-5a), 3.81 (dd, 1H, *J* 4.2 Hz, 12.9 Hz, H-5b), 3.75 (s, 3H, $C_6H_4OCH_3$), 2.93 (br d, 1H, O*H*), 1.54, 1.36 (2s, 6H, 2×isopropylidene-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.8, 136.6, 118.7(2), 114.7(2) (ArC), 110.2 (isopropylidene-C), 101.5 (C-1), 77.9, 72.9, 72.4, 62.7, 55.4 ($C_6H_4OCH_3$), 27.8, 25.8 (2×isopropylidene-CH_3). HRMS calcd for $C_{15}H_{24}O_6N$ (M+NH_4): 314.1604; found 314.1602.

4.1.4. *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-isopropylidene-α-L-arabinopyranoside (11). To a solution of compound **6** (3 g, 4.1 mmol) in CH_3CN–H_2O (9:1, 30 mL), CAN (4.5 g, 8.2 mmol) was added and the mixture was stirred at room temperature for 30 min when all starting material was converted to a slower moving spot (TLC). After evaporating the solvents in vacuo, the residue was partitioned with CH_2Cl_2 and water. The organic phase was collected, dried (Na_2SO_4) and evaporated. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (2:1). The resulting product was dissolved in CH_2Cl_2 (25 mL), CCl_3CN (616 μL, 6.15 mmol) was added followed by DBU (674 μL, 4.5 mmol) and the solution was stirred at room temperature for 1 h until the starting material was converted completely to a faster running spot (TLC). After evaporation of the solvents, the crude product was purified by flash chromatography to afford pure compound **7** (2.5 g, 79%) as a white foam. This compound was used for the next step without any further characterization, as glycosyl trichloroacetimidates are relatively unstable on storing.

A solution of **7** (2.5 g, 3.2 mmol), **10** (870 mg, 2.9 mmol) and MS 4 Å (1.5 g) in dry CH_2Cl_2 (25 mL) was stirred under nitrogen for 1 h. After cooling the mixture at −40 °C,

H_2SO_4–silica (20 mg) was added and the mixture was allowed to stir at the same temperature for 5 h until the acceptor **10** was completely consumed (TLC). The mixture was neutralized with Et_3N and filtered through a pad of Celite. The filtrate was evaporated in vacuo and the crude product was purified by flash chromatography using *n*-hexane–EtOAc (1.5:1) to afford pure trisaccharide **11** (2.4 g, 89%) as a white foam. $[\alpha]_D^{25}$ +48 (*c* 1.1, $CHCl_3$). IR (KBr): 1751, 1724, 1635, 1601, 1363, 1221, 1042 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32–7.24 (m, 5H, ArC), 6.97, 6.75 (2d, 4H, $C_6H_4OCH_3$), 5.28 (br s, 2H, H-1′, H-2′), 5.08–5.01 (m, 3H, H-2‴, H-3‴, H-4‴), 4.87 (d, 1H, *J* 6.9 Hz, H-1‴), 4.77, 4.55 (2d, 2H, *J* 11.4 Hz, AB system, CH_2Ph), 4.67 (d, 1H, *J* 7.5 Hz, H-1), 4.33 (m, 1H, H-4), 4.24–4.17 (m, 2H, H-2, H-3), 4.13–3.96 (m, 5H, H-5a, H-3′, H-5′, H-6a″, H-6b″), 3.91 (dd, 1H, *J* 4.8 Hz, 12.6 Hz, H-5b), 3.74 (s, 3H, $C_6H_4OCH_3$), 3.59 (m, 1H, H-5″), 3.44 (t, 1H, *J* 9.3 Hz, H-4′), 2.13, 2.07, 1.99, 1.95, 1.65 (5s, 15H, 5×$COCH_3$), 1.53, 1.31 (2s, 6H, 2×isopropylidene-CH_3), 1.30 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.2, 169.8(2), 168.9(2) (5×$COCH_3$), 155.1, 151.2, 138.4, 128.2(2), 127.4, 127.0(2), 118.0(2), 114.4(2) (ArC), 110.6 (isopropylidene-C), 100.7 (C-1″), 99.8 (C-1), 95.8 (C-1″), 79.3, 78.8, 77.9, 75.2, 74.5, 72.9, 72.3, 71.6, 71.5, 71.0, 67.8, 67.4, 62.4 (C-5), 61.3 (C-6″), 55.3 ($C_6H_4OCH_3$), 27.6, 25.8 (2×isopropylidene-CH_3), 20.9, 20.5(3), 20.4 (5×$COCH_3$), 17.8 (C–CH_3). HRMS calcd for $C_{44}H_{60}O_{20}N$ (M+NH_4): 922.3709; found 922.3707.

4.1.5. *p*-Methoxyphenyl β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside (1). To a solution of compound **11** (2 g, 2.2 mmol) in MeOH (20 mL) was added Pd–C (10% Pd on activated charcoal, 50 mg) and the mixture was stirred under hydrogen (40 psi) for 6 h until the starting material was completely converted to a slower running spot (TLC). The mixture was filtered through a pad of Celite and washed with hot MeOH to extract the product completely from the charcoal. The filtrate was evaporated in vacuo and the residue was dissolved in AcOH–H_2O (9:1, 30 mL) and the solution was stirred at 80 °C for 2 h. After evaporating the solvents and co-evaporating with toluene, the residue was dissolved in dry MeOH (30 mL). NaOMe (0.5 M in MeOH) was added and the solution was allowed to stir at room temperature for 3 h. Then the solution was neutralized with DOWEX 50W H^+, filtered and evaporated in vacuo to furnish pure compound **1** (970 mg, 78%) as amorphous white powder. $[\alpha]_D^{25}$ +82 (*c* 1.0, H_2O); ^1H NMR (300 MHz, D_2O) δ: 7.03, 6.88 (2d, 4H, $C_6H_4OCH_3$), 5.27 (d, 1H, *J* 1.5 Hz, H-1′), 4.63 (d, 1H, *J* 7.8 Hz, H-1″), 4.57 (d, 1H, *J* 7.2 Hz, H-1), 4.20 (m, 2H, H-2, H-3′), 4.02–3.77 (m, 8H, H-2′, H-4, H-4′, H-5a, H-5b, H-5′, H-6a″, H-6b″), 3.63 (m, 2H, H-3, H-4″), 3.52 (m, 3H, H-2″, H-3″, H-5″), 3.72 (s, 3H, $C_6H_4OCH_3$), 1.16 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, D_2O) δ: 151.4, 148.3, 115.0, 113.8 (ArC), 101.0 (C-1″), 99.7 (C-1), 98.0 (C-1′), 78.8, 76.0(2), 75.8(2), 72.9(2), 71.4, 69.7, 68.7, 68.5, 61.6, 60.9, 54.5 ($C_6H_4OCH_3$), 15.5 (C–CH_3). HRMS calcd for $C_{24}H_{36}O_{15}Na$ (M+Na): 587.1952; found 587.1949.

4.1.6. *p*-Tolyl 2,3,4-tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (14). To a solution of compound **12** (2 g, 7.0 mmol) in dry pyridine (30 mL), TBDPS-Cl (2.4 mL, 9.1 mmol) was added and the solution was stirred for 6 h at room temperature until the starting material was completely consumed (TLC). Then Ac_2O (2.4 mL, 25.0 mmol) was added and stirring was continued for another 2 h at room temperature. The solvents were evaporated in vacuo and the residue was dissolved in CH_2Cl_2 (30 mL), washed successively with ice-cold 1 M HCl (2×30 mL), $NaHCO_3$ (2×30 mL) and brine (30 mL). The organic layer was separated, dried (Na_2SO_4) and evaporated to syrup. The crude product was purified by flash chromatography using *n*-hexane–EtOAc (5:1) to afford pure **14** (4 g, 89%) as a colourless syrup. $[\alpha]_D^{25}$ +83 (*c* 1.0, $CHCl_3$). IR (neat): 1751, 1373, 1228, 1063, 772 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.63–7.00 (m, 14H, ArH), 5.16 (t, 1H, *J* 9.3 Hz, H-4), 5.11 (t, 1H, *J* 9.3 Hz, H-3), 4.92 (t, 1H, *J* 9.3 Hz, H-2), 4.62 (d, 1H, *J* 9.3 Hz, H-1), 3.77 (dd, 1H, *J* 1.5 Hz, 11.4 Hz, H-6a), 3.69 (dd, 1H, *J* 4.5 Hz, 11.4 Hz, H-6b), 3.55 (m, 1H, H-5), 2.30 (s, 3H, $SC_6H_4CH_3$), 2.07, 2.01, 1.86 (3s, 9H, 3×$COCH_3$), 1.05 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.9, 168.7, 168.6 (3×$COCH_3$), 138.2, 135.6, 135.5, 133.7, 132.9, 132.8, 129.6, 129.5, 127.7 (ArC), 96.1 (C-1), 85.5, 78.6, 74.5, 69.9, 68.0, 62.3 (C-6), 26.7 ($C(CH_3)_3$), 21.1, 20.6, 20.5 (3×$COCH_3$), 18.5 ($C(CH_3)_3$). HRMS calcd for $C_{35}H_{46}O_8NSSi$ (M+NH_4): 668.2713; found 668.2714.

4.1.7. *p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranoside (16). A mixture of compound **14** (3.7 g, 5.8 mmol), compound **15** (1.5 g, 4.8 mmol) and MS 4 Å (2 g) in dry CH_2Cl_2 (40 mL) was stirred under nitrogen for 1 h. NIS (1.6 g, 7.0 mmol) was added and the mixture was cooled to 10 °C using ice-water bath. After stirring for 15 min, H_2SO_4–silica (25 mg) was added and stirring was continued for another 45 min when the acceptor **15** was completely consumed (TLC). The mixture was immediately filtered through a pad of Celite and the filtrate was washed successively with $Na_2S_2O_3$ (2×30 mL), $NaHCO_3$ (2×30 mL) and brine (30 mL). The organic layer was collected, dried (Na_2SO_4) and evaporated in vacuo. The crude product was purified by flash chromatography using *n*-hexane–EtOAc (3:1) as eluent to afford pure **16** (3.5 g, 86%) as white foam. $[\alpha]_D^{25}$ +46 (*c* 1.1, $CHCl_3$). IR (KBr): 1763, 1723, 1639, 1598, 1367, 1235, 1047 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.67–7.32 (m, 10H, ArH), 6.96, 6.80 (2d, 4H, $C_6H_4OCH_3$), 5.57 (s, 1H, H-1), 5.25 (t, 1H, *J* 9.3 Hz, H-4′), 5.22 (t, 1H, *J* 9.3 Hz, H-3′), 5.00 (d, 1H, *J* 6.3 Hz, H-1′), 4.99 (dd, 1H, *J* 6.3 Hz, 9.3 Hz, H-2′), 4.29 (br d, 1H, *J* 6.3 Hz, H-2), 4.22 (t, 1H, *J* 7.2 Hz, H-4), 3.83–3.64 (m, 7H, H-3, H-5, H-6a″, H-6b″, $C_6H_4OCH_3$), 3.52 (m, 1H, H-5′), 2.09, 2.00, 1.91 (3s, 9H, 3×$COCH_3$), 1.44, 1.35 (2s, 6H, 2×isopropylidene-CH_3), 1.26 (d, 3H, *J* 6.3 Hz, C–CH_3), 1.04 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.0, 169.0, 168.7 (3×$COCH_3$), 154.9, 150.0, 135.5, 135.4, 132.9, 132.6, 129.7, 127.7, 117.7, 114.5 (ArC), 109.2 (isopropylidene-C), 99.6 (C-1′), 96.0 (C-1), 79.2, 78.2, 76.0, 74.3, 73.4, 71.7, 68.4, 64.8, 61.9 (C-6′), 55.3 ($C_6H_4OCH_3$), 27.9, 26.4 (2×isopropylidene-CH_3), 26.6 ($C(CH_3)_3$), 20.6, 20.5, 20.4 (3×$COCH_3$), 19.1 ($C(CH_3)_3$), 17.4 (C–CH_3). HRMS calcd for $C_{44}H_{60}O_{14}NSi$ (M+NH_4): 854.3783; found 854.3785.

4.1.8. *p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-

α-L-rhamnopyranoside (17). A solution of compound **16** (3 g, 3.6 mmol) in AcOH–H_2O (8:1, 30 mL) was stirred at 80 °C for 2 h. After evaporating the solvents, the residue was dissolved in pyridine (15 mL), Ac_2O (850 μL, 9.0 mmol) was added and the solution was stirred at room temperature for 3 h. Then the solvents were evaporated and the residue was dissolved in CH_2Cl_2 (30 mL). The solution was washed successively with ice-cold 1 M HCl (2×30 mL), $NaHCO_3$ (2×30 mL) and brine (30 mL). The organic layer was separated, dried (Na_2SO_4) and evaporated in vacuo. The crude product was purified by flash chromatography using *n*-hexane–EtOAc (2:1) as eluent to give pure **17** (2.7 g, 85%) as white foam. $[\alpha]_D^{25}$ +59 (*c* 1.1, $CHCl_3$). IR (KBr): 1754, 1378, 1226, 1067, 763 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.66–7.34 (m, 10H, ArH), 6.98, 6.77 (2d, 4H, $C_6H_4OCH_3$), 5.43 (dd, 1H, *J* 3.6 Hz, 9.9 Hz, H-3), 5.31 (dd, 1H, *J* 1.5 Hz, 3.6 Hz, H-2), 5.27 (br s, 1H, H-1), 5.11 (t, 1H, *J* 9.3 Hz, H-4′), 5.06 (t, 1H, *J* 9.3 Hz, H-3′), 4.94 (t, 1H, *J* 9.3 Hz, H-2′), 4.69 (d, 1H, *J* 7.8 Hz, H-1′), 3.95 (m, 1H, H-5), 3.75 (s, 3H, $C_6H_4OCH_3$), 3.73–3.69 (m, 3H, H-4, H-6a′, H-6b′), 3.56 (m, 1H, H-5′), 2.13 (2), 2.02, 2.00, 1.86 (4s, 15H, 5×$COCH_3$), 1.38 (d, 3H, *J* 6.0 Hz, C–CH_3), 1.06 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.3, 169.6, 169.4, 169.1, 168.8 (5×$COCH_3$), 155.2, 150.0, 135.6, 133.0, 132.8, 129.9, 129.8, 127.8, 117.9, 114.5 (ArC), 100.9 (C-1′), 96.5 (C-1), 76.8, 74.5, 73.4, 71.4, 71.3, 70.2, 68.5, 67.5, 62.3 (C-6′), 55.4 ($C_6H_4OCH_3$), 26.8 [$C(CH_3)_3$], 21.0, 20.9, 20.6, 20.4(2) (5×$COCH_3$), 18.5 [$C(CH_3)_3$], 17.7 (C–CH_3). HRMS calcd for $C_{45}H_{60}O_{16}NSi$ (M+NH_4): 898.3681; found 898.3683.

4.1.9. Methyl 2,3,4-tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (20). To a solution of compound **17** (2.5 g, 2.8 mmol) in CH_3CN–H_2O (9:1, 30 mL), CAN (3 g, 5.6 mmol) was added and the mixture was stirred at room temperature for 30 min when the starting material was completely converted to slower moving component (TLC). The solvents were evaporated and residue was dissolved in CH_2Cl_2 (30 mL), washed with H_2O (30 mL), $NaHCO_3$ (30 mL) and brine (30 mL). The organic layer was collected, dried (Na_2SO_4) and evaporated in vacuo. The residue was dissolved in dry CH_2Cl_2 (20 mL) followed by the addition of CCl_3CN (420 μL, 4.2 mmol) and DBU (465 μL, 3.1 mmol). The solution was stirred at room temperature for 1 h when the starting material was completely converted to a faster running spot (TLC). Solvents were evaporated and the residue was charged on a flash column directly and eluted with *n*-hexane–EtOAc (3:1) to afford pure **18** (2.1 g, 81%).

A mixture of compound **18** (2 g, 2.2 mmol), compound **19** (695 mg, 1.8 mmol) and MS 4 Å (2 g) was stirred under nitrogen for 1 h. After cooling the mixture to −40 °C, H_2SO_4–silica (20 mg) was added and the mixture was allowed to stir at the same temperature for another 6 h when the starting acceptor **19** was completely consumed. The mixture was neutralized with Et_3N and filtered through Celite and the filtrate was evaporated in vacuo. The residue was purified by flash chromatography using *n*-hexane–EtOAc (2:1) to afford pure compound **20** (1.7 g, 84%) as white foam. $[\alpha]_D^{25}$ +78 (*c* 1.0, $CHCl_3$). IR (KBr): 1757, 1721, 1636, 1593, 1364, 1230, 1043 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.01–7.29 (m, 20H, ArH), 5.61 (s, 1H, C*H*Ph), 5.19 (t, 1H, *J* 9.6 Hz, H-4″), 5.16 (dd, 1H, *J* 3.6 Hz, 9.6 Hz, H-3′), 5.06 (m, 3H, H-1′, H-2′, H-3″), 4.92 (m, 3H, H-1, H-2″, H-2), 4.56 (d, 1H, *J* 7.8 Hz, H-1″), 4.33 (m, 2H, H-4′, H-5′), 4.08 (m, 1H, H-5″), 3.88 (m, 1H, H-5), 3.79 (m, 2H, H-6a, H-6b), 3.68 (dd, 1H, *J* 2.1 Hz, 11.4 Hz, H-6a″), 3.64 (dd, 1H, *J* 4.2 Hz, 11.4 Hz, H-6b″), 3.49 (t, 2H, H-3, H-4), 3.38 (s, 3H, OCH_3), 1.99, 1.98(2), 1.86, 1.84 (5s, 15H, 5×$COCH_3$), 1.05 (s, 9H, $C(CH_3)_3$), 0.85 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 170.2, 169.2, 168.9, 168.8, 168.7 (5×$COCH_3$), 165.3 (*C*OPh), 136.9, 135.5, 133.1, 132.8, 132.7, 129.9, 129.8, 129.7, 129.3, 129.1, 128.2, 128.1, 127.7, 126.2 (ArC), 101.7 (*C*HPh), 100.8 (C-1″), 98.2 (C-1), 97.8 (C-1′), 79.4, 76.7, 74.6, 74.3, 73.9, 73.5, 71.3, 71.2, 70.0, 68.8, 68.4, 66.9, 62.9 (C-6), 62.0 (C-6″), 55.3 (OCH_3), 26.7 ($C(CH_3)_3$), 20.9, 20.6, 20.5, 20.4, 20.3 (5×$COCH_3$), 19.2 ($C(CH_3)_3$), 16.9 (C–CH_3). HRMS calcd for $C_{59}H_{74}O_{21}NSi$ (M+NH_4): 1160.4523; found 1160.4525.

4.1.10. Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (21). To a stirred solution of compound **20** (1.5 g, 1.3 mmol) in dry THF (20 mL) at 0 °C was added AcOH (82 μL, 1.4 mmol) followed by Bu_4NF (1 N in THF, 6.6 mL) and the solution was allowed to stir at room temperature for 12 h when the starting material was completely converted to a slower moving spot (TLC). The solvents were evaporated at temperature <30 °C in vacuo. The crude product was purified by flash chromatography using *n*-hexane–EtOAc (1:1) as eluent to afford pure compound **21** (985 mg, 83%) as a colourless glass. $[\alpha]_D^{25}$ +83 (*c* 1.1, $CHCl_3$). IR (neat): 1754, 1719, 1634, 1597, 1367, 1223, 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.99–7.34 (m, 10H, ArH), 5.60 (s, 1H, C*H*Ph), 5.28 (dd, 1H, *J* 1.8 Hz, 9.6 Hz, H-3′), 5.12 (m, 3H, H-1′, H-2′, H-4″), 4.91 (m, 3H, H-1, H-2″, H-3″), 4.77 (dd, 1H, *J* 1.8 Hz, 9.6 Hz, H-2), 4.50 (d, 1H, *J* 7.8 Hz, H-1″), 4.28 (m, 2H, H-4′, H-5′), 4.01 (m, 1H, H-5″), 3.81 (m, 1H, H-5), 3.78–3.70 (m, 2H, H-6a, H-6b), 3.61–3.42 (m, 4H, H-3, H-4, H-6a″, H-6b″), 3.38 (s, 3H, OCH_3), 2.10, 2.07, 1.98(2), 1.88 (5s, 15H, 5×$COCH_3$), 0.81 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.0, 169.3(2), 168.8(2) (5×$COCH_3$), 165.3 (*C*OPh), 133.2, 129.9, 129.2, 128.3, 128.1, 126.3 (ArC), 101.6 (*C*HPh), 100.4 (C-1″), 98.2 (C-1), 97.7 (C-1′), 79.4, 76.7, 75.6, 74.6, 73.9, 73.6, 71.2, 71.0, 69.9, 69.0, 68.8, 62.8(2), 55.3 (OCH_3), 20.8, 20.7, 20.6, 20.5, 20.4 (5×$COCH_3$), 17.1 (C–CH_3). HRMS calcd for $C_{43}H_{56}O_{21}N$ (M+NH_4): 922.3345; found 922.3343.

4.1.11. Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3-di-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosiduronic acid (22). To a solution of compound **21** (520 mg, 0.6 mmol) in CH_2Cl_2 (14 mL) and H_2O (3 mL) was added aq NaBr (1 M, 320 μL), aq tetrabutylammonium bromide (1 M, 640 μL), TEMPO (30 mg, 0.3 equiv) and saturated aq $NaHCO_3$ (1.6 mL) at 0 °C. To the resulting mixture, aq NaOCl (1.9 mL) was added and the mixture was allowed to stir for 1.5 h when the temperature was raised from 0 °C to room temperature. At this point TLC showed complete

conversion of the starting material to a faster moving spot, presumably the corresponding aldehyde derivative. The mixture was neutralized with 1 M HCl (~150 μL) to keep the pH of the mixture at 6–7. Then *tert*-butanol (8.8 mL), 2-methyl-but-2-ene (2 M in THF, 18 mL), $NaOCl_2$ (640 mg) and NaH_2PO_4 (510 mg) were added and the mixture was allowed to stir at room temperature for another 4 h when TLC showed complete conversion. The mixture was diluted with saturated NaH_2PO_4 (30 mL) and the product was extracted with EtOAc (3×20 mL). The combined organic layer was dried (Na_2SO_4) and evaporated. The crude product thus obtained was purified by flash chromatography using *n*-hexane–EtOAc (1:4) to neat EtOAc to afford pure compound **22** (410 mg, 78%) as a light yellow syrup. $[\alpha]_D^{25}$ +68 (*c* 1.0, $CHCl_3$). IR (neat): 2365, 1754, 1597, 1381, 1226, 1046, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.97–7.30 (m, 10H, ArH), 5.55 (s, 1H, C*H*Ph), 5.26 (dd, 1H, *J* 1.8 Hz, 9.6 Hz, H-3′), 5.13 (m, 3H, H-1′, H-2′, H-4″), 4.88 (m, 3H, H-1, H-2″, H-3″), 4.78 (dd, 1H, *J* 1.8 Hz, 9.6 Hz, H-2), 4.62 (d, 1H, *J* 7.8 Hz, H-1″), 4.33 (m, 2H, H-4′, H-5′), 4.03 (m, 1H, H-5″), 3.88 (m, 1H, H-5), 3.81–3.70 (m, 3H, H-6a, H-6b, H-3), 3.61 (t, 1H, *J* 9.6 Hz, H-4), 3.38 (s, 3H, OCH_3), 2.03, 2.00, 1.97(2), 1.90 (5s, 15H, 5×COCH_3), 0.84 (d, 3H, *J* 6.0 Hz, C–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.4 (*C*OOH), 169.8, 169.5, 169.1(3) (5×CO*C*H_3), 165.4 (*C*OPh), 133.2, 129.8, 129.1, 128.9, 128.3, 128.1, 126.1 (ArC), 101.5 (*C*HPh), 100.5 (C-1″), 98.2 (C-1), 97.7 (C-1′), 79.4, 74.7, 73.6, 72.8, 71.2, 71.1, 69.7, 69.6, 68.8, 62.7, 55.3 (O*C*H_3), 20.8, 20.5, 20.4(2), 20.3 (5×CO*C*H_3), 16.7 (C–*C*H_3). HRMS calcd for $C_{43}H_{50}O_{22}Na$ (M+Na): 941.2691; found 941.2693.

4.1.12. Methyl β-D-glucopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-α-D-glucopyranosiduronic acid (2). A solution of compound **22** (400 mg, 0.4 mmol) in AcOH–H_2O (9:1, 10 mL) was stirred at 80 °C for 2 h when the starting material was completely converted to a slower moving spot (TLC). The solvents were evaporated and co-evaporated with toluene to remove AcOH and H_2O completely. Then the residue was dissolved in dry MeOH (10 mL) and NaOMe (0.5 M in MeOH) was added and the solution was stirred at room temperature for 3 h. Then after neutralizing with DOWEX 50W H^+, the solvents were evaporated in vacuo to afford pure compound **2** (180 mg, 81%) as white amorphous powder. $[\alpha]_D^{25}$ +69 (*c* 1.1, H_2O). IR (KBr): 2353, 1687, 1197, 785 cm^{-1}; ^1H NMR (300 MHz, D_2O) δ: 4.96 (br s, 1H, H-1′), 4.65 (d, 1H, *J* 1.8 Hz, H-1), 4.63 (d, 1H, *J* 8.1 Hz, H-1″), 3.94 (m, 2H, H-2′, H-3), 3.82 (dd, 1H, *J* 3.3 Hz, 9.6 Hz, H-3′), 3.72 (dd, 1H, *J* 1.8 Hz, 12.3 Hz, H-6a), 3.67–3.53 (m, 6H, H-2, H-2′, H-2″, H-3″, H-4, H-4″), 3.43 (m, 1H, H-5″), 3.40 (t, 1H, *J* 9.6 Hz, H-4′), 3.31 (s, 3H, C_6H_4OC*H*$_3$), 3.28 (m, 1H, H-5′), 3.18 (m, 1H, H-5), 1.19 (d, 3H, *J* 6.3 Hz, C–CH_3). ^{13}C NMR (75 MHz, D_2O) δ: 171.5 (*C*OOH), 102.9 (C-1″), 100.9 (C-1), 99.4 (C-1′), 81.0, 80.1, 75.5, 73.6, 71.7(3), 71.5, 70.3, 70.2, 67.9, 67.2, 60.5 (C-6), 55.0 (O*C*H_3), 16.6 (C–*C*H_3). HRMS calcd for $C_{19}H_{32}O_{16}Na$ (M+Na): 539.1588; found 539.1586.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.077.

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