Carbohydrate Research, 194 (1989) 95–114
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A HIGHLY STEREOCONTROLLED SYNTHESIS OF THE PROPYL GLYCOSIDE OF A DECAGALACTURONIC ACID, A MODEL COMPOUND FOR THE ENDOGENOUS PHYTOALEXIN ELICITOR-ACTIVE OLIGOGALACTURONIC ACIDS*

YOSHIAKI NAKAHARA† AND TOMOYA OGAWA†
RIKEN (The Institute of Physical and Chemical Research), Wako-shi, Saitama 351-01 (Japan)
(Received January 14th, 1989; accepted for publication, May 6th, 1989)

ABSTRACT

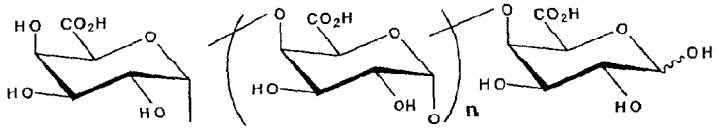
Propyl *O*-(α-D-galactopyranosyluronic acid)-[(1→4)-*O*-(α-D-galactopyranosyluronic acid)]$_8$-(1→4)-β-D-galactopyranosiduronic acid, a model compound for a phytoalexin-elicitor-active oligogalacturonic acid, was synthesized in a highly stereocontrolled manner. *O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-D-galactopyranosyl fluoride, *O*-(2,3-di-*O*-benzyl-4,6-*O*-isopropylidene-α-D-galactopyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-D-galactopyranosyl fluoride, and allyl *O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside were employed as the key intermediates for the stereoselective glycan chain elongation. Transformation of ten primary hydroxyl groups into carboxylic acid groups was achieved efficiently in two steps.

INTRODUCTION

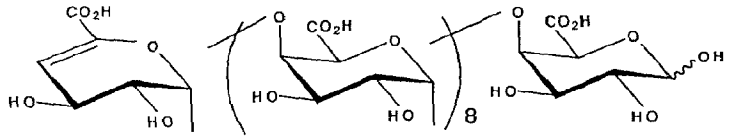
Fragments of plant cell-wall homogalacturonan induce a series of enzymic reactions in plant tissues to synthesize, against invading pathogens, defence substances such as phytoalexins in both soy bean[2,3] and caster bean[4], proteinase inhibitor I in tomato[5], and ethylene and hydroxyproline-rich glycoprotein in melon[6]. Albersheim *et al.*[2] fractionated the oligogalactosiduronic acids released from plant cell-wall pectin by partial acid hydrolysis and suggested that the most active phytoalexin-elicitor fractions comprised dodeca-α-(1→4)-galactosiduronic acid **1** (n = 10). Another active fragment, produced by pectic-degrading enzymes, was reported[3] to be a deca-α-(1→4)-galactosiduronic acid (**2**) containing hexopyranos-4-enyluronic acid at the non-reducing terminus.

*Synthetic Studies on Plant Cell Wall Glycans, Part 5. For Part 4, see ref. 1.
†Authors for enquiries.

0008-6215/89/$ 03.50



1



2

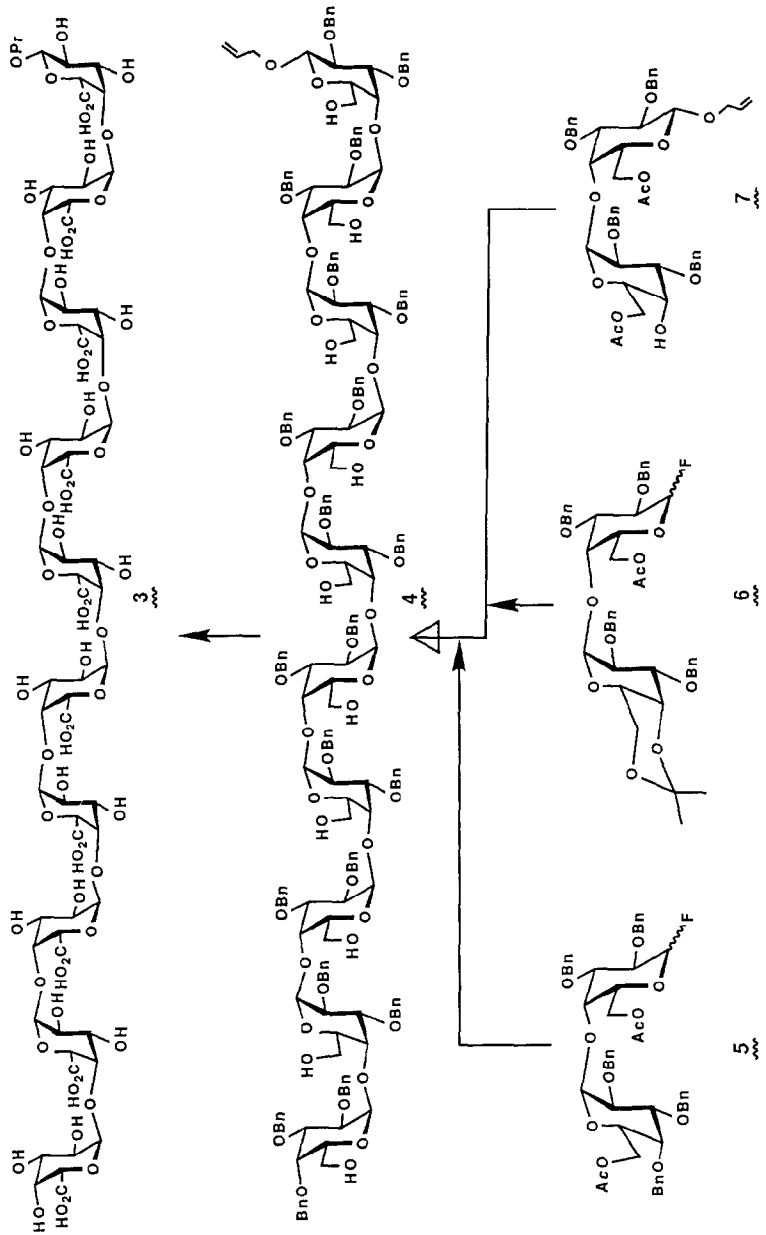
Due to the scarcity of the purified oligosaccharides isolated from plant cell-wall, the development of practical and unambiguous routes of synthesis is necessary in order to provide authentic compounds for the biological study of plant defence mechanisms[7]. In continuation of our studies of the syntheses of monosaccharide synthons[8] and their use in the synthesis of (1→4)-α-linked galacto-oligosides with high stereoselectivity[9], we now describe a stereoselective synthesis of α-D-GalA-[(1→4)-α-D-GalA]$_8$-(1→4)-β-D-GalA-1→OPr (**3**), a derivative of α-(1→4)-linked decagalactosiduronic acid[10].

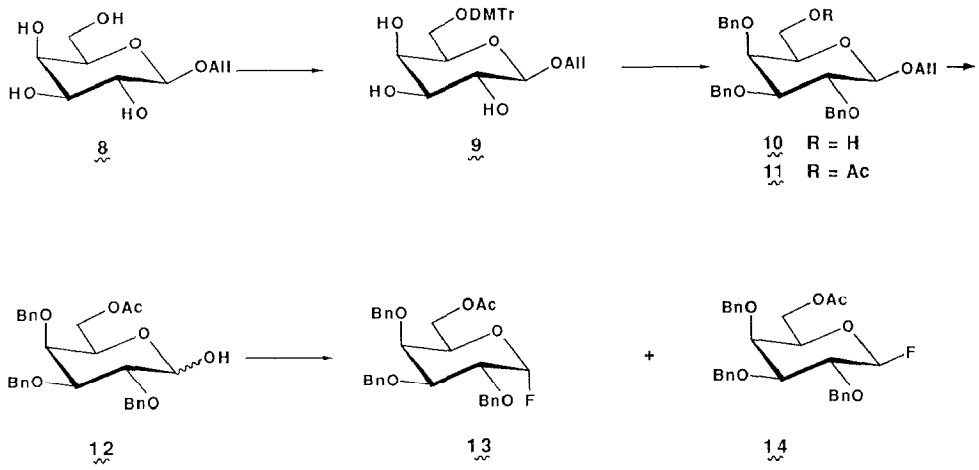
RESULTS AND DISCUSSION

Based on the retrosynthetic analysis of the target molecule **3**, a synthetic plan **3**–**7** was designed which involved the oxidative transformation of a suitably protected α-(1→4)-linked decagalactopyranoside **4** constructed from the galactobiosyl synthons **5**–**7**.

The synthon **5**, intended as the non-reducing terminal biosyl unit, was prepared as follows. Allyl β-D-galactopyranoside[11] (**8**) was selectively protected with the 4,4'-dimethoxytrityl group to give 82% of **9** which, on benzylation followed by cleavage of the trityl ether, produced 58% of **10**[12]. Acetylation of **10** into **11** (96%), followed by removal[13] of the allyl group by treatment first with tris(triphenylphosphine)rhodium(I) chloride and 1,4-diazabicyclo[2.2.2]octane in water–ethanol–benzene, then with mercuric chloride and mercuric oxide in aqueous acetone, gave the hemiacetal **12** (96%). Treatment of **12** with diethylaminosulfur trifluoride[14] (DAST) in tetrahydrofuran afforded 95% of a 9:11 αβ-mixture of the glycosyl fluorides **13** and **14**. In the following formulae, All = allyl.

Glycosyl acceptors **17** and **18** were prepared by selective acetylation of the known compounds **15**[8] and **16**[8], respectively. A highly stereoselective glycosylation reaction of **17** with **13** occurred smoothly in the presence of $SnCl_2$, $AgClO_4$, and

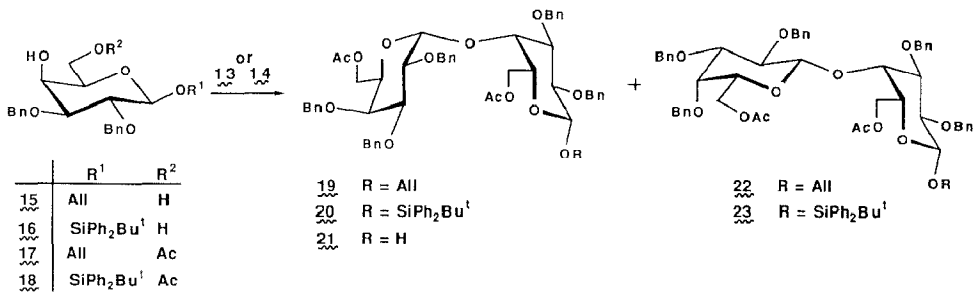

3
4
5
6
7



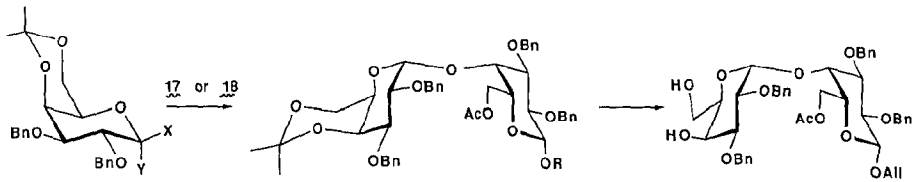
molecular sieves 4A in dry ether[15] to give 87% of the α-linked galactobiose derivative **19** and a 9% yield of the β isomer **22**. Similarly, the reaction between **14** and **18** gave **20** (78%) and **23** (16%). The structures of coupling products were indicated by the n.m.r. data[16]. Deallylation of **19**, as described above, gave 93% of **21**, which was also obtainable (95%) from **20** by desilylation with tetrabutylammonium fluoride and acetic acid in tetrahydrofuran[17]. Treatment of **21** with DAST gave the galactobiosyl donor **5** (97%) as a 3:7 $\alpha\beta$-mixture.

The galactobiosyl unit **6**, corresponding to the middle part of **4**, was prepared as follows. The hemiacetal **24**[8] was fluorinated with DAST to give 89% of a 1.3:1 $\alpha\beta$-mixture of **25** and **26**. Glycosylation[15] of **18** with the α-fluoride **25** was highly stereoselective and gave 84% of **28** as the sole product, which, on desilylation (92%) and fluorination (98%), was converted into the desired donor **6** ($\alpha\beta$-ratio 3:7) via **29**. Use of the β-fluoride **26** for this glycosylation also afforded the α-glycoside **28** (96%). Therefore, the high α-selectivity in the reactions of the donors **25** and **26** is due, most probably, to the formation of a common oxocarbonium ion intermediate which is attacked by a nucleophile exclusively from the α face.

The third synthon **7**, intended as the reducing-end galactobiosyl unit, was



	R^1	R^2
15	All	H
16	$SiPh_2Bu^t$	H
17	All	Ac
18	$SiPh_2Bu^t$	Ac



	X	Y
24	H,	OH
25	H	F
26	F	H

27 R = All
28 R = $SiPh_2Bu^t$
29 R = H

30

prepared by selective acetylation of the diol **30**, which was obtained as the major product (74%) when the coupling reaction[15] of either **25** or **26** and **17** was worked-up without pyridine-quenching and after storage for 20 h at room temperature.

Using the synthons **5–7**, the synthesis of **4** was undertaken as follows. Glycosylation[15] of **7** with **6** promoted by tin(II) chloride and silver perchlorate proceeded with remarkable stereocontrol to give the tetrasaccharide derivativve **31**, which was deisopropylidenated with aq. 80% acetic acid to yield **32** (84% overall yield). The ^{13}C-n.m.r. spectrum of **32** contained signals for anomeric carbons at 99.0, 99.6, and 99.7 p.p.m. (each with a $^1J_{C,H}$ value of 169 Hz) for C-1bcd and at 102.8 p.p.m. (with a $^1J_{C,H}$ value of 160 Hz) for C-1a, which indicated[16] the configuration at the newly formed linkage at C-1c to be α. The derivative **32** was also synthesized (44% overall yield) by stepwise additions of a monosaccharide synthon **25** (or **26**) to **7** in four steps via **34, 35,** and **36**.

After selective acetylation of **32** to give **33** (87%), glycosylation with **6** gave the hexasaccharide derivative **37**, which was hydrolyzed immediately to give **38** (77% overall yield). Mono-*O*-acetylation of **38** gave **39** (85%), which was glycosylated with 2 equiv. of **6** in dichloroethane to give the octasaccharide derivative **40**. When ether was used as the solvent, the yield of **40** was lowered probably due to the low solubility of **39** in ether. Deisopropylidenation of **40** gave **41** (83% overall yield), the ^{13}C-n.m.r. spectrum of which contained signals at 99.2, 99.5, and 99.7 p.p.m. (4:1:2) for C-1bcdefgh with $^1J_{C,H}$ values of 169 Hz, and at 103.0 p.p.m. for C-1a with a $^1J_{C,H}$ value of 159 Hz. Monoacetylation of **41** afforded 87% of the octa-acetate **42**, glycosylation of which with 2 equiv. of **5** in dichloroethane proceeded with remarkable stereocontrol to give the decasaccharide derivative **43** (76%). The ^{1}H-n.m.r. spectrum of **43** contained 10 signals for OAc groups. Deacetylation of **43** with methanolic sodium methoxide afforded 84% of the key intermediate **4**.

The conversion **4** into **3** was examined in two steps. Swern oxidation[18] of **4** afforded a labile deca-aldehyde (**44**) which was immediatley oxidized[19] with freshly prepared aqueous $NaClO_2$ to give 62% of the expected decacarboxylic acid **45**. Treatment of **45** with ethereal diazomethane gave the methyl ester **46**, the ^{1}H-n.m.r. spectrum of which showed ten singlets for CO_2Me groups.

7
6
31 R¹, R² = >C(CH₃)₂
32 R¹ = R² = H
33 R¹ = H, R² = Ac
34 R¹, R² = >C(CH₃)₂
35 R¹ = R² = H
36 R¹ = H, R² = Ac
25 or 26
7
37 R¹, R² = C(CH₃)₂
38 R¹ = R² = H
39 R¹ = H, R² = Ac
40 R¹, R² = C(CH₃)₂
41 R¹ = R² = H
42 R¹ = H, R² = Ac
43 R = CH₂OAc
44 R = CH₂OH
45 R = CHO
46 R = COOCH₃

Catalytic hydrogenation of **45**, without further purification, over 10% Pd/C in aq. methanol gave the crude decagalactosiduronic acid **3**, anion-exchange chromatography[20] of which on MonoQ revealed minor by-products. In order to obtain pure **45** for hydrogenolysis, the methyl ester **46**, which was easily purified by preparative t.l.c., was treated with LiI in boiling pyridine[21] to give pure **45**, and catalytic hydrogenation then gave **3** which was purified further by fractionation on MonoQ. The structure of **3**, assigned by the route of synthesis, was confirmed by comparison of the ^{1}H-n.m.r. data with those of the related compounds[3,22] and by f.a.b.-m.s. using acidified thioglycerol as the matrix[23], which gave the $[M^+ - 1]$ ion with *m/z* 1819 expected for **3**.

The synthesis of the phytoalexin-elicitor active dodecagalactosiduronic acid **1** (n = 10), isolated from plant cell-wall pectin, is now being investigated.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter for solutions in $CHCl_3$ at 25°, unless noted otherwise. Column chromatography was performed on Silica Gel (Merck 70–230 mesh). T.l.c. and high-performance (h.p.) t.l.c. were performed on Silica Gel 60 F_{254} (Merck). Molecular sieves were purchased from Nakarai Chemicals. N.m.r. spectra were recorded with either JEOL GX400 [^{1}H (400 MHz)] or FX90Q [^{13}C (22.50 MHz)] spectrometers. The values of δ_C and δ_H are expressed in p.p.m. downfield from the signal for internal Me_4Si, for solutions in $CDCl_3$, unless noted otherwise. Values of δ_H (D_2O) are expressed in p.p.m. downfield from the signal for Me_4Si by reference to internal Me_3COH (1.230 p.p.m.).

*Allyl 6-O-(4,4'-dimethoxytriphenylmethyl)-β-*D*-galactopyranoside* (**9**). — To a solution of **8** (2.0 g, 3.8 mmol) in dry pyridine (20 mL) was added 4,4'-dimethoxytrityl chloride (3.4 g, 10.0 mmol). The mixture was stirred for 2.5 h at room temperature, water (1 mL) was added, most of pyridine was evaporated *in vacuo*, and the residue was extracted with $CHCl_3$. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was chromatographed on silica gel (250 g) in $CHCl_3$–MeOH–pyridine (95:5:1) to give **9** (3.9 g, 82.2%), $[\alpha]_D^{22}$ −26° (*c* 1.2), R_F 0.35 (9:1 $CHCl_3$–MeOH). N.m.r. data: ^{1}H, δ 3.78 (s, 6 H, 2 OMe), 5.20 (m, 1 H, CH=CH_2), 5.35 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH_2); ^{13}C, δ 55.2, 62.7, 69.2, 69.9, 72.0, 73.7, 73.9, 86.3, 102.0 (C-1), 113.2, 117.7, 123.7, 126.7, 127.7, 128.1, 130.1, 134.0, 136.0, 144.8, 149.6, 158.5.

Anal. Calc. for $C_{30}H_{34}O_8$: C, 68.95; H, 6.56. Found: C, 68.84; H, 6.58.

*Allyl 2,3,4-tri-*O*-benzyl-β-*D*-galactopyranoside* (**10**). — NaH (60% in mineral oil; 950 mg, 23.8 mmol) was washed with *n*-hexane and to a suspension in dry *N,N*-dimethylformamide was added dropwise a solution of **9** (2.74 g, 5.2 mmol) in dry *N,N*-dimethylformamide (20 mL) with stirring at room temperature. Stirring

was continued for 1 h, the mixture was cooled (ice–water bath), and a solution of benzyl bromide (4.03 g, 23.5 mmol) in dry *N,N*-dimethylformamide (2.5 mL) was added dropwise. The mixture was stirred overnight at room temperature, and water (10 mL) was added to decompose the excess of NaH. After dilution with water (300 mL), the mixture was extracted with ether–toluene (1:1). The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was stirred with 1% benzenesulfonic acid in $CHCl_3$–MeOH (7:3, 60 mL) at room temperature for 30 min, then diluted with $CHCl_3$ (300 mL), washed with sat. aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was chromatographed on silica gel (250 g) in *n*-hexane–EtOAc (3:2) to give **10** (1.49 g, 58%), m.p. 76–76.5° (from *n*-hexane), $[\alpha]_D^{22}$ −33° (*c* 0.6), R_F 0.47 (7:3 *n*-hexane–EtOAc). N.m.r. data: ^1H, δ 3.35 (bt, 1 H, *J* 5.9 Hz, H-5), 3.47 (m, 1 H, H-6), 3.53 (dd, 1 H, *J* 2.9 Hz and 9.8 Hz, H-3), 3.74 (m, 1 H, H-6), 3.77 (d, 1 H, *J* 2.4 Hz, H-4), 4.66 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.74 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.78 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.81 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.95 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.96 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 5.18 (m, 1 H, $CH{=}CH_2$), 5.32 (m, 1 H, $CH{=}CH_2$), 5.95 (m, 1 H, $CH{=}CH_2$), 7.33 (m, 15 H, 3 Ph); ^{13}C, δ 62.0, 70.3, 73.4, 74.2, 74.7, 75.2, 79.7, 82.4, 103.2 (C-1), 117.0, 127.5, 127.6, 127.8, 128.1, 128.2, 128.4, 128.5, 134.3, 138.4, 138.8.

Anal. Calc. for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.49; H, 7.02.

*Allyl 6-O-acetyl-2,3,4-tri-O-benzyl-β-*D*-galactopyranoside* (**11**). — To a solution of **10** (1.2 g, 2.4 mmol) in dry pyridine (15 mL) was added acetyl chloride (0.35 mL, 4.9 mmol) with stirring and cooling (ice–water bath). The mixture was allowed to warm to room temperature, stirred for 2 h, diluted with water (10 mL), and then concentrated *in vacuo* to remove most of pyridine. The residue was extracted with ether and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was chromatographed on silica gel (150 g) in *n*-hexane–EtOAc (4:1) to give **11** (1.25 g, 96%), $[\alpha]_D^{22}$ −26° (*c* 1.1), R_F 0.43 (7:3 *n*-hexane–EtOAc). N.m.r. data: ^1H, δ 1.96 (s, 3 H, Ac), 3.51 (m, 1 H, H-5), 3.53 (dd, 1 H, *J* 2.9 and 9.8 Hz, H-3), 3.77 (d, 1 H, *J* 2.0 Hz, H-4), 3.88 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2), 4.05 (dd, 1 H, *J* 6.4 and 11.2 Hz, H-6), 4.12 (m, 1 H, $CH_2CH{=}CH_2$), 4.21 (dd, 1 H, *J* 6.6 and 11.2 Hz, H-6), 4.40 (d, 1 H, *J* 7.6 Hz, H-1), 4.41 (m, 1 H, $CH_2CH{=}CH_2$), 4.67 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.75 (m, 2 H, CH_2Ph), 4.82 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.93 (m, 2 H, CH_2Ph), 5.18 (m, 1 H, $CH{=}CH_2$), 5.32 (m, 1 H, $CH{=}CH_2$), 5.94 (m, 1 H, $CH{=}CH_2$), 7.31 (m, 15 H, 3 Ph); ^{13}C, δ 20.7, 63.1, 70.2, 72.2, 73.5, 74.3, 75.2, 79.5, 82.3, 103.0 (C-1), 117.1, 127.5, 128.1, 128.2, 128.4, 134.2, 138.3, 170.3 (C=O).

Anal. Calc. for $C_{32}H_{36}O_7$: C, 72.16; H, 6.81. Found: C, 71.56; H, 6.76.

*6-O-Acetyl-2,3,4-tri-O-benzyl-*D*-galactopyranose* (**12**). — A mixture of **11** (470 mg, 0.88 mmol), tris(triphenylphosphine)rhodium(I) chloride (65 mg), and 1,4-diazabicyclo[2.2.2]octane (DABCO, 21 mg) in EtOH–benzene–H_2O (7:3:1, 50 mL) was heated under reflux for 2 days, then cooled, filtered through Celite, and concentrated *in vacuo*. A solution of the residue in acetone–H_2O (9:1, 11 mL) was

stirred with $HgCl_2$ (850 mg) and HgO (17 mg) at room temperature for 1 h, then concentrated *in vacuo*, and the residue was extracted with $CHCl_3$. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was chromatographed on silica gel (50 g) in *n*-hexane–EtOAc (3:2) to give **12** (418 mg, 96.2%), m.p. 96–98° (from *n*-hexane–benzene). ^{13}C-N.m.r. data: δ 20.8, 63.6, 68.9, 72.7, 73.3, 73.6, 74.5, 74.7, 75.0, 76.7, 78.7, 80.7, 82.2, 91.8 (C-1, α anomer), 97.9 (C-1, β anomer), 127.5, 128.0, 128.3, 128.4, 138.1, 138.3, 170.6 (C=O).

Anal. Calc. for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.41; H, 6.50.

6-O-Acetyl-2,3,4-tri-O-benzyl-α- (**13**) *and -β-*D*-galactopyranosyl fluoride* (**14**). — To a solution of **12** (418 mg, 0.85 mmol) in dry tetrahydrofuran (3 mL) was added diethylaminosulfur trifluoride (DAST; 150 μL, 1.14 mmol) with stirring in an ice–MeOH bath. Stirring was continued at room temperature for 30 min, MeOH (0.5 mL) was added, and the mixture was concentrated *in vacuo*. The residue was extracted with ether–EtOAc (1:1), and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was chromatographed on silica gel (50 g) in *n*-hexane–EtOAc (7:3) to give oily **13** (179 mg, 42.7%) and then crystalline **14** (219 mg, 52.2%). Compound **13** had $[\alpha]_D^{22}$ +1.2° (*c* 0.5), R_F 0.38 (7:3 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 2.00 (s, 3 H, Ac), 4.62 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 4.73 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.79 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.86 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.88 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.99 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 5.52 (dd, 1 H, *J* 2.7 and 53.5 Hz, H-1), 7.27–7.41 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{29}H_{31}FO_6$: C, 70.43; H, 6.32; F, 3.84. Found: C, 70.40; H, 6.31; F, 3.78.

Compound **14** had m.p. 70° (from *n*-hexane–benzene), $[\alpha]_D^{22}$ +11° (*c* 0.3), R_F 0.30 (7:3 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 2.00 (s, 3 H, Ac), 3.57 (dd, 1 H, *J* 2.2 and 9.3 Hz, H-3), 3.70 (bt, 1 H, H-5), 3.81 (bd, 1 H, *J* 1.7 Hz, H-4), 3.96 (ddd, 1 H, *J* 6.6, 9.3, and 12.7 Hz, H-2), 4.16 (dd, 1 H, *J* 5.1 and 11.5 Hz, H-6), 4.26 (dd, 1 H, *J* 7.3 and 11.5 Hz, H-6), 4.64 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 4.74 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.76 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.81 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.95 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 5.19 (dd, 1 H, *J* 6.6 and 52.7 Hz, H-1), 7.34 (m, 15 H, 3 Ph).

Anal. Found: C, 70.43; H, 6.32.

*Allyl 6-O-acetyl-2,3-di-O-benzyl-β-*D*-galactopyranoside* (**17**). — A solution of **15**[8] (915 mg, 2.3 mmol) in dry pyridine (20 mL) was treated with acetyl chloride (180 μL, 2.5 mmol) essentially as described for **11**. The crude product was chromatographed on silica gel (100 g) in *n*-hexane–EtOAc (1:1) to give, first, an oily diacetate (88 mg, 7.9%) and then **17** (787 mg, 77.8%), m.p. 91.5–92° (from *n*-hexane–EtOAc), $[\alpha]_D^{22}$ +0.8° (*c* 0.8), R_F 0.56 (1:1 toluene–EtOAc). ^{1}H-N.m.r. data: δ 2.08 (s, 3 H, Ac), 3.49 (dd, 1 H, *J* 3.4 and 9.3 Hz, H-3), 3.58 (bt, 1 H, H-5), 3.67 (dd, 1 H, *J* 7.8 and 9.5 Hz, H-2), 3.92 (m, 1 H, H-4), 4.15 (m, 1 H, C*H*$_2$CH=CH$_2$), 4.32 (dd, 1 H, *J* 5.9 and 11.2 Hz, H-6), 4.35 (dd, 1 H, *J* 6.6 and

11.2 Hz, H-6), 4.40 (d, 1 H, *J* 7.8 Hz, H-1), 4.42 (m, 1 H, $CH_2CH=CH_2$), 4.71 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.73 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.75 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.93 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 5.20 (m, 1 H, $CH=CH_2$), 5.34 (m, 1 H, $CH=CH_2$), 5.96 (m, 1 H, $CH=CH_2$), 7.33 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{25}H_{30}O_7$: C, 67.86; H, 6.83. Found: C, 67.81; H, 6.84.

The diacetate had R_F 0.67. ^{1}H-N.m.r. data: δ 2.06 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 5.18 (m, 1 H, $CH=CH_2$), 5.32 (m, 1 H, $CH=CH_2$), 5.95 (m, 1 H, $CH=CH_2$), 7.31 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{27}H_{30}O_8$: C, 66.92; H, 6.66. Found: C, 66.99; H, 6.69.

tert-*Butyldiphenylsilyl 6-O-acetyl-2,3-di-O-benzyl-β-*D*-galactopyranoside* (**18**). — Selective mono-acetylation of **16** (350 mg, 0.58 mmol) was carried out as described for **17**. Chromatography of the crude product gave a diacetate (33 mg, 8.3%) and **18** (306 mg, 81.7%) as oily products.

Compound **18** had $[\alpha]_D^{25}$ +30° (*c* 0.9), R_F 0.53 (3:2 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 1.11 (s, 9 H, CMe_3), 1.94 (s, 3 H, Ac), 3.34 (bt, 1 H, H-5), 3.43 (dd, 1 H, *J* 3.5 and 9.5 Hz, H-3), 3.72 (dd, 1 H, *J* 7.6 and 9.5 Hz, H-2), 3.84 (m, 1 H, H-4), 4.12 (dd, 1 H, *J* 7.1 and 11.4 Hz, H-6), 4.18 (dd, 1 H, *J* 5.4 and 11.4 Hz, H-6), 4.58 (d, 1 H, *J* 7.6 Hz, H-1), 4.65 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.69 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.82 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.95 (d, 1 H *J* 11.0 Hz, CH_2Ph), 7.29, 7.38, and 7.72 (3 m, 14, 2, and 4 H, 4 Ph).

Anal. Calc. for $C_{38}H_{44}O_7Si$: C, 71.22; H, 6.92. Found: C, 70.86; H, 6.89.

The diacetate had $[\alpha]_D^{25}$ +47° (*c* 1.2), R_F 0.64. ^{1}H-N.m.r. data: δ 1.11 (s, 9 H, CMe_3), 1.94 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 3.49 (dd, 1 H, *J* 3.4 and 9.5 Hz, H-3), 3.50 (bt, 1 H, H-5), 3.68 (dd, 1 H, *J* 7.6 and 9.5 Hz, H-2), 3.88 (dd, 1 H, *J* 7.1 and 11.2 Hz, H-6), 4.01 (dd, 1 H, *J* 6.1 and 11.2 Hz, H-6), 4.46 (d, 1 H, *J* 11.2 Hz, CH_2Ph), 4.64 (d, 1 H, *J* 7.6 Hz, H-1), 4.70 (d, 1 H, *J* 11.2 Hz, CH_2Ph), 4.84 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.92 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 5.41 (m, 1 H, H-4), 7.27, 7.39, and 7.71 (3 m, 14, 2, and 4 H, 4 Ph).

Anal. Calc. for $C_{40}H_{46}O_8Si$: C, 70.35; H, 6.79. Found: C, 69.53; H, 6.74.

Allyl O-(6-O-acetyl-2,3,4-tri-O-benzyl-α- (**19**) *and -β-*D*-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-*D*-galactopyranoside* (**22**). — A mixture of **13** (83 mg, 0.17 mmol) and **17** (58 mg, 0.13 mmol) in dry ether (4 mL) was added under argon with stirring and cooling (~ −20°) to a mixture of $SnCl_2$ (65 mg, 0.34 mmol), $AgClO_4$ (70 mg, 0.34 mmol), and dry powdered molecular sieves 4A (400 mg). The mixture was allowed to warm to ambient temperature and stirring was continued for 4 h. The mixture was filtered through Celite, washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on silica gel (200 g) in *n*-hexane–EtOAc (13:7) to afford **19** (105 mg, 86.9%) and then **22** (11 mg, 8.7%).

Compound **19** had $[\alpha]_D^{23}$ +27° (*c* 1.1), R_F 0.28 (7:3 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.79 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 3.38 (dd, 1 H, *J* 2.9 and 9.8 Hz, H-3a), 3.49 (bt, 1 H, H-5a), 3.66 (dd, 1 H, *J* 7.6 and 10.0 Hz, H-2a), 3.86 (d, 1 H, *J* 2.7 Hz, H-4), 4.36 (d, 1 H, *J* 7.6 Hz, H-1a), 5.21 (m, 1 H, $CH=CH_2$), 5.35 (m, 1

H, CH=CH_2), 5.96 (m, 1 H, CH=CH$_2$), 7.23–7.44 (m, 25 H, 5 Ph); ^{13}C, δ 20.8 (COCH_3), 62.7, 69.0, 70.4, 72.5, 72.7, 73.0, 73.8, 74.6, 74.8, 75.0, 75.4, 76.6, 78.9, 80.2, 100.2 ($^1J_{C,H}$ 168.5 Hz, C-1b), 103.2 ($^1J_{C,H}$ 158.7 Hz, C-1a), 117.2, 127.5, 128.2, 134.2, 138.4, 138.5, 138.8, 170.0 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{54}H_{60}O_{13}\cdot H_2O$: C, 69.36; H, 6.47. Found: C, 69.45; H, 6.38.

Compound **22** had $[\alpha]_D^{22}$ +7.4° (*c* 0.8), R_F 0.17. N.m.r. data: ^{1}H, δ 1.97 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 4.39 (d, 1 H, *J* 7.8 Hz, H-1a), 5.19 (m, 1 H, CH=CH_2), 5.33 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, CH=CH$_2$), 7.19–7.46 (m, 25 H, 5 Ph); ^{13}C, δ 20.8 (COCH_3), 63.2, 64.3, 70.2, 71.8, 72.2, 72.3, 73.0, 73.6, 74.3, 74.7, 75.0, 75.3, 79.6, 79.8, 81.6, 82.0, 102.9 ($^1J_{C,H}$ 158.7 Hz, C-1a or C-1b), 103.2 ($^1J_{C,H}$ 158.7 Hz, C-1a or C-1b), 117.1, 127.2, 127.5, 127.8, 128.1, 128.2, 128.5, 134.3, 138.5, 170.5 (C=O), 170.7 (C=O).

Anal. Calc. for $C_{54}H_{60}O_{13}$: C, 70.73; H, 6.59. Found: C, 70.32; H, 6.55.

tert-*Butyldiphenylsilyl* O-*(6*-O-*acetyl-2,3,4-tri*-O-*benzyl-α*- (**20**) *and* -*β*-D-*galactopyranosyl-(1→4)-6*-O-*acetyl-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**23**). — Glycosylation of **14** (1.10 g, 2.22 mmol) and **18** (1.06 g, 1.65 mmol) was carried out with $SnCl_2$ (850 mg, 4.48 mmol), $AgClO_4$ (935 mg, 4.51 mmol), and powdered molecular sieves 4A (4.0 g) in dry ether (50 mL) and toluene (5 mL) at −10 to 5° for 2.5 h. Work-up, as described above for **19**, followed by chromatography on silica gel (200 g) in *n*-hexane–EtOAc (3:1) afforded **20** (1.47 g, 79.7%) and **23** (0.30 g, 16.3%).

Compound **20** had $[\alpha]_D^{22}$ +40° (*c* 0.8), R_F 0.41 (7:3 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.13 (s, 9 H, CMe$_3$), 1.78 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 3.25 (bt, 1 H. H-5a), 3.29 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.71 (dd, 1 H, *J* 7.3 and 10.0 Hz, H-2a), 3.81 (d, 1 H, *J* 2.7 Hz, H-4), 4.59 (d, 1 H, *J* 7.1 Hz, H-1a), 7.21–7.39, 7.45, and 7.71 (m, bd, m, 29, 2, and 4 H, 7 Ph); ^{13}C, δ 19.3 (*C*Me$_3$), 20.7 (COCH_3), 27.1 [C(CH_3)$_3$], 62.7, 62.8, 69.1, 72.3, 72.6, 73.8, 74.6, 75.1, 76.8, 78.8, 80.3, 80.9, 98.1 ($^1J_{C,H}$ 152.6 Hz, C-1a), 100.0 ($^1J_{C,H}$ 168.5 Hz,C-1b), 127.2, 127.4, 127.5, 127.9, 128.0, 128.1, 128.2, 128.4, 129.5, 133.8, 135.8, 136.0, 138.3, 138.6, 170.0 (*C*=O), 170.2 (*C*=O).

Anal. Calc. for $C_{67}H_{74}O_{13}Si$: C, 72.15; H, 6.69. Found: C, 71.65; H, 6.66.

Compound **23** had $[\alpha]_D^{23}$ +17° (*c* 0.6), R_F 0.30. ^{1}H-N.m.r. data: δ 1.10 (s, 9 H, CMe$_3$), 1.90 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 3.38 (bt, 1 H, H-5a or H-5b), 3.40 (bt, 1 H, H-5a or H-5b), 3.43 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a or H-3b), 3.48 (dd, 1 H, *J* 3.2 and 9.5 Hz, H-3a or H-3b), 3.73 (d, 1 H, *J* 2.2 Hz, H-4a or H-4b), 3.83 (m, 2 H, H-2a,2b), 4.02 (dd, 1 H, *J* 6.1 and 11.2 Hz, H-6), 4.09 (dd, 1 H, *J* 7.3 and 11.7 Hz, H-6), 4.26 (dd, 1 H, *J* 4.2 and 11.7 Hz, H-6), 4.55 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.61 (d, 1 H, *J* 7.3 Hz, H-1a), 4.86 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.86 (d, 1 H, *J* 10.8 Hz, CH_2Ph), 4.89 (d, 1 H, *J* 7.6 Hz, H-1b), 4.99 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 5.23 (d, 1 H, *J* 11.2 Hz, CH_2Ph), 7.14–7.39, 7.50, and 7.50–7.73 (m, bd, m, 29, 2, and 4 H, 7 Ph); ^{13}C, δ 19.2 (*C*Me$_3$), 20.7 (COCH_3)$_3$, 27.0 [C(CH_3)$_3$], 63.2, 64.3, 70.8, 72.2, 72.9, 73.6, 73.9, 74.4, 74.8, 75.3, 79.6, 81.6, 82.0, 82.2, 98.1 ($^1J_{C,H}$

160.5 Hz, C-1a), 102.8 ($^1J_{C,H}$ 156.3 Hz, C-1b), 127.2, 127.4, 127.5, 127.7, 128.0, 128.3, 129.5, 133.6, 135.8, 136.0, 138.4, 138.8, 139.2, 170.4 (*C*=O), 170.6 (*C*=O).

Anal. Found: C, 71.65; H, 6.65.

*O-(6-O-Acetyl-2,3,4-tri-O-benzyl-α-*D*-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-*D*-galactopyranose* (**21**). — (*a*) *From* **19**. Deallylation of **19** (446 mg, 0.49 mmol), as described for **12**, followed by chromatography on silica gel (50 g) in *n*-hexane–EtOAc (9:11) gave **21** (397 mg, 93.1%) as an αβ-mixture. ^{1}H-N.m.r. data: δ 1.80 (1.81) (s, 3 H, Ac), 2.01 (s, 3 H, Ac).

Anal. Calc. for $C_{51}H_{56}O_{13}$: C, 69.85; H, 6.44. Found: C, 69.78; H, 6.40.

(*b*) *From* **20**. To a mixture of **20** (1.47 g, 1.32 mmol) and AcOH (540 μL, 9.43 mmol) in dry tetrahydrofuran (39 mL) was added M *n*-Bu_4NF–tetrahydrofuran (5.4 mL, 5.4 mmol). The mixture was stirred at room temperature for 5 days, most of the solvent was evaporated *in vacuo*, and the residue was extracted with ether–EtOAc (1:1). The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Chromatography of the crude product on silica gel (100 g) afforded **21** (1.10 g, 95.2%).

*O-(6-O-Acetyl-2,3,4-tri-O-benzyl-α-*D*-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-*D*-galactopyranosyl fluoride* (**5**). — As described for **13** and **14**, treatment of **21** (427 mg, 0.49 mmol) with DAST (100 μL, 0.76 mmol) in dry tetrahydrofuran (1.6 mL), followed by column chromatography of the product on silica gel (50 g) in *n*-hexane–EtOAc (7:3), gave **5** (416 mg, 97.2%) as an αβ-mixture (αβ-ratio 3:7), R_F 0.28 and 0.23 (7:3 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 1.81 (1.82) (s, 3 H, Ac), 2.03 (2.02) (s, 3 H, Ac), 5.20 (dd, *J* 5.9 and 52.7 Hz, H-1a of β isomer), 5.62 (dd, *J* 2.8 and 54.7 Hz, H-1a of α isomer).

Anal. Calc. for $C_{51}H_{55}FO_{12}$: C, 69.69; H, 6.31; F, 2.16. Found: C, 69.41; H, 6.29; F, 2.03.

2,3-Di-O-benzyl-4,6-O-isopropylidene-α- (**25**) *and -β-*D*-galactopyranosyl fluoride* (**26**). — A solution of **24**[8] (690 mg, 1.72 mmol) in tetrahydrofuran was treated with DAST (300 μL, 2.27 mmol) as described above. Chromatography of the crude product on silica gel (75 g) in *n*-hexane–EtOAc (13:7) afforded oily **25** (353 mg, 50.9%) and crystalline **26** (262 mg, 37.8%). Compound **25** had $[\alpha]_D^{23}$ +27° (*c* 1.4), R_F 0.59 (1:1 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 1.42 (s, 3 H, Me), 1.48 (s, 3 H, Me), 3.66 (bs, 1 H, H-5), 4.16 (bd, 1 H, H-4), 4.71 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.72 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.84 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.92 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 5.64 (dd, 1 H, *J* 2.7 and 53.6 Hz, H-1), 7.35 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{23}H_{27}FO_5$: C, 68.64; H, 6.76; F, 4.72. Found: C, 68.17; H, 6.74; F, 4.23.

Compound **26** had m.p. 120–121° (from *n*-hexane–EtOAc), R_F 0.50. ^{1}H-N.m.r. data: δ 1.43 (s, 3 H, Me), 1.52 (s, 3 H, Me), 3.34 (bs, 1 H, H-5), 3.50 (dd, 1 H, *J* 2.8 and 9.8 Hz, H-3), 3.92 (m, 1 H, H-2), 3.96 (dd, 1 H, *J* 2.1 and 12.8 Hz, H-6), 4.02 (bd, 1 H, *J* 12.8 Hz, H-6), 4.07 (bs, 1 H, H-4), 4.70 (d, 1 H, *J* 12.4 Hz, CH_2Ph), 4.78 (d, 1 H, *J* 12.4 Hz, CH_2Ph), 4.82 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.86

(d, 1 H, *J* 11.0 Hz, CH_2Ph), 5.16 (dd, 1 H, *J* 7.0 and 53.1 Hz, H-1), 7.35 (m, 10 H, 2 Ph).

Anal. Found: C, 68.44; H, 6.77; F, 4.63.

Allyl O-*(2,3-di*-O-*benzyl-4,6*-O-*isopropylidene-α*-D-*galactopyranosyl)-(1→4)-6*-O-*acetyl-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**27**) *and allyl* O-*(2,3-di*-O-*benzyl-α*-D-*galactopyranosyl)-(1→4)-6*-O-*acetyl-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**30**). — (*a*) Reaction of **26** (80 mg, 0.20 mmol) and **17** (73 mg, 0.17 mmol) was carried out with $SnCl_2$ (76 mg, 0.40 mmol), $AgClO_4$ (84 mg, 0.40 mmol), and powdered molecular sieves 4A (400 mg) in 10:1 dry ether–dry toluene (5.5 mL) at −15° to ~room temperature for 20 h, and the mixture was worked-up as described for **19**. The crude product was chromatographed on silica gel (17 g) in toluene–EtOAc (7:3–1:1) to give **27** (5.5 mg, 4.0%) and **30** (96 mg, 74.1%). The former contained some impurities and was treated with aq. 80% AcOH at 60° for 1 h to give more **30**.

Compound **27**. ^{1}H-N.m.r. data: δ 1.33 (s, 3 H, Me), 1.43 (s, 3 H, Me), 2.04 (s, 3 H, Ac).

Compound **30** had $[\alpha]_D^{22}$ +39° (*c* 1.8). N.m.r. data: ^{1}H, δ 2.01 (s, 3 H, Ac), 3.40 (dd, 1 H, *J* 2.9 and 10.0 Hz, H-3a), 3.51 (bt, 1 H, *J* 6.6 Hz, H-5a), 3.65 (dd, 1 H, *J* 7.6 and 10.0 Hz, H-2a), 3.86 (dd, 1 H, *J* 3.4 and 9.8 Hz, H-2b), 3.97 (dd, 1 H, *J* 3.2 and 9.8 Hz, H-3b), 4.15 (m, 1 H, CH_2CH=CH_2), 4.38 (d, 1 H, *J* 7.6 Hz, H-1a), 4.93 (d, 1 H, *J* 3.4 Hz, H-1b), 5.22 (m, 1 H, CH=CH_2), 5.36 (m, 1 H, CH=CH_2), 5.97 (m, 1 H, C*H*=CH$_2$), 7.26–7.38 (m, 20 H, 4 Ph); ^{13}C, δ 20.8 (CO*C*H$_3$), 62.6, 63.0, 69.1, 70.1, 70.4, 72.4, 73.1, 73.7, 74.9, 76.0, 76.6, 77.7, 78.5, 80.6, 100.5 ($^1J_{C,H}$ 168.5 Hz, C-1b), 103.1 ($^1J_{C,H}$ 156.3 Hz, C-1a), 117.2, 127.5, 127.8, 128.1, 128.2, 128.4, 134.1, 137.9, 138.1, 138.5, 170.3 (*C*=O).

Anal. Calc. for $C_{45}H_{52}O_{12}$: C, 68.86; H, 6.68. Found: C, 68.56; H, 6.67.

tert-*Butyldiphenylsilyl* O-*(2,3-di*-O-*benzyl-4,6*-O-*isopropylidene-α*-D-*galacto-pyranosyl)-(1→4)-6*-O-*acetyl-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**28**). — (*a*) Reaction of **25** (649 mg, 1.61 mmol) and **18** (729 mg, 1.14 mmol) was achieved at −20 to −15° for 1.5 h in the presence of $SnCl_2$ (620 mg, 3.27 mmol), $AgClO_4$ (680 mg, 3.28 mmol), and powdered molecular sieves 4A (3.0 g) in dry ether (37 mL). The mixture was diluted with dry pyridine (4 mL), filtered through Celite, and worked-up as described for **19**. Chromatography of the crude product on silica gel (150 g) in toluene–EtOAc–pyridine (75:25:1) afforded **28** (978 mg, 84.0%), $[\alpha]_D^{21}$ +72° (*c* 1.5), R_F 0.46 (7:3 toluene–EtOAc). N.m.r. data: ^{1}H, δ 1.16 (s, 9 H, CMe$_3$), 1.36 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.93 (s, 3 H, Ac), 3.17 (bd, 1 H, *J* 12.0 Hz, H-6b), 3.23 (bt, 1 H, *J* 7.1 Hz, H-5a), 3.26 (dd, 1 H, *J* 2.7 and 10.0 Hz, H-3a), 3.42 (bd, 1 H, *J* 12.0 Hz, H-6b), 3.63 (dd, 1 H, *J* 7.3 and 10.0 Hz, H-2a), 3.73 (bs, 1 H, H-4b), 3.87 (d, 1 H, *J* 2.7 Hz, H-4a), 4.15 (dd, 1 H, *J* 6.5 and 10.7 Hz, H-6a), 4.27 (dd, 1 H, *J* 7.5 and 10.7 Hz, H-6a), 4.51 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.58 (d, 1 H, *J* 7.3 Hz, H-1a), 4.67 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.75 (d, 1 H, *J* 11.7 Hz, CH_2Ph), 4.79 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.83 (d, 1 H, *J* 11.2 Hz, CH_2Ph), 4.88 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 7.20–7.39, 7.48, and 7.72 (3 m, 24, 2, and 4 H, 5 Ph); ^{13}C, δ 18.3

(CH_3), 19.2 (CMe_3), 20.6 ($COCH_3$), 27.1 [$C(CH_3)_3$], 29.5 (CH_3), 61.6, 62.5, 62.7, 67.7, 72.0, 72.3, 74.0, 74.1, 74.8, 80.0, 80.5, 98.2 ($^1J_{C,H}$ 152.6 Hz, C-1a), 98.3 (O–CMe_2–O), 100.5 ($^1J_{C,H}$ 169.7 Hz, C-1b), 127.1, 127.3, 127.4, 127.5, 127.6, 128.0, 128.1, 128.2, 129.5, 133.6, 135.7, 135.9, 138.1, 138.5, 138.7, 170.0 (C=O).

Anal. Calc. for $C_{61}H_{70}O_{12}Si$: C, 71.60; H, 6.90. Found: C, 71.32; H, 6.85.

(*b*) Reaction of **26** (550 mg, 1.37 mmol) and **18** (625 mg, 0.98 mmol), as described in (*a*) using $SnCl_2$ (525 mg, 2.77 mmol), $AgClO_4$ (575 mg, 2.77 mmol), and molecular sieve 4A (3.0 g) in dry Et_2O (32 mL), gave **28** (955 mg, 95.7%).

O-(2,3-Di-O-benzyl-4,6-O-isopropylidene-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-D-galactopyranose (**29**). — Desilylation of **28** (1.22 g, 1.19 mmol) as described above for **21**, followed by chromatography on silica gel (150 g) in toluene–EtOAc–pyridine (65:35:1), gave **29** (0.86 g, 91.9%). N.m.r. data: ^1H, δ 1.32 (s, 3 H, Me), 1.43 (s, 3 H, Me), 2.02 (s, 3 H, Ac); ^{13}C, δ 18.2 (CH_3), 20.8 ($COCH_3$), 29.4 (CH_3), 91.4 (C-1a, for α anomer), 97.7 (C-1a, for β anomer), 98.4 (O-CMe_2-O), 100.3 (C-1b), 170.3 (C=O).

Anal. Calc. for $C_{45}H_{52}O_{12}$: C, 68.86; H, 6.68. Found: C, 68.63; H, 6.69.

O-(2,3-Di-O-benzyl-4,6-O-isopropylidene-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-D-galactopyranosyl fluoride (**6**). — Treatment of **29** (534 mg, 0.68 mmol) with DAST (145 μL, 1.10 mmol) in dry tetrahydrofuran (3 mL), as described for **13**, and chromatography of the product on silica gel (50 g) in *n*-hexane–EtOAc–pyridine (130:70:1) afforded **6** (525 mg, 98.1%) as an αβ-mixture (αβ-ratio 3:7), R_F 0.60 and 0.55 (1:1 *n*-hexane–EtOAc). ^1H-N.m.r. data: δ 1.354 (1.345) (s, 3 H, Me), 1.439 (1.445) (s, 3 H, Me), 2.06 (s, 3 H, Ac), 5.18 (dd, *J* 6.6 and 53.0 Hz, H-1a for β anomer), 5.66 (bd, *J* 54.9 Hz, H-1a for α anomer).

Anal. Calc. for $C_{45}H_{51}FO_{11}$: C, 68.69; H, 6.53; F, 2.41. Found: C, 68.88; H, 6.51; F, 2.42.

Allyl O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**7**). — Selective mono-acetylation of **30** (369 mg, 0.47 mmol) was carried out as described above with acetyl chloride (42 μL, 0.59 mmol) in dry pyridine (3.5 mL) at 0° (ice-cooled) for 1.5 h. Chromatography of the product on silica gel (50 g) in *n*-hexane–EtOAc (3:2) gave **7** (349 mg, 89.8%), $[\alpha]_D^{20}$ +37° (*c* 0.8), R_F 0.40 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^1H, δ 1.91 (s, 3 H, Ac), 2.01 (s, 3 H, Ac); ^{13}C, δ 20.8 ($COCH_3$), 62.9, 67.4, 68.1, 70.4, 72.5, 72.7, 73.8, 75.0, 75.9, 76.1, 77.6, 78.9, 80.2, 100.2 (C-1a), 103.0 (C-1b), 117.3, 127.6, 127.9, 128.1, 128.3, 128.5, 134.2, 138.2, 138.4, 138.8, 170.4 (C=O).

Anal. Calc. for $C_{47}H_{54}O_{13}$: C, 68.27; H, 6.58. Found: C, 68.28; H, 6.61.

Allyl O-(2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**35**). — Reaction of **26** (85 mg, 0.21 mmol) and **7** (125 mg, 0.15 mmol) in the presence of $SnCl_2$ (81 mg, 0.43 mmol), $AgClO_4$ (89 mg, 0.43 mmol), and powdered molecular sieves 4A (400 mg) in dry ether–dry toluene (5.5 mL, 0.5 mL) was carried out at −15 to −5° for 6 h. After an addition of pyridine (0.5 mL), the mixture was worked-up as described above for **19**. The crude product was

chromatographed on silica gel (20 g) in toluene–EtOAc–pyridine (75:25:1) to give **34** (170 mg), R_F 0.47 (7:3 toluene–EtOAc), which still contained some impurities. H.p.l.c. indicated 86.6% purity. Crude **34** was heated in aq. 80% AcOH (3 mL) at 60° for 30 min, the mixture was concentrated *in vacuo*, and the residue was chromatographed on silica gel (20 g) in *n*-hexane–EtOAc (2:3) to afford **35** (138 mg, 78.1%), $[\alpha]_D^{19}$ +42° (*c* 0.9), R_F 0.23 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.90 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 3.37 (dd, 1 H, *J* 2.9 and 10.0 Hz, H-3a), 3.49 (bt, 1 H, H-5a), 4.36 (d, 1 H, *J* 7.8 Hz, H-1a), 4.92 (d, 1 H, *J* 2.7 Hz, H-1c), 5.02 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.96 (m, 1 H, C*H*=CH$_2$), 7.24–7.44 (m, 30 H, 6 Ph); ^{13}C, δ 20.7 (CO*C*H$_3$), 99.6 ($^1J_{C,H}$ 169.7 Hz, C-1b or C-1c), 99.7 ($^1J_{C,H}$ 169.7 Hz, C-1b or C-1c), 102.8 ($^1J_{C,H}$ 159.9 Hz, C-1a), 169.7 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{67}H_{76}O_{18}$: C, 68.82; H, 6.55. Found: C, 68.52; H, 6.55.

Allyl O-*(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranoside* (**36**). — Acetylation of **35** (208 mg, 0.18 mmol) with acetyl chloride (16 μL, 0.23 mmol) in dry pyridine (1.5 mL) at 0° for 1 h, as described above, and chromatography of the product gave **36** (189 mg, 87.7%). A trace (<5%) of tetra-acetate was eluted in a less polar fraction. Compound **36** had $[\alpha]_D^{20}$ +39° (*c* 0.7), R_F 0.56 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.90 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 3.36 (dd, 1 H, *J* 2.9 and 9.8 Hz, H-3a), 3.48 (bt, 1 H, *J* 6.6 Hz, H-5a), 3.62 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.35 (d, 1 H, *J* 7.6 Hz, H-1a), 4.92 (d, 1 H, *J* 2.9 Hz, H-1c), 4.99 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH$_2$), 7.23–7.44 (m, 30 H, 6 Ph); ^{13}C, δ 20.8 (CO*C*H$_3$), 99.4, 99.6 (C-1b and C-1c), 102.9 (C-1a), 169.8 (C=O), 170.2 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{69}H_{78}O_{19}$: C, 68.42; H, 6.49. Found: C, 68.64; H, 6.49.

Allyl O-*(2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galacto-pyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranoside* (**32**). — (*a*) *By coupling of* **26** *and* **36**. Reaction of **26** (74 mg, 0.18 mmol) and **36** (158 mg, 0.13 mmol) was carried out in the presence of $SnCl_2$ (70 mg, 0.37 mmol), $AgClO_4$ (77 mg, 0.37 mmol), and molecular sieves 4A (400 mg) in dry ether–toluene (4.5 mL, 0.5 mL) at −20 to −5° for 6 h. Pyridine (0.5 mL) was then added and the mixture was worked-up as described above. The crude product was chromatographed on silica gel (20 g) in toluene–EtOAc–pyridine (75:25:1) to afford slightly impure **31** (185 mg), which, without further purification, was treated with aq. 80% AcOH (2.5 mL) at 60° for 30 min. The solution was concentrated *in vacuo*, and the residue was chromatographed on silica gel (20 g) in *n*-hexane–EtOAc (2:3) to give **32** (132 mg, 65.1%), $[\alpha]_D^{19}$ +46° (*c* 0.6), N.m.r. data: ^{1}H, δ 1.92 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 4.35 (d, 1 H, *J* 7.6 Hz, H-1a), 4.92 (d, 1 H, *J* 3.2 Hz, H-1c), 4.96 (d, 1 H, *J* 3.4 Hz, H-1d), 5.00 (d, 1 H, *J* 2.9 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH$_2$), 7.22–7.44 (m, 40 H, 8 Ph); ^{13}C,

δ 20.8 ($COCH_3$), 99.0, 99.6, 99.7 ($^1J_{C,H}$ 168.5 Hz, C-1bcd), 102.8 ($^1J_{C,H}$ 159.9 Hz, C-1a), 169.7 (C=O), 169.9 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{89}H_{100}O_{24}$: C, 68.80; H, 6.49. Found: C, 68.65; H, 6.50.

(*b*) *By coupling of* **6** *and* **7**. Glycosylation of **6** (115 mg, 0.15 mmol) and **7** (93 mg, 0.11 mmol) was performed with $SnCl_2$ (56 mg, 0.30 mmol), $AgClO_4$ (62 mg, 0.30 mmol), and molecular sieves 4A (320 mg) in dry ether (4 mL) at −20 to −5° for 5 h. The mixture was worked-up as described above, to give **31** (159 mg) which was deisopropylidenated to give **32** (145 mg, 83.5%).

Allyl O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**33**). — Selective mono-acetylation of **32** (265 mg, 0.17 mmol) with acetyl chloride (15 μL, 0.21 mmol) in dry pyridine (1.5 mL) at 0° for 1.5 h as described above, followed by chromatography on silica gel (30 g) in *n*-hexane–EtOAc (3:2), afforded **33** (237 mg, 87.1%), $[\alpha]_D^{19}$ +39° (*c* 1.1), R_F 0.35 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^1H, δ 1.91 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 2.04 (s, 3 H, Ac), 3.35 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.47 (bt, 1 H, *J* 6.8 Hz, H-5a), 3.61 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.34 (d, 1 H, *J* 7.6 Hz, H-1a), 4.91 (d, 1 H, *J* 3.4 Hz), 4.92 (d, 1 H, *J* 3.2 Hz), (H-1c, H-1d), 5.00 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH_2), 7.23–7.42 (m, 40 H, 8 Ph); ^{13}C, δ 20.8 ($COCH_3$), 99.2, 99.5 (C-1bcd), 102.8 (C-1a), 169.7 (C=O), 169.9 (C=O), 170.1 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{91}H_{102}O_{25}$: C, 68.49; H, 6.44. Found: C, 68.35; H, 6.41.

Allyl O-(2,3-di-O-benzyl-α-D-galactopyranosyl)-[(1→4)-O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)]$_4$-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**38**). — Reaction of **6** (72 mg, 92 μmol) and **33** (105 mg, 66 μmol) was carried out with $SnCl_2$ (36 mg, 190 μmol), $AgClO_4$ (39 mg, 188 μmol), and molecular sieves 4A (200 mg) in dry ether (2.5 mL) at −5 to 0° for 2.5 h. Column chromatography of the crude product gave **37** (137 mg), h.p.l.c. analysis of which indicated 93% purity. N.m.r. data: ^1H, δ 1.32 (s, 3 H, Me), 1.40 (s, 3 H, Me), 1.91 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 2.02 (s, 3 H, Ac); ^{13}C, δ 18.2 (CH_3), 20.8 ($COCH_3$), 29.4 (CH_3), 98.2 (-O-*C*Me_2-O-), 99.0, 99.6, 100.1 (C-1bcdef, 3:1:1), 102.8 (C-1a), 169.4 (C=O), 169.7 (C=O), 169.9 (C=O), 170.2 (C=O).

Crude **37** was treated with aq. 80% AcOH as described above. The product was chromatographed on silica gel (15 g) in *n*-hexane–EtOAc (2:3) to give **38** (117 mg, 76.6%), $[\alpha]_D^{21}$ +52° (*c* 0.9). N.m.r. data: ^1H, δ 1.89 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 3.34 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.47 (bt, 1 H, H-5a), 3.60 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.34 (d, 1 H, *J* 7.6 Hz, H-1a), 4.90 (d, 1 H, *J* 3.2 Hz), 4.93 (m, 3 H), (H-1cdef), 4.98 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH_2), 7.17–7.40 (m, 60 H, 12 Ph); ^{13}C, δ 20.8 ($COCH_3$), 99.1 ($^1J_{C,H}$ 168.5 Hz), 99.6 ($^1J_{C,H}$ 170.9 Hz), (C-1bcdef 3:2), 102.9 ($^1J_{C,H}$ 156.3 Hz, C-1a), 169.6 (C=O), 169.7 (C=O), 169.9 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{133}H_{148}O_{36}$; C, 68.78; H, 6.42. Found: C, 68.80; H, 6.45.

Allyl O-*(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-[(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)]$_4$-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranoside* (**39**). — The reaction of **38** (212 mg, 91 μmol) in dry pyridine (1.5 mL) with acetyl chloride (8 μL, 113 μmol) was carried out essentially as described for **7**. The crude product was chromatographed on silica gel (30 g) in *n*-hexane–EtOAc (3:2–1:1) to give **39** (184 mg, 85.2%), $[\alpha]_D^{21}$ +45° (*c* 0.7), R_F 0.30 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.88 (s, 3 H, Ac), 1.90 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.94 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 3.34 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.47 (bt, 1 H, *J* 6.8 Hz, H-5a), 3.60 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.34 (d, 1 H, *J* 7.6 Hz, H-1a), 4.89 (d, 2 H, *J* 3.2 Hz), 4.92 (d, 1 H, *J* 3.2 Hz), 4.93 (d, 1 H, *J* 3.2 Hz), (H-1cdef), 4.98 (d, 1 H, *J* 2.9 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH$_2$), 7.16–7.45 (m, 60 H, 12 Ph); ^{13}C, δ 20.8 (CO*C*H$_3$), 99.2, 99.4 (C-1bcdef), 102.8 (C-1a), 169.7 (C=O), 169.9 (C=O), 170.1 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{135}H_{150}O_{37}$: C, 68.58; H, 6.39. Found: C, 68.10; H, 6.34.

Allyl O-*(2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-[(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)]$_6$-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranoside* (**41**). — Reaction of **6** (42 mg, 53.4 μmol) and **39** (62 mg, (26.2 μmol) was performed in dry dichloroethane (3 mL) in the presence of $SnCl_2$ (22 mg, 116 μmol), $AgClO_4$ (25 mg, 120 μmol), and molecular sieves 4A (150 mg) at −15 to 0° for 4 h. After addition of pyridine (0.5 mL), the mixture was worked-up as described above. The crude product was chromatographed on silica gel (10 g) in toluene–EtOAc–pyridine (75:25:1) to give **40** (79 mg) contaminated by small amounts of impurities. Deisopropylidenation of **40** and chromatography of the crude product on silica gel (10 g) in $CHCl_3$–acetone (97:3) afforded **41** (67 mg, 82.7%), $[\alpha]_D^{22}$ +50° (*c* 0.7). N.m.r. data: ^{1}H, δ 1.88 (s, 3 H, Ac), 1.91 (s, 12 H, 4 Ac), 1.93 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 3.34 (dd, 1 H, *J* 2.9 and 9.8 Hz, H-3a), 3.46 (bt, 1 H, H-5a), 3.60 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.34 (d, 1 H, *J* 7.8 Hz, H-1a), 4.89–4.92 (m, 6 H, H-1cdefgh), 4.98 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, C*H*=CH$_2$), 7.15–7.36 (m, 80 H, 16 Ph); ^{13}C, δ 20.8 (CO*C*H$_3$), 99.2, 99.7 ($^1J_{C,H}$ 168.5 Hz, 5:2, C-1bcdefgh), 103.0 ($^1J_{C,H}$ 158.7 Hz, C-1a), 169.7 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{177}O_{196}O_{48}$: C, 68.77; H, 6.39. Found: C, 68.63; H, 6.36.

Allyl O-*(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)-[(1→4)-*O*-(6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-galactopyranosyl)]$_6$-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranoside* (**42**). — Acetylation of **41** (113 mg, 36.6 μmol), with acetyl chloride (3.5 μL, 49.2 μmol) in dry pyridine (0.7 mL) at 0° for 3 h, gave **42** (99 mg, 86.4%), $[\alpha]_D^{21}$ +42° (*c* 0.6), R_F 0.30 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.88 (s, 3 H, Ac), 1.90 (s, 3 H, Ac), 1.91 (s, 12 H, 4 Ac), 1.93 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 3.34 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.46 (bt, 1 H, H-5a), 3.60 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.33 (d, 1 H, *J* 7.6 Hz, H-1a), 4.89 (m, 6 H, H-1cdefgh), 4.98 (d, 1 H, *J* 3.4 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.33 (m, 1 H,

CH=CH_2), 5.95 (m, 1 H, CH=CH$_2$), 7.16–7.38 (m, 80 H, 16 Ph); ^{13}C, δ 20.8 (COCH_3), 99.2, 99.5, 99.6 (C-1bcdefgh), 169.6 (C=O), 169.7 (C=O), 169.9 (C=O), 170.2 (C=O), 170.3 (C=O).

Anal. Calc. for $C_{179}H_{198}O_{49}$: C, 68.61; H, 6.37. Found: C, 68.48; H, 6.38.

Allyl O-(6-O-acetyl-2,3,4-tri-O-benzyl-α-D-galactopyranosyl)-[(1→4)-O-(6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranosyl)]$_8$-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside (**43**). — Glycosylation of **42** (57 mg, 18.2 μmol) with **5** (33 mg, 37.5 μmol) was achieved in dry dichloroethane (2 mL), using $SnCl_2$ (15 mg, 79 μmol), $AgClO_4$ (18 mg, 87 μmol), and powdered molecular sieves 4A (150 mg) at −15° to room temperature for 7 h, and the mixture was worked-up as described above. The crude product was chromatographed on silica gel (10 g) in *n*-hexane–EtOAc (3:2) to give **43** (55 mg, 75.7%), $[\alpha]_D^{23}$ +51° (*c* 0.4), R_F 0.52 (1:1 *n*-hexane–EtOAc). N.m.r. data: ^{1}H, δ 1.752 (s, 3 H, Ac), 1.859 (s, 3 H, Ac), 1.901 (s, 9 H, 3 Ac), 1.908 (s, 3 H, Ac), 1.913 (s, 3 H, Ac), 1.921 (s, 3 H, Ac), 1.932 (s, 3 H, Ac), 2.029 (s, 3 H, Ac), 3.34 (dd, 1 H, *J* 2.9 and 9.8 Hz, H-3a), 3.47 (bt, 1 H, H-5a), 3.60 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a), 4.34 (d, 1 H, *J* 7.6 Hz, H-1a), 4.88 (m, 8 H, H-1cdefghij), 4.98 (d, 1 H, *J* 3.2 Hz, H-1b), 5.20 (m, 1 H, CH=CH_2), 5.34 (m, 1 H, CH=CH_2), 5.95 (m, 1 H, CH=CH$_2$), 7.16–7.41 (m, 105 H, 21 Ph); ^{13}C, δ 20.8 (COCH_3), 99.2 (br, $^1J_{C,H}$ 167.2 Hz, C-1bcdefghij), 169.7 (C=O), 170.0 (C=O).

Anal. Calc. for $C_{230}H_{252}O_{61}$: C, 69.19; H, 6.36. Found: C, 69.26; H, 6.38.

Allyl O-(2,3,4-tri-O-benzyl-α-D-galactopyranosyl)-[1→4)-O-(2,3-di-O-benzyl-α-D-galactopyranosyl)]$_8$-(1→4)-2,3-di-O-benzyl-β-D-galactopyranoside (**4**). — To a solution of **43** (80 mg, 20.0 μmol) in dry tetrahydrofuran (0.2 mL) was added methanolic 0.1M NaOMe (1.5 mL). The mixture was stirred overnight at room temperature, dry toluene (1 mL) was added to the mixture, and the stirring was continued for 20 h. The mixture was treated with excess of Amberlyst 15 (H^+) resin, filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel (10 g) in *n*-hexane–EtOAc (9:11–7:13) to give **4** (60 mg, 83.8%), $[\alpha]_D^{25}$ +70° (*c* 0.3). ^{1}H-N.m.r. data: δ 4.32 (d, 1 H, *J* 7.6 Hz, H-1a), 4.36 (m, 1 H, CH_2CH=CH$_2$), 5.18 (m, 1 H, CH=CH_2), 5.31 (m, 1 H, CH=CH_2), 5.92 (m, 1 H, CH=CH$_2$), 7.27–7.54 (m, 105 H, 21 Ph).

Anal. Calc. for $C_{210}H_{232}O_{51}\cdot H_2O$: C, 70.26; H, 6.57. Found: C, 69.99; H, 6.51.

Oxidation of **4**. — To a solution of oxalyl chloride (22 μL, 252 μmol) in dry CH_2Cl_2 (0.5 mL) was added a solution of dry dimethyl sulfoxide (38 μL, 535 μmol) in dry CH_2Cl_2 (108 μL) under argon with stirring and cooling (dry ice–acetone). After 5 min, a solution of **4** (17 mg, 47.6 μmol) in dry CH_2Cl_2 (0.3 mL) was added, stirring was continued for 15 min, then *N,N*-di-isopropylethylamine (187 μL, 1.07 mmol) was added. After 5 min, the mixture was allowed to warm to room temperature, stirred for another 15 min, diluted with $CHCl_3$, washed successively with dil. HCl, water, and brine, dried (Na_2SO_4), and concentrated *in vacuo*. A solution of the resulting crude aldehyde **44** in CH_3CN (165 μL) was stirred with 7.4% NaH_2PO_4 buffer (45 μL), aq. 31% hydrogen peroxide (11 μL), and aq. 10%

$NaClO_2$ (165 μL) at room temperature overnight. The mixture was diluted with water, acidified with 0.1M HCl (pH 2–3), and extracted with EtOAc. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on silica gel (3 g) in $CHCl_3$–AcOH (9:1) to give allyl *O*-(2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronic acid)-[(1→4)-*O*-(2,3-di-*O*-benzyl-α-D-galactopyranosyluronic acid)]$_8$-(1→4)-2,3-di-*O*-benzyl-β-D-galactopyranosiduronic acid (**45**; 11 mg, 62.3%), $[\alpha]_D^{20}$ +134° (*c* 0.3). ^{1}H-N.m.r. data: δ 5.07 (d, 1 H, *J* 3.4 Hz), 5.13 (m, 7 H), and 5.20 (d, 1 H, *J* 3.1 Hz), for H-1bcdefghij, 5.29 (m, 1 H, CH=CH_2), 5.41 (m, 1 H, CH=CH_2), 6.00 (m, 1 H, C*H*=CH_2), and 7.23–7.33 (m, 105 H, 21 Ph).

Conversion of **45** *into* O-*(methyl 2,3,4-tri*-O-*benzyl*-α-D-*galactopyranosyluronate)*-[*(1→4)*-O-*(methyl 2,3-di*-O-*benzyl*-α-D-*galactopyranosylonate)*]$_8$-*(1→4)*-[*methyl (allyl 2,3-di*-O-*benzyl*-β-D-*galactopyranosid)uronate*] (**46**). — A solution of **45** (8 mg, 2.2 μmol) in EtOAc (0.5 mL) was treated with an excess of ethereal diazomethane, then concentrated *in vacuo*. The residue was purified by preparative t.l.c. using toluene–EtOAc (7:3), to give **46** (5 mg, 60%), R_F 0.69 (1:1 *n*-hexane–EtOAc). ^{1}H-N.m.r. data: δ 3.077, 3.178, 3.197, 3.199, 3.203, 3.219, 3.233, 3.327, 3.408, and 3.654 (10 s, each 3 H, 10 Me), 5.20 (m, 1 H, CH=CH_2), 5.35 (m, 1 H, CH=CH_2), 5.97 (m, 1 H, C*H*=CH_2), 7.11–7.41 (m, 105 H, 21 Ph).

Conversion of **46** *into* **45**. — A mixture of **46** (5 mg, 1.3 μmol) and LiI (15 mg, 112 μmol) in dry pyridine (2 mL) was heated under reflux under argon for 30 h, then concentrated *in vacuo*. A solution of the residue in water (10 mL) was acidified with dil. HCl (pH 2) and extracted with EtOAc, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by preparative t.l.c. with $CHCl_3$–acetone–AcOH (17:1:2). A solution of the product in EtOAc was washed with dil. HCl, water, and brine, dried (Na_2SO_4), and concentrated *in vacuo* to afford **45** (2.5 mg, 52%).

Hydrogenation of **45** *to give propyl* O-*(*α-D-*galactopyranosyluronic acid)*-[*(1→4)*-O-*(*α-D-*galactopyranosyluronic acid)*]$_8$-*(1→4)*-β-D-*galactopyranosiduronic acid* **3**. — A mixture of **46** (2.5 mg, 0.67 μmol) and 10% Pd/C (5 mg) in aq. 70% MeOH was stirred in an atmosphere of hydrogen at room temperature for 5 days, then filtered through Celite, and concentrated *in vacuo*. A solution of the residue in aq. 50% MeOH was passed through a short column of Sephadex LH-20, and the resulting crude product was purified by anion-exchange chromatography on Mono-Q (HR 5/5) with a linear gradient of $NH_4 \cdot HCO_3$ buffer (0.2→0.4M). Fractions were assayed for uronosyl residue by the *m*-hydroxybiphenyl method[24]. The fractions containing **3** were combined and concentrated *in vacuo* at 70°. Water was evaporated several times from the residue to remove the contaminating hydrogencarbonate and leave **3** (1.1 mg). Mass spectrum: *m/z* (M − 1) 1819 (M^+ − 1). ^{1}H-N.m.r. data [D_2O, internal ^{t}BuOH (δ 1.23), 80°]: δ 0.91 (t, 3 H, *J* 7.3 Hz, CH_2CH_3), 1.63 (m, 2 H, CH_2CH_3), 3.51 (dd, 1 H, *J* 7.8 and 9.9 Hz, H-2a), 3.64 (dt, 1 H, *J* 6.8 and 9.8 Hz, $OCH_2CH_2CH_3$), 3.70–3.82 (m, 10 H, H-2bcdefghij, H-3a), 3.88 (dt, 1 H, *J* 6.9 and 10.0 Hz, $OCH_2CH_2CH_3$), 3.91 (dd, 1 H, *J* 3.4 and 10.7 Hz, H-3j), 4.00 (bd, 8 H, H-3bcdefghi), 4.30 (b, 1 H, H-5a), 4.34 (b, 1 H, H-4j),

4.41 (b, 1 H, H-4a), 4.44 (d, 1 H, *J* 7.8 Hz, H-1a), 4.49 (b, 8 H, H-4bcdefghi), 4.99 (b, 9 H, H-bcdefghij), 5.09 (b, 9 H, H-1bcdefghij).

ACKNOWLEDGMENTS

We thank Drs. P. Albersheim, A. G. Darvill, M. G. Hahn, and W. S. York for assistance with the chromatographic, mass spectrometric, and n.m.r. analyses, which were made possible by a research grant from the U.S. Department of Energy No. DE-FG-09-87-ER13810 to the Complex Carbohydrate Research Center of the University of Georgia. We thank Dr. J. Uzawa and Mrs. T. Chijimatsu for recording and measuring the n.m.r. spectra, Dr. H. Yamazaki and his staff for the elemental analyses, and Ms. A. Takahashi and Ms. K. Moriwaki for technical assistance.

REFERENCES

1 Y. NAKAHARA AND T. OGAWA, *Tetrahedron Lett.*, 30 (1989) 87–90.
2 E. A. NOTHNAGEL, M. MCNEIL, P. ALBERSHEIM, AND A. DELL, *Plant Physiol.*, 71 (1983) 916–926; M. G. HAHN, A. G. DARVILL, AND P. ALBERSHEIM, *ibid.*, 68 (1981) 1161–1169.
3 K. R. DAVIS, G. D. LYON, A. G. DARVILL, AND P. ALBERSHEIM, *Plant Physiol.*, 74 (1984) 52–60; K. R. DAVIS, A. G. DARVILL, P. ALBERSHEIM, AND A. DELL, *ibid.*, 80 (1986) 568–577.
4 D. F. JIN AND C. A. WEST, *Plant Physiol.*, 74 (1984) 989–992.
5 P. BISHOP, D. J. MAKUS, G. PEARCE, AND C. A. RYAN, *Proc. Natl. Acad. Sci. U.S.A.*, 78 (1981) 3536–3540.
6 D. ROBY, A. TOPPAN, AND M.-T. ESQUERRÉ-TUGAYÉ, *Plant Physiol.*, 77 (1985) 700–704.
7 A. G. DARVILL AND P. ALBERSHEIM, *Annu. Rev. Plant Physiol.*, 35 (1984) 243–275; M. MCNEIL, A. G. DARVILL, S. C. FRY, AND P. ALBERSHEIM, *Annu. Rev. Biochem.*, 53 (1984) 625–663.
8 Y. NAKAHARA AND T. OGAWA, *Carbohydr. Res.*, 173 (1988) 306–315.
9 Y. NAKAHARA AND T. OGAWA, *Tetrahedron Lett.*, 28 (1987) 2731–2734.
10 Y. NAKAHARA AND T. OGAWA, *Carbohydr. Res.*, 167 (1987) c1–c7.
11 E. BOURQUELET AND M. BRIDEL, *C.R. Acad. Sci.*, 156 (1913) 1104–1106; R. GIGG AND C. D. WARREN, *J. Chem. Soc.*, (1965) 2205–2210; R. T. LEE AND Y. C. LEE, *Carbohydr. Res.*, 37 (1974) 193–201; L. R. SCHROEDER, K. M. COUNTS, AND F. C. HAIGH, *ibid.*, 37 (1974) 368–372; K. JAMES AND R. V. STICK, *Aust. J. Chem.*, 29 (1976) 1159–1162; J.-C. JACQUINET AND P. SINAŸ, *Tetrahedron*, 35 (1979) 365–371.
12 P. A. GENT AND R. GIGG, *J. Chem. Soc., Perkin Trans. 1*, (1974) 1835–1839.
13 E. J. COREY AND J. W. SUGGS, *J. Org. Chem.*, 38 (1973) 3224; P. A. GENT AND R. GIGG, *J. Chem. Soc., Chem. Commun.*, (1974) 277–278.
14 W. ROSENBROOK, JR., D. A. RILEY, AND P. A. LARTEY, *Tetrahedron Lett.*, 26 (1985) 3–4; G. H. POSNER AND S. R. HAINES, *ibid.*, 26 (1985) 5–8.
15 T. MUKAIYAMA, Y. MURAI, AND S. SHODA, *Chem. Lett.*, (1981) 1537–1545.
16 K. BOCK, I. LUNDT, AND C. PEDERSEN, *Tetrahedron Lett.*, (1973) 1037–1040; K. BOCK AND C. PEDERSEN, *J. Chem. Soc., Perkin Trans. 2*, (1974) 293–297.
17 W. KINZY AND R. R. SCHMIDT, *Justus Liebigs Ann. Chem.*, (1985) 1537–1545.
18 K. OMURA AND D. SWERN, *Tetrahedron*, (1978) 1651–1660; R. E. IRELAND AND D. W. NORBECK, *J. Org. Chem.*, 50 (1985) 2198–2200.
19 E. DALCANALE AND F. MONTANARI, *J. Org. Chem.*, 51 (1986) 567–569.
20 F. CERVONE, M. G. HAHN, G. DELORENZO, A. DARVILL, AND P. ALBERSHEIM, submitted for publication.
21 J. MCMURRY, *Org. React.*, 24 (1976) 187–224.
22 W. S. YORK, personal communication; B. MATSUHIRO, A. B. ZANLUNGO, AND G. G. S. DUTTON, *Carbohydr. Res.*, 97 (1981) 11–18.
23 M. G. HAHN AND P. ALBERSHEIM, unpublished data.
24 N. BLUMENKRANTZ AND G. ASBOE-HANSEN, *Anal. Biochem.*, 54 (1973) 484–489.