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# SUGAR ORTHO ESTERS

## PART VIII[1]. SYNTHESIS OF 4-*O*-METHYL-D-GLUCURONIC ACID DERIVATIVES

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ABSTRACT

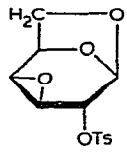
1,6:3,4-Dianhydro-2-*O*-tosyl-β-D-galactopyranose was converted into the triacetate of methyl 4-*O*-methyl-D-glucuronate *via* 1,6:2,3-dianhydro-4-*O*-methyl-β-D-mannopyranose and 4-*O*-methyl-D-glucose. The 1,2-(methyl orthoacetate) of methyl 3-*O*-acetyl-4-*O*-methyl-D-glucuronate was prepared and used for the glycosylation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose. The aldobiouronic acid derivative thus obtained was converted into the known amide of methyl 6-*O*-(4-*O*-methyl-β-D-glucopyranosyluronic acid)-α-D-galactopyranoside.

## INTRODUCTION

4-*O*-Methyl-D-glucuronic acid occurs in plant polysaccharides[2]. Partial, acid hydrolysis of such polymers gives, typically[3], oligosaccharides containing 4-*O*-methyl-D-glucuronic acid at the non-reducing end. There are no examples of glycosidation (other than with lower alcohols) or convenient synthesis of 4-*O*-methyl-D-glucuronic acid. The available synthesis[4] and the isolation from plant sources[5] are not amenable to large-scale preparation. We now describe the synthesis of a series of derivatives of 4-*O*-methyl-D-glucuronic acid, including the ortho ester which has been used for the synthesis of an aldobiouronic acid.

## RESULTS AND DISCUSSION

The starting material, 1,6:2,3-dianhydro-4-*O*-methyl-β-D-mannopyranose (**3**), was prepared from 1,6:3,4-dianhydro-2-*O*-tosyl-β-D-galactopyranose[6] (**1**) *via* 1,6-anhydro-4-*O*-methyl-2-*O*-tosyl-β-D-glucopyranose (**2**) by the known reaction sequence[7], but with improvements at both stages. Conditions were found for the alkali-catalyzed cleavage of the epoxide ring of **3** which gave 1,6-anhydro-4-*O*-methyl-β-D-glucopyranose (**4**) in nearly quantitative yield. The anhydride **4** was characterized as the known[8] dibenzoate **5** and the diacetate **6**. Acid-catalysed hydrolysis of **4** afforded 4-*O*-methyl-D-glucose (**7**) in high yield. The physical constants of **7**, as well as those of its crystalline acetate **8**, were in agreement with the literature data[5,9].

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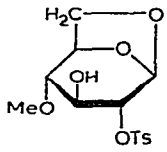


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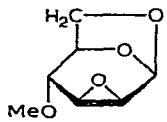


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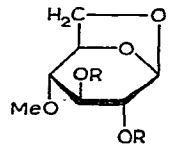


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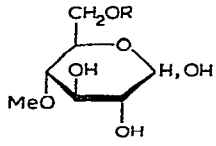
5 R = Bz
6 R = Ac

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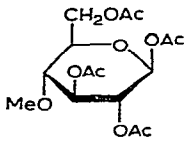


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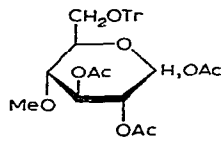


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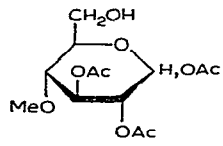
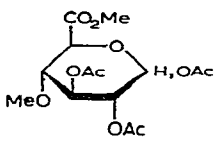


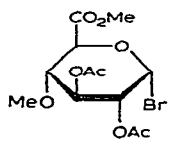

11
11a β anomer

Tritylation of **7** gave the 6-trityl ether **9** which, with acetic anhydride–pyridine, afforded an anomeric mixture of acetates **10**. Detritylation of **10** with hydrogen bromide in glacial acetic acid gave the triacetate **11** (as an anomeric mixture). Two stages of this sequence (**7**→**9** and **10**→**11**) were accompanied by side reactions and gave relatively low yields of the products (46.5 and 44%, respectively).

Surprisingly, all attempts to convert the diacetate **6** directly into the β-triacetate **11a** by successive treatment with titanium tetrachloride and mercury(II) acetate failed (*cf.* refs. 10–12). Instead, the tetra-acetate of 4-*O*-methyl-D-glucose was formed in moderate yield.




12

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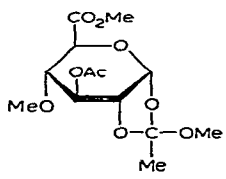


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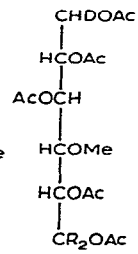
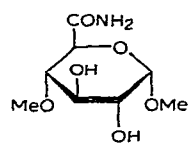



15a R = H
15b R = D




16

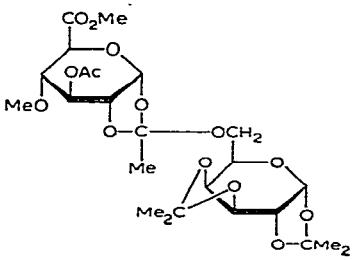
Oxidation of the triacetate **11** with potassium permanganate in acetic acid, followed by methylation with diazomethane, gave methyl 1,2,3-tri-*O*-acetyl-4-*O*-methyl-D-glucuronate (**12**). Treatment of **12** with hydrogen bromide in acetic acid gave **13**, which condensed with methanol under conditions used for the preparation of sugar 1,2-(ortho esters) from 1,2-*cis*-acylglycosyl bromides[13–15]. Methyl 3-*O*-acetyl-4-*O*-methyl-D-glucuronate 1,2-(methyl orthoacetate) (**14**) was thus obtained in good yield. The structures of the compounds synthesized were confirmed as follows.

Reduction of the triacetate **11** and of the methyl ester **12** with sodium boro-

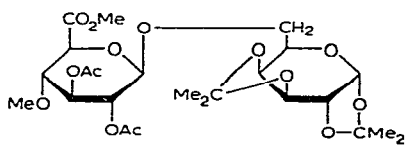
deuteride, followed by acetylation, gave the D-glucitol derivatives **15a** and **15b**, respectively. The mass-spectral data for these compounds were in good agreement with those described for acetates of 4-*O*-(3-*O*-)methylhexitols[16]. In both spectra, the peaks of ions containing C-1 were shifted by one mass unit; in the spectrum of **15b**, the peaks of ions containing C-6 were shifted by two mass units. These data prove both the position of the OMe group (at C-4) and the structure **12** as the derivative of 4-*O*-methylhexuronic acid. In addition, the triacetate **12** was converted into the known[17] crystalline amide of methyl 4-*O*-methyl-α-D-glucopyranosiduronic acid (**16**) by the application in sequence of deacetylation, acidic methanolysis, and ammonolysis.

Compound **14** was completely hydrolysable under conditions characteristic for sugar ortho esters[14,15]. The p.m.r. spectrum of **14** contained, *inter alia*, signals for the C-Me ($\delta$ 1.65) and O-Me ($\delta$ 3.15) groups of the orthoacetate, and for OAc ($\delta$ 2.01), OMe-4 ($\delta$ 3.38), and $CO_2Me$ ($\delta$ 3.70). On the basis of the chemical shift of the C-Me group, the compound is believed to be essentially the O-Me-*exo*-(C-Me-*endo*-)-isomer (*cf.* refs. 15 and 18). The $J_{1,2}$ value (5 Hz) of the ortho ester **14** is in agreement with the typical value for 1,2-(ortho esters) of gluco-, galacto-, and xylopyranoses[15,18–20].

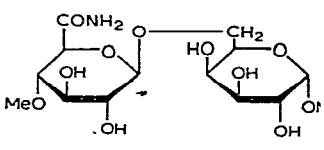
The reactivity of the ortho ester **14** as a glycosylating reagent was studied by using 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose and the two-stage glycosylation technique[21] involving nitromethane–mercury(II) bromide[14]. At a low concentration of the catalyst (re-esterification conditions[15,21]), the ortho ester intermediate **17** was the main product. Under the conditions of glycosylation[15] [*i.e.* with a relatively high concentration of mercury(II) bromide], **17** was converted into the disaccharide derivative **18** (43%). Each stage of this synthesis proceeded more slowly than in the corresponding reactions of the ortho esters of neutral aldoses[14,15] and of D-glucuronic acid[22].




17




18




19

The structure of the synthetic disaccharide was proved as follows. The specific rotation (−69.5°) of **18** is closely similar to that (−64°) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(2,3,4-tri-*O*-acetyl-β-D-glucopyranosyluronic acid)-α-D-galactopyranose methyl ester[22]. The specific rotation of disaccharides containing a 4-*O*-methyl-D-glucuronic acid residue are very close to those of the analogues containing D-glucuronic acid[3]. Calculation of the rotation for **18**, using the Klyne rule, was not possible because

the data for corresponding lower glycosides were not available. The p.m.r. spectrum of **18** contained, *inter alia*, signals for the Me groups of the isopropylidene residues ($\delta$ 1.18, 1.29, and 1.37), acetyl groups ($\delta$ 1.91 and 1.88), and ether and ester groups ($\delta$ 3.28 and 3.65, respectively). Compound **18** was characterized as the known[23] crystalline amide **19**, which was obtained by application in sequence of deacetylation, acid-catalyzed methanolysis, and ammonolysis.

## EXPERIMENTAL

The solvents for the operations with the ortho ester were purified as previously described[21]. T.l.c. was performed on silica gel plates, using chloroform–acetone mixtures: *A* 95:5, *B* 1:1. P.c. was performed on "Leningradskaya S" paper, using 1-butanol–pyridine–water (6:4:3). Neutral alumina (Brockmann III) was used for column chromatography. Evaporation of solvents was performed *in vacuo* at 40°. M.p.s. were determined with a Kofler apparatus. Specific rotations were determined with a Perkin–Elmer 141 polarimeter. P.m.r. spectra were recorded at 60 MHz with HMDS as internal standard, with a Varian D-A60-IL spectrometer. Mass spectra were recorded with a Varian CH-6 MAT instrument.

*1,6-Anhydro-4-*O*-methyl-2-*O*-tosyl-β-*D*-glucopyranose* (**2**). — To a solution of **1**[6] (50 g, 168 mmoles) in dry benzene (80 ml), a freshly prepared solution of conc. sulphuric acid (8 ml, 150 mmoles) in dry methanol (50 ml) was added and the mixture was boiled under reflux for 4.5 h (homogeneous solution formed in 0.5 h). The solution was then diluted with benzene (100 ml), washed with water (4 × 50 ml) until neutral, filtered through cotton wool, and evaporated. The residue was crystallized from chloroform–carbon tetrachloride (1:4, 250 ml) at −78°, and the product (42 g) thus obtained was recrystallized from aqueous ethanol to yield **2** (38.9 g, 70%), m.p. 87–89°, $[\alpha]_D$ −41° (*c* 1.1, chloroform); lit.[7] m.p. 89–90°, $[\alpha]_D$ −43.6°.

*1,6:2,3-Dianhydro-4-*O*-methyl-β-*D*-mannopyranose* (**3**). — To a stirred solution of **2** (35 g, 106 mmoles) in chloroform (200 ml), methanolic sodium methoxide (218 mmoles, prepared from 5 g of sodium and 100 ml of methanol) was added slowly. After 2 h at room temperature, the mixture was filtered, diluted with chloroform (200 ml), washed with water (5 × 20 ml), filtered through cotton wool, and evaporated. Crystallization of the residue from methanol (−78°) gave **3** (14.2 g, 85%), m.p. 56–58°, $[\alpha]_D$ −48° (*c* 1.2, methanol), lit.[7] m.p. 52–58°, $[\alpha]_D$ −40.2°.

*1,6-Anhydro-4-*O*-methyl-β-*D*-glucopyranose* (**4**). — M Potassium hydroxide (200 ml) was added to **3** (20 g, 126 mmoles) and the mixture was boiled under reflux for 12 h. The cooled mixture was washed with chloroform (3 × 100 ml), and the aqueous layer was neutralized with QU-2($H^+$) resin. The resin was washed with methanol (5 × 100 ml), and the combined aqueous and methanolic solutions were evaporated to dryness. The residue crystallized on drying *in vacuo* to give **4** (20.5 g, 92%), m.p. 61–66°, $[\alpha]_D$ −62° (*c* 3.19, acetone); lit.[8] m.p. 67–68°, $[\alpha]_D$ −65.4°.

The diacetate (**6**) of **4**, prepared conventionally using sodium acetate–acetic anhydride, had m.p. 39–41°, $[\alpha]_D$ −36.5° (*c* 1.2, chloroform) (Found: C, 50.55;

H, 6.24. $C_{11}H_{16}O_7$ calc.: C, 50.78; H, 6.16%). P.m.r. data ($CCl_4$): $\delta$ 2.08 (*s*, 3H, OAc), 2.12 (*s*, 3H, OAc), 3.48 (*s*, 3H, 4-OMe), 5.33 (*s*, 1H, H-1).

The dibenzoate **5** had m.p. 110°, $[\alpha]_D$ +92° (*c* 1.48, chloroform); lit.[8] m.p. 110–112°, $[\alpha]_D$ +92°.

*4-O-Methyl-D-glucose* (**7**). — A solution of **4** (23.8 g, 135 mmoles) in M sulphuric acid (320 ml) was boiled under reflux for 4 h, then cooled, washed with chloroform (3 × 100 ml), and neutralized with IRA-410($HCO_3^-$) resin. The resin was washed with methanol (5 × 100 ml), and the combined aqueous and methanolic solutions were evaporated to give **7** as a chromatographically homogeneous (p.c.) syrup (24 g, 91%), $[\alpha]_D$ +59° (*c* 1.05, equil., water); lit.[9] $[\alpha]_D$ +58.4° (equil., water) (Found: C, 43.53; H, 7.33. $C_7H_{14}O_6$ calc.: C, 43.29; H, 7.22%).

The $\beta$-tetra-acetate (**8**) of **7**, prepared conventionally with sodium acetate–acetic anhydride, had m.p. 104° (from ethanol), $[\alpha]_D$ −9.4° (*c* 1.58, chloroform); lit.[9] m.p. 103–104°, $[\alpha]_D$ −10.2°. P.m.r. data ($CDCl_3$): $\delta$ 1.90–2.20 (*m*, 12H, 4OAc), 3.20 (*s*, 3H, 4-OMe), 5.65 (*d*, 1H, H-1, $J_{1,2}$ 8.0 Hz).

*1,2,3-Tri-O-acetyl-4-O-methyl-D-glucopyranose* (**11**). — A solution of dry **7** (18 g, 93 mmoles) in freshly distilled, dry pyridine (150 ml) was treated with chlorotriphenylmethane (30 g, 104 mmoles). After 3 days at room temperature, the solution was poured into water, and the mixture was extracted with chloroform (3 × 100 ml). The combined extracts were evaporated and the residue, containing compounds with $R_F$ 0.06, 0.38, 0.57, and 0.81 (solvent *B*), was eluted from a column (4 cm, area 80 $cm^2$) of alumina, using a gradient of solvents carbon tetrachloride–chloroform–methanol–water, to give the 6-trityl ether **9** ($R_F$ 0.38; 19 g, 46.5%), $[\alpha]_D$ +27.5° (*c* 0.9, chloroform). A solution of **9** (19 g) in pyridine (70 ml) was treated with acetic anhydride (50 ml, 530 mmoles) at room temperature for 3 days. The mixture was then poured into water and extracted with chloroform (2 × 200 ml), and the combined extracts were washed with water, saturated, aqueous sodium hydrogen carbonate, and water, and evaporated to yield chromatographically homogeneous (solvent *A*) triacetate **10** (24.5 g, $[\alpha]_D$ +56° (*c* 0.84, chloroform),

A solution of **10** (24 g, 43 mmoles) in glacial acetic acid (125 ml) was treated with a 30% solution of hydrogen bromide in glacial acetic acid (15 ml). After 2 min at room temperature, the mixture was quickly filtered into ice–water, insoluble material (TrOH) was washed with ice–water, and the combined filtrate and washings were extracted with chloroform. The extracts were washed with saturated, aqueous sodium hydrogen carbonate and evaporated. The residue, which contained compounds with $R_F$ 0.17, 0.48, and 0.70 (solvent *A*), was eluted from a column (23 × 2 cm) of silica gel, using the solvent carbon tetrachloride–chloroform–acetone, to give **11** ($R_F$ 0.17; 6 g, 43.8% from **10**), $[\alpha]_D$ −48° (*c* 2.06, chloroform) (Found: C, 48.74; H, 6.26. $C_{13}H_{20}O_9$ calc.: C, 48.79; H, 6.55%).

*Methyl 1,2,3-tri-O-acetyl-4-O-methyl-D-glucopyranuronate* (**12**). — To a solution of **11** (3 g, 9.4 mmoles) in acetic acid (60 ml), finely powdered potassium permanganate (4.5 g, 28 mmoles) was added and the mixture was stirred for 20 h at room temperature. The mixture was then diluted with chloroform (80 ml), and oxalic

acid dihydrate (20 g) suspended in water (20 ml) was added. The mixture was stirred until colourless (2–3 h), the organic layer was separated, and the aqueous layer was extracted with chloroform (3 × 20 ml). The combined chloroform solutions were evaporated to give a residue (2.0 g) which contained two components with $R_F$ (solvent *B*) 0.45 (minor) and 0.05 (uronic acid, major component). The latter was isolated by elution from a column (17 × 1 cm) of silica gel, using the solvent gradient chloroform–methanol. To the combined fractions containing chromatographically homogeneous uronic acid derivative, excess of an ethereal solution of diazomethane was added. After 30 min at room temperature, the yellow solution was evaporated and the residue was eluted from a column (15 × 1 cm) of silica gel, using the solvent gradient carbon tetrachloride–chloroform–acetone, to give **12** (1.40 g, 43%), $[\alpha]_D$ +42.5° (*c* 0.8, chloroform), $R_F$ 0.53 (solvent *A*) (Found: C, 48.28; H, 5.89. $C_{14}H_{20}O_{10}$ calc.: C, 48.27; H, 5.75%). P.m.r. data ($CDCl_3$): $\delta$ 1.90–2.20 (*m*, 9H, 3OAc), 3.40 (*s*, 3H, 4-OMe), 3.75 (*s*, 3H, $CO_2Me$), 5.70 (*d*, 0.45H, $\alpha$H-1, $J_{1,2}$ 7.5 Hz), 6.20 (*d*, 0.55H, $\beta$H-1, $J_{1,2}$ 3.5 Hz).

*Methyl 4-*O*-methyl-*α*-*D*-glucopyranosiduronamide* (**16**). — A solution of **12** (0.5 g, 1.44 mmole) in methanol (5 ml) and M methanolic sodium methoxide (0.1 ml) was stored for 4 h at room temperature, then neutralized with QU-2($H^+$) resin, and evaporated. A solution of the residue in 4% methanolic hydrogen chloride (25 ml) was boiled under reflux for 6 h, then neutralized with IRA-410($HCO_3^-$) resin, and evaporated. Saturated, methanolic ammonia (20 ml) was added to the residue and, after 2 days at room temperature, the mixture was evaporated to yield an anomeric mixture of glycosides (100 mg, 33%). Three recrystallizations from methanol gave **16** (30 mg), m.p. 234°, $[\alpha]_D$ +136° (*c* 0.8, water); lit.[17] m.p. 236°, $[\alpha]_D$ +150°.

*1,2,3,5,6-Penta-*O*-acetyl-4-*O*-methyl-*D*-glucitol*-1-d (**15a**) *and* 1,6,6-$d_3$ (**15b**). — To a solution of **11** (10 mg) in methanol (5 ml), sodium borodeuteride (10 mg) was added. After 2 h at room temperature, acetic acid (1 ml) was added, the mixture was evaporated to dryness, and methanol (3 × 3 ml) was distilled from the residue, which was then dried *in vacuo*, dissolved in a mixture of pyridine (1 ml) and acetic anhydride (0.5 ml), and stored overnight. The solution was diluted with chloroform, washed with water, saturated, aqueous hydrogen carbonate, and water, and evaporated, and the residue was dried *in vacuo* to give **15a** (5 mg). The mass spectrum showed, *inter alia*, the following peaks: *m/e* 262 (28%), 202 (10), 189 (68), 129 (100), 71 (70).

When the triacetate **12** (5 mg) was reduced, as described above, **15b** (3 mg) was obtained, the mass spectrum of which showed peaks, *inter alia*, at *m/e* 262 (34%), 202 (9), 191 (58), 131 (90), 71 (100).

*Methyl 3-*O*-acetyl-4-*O*-methyl-*α*-*D*-glucuronate 1,2-(methyl orthoacetate)* (**14**). — To **12** (1 g, 4.0 mmoles), a 30% solution of hydrogen bromide in glacial acetic acid (13 ml) was added and the mixture was stored at room temperature for 4 h. The mixture was then diluted with toluene and evaporated, and toluene was evaporated from the residue, which was then dried *in vacuo* to give syrupy **13** (1.4 g), $[\alpha]_D$ +158° (*c* 2.4, chloroform).

To a solution of **13** in nitromethane (12 ml), a mixture of methanol (1.84 ml,

45 mmoles) and 2,4,6-trimethylpyridine (0.6 ml, 4.5 mmoles) was added, and the solution was kept at 35° until reaction was complete (t.l.c. monitoring, solvent *A*) in ~3 days. The solution was diluted with ether (100 ml), washed successively with water, M silver nitrate (4 ml), saturated, aqueous sodium chloride, and water. The organic layer was then evaporated and the residue, which contained **14** ($R_F$ 0.60, solvent *A*) with a contaminant ($R_F$ 0.15), was eluted from a column (17 × 2 cm) of florisil, using the solvent gradient carbon tetrachloride–chloroform–acetone to give **14** (0.8 g, 62%), $[\alpha]_D$ +1.45° (*c* 2.2, chloroform) (Found: C, 49.16; H, 6.34. $C_{13}H_{20}O_9$ calc.: C, 48.74; H, 6.26%). The compound was completely hydrolysable under the conditions of the hydrolytic test for sugar ortho esters[14]. P.m.r. data ($CDCl_3$): $\delta$ 1.65 (*s*, 3H, *endo*-C-Me), 2.01 (*s*, 3H, OAc), 3.15 (*s*, 3H, *exo*-O-Me), 3.38 (*s*, 3H, 4-OMe), 3.70 (*s*, 3H, $CO_2Me$), 5.58 (*d*, 1H, H-1, $J_{1,2}$ 5.0 Hz).

*1,2:3,4-Di-O-isopropylidene-6-O-(methyl 2,3-di-O-acetyl-4-O-methyl-β-D-glucopyranosyluronate)-α-D-galactopyranose* (**18**). — A solution of **14** (190 mg, 0.60 mmole) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (155 mg, 0.60 mmole) in nitromethane (30 ml) was distilled at atmosphetic pressure. When 15 ml of solvent had distilled, mercury(II) bromide (1.5 mg, 4.2 μmoles) was added, and the mixture was distilled with simultaneous addition of fresh solvent to maintain a constant volume (15 ml). After 8 h, the re-esterification was nearly complete (t.l.c., hydrolytic test data[14]). More mercury(II) bromide (10 mg, 28 μmoles) was then added, and the solution was boiled under reflux for 10 h, then diluted with benzene (100 ml), washed with water, and evaporated. The residue was dissolved in a mixture of acetone and 0.05M sulphuric acid (0.5 ml). After 1 h at room temperature, the solution was neutralized with IRA-410($HCO_3^-$) resin and evaporated, and the residue was eluted from a column (15 cm, area 0.51 $cm^2$) of alumina, using a solvent gradient carbon tetrachloride–chloroform–acetone, to give **18** (140 mg, 43%), $[\alpha]_D$ −69.5° (*c* 1.08, chloroform) (Found: C, 52.05; H, 6.29. $C_{24}H_{36}O_{14}$ calc.: C, 52.50; H, 6.56%). P.m.r. data ($CCl_4$): $\delta$ 1.18, 1.29, 1.37 (3*s*, ratio 2:1:1, 12H, 4 isopropylidene C-Me); 1.88, 1.91 (2*s*, 6H, 2OAc); 3.28 (*s*, 3H, 4-OMe); 3.65 (*s*, 3H, $CO_2Me$); 5.33 (*d*, 1H, H-1, $J_{1,2}$ 5.0 Hz).

*Methyl 6-O-(4-O-methyl-β-D-glucopyranosyluronamide)-α-D-galactopyranoside* (**19**). — A solution of **18** (140 mg, 0.24 mmole) in methanol (5 ml) and M methanolic sodium methoxide (0.1 ml) was stored for 3 h at room temperature, then neutralized with QU-2($H^+$) resin, and evaporated. A solution of the product (100 mg) in 4% methanolic hydrogen chloride (15 ml) was left for 5 days at room temperature, then neutralized with IRA-410($HCO_3^-$) resin, and evaporated. Saturated, methanolic ammonia (20 ml) was added to the residue, and the mixture was kept in a sealed tube for 2 days at room temperature and then evaporated. Crystallisation of the residue from methanol–ether gave **19** (25 mg, 27%), m.p. 262–264°; lit.[23] m.p. 267°.

*The reaction of 2,3-di-O-acetyl-1,6-anhydro-4-O-methyl-β-D-glucopyranose with titanium tetrachloride.* — A solution of **6** (2.2 g, 8.5 mmoles) in chloroform (20 ml, purified as previously described[11]) was treated with acetic acid (0.14 ml) and titanium tetrachloride (2 ml, 18.5 mmoles). The yellow mixture was boiled under reflux for

3 h, then diluted with chloroform (100 ml), washed with ice–water until neutral, filtered through cotton wool, and evaporated. A saturated solution of mercury(II) acetate in acetic acid (5 ml) was added to the residue (1.50 g) and the resulting solution was kept for 2 h at room temperature. The solution was then diluted with chloroform (50 ml), washed with water (4 × 15 ml), and evaporated. Crystallisation of the residue from aqueous ethanol yielded the tetra-acetate **8** (160 mg), m.p. and m.m.p. 104°. The mother liquors did not contain (t.l.c.) any triacetate.

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