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Synthesis of (1→4)-linked galacturonic acid trisaccharides, a proposed plant wound-hormone and a stereoisomer*

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ABSTRACT

Syntheses of α-GalA-(1→4)-α-GalA-(1→4)-GalA, a proposed plant wound-hormone, and its stereoisomer β-GalA-(1→4)-α-GalA-(1→4)-GalA are described. The key intermediates, *tert*-butyldiphenylsilyl *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)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside and *tert*-butyldiphenylsilyl *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-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, were prepared by stereoselective α-glycosylation of *tert*-butyldiphenylsilyl 6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside with *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 and *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzyl-D-galactopyranosyl fluoride, respectively. The corresponding β isomers were minor products. Characteristic features in the n.m.r. data of the key intermediates are discussed.

INTRODUCTION

Small fragments of plant cell-wall pectic polysaccharides, such as the galacturonic acid trisaccharide **1a**, have been proposed to behave as hormone-like substances which may induce a second messenger that would be systemically transported throughout the plant tissues in the tomato and induce the synthesis and accumulation of proteinase inhibitor I, one of the defence substances produced by plants against invading microbes or insects[2].

As part of a project on the synthesis of plant cell-wall glycans, we have achieved[1,3] a stereocontrolled total synthesis of the decasaccharide propyl glycoside **1c**, a synthetic model for the phytoalexin elicitor-active galacturonic acid oligosaccharides **1b**[4]. The allyl galactodecaoside **2** was a key intermediate which was transformed into the corresponding uronic acid glycoside **1d**. However, liberation of the anomeric hydroxyl group was not achieved. In a preliminary study of the tris(triphenylphosphine)rhodium (I) chloride-mediated deallylation of allyl galactosides, undesired oxidation of the allyl to the 2-oxopropyl group was encountered.

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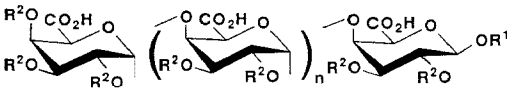
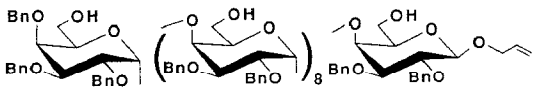
In order to synthesize galacturonic acid oligosaccharides of the type released by the degradation of pectin, an alternative to the allyl group for protecting HO-1 was necessary. Galactobioses have been synthesised by way of the stable *tert*-butyldiphenylsilyl glycosides[5], and the mild conditions used for desilylation[6] make feasible the regeneration of HO-1 in a late stage of the syntheses of galacturonic acid oligosaccharides.

We now describe a practical approach to the synthesis of such oligosaccharides, using 1-O-*tert*-butyldiphenylsilylated intermediates, which led to a total synthesis of α-GalA-(1→4)-α-GalA-(1→4)-GalA (**1a**), a putative plant wound-hormone, and its stereoisomer, β-GalA-(1→4)-α-GalA-(1→4)-GalA (**3**).



1 a n = 1 $R^1 = R^2 = H$
b n = 5 ~ 11 $R^1 = R^2 = H$
c n = 8 R^1 = n-Pr, $R^2 = H$
d n = 8 R^1 = Allyl, R^2 = Bn



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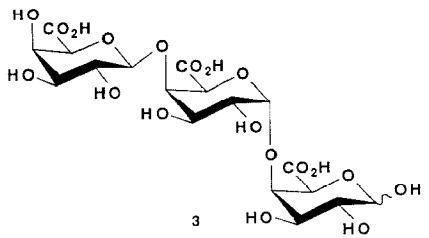

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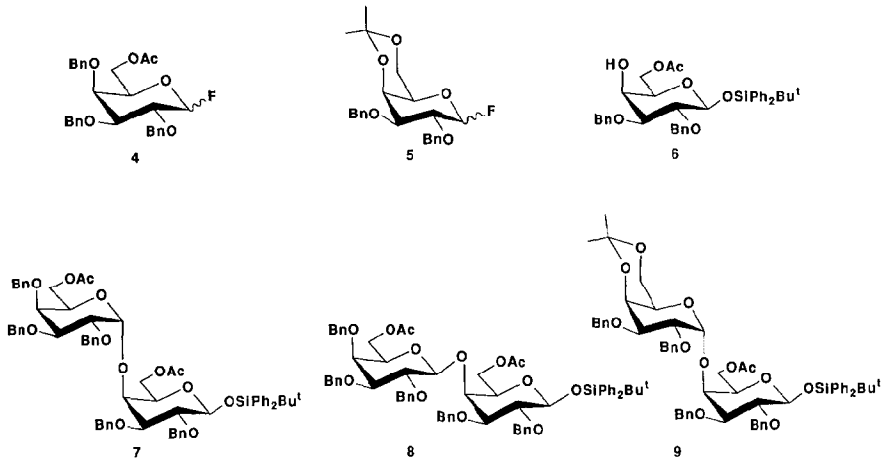
RESULTS AND DISCUSSION

The *tert*-butyldiphenylsilyl galactobiosides **7** and **9** were prepared by stereoselective glycosylation using the galactopyranosyl fluorides **4** and **5** as the donors[1,3,5]. Under the conditions ($SnCl_2$, $AgClO_4$, MS4A, ether) described by Mukaiyama *et al.*[7], glycosylation of **6** with **5** afforded the α-linked galactobioside derivative **9** as the sole coupling product. On the other hand, the reaction of **6** with **4** gave a mixture of the α-linked galactobioside derivative **7** and the β isomer **8** in the ratio 4.3–5:1.

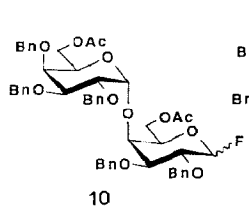


As the stereochemical outcome of the glycosylation reaction strongly depends on the choice of the promoter and the protecting groups in the donors, tin(II) trifluoromethanesulfonate[8] and tributyltin trifluoromethanesulfonate[9] were examined as alternative promoters, since each has been reported to activate a glycosyl fluoride[10]. These stannyl salts smoothly promoted the reaction of **5** with **6** to yield, exclusively, the α-linked product **9**. In contrast, they displayed lower stereoselectivity for the reaction of **4** with **6**. Thus, the use of tin(II) trifluoromethanesulfonate gave 96.5% of a mixture of **7** and **8** in the ratio 2.6:1, and the use of tributyltin trifluoromethanesulfonate gave 93.4% of a 1.6:1 mixture. The α and β isomers were distinguished on the basis of the n.m.r. data. The configurations at C-1 were assignable from either of the $J_{C\text{-}1,H\text{-}1}$ values[11] or the chemical shifts of the resonances of the anomeric carbons[12]. Thus, for the (1→4)-linked galacto-oligosaccharides, the signals for C-1α appeared at ~100 p.p.m. and those for C-1β at ~103 p.p.m..

The galactobiosides **7**–**9** were converted into the *tert*-butyldiphenylsilyl galactotrioside derivatives **15** and **17**, suitable precursors for the α-(1→4)-linked galacturonic acid trisaccharide **1a** and its stereoisomer as follows.

Transformation of **7** into the galactobiosyl fluoride **10** has been reported[1,5]. In a similar manner, the stereoisomer **12** was prepared from **8** by desilylation with tetrabutylammonium fluoride–acetic acid in tetrahydrofuran[6] and treatment of the resulting hemiacetal **11** with diethylaminosulfur trifluoride (DAST) in tetrahydrofuran[13]. The product **12** was obtained as a 1:3 $\alpha\beta$-mixture. Compound **9** was converted into the galactobiosyl acceptor **14** by acid-catalyzed *O*-deisopropylidenation followed by selective acetylation of the resulting diol **13**.

Glycosylation of **6** with **10** gave 76.8% of the galactotrioside derivative **15** as the sole product by using stannous chloride and silver perchlorate in ether. When the same reaction was carried out in 1,2-dichloroethane, lower stereoselectivity was observed and 3.9% of the β-linked isomer **16** was obtained in addition to 68.3% of **15**. In contrast, glycosylation of **6** with the β-(1→4)-linked galactobiosyl donor **12** gave both the α- (**17**,



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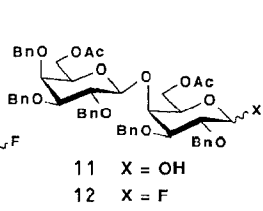
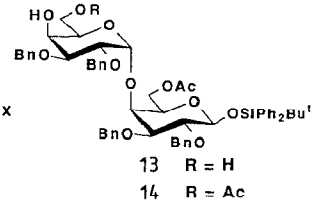
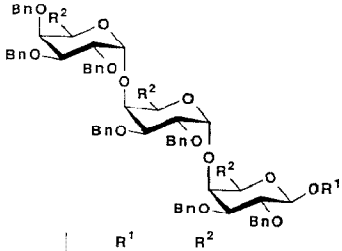


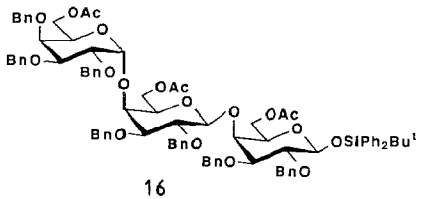
11 X = OH
12 X = F



13 R = H
14 R = Ac



	R^1	R^2
15	$SiPh_2Bu^t$	CH_2OAc
19	〃	CH_2OH
20	〃	CHO
21	〃	COOH
22	〃	$COOCH_3$
23	H	COOH



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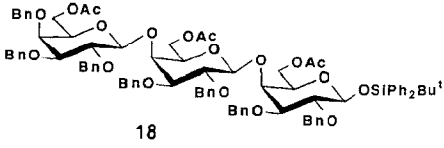

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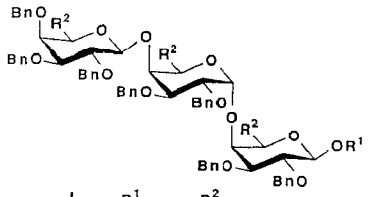
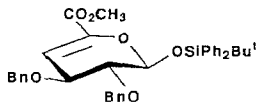


	R^1	R^2
17	$SiPh_2Bu^t$	CH_2OAc
24	〃	CH_2OH
25	〃	CHO
26	〃	COOH
27	〃	$COOCH_3$
28	H	COOH



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73.3%) and β-linked (**18**, 4.6%) trisaccharide derivatives, even in ether. Apparently, the α-D-galactopyranosyl residue at C-4a in the donor **10** promotes higher α-stereoselectivity than the β-D-galactopyranosyl residue at C-4a in the donor **12**. The galactotrioside derivative **17** was also produced as a minor product (11.6%) in the reaction of **4** with the galactobiosyl acceptor **14**, in which **15** was the major product (63.3%). The structural assignment of these products was based on comparison of their ^{1}H- and ^{13}C-n.m.r. data[11,12].

The presence of a characteristic signals for ^{t}Bu and three OAc groups in the ^{1}H-n.m.r. spectra of **15**–**18** demonstrated that they were stereoisomeric trisaccharide derivatives. The anomeric configurations of **15** and **17** were assignable on the basis of the $J_{C\text{-}1,H\text{-}1}$ values, and the structures of **16** and **18** were assigned by the values of chemical

shift of the resonances for the anomeric carbon atoms (see Experimental). The isomers (**16**–**18**) that involved at least one β linkage exhibited one or two doublets for benzylic hydrogen at lower field than δ 5.00 [*e.g.*, **16** δ 5.20 (J 11.0 Hz), **17** δ 5.09 (J 11.6 Hz), **18** δ 5.00 (J 11.0 Hz) and 5.14 (J 11.0 Hz)], whereas no such low-field signal was observed for the isomer **15**. Although the benzylic proton which is deshielded in each of **16**–**18** cannot be specified, this characteristic feature helped to confirm the configuration of the glycosidic linkages.

Among the above galactotrioside derivatives, **15** and **17** were obtained in amounts sufficient for further transformations to the corresponding uronides. Deacetylation of **15** with methanolic sodium methoxide gave **19** (96%). Oxidation of **19** to the uronic acid **21** was carried out in two steps[1,3]. Swern oxidation[14] converted **19** into the aldehyde **20** which, without purification, was further oxidized[15] with aqueous sodium chlorite to give **21** (86% after chromatography). The structure of **21** was established after treatment with ethereal diazomethane to give the methyl ester **22**, the ^{1}H-n.m.r. spectrum of which contained three singlets for methyl groups at δ 3.26, 3.38, and 3.48. Purification of such a large molecule as the decacarboxylic acid **1d** was laborious, as reported[1] in the synthesis of **1c**. A pure sample of **1d** was obtained by methyl esterification, chromatography, and hydrolysis. This procedure was applied also to purify the tricarboxylic acid **21**. For the regeneration of **21** from **22**, an S_N2 type demethylation procedure[16] (LiI, pyridine) gave an acceptable yield (69%), whereas saponification was unsuitable probably because of β-elimination.

Desilylation of **21** with tetrabutylammonium fluoride in the presence of acetic acid[6] afforded **23** (86%), which was then hydrogenated (10% Pd–C) to complete the total synthesis of the α-(1→4)-linked galacturonic acid trisaccharide **1a**. Purification by anion-exchange chromatography gave a homogeneous sample of **1a**, the ^{1}H-n.m.r. spectral data of which were coincident with that of the sample derived from natural pectins.

Likewise, the stereoisomeric galactotrioside derivative **17** was transformed into the uronic acid **3**. Deacetylation of **17** (79%) was followed by the two-step oxidation to give the tricarboxylic acid **26** (80%). The signals for the corresponding trimethyl ester **27** appeared at δ 3.23, 3.33, and 3.43. Regeneration of **26** from **27** was also examined. On heating **27** with lithium iodide in dry pyridine for 7 h, 57% of **26** was obtained together with the elimination product **29**. Desilylation of **26** followed by hydrogenolysis afforded the galacturonic acid trisaccharide **3**, the anion-exchange chromatographic behavior and ^{1}H-n.m.r. spectrum of which were compatible with the assigned structure.

The results reported demonstrate a practical method for synthesizing α-(1→4)-linked galacturonic acid oligosaccharides. A total synthesis of a galacturonic acid dodecasaccharide, a phytoalexin-elictor active oligomer, using this methodology, will be reported elsewhere.

EXPERIMENTAL

General. — 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). Flash chromatography was performed on columns of Wako Gel C-300 (200–300 mesh). T.l.c. and h.p.t.l.c. were performed on Silica Gel 60 F_{254} (Merck). N.m.r. spectra were recorded with a JEOL GX500 [^1H (500 MHz)] or FX90Q [^{13}C (22.50 MHz)] spectrometer. Chemical shifts are expressed in p.p.m. downfield from the signal for internal Me_4Si, for solutions in $CDCl_3$, unless noted otherwise, and, for solutions in D_2O, in p.p.m. downfield from the signal for Me_4Si, by reference to internal Me_3COH (1.230).

tert-*Butyldiphenylsilyl* O-(*6-O-acetyl-2,3,4-tri-O-benzyl-α- and -β-*D*-galactopyranosyl*)-(1→4)-6-O-*acetyl-2,3-di-O-benzyl-β-*D*-galactopyranoside (**7** *and* **8**). — (*a*) *With Sn(OTf)$_2$ as the promoter.* A mixture of **4** (ref. 1) (88 mg, 0.18 mmol) and **6** (ref. 1) in dry ether (5 mL) was added to a stirred mixture of $Sn(OTf)_2$[8] (150 mg, 0.36 mmol) and powdered molecular sieves 4 Å (220 mg) under Ar at −10°. After stirring for 1 h at −10° to −4°, the reaction was stopped by quenching with pyridine (1 mL). The mixture was filtered through Celite and extracted with EtOAc–ether (1:1), and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (20 g) with hexane–EtOAc (3:1) gave **7** (87 mg, 69.4%) and then **8** (34 mg, 27.1%). The physical data of **7** and **8** were identical with those described[1].

(*b*) *With* n-*Bu$_3$SnOTf as the promoter.* To a mixture of **4** (88 mg, 0.18 mmol), **6** (72 mg, 0.11 mmol), and powdered molecular sieves 4 Å (230 mg) in dry ether (3 mL) was added ethereal 0.16M *n*-Bu_3SnOTf[9] (3 mL) with stirring under Ar at −10°. The stirred mixture was allowed to warm to room temperature overnight, then filtered through Celite, and stirred with saturated aq. KF (10 mL) for 4 h. The precipitate was removed, the filtrate was extracted with EtOAc, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (20 g) with hexane–EtOAc (4:1) gave **7** (72 mg, 57.5%) and **8** (45 mg, 35.9%).

tert-*Butyldiphenylsilyl* 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* (**9**). — (*a*) *With Sn(OTf)$_2$ as the promoter.* Reaction of **5** (ref. 1) (81 mg, 0.20 mmol) with **6** (73 mg, 0.11 mmol), as described above, gave **9** (72 mg, 61.8%) and its *O*-deisopropylidenated derivative **13** (10 mg, 8.9%) after chromotagraphy on silica gel (20 g) with hexane–EtOAc–pyridine (60:40:1). The physical data of **9** and **13** were identical with those described[1].

(*b*) *With* n-*Bu$_3$SnOTf as the promoter.* Reaction of **5** (81 mg, 0.20 mmol) with **6** (73 mg, 0.11 mmol) was carried out in dry ether (3 mL) with an ethereal solution of 0.16M *n*-Bu_3SnOTf (4 mL) and powdered molecular sieves 4 Å (200 mg) at −7° for 2 h. The mixture was worked-up as described above and chromatography on silica gel (20 g) with hexane–EtOAc–pyridine (60:40:1) afforded **9** (88 mg, 75.5%) as the sole product.

O-*(6-O-Acetyl-2,3,4-tri-O-benzyl-β-*D*-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-*

di-O-benzyl-D-galactopyranose (**11**). — To a mixture of **8** (295 mg, 0.26 mmol) and AcOH (110 μL, 1.92 mmol) in dry tetrahydrofuran (8mL) was added M *n*-Bu_4NF–tetrahydrofuran (1.1 mL, 1.1 mmol). The mixture was stirred at room temperature for 3 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*. Column chromatography of the crude product on silica gel (25 g) with hexane–EtOAc (1:1) gave **11** (200 mg, 86.2%), R_F 0.25 and 0.21 (1:1 hexane–EtOAc). ^{1}H-N.m.r. data: δ 1.97 (1.96) (s, 3 H, Ac), 2.04 (2.05) (s, 3 H, Ac).

Anal. Calc. for $C_{51}H_{56}O_{13}$: C, 69.85; H, 6.45. Found: C, 69.47; H, 6.40.

O-*(6-O-Acetyl-2,3,4-tri-O-benzyl-β-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-D-galactopyranosyl fluoride* (**12**). — To a stirred solution of **11** (166 mg, 0.19 mmol) in dry tetrahydrofuran (1 mL) at −10° was added diethylaminosulfur trifluoride (DAST, 40 μL, 0.30 mmol). The mixture was allowed to warm to room temperature, a few drops of MeOH were added, 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*. Column chromatography of the residue on silica gel (25 g) with hexane–EtOAc (7:3) gave **12** (162 mg, 97.4%) as a 1:3 αβ-mixture, R_F 0.47 and 0.41 (1:1, hexane–EtOAc). ^{1}H-N.m.r. data: δ 1.97 (s, 3 H, Ac), 2.05 (2.06) (s, 3 H, Ac).

Anal. Calc. for $C_{51}H_{55}FO_{12}$: C, 69.69; H, 6.31. Found: C, 69.89; H, 6.31.

tert-*Butyldiphenylsilyl* O-*(2,3-di-O-benzyl-α-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-α-D-galactopyranoside* (**13**). — A mixture of **9** (1.37 g, 1.34 mmol), tetrahydrofuran (5 mL), and aq. 80% AcOH (30 mL) was stirred at room temperature for 2 days, then concentrated. Column chromatography of the residue on silica gel (120 g) with toluene–EtOAc (3:2) gave **13** (1.20 g, 91.2%), $[\alpha]_D^{27}$ +54° (*c* 1.4). N.m.r. data: ^{1}H, δ 1.14 (s, 9 H, ^{t}Bu), 1.88 (s, 3 H, Ac), 3.27 (bt, 1 H, *J* 6.34 Hz, H-5a), 3.31 (dd, 1 H, *J* 2.7 and 10.0 Hz, H-3a), 3.52 (m, 1 H, H-6b), 3.62 (dd, 1 H, *J* 5.1 and 11.5 Hz, H-6b), 3.69 (dd, 1 H, *J* 7.3 and 10.0 Hz, H-2a), 3.78 (bd, 1 H, *J* 2.4 Hz, H-4a), 3.88 (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), 4.07 (bt, 1 H, H-5b), 4.09 (b, 1 H, H-4b), 4.15 (dd, 1 H, *J* 6.6 and 11.2 Hz, H-6a), 4.24 (dd, 1 H, *J* 6.4 and 11.2 Hz, H-6a), 4.60 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.61 (d, 1 H, *J* 7.3 Hz, H-1a), 4.68 (d, 1H, *J* 11.7 Hz, C*H*$_2$Ph), 4.71 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.76 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.80 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.83 (d, 1 H, *J* 11.7 Hz, C*H*$_2$Ph), 4.84 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.91 (d, 1 H, *J* 3.4 Hz, H-1b), 4.96 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 7.23–7.42 (m, 26 H, aromatic H), 7.70–7.74 (m, 4 H, aromatic H); ^{13}C, δ 19.3 (*C*Me$_3$), 20.7 (*C*H$_3$CO), 27.1 [C(*C*H$_3$)$_3$], 62.7, 63.1, 69.5, 70.1, 72.6, 73.1, 73.8, 75.1, 76.1, 76.3, 77.5, 80.7, 98.3 (C-1a), 100.2 (C-1b), 127.3, 127.4, 127.5, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 130.0, 133.7, 135.8, 136.0, 138.0, 138.1, 138.6, 170.2 (C=O).

Anal. Calc. for $C_{54}H_{66}O_{12}Si$: C, 70.85; H, 6.77. Found: C, 70.47; H, 6.74.

tert-*Butyldiphenylsilyl* 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* (**14**). — To an ice-cooled solution of **13** (1.38 g, 1.40 mmol) in dry pyridine (15 mL) was added acetyl chloride (125 μL, 1.76 mmol) with stirring. After stirring at 0–10° for 3 h, a few drops of water were

added, the mixture was concentrated *in vacuo*, the residue was extracted with EtOAc, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated. Column chromatography of the residue on silica gel (150 g) with toluene–EtOAc (3:1) gave a triacetate (0.10 g, 6.7%) and then **14** (1.25 g, 86.9%), $[\alpha]_D^{23}$ +55° (*c* 0.7), R_F 0.35 (7:3 toluene–hexane). N.m.r. data: ^{1}H, δ 1.12 (s, 9 H, ^{t}Bu), 1.88 (s, 3 H, Ac), 1.90 (s, 3 H, Ac), 3.26 (t, 1 H, *J* 6.6 Hz, H-5a), 3.30 (dd, 1 H, *J* 2.8 and 9.8 Hz, H-3a), 3.71 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-2a), 3.81 (d, 1 H, *J* 2.4 Hz, H-4a), 3.89 (dd, 1 H, *J* 3.4 and 9.8 Hz, H-2b), 4.01 (dd, 1 H, *J* 3.1 and 9.8 Hz, H-3b), 4.04 (dd, 1 H, *J* 6.1 and 11.0 Hz, H-6b), 4.05 (bs, 1 H, H-4b), 4.13 (dd, 1 H, *J* 7.0 and 11.3 Hz, H-6a), 4.19 (dd, 1 H, *J* 7.0 and 11.3 Hz, H-6a or H-6b), 4.23 (dd, 1 H, *J* 6.1 and 11.3 Hz, H-6a or H-6b), 4.35 (t, 1 H, *J* 6.4 Hz, H-5b), 4.60 (d, 1 H, *J* 7.3 Hz, H-1a), 4.65 (d, 1 H, *J* 12.8 Hz, C*H*$_2$Ph), 4.70 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.72 (d, 1 H, *J* 12.8 Hz, C*H*$_2$Ph), 4.78 (d, 1 H, *J* 11.3 Hz, C*H*$_2$Ph), 4.80 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.83 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.86 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.94 (d, 1 H, *J* 3.4 Hz, H-1b), 4.96 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 7.22–7.42 (m, 26 H, aromatic H), 7.69–7.73 (m, 4 H, aromatic H); ^{13}C, δ 19.3 (*C*Me$_3$), 20.7 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 27.1 [C(*C*H$_3$)$_3$], 62.7, 63.0, 67.6, 68.1, 72.3, 72.6, 73.9, 75.0, 75.5, 76.2, 77.4, 80.2, 80.8, 98.1 (C-1a), 99.8 (C-1b), 127.2, 127.4, 127.5, 127.9, 128.1, 128.3, 129.5, 135.8, 136.0, 138.2, 138.3, 138.7, 170.5 (C=O), 170.2 (C=O).

Anal. Calc. for $C_{60}H_{68}O_{13}Si$: C, 70.29; H, 6.69. Found: C, 70.27; H, 6.69.

Triacetate: R_F 0.56 (7:3 toluene–EtOAc). ^{1}H-N.m.r. data: δ 1.13 (s, 9 H, ^{t}Bu), 1.88 (s, 3 H, Ac), 1.92 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 5.56 (m, 1 H, H-4b).

tert-*Butyldiphenylsilyl* 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- and -β-D-galactopyranosyl)-(1→4)-6-O-acetyl-2,3-di-O-benzyl-β-D-galactopyranoside* (**15** *and* **16**).— (*a*) *With 1,2-dichloroethane as the solvent.* To a mixture of $SnCl_2$ (72 mg, 0.38 mmol), $AgClO_4$ (87 mg, 0.42 mmol), and powdered molecular sieves 4 Å (500 mg) was added a solution of **10** (ref. 1) (106 mg, 0.12 mmol) and **6** (77 mg, 0.12 mmol) in 1,2-dichloroethane (8 mL) with stirring at −10°. Stirring was continued from −10° to room temperature during 7.5 h, pyridine (0.5 mL) was added, the mixture was filtered through Celite and extracted with $CHCl_3$, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (25 g) with hexane–EtOAc (3:1) gave **15** (114 mg, 63.3%), and a mixture (28 mg, 15.5%) of **15** and **16**. Preparative t.l.c. (hexane–EtOAc, 3:2) of the latter mixture gave **15** (9 mg) and **16** (7 mg).

Compound **15** had $[\alpha]_D^{20}$ +40° (*c* 0.5), R_F 0.51. N.m.r. data: ^{1}H, δ 1.12 (s, 9 H, ^{t}Bu), 1.84 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 1.91 (s, 3 H, Ac), 3.22 (bt, 1 H, *J* 6.6 Hz, H-5a), 3.25 (dd, 1 H, *J* 2.7 and 10.0 Hz, H-3a), 3.65 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-2a), 4.55 (d, 1 H, *J* 7.3 Hz, H-1a); ^{13}C, δ 19.2 (*C*Me$_3$), 20.7 (*C*H$_3$CO), 27.0 [C(*C*H$_3$)$_3$], 98.0 ($J_{C\text{-}1,H\text{-}1}$ 155.0 Hz, C-1a), 99.5 ($J_{C\text{-}1,H\text{-}1}$ 167.2 Hz, C-1b or C-1c), 99.6 ($J_{C\text{-}1,H\text{-}1}$ 168.5 Hz, C-1b or C-1c), 169.8 (C=O), 169.9 (C=O), 170.2 (C=O).

Anal. Calc. for $C_{89}H_{98}O_{19}Si$: C, 71.27; H, 6.59. Found: C, 70.89; H, 6.57.

Compound **16** had $[\alpha]_D^{20}$ +37° (*c* 0.4), R_F 0.45. N.m.r. data: ^{1}H, δ 1.09 (s, 9 H, ^{t}Bu), 1.82 (s, 3 H, Ac), 1.85 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 5.20 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph); ^{13}C, δ 1.93 (*C*Me$_3$), 20.8 (*C*H$_3$CO), 27.0 [C(*C*H$_3$)$_3$], 98.1 (C-1a), 100.4 (C-1c), 102.5 (C-1b), 170.2 (C=O), 170.3 (C=O), 170.4 (C=O).

Anal. Calc. for $C_{89}H_{98}O_{19}Si \cdot H_2O$: C, 70.43; H, 6.64. Found: C, 70.39; H, 6.48.

(*b*) *With ether as the solvent.* Reaction of **10** (270 mg, 0.31 mmol) and **6** (200 mg, 0.31 mmol) was carried out in dry ether (20 mL) by using $SnCl_2$ (185 mg, 0.96 mmol), $AgClO_4$ (220 mg, 1.06 mmol), and powdered molecular sieve 4 Å (1.5 g) at $-10°$ to $-5°$ for 1.5 h. After work-up as described above, column chromatography of the crude product gave **15** (354 mg, 76.8%) and no detectable amount of **16**.

tert-*Butyldiphenylsilyl* O-(6-O-*acetyl-2,3,4-tri*-O-*benzyl-β*-D-*galactopyranosyl*)-(1→4)-O-(6-O-*acetyl-2,3-di*-O-*benzyl-α- and -β*-D-*galactopyranosyl*)-(1→4)-6-O-*acetyl-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**17** *and* **18**). — In the manner described for **15** and **16**, **12** (140 mg, 0.16 mmol) and **6** (102 mg, 0.16 mmol) were reacted in dry ether to afford a mixture of **6**, **17**, and **18** after 3 h. Column chromatography of the crude product gave **17** (145 mg) and a mixture (73 mg) of **6**, **17**, and **18**, t.l.c. (toluene–EtOAc, 4:1) of which gave **17** (30 mg, total 73.3%), **6** (19 mg), and **18** (11 mg, 4.6%).

Compound **17** had $[\alpha]_D^{20}$ +39° (*c* 1.3), R_F 0.65 (7:3 toluene–EtOAc). N.m.r. data: ^{1}H, δ 1.11 (s, 9 H, ^{t}Bu), 1.84 (s, 3 H, Ac); 1.85 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 3.24 (bt, 1 H, *J* 6.4 Hz, H-5a), 3.29 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a), 3.43 (bt, 1 H, *J* 6.3 Hz, H-5c), 3.48 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3c), 3.71 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-2a), 3.73 (d, 1 H, *J* 2.1 Hz, H-4c), 3.80 (dd, 1 H, *J* 7.6 and 9.5Hz, H-2c), 3.83 (d, 1 H, *J* 2.1 Hz, H-4a), 4.58 (d, 1 H, *J* 7.3 Hz, H-1a), 4.89 (d, 1 H, *J* 7.6 Hz, H-1c), 5.01 (d, 1 H, *J* 3.4 Hz, H-1b), 5.09 (d, 1 H, *J* 11.6 Hz, C*H*$_2$Ph); ^{13}C, δ 19.2 (*C*Me$_3$), 20.8 (*C*H$_3$CO), 27.0 [C(*C*H$_3$)$_3$], 98.0 ($J_{C-1,H-1}$ 155.0 Hz, C-1a), 99.6 ($J_{C-1,H-1}$ 168.5 Hz, C-1b), 102.8 ($J_{C-1,H-1}$ 162.4 Hz, C-1c), 170.2 (C=O), 170.4 (C=O).

Anal. Calc. for $C_{89}H_{98}O_{19}Si$: C, 71.27; H, 6.59. Found: C, 70.94; H, 6.59.

Compound **18** had $[\alpha]_D^{24}$ +22.5° (*c* 0.5), R_F 0.55. N.m.r. data: ^{1}H, δ 1.08 (s, 9 H, ^{t}Bu), 1.89 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 4.59 (d, 1 H, *J* 7.3 Hz, H-1a), 4.86 (d, 1 H, *J* 7.6 Hz, H-1b or H-1c), 4.88 (d, 1 H, H-1b or H-1c), 5.00 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 5.14 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph); ^{13}C, δ 1.93 (*C*Me$_3$), 20.9 (*C*H$_3$CO), 27.0 [C(*C*H$_3$)$_3$], 98.1 (C-1a), 102.7 (C-1b or C-1c), 103.1 (C-1b or C-1c), 170.5 (C=O), 170.7 (C=O).

Anal. Calc. for $C_{89}H_{98}O_{19}Si \cdot H_2O$: C, 70.42; H, 6.51. Found: C, 70.61; H, 6.62.

Alternative preparation of **15** *and* **17**. — Reaction of **4** (145 mg, 0.29 mmol) and **14** (230 mg, 0.22) with $SnCl_2$ (112 mg, 0.59 mmol), $AgClO_4$ (122 mg, 0.59 mmol), and powdered molecular sieve 4 Å (1 g) in dry ether (12 mL) was performed at $-10°$ to room temperature for 4 h. Column chromatography ($CHCl_3$–EtOAc, 95:5) of the product on silica gel (35 g) gave **15** (213 mg, 63.3%), R_F 0.58, and **17** (39 mg, 11.6%), R_F 0.46.

tert-*Butyldiphenylsilyl* O-(2,3,4-*tri*-O-*benzyl-α*-D-*galactopyranosyl*)-(1→4)-O-(2,3-*di*-O-*benzyl-α*-D-*galactopyranosyl*)-(1→4)-2,3-*di*-O-*benzyl-β*-D-*galactopyranoside* (**19**). — A mixture of **15** (200 mg, 0.13 mmol), tetrahydrofuran (0.5 mL), and methanolic 0.1M NaOMe (2 mL) was stirred at room temperature overnight, then neutralised with Amberlyst 15 (H^+) resin, and concentrated. Column chromatography of the residue on silica gel (25 g) with toluene–EtOAc (3:2) gave **19** (175 mg, 95.5%), $[\alpha]_D^{20}$ +47° (*c* 0.6). N.m.r. data: ^{1}H, δ 1.09 (s, 9 H, ^{t}Bu), 4.55 (d, 1 H, *J* 7.4 Hz, H-1a), 4.88 (d, 1 H, *J* 3.2 Hz, H-1b or H-1c), 4.91 (d, 1 H, *J* 3.2 Hz, H-1b or H-1c; ^{13}C, δ 19.2 (*C*Me$_3$), 27.1 [C(*C*H$_3$)$_3$], 98.3 (C-1a), 99.8 (C-1b or C-1c), 100.8 (C-1b or C-1c).

Anal. Calc. for $C_{83}H_{92}O_{16}Si$: C, 72.57; H, 6.75. Found: C, 72.59; H, 6.78.

tert-*Butyldiphenylsilyl* O-*(2,3,4-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2,3-di*-O-*benzyl-α*-D-*galactopyranosyl)-(1→4)-2,3-di*-O-*benzyl-β*-D-*galactopyranoside* (**24**). — Deacetylation of **17** (165 mg, 0.11 mmol), as described above, gave **24** (119 mg, 78.7%), $[\alpha]_D^{24}$ +45° (*c* 0.6). N.m.r. data: ^{1}H, δ 1.10 (s, 9 H, ^{t}Bu), 3.29 (dd, 1H, *J* 3.0 and 9.8 Hz, H-3a), 3.67 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-2a), 3.90 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2c), 4.58 (d, 1 H, *J* 7.3 Hz, H-1a), 4.70 (d, 1 H, *J* 7.6 Hz, H-1c), 4.88 (d, 1 H, *J* 3.1 Hz, H-1b); ^{13}C, δ 19.2 (CMe_3), 27.1 [$C(CH_3)_3$], 98.3 (C-1a), 100.1 (C-1b), 104.5 (C-1c).

Anal. Calc. for $C_{83}H_{92}O_{16}Si$: C, 72.57; H, 6.75. Found: C, 72.03; H, 6.76.

tert-*Butyldiphenylsilyl* O-*(2,3,4-tri*-O-*benzyl-α*-D-*galactopyranosyluronic acid)-(1→4)*-O-*(2,3-di*-O-*benzyl-α*-D-*galactopyranosyluronic acid)-(1→4)-2,3-di*-O-*benzyl-β*-D-*galactopyranosiduronic acid* (**21**). — To a solution of oxalyl chloride (116 μL, 1.33 mmol) in dry CH_2Cl_2 (3 mL) was added dry methyl sulfoxide (200 μL, 2.81 mmol) at −78° under Ar. After 15 min, a solution of **19** (123 mg, 0.09 mmol) in dry CH_2Cl_2 (2 mL) was added, stirring was continued for 30 min, *N,N*-di-isopropylethylamine (1 mL, 5.74 mmol) was added, and, after 5 min, the cooling bath was removed. The mixture was stirred for another 30 min, diluted with $CHCl_3$, washed successively with dil HCl, water, and brine, dried (Na_2SO_4), and concentrated to give the crude trialdehyde **20**, a solution of which in ^{t}BuOH (3.7 mL) and 2-methyl-2-butene (1.4 mL, 16.7 mmol) was stirred overnight with a solution of $NaClO_2$ (230 mg, 2.54 mmol) and NaH_2PO_4 (230 mg) in water (2.3 mL). The mixture was concentrated *in vacuo*, diluted with water, and extracted with hexane. Then the aqueous layer was acidified with M HCl and extracted with EtOAc. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (25 g) with $CHCl_3$–AcOH (97:3) gave **21** (109 mg, 86%), $[\alpha]_D^{20}$ +93° (*c* 0.3). N.m.r. data: ^{1}H, δ 1.17 (s, 9 H, ^{t}Bu), 3.25 (dd, 1 H, *J* 2.7 and 10.0 Hz, H-3a), 3.57 (dd, 1 H, *J* 7.3 and 10.0 Hz, H-2a), 4.59 (d, 1 H, *J* 7.3 Hz, H-1a), 5.08 (m, 2 H, H-1b,c); ^{13}C, δ 19.1 (CMe_3), 26.9 [$C(CH_3)_3$], 98.3, 98.7, 99.4 (C-1a,1b,1c), 167.8 (C=O), 169.0 (C=O).

Anal. Calc. for $C_{83}H_{86}O_{19}Si{\cdot}H_2O$: C, 69.54; H, 6.19. Found: C, 69.11; H, 6.07.

tert-*Butyldiphenylsilyl* O-*(2,3,4-tri*-O-*benzyl-β*-D-*galactopyranosyluronic acid)-(1→4)*-O-*(2,3-di*-O-*benzyl-α*-D-*galactopyranosyluronic acid)-(1→4)-2,3-di*-O-*benzyl-β*-D-*galactopyranosiduronic acid* (**26**). — Oxidation of **24** (96 mg, 0.07 mmol), as described for **21**, afforded **26** (79 mg, 79.9%), $[\alpha]_D^{24}$ +75° (*c* 1.1). N.m.r. data: ^{1}H, δ 1.10 (s, 9 H, ^{t}Bu), 3.29 (dd, 1 H, *J* 2.8 and 10.1 Hz, H-3a), 3.48 (dd, 1 H, *J* 3.1 and 9.8 Hz, H-3c), 3.64 (dd, 1 H, *J* 7.6 and 10.1 Hz, H-2a), 3.75 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2c), 4.61 (d, 1 H, *J* 7.6 Hz, H-1a or H-1c), 5.12 (d, 1 H, *J* 2.7 Hz, H-1b); ^{13}C, δ 19.1 (CMe_3), 26.9 [$C(CH_3)_3$], 98.3 (C-1a), 99.3 (C-1b), 103.1 (C-1c), 167.6 (C=O), 169.2 (C=O).

O-*(Methyl 2,3,4-tri*-O-*benzyl-α*-D-*galactopyranosyluronate)-(1→4)*-O-*(methyl 2,3-di*-O-*benzyl-α*-D-*galactopyranosyluronate)-(1→4)-[methyl* (tert-*butyldiphenylsilyl 2,3-di*-O-*benzyl-β*-D-*galactopyranosid)uronate]* (**22**). — A solution of **21** (45 mg, 0.03 mmol) in EtOAc (1 mL) was treated with a large excess of fresh ethereal diazomethane, then concentrated. Column chromatography of the residue on silica gel (5 g) with hexane–EtOAc (7:3) gave **22** (39 mg, 84.2%), $[\alpha]_D^{25}$ +66° (*c* 0.8). N.m.r. data: ^{1}H, δ 1.17

(s, 9 H, ^{t}Bu), 3.26 (s, 3 H, OMe), 3.38 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.63 (dd, 1 H, *J* 7.6 and 10.1 Hz, H-2a), 3.78 (dd, 1 H, *J* 2.7 and 10.1 Hz, H-3a), 4.50 (d, 1 H, *J* 7.6 Hz, H-1a), 5.05 (d, 1 H, *J* 3.4 Hz, H-1b or H-1c), 5.28 (d, 1 H, *J* 3.4 Hz, H-1b or H-1c); ^{13}C, δ 19.3 (CMe_3), 27.1 [$C(CH_3)_3$], 51.7 (OCH_3), 51.8 (OCH_3), 51.9 (OCH_3), 98.1 (C-1a), 98.8, 99.5 (C-1b, C-1c), 168.1 (C=O), 168.8 (C=O), 169.5 (C=O).

Anal. Calc. for $C_{86}H_{92}O_{19}Si \cdot H_2O$: C, 69.99; H, 6.42. Found: C, 69.61; H, 6.48.

O-*(Methyl 2,3,4-tri*-O-*benzyl-β*-D-*galactopyranosyluronate)-(1→4)*-O-*(methyl 2,3-di*-O-*benzyl-α*-D-*galactopyranosyluronate)-(1→4)*-[*methyl* (tert-*butyldiphenylsilyl 2,3-di*-O-*benzyl-β*-D-*galactopyranosid)uronate*] (**27**). — Esterification of **26** (62 mg, 0.045 mmol) with ethereal diazomethane followed by column chromatography, as described for **22**, afforded **27** (45 mg, 70.5%), $[\alpha]_D^{25}$ +73° (*c* 0.6). N.m.r. data: ^{1}H, δ 1.16 (s, 9 H, ^{t}Bu), 3.23 (s, 3 H, OMe), 3.33 (dd, 1 H, *J* 2.7 and 9.8 Hz, H-3a or H-3c), 3.43 (dd, 1 H, *J* 3.1 and 9.8 Hz, H-3a or H-3c), 3.53 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.69 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-2a or H-2c), 3.70 (dd, 1 H, *J* 7.6 and 9.8 Hz, H-2a or H-2c), 3.96 (dd, 1 H, *J* 3.4 and 10.1 Hz, H-2b), 4.09 (dd, 1 H, *J* 2.8 and 10.1 Hz, H-3b), 5.33 (d, 1 H, *J* 3.4 Hz, H-1b); ^{13}C, δ 19.4 (CMe_3), 27.1 [$C(CH_3)_3$], 51.8 (OCH_3), 51.9 (OCH_3), 52.3 (OCH_3), 98.1 (C-1a), 99.3 (C-1b), 102.1 (C-1c), 168.1 (C=O), 168.4 (C=O), 168.8 (C=O).

Anal. Calc. for $C_{86}H_{92}O_{19}Si$: C, 70.86; H, 6.36. Found: C, 70.60; H, 6.36.

Regeneration of **21** *from* **22**. — A mixture of **22** (13.5 mg, 9.3 μmol) and anhydrous LiI (36 mg, 0.27 mmol) in dry pyridine (3.5 mL) was heated under reflux under argon for 7 h, then concentrated *in vacuo*. A solution of the residue in water was acidified with dil. HCl and extracted with EtOAc, and the extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. Preparative t.l.c. ($CHCl_3$–AcOH, 97:3) of the residue gave a fraction which was dissolved in EtOAc, and the solution was washed with dil HCl, water, and brine, dried (Na_2SO_4), and concentrated to give **21** (9 mg, 69%).

Regeneration of **26** *from* **27**. — As described above, a mixture of **27** (29 mg, 19.9 μmol) and LiI (75 mg, 0.56 mmol) in dry pyridine (7.5 mL) was heated for 7 h. Preparative t.l.c. of the crude product afforded **26** (16 mg, 57%) and **29** (5 mg) as a less polar material. Compound **29**, ^{1}H-n.m.r. data: δ 1.08 (s, 9 H, ^{t}Bu), 3.73 (s, 3 H, OMe), 3.78 (bt, 1 H, H-2), 4.09 (bt, 1 H, H-3), 4.57 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.59 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.62 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.69 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 5.29 (d, 1 H, *J* 5.2 Hz, H-1), 6.19 (d, 1 H, *J* 3.7 Hz, H-4).

O-*(2,3,4-Tri*-O-*benzyl-α*-D-*galactopyranosyluronic acid)-(1→4)*-O-*(2,3-di*-O-*benzyl-α*-D-*galactopyranosyluronic acid)-(1→4)-(2,3-di*-O-*benzyl*-D-*galactopyranuronic acid* (**23**). — A mixture of **21** (21 mg, 14.8 μmol), AcOH (15 μL, 0.26 mmol), and M tetrabutylammonium fluoride/tetrahydrofuran (150 μL, 0.15 mmol) in dry tetrahydrofuran (1.2 mL) was stirred at room temperature for 4 days, then diluted with water (15 mL), acidified with dil. HCl, and extracted with EtOAc. The extract was washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. T.l.c. ($CHCl_3$–MeOH–AcOH 18:1:1) of the residue gave a fraction which was dissolved in EtOAc, and the solution was washed with dil. HCl, water, and brine, dried (Na_2SO_4), and concentrated to give **23** (15 mg, 86%).

Anal. Calc. for $C_{67}H_{68}O_{19}\cdot H_2O$: C, 67.33; H, 5.90. Found: C, 67.61; H, 5.98.

O-(*2,3,4-Tri*-O-*benzyl*-β-D-*galactopyranosyluronic acid*)-(*1→4*)-O-(*2,3-di*-O-*benzyl*-α-D-*galactopyranosyluronic acid*)-(*1→4*)-*2,3-di*-O-*benzyl*-D-*galactopyranuronic acid* (**28**). — Desilylation of **26** (15 mg, 10.6 μmol), as described above for **23**, gave **28** (11 mg, 88.2%).

Anal. Calc. for $C_{67}H_{68}O_{19}\cdot H_2O$: C, 67.33; H, 5.90. Found: C, 67.62; H, 5.86.

O-(α-D-*Galactopyranosyluronic acid*)-(*1→4*)-O-(α-D-*galactopyranosyluronic acid*)-(*1→4*)-D-*galactopyranuronic acid* (**1a**). — A solution of **23** (15 mg, 12.7 μmol) in aq. 80% MeOH (10 mL) was stirred with 10% Pd–C (10 mg) under hydrogen at room temperature for 3 days, then filtered through Celite, and concentrated *in vacuo*. Short-column (2 mL) chromatography of the residue on Sephadex LH-20 with 50% aq. MeOH removed traces of impurities. Further purification was effected by anion-exchange chromatography on Mono-Q (HR 5/5), using a linear NH_4HCO_3 gradient (0.2→0.4M)[1]. Fractions were assayed for uronosyl residue by the *m*-hydroxybiphenyl method[17] (*A* at 520 nm). The fractions having a maximal content of **1a** were combined and concentrated *in vacuo* at 70°. Water was distilled several times from the residue to leave **1a** (4.7 mg). ^{1}H-N.m.r. data [D_2O, internal ^{t}BuOH (δ 1.23), 80°]; δ 3.49 (dd, *J* 7.6, 9.8 Hz, H-2aβ), 3.60–3.85 (m, H-2aα,2b,2c, H-3aβ), 3.90 (dd, *J* 3.4, 10.1 Hz, H-3), 3.97–4.01 (m), 4.05 (s, H-5aβ), 4.29 (bs, H-4c), 4.38 (bs, H-5aα), 4.43 (bs, H-4aβ), 4.44 (bs, H-4b), 4.58 (d, *J* 7.6 Hz, H-1aβ), 4.70 (m, H-5b), 4.71 (bs, H-5c), 5.10 (bs, H-1b or H-1c), 5.13 (bs, H-1b or H-1c), 5.31 (bs, H-1aα).

Anal. Calc. for $C_{18}H_{26}O_{19}\cdot 0.5H_2O$: C, 38.94; H, 4.90. Found: C, 38.91; H, 4.83.

O-(β-D-*Galactopyranosyluronic acid*)-(*1→4*)-O-(α-D-*galactopyranosyluronic acid*)-(*1→4*)-D-*galactopyranuronic acid* (**3**). — Hydrogenolysis of **28** (10 mg, 8.5 μmol) with 10% Pd/C (7 mg) in 80% MeOH (7 mL), as described above for **1a**, followed by anion-exchange chromatography (Mono-Q) afforded **3** (4.5 mg). ^{1}H-N.m.r. data (D_2O, 60°): δ 3.49 (dd, *J* 7.6 and 10.1 Hz, H-2aβ), 3.55 (bt, 1 H, H-2c), 3.67 (dd, 1 H, *J* 3.4 and 9.8 Hz, H-3c), 3.74 (dd, *J* 3.1 and 10.1 Hz, H-3aβ), 3.82 (dd, *J* 3.7 and 10.7 Hz, H-2aα), 4.05 (bs, H-5aβ), 4.59 (d, *J* 7.6 Hz, H-1aβ), 4.70 (d, 1 H, *J* 7.6 Hz, H-1c), 4.79 (m, 1 H, H-5b), 5.13 (d, 1 H, *J* 2.8 Hz, H-1b), 5.31 (d, *J* 3.7 Hz, H-1aα).

Anal. Calc. for $C_{18}H_{26}O_{19}$: C, 39.57; H, 4.80. Found: C, 39.25; H, 5.05.

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