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Oligosaccharides related to xyloglucan: synthesis and X-ray crystal structure of methyl 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranoside

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Abstract

The disaccharides methyl 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranoside and methyl 2-*O*-(α-L-fucopyranosyl)-α-D-galactopyranoside have been synthesised using the assisted halide reaction of tri-*O*-benzyl-α-L-fucopyranosyl bromide with methyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside and methyl 3,4,6-tri-*O*-benzyl-α-D-galactopyranoside to construct the interresidue glycosidic linkages. A crystal structure of methyl 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranoside was determined using Mo-$K\alpha$ X-ray data at 183 K. The space group is P_1 (No. 1) with the unit cell containing two molecules of the disaccharide with unique conformations and a water molecule. The structure was refined to $R = 0.0566$ for 2969 reflections. The L-fucopyranosyl and D-galactopyranosyl residues have the nominal $^1C_4$ and $^4C_1$ conformations, respectively. The interresidue torsion angles are comparable with those generated in a recent molecular modelling study. © 1996 Elsevier Science Ltd.

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

1. Introduction

Xyloglucan [1], a major polysaccharide present in the primary cell walls of dicotyledonous plants, contains oligosaccharide components that are biologically active [1–5]. Of these, XG9 [2,6], a nonasaccharide formed by enzymatic degradation of xyloglucan,

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has been shown to occur in vivo through polysaccharide breakdown and to inhibit the auxin-induced (2,4-dichlorophenoxyacetic acid) elongation of pea stem segments. Synthetic [4,5] and natural XG5 [4] (pentasaccharide), XG11 [4] (undecasaccharide), and the unrelated (in origin) human milk trisaccharide, 2′-*O*-fucosyl-lactose [1] have been shown to have similar effects.

A common structural feature of these biologically active oligomers is a terminal α-L-fucopyranosyl residue. It appears that this functionality is essential for anti-auxin activity as non-fucosylated xyloglucan oligomers are inactive. However, it has been shown that this residue is not solely responsible for the activity as neither L-fucose nor methyl α-L-fucopyranoside inhibits the auxin-induced elongation of peak segments [3]. The other common structural feature of XG5, XG9, XG10, XG11, and 2′-*O*-fucosyl-lactose is a terminal 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl unit. Due to the activity of 2′-*O*-fucosyl-lactose McDougal and Fry [3] have postulated that only the fucosyl–galactose portion of the trisaccharide side chain of XG9 may be necessary for its biological activity. However, despite the availability of 2-*O*-(α-L-fucopyranosyl)-D-galactose [7], this theory has yet to be tested.

As part of a programme involving the utilisation of xyloglucan from apple pomace, an investigation of the minimum structural requirements for the anti-auxin activity exhibited by the aforementioned oligomers was planned. For this study we synthesised the disaccharides, methyl 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranoside (**1**) and methyl 2-*O*-(α-L-fucopyranosyl)-α-D-galactopyranoside (**2**). We envisaged that a conformational study of analogues of the xyloglucan side chain might give further information on possible binding and recognition elements.

In this paper we report new syntheses of the disaccharides **1** and **2**. Furthermore, a single-crystal X-ray structure for **1** has been determined and compared with a recently published molecular modelling study. Our investigation not only impacts on the chemistry of xyloglucans, but also that of the blood group substances [8] and an antigen [9] isolated from breast-cancer cell lines MCF7. The 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl moiety is common to these groups of carbohydrates and is an important immunodominant disaccharide unit of the A, B, H, and Le^b blood group antigenic determinants. To the authors' knowledge no other high-resolution crystal structures of **1** or related oligomers have been reported in detail.

2. Results and discussion

Our attention was directed to both anomers of methyl 2-*O*-(α-L-fucopyranosyl)-D-galactopyranoside. The β-methyl glycoside **1** has the same anomeric stereochemistry as the terminal disaccharide of both the xyloglucan side chain and the Lewis H blood group antigen, and as such it has received the attention of other workers. Both anomers have been previously synthesised by chemical methods [10], and **1** has also been synthesised by enzymatic methods [11,12].

For expediency, the galactosyl acceptors for the synthesis of both **1** and **2** were prepared from a common intermediate, 3,4,6-tri-*O*-benzyl-α-D-galactopyranose 1,2-(methyl orthoacetate) (**3**) [13], and the interresidue glycosidic linkages were formed

using the assisted halide approach of Lemieux [14]. An orthoester rearrangement of **3** using the method of Doboszewski et al. [15] gave the methyl galactoside **4** as a microanalytically pure clear syrup in 87% yield. The coupling constant associated with the anomeric proton (δ 4.28, $J_{1,2}$ 8 Hz) clearly indicated the β-D-configuration, and the three-proton singlet at δ 2.03 was attributed to the C-2 acetate. Zemplén deacetylation (NaOMe–MeOH) gave after recrystallisation, the known galactoside **5** in 70% yield. Reaction of the acceptor **5** with the freshly prepared fucosyl donor **6** in the presence of tetraethylammonium bromide gave, after purification by column chromatography, the protected disaccharide **7** in a 96% yield as a microanalytically pure syrup. The coupling constants of the anomeric resonances due to H-1′ (δ 5.63, $J_{1',2'}$ 3.5 Hz) and H-1 (δ 4.37, $J_{1,2}$ 7.5 Hz) were consistent with the anomeric configurations (α and β, respectively). Both the ^{1}H and ^{13}C NMR spectra were fully assigned with the aid of COSY, DEPT, and HETCOR experiments. Hydrogenolytic debenzylation (H_2, Pd/C) and purification of the product by reversed-phase column chromatography gave the target disaccharide **1** as a crystalline solid in 72% yield. Slow recrystallisation from a mixture of *n*-propyl acetate and wet methanol gave single crystals of a hemihydrate suitable for X-ray diffraction studies. The optical rotation of the product ($-112°$) was significantly different from that reported in the literature (Flowers [10], $-70°$). However, the ^{1}H NMR spectrum showed the expected one-proton doublets at δ 5.10 ($J_{1',2'}$ 4 Hz) due to H-1′ and at δ 4.39 ($J_{1,2}$ 8 Hz) due to H-1, and the ^{13}C NMR spectrum was in good agreement with that in the literature [12].

The α-methyl glycoside (**2**) was prepared using a similar strategy. Refluxing the orthoester **3** in methanolic hydrochloric acid gave a 3:1 mixture of the methyl glycosides **8** and **5**, which proved to be chromatographically inseparable. Three crystallisations from diethyl ether and hexanes gave the methyl 3,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**8**) in 13% yield. Reaction of **8** with the freshly prepared donor **6** in the presence of tetraethylammonium bromide gave the protected disaccharide **9** in a 71% yield as a microanalytically pure crystalline solid. Hydrogenolytic debenzylation of **9**, followed by purification by reversed-phase column chromatography gave methyl 2-*O*-(α-L-fucopyranosyl)-α-D-galactopyranoside (**2**) as a crystalline solid in 68% yield. The mp, optical rotation, and ^{1}H NMR data were in good agreement with those reported by Flowers [10].

With the successful syntheses of **1** and **2** completed, we felt that an X-ray crystallographic study of the β-methyl glycoside would provide important structural information. Oligosaccharides in solution are flexible molecules that can adopt a variety of conformation that are generally populated to different extents. However, in the crystalline state the conformation is determined to some extent by crystal packing requirements. These include space-fitting and stabilisation of the conformation by interactions such as hydrogen bonding and van der Waals forces. Thus the conformation of an oligosaccharide in a crystalline form may not represent the most favoured in solution, but one of the possible conformations that the oligosaccharide could adopt.

Suitable crystals of the β-methyl glycoside **1** were obtained by slow crystallisation from *n*-propyl acetate and wet methanol. Crystallographic parameters are given in Table 1. The unit cell included two molecules of the disaccharide that adopted two unique but similar (almost indistinguishable) conformations (i.e., **1a** and **1b**), and a water molecule.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{13}H_{24}O_{10.50}$
Formula weight	348.32
Temperature (K)	183(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*1 (No. 1)
Unit cell dimensions	$a = 4.930(2)$ Å; $\alpha = 92.72(3)°$
	$b = 11.140(4)$ Å; $\beta = 99.57(4)°$
	$c = 14.759(7)$ Å; $\gamma = 102.70(3)°$
Volume (Å^3)	776.8(6)
Z	2

The configuration, conformations, and atom numbering scheme are shown in Fig. 1. Atomic coordinates [1] of the non-hydrogen atoms are listed in Table 2. The main difference in the conformers **1a** and **1b** is the position of some of the hydroxyl protons that result from the hydrogen-bonding network. As expected the L-fucopyranosyl and D-galactopyranosyl residues adopted the $^1C_4$ and $^4C_1$ conformations, respectively. A comparison of bond angles and bond lengths of the fucosyl residue of **1** (Table 3) with values obtained from the crystal structure of methyl α-L-fucopyranose [16] shows no significant differences for the ring conformation. A similar comparison of the conformation of the β-galactopyranosyl ring of **1** shows no significant differences from data reported for the crystal conformation [17,18] of methyl β-D-galactopyranoside. Selected torsion angles for each of the molecules in the unit cell are given in Table 4.

The crystal packing projected along the *x*-axis is depicted in Fig. 2. The molecules are stacked in arrays along the *x*-axis with individual stacks interlinked by a network of hydrogen bonds (hydrogen bonds are shown as dotted lines). Molecules within each array are linked by a hydrogen-bonding network of the C-3 and C-4 hydroxyl groups of the galactose residue of one molecule, water of crystallisation, and the C-2, C-3 and C-4 hydroxyl groups of the fucosyl residues of the adjacent molecules. The arrays are linked together by hydrogen bonding between the C-6 hydroxyl groups of galactose residues of adjacent molecules. The arrays are also linked by van der Waals interactions between the methyl aglycone of the galactosyl residue and the methyl group of the fucosyl residues. No interresidue intramolecular hydrogen bonds are present in the crystal structure of **1**. Possible hydrogen bonds are listed in Table 5.

Several molecular modelling studies of the disaccharide **1** and related compounds have been carried out to probe the anomeric conformation. Lemieux et al. [19] found a global minimum for the fucosyl linkage of 2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranose at $\phi_H = 40°$ and $\psi_H = 20°$ using HSEA calculations. Furthermore, a study of

[1] Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

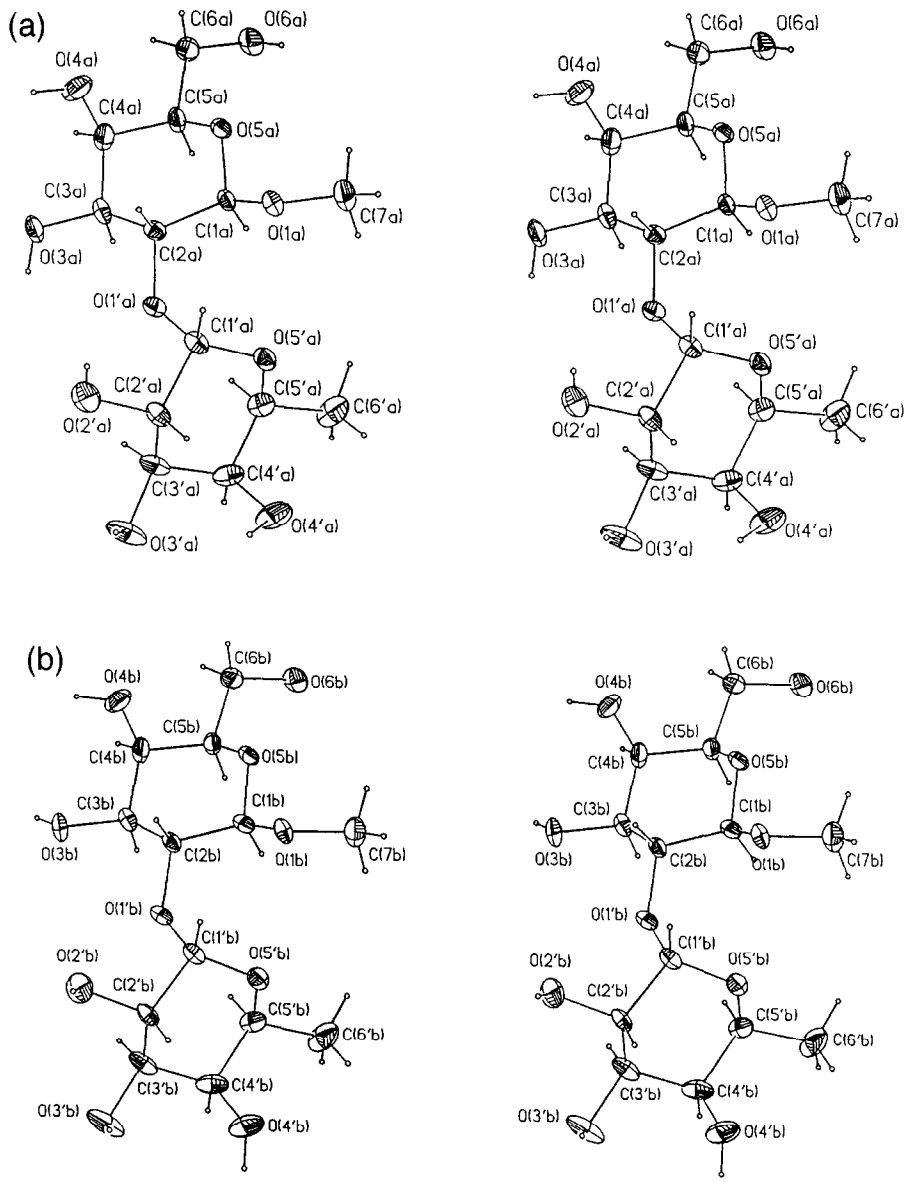


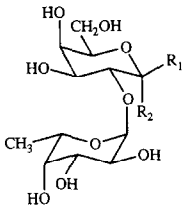
Fig. 1. Stereoviews of the two unique molecules of **1** showing atom numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

the human B blood-group determinant methyl (2-*O*-α-L-fucopyranosyl)-(3-*O*-α-D-galactopyranosyl)-β-D-galactopyranoside (**10**) predicted the energy minimum of the fucosyl linkage at $\phi_H = 55°$ and $\psi_H = 20°$ [20]. Lemieux [21] reported that an unpublished crystal structure determination of the trisaccharide had been carried out by Ball, and that the structure was almost identical to the preferred conformer predicted by these

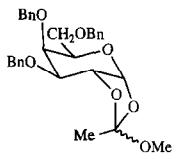
Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	U(eq)
C(1A)	−6932(9)	8562(4)	−2374(3)	15(1)
O(1A)	−9156(6)	9152(3)	−2548(2)	19(1)
C(7A)	−9964(12)	9284(5)	−3508(4)	29(1)
C(2A)	−5665(9)	8766(4)	−1344(3)	16(1)
O(1′A)	−3870(6)	9979(3)	−1081(2)	18(1)
C(3A)	−3716(9)	7909(4)	−1084(3)	19(1)
O(3A)	−2987(7)	7974(3)	−98(2)	24(1)
C(4A)	−4952(11)	6582(5)	−1468(3)	24(1)
O(4A)	−7237(9)	6002(3)	−1024(3)	36(1)
C(5A)	−5995(10)	6757(4)	−2504(3)	20(1)
O(5A)	−8102(6)	7291(3)	−2646(2)	18(1)
C(6A)	−7304(12)	5315(5)	−3003(3)	26(1)
O(6A)	−7745(8)	5358(3)	−3979(2)	27(1)
C(1′A)	−5180(9)	10984(4)	−1171(3)	17(1)
C(2′A)	−3675(9)	11978(4)	−390(3)	19(1)
O(2′A)	−3727(9)	11470(4)	483(3)	35(1)
C(3′A)	−660(9)	12561(4)	−489(4)	23(1)
O(3′A)	493(8)	13588(4)	193(3)	39(1)
C(4′A)	−640(10)	12987(4)	−1459(4)	23(1)
O(4′A)	−1957(9)	14012(3)	−1565(3)	36(1)
C(5′A)	−2218(11)	11931(5)	−2182(3)	23(1)
O(5′A)	−5080(7)	11472(3)	−2032(2)	20(1)
C(6′A)	−2478(15)	12312(5)	−3153(4)	38(1)
C(1B)	3251(9)	12894(4)	3687(3)	17(1)
O(1B)	637(6)	12316(3)	3863(2)	19(1)
C(7B)	641(12)	12183(5)	4817(3)	28(1)
C(2B)	3298(9)	12704(4)	2659(3)	16(1)
O(1′B)	3617(7)	11482(3)	2390(2)	19(1)
C(3B)	5854(9)	13556(4)	2393(3)	19(1)
O(3B)	5528(7)	13490(3)	1408(2)	24(1)
C(4B)	6317(10)	14889(5)	2786(3)	22(1)
O(4B)	4169(9)	15455(3)	2339(3)	36(1)
C(5B)	6323(10)	14888(4)	3818(3)	19(1)
O(5B)	3654(7)	14172(3)	3959(2)	19(1)
C(6B)	6761(11)	16149(4)	4313(3)	25(1)
O(6B)	7238(7)	16102(3)	5298(2)	26(1)
C(1′B)	1386(9)	10477(4)	2483(3)	17(1)
C(2′B)	1121(9)	9475(4)	1701(3)	19(1)
O(2′B)	716(9)	9997(4)	830(3)	35(1)
C(3′B)	3648(10)	8906(5)	1805(4)	24(1)
O(3′B)	3097(8)	7875(4)	1120(3)	40(1)
C(4′B)	4206(10)	8467(4)	2771(4)	26(1)
O(4′B)	1977(8)	7459(3)	2873(3)	34(1)
C(5′B)	4401(10)	9530(4)	3495(3)	23(1)
O(5′B)	1860(7)	9986(3)	3342(2)	21(1)
C(6′B)	4736(15)	9160(6)	4475(4)	42(2)
O(1)	8444(43)	5726(13)	655(9)	82(5)
O(1′)	6613(19)	5744(9)	663(6)	24(2)

calculations. The relevant torsion angles were $\phi_H = 52°$ and $\psi_H = 28°$. He postulated that the close comparison justified the role of the *exo*-anomeric effect in HSEA calculations. However, in the current crystallographic study the corresponding torsion angles of the fucosyl linkage of **1** ($\phi_H = 28°$ and $\psi_H = -57°$) are significantly different.



1 R_1 = OMe, R_2 = H
2 R_1 = H, R_2 = OMe



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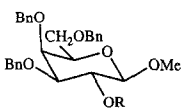
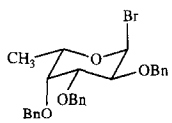


4 R = Ac
5 R = H



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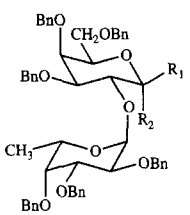
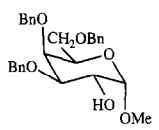


7 R_1 = OMe, R_2 = H
9 R_1 = H, R_2 = OMe



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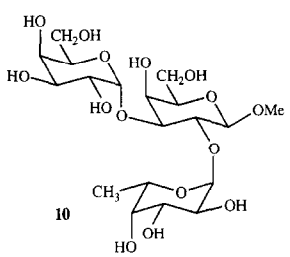

10

A molecular modelling and molecular dynamics study of **1** has been carried out by Yan and Bush using the CHARMM force field modified for carbohydrates [22]. They predicted that **1** could adopt a range of conformations with a global energy minimum at $\phi = -72°$ and $\psi = 126°$ ($\phi_H = 48°$ and $\psi_H = 6°$) and a less population minimum at $\phi = -86°$ and $\psi = 57°$ ($\phi_H = 34°$ and $\psi_H = -63°$). Our crystallographic study supports this, with the corresponding torsion angles being $\phi = -93°$ and $\psi = 65°$ ($\phi_H = 28°$ and $\psi_H = -57°$). Thus the crystal conformation of **1** falls within the well associated with the higher energy minimum while that of the trisaccharide **10** falls within the global minimum.

Table 3
Bond lengths (Å) and angles (°) for **1**

C(1A)–O(1A)	1.392(5)	C(1B)–O(1B)	1.380(6)
C(1A)–O(5A)	1.417(5)	C(1B)–O(5B)	1.422(5)
C(1A)–C(2A)	1.531(6)	C(1B)–C(2B)	1.526(6)
O(1A)–C(7A)	1.430(6)	O(1B)–C(7B)	1.422(6)
C(2A)–O(1′A)	1.439(5)	C(2B)–O(1′B)	1.448(5)
C(2A)–C(3A)	1.516(6)	C(2B)–C(3B)	1.523(6)
O(1′A)–C(1′A)	1.411(5)	O(1′B)–C(1′B)	1.416(6)
C(3A)–O(3A)	1.435(5)	C(3B)–O(3B)	1.431(5)
C(3A)–C(4A)	1.513(7)	C(3B)–C(4B)	1.522(7)
C(4A)–O(4A)	1.443(6)	C(4B)–O(4B)	1.434(6)
C(4A)–C(5A)	1.529(6)	C(4B)–C(5B)	1.522(6)
C(5A)–O(5A)	1.438(6)	C(5B)–O(5B)	1.434(6)
C(5A)–C(6A)	1.508(7)	C(5B)–C(6B)	1.507(7)
C(6A)–O(6A)	1.425(6)	C(6B)–O(6B)	1.438(6)
C(1′A)–O(5′A)	1.409(6)	C(1′B)–O(5′B)	1.409(6)
C(1′A)–C(2′A)	1.529(6)	C(1′B)–C(2′B)	1.536(6)
C(2′A)–O(2′A)	1.434(6)	C(2′B)–O(2′B)	1.437(6)
C(2′A)–C(3′A)	1.520(6)	C(2′B)–C(3′B)	1.507(7)
C(3′A)–O(3′A)	1.435(6)	C(3′B)–O(3′B)	1.441(6)
C(3′A)-C(4′A)	1.529(7)	C(3′B)–C(4′B)	1.532(8)
C(4′A)–O(4′A)	1.434(6)	C(4′B)–O(4′B)	1.421(6)
C(4′A)–C(5′A)	1.526(7)	C(4′B)–C(5′B)	1.532(7)
C(5′A)–O(5′A)	1.448(6)	C(5′B)–O(5′B)	1.421(6)
C(5′A)–C(6′A)	1.507(7)	C(5′B)–C(6′B)	1.515(7)
O(1A)–C(1A)–O(5A)	106.3(3)	O(1B)–C(1B)–O(5B)	106.8(3)
O(1A)–C(1A)–C(2A)	109.2(3)	O(1B)–C(1B)–C(2B)	109.8(4)
O(5A)–C(1A)–C(2A)	110.9(3)	O(5B)–C(1B)–C(2B)	110.2(4)
C(1A)–O(1A)–C(7A)	112.4(3)	C(1B)–O(1B)–C(7B)	112.9(4)
O(1′A)–C(2A)–C(3A)	103.7(3)	O(1′B)–C(2B)–C(3B)	103.3(3)
O(1′A)–C(2A)–C(1A)	112.8(4)	O(1′B)–C(2B)–C(1B)	112.6(4)
C(3A)–C(2A)–C(1A)	111.0(4)	C(3B)–C(2B)–C(1B)	111.8(4)
C(1′A)–O(1′A)–C(2A)	116.7(3)	C(1′B)–O(1′B)–C(2B)	116.6(3)
O(3A)–C(3A)–C(2A)	108.9(4)	O(3B)–C(3B)–C(2B)	109.0(4)
O(3A)–C(3A)–C(4A)	109.9(4)	O(3B)–C(3B)–C(4B)	110.4(4)
C(2A)–C(3A)–C(4A)	113.7(4)	C(2B)–C(3B)–C(4B)	113.0(4)
O(4A)–C(4A)–C(3A)	111.7(4)	O(4B)–C(4B)–C(3B)	111.0(4)
O(4A)–C(4A)–C(5A)	110.5(4)	O(4B)–C(4B)–C(5B)	111.1(4)
C(3A)–C(4A)–C(5A)	108.0(4)	C(3B)–C(4B)–C(5B)	108.0(4)
O(5A)–C(5A)–C(6A)	107.1(4)	O(5B)–C(5B)–C(6B)	107.3(4)
O(5A)–C(5A)–C(4A)	108.9(4)	O(5B)–C(5B)–C(4B)	108.8(4)
C(6A)–C(5A)–C(4A)	115.1(4)	C(6B)–C(5B)–C(4B)	114.6(4)
C(1A)–O(5A)–C(5A)	111.8(3)	C(1B)–O(5B)–C(5B)	112.7(3)
O(6A)–C(6A)–C(5A)	111.8(4)	O(6B)–C(6B)–C(5B)	111.5(4)
O(1′A)–C(1′A)–O(5′A)	112.1(3)	O(1′B)–C(1′B)–O(5′B)	112.2(3)
O(1′A)–C(1′A)–C(2′A)	108.0(4)	O(1′B)–C(1′B)–C(2′B)	107.9(3)
O(5′A)–C(1′A)–C(2′A)	110.1(4)	O(5′B)–C(1′B)–C(2′B)	109.8(4)
O(2′A)–C(2′A)–C(3′A)	110.7(4)	O(2′B)–C(2′B)–C(3′B)	110.9(4)
O(2′A)–C(2′A)–C(1′A)	109.9(4)	O(2′B)–C(2′B)–C(1′B)	109.2(4)
C(3′A)–C(2′A)–C(1′A)	112.6(4)	C(3′B)–C(2′B)–C(1′B)	112.1(4)
O(3′A)–C(3′A)–C(2′A)	109.5(4)	O(3′B)–C(3′B)–C(2′B)	109.0(4)

Table 3 (continued)

O(3'A)–C(3A)–C(4'A)	110.4(4)	O(3'B)–C(3'B)–C(4'B)	109.9(4)
C(2'A)–C(3'A)–C(4'A)	109.5(4)	C(2'B)–C(3'B)–C(4'B)	109.9(4)
O(4'A)–C(4'A)–C(3'A)	110.0(4)	O(4'B)–C(4'B)–C(3'B)	110.0(4)
O(4A)–C(4'A)–C(5'A)	109.5(4)	O(4'B)–C(4'B)–C(5'B)	109.4(4)
C(3'A)–C(4'A)–C(5'A)	110.2(4)	C(3'B)–C(4'B)–C(5'B)	109.5(4)
O(5'A)–C(5'A)–C(6'A)	106.1(5)	O(5'B)–C(5'B)–C(6'B)	106.1(5)
O(5'A)–C(5'A)–C(4'A)	110.5(4)	O(5'B)–C(5'B)–C(4'B)	110.4(4)
C(6'A)–C(5'A)–C(4'A)	113.1(4)	C(6'B)–C(5'B)–C(4'B)	113.5(5)
C(1'A)–O(5'A)–C(5'A)	112.8(3)	C(1'B)–O(5'B)–C(5'B)	113.1(4)

Table 4
Selected torsion and bond angles (°) for the crystal conformations of **1a** and **1b**

Torsion		Molecule **1a**	Molecule **1b**
O(5')–C(1')–O(1')–C(2)	ϕ	−92.7(4)	−92.5(4)
H(1')–C(1')–O(1')–C(2)	ϕ_H	+27.8(4)	28.2(4)
C(1')–O(1')–C(2)–C(1)	ψ	+65.0(5)	+64.4(5)
C(1')–O(1')–C(2)–H(2)	ψ_H	−57.7(3)	−58.0(3)
O(5)–C(5)–C(6)–O(6)	ω	+69.5(5)	+69.2(5)
C(1')–O(1)–C(2)	τ	+116.7(3)	+116.6(3)

Standard nomenclature for dihedral angles used throughout this study are those adopted by the International Union of Pure and Applied Chemistry and International Union of Biologists [29]. The glycosidic torsion angles given by the terms ϕ_H and ψ_H are those defined by Lemieux et al. [30].

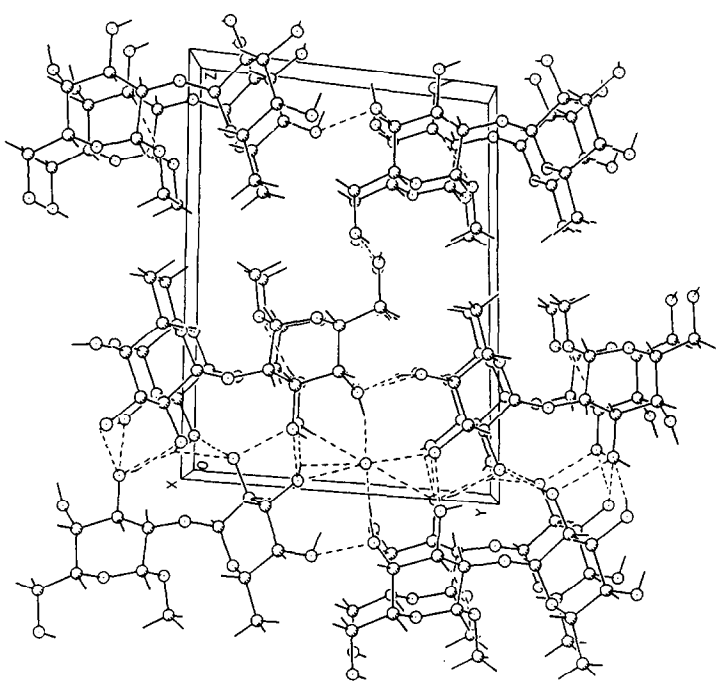

Fig. 2. Unit cell contents of **1** projected down the *x*-axis. Possible hydrogen bonds are indicated by dashed lines.

Table 5
Possible hydrogen bonds [31], bond lengths, and angles in the crystal structure of **1**

D–H · · · A	[a]	D · · · A (Å)	H · · · A (Å) [b]	D–H · · · A (°) [b]
O3a–H · · · O1′a	0	2.795(5)	2.609	91.4
O3a–H · · · O2′b	0	2.711(5)	1.802	162.5
O3a–H · · · O3′b	0	3.257(5)	2.856	107.0
O4a–H · · · O3a	0	2.797(5)	2.581	93.4
O6a–H · · · O5a	0	2.902(5)	2.614	98.3
O3′a–H · · · O2′a	0	2.883(6)	2.536	102.2
O4′a–H · · · O3′a	0	2.781(6)	2.292	111.9
O4b–H · · · O3b	0	2.792(6)	2.645	89.1
O2′b–H · · · O1′a	0	3.305(5)	2.594	133.0
O2′b–H · · · O3a	0	2.711(5)	2.064	124.8
O2′b–H · · · O2′a	0	3.007(7)	2.534	111.5
O3′b–H · · · O3a	0	3.257(5)	2.499	138.0
O3b–H · · · O3′a	1	3.253(6)	2.523	134.8
O4′b–H · · · O4b	2	2.819(6)	1.913	161.9
O4a–H · · · O1	3	2.02(2)	1.789	89.7
O4a–H · · · O1′	3	2.11(1)	1.777	97.4
O2′a–H · · · O2′b	4	3.005(6)	2.093	163.8
O4a–H · · · O1′	4	2.94(1)	2.054	156.0
O3′b–H · · · O1	4	2.89(2)	2.148	135.5
O3′b–H · · · O1′	4	3.479(9)	2.614	153.6
O4a–H · · · O1	4	3.50(2)	2.715	141.2
O3′a–H · · · O3b	4	3.253(6)	2.327	169.5
O3′a–H · · · O1	6	2.88(2)	2.388	112.5
O4b–H · · · O1	7	3.50(2)	2.707	142.6
O4b–H · · · O1′	7	2.93(1)	2.046	156.0
O3b–H · · · O1′	7	2.77(1)	2.242	114.8
O3b–H · · · O1	7	2.96(2)	2.187	138.5

[a] Equivalent positions: (0) X, Y, Z; (1) $+X+1, +Y, +Z$; (2) $+X, +Y-1, +Z$; (3) $-X, -Y+1, -Z$; (4) $+X-1, +Y, +Z$; (5) $-X-1, -Y+1, -Z$; (6) $+X-1, +Y+1, +Z$; (7) $+X, +Y+1, +Z$.
[b] Values normalised following refs. [32,33].

In conclusion, we have reported the syntheses of both anomers of methyl 2-*O*-(α-L-fucopyranosyl)-D-galactopyranoside (i.e., **1** and **2**). The β-anomer **1** represents the terminal disaccharide unit of one of the side chains of xyloglucan, and that of the H blood-group determinant. A crystal structure has been determined for **1**, and a comparison of the torsion angles with those generated by a recent molecular modelling study has been made. A study of the growth inhibiting activity of **1**, **2**, and related oligomers is planned.

3. Experimental

General.—Mps were measured on a Gallenkamp capillary melting point apparatus and are uncorrected. Optical rotations were measured at 25 °C using a Jasco DIP370 digital polarimeter. Varian Gemini 200 and VXR300 spectrometers were used to obtain

^{1}H (200 and 300 MHz) and ^{13}C (50 and 75 MHz) NMR spectra. All spectra were measured on solutions of the compound in deuteriochloroform using tetramethylsilane as an internal reference or deuterium oxide using methanol (δ 3.32) as an internal reference, unless otherwise stated. Chemical shifts are reported as parts per million (ppm) using the δ scale. Coupling constants (J) are reported to $\pm$0.5 Hz. IR spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrophotometer. FAB mass spectra were recorded on a Kratos MSORF mass spectrometer using *m*-nitrobenzyl alcohol as the matrix and xenon as the ionising gas. Elemental analyses were carried out by Dr. R.G. Cunninghame and associates at the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Thin-layer chromatography (TLC) was performed on E. Merck Silica Gel DC Alurolle Kieselgel 60F$_{254}$ plates and were visualised under an UV lamp and/or with a spray consisting of 5% w/v sulfuric acid in ethanol with subsequent heating. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). All column chromatography solvents were reagent grade. Reversed-phase HPLC was performed using a Jasco PU-980 pump, a Jasco 830-RI refractive index detector, a Rheodyne model 761 injector fitted with a 1 mL sample loop, and an Activon ODS (250 × 10 mm) column. The flow rate was typically 1–2 mL/min. All other solvents and reagents were purified using the methods outlined in ref. [34].

Methyl 2-O-acetyl-3,4,6-tri-O-benzyl-β-D-galactopyranoside (**4**).—A solution of 3,4,6-tri-*O*-benzyl-α-D-galactopyranose 1,2-(methyl orthoacetate) (**3**) [13] (0.38 g, 0.75 mmol), 2,2,2-trichloroethanol (0.15 mL) and mercuric bromide (0.12 g, mmol) in nitromethane (5.3 mL) was stirred for 16 h at room temperature. The solvent was removed under reduced pressure, and the crude material was purified by column chromatography on silica gel (3:2 ether–hexanes as eluent) to give methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**4**) (TLC, R_f 0.33) (0.33 g, 87%) as a clear syrup: $[\alpha]_D$ 0° (*c* 1, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 2.03 (3 H, s, OAc), 3.45 (3 H, s, OCH_3), 3.47–3.67 (4 H, m), 3.95 (1 H, br d, *J* 3.0 Hz, H-4), 4.28 (1 H, d, *J* 8.0 Hz, H-1), 4.42–4.71 (5 H, m), 4.93 (1 H, d, *J* 12.0 Hz, one of CH_2Ph), 5.36 (1 H, dd, *J* 8.0 and 10.0 Hz, H-2), and 7.20–7.40 (15 H, m, 3 × Ph); δ_C (75 MHz, $CDCl_3$) 20.9 (OAc), 56.1 (OCH_3), 68.6 (C-6), 71.0 (C-2), 71.85, 73.4, and 74.3 (3 × CH_2Ph), 72.5 (C-4), 73.5 (C-5), 80.2 (C-3), 101.9 (C-1), 127–129 and 137.6–138.3 (3 × Ph).

Methyl 3,4,6-tri-O-benzyl-β-D-galactopyranoside (**5**).—A solution of the galactoside **4** (4.03 g, 7.96 mmol) in methanol (50 mL) was added to a solution of sodium methoxide in methanol [formed by the addition of sodium (0.05 g) to methanol (50 mL)]. The mixture was stirred for 24 h, after which time it was neutralised by the addition of a small amount of HCl (0.5 M) and then concentrated to approximately half of its original volume. Dichloromethane (200 mL) was added, and the mixture was washed with water (3 × 500 mL). The organic layer was dried over magnesium sulfate and concentrated in vacuo to give a white crystalline solid (3.16 g). Recrystallisation from ether–hexanes gave the title compound **5** (2.60 g, 70%) as white needles: mp 99 °C (lit. [13] 99–99.5°); $[\alpha]_D$ −5.4° (*c* 0.7, $CHCl_3$) [lit. [13] −5.4° (*c* 1, $CHCl_3$)]; δ_H (200 MHz, $CDCl_3$) 1.97 (1 H, d, *J* 2.0 Hz, exchangeable in D_2O, OH), 3.43 (1 H, dd, *J* 3.0 and 9.5 Hz, H-3), 3.53 (3 H, s, CH_3O), 3.59–3.66 (3 H, m, H-5 and H-6), 3.88–3.98 (2 H, m, H-2 and H-4), 4.18 (1 H, d, *J* 7.5 Hz, H-1), 4.43 and 4.50 (2 H, ABq, *J* 12.0 Hz,

CH_2Ph), 4.57–4.77 (3 H, m, CH_2Ph), 4.88 (1 H, ABd, J 12.0 Hz, CH_2Ph), 7.2–7.4 (15 H, m, $3 \times Ph$); δ_C (75 MHz, $CDCl_3$) 56.99 (CH_3O), 68.69 (C-6), 71.27 (C-2), 72.36, 73.59, and 74.52 (CH_2Ph), 72.75 (C-4), 73.70 (C-5), 81.99 (C-3), 104.11 (C-1), 127–129 and 137–139 (Ph); FABMS (positive ion): m/z 465 (MH^+, 19%), 341 ($[MH - MeOH - BnH]^+$, 10%), 307 ($[MH - MeOH - BnOH - H_2O]^+$, 53%), 289 ($[MH - MeOH - BnOH - 2H_2O]^+$, m/z, 32%), 154 (100%). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.40; H, 6.64.

Methyl 3,4,6-tri-O-benzyl-2-O-(tri-O-benzyl-α-L-fucopyranosyl)-β-D-galactopyranoside (**7**).—Freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (**6**) [23] (2.2 g, 4.3 mmol) was added to a mixture of the galactoside **5** (1.00 g, 2.2 mmol), tetraethylammonium bromide (2.20 g, 11 mmol), and powdered 4 Å molecular sieves (2.2 g) in dichloromethane (14.5 mL). The mixture was shaken for 4.5 days and then filtered through a Celite® pad. Further dichloromethane (100 mL) was added, and the organic mixture was washed with water (2×100 mL). The water wash was extracted with dichloromethane (2×50 mL), and the combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure, followed by purification by column chromatography using silica gel (2:3 ether–hexanes as eluent; TLC, R_f 0.33) gave the title compound **7** (1.87 g, 96%) as a clear syrup: $[\alpha]_D$ −54° (c 0.7, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.12 (3 H, d, J 6.5 Hz, H-6′), 3.45 (3 H, s, CH_3O), 3.56–3.63 (3 H, m, H-6 and H-5), 3.69 (1 H, d, J 2.0 Hz, H-4′), 3.72 (1 H, dd, J 2.5 and 9.5 Hz, H-3), 3.91–3.96 (2 H, m, H-3′ and H-4), 4.03 (1 H, dd, J 10.0 and 4.0 Hz, H-2′), 4.20 (1 H, dd, J 9.5 and 8.0 Hz, H-2), 4.29 (1 H, br q, J 6.5, 6.5, and 6.5 Hz, H-5′), 4.37 (1 H, d, J 7.5 Hz, H-1), 4.42 and 4.47 (2 H, ABq, J 12.0 Hz, CH_2Ph), 4.49–4.95 (10 H, m, $5 \times CH_2Ph$), 5.63 (1 H, d, J 3.5 Hz, H-1′), 7.0–7.4 (30 H, m, $6 \times Ph$); δ_C (75 MHz, $CDCl_3$) 16.46 (C-6′), 56.50 (CH_3O), 66.33 (C-5′), 68.86 (C-6), [71.24, 72.59, 72.99, 73.65, 74.36, and 74.62 ($6 \times CH_2Ph$)], 71.97 (C-4), 72.89 (C-2), 73.23 (C-5), 75.69 (C-2′), 77.78 (C-4′), 79.73 (C-3′), 84.01 (C-3), 97.44 (C-1′), 102.93 (C-1), 126–129 (CH_2Ph), 138–139 (CH_2Ph); FABMS (positive ion): m/z 880 (M^+, 2%), 879 ($[M - H]^+$, 3%), 757 (2%), 417 (2%), 325 (11%), 307 (17%), 289 (12%), 271 (29%), 181 (100%). Anal. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.63; H, 6.97.

Methyl 2-O-(α-L-fucopyranosyl)-β-D-galactopyranoside (**1**).—A mixture of the disaccharide **7** (1.67 g, 1.89 mmol) and 10% palladium-on-charcoal (0.20 g) in glacial acetic acid (100 mL) under an atmosphere of hydrogen was shaken for 4 days. Filtration through a pad of Celite® and removal of the solvent under reduced pressure gave a syrup (0.76 g). Purification by C-18 reversed-phase column chromatography (99:1 water–methanol as eluent) gave the title compound **1** (0.46 g, 72%) as a clear syrup that crystallised on standing. Recrystallisation from methanol and propyl acetate gave single crystals suitable for X-ray crystal structure determination. Mp 171 °C; $[\alpha]_D$ −112° (c 0.5 H_2O) [lit. [10] −70.1° (c 0.88, H_2O)]; δ_H (300 MHz, D_2O) 1.18 (3 H, d, J 6.5 Hz, H-6′), 3.49 (1 H, dd, J 9.5 and 8 Hz, H-2), 3.55 (3 H, s, CH_3O), 3.62–3.90 (8 H, m), 4.23 (1 H, q, J 6.5 Hz, 6.5, and 6.5 Hz, H-5′), 4.39 (1 H, d, J 8 Hz, H-1), 5.10 (1 H, d, J 4 Hz, H-1′); δ_C (75 MHz, D_2O) 16.50 (C-6′), 58.41 (CH_3O), 62.25 (C-6), 68.17 (C-5′), 69.75 (C-2′), 70.06 (C-4), 70.90 (C-3′), 73.22 (C-4′), 74.56 (C-3), 76.20 (C-5), 79.52 (C-2), 101.38 (C-1′), 104.02 (C-1); FABMS (positive ion): m/z 341 ($[MH]^+$, 12%), 307 ($[M - MeOH - H]^+$, 85%), 289 ($[MH - MeOH - H_2 - H_2O]^+$, 69%), 137

(100%). Anal. Calcd for $C_{13}H_{24}O_{10} \cdot 0.5H_2O$: C, 44.70; H, 7.21. Found: C, 44.86; H, 7.28.

X-ray crystallography.—Slow recrystallisation of **1** from methanol–*n*-propyl acetate gave colourless plates. Precession photography, using Cu-$K\alpha$ radiation, indicated a triclinic unit cell. The choice of the non-centrosymmetric alternative P_1 (No. 1) [24] was imposed by the chirality of the molecule and vindicated by the successful solution and refinement. Details of the crystal data collection are given in Table 1. Data were corrected for Lorentz and polarisation effects using SHELXTL [25]; absorption corrections were not applied.

The structure was solved by direct methods using SHELXS-86 [26]; the chosen E-map revealed the position of all of the non-hydrogen atoms from the two discrete molecules in the unit cell. The structure was refined on F_o^2 using SHELXL-93 [27] with the hydrogen atoms included as fixed contributions to F_c. A difference Fourier map indicated the presence of an additional heavy atom, disordered over two positions. This was presumed to be the oxygen atom of a solvent water molecule and was refined appropriately with equal occupancy for each position. H atoms of the disordered water were not included. All non-hydrogen atoms were refined anisotropically and this model of the structure converged with $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.0566$ ($F > 2F$, 2969 reflections), and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.1436$ (all data), $w^{-1} = {}^2(F_o^2) = (0.0761P)^2 + 0.61P$, and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The final difference Fourier map was essentially flat with residual electron density max = 0.57, min = −0.34 e Å^{-3}.

*Methyl 3,4,6-tri-*O*-benzyl-α-*D*-galactopyranoside* (**8**).—A solution of the orthoacetate **3** (5.10 g, 10.1 mmol) in 2% methanolic hydrochloric acid (500 mL) was refluxed for 16 h. The solution was concentrated under reduced pressure (ca. 30 mL) and dichloromethane was added. The mixture was washed with water (200 mL), satd sodium hydrogencarbonate solution (200 mL) and again with water (200 mL). The organic layer was dried over magnesium sulfate, and removal of the solvent under reduced pressure gave the product as 3:1 mixture of the α and β anomers **8** and **5** (4.78 g, 100%) as a white crystalline material. Three repeated crystallisations from ether–hexane gave the title compound **8** (0.62 g, 13%) as white needles: mp 83° (lit. [28] 85–88.5°); $[\alpha]_D$ +86° (*c* 0.65, $CHCl_3$) [lit. [28] +94° (*c* 0.7 $CHCl_3$)]; δ_H (300 MHz, $CDCl_3$) 2.14 (1 H, br s, exchangeable in D_2O, OH), 3.41 (3 H, s, CH_3O), 3.59 (2 H, m, H-6), 3.70 (1 H, dd, *J* 3.0 and *J* 10.0 Hz, H-3), 3.91 (1 H, br t, *J* 6.5 and 6.5 Hz, H-5), 3.98 (1 H, br d, *J* 2.5 Hz, H-4), 4.17 (1 H, dd, *J* 10.0 and 4.0 Hz, H-2), 4.43 and 4.52 (2 H, ABq, *J* 12.0 Hz, CH_2Ph), 4.57 and 4.89 (2 H, ABq, *J* 11.0 Hz, CH_2Ph), 4.67 and 4.74 (2 H, ABq, *J* 12.0 Hz, CH_2Ph), 4.85 (1 H, d, *J* 4.0 Hz, H-1), 7.2–7.4 (15 H, m, 3 × Ph); δ_C (75 MHz, $CDCl_3$) 55.42 (CH_3O), 68.95 (C-6), 69.03 (C-2), 69.59 (C-5), [72.41, 73.54, and 74.67 (CH_2Ph)], 73.98 (C-4), 79.59 (C-3), 99.65 (C-1), 127–129 and 137–139 (Ph); FABMS (positive ion): *m/z* 465 ($[MH]^+$, 19%), 341 ($[MH - MeOH - BnH]^+$, 11%), 307 ($[MH - MeOH - BnOH - H_2O]^+$, 58%), 289 ($[MH - MeOH - BnOH - 2H_2O]^+$, 45%), 154 (100%). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.37; H, 7.01.

*Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(tri-*O*-benzyl-α-*L*-fucopyranosyl)-α-*D*-galactopyranoside* (**9**).—Freshly prepared 2,3,4-tri-O-benzyl-α-L-fucopyranosyl bromide (**6**) (0.900 g, 1.75 mmol) was added to a mixture of the galactoside **8** (0.400 g, 0.86 mmol),

tetraethylammonium bromide (0.350 g, 1.7 mmol), and powered 4 Å molecular sieves (0.90 g) in dichloromethane (7 mL). The mixture was shaken for 4.5 days and then filtered through a Celite® pad. Additional dichloromethane (100 mL) was added, and the organic mixture was washed with water (2 × 100 mL). The water wash was extracted with dichloromethane (2 × 50 mL), and the combined extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure, followed by column chromatography on silica gel (1:1 ether–hexane as eluent) and crystallisation from ether–hexane, gave the title compound **9** (0.542 g, 71%) as white crystals: mp 106–108 °C; $[\alpha]_D$ −11° (c 0.5, $CHCl_3$); δ_H (300 MHz, $CDCl_3$) 1.09 (3 H, d, *J* 6.5 Hz, H-6′), 3.33 (3 H, s, CH_3O), 3.51–3.54 (2 H, m), 3.68 (1 H, br s), 3.83–3.89 (3 H, m), 4.01–4.13 (4 H, m), 4.39 and 4.48 (2 H, ABq, *J* 12.0 Hz, CH_2Ph), 4.57–5.04 (12 H, m, 5 × CH_2Ph, H-1′ and H-1); δ_C (75 MHz, $CDCl_3$) 16.85 (C-6′), 55.01 (CH_3O), 66.77, 69.22 (C-5′), 69.27 (C-6), [72.73, 73.09, 73.55, 73.76, 74.81, and 74.89 (6 × CH_2Ph)], 75.94, 76.38, 77.63, 77.75, 79.01, 79.06, 99.69, 100.66, 127–129 (Ph), [138.02, 138.68, 138.73 (2 C), 139.13, 139.45 (6 × Ph)]; FABMS (positive ion): *m/z* 881 ($[MH]^+$, 2%), 880 (M^+, 2%), 879 ($[M - H]^+$, 2%), 849 ($[MH - H_2O]^+$, 2%), 757 (1%), 463 (2%), 431 (3%), 417 (2%), 325 (8%), 307 (33%), 289 (22%), 271 (18%), 181 (88%), 154 (100%). Anal. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86. Found: C, 74.63; H, 6.81%.

Methyl-2-O-(α-L-fucopyranosyl)-α-D-galactopyranoside (**2**).—A mixture of the disaccharide **9** (0.144 g, 0.129 mmol) and 10% palladium-on-charcoal (0.15 g) in ethanol (15 mL) under an atmosphere of hydrogen was shaken for 4 days. Filtration through a pad of Celite® and removal of the solvent under reduced pressure gave a syrup (0.20 g). The crude product was eluted through a Sep-Pak® C-18 cartridge (1:4 methanol–water as eluent) and purified further by semipreparative HPLC (C-18, 1:9 methanol–water as eluent) gave the title compound **2** (0.035 g) as a clear syrup. Crystallisation from methanol and *n*-propyl acetate gave **2** (0.030 g, 68%) as white crystals: mp 202–203 °C (lit. [10] 202–204°); $[\alpha]_D$ +2° (*c* 0.1, H_2O) [lit. [10] 0.9° (*c* 1.15, H_2O)]; δ_H (300 MHz, D_2O) 1.22 (3 H, d, *J* 6.5 Hz, H-6′), 3.41 (3 H, s, CH_3O), 3.73–4.04 (8 H, m), 4.00 (1 H, d, *J* 3.0 Hz), 4.07 (1 H, br q, *J* 6.5, 6.5, and 6.5 Hz, H-5′), 4.94 (1 H, d, *J* 4.0 Hz, H-1*[2]), 5.03 (1 H, d, *J* 4.0 Hz, H-1*); δ_C (75 MHz, $CDCl_3$) 16.81 (C-6′), 55.99 (CH_3O), 62.46 (C-6), 68.58, 69.62 (2 C), 70.52, 70.62, 71.89, 72.98, 79.34, 100.19 (C-1*), 102.89 (C-1′*); FABMS (positive ion): *m/z* 363 ($[MNa]^+$, 28%), 341 ($[MH]^+$, 10%), 307 ($[M - MeOH - H]^+$, 46%), 289 ($[M - MeOH - H_2O - H]^+$, 30%) 219 (14%), 154 (100%).

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[2] Order of assignments may be reversed for *.

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