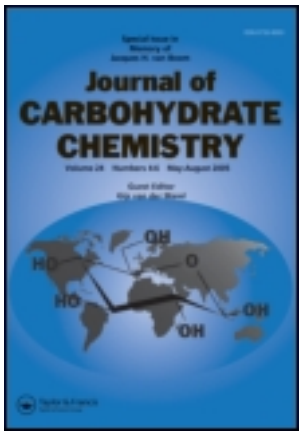

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SYNTHESIS OF O-METHYLATED DISACCHARIDES RELATED TO EXCRETORY/ SECRETORY ANTIGENS OF TOXOCARA LARVAE

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SYNTHESIS OF *O*-METHYLATED DISACCHARIDES RELATED TO EXCRETORY/ SECRETORY ANTIGENS OF *TOXOCARA* LARVAE[1]

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ABSTRACT

The disaccharides 2-*O*-Me-α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→*O*Allyl) **12**, α-L-Fuc*p*-(1→2)-4-*O*-Me-β-D-Gal*p*-(1→*O*Allyl) **15**, and 2-*O*-Me-α-L-Fuc*p*-(1→2)-4-*O*-Me-β-D-Gal*p*-(1→*O*Allyl) **18** have been synthesized. Glycosylation reactions were performed using ethyl 1-thiofucopyranosides as glycosyl donors and *N*-iodosuccinimide-triflic acid as the activating agent. The *O*-methylated disaccharides correspond to highly immunogenic *O*-glycan antigens occurring at the surface of *Toxocara canis* and *Toxocara cati* larvae.

INTRODUCTION

Toxocara canis and *Toxocara cati* are parasitic roundworms usually occurring in dogs and cats, which may cause severe infections in a human host affecting eyes, liver and the central nervous system.[2] The surface coat of the parasitic nematode larvae represents the major immunological challenge to the host immune system.[3] In particular, glycoproteins being present in multiple copies at the outer layer elicit a strong immune response, are subsequently released from the surface and divert the immune attack from the mobile nematode. The structure of the excreted and secreted glycoproteins (TES antigens) from *Toxocara canis* investigated by MS analysis of alditol acetates revealed the presence of the trisaccharide backbone α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→3)-D-Gal*p*NAc.[4] The fucose part has been found to be *O*-methylated at the 2-position. In addition, ~50% of the glycans

contained a 4-*O*-methyl group at the galactopyranosyl unit, which is also the prominent structure found in *T. cati* glycans. The anomeric configuration of the Gal*p*NAc residue has yet to be elucidated. Monoclonal anti-carbohydrate antibodies which have been raised against the TES antigens bind to different sites within the larval parasite.[5] For a detailed immunochemical characterization of those monoclonal antibodies, we have synthesized three potential carbohydrate ligands which are *O*-methylated either at position 2 of the fucopyranosyl moiety or at position 4 of the galactopyranosyl unit or at both positions. Herein we report on the synthesis of the corresponding disaccharide allyl glycosides, which may be converted into spacer-elongated derivatives to be coupled to proteins.[6]

RESULTS AND DISCUSSION

For the synthesis of the allyl galactopyranoside acceptor derivatives, the known[7] allyl β-D-galactopyranoside **1** was reacted with anisaldehyde dimethyl acetal in the presence of *p*-toluenesulphonic acid in MeCN to give the crystalline 4,6-*O*-*p*-methoxybenzylidene derivative **2** in 81% yield.[8] Regioselective protection of the 3-OH group was achieved in 77% yield by reaction of the 2,3-*O*-dibutylstannylene intermediate with *p*-methoxybenzyl chloride / tetra-*n*-butylammonium iodide[9] to furnish the acceptor **3**.

For the subsequent introduction of the 4-*O*-methyl group, compound **3** was *O*-acetylated with acetic anhydride / pyridine to afford compound **4** in 92% yield. The ^{1}H NMR spectrum of **4** displayed a downfield shift for H-2 to 5.36 ppm, thereby confirming the structural assignment of the 3-*O*-*p*-methoxybenzyl substituent. Reductive ring opening of the benzylidene acetal[10] using $NaCNBH_3$ / trifluoroacetic acid in DMF furnished the 6-*O*-*p*-methoxybenzyl ether derivative **5** in 70% yield and the 4-*O*-*p*-methoxybenzyl isomer in 20% yield. Methylation of **5** was performed with MeI / NaH in DMF to give compound **6** in 87% yield. Removal of the 2-*O*-acetyl group was accomplished by treatment of **6** with Bu_4NOH in aq 1,4-dioxane, which gave the 4-*O*-methyl-galactopyranoside acceptor **7** in 82% yield (Scheme 1).

For the synthesis of the α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→*O*Allyl) disaccharide[11] derivatives, *S*-ethyl β-L-fucopyranosides were used as glycosyl donors. They were synthesized by *O*-acetylation (of known precursors[12]) to give the 3,4-di-*O*-acetyl derivatives **8** and **9**, respectively. Coupling of the glycosyl donors with the galactopyranoside acceptor derivatives was carried out under iodonium ion activation of the thioglycoside using *N*-iodosuccinimide and trifluoromethanesulphonic acid at −20°C in dichloromethane-diethyl ether.[13] Coupling of donor **9** with acceptor **3** gave the α-(1→2)- linked disaccharide derivative **10** in 58% yield together with the β-(1→2)-linked isomer (18%). The ^{1}H NMR spectrum of **10** showed a doublet for H-1′ at 5.53 ppm with a coupling constant of 3.7 Hz. Similar reactions with the 4-*O*-methylated acceptor **7** and the thiofucopyranoside donors **8** and **9** proceeded with better anomeric selectivity to furnish disaccharide **13** in 83% yield (and 6% of the β-isomer) and the dimethylated disaccharide **16** in 88% yield

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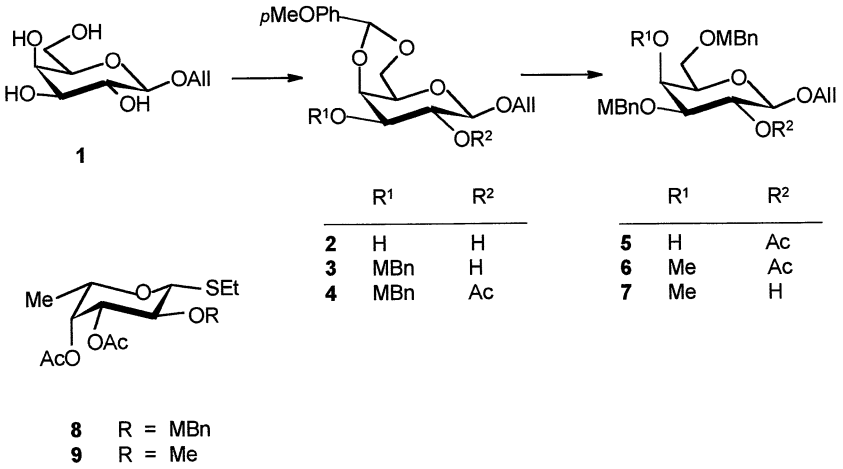


Scheme 1.

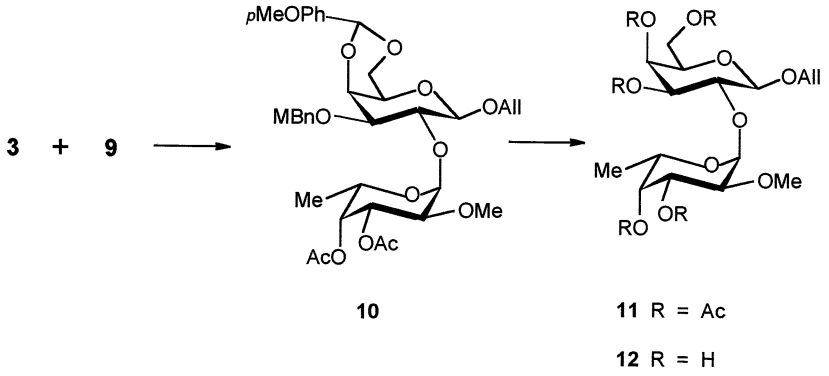
(and 11% of the β-isomer, respectively). Acid hydrolysis of the *p*-methoxybenzyl or *p*-methoxybenzylidene group of derivatives **10** and **13** with 90% aq TFA followed by *O*-acetylation afforded the penta-*O*-acetyl disaccharides **11** and **14** in 84% and 65% yield, respectively. The *p*-methoxybenzyl ether groups of compound **16** were cleaved by the action of ceric ammonium nitrate. Subsequent *O*-acetylation gave the dimethylated disaccharide **17** in 76% overall yield. Zemplén de-*O*-acetylation of the acetylated disaccharides and final purification furnished the disaccharides 2-*O*-Me-α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→*O*Allyl) **12**, α-L-Fuc*p*-(1→2)-4-*O*-Me-β-D-Gal*p*-(1→*O*Allyl) **15** and 2-*O*-Me-α-L-Fuc*p*-(1→2)-4-*O*-Me-β-D-Gal*p*-(1→*O*Allyl) **18** in 92%, 96% and 97% yield, respectively (Scheme 2).

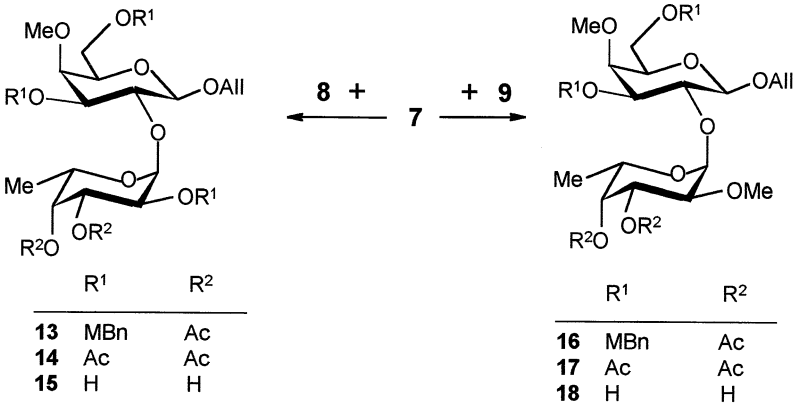
Structural assignments were confirmed by the ^{13}C NMR data (based on HMQC and HMBC spectra, Table 1) and compare favorably with data of related *O*-methylated oligosaccharides.[14]

The synthesis of the trisaccharides and immunochemical data derived from neoglycoconjugates will be published elsewhere.

EXPERIMENTAL

General methods. Melting points were determined with a Kofler hot stage and are uncorrected. Optical rotations were measured with a Perkin-Elmer 243 B polarimeter. ^1H NMR spectra were recorded with a Bruker DPX 300 instrument and tetramethylsilane or DSS as internal standards; coupling constants are first order. Homo- and heteronuclear 2D NMR spectroscopy was performed with Bruker standard software. Thin-layer chromatography was performed on Merck precoated plates (5 x 10 cm, layer thickness 0.25 mm, Silica Gel $60F_{254}$); spots were detected by spraying with anisaldehyde-H_2SO_4 reagent. Column chromatography was per-





Scheme 2.

Table 1. ^{13}C NMR Chemical Shifts[a] (ppm) for Disaccharides **12**, **15** and **18**.

Unit	Carbon	**12**	**15**	**18**
α-L-Fuc*p*	C-1	96.85	100.69	97.29
	C-2	77.77	69.37	78.16
	C-3	68.98	70.58	69.37
	C-4	72.17	72.91	72.57
	C-5	66.89	67.84	67.29
	C-6	15.75	16.42	16.17
β-D-Gal*p*	C-1	100.99	101.54	101.30
	C-2	76.24	78.36	76.89
	C-3	74.18	75.02	74.89
	C-4	69.47	80.32	80.33
	C-5	75.31	76.16	75.83
	C-6	61.34	61.51	61.29
*O*All	C-1	133.72	134.41	134.15
	C-2	119.55	120.13	119.94
	C-3	71.40	71.97	71.77
*O*Me		57.84	62.45	62.34 (*O*-4)
				58.20 (*O*-2′)

[a] Spectra were recorded in D_2O at 295 K.

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formed on Merck Lichroprep columns (size *A*, 24 × 1; *B*, 31 × 2.5 and *C*, 44 × 3.7 cm; silica gel 40–63 μm) under pressure (0.2 MPa). Elemental analyses were performed by Dr. J. Theiner, Mikroanalytisches Laboratorium am Institut für Physikalische Chemie, Universität Wien.

Allyl 4,6-*O*-*p*-Methoxybenzylidene-β-D-galactopyranoside (2). A mixture of **1** (800 mg, 3.63 mmol), anisaldehyde dimethyl acetal (800 μL, 4.40 mmol) and *p*-toluenesulphonic acid monohydrate (100 mg) in dry acetonitrile (20 mL) was stirred for 4 h at rt. Neutralization with triethylamine (0.5 mL) and evaporation of the solvent gave a residue which was purified on silica gel (*C*, 50:1 $CHCl_3$/EtOH) to furnish **2** as colorless crystals. Yield: 1.0 g (81%); mp 179°C (hexane/EtOAc). $[\alpha]_D^{20}$ +44° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.45 - 6.80 (m, 4H, arom H), 5.97 (m, 1H, -CH=), 5.51 (s, 1H, MeOPhCH), 5.33 (dq, 1H, $=CH_{2trans}$), 5.23 (dq, 1H, $=CH_{2cis}$), 4.45 (ddt, 1H, OCH_2), 4.35 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.33 (dd, 1 H, $J_{5,6a}$ = 1.4, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.20 (d, 1H, $J_{3,4}$ = 3.9 Hz, H-4), 4.14 (ddt, 1H, OCH_2), 4.07 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.81 (s, 3H, OMe), 3.77 (ddd, 1H, $J_{2,3}$ = 9.4, $J_{2,OH}$ = 1.8 Hz, H-2), 3.68 (ddd, 1H, $J_{3,OH}$ = 9.3 Hz, H-3), 3.47 (m, 1H, H-5) and 2.45–2.40 (m, 2H, OH).

Anal. Calcd for $C_{17}H_{22}O_7$ (338.36): C, 60.35; H, 6.55. Found: C, 59.83; H, 6.41.

Allyl 3-*O*-*p*-Methoxybenzyl-4,6-*O*-*p*-methoxybenzylidene-β-D-galactopyranoside (3). A mixture of **2** (1.1 g, 2.4 mmol) and dibutyltin oxide (800 mg, 3.21 mmol) in toluene (100 mL) was refluxed for 4 h with azeotropic removal of water. The solution was concentrated and the residue was dissolved in CH_3CN (20 mL). Tetrabutylammonium iodide (1.2 g, 3.24 mmol) and *p*-methoxybenzyl chloride (1.2 mL, 8.85 mmol) were added, and the mixture was refluxed overnight. Evaporation of the solvents gave a residue which was purified on silica gel (*C*, 1:1 hexane/EtOAc) to give **3** as colorless crystals, mp 182°C (hexane/EtOAc). Yield : 1.15 g (77%); $[\alpha]_D^{20}$ +43° (*c* 0.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.50 - 6.80 (m, 8H, arom H), 5.98 (m, 1H, -CH=), 5.43 (s, 1H, MeOPhCH), 5.34 (dq, 1H, $=CH_{2trans}$), 5.23 (dq, 1H, $=CH_{2cis}$), 4.73 and 4.67 (AB, 2 H, $J_{A,B}$ = 11.9 Hz, OCH_2Ph), 4.44 (ddt, 1H, OCH_2), 4.37 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.31 (dd, 1H, $J_{5,6a}$ = 1.4, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.15 (ddt, 1H, OCH_2), 4.11 (d, 1H, $J_{3,4}$ = 3.6 Hz, H-4), 4.07-3.97 (m, 2H, H-2, H-6b), 3.81 (s, 6H, 2 OMe), 3.48 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-3), 3.35 (m, 1H, H-5) and 2.47 (d, 1H, $J_{2,OH}$ = 1.9 Hz, OH).

Anal. Calcd for $C_{25}H_{30}O_8$ (458.51): C, 65.49; H, 6.59. Found: C, 64.84; H, 6.54.

Allyl 2-*O*-Acetyl-3-*O*-*p*-methoxybenzyl-4,6-*O*-*p*-methoxybenzylidene-β-D-galactopyranoside (4). A solution of **3** (800 mg, 1.74 mmol) and a catalytic amount of 4-*N*,*N*-dimethylaminopyridine in dry pyridine (10 mL) was stirred with acetic anhydride (1 mL) overnight at rt. MeOH (2 mL) was added, and the solution was coevaporated three times with addition of toluene and concentrated. Purification of the residue on silica gel (*C*, 2:1 hexane/EtOAc) furnished **4** as colorless

crystals, mp 141°C (hexane/EtOAc). Yield: 800 mg (92%); $[\alpha]_D^{20}$ +46° (*c* 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.50–6.80 (m, 8H, arom H), 5.85 (m, 1H, -CH=), 5.43 (s, 1H, MeOPhCH), 5.36 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.1 Hz, H-2), 5.26 (dq, 1H, $=CH_{2trans}$), 5.15 (dq, 1H, $=CH_{2cis}$), 4.62 and 4.55 (AB, 2H, $J_{A,B}$ = 12.3 Hz, OCH_2Ph), 4.45 (d, 1H, H-1), 4.35 (ddt, 1H, OCH_2), 4.29 (dd, 1H, $J_{5,6a}$ = 1.6, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.12 (d, 1H, $J_{3,4}$ = 3.5 Hz, H-4), 4.10 (ddt, 1H, OCH_2), 4.01 (dd, 1H, $J_{5,6b}$ = 1.8 Hz, H-6b), 3.80 (s, 6H, 2 OMe), 3.56 (dd, 1H, H-3), 3.32 (m, 1H, H-5), and 2.06 (s, 3H, Ac).

Anal. Calcd for $C_{27}H_{32}O_9$ (500.54): C, 64.79; H, 6.44. Found: C, 64.39; H, 6.28.

Allyl 2-*O*-Acetyl-3,6-di-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (5). A suspension of **4** (200 mg, 0.4 mmol), 4 Å molecular sieves (0.4 g) in DMF (5 mL) and $NaCNBH_3$ (450 mg, 7.16 mmol) was stirred under Ar at rt. After 15 min, trifluoroacetic acid (400 μL, 5.19 mmol) in DMF (2 mL) was added dropwise at 0°C. The suspension was stirred overnight at room temperature. Triethylamine (0.5 mL) was added, and the mixture was filtered over a pad of Celite. The filtrate was concentrated and the residue was purified on a column of silica gel (*C*, 3:2 hexane/EtOAc) to give **5** as a syrup. Yield: 140 mg (70%); $[\alpha]_D^{20}$ +8° (*c* 0.8, $CHCl_3$).^1H NMR ($CDCl_3$) δ 7.35 - 6.85 (m, 8H, arom H), 5.85 (m, 1H, -CH=), 5.26 (dq, 1H, $=CH_{2trans}$), 5.20 (dd, 1H, $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.8 Hz, H-2), 5.16 (dq, 1H, $=CH_{2cis}$), 4.63 and 4.48 (AB, 2H, $J_{A,B}$ = 11.9 Hz, OCH_2Ph), 4.53 (s, 2H, OCH_2Ph), 4.38 (d, 1H, H-1), 4.33 (ddt, 1H, OCH_2), 4.15–4.00 (m, 2H, H-4, OCH_2), 3.82 (s, 6H, 2 OMe), 3.81 (dd, 1H, $J_{5,6a}$ = 6.2, $J_{6a,6b}$ = 9.9 Hz, H-6a), 3.72 (dd, 1H, $J_{5,6b}$ = 5.8 Hz, H-6b), 3.70 (dd, 1H, H-5), 3.47 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 2.56 (bs, 1H, OH), and 2.05 (s, 3H, Ac).

Anal. Calcd for $C_{27}H_{34}O_9$ (502.57): C, 64.53; H, 6.82. Found: C, 64.10; H, 6.83. Further elution afforded the 4-*O*-isomer as a syrup. Yield: 40 mg (20%).

Allyl 2-*O*-Acetyl-3,6-di-*O*-*p*-methoxybenzyl-4-*O*-methyl-β-D-galactopyranoside (6). A suspension of **5** (95 mg, 0.19 mmol) in dry DMF (3 mL) and NaH (12 mg, 80% in oil, 0.4 mmol) was stirred at rt. After stirring for 15 min, MeI (60 μL, 0.96 mmol) was added at −20°C and stirring was continued for 2 h. The mixture was diluted with CH_2Cl_2, filtered over a pad of Celite, washed with 10% aq $Na_2S_2O_3$, satd aq $NaHCO_3$ and dried (Na_2SO_4). Concentration of the solution and purification of the residue on a column of silica gel (*C*, 3:2 hexane/EtOAc) afforded **6** as a syrup. Yield: 85 mg (87%); $[\alpha]_D^{20}$ +8° (*c* 1.2, $CHCl_3$).^1H NMR ($CDCl_3$) δ 7.27–6.75 (m, 8H, arom H), 5.81 (m, 1H, -CH=), 5.25 (dd, 1H, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.8, H-2), 5.22 (dq, 1H, $=CH_{2trans}$), 5.12 (dq, 1H, $=CH_{2cis}$), 4.64, 4.51 and 4.46 (AB, 4H, $J_{A,B}$ 11.5 Hz, 2 OCH_2Ph), 4.35 (d, 1H, H-1), 4.28 (ddt, 1H, OCH_2), 4.03 (ddt, 1H, OCH_2), 3.81, 3.80 (2 s, 6H, 2 MeOPh), 3.71 (dd, 1H, $J_{5,6a}$ = 7.5, $J_{6a,6b}$ = 9.0 Hz, H-6a), 3.66 (d, 1H, $J_{3,4}$ = 3.0 Hz, H-4), 3.60 (dd, 1H, $J_{5,6b}$ = 5.4 Hz, H-6b), 3.54 (s, 3H, OMe), 3.51 (dd, 1H, H-5), 3.43 (dd, 1H, H-3), and 2.02 (s, 3H, Ac).

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Anal. Calcd for $C_{28}H_{36}O_9$ (516.59): C, 65.10; H, 7.02. Found: C, 64.90; H, 6.92.

Allyl 3,6-Di-*O*-*p*-methoxybenzyl-4-*O*-methyl-β-D-galactopyranoside (7). Compound **6** (65 mg, 0.13 mmol) was dissolved in 90% aq dioxane (5 mL), and 40% aq tetra-*n*-butylammonium hydroxide (100 μL, 0.22 mmol) was added. After stirring for 4 h at rt, the solution was neutralized by addition of Dowex 50 (H^+) resin, the resin was filtered off, and the filtrate was concentrated. The residue was purified on a column of silica gel (*C*, 3:2 hexane/EtOAc) to give **7** as a syrup. Yield: 48 mg (82%); $[\alpha]_D^{20}$ −5° (*c* 1.2, $CHCl_3$).^{1}H NMR ($CDCl_3$) δ 7.35–6.85 (m, 8H, arom H), 5.92 (m, 1H, =CH-), 5.28 (dq, 1H, $=CH_{2trans}$), 5.17 (dq, 1H, $=CH_{2cis}$), 4.71, 4.60, 4.51 and 4.46 (AB, 4H, $J_{A,B}$ = 11.5 Hz, OCH_2Ph), 4.35 (ddt, 1H, OCH_2), 4.27 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.08 (ddt, 1H, OCH_2), 4.00–3.79 (m, 7H, H-2, 2 MeOPh), 3.70 (dd, 1H, $J_{5,6a}$ = 7.6, $J_{6a,6b}$ = 8.9 Hz, H-6a), 3.64 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-4), 3.59 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, H-6b), 3.56 - 3.50 (m, 4H, H-5, OMe), 3.36 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-3), and 2.31 (bs, 1H, OH).

Anal. Calcd for $C_{26}H_{34}O_8$ (474.55): C, 65.81; H, 7.22. Found: C, 65.76; H, 7.27.

***S*-Ethyl 3,4-Di-*O*-acetyl-2-*O*-*p*-methoxybenzyl-1-thio-β-L-fucopyranoside (8).** A solution of *S*-ethyl 3,4-*O*-isopropylidene-2-*O*-*p*-methoxybenzyl-1-thio-β-L-fucopyrano-side (150 mg, 0.41 mmol) in CH_2Cl_2 (10 mL) was treated with 90% aq trifluoroacetic acid (150 μL) at −35°C for 2 h. Triethylamine (0.5 mL) was added, and the solvent was evaporated. The residue was dissolved in pyridine (3 mL) and stirred with a catalytic amount of 4-*N*,*N*-dimethylaminopyridine and acetic anhydride (1 mL) for 48 h at rt. Methanol (2 mL) was added, and the solution was concentrated. Purification of the residue on silica gel (*C*, 3:1 hexane/EtOAc) afforded **8** as a syrup; Yield: 65 mg (39%).[$\alpha]_D^{20}$ −9° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.30–6.80 (m, 4H, arom. H), 5.25 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-4), 4.99 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-3), 4.78 and 4.54 (d, 2H, $J_{A,B}$ = 10.5 Hz, OCH_2Ph), 4.54 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 3.79 (s, 1H, OMe), 3.76 (dd, 1H, $J_{5,6}$ = 6.4 Hz, H-5), 3.62 (dd, 1H, H-2), 2.77 (m, 2H, SCH_2), 2.15 and 1.97 (2 s, 6H, 2 Ac), 1.33 (t, 3H, CH_2CH_3), and 1.20 (d, 3H, H-6).

Anal. Calcd for $C_{20}H_{28}O_7S$ (412.51): C, 58.24; H, 6.84. Found: C, 57.95; H, 6.78.

***S*-Ethyl 3,4-Di-*O*-acetyl-2-*O*-methyl-1-thio-β-L-fucopyranoside (9).** A solution of *S*-ethyl 3,4-*O*-isopropylidene-2-*O*-methyl-1-thio-β-D-fucopyranoside (500 mg, 1.91 mmol) in CH_2Cl_2 (40 mL) was treated with 90% aq trifluoroacetic acid (1 mL) at rt for 2 h. Triethylamine (0.5 mL) was added, and the solvent was evaporated. The residue was dissolved in pyridine (20 mL) and stirred with a catalytic amount of 4-*N*,*N*-dimethylaminopyridine and acetic anhydride (3 mL) for 48 h at rt. Methanol (6 mL) was added, and the solution was concentrated. Purification of the residue on silica gel (*C*, 3:1 hexane/EtOAc) afforded **9** as a syrup.Yield:

520 mg (89%); $[\alpha]_D^{20}$ +17° (*c* 0.6, $CHCl_3$).^{1}H NMR ($CDCl_3$) δ 5.24 (dd, 1H, $J_{5,4}$ = 1.0, $J_{3,4}$ = 3.4 Hz, H-4), 4.93 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-3), 4.43 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 3.76 (dd, 1H, $J_{5,6}$ = 6.5 Hz, H-5), 3.52 (s, 3H, OMe), 3.35 (dd, 1H, H-2), 2.77 (m, 2H, SCH_2), 2.16, 2.04 (2 s, 6H, 2 Ac), 1.32 (t, 3H, CH_2CH_3), and 1.19 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6).

Anal. Calcd for $C_{13}H_{22}O_6S$ (306.38): C, 50.96; H, 7.24. Found: C, 51.26; H, 7.41.

Allyl (3,4-Di-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-(1(2)-3-*O*-*p*-methoxy-benzyl-4,6-*O*-*p*-methoxybenzylidene-β-D-galactopyranoside (10). To a suspension of **3** (95 mg, 0.21 mmol), **9** (83 mg, 0.27 mmol), and powdered molecular sieves 4 Å (0.2 g) in CH_2Cl_2/Et_2O (1:1, v/v, 2 mL) was added a solution of *N*-iodosuccinimide (16 mg) and trifluoromethanesulphonic acid (4 μL) in CH_2Cl_2/Et_2O (1:1, v/v, 2 mL) at −20°C under Ar. The mixture was stirred at 0°C for 1 h, diluted with CH_2Cl_2 (50 mL), and filtered over a pad of Celite. The filtrate was washed with 10% aq $Na_2S_2O_3$, aq satd $NaHCO_3$, dried (Na_2SO_4) and concentrated. Purification of the residue on silica gel (*C*, 3:1:1 toluene/EtOAc/MeOH, v/v/v) gave **10** as a syrup. Yield: 77 mg (53%); $[\alpha]_D^{20}$ −47° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.45–6.75 (m, 8H, arom H), 5.93 (m, 1H, -CH=), 5.53 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1′), 5.36 (s, 1H, PhCH), 5.34 - 5.15 (m, 4H, H-3′, H-4′, $=CH_{2trans}$, $=CH_{2cis}$), 4.66 and 4.56 (AB, 2H, $J_{A,B}$ = 11.4 OCH_2Ph), 4.62 (dd, 1H, $J_{5',6'}$ = 6.5 Hz, H-5′), 4.48 (d, 1H, $J_{1,2}$ = 7.8, H-1), 4.40 (ddt, 1H, OCH_2), 4.28 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.14–4.02 (m, 3H, H-2, H-4, OCH_2), 3.98 (dd, 1H, $J_{5,6a}$ = 1.6 Hz, H-6b), 3.81 and 3.79 (2 s, 6H, 2 MeOPh), 3.72 (dd, 1H, $J_{2,3}$ = 9.5, $J_{3,4}$ = 3.7 Hz, H-3), 3.56 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2′), 3.36 (s, 3H, OMe), 3.31 (m, 1H, H-5), 2.14 and 2.01 (2 s, 6H, 2 Ac), and 1.04 (d, 3H, H-6′).

Anal. Calcd for $C_{36}H_{46}O_{14}$ (702.76): C, 61.53; H, 6.60. Found: C, 61.26; H, 6.51. Further elution furnished the β-isomer as a syrup. Yield: 25 mg (18%); ^{1}H NMR ($CDCl_3$) for anomeric protons δ 4.92 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), and 4.45 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1).

Allyl (3,4-Di-*O*-acetyl-2-*O*-*p*-methoxybenzyl-β-L-fucopyranosyl)-(1→2)-3,6-di-*O*-*p*-methoxybenzyl-4-*O*-methyl-β-D-galactopyranoside (13). Compound **7** (45 mg, 0.10 mmol) was reacted with **8** (50 mg, 0.12 mmol) in the same way as described for **10**. Purification of the residue on silica gel (*C*, 3:2 hexane/EtOAc) afforded **13** as syrup. Yield: 65 mg (83%); $[\alpha]_D^{20}$ −60° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ7.30–6.50 (m, 12H, arom H), 5.90 (m, 1H, -CH=), 5.57 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1′), 5.35 - 5.10 (m, 4H, H-3′, H-4′, $=CH_{2trans}$, $=CH_{2cis}$), 4.71 and 4.28 (AB, 2H, $J_{A,B}$ = 11.9 Hz, OCH_2Ph), 4.65 (dd, 1H, $J_{5',6'}$ = 6.5 Hz, H-5′), 4.52–4.40 (m, 5H, H-1, 2 OCH_2Ph), 4.35 (ddt, 1H, OCH_2), 4.10–3.95 (m, 2H, H-2, OCH_2), 3.80, 3.79 and 3.75 (3 s, 9H, 3 MeOPh), 3.75 (dd, 1H, $J_{2',3'}$ = 10.7 Hz, H-2′), 3.72–3.49 (m, 5H, H-3, H-4, H-5, H-6a, H-6b), 3.48 (s, 3H, OMe), 2.06 and 1.95 (2 s, 6H, 2 Ac), and 1.02 (d, 3H, H-6′).

Anal. Calcd for $C_{44}H_{56}O_{15}$ (824.93): C, 64.07; H, 6.84. Found: C, 63.56; H, 6.77. Further elution furnished the β-isomer as a syrup. Yield: 6 mg (7%). ^{1}H NMR

($CDCl_3$) for anomeric protons δ 4.96 (d, 1H, $J_{1',2'} = 7.8$ Hz, H-1′), and 4.37 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1).

Allyl (3,4-Di-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→2)-3,6-di-*O*-*p*-methoxybenzyl-4-*O*-methyl-β-D-galactopyranoside (16). To a mixture of **7** (45 mg, 0.09 mmol), **9** (40 mg, 0.13 mmol) and powdered molecular sieves 4 Å (0.2 g) in CH_2Cl_2/Et_2O (1:1, v/v, 2 mL) was added a solution of *N*-iodosuccinimide (16 mg) and trifluoromethanesulphonic acid (4 μL) in CH_2Cl_2/Et_2O (1:1, v/v, 2 mL) at −20°C under Ar. The suspension was stirred at 0°C for 1 h, diluted with CH_2Cl_2 (50 mL) and filtered over Celite. The filtrate was washed with 10% aq $Na_2S_2O_3$, aq $NaHCO_3$, dried over Na_2SO_4 and concentrated. Purification of the residue on silica gel (*B*, 3:1 hexane/EtOAc) gave contaminated product **16**, which could not be further purified at this stage. Yield: 60 mg (88%). ^{1}H NMR ($CDCl_3$) δ 7.30–6.80 (m, 8H, arom H), 5.88 (m, 1H, -CH=), 5.55 (d, 1H, $J_{1',2'} = 3.7$ Hz, H-1′), 5.35–5.10 (m, 4H, H-3′, H-4′, $=CH_{2trans}$, $=CH_{2cis}$), 4.71 and 4.53 (AB, 2H, $J_{AB} = 11.1$ Hz, OCH_2Ph), 4.62 (dd, 1H, $J_{5',6'} = 6.5$ Hz, H-5′), 4.48 and 4.47 (2 s, 2H, OCH_2Ph), 4.43 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1), 4.35 (ddt, 1H, OCH_2), 4.10–3.95 (m, 2H, H-2, OCH_2), 3.81 and 3.79 (2 s, 6H, 2 MeOPh), 3.70–3.50 (m, 6H, H-3, H-4, H-5, H-6a, H-6b, H-2′), 3.49 and 3.30 (2 s, 3H, 2 OMe), 2.13 and 1.99 (2s, 6H, 2 Ac), and 1.02 (d, 3H, H-6′).

Further elution furnished the β-isomer as a syrup. Yield: 8 mg (11%). ^{1}H NMR ($CDCl_3$) for anomeric protons δ 4.87 (d, 1H, $J_{1',2'} = 7.7$ Hz, H-1′), and 4.37 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1)

Allyl (3,4-Di-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→2)-3,4,6-tri-*O*-ace-tyl-β-D-galactopyranoside (11). A solution of **10** (28 mg, 0.04 mmol) in CH_2Cl_2 (3 mL) was treated with aq 90% trifluoroacetic acid (100 μL) at rt for 1 h. The mixture was neutralized with triethylamine (0.5 mL), and the solvent was evaporated. The residue was dissolved in pyridine (2 mL) and stirred with a catalytic amount of 4-*N*,*N*-dimethylaminopyridine and acetic anhydride (200 μL) overnight at rt. MeOH (1 mL) was added, and the solution was concentrated. Purification of the residue on silica gel (*B*, 1:2 hexane/EtOAc) afforded **11** as a syrup. Yield: 15 mg (65%); $[\alpha]_D^{20}$ −46° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 1H, -CH=), 5.37 (d, 1H, $J_{3,4} = 3.4$ Hz, H-4), 5.32 (dq, 1H, $=CH_{2trans}$), 5.28–5.15 (m, 4H, H-1′, H-3′, H-4′, $=CH_{2cis}$), 5.10 (dd, 1H, $J_{2,3} = 10.1$ Hz, H-3), 4.55 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1), 4.51 (dd, 1H, $J_{5',6'} = 6.5$ Hz, H-5′), 4.40 (ddt, 1H, OCH_2), 4.25–4.05 (m, 3H, H-6a, H-6b, OCH_2), 3.98 (dd, 1H, H-2), 3.87 (dd, 1H, $J_{5,6a} = J_{5,6b} = 6.7$ Hz, H-5), 3.61 (dd, 1H, $J_{1',2'} = 3.7$, $J_{2',3'} = 10.1$ Hz, H-2′), 3.39 (1 s, 3H, OMe), 2.15, 2.12, 2.05, 2.00 and 1.99 (5s, 15H, 5 Ac), and 1.08 (d, 3H, H-6′).

Anal. Calcd for $C_{26}H_{38}O_{15}$ (590.58): C, 52.88; H, 6.49. Found: C, 53.20; H, 6.44.

Allyl (2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl)-(1→2)-3,6-di-*O*-acetyl-4-*O*-methyl-β-D-galactopyranoside (14). A solution of **13** (55 mg, 0.07 mmol) in CH_2Cl_2 (8 mL) was treated with aq 90% trifluoroacetic acid (150 μL) at rt for 1 h.

The mixture was neutralized with triethylamine (0.5 mL), and the solvent was evaporated. The residue was dissolved in pyridine (3 mL) and stirred with a catalytic amount of 4-*N*,*N*-dimethylaminopyridine and acetic anhydride (400 μL) overnight at rt. MeOH (1 mL) was added, and the solution was concentrated. Purification of the residue on silica gel (*B*, 1:1 hexane/EtOAc) afforded **14** as a syrup. Yield: 33 mg (84%); $[\alpha]_D^{20}$ −117° (*c* 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ5.90 (m, 1H, =CH-), 5.40 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1′), 5.40 (dd, 1H, $J_{2',3'}$ = 10.9, $J_{3',4'}$ = 3.4 Hz, H-3′), 5.29 (dq, 1H, $=CH_{2trans}$), 5.26–5.18 (m, 2H, H-4′, $=CH_{2cis}$), 5.02 (dd, 1H, H-2′), 4.94 (dd, 1H, $J_{2,3}$ = 9.9, $J_{3,4}$ = 3.0 Hz, H-3), 4.57 (dd, 1H, $J_{5',6'}$ = 6.5 Hz, H-5′), 4.45 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.38 (ddt, 1H, OCH_2), 4.32 (dd, 1H, $J_{5,6a}$ = 6.4, $J_{6a,6b}$ = 11.1 Hz, H-6a), 4.18 (dd, 1H, $J_{5,6b}$ = 6.6 Hz, H-6b), 4.08 (ddt, 1H, OCH_2), 4.06 (dd, 1H, H-2), 3.67 (dd, 1H, H-5), 3.57 (d, 1H, H-4), 3.46 (1 s, 3H, OMe), 2.14, 2.11, 2.08, 2.02 and 1.98 (5 s, 15H, 5 Ac), and 1.06 (d, 3H, H-6′).

Anal. Calcd for $C_{26}H_{38}O_{15}$ (590.58): C, 52.88; H, 6.49. Found: C, 53.58; H, 6.43.

Allyl (3,4-Di-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-(1→2)-3,6-di-*O*-acetyl-4-*O*-methyl-β-D-galactopyranoside (17). To a solution of **16** (54 mg, 0.08 mmol) in 9:1 CH_3CN/H_2O (5 mL) was added ceric ammonium nitrate (300 mg, 0.55 mmol) and 2 drops of pyridine, and the mixture was stirred for 2 h at rt. Additional ceric ammonium nitrate (100 mg) was added and stirring was continued for 1 h. The mixture was diluted with CH_3CN (10 mL), filtered over a pad of Celite, and the solvent was evaporated. The residue was dissolved in pyridine (3 mL) and stirred with a catalytic amount of 4-*N*,*N*-dimethylaminopyridine and acetic anhydride (0.5 mL) at rt for 12 h. MeOH (2 mL) was added, and the solution was concentrated. Purification of the residue on silica gel (*B*, 2:1 hexane/EtOAc) afforded **16** as a syrup. Yield: 32 mg (76%); $[\alpha]_D^{20}$ −88° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 5.89 (m, 1H, -CH=), 5.35 - 5.10 (m, 5H, H-1′, 3′, 4′, $=CH_{2trans}$, $=CH_{2cis}$), 4.98 (dd, 1H, $J_{2,3}$ = 10.3, $J_{3,4}$ = 3.0 Hz, H-3), 4.56 (dd, 1H, $J_{5',6'}$ = 6.5 Hz, H-5′), 4.45 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.40–4.25 (m, 2H, H-6a, OCH_2), 4.17 (dd, 1H, $J_{5,6b}$ = 6.5, $J_{6a,6b}$ = 11.1 Hz, H-6b), 4.13–4.00 (m, 2H, H-2, OCH_2), 3.75 - 3.55 (m, 3H, H-4, 5, 2′), 3.46 and 3.41 (2 s, 6H, 2 OMe), 2.14, 2.11, 2.07 and 1.99 (4 s, 12H, 4 Ac), and 1.04 (d, 3H, H-6′).

Anal. Calcd for $C_{25}H_{38}O_{14}$ (562.57): C, 53.38; H, 6.81. Found: C, 53.61; H, 6.62.

Allyl 2-*O*-Methyl-α-L-fucopyranosyl-(1→2)-β-D-galactopyranoside (12). A solution of **11** (19 mg, 0.032 mmol) in dry MeOH (3 mL) was stirred with 0.1 M methanolic NaOMe (200 μL) overnight at rt. The pH of the solution was adjusted to 7.0 by addition of Dowex 50 (H^+) resin, the resin was filtered off, and the filtrate was concentrated. Purification of the residue on silica gel (*A*, 1:2 MeOH/EtOAc) afforded **12** as a syrup. Yield: 12 mg (96%); $[\alpha]_D^{20}$ −134° (*c* 0.6, MeOH). ^{1}H NMR (D_2O) δ 5.97 (m, 1H, -CH=), 5.44 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1′), 5.35 (dq, 1H, $=CH_{2trans}$), 5.27 (dq, 1H, $=CH_{2cis}$), 4.52 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.38 (ddt, 1H, OCH_2), 4.31 (dd, 1H, $J_{5',6'}$ = 6.6 Hz, H-5′), 4.21 (ddt, 1H, OCH_2), 3.90–3.63 (m,

7H, H-3, H-4, 5, 6a, 6b, 3′, 4′), 3.60 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.49 (s, 3H, OMe), 3.47 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2′), and 1.17 (d, 3H, H-6′).

Anal. Calcd for $C_{16}H_{28}O_{10}$ (380.39): C, 50.52; H, 7.42. Found: C, 49.69; H, 7.19.

Allyl α-L-Fucopyranosyl-(1→2)-4-*O*-methyl-β-D-galactopyranoside (15). A solution of **14** (27 mg, 0.046 mmol) in dry MeOH (5 mL) was stirred with 0.1 M methanolic NaOMe (100 μL) for 48 h at rt. The pH of the solution was adjusted to 7.0 by addition of Dowex 50 (H^+) resin, the resin was filtered off, and the residue was concentrated. Purification of the residue on silica gel (*A*, 1:3 MeOH/EtOAc) afforded **15** as a syrup. Yield: 16 mg (92%); $[\alpha]_D^{20}$ −129° (*c* 0.9, MeOH). ^{1}H NMR (D_2O) δ 5.98 (m, 1H, -CH=), 5.35 (dq, 1H, $=CH_{2trans}$), 5.28 (dq, 1H, $=CH_{2cis}$), 5.17 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.50 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.37 (ddt, 1H, OCH_2), 4.31 (dd, 1H, $J_{5',6'}$ = 6.6 Hz, H-5′), 4.21 (ddt, 1H, OCH_2), 3.95–3.73 (m, 6H, H-3, 6a, 6b, 2′, 3′, 4′), 3.68 (dd, 1H, $J_{5,6a}$ = 6.4 $J_{5,6b}$ = 6.2 Hz, H-5), 3.62 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4), 3.60–3.45 (m, 4H, H-2, OMe), and 1.18 (d, 3H, H-6′).

Anal. Calcd for $C_{16}H_{28}O_{10}$ (380.39): C, 50.52; H, 7.42. Found: C, 49.82; H, 7.31.

Allyl 2-*O*-Methyl-α-L-fucopyranosyl-(1→2)-4-*O*-methyl-β-D-galactopyrano-side (18). A solution of **17** (22 mg, 0.039 mmol) in dry MeOH (3 mL) was stirred with 0.1 M methanolic NaOMe (100 μL) for 3 h at rt. The pH of the solution was adjusted to 7.0 by addition of Dowex 50 (H^+) resin, the resin was filtered off, and the residue was concentrated. Purification of the residue on silica gel (*A*, 1:3 MeOH/EtOAc) afforded **18** as a syrup. Yield: 15 mg (97%); $[\alpha]_D^{20}$ −138° (*c* 0.7, MeOH). ^{1}H NMR (D_2O) δ 5.96 (m, 1H, -CH=), 5.41 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1′), 5.33 (dq, 1H, $=CH_{2trans}$), 5.26 (dq, 1H, $=CH_{2cis}$), 4.49 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.40–4.25 (m, 2H, H-5′, OCH_2), 4.19 (ddt, 1H, OCH_2), 4.00–3.70 (m, 5H, H-3, 6a, 6b, 3′, 4′), 3.67 (dd, 1H, $J_{5,6a}$ = 5.8, $J_{5,6b}$ = 6.8 Hz, H-5), 3.60–3.40 (m, 9H, H-2, 4, 2′, 2 OMe), 1.06 (d, 3H, $J_{5',6'}$ = 6.5 Hz, H-6′).

Anal. Calcd for $C_{17}H_{30}O_{10}$ (394.42): C, 51.77; H, 7.67. Found: C, 51.02; H, 7.43

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