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Oligosaccharides related to xyloglucan: synthesis and X-ray crystal structure of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside and the synthesis of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-xylopyranoside

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Abstract

Trisaccharides, methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside and methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-xylopyranoside, which are related to the side chain of xyloglucan have been synthesised. The β-galactopyranosyl linkage of each was constructed using silver trifluoromethanesulfonate-promoted glycosylations of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl chloride and the corresponding anomer of methyl 3,4-tri-*O*-benzyl-D-xylopyranoside. The resulting disaccharides were deacetylated and fucosylated using assisted halide reactions with tri-*O*-benzyl-α-L-fucopyranosyl bromide. Hydrogenolytic debenzylation of the resulting protected trisaccharides gave the methyl glycosides of the fucose-containing xyloglucan side chain. The structure of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside as the monohydrate was confirmed by an X-ray crystallographic study.

Keywords: Oligosaccharides; Xyloglucan; Synthesis; X-ray structure

1. Introduction

Xyloglucan is a major polysaccharide present in the cell walls of dicotyledonous plants and may play an important role in dicot cell expansion and growth [1]. It has been proposed that xyloglucan cross-links cellulose microfibrils by hydrogen bonding. During cell expansion, cell-wall-modifying enzymes act on xyloglucan and break these cross-links. Alternatively, proteins, known as expansins, loosen the xyloglucan binding to the cellulose microfibrils and so allow cell-wall expansion [2]. Oligosaccharides originating from the enzymic hydrolyses of xyloglucan have been shown to inhibit the 2,4-D-induced growth of excised pea-stem segments [1,3–6]. Of these oligosaccharides, the nonasaccharide XXFG [3,6] exhibited the greatest activity. However, the activity of α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→4)-D-glu-

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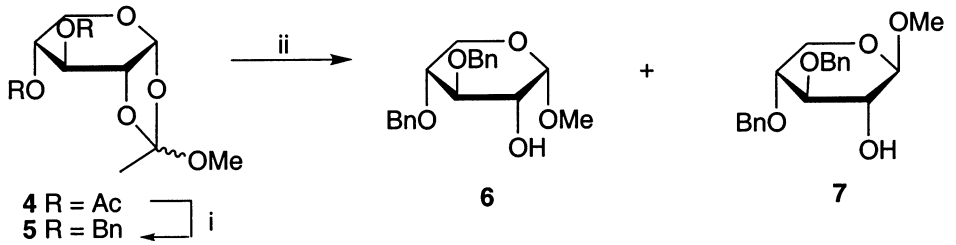
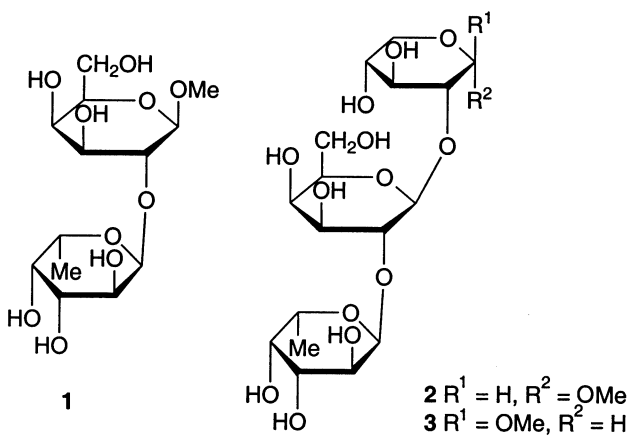


Scheme 1. Reagents and conditions: (i) NaH, BnCl, DMF; (ii) 2% HCl–MeOH.

cose in the pea-stem bio-assay led McDougall and Fry [4] to postulate that only part of XXFG is necessary for its biological activity.

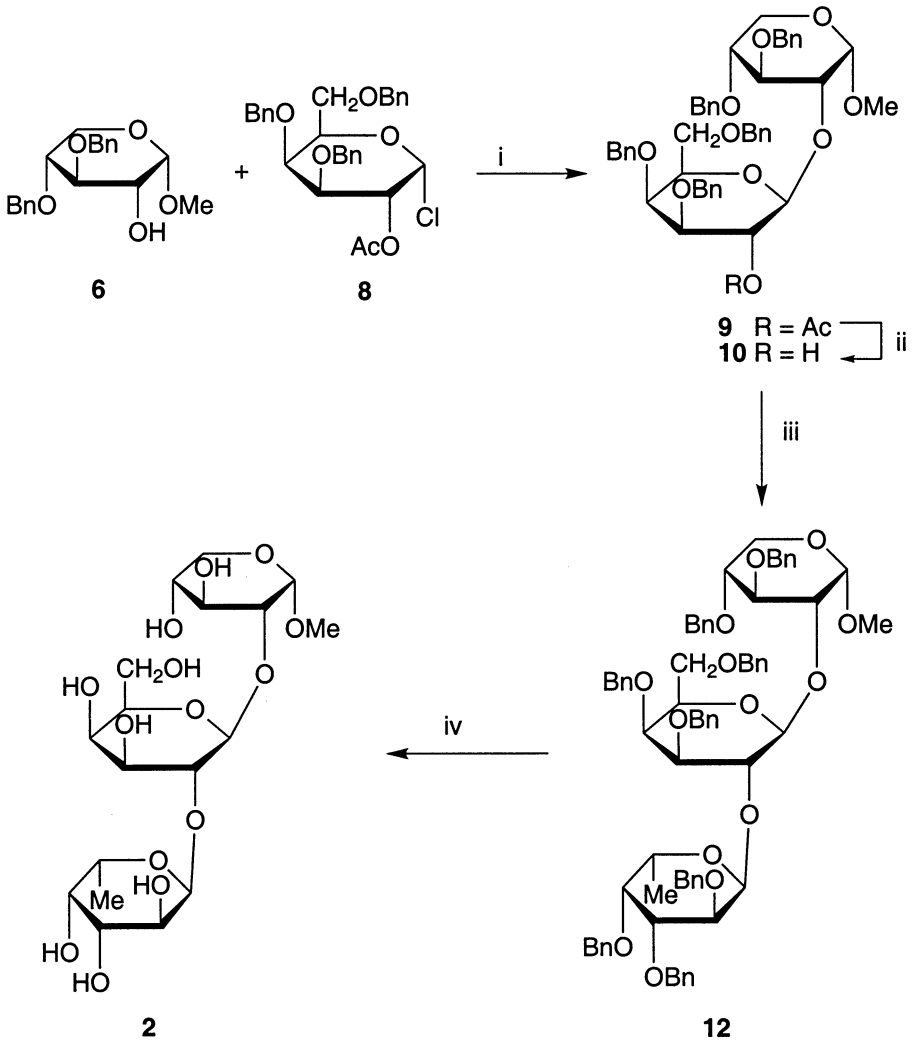
We have previously reported the syntheses of the disaccharides methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranoside (**1**) and methyl α-L-fucopyranosyl-(1→2)-α-D-galactopyranoside, and the single-crystal X-ray structure of the former [7]. The crystal-structure conformation of **1** was similar to low-energy conformations determined from molecular modelling studies reported by both Lemieux et al. [8] and Yan and Bush [9]. In this paper we report the synthesis of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside (**2**) and its single-crystal X-ray structure and the synthesis of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-xylopyranoside (**3**). The trisaccharide **2** is the α-methyl glycoside of the fucose-containing side chain of fucogalactoxyloglucan and XXFG.



2. Results and discussion

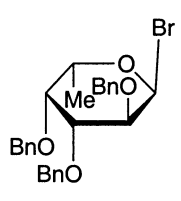
The initial focus of this work was the synthesis of both anomers of the methyl glycoside of the main trisaccharide side chain of xyloglucan. The α-methyl anomer possesses the same anomeric configuration as the trisaccharide side chain in xyloglucan. For expediency, the xyloside acceptors for both syntheses were prepared from the common precursor **4** (Scheme 1). Benzylation of the orthoester **4** was effected using standard conditions to give orthoester **5** in good yield. Methanolysis of **5** in 2% hydrochloric acid in methanol gave a 3:1 mixture of the known xylosides **6** [10] and **7** [11]. Separation of the anomers was achieved by column chromatography and fractional crystallisation to give **6** and **7** in yields of 42 and 19%, respectively.

The synthesis of target trisaccharide **2** is shown in Scheme 2. The reaction of **6** with the galactosyl donor **8** [12] promoted by silver trifluoromethanesulfonate gave the disaccharide **9** in 62% yield. In the ^{1}H NMR spectrum, the resonance due to the anomeric proton (H-1′) of the inter-residue glycosidic linkage was obscured. However, the β-anomeric configuration was apparent from the magnitude of the coupling constants of the signal H-2′, which resonated as a doublet of doublets at δ 5.44 with coupling constants $J_{1',2'}$ and $J_{2',3'}$ of 8 and 10 Hz, respectively. Deacetylation of **9** under standard conditions gave disaccharide **10** in 79% yield. The lack of a signal due to an acetate methyl in the ^{1}H NMR spectrum confirmed deacetylation, and the doublet at δ 4.47 with a coupling constant $J_{1',2'}$ of 8 Hz indicated the β-anomeric stereochemistry of the glycosidic linkage. α-Fucosylation of **10** was achieved using the assisted halide approach [13]. Treatment of **10** with tri-*O*-benzyl-α-L-fucopyranosyl bromide **11** [14], and tetraethylammonium bromide gave the protected trisaccharide **12** in good yield as a slightly impure syrup. The ^{1}H NMR spectrum of the syrup was consistent with the proposed



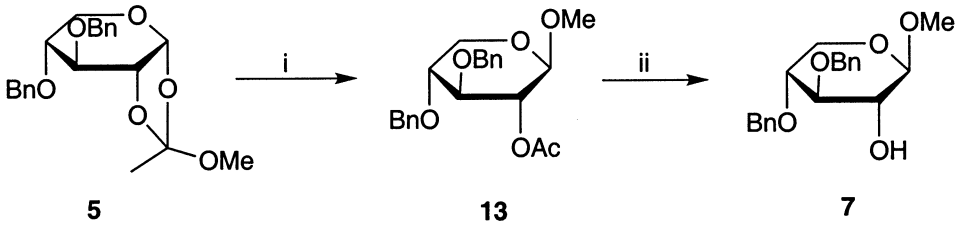
Scheme 2. Reagents and conditions: (i) AgOTf, CH_2Cl_2, −50 to −30 °C; (ii) NaOMe, MeOH; (iii) **11**, Et_4NBr, 4 Å sieves, CH_2Cl_2; (iv) H_2, Pd, MeOH and EtOAc.

structure and showed an upfield three-proton doublet at δ 1.16 (J 6 Hz), which was assigned to the H-6″ of the fucose residue. A clearly resolved doublet at δ 5.81 ($J_{1'',2''}$ 3 Hz) confirmed the α anomeric configuration of the new glycosidic linkage. Furthermore, the ^{13}C NMR spectrum was consistent with the proposed structure and showed three resonances in the anomeric region at δ 97.5, 99.5 and 101.4 assigned to C-1″, C-1, and C-1′, respectively.



Hydrogenolytic debenzylation of **12** and purification by semi-preparative reversed-phase high-performance liquid chromatography (HPLC) gave the target trisaccharide **2** in 59% yield from **10** as a white crystalline solid. Compound **2** analysed as a hydrate and produced an $[M-H]^-$ ion in the negative-ion FAB mass spectrum. The spectroscopic data were consistent with the proposed structure. The anomeric protons were clearly resolved in the ^1H NMR spectrum with the doublets at δ 4.62 ($J_{1',2'}$ 7.5 Hz), 4.98 ($J_{1,2}$ 3 Hz) and 5.27 ($J_{1'',2''}$ 4 Hz) assigned to H-1′, H-1, and H-1″, respectively.

Our attention turned to the synthesis of the β-methyl glycoside of the xyloglucan side chain. A similar approach to that described above for the synthesis of **2** using the xyloside



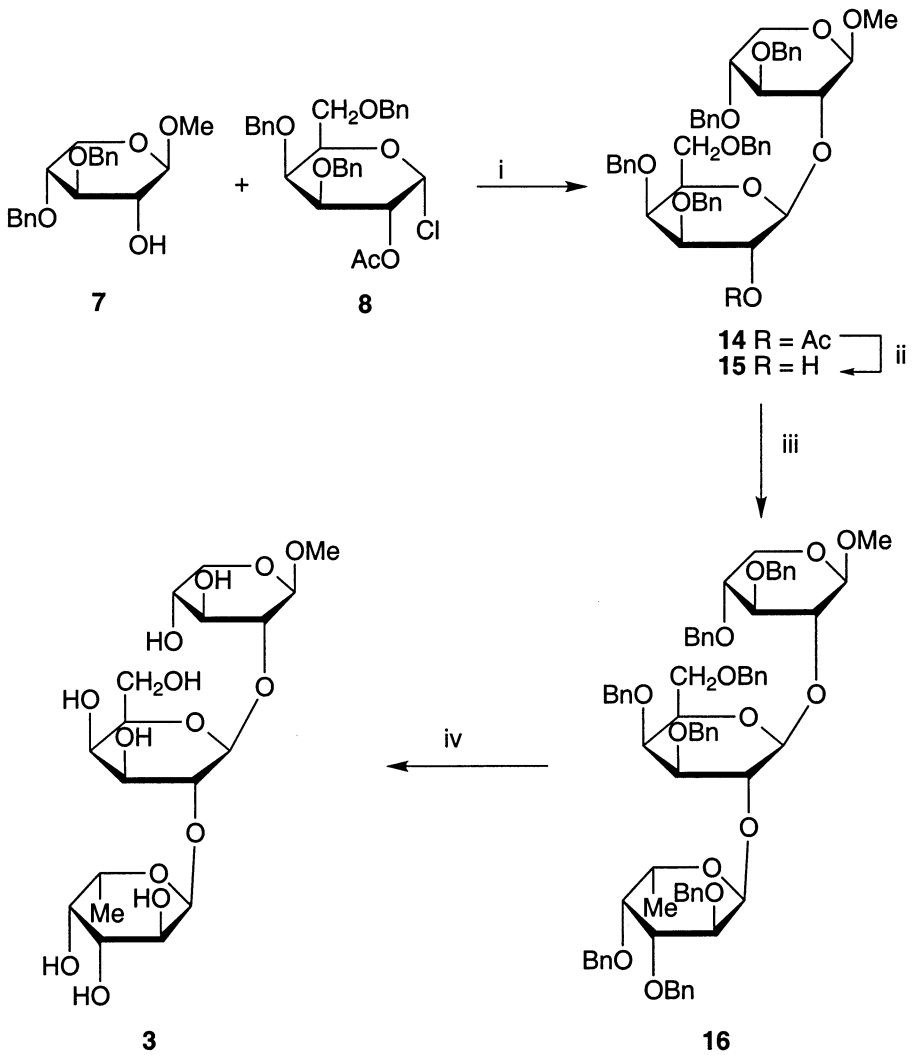
5 13 7

Scheme 3. Reagents and conditions: (i) Cl_3CCH_2OH, $HgCl_2$, CH_3NO_2; (ii) NaOMe, MeOH.

acceptor **7** would be employed. However, a more effective synthesis of this starting material was required (Scheme 3). Treatment of a nitromethane solution of orthoester **5** with 2,2,2-trichloroethanol and mercuric chloride gave methyl xyloside **13** as a slightly impure syrup. Deacetylation using standard conditions gave acceptor **7** in a 70% overall yield from **5**. A silver trifluoromethanesulfonate promoted glycosylation of **7** and the galactosyl donor **8** gave the protected disaccharide **14** as a slightly impure syrup (Scheme 4). Zemplén deacetylation gave the disaccharide **15** in 62% yield from **7** as white crystals from ether and hexanes. The resonances due to the anomeric protons of both **14** and **15** were obscured in their ^{1}H NMR spectra. However, the anomeric configurations at C-l and C-l′ could be assigned as β from the chemical shifts of their anomeric carbon resonances at δ 103.8 and 104.7 in the ^{13}C NMR spectrum. Fucosylation of **15** with bromide **11** was achieved using the assisted halide method to give the trisaccharide **16** as a syrup. The α configuration of the new glycosidic linkage was evident from the magnitude of the coupling constant of the resonance attributed to H-l″ ($J_{1'',2''}$ 3.5 Hz). Hydrogenolytic debenzylation gave the target disaccharide **3** (38% from **15**) as a white solid after purification by reversed-phase column chromatography. The analytical and spectroscopic data were consistent with the proposed structure with the ^{1}H NMR spectrum, showing doublets at δ 4.91 ($J_{1,2}$ 8 Hz) and 5.24 ($J_{1'',2''}$ 4 Hz) assigned to H-l and H-l″, respectively. The signal for H-l′ of the galactosyl residue was obscured by other proton resonances. The ^{13}C NMR spectrum showed the expected 18 resonances with the three resonances at δ 100.1, 101.9, and 103.6 being assigned to the anomeric carbons C-l″, C-l′, and C-l, respectively. The negative-ion FAB mass spectrum was also consistent with the proposed structure and showed a signal at m/z 471 attributed to the $[M-H]^-$ ion.

Unambiguous confirmation of the structure of trisaccharide **2** was gained from an X-ray crystallographic study. Suitable crystals of **2** were obtained by slow crystallisation from aqueous acetonitrile. Crystallographic parameters are given in Table 1. The asymmetric unit contains a molecule of the trisaccharide and a molecule of water. The configuration, conformation and atom numbering are shown in Fig. 1. Atomic coordinates of the non-hydrogen atoms are listed in Table 2. Bond lengths and angles of each residue compare well to those of the corresponding residues in the crystal structures of methyl α-L-fucopyranoside [15], methyl β-D-galactopyranoside [16,17] and methyl α-D-xylopyranoside [18]. Major torsion angles for **2** are given in Table 3. The endocyclic conformation angles (entries 1–6, Table 3) confirm the expectation that the fucosyl, galactosyl and xylosyl units are in the $^1C_4$, $^4C_1$ and $^4C_1$ chair conformations, respectively. Both the hydroxymethyl group in the galactosyl and α-*O*-methyl group in the xylosyl units are in gauche plus domains (entries 7 and 8, Table 3). The interglycosyl conformation angles ϕ and ψ (entries 9 and 10, Table 3) indicate some differences with respect to **1** for the first linkage; **1** ($\phi_1 = -92.7°$ and $\psi_1 = 65.0°$) and **2** ($\phi_1 = -134.1°$ and $\psi_1 = 104.3°$)[2]. We believe that this variation is probably due to inter-residue hydrogen bonds between the hydroxyl groups at the C-3 of the galactosyl and C-2 of the fucosyl residues, and the C-3

[2] ϕ defined as O(5″)–C(1″)–O(1″)–C(2′) and ψ as C(1″)–O(1″)–C(2′)–C(1′) (see Table 3) in accordance with Ref. [24].



Scheme 4. Reagents and conditions: (i) AgOTf, CH_2Cl_2, -50 to -40 °C; (ii) NaOMe, MeOH; (iii) **11**, Et_4NBr, 4 Å sieves, CH_2Cl_2; (iv), H_2, Pd, MeOH and EtOAc.

hydroxyl group of the xylosyl and the ring oxygen of the fucosyl residues, evidenced in the crystal structure of **2**, that stabilise the observed conformation, which has the glycosidic torsion angles between the galactosyl and xylosyl residues, $\phi_1 = -91.8°$ and $\psi_1 = 68.2°$.

The molecular packing projected along the x-axis is depicted in Fig. 2. The molecules are stacked in arrays along the x-axis with individual stacks inter-linked by a network of hydrogen bonds. Molecules within each array are linked by hydrogen bonds, some involving the water molecule. A series of intermolecular hydrogen bonds (Table 4), some mediated by water molecules, provide stability to the crystal structure.

In conclusion, we have reported the syntheses of both anomers of methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-D-xylopyranoside (i.e., **2** and **3**). The α anomer, **2**, represents the trisaccharide unit of one of the side chains of xyloglucan.

3. Experimental

General methods.—For general experimental details see Ref. [7]. The ^1H NMR resonances of the oligosaccharides were assigned on the basis of 2D ^1H COSY and ^1H–^{13}C chemical shift correlation experiments.

3,4-Di-O-benzyl-1,2-O-methoxyethylidene-α-D-xylopyranose (**5**).—A solution of 3,4-di-*O*-

acetyl-1,2-*O*-methoxyethylidene-α-D-xylopyranose (**4**) [19] (15.9 g, 54.7 mmol) in DMF (100 mL) at −10 °C was added dropwise to a stirred suspension of sodium hydride (9.0 g, 380 mmol) in DMF (50 mL) at −10 °C. The resulting mixture was placed in an ice-bath, and benzyl chloride (30 mL) was added dropwise with stirring, over a period of 50 min. The mixture was then stirred for 12 h at room temperature (rt) and then poured onto crushed ice (300 g). The resultant aq mixture was extracted with CH_2Cl_2 (200 mL), and the organic extract was washed with dilute sodium chloride solution (4 × 200 mL) and finally with water (200 mL). The extract was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification of the residue by silica-gel column chromatography (1:4–1:1 ether–hexanes gradient elution) gave the title compound **5** [14.7 g, 38.0 mmol, 69%; TLC (1:1 ether–hexanes], R_f 0.38) as a syrup: $[\alpha]_D$ +20° (*c* 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67 (s, 3 H, CH_3), 3.29 (s, 3 H, CH_3O), 3.62–3.65 (m, 2 H, H-4 and H-5a), 3.81 (d, 1 H, *J* 6 Hz, H-5b), 3.87 (br t, 1 H, *J* 4 Hz and 4 Hz, H-3), 4.33 (dd, 1 H, *J* 3.5 and *J* 5 Hz, H-2), 4.54–4.73 (m, 4 H, 2 × CH_2Ph), 5.60 (d, 1 H, *J* 5 Hz, H-1), 7.20–7.40 (m, 10 H, 2 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3 (CH_3), 50.3 (CH_3O), 60.6 (C-5), 71.9 (CH_2Ph), 72.3 (CH_2Ph), 74.1 (C-4), 76.5 (C-2), 78.0 (C-3), 97.5 (C-1), 121.7 ($CH_3\mathbf{C}O_3$), 127–129 (Ph), 137.7 and 138.0 (Ph); FABMS: *m*/*z* 356 ($[MH-CH_3O]^+$, 18%), 355 ($[M-CH_3O]^+$, 72%), 313 ($[MH-C_2H_6CO_2]^+$, 20%), 307 (37%), 289 (28%), 247 (26%). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found C, 68.36; H, 6.70.

Table 1
Crystal data and structure refinement for methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside monohydrate (**2**) as a monohydrate

Empirical formula	$C_{18}H_{34}O_{15}$
Formula weight	490.45
Temperature (K)	183(5)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	4.8570(10)
b (Å)	19.514(4)
c (Å)	22.859(5)
V (Å^3)	2166.6(8)
Z	4
D_{calcd} (Mg m^{-3})	1.504
Absorption coefficient (mm^{-1})	0.132
F(000)	1048
Crystal size (mm^3)	0.78 × 0.10 × 0.04
θ Range for data collection (°)	2.06–22.48
Index ranges	$-5 \le h \le 0$, $-1 \le k \le 21$, $-1 \le l \le 24$
Reflections collected	1908
Independent reflections	1856 [$R_{int} = 0.0955$]
Completeness to $\theta = 22.48°$	99.9%
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1856/0/308
Goodness-of-fit on F^2	0.964
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$, $wR_2 = 0.1119$
R indices (all data)	$R_1 = 0.0595$, $wR_2 = 0.1161$
Absolute structure parameter	2(2)
Largest difference peak and hole (e Å^{-3})	0.285 and −0.304

Methyl 3,4-di-O-*benzyl*-α-D-*xylopyranoside* (**6**) *and methyl 3,4-di*-O-*benzyl*-β-D-*xylopyranoside* (**7**)

Method A. Orthoacetate **5** (5.39 g, 13.9 mmol) in 2% methanolic HCl (400 mL) was heated at reflux for 16 h. The solution was concentrated by rotary evaporation to ca. 30 mL, and CH_2Cl_2 (100 mL) was added. The CH_2Cl_2 solution was washed with water (200 mL), satd aq $NaHCO_3$ (200 mL), and water (200 mL). The solution was then dried ($MgSO_4$) and concentrated in vacuo to give a 76:24 mixture of **6** and **7**. Purification by silica-gel column chromatography (1:1 ether–hexanes as eluent) gave the title compounds **6** [2.56 g, TLC (ether), R_f 0.43] and **7** [1.01 g, TLC (ether), R_f 0.51] as slightly impure white solids. Purification of the lower R_f fraction by crystallisation from ether–hexanes gave **6** (2.00 g, 5.81 mmol, 42%): mp 100 °C, lit. 90 °C [10]; $[\alpha]_D$ +98° (*c* 0.5, $CHCl_3$), lit. +56° [10]; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.27 (d, 1 H, *J* 7.5 Hz, OH), 3.42 (s, 3 H, CH_3O), 3.50–3.75 (m, 5 H), 4.59–4.75 (m, 3 H, CH_2Ph and H-1), 4.81 (d, 1 H, *J* 11.5 Hz, CH_2Ph), 4.90 (d, 1 H, *J* 11.5 Hz, CH_2Ph), 7.20–7.40 (m, 10 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4 (CH_3O), 60.4 (C-5), 72.3, 73.2,

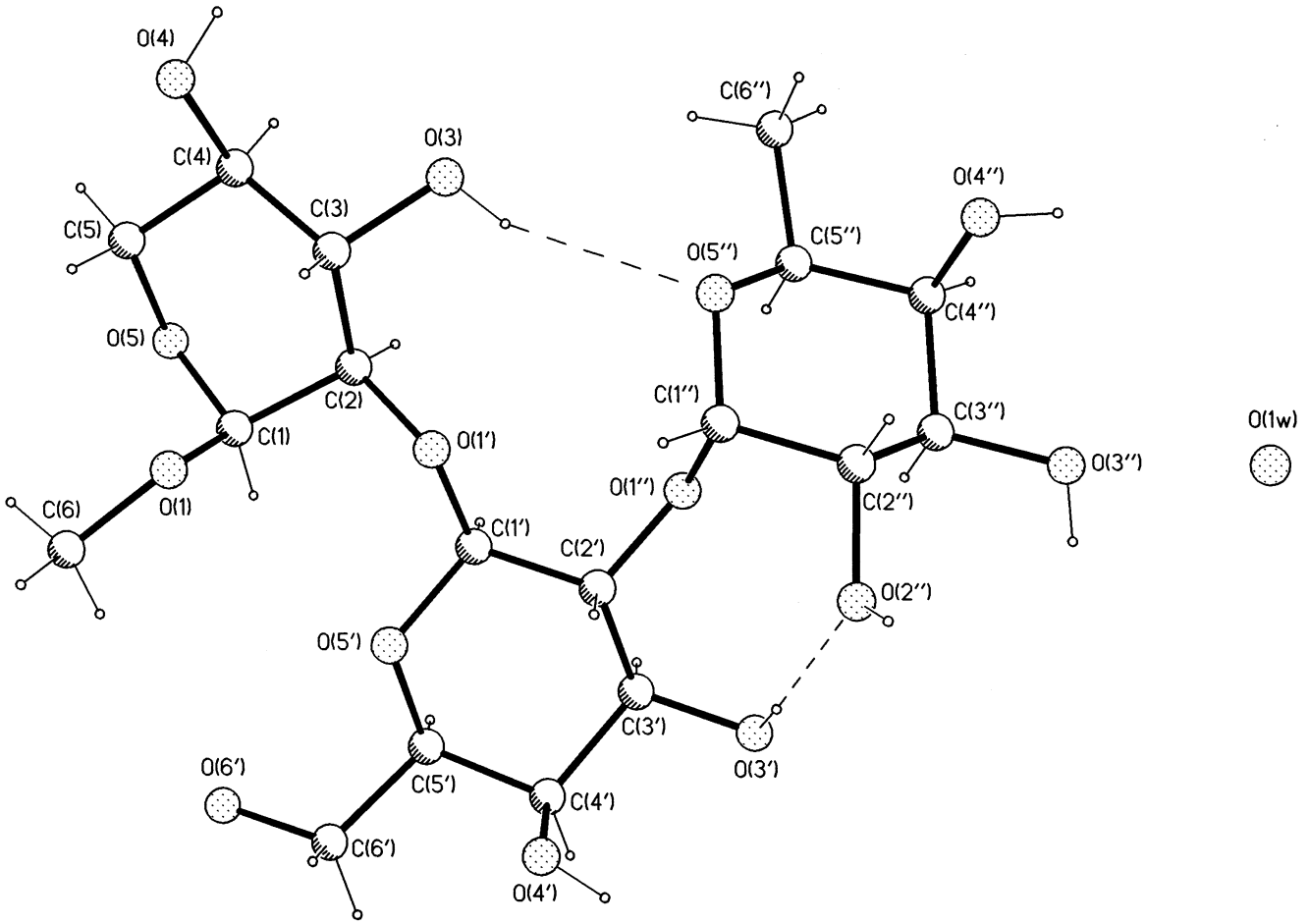


Fig. 1. A view of the molecular structure of **2** with atom labelling and inter-residue hydrogen bonds (dashed lines). O(1w) is the water molecule.

75.2, 77.6, 81.7, 99.5 (C-1), 127–129, 138.2 and 138.7 (Ph); FABMS: m/z 345 ($[MH]^+$, 7%), 343 ($[M-H]^+$, 27%), 301 (8%), 253 (11%), 221 (13%), 205 (20%) and 181 (100%). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found C, 69.92; H, 6.93. Purification of the higher R_f fraction by crystallisation from ether–hexanes gave **7** (0.89 g, 2.58 mmol, 19%): mp 97 °C, lit. 97 °C [11]. $[\alpha]_D$ −37° (c 0.5, $CHCl_3$), lit. −37° [11].

Method B.—Orthoester **5** (1.93 g, 4.98 mmol) was dissolved in nitromethane (25.0 mL), and 2,2,2-trichloroethanol (0.60 mL) and mercuric chloride (0.40 g) were added and the mixture was stirred for 16 h at rt. The mixture was filtered, and the filtrate was concentrated to a small volume that was dissolved in CH_2Cl_2 (100 mL) and washed twice with water (ca. 100 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give crude methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-xylopyranoside (**13**) (2.41 g) as an impure syrup: ^{1}H NMR (200 MHz, $CDCl_3$) inter alia δ 1.99 (s, 3 H, CH_3CO), 3.44 (s, 3 H, CH_3O), 3.99 (dd, 1 H, J 5 and J 12 Hz), 4.15 (d, 1 H, J 8 Hz), 7.2–7.4 (m, 5 H, Ph). The crude product was dissolved in a mixture of ether (30 mL) and MeOH (30 mL) containing a catalytic amount of NaOMe. The solution was stirred for 16 h, concentrated to a small volume, and CH_2Cl_2 (100 mL) was added. The solution was washed with 0.5 M HCl (100 mL), water (100 mL), satd aq $NaHCO_3$ (100 mL) and finally again with water (100 mL). The organic layer was dried ($MgSO_4$), concentrated in vacuo, and the product crystallised from a mixture of ether–hexanes to give **7** (0.483 g, 1.40 mmol, 28% from **5**). The mother liquor was concentrated and purified by silica-gel column chromatography [1:1 ether–hex-

anes, TLC (ether), R_f 0.51], to give additional **7** (0.724 g, 2.10 mmol, 42%). The total yield of **7** was 70%.

Methyl 2-O-acetyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→2)-3,4-di-O-benzyl-α-D-xylopyranoside (**9**).—A mixture of silver triflate (1.1 g, 4.3 mmol) and powdered 4 Å molecular sieves (2.1 g) in CH_2Cl_2 (10 mL) was stirred for 15 min at rt. After cooling to −50 °C, acceptor **6** (0.62 g, 1.8 mmol) was added and the solution was stirred for a further 15 min. A solution of galactosyl chloride **8** [12] (0.96 g, 1.9 mmol) in CH_2Cl_2 (3.0 mL) was added dropwise, and the solution was stirred for 10 min. The reaction mixture warmed to −30 °C at which temperature it was held for 60 min, while stirring was continued. The solution was neutralised with Et_3N, washed with ice-cold aq 1 M sodium thiosulfate, and filtered through Celite®. The filtrate was washed with 1 M HCl, satd aq $NaHCO_3$, and water, dried over $MgSO_4$, and concentrated in vacuo. The product was purified by silica-gel column chromatography [3:2 ethyl acetate–hexanes as eluent; TLC (1:1 ethyl acetate–hexanes), R_f 0.52] to give **9** (1.5 g) as a slightly impure syrup. The product was dissolved in a small amount of CH_2Cl_2. The addition of ether and hexanes to the solution gave a gel. Ultrasonication of the mixture yielded **9** as an amorphous white solid (0.91 g, 1.1 mmol, 62%): mp 135 °C; $[\alpha]_D$ +37° (*c* 0.25, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.78 (s, 3 H, CH_3CO), 3.33 (s, 3 H, CH_3O), 3.40–3.62 (m, 9 H), 3.80–3.89 (m, 1 H), 3.93 (d, 1 H, *J* 3 Hz, H-4′), 4.41–4.84 (m, 11 H), 4.93 (d, 1 H, *J* 11.5 Hz, CH_2Ph), 5.44 (dd, 1 H, *J* 8 Hz and *J* 10 Hz, H-2′), 7.2–7.4 (m, 25 H, 5 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$); δ 21.0 (CH_3CO), 55.3 (CH_3O), 59.7 (C-5), 68.7 (C-6′), 71.3 (C-2′), 71.9 (CH_2Ph), 72.6 (C-4′), 73.4 (CH_2Ph), 73.6 (CH_2Ph), 73.6, 74.5 (CH_2Ph), 75.3 (CH_2Ph), 78.4, 79.7, 80.6, 80.7 (C-3′), 99.6 (C-1), 102.4 (C-1′), 127–129, 137.8, 137.9, 138.4, 138.5, 139.0; FABMS *m/z* 842 (5%), 841 ($[MNa]^+$, 8%), 818 ($[M]^+$, 3%), 817 ($[M-H]^+$, 5%), 680 (6%), 679 (13%), 475 (28%), 383 (21%), 307 (44%), 295 (46%), 289 (25%), 277 (61%), and 181 (100%); Anal. Calcd for $C_{49}H_{54}O_{11}$: C, 71.86; H, 6.65. Found C, 71.86; H, 6.70.

Methyl3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→2)-3,4-di-O-benzyl-α-D-xylopyranoside (**10**).—Compound **9** (0.840 g, 1.03 mmol) was dissolved in ether (80 mL), and MeOH (60 mL) containing a catalytic amount of NaOMe was added. The mixture was stirred for 16 h and concentrated. Dichloromethane (200 mL) was added, the solution was washed with water until neutral, dried over $MgSO_4$ and concentrated in vacuo (0.733 g, 0.944 mmol, 92%). Crystallisation of the crude product from ether–hexanes gave the title compound **10** (0.613 g, 0.789 mmol, 79%) as fine white crystals: mp 120–121 °C; $[\alpha]_D$ +22° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz,

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2** [a]

	x	*y*	*z*	U_{eq}
O(1″)	7123(8)	8710(2)	7111(1)	13(1)
C(1″)	9126(13)	8892(3)	6682(2)	12(1)
C(2″)	8494(12)	8495(3)	6120(2)	14(1)
O(2″)	8549(9)	7773(2)	6259(2)	17(1)
C(3″)	5719(13)	8692(3)	5894(2)	14(1)
O(3″)	5028(9)	8341(2)	5354(1)	17(1)
C(4″)	5578(13)	9468(3)	5792(2)	14(1)
O(4″)	7487(9)	9661(2)	5340(2)	21(1)
C(5″)	6355(13)	9834(3)	6362(2)	16(1)
O(5″)	9016(8)	9609(2)	6579(1)	13(1)
C(6″)	6545(16)	10,609(3)	6294(3)	28(2)
C(1′)	8543(13)	8670(3)	8127(2)	15(1)
O(1′)	10,665(9)	9146(2)	8024(1)	15(1)
C(2′)	8096(12)	8258(3)	7563(2)	13(1)
C(3′)	5906(14)	7725(3)	7677(2)	15(1)
O(3′)	5300(10)	7342(2)	7159(2)	22(1)
C(4′)	6828(13)	7243(3)	8170(2)	15(1)
O(4′)	9180(9)	6860(2)	8017(2)	21(1)
C(5′)	7501(14)	7680(3)	8708(2)	15(1)
O(5′)	9534(8)	8207(2)	8573(1)	14(1)
C(6′)	8763(14)	7248(3)	9189(2)	17(1)
O(6′)	8949(9)	7607(2)	9739(1)	18(1)
C(1)	11,013(13)	9600(3)	9032(2)	13(1)
O(1)	13,529(8)	9297(2)	9103(1)	16(1)
C(6)	13,895(15)	9019(3)	9691(2)	23(2)
C(2)	10,471(14)	9762(3)	8381(2)	15(1)
C(3)	12,618(13)	10,263(3)	8136(2)	15(1)
O(3)	11,711(10)	10,527(2)	7571(2)	21(1)
C(4)	12,966(13)	10,885(3)	8531(2)	15(1)
O(4)	15,582(8)	11,207(2)	8435(2)	16(1)
C(5)	13,037(13)	10,701(3)	9188(2)	18(1)
O(5)	10,792(8)	10,249(2)	9340(2)	17(1)
O(1W)	7558(9)	7919(2)	4330(2)	18(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Major conformation angles (°) in the trisaccharide **2** [a]

Entry	Atoms	α-L-Fuc		α-D-Gal	α-D-Xyl
1	θ (C1–C2–C3–C4)	56.8	−60.1		−49.6
2	θ (C2–C3–C4–C5)	−55.1	55.8		42.4
3	θ (C3–C4–C5–O5)	54.8	−55.3		−48.5
4	θ (C4–C5–O5–C1)	−58.2	60.7		63.0
5	θ (C5–O5–C1–C2)	58.6	−63.0		−68.6
6	θ (O5–C1–C2–C3)	−58.0	62.5		61.3
7	χ (O5–C5–C6–O6)		69.7		
8	θ (O5–C1–O1–C6)				72.4
9	ϕ (O5′–C1′–O1′–C2)	−134.1		−91.8	
10	ψ (C1′–O1′–C2–C1)	104.3		68.2	

[a] All θs and χ denote intra-residue angles. ϕ and ψ refer to inter-residue angles and the prime denotes the non-reducing end atom.

$CDCl_3$): δ 2.51 (br s, 1 H, OH), 3.34–3.41 (m, 1 H), 3.36 (s, 3 H, CH_3O), 3.49–3.67 (m, 7 H), 3.87 (d, 1 H, *J* 4.5 Hz, H-4′), 3.89–3.96 (m, 1 H), 4.02 (dd, 1 H, *J* 7.5 and *J* 9.5 Hz, H-2′), 4.42 (s, 2 H, CH_2Ph), 4.47 (d, 1 H, *J* 8 Hz, H-1′), 4.56–4.93 (m, 9 H), 7.2–7.4 (m, 25 H, 5 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$), 55.1 (CH_3O), 59.7 (C-5), 68.7 (C-6′), 71.4 (C-2′), 72.5 (CH_2Ph), 73.3 (C-4′), 73.5 (2 × CH_2Ph), 73.8, 74.6 (CH_2Ph), 75.7 (CH_2Ph), 78.6, 79.3, 80.6, 81.7 (C-3′), 99.5 (C-1), 104.9 (C-1′), 127–129 (Ph), 137–139 (Ph); FABMS: *m/z* 777 ($[MH]^+$, 1%), 775 ($[M-H]^+$, 1%), 181 (78%), and 154 (100%); Anal. Calcd for $C_{47}H_{52}O_{10}$: C, 72.66; H, 6.75. Found C, 72.67; H, 6.68.

Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-α-D-xylopyranoside (**2**). —A mixture of acceptor **10** (0.285 g, 0.367 mmol), dry tetraethylammonium bromide (0.320 g, 1.53 mmol), and powdered 4 Å molecular sieves (0.860 g) was stirred in dry CH_2Cl_2 (7.4 mL). Freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (**11**) (0.191 g, 0.371 mmol) was added, and the mixture was shaken at ambient temperature for 5 days. The solids were removed by filtration through Celite®, and the filtrate was diluted with CH_2Cl_2 (100 mL). The filtrate was washed twice with water (100 mL) while extracting each wash with CH_2Cl_2 (50 mL). The CH_2Cl_2 extracts were combined, dried ($MgSO_4$) and concentrated in vacuo to a syrup. The crude product was purified by silica-gel column chromatography (1:2 EtOAc–hexanes as eluent) to give impure methyl 2,3,4-tri-O-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-O-benzyl-β-D-galactopyranosyl-(1→2)-3,4-di-O-benzyl-α-D-xylopyranoside (**12**) [TLC (1:2 EtOAc–hexanes), R_f 0.65] (0.394 g) as a syrup. ^1H NMR (300 MHz, $CDCl_3$) inter alia δ 1.16 (d, 3 H, *J* 6.5 Hz, H-6″), 3.27 (s, 3 H, CH_3O), 3.33–4.10 (m, 13 H), 4.24 (dd, 1 H, *J* 8 and 10 Hz), 4.34–5.02 (m, 19 H), 5.81 (d, 1 H, *J* 3 Hz), 6.95–7.60 (m, 40 H, 8 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.0 (C-6″), 54.8 (CH_3O), 59.6 (C-5), 66.6, 68.2 (C-6′), 71.4 (CH_2Ph), 72.3, 72.5 (2 C, CH_2Ph and CH), 72.8 (CH_2Ph), 73.3, 73.4 (CH_2Ph), 73.7 (CH_2Ph), 74.4, 74.6 (CH_2Ph), 74.8 (CH_2Ph), 75.6 (CH_2Ph), 76.5, 78.3 78.8, 79.7, 82.2, 84.5, 97.5 (C-1″), 99.5 (C-1), 101.4 (C-1′), 126-129 (Ph), 137–139 (Ph).

The impure per-*O*-benzylated trisaccharide **12** (0.342 g, 0.286 mmol) was dissolved in MeOH (20 mL). Ethyl acetate (5 mL) and 10% palladium-on-charcoal catalyst (200 mg) were added (Caution! extreme fire danger), and the mixture was shaken under an atmosphere of hydrogen at atmospheric pressure for 4 days. The catalyst was removed by filtration through Celite®, and the solution was concentrated to dryness. The product was dissolved in water (40 mL) and passed through a Sepak® C-18 cartridge. The cartridge was further eluted with 4:1 water–EtOH (20 mL). Removal of the solvent from the combined elutions and then purification by semi-prepar-

ative reversed-phase HPLC (1:19 MeOH–water as eluent) gave **2** (0.089 g, 0.188 mmol, 59% from **10**) as a white crystaline solid: mp 267–271 °C; $[\alpha]_D$ −36° (*c* 0.1, H_2O); ^1H NMR (300 MHz, D_2O): δ 1.19 (d, 3 H, *J* 6.5 Hz, H-6″), 3.36 (s, 3 H, CH_3O), 3.40–3.90 (m, 22 H), 4.49 (br q, 1 H, *J* 6.5, *J* 6.5, and *J* 6.5 Hz, H-5″), 4.62 (d, 1 H, *J* 7.5 Hz, H-1′), 4.98 (d, 1 H, *J* 3 Hz, H-1), 5.27 (d, 1 H, *J* 4 Hz, H-1″); ^{13}C NMR (75 MHz, D_2O): δ 16.7 (C-6″), 56.1 (CH_3O), 61.7, 62.2, 68.4, 69.8, 70.2, 70.8, 71.2, 73.3, 73.7, 74.7, 76.1, 78.0, 81.1, 100.5 (C-1 and C-1″), 104.4 (C-1′). FABMS, (negative ion mode) *m/z* 471 ($[M-H]^-$, 42%), 325 (12%), 313 (12%), 297 (87%), 295 (56%), 276 (12%), 265 (24%), 192 (19%), 175 (23%), 148 (100%); Anal. Calcd for $C_{18}H_{32}O_{14}\cdot H_2O$: C, 44.07; H, 6.99. Found C, 44.07; H, 6.82.

Methyl 3,4,6-tri-O-*benzyl*-β-D-*galactopyranosyl*-(1→2)-3,4-*di*-O-*benzyl*-β-D-*xylopyranoside* (**15**).—A mixture of silver triflate (1.5 g, 5.8 mmol) and powdered 4 Å molecular sieves (2.5 g) in CH_2Cl_2 (12 mL) was stirred for 15 min at rt. After cooling to −50 °C, acceptor **7** (0.62 g, 1.81 mmol) was added, and the solution was stirred for a further 15 min. A solution of the galactosyl chloride **8** (1.00 g, 2.0

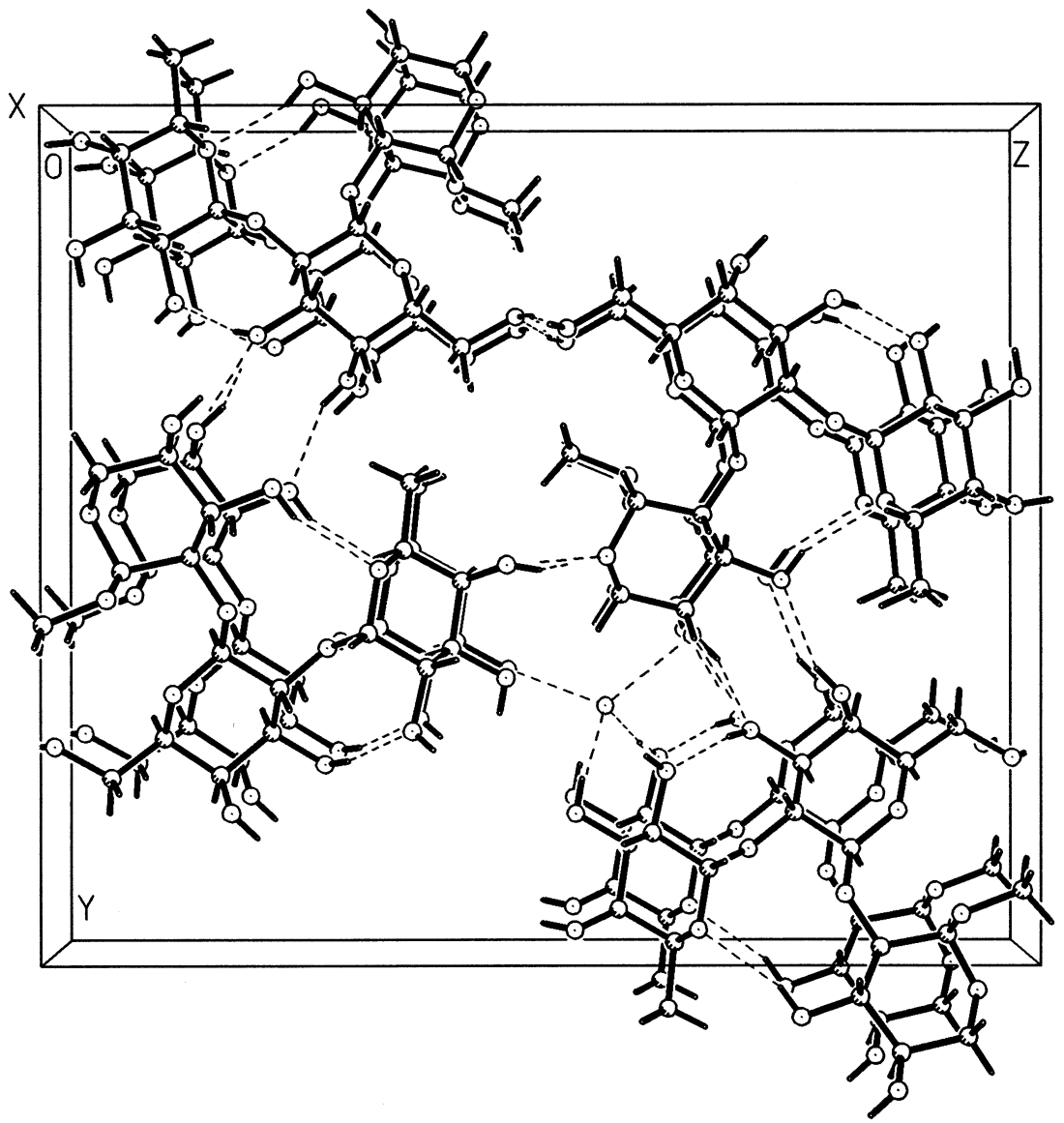


Fig. 2. Molecular packing in the crystal structure of **2** shows the stacking of trisaccharides along the *x*-axis. Each water molecule is hydrogen bonded to four surrounding trisaccharides.

Table 4
Intra- and intermolecular hydrogen bonds for **2** [a]

D–H…A	Distance (Å)		Angle (°)
	(H…A)	(D…A)	(D–H…A)
O(2″)–H(2A) …O(1W) # 1	1.91	2.726(5)	171.5
O(3″)–H(3A) …O(1W) # 2	2.07	2.830(5)	154.5
O(4″)–H(4A) …O(5) # 3	2.01	2.792(5)	159.9
O(3′)–H(3′1) …O(2″)	1.94	2.725(5)	159.8
O(4′)–H(4′1) …O(3) # 4	2.19	2.959(5)	155.7
O(6′)–H(6′) …O(6′) # 5	1.93	2.739(3)	171.3
O(3)–H(3′2) …O(5″)	2.39	3.172(5)	160.6
O(4)–H(4′2) …O(3′) # 6	1.86	2.634(5)	157.3

[a] D–H is 0.82 Å. Symmetry transformations used to generate equivalent atoms: # 1 $x+1/2, -y+3/2, -z+1$; # 2 $x-1/2, -y+3/2, -z+1$; # 3 $-x+3/2, -y+2, z-1/2$; # 4 $-x+2, y-1/2, -z+3/2$; # 5 $x-1/2, -y+3/2, -z+2$; # 6 $-x+2, y+1/2, -z+3/2$.

mmol) in CH_2Cl_2 (6.0 mL) was added, and the solution was stirred for 10 min. The reaction mixture was warmed to −40 °C and stirred for a further 30 min. The solution was neutralised with triethylamine, washed with ice-cold aq 1 M sodium thiosulfate, and filtered through Celite®. The filtrate was washed with 1 M HCl, satd aq $NaHCO_3$, water, and dried over $MgSO_4$. Removal of the solvent in vacuo gave methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→2)-3,4-di-*O*-benzyl-β-D-xylopyranoside (**14**) (1.61 g) as a slightly impure clear syrup. ^{1}H NMR data (200 MHz, $CDCl_3$): inter alia δ 1.77 (s, 3 H, OAc), 3.39 (CH_3O), 5.39 (dd, 1 H, *J* 10 and 8 Hz, H-2′), 7.20–7.40 (m, 25 H, 5 × Ph).

Crude **14** (1.60 g, 1.95 mmol) was dissolved in ether (50 mL) and MeOH (50 mL) containing a small amount of NaOMe. The mixture was stirred for 24 h and concentrated. Dichloromethane (200 mL) was added, and the solution was washed with water until neutral and dried over $MgSO_4$. Removal of the solvent in vacuo and purification of the residue by silica-gel column chromatography (silica-gel, 1:2 EtOAc–hexanes as eluent) gave **15** [1.05 g, 1.35 mmol, 75% from **7**; TLC (1:2 EtOAc–hexanes), R_f 0.15]. Crystallisation from ether–hexanes gave **15** (0.87 g, 1.12 mmol, 62% from **7**) as white crystals: mp 113 °C; $[\alpha]_D$ −16° (*c* 1.0, $CHCl_3$); ^{1}H NMR data (200 MHz, $CDCl_3$): δ 1.66 [br s, 1 H, OH], 3.24 (dd, 1 H, *J* 12 and *J* 8 Hz), 3.38 (dd, 1 H, *J* 10 and *J* 3 Hz), 3.43 (s, 3 H, CH_3O), 3.48–3.69 (m, 6 H), 3.84–3.96 (m, 3 H), 4.29–4.95 (m, 12 H), 7.20–7.40 (m, 25 H, 5 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 57.2 (CH_3O), 62.5 (C-5), 68.7 (C-6′), 72.6 (CH_2Ph), 72.8 (CH_2Ph), 72.9, 73.4 (CH_2Ph), 73.7, 74.0, 74.5 (CH_2Ph), 75.2 (CH_2Ph), 77.6, 80.6, 81.2, 81.4, 103.8 (C-1), 104.7 (C-1′), 127–129, 137.8, 137.8, 137.9, 138.6, 138.8; FABMS *m/z* 777 ($[MH]^+$, 1%), 775 ($[M-H]^+$, 1%), 745 ($[M-CH_3O]^+$, 2%), 637 (2%), 371 (6%), 327 (16%), 307 (6%), 289 (8%), 283 (41%), 239 (75%), 195 (88%), 181 (81%), 150 (100%). Anal. Calcd for $C_{47}H_{52}O_{10}$: C, 72.66; H, 6.75. Found C, 72.75; H, 6.70.

Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-xylopyranoside (**3**). —Freshly prepared bromide **11** (0.191 g, 0.371 mmol) was added to a mixture of **15** (0.285 g, 0.367 mmol), dry tetraethylammonium bromide (0.320 g, 1.53 mmol), and powdered 4 Å molecular sieve (0.860 g) in anhyd CH_2Cl_2 (7.4 mL), and the mixture was shaken for 5 days at ambient temperature. The solids were removed by filtration through Celite®, and CH_2Cl_2 (100 mL) was added. The filtrate was washed twice with water (100 mL), while extracting each wash with CH_2Cl_2 (50 mL). The CH_2Cl_2 extracts were combined and dried ($MgSO_4$) and concentrated to a syrup in vacuo. The product was purified by silica-gel column chromatography (1:2 EtOAc–hexanes as eluent; TLC, R_f 0.59) to give methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→2)3,4-di-*O*-benzyl-β-D-xylopyranoside (**16**) (0.309 g) as a slightly impure syrup: ^{1}H NMR (200 MHz, $CDCl_3$) inter alia δ 1.15 (d, 3 H, *J* 6.5 Hz, H-6″), 3.19–4.24 (m, 15 H), 3.41 (s, 3 H, CH_3O), 4.38–5.01 (m, 18 H), 5.76 (d, 1 H, *J* 3.5, H-1″), 6.98–7.52 (m, 40 H, 8 × Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.7 (C-6″), 56.3 (CH_3O), 63.3 (C-5), 66.3 (C-5″), 68.4 (C-6′), [71.2, 72.5, 72.8, 73.2, 73.5, 74.6, 74.7, 75.2 (8 × CH_2Ph)], 72.5, 73.0, 73.3, 75.5, 76.3, 77.9,

79.5, 84.2, 84.5, 97.5 (C-1″), 100.4, 102.9, 126–129 (Ph), 137.9–138.9 (Ph).

A mixture of per-*O*-benzylated trisaccharide **16** (0.258 g) and 10% palladium-on-charcoal (0.200 g) in MeOH (40 mL) [Caution! extreme fire hazard] and EtOAc (5 mL) was shaken under an atmosphere of hydrogen at atmospheric pressure for 4 days. The catalyst was removed by filtration through Celite®, and the solution was concentrated to dryness by rotary evaporation. The product was dissolved in water (40 mL) and passed through a Sepak® C-18 cartridge. The cartridge was further eluted with 1:4 EtOH–water (20 mL). Removal of the solvent from the combined elutions and further purification by semi-preparative reversed-phase HPLC (1:19 MeOH–water) gave **3** (0.055 g, 38% from acceptor **15**) as a white solid: mp 134–138 °C; $[\alpha]_D$ −116° (*c* 0.1, H_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (d, 3 H, *J* 6.5 Hz, H-6″), 3.29 (dd, 1 H, *J* 11.5 and 10 Hz), 3.51 (s, 3 H, CH_3O), 3.53–3.90 (m, 11 H), 3.95 (dd, 1 H, *J* 11.5 and 5 Hz), 4.38–4.44 (m, 2 H, H-5″ and H-1′), 4.91 (d, 1 H, *J* 8 Hz, H-1), 5.24 (d, 1 H, *J* 4 Hz, H-1″); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.8 (C-6″), 58.0 (CH_3O), 62.3 (C-5), 66.2 (C-6′), 68.1 (C-5″), 69.7, 70.4, 70.7, 70.9, 73.1, 74.9, 76.3, 77.9, 78.2, 78.3, 100.7 (C-1″), 101.9 (C-1′), 103.6 (C-1); FABMS (negative ion mode) *m*/*z* 471 ($[M-H]^-$, 63%), 423 (16%), 408 (27%), 386 (42%), 360 (13%), 338 (17%), 316 (34%), 276 (63%), 265 (20%), 192 (16%), 175 (20%), 148 (100%). Anal. Calcd for $C_{18}H_{32}O_{14}\cdot H_2O$: C, 44.07; H, 6.99. Found C, 43.92; H, 6.77.

Crystallography.—Slow recrystallisation of **2** from CH_3CN and water gave a crystal suitable for single-crystal X-ray diffraction analysis. Data were collected on a Nicolet R3M four-circle computer-controlled diffractometer, with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) at 183 K. Cell dimensions were derived from the angular measurement of 26 strong reflections in the range $7 < 2\theta < 23°$. A total of 1856 independent reflections were measured in the ω scan mode at a scan speed of 4.00° min^{-1}. Systematic absences within the data uniquely determined the orthorhombic space group as $P2_12_12_1$ (no 19) [20]. Data were corrected for Lorentz and polarisation effects using SHELXTL [21].

The structure was solved by direct methods using SHELXS-86 [22] and refined on F_o^2 using SHELXL-97 [23] with the hydrogen atoms included as fixed contributions to F_c. A difference Fourier map following the location of the expected non-hydrogen atoms showed a high peak, which could be assigned to the oxygen atom of a water solvate. Inclusion of this atom in the refinement led to a significant improvement in the residuals. The H atoms of the water were not included. All non-hydrogen atoms were refined anisotropically, and the final difference Fourier map was essentially flat. Complex neutral-atom scattering factors [23] were employed. At convergence $R_1 = 0.0470$ and $wR_2 = 0.1119$ for 1856 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0595$ and $wR_2 = 0.1161$ for all data; the goodness of fit was 0.980. The final difference map showed no peaks greater than 0.285 or less than −0.304 e Å^{-3}. Final atomic coordinates are listed in Table 2.

Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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