Supporting Information

Synthesis of a 2,3,4-triglycosylated rhamnoside fragment of rhamnogalacturonan-II side chain A using a late stage oxidation approach

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Structure of the side-chain A octasaccharide of rhamnogalacturonan-II, shown attached to a polygalacturonan backbone. The target tetrasaccharide fragment is highlighted.

Experimental Section

General Methods. Reactions were carried out in dry solvents using septa and syringes for addition of reagents. Commercially available anhydrous DMF and Et₂O were used, CH₂Cl₂ was distilled from CaH₂, MeOH was distilled from Mg(OMe)₂, pyridine was distilled from P₂O₅ and stored over 4 Å molecular sieves. Cation-exchange resin was washed with water and dry MeOH before use. TLC was performed on precoated aluminium plates. Compounds were visualized by exposure to UV light or by immersion in 5% ethanolic H₂SO₄ followed by heating to 150 °C. Solutions of reaction products were dried over MgSO₄ and solvents were evaporated under reduced pressure at 25–40 °C. Column chromatography was performed on silica gel (40–70 μm). Optical rotations were measured at 25 °C. ¹H and ¹³C NMR spectra were recorded at 24 °C with at 300 and 75 MHz, respectively, or at 400 and 100 MHz, respectively, using TMS (for solution in CDCl₃) or MeOH (δ 49.9, for solutions in D₂O) as internal standards. Resonance allocations were made with the aid of COSY and gHSQC experiments. Accurate electrospray ionisation mass spectra (ESI-MS) were obtained using positive ionization mode. For compounds with molecular masses >1000 low resolution ESI-MS were obtained on the same instrument and experimental data were matched to theoretical isotope patterns. ESI-MS for compounds **1** and **20** were obtained on instrument operating in negative ionization mode.

¹H NMR spectrum of compound 1

^{13}C NMR spectrum of compound 1

HSQC NMR spectrum of compound 1

^1H NMR spectrum of compound 2

^{13}C NMR spectrum of compound 2

HSQC NMR spectrum of compound 2

¹H NMR spectrum of compound 3

^{13}C NMR spectrum of compound 3

¹H NMR spectrum of compound 4

^{13}C NMR spectrum of compound 4

¹H NMR spectrum of compound 10

^{13}C NMR spectrum of compound 10

^1H NMR spectrum of compound 11

^{13}C NMR spectrum of compound 11

HSQC NMR spectrum of compound 11

^1H NMR spectrum of compound 12

¹³C NMR spectrum of compound 12

¹H NMR spectrum of compound 13

^{13}C NMR spectrum of compound 13

¹H NMR spectrum of compound 14

^{13}C NMR spectrum of compound 14

^1H NMR spectrum of compound 16

^{13}C NMR spectrum of compound 16

^1H NMR spectrum of compound 17

^{13}C NMR spectrum of compound 17

¹H NMR spectrum of compound **18**

¹³C NMR spectrum of compound **18**

HSQC NMR spectrum of compound 18

^1H NMR spectrum of compound 19

^{13}C NMR spectrum of compound 19

^1H NMR spectrum of compound 20

^{13}C NMR spectrum of compound 20