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PARTIAL TOLUENE-*p*-SULPHONYLATION STUDIES OF METHYL 6-*O*-TRITYL-*β*-D-GALACTOFURANOSIDE

PART I. SYNTHESIS OF 2,5- AND 3,5-DIMETHYL ETHERS OF D-GALACTOSE*

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INTRODUCTION

Although the di-*O*-methyl derivatives of D-galactopyranose have been known for some time, little is known about the furanoid analogues. In 1960, Siddiqui and Adams described the isolation and characterization of 3,5-di-*O*-methyl-D-galactose[1] from a methylated polysaccharide of *Gibberella fujikuroi*. The present communication deals with the synthesis of 3,5-di-*O*-methyl-D-galactose and also of 2,5-di-*O*-methyl-D-galactose, which was hitherto undescribed. The paper also describes an alternative synthesis of 3-*O*-methyl- and 2,3-di-*O*-methyl-D-galactose.

RESULTS AND DISCUSSION

The sequence of reactions which led to these syntheses was as follows. Methyl-*β*-D-galactofuranoside was tritylated to yield the crystalline methyl 6-*O*-trityl-*β*-D-galactofuranoside. The trityl derivative was partially tosylated** to give a mixture of tosyl derivatives that were separated by chromatography on silica gel and designated compounds **1**, **2**, **3** and **4**, in the order of their increasing R_F values (t.l.c.). Fraction 1 was successively methylated, detosylated, detritylated, and hydrolyzed to yield a dimethyl ether, which, on demethylation, gave galactose. The paper-chromatographic and electrophoretic behaviour and specific optical rotation of the ether agreed with those of the known 2,3-di-*O*-methyl-D-galactose. The ether gave a crystalline aniline derivative, which had the same m.p. and $[\alpha]_D$ as 2,3-di-*O*-methyl-*N*-phenyl-D-galactosylamine. Compound **1**, therefore, was methyl 5-*O*-tosyl-6-*O*-trityl-*β*-D-galactofuranoside.

Compound **2**, when subjected to the above-mentioned procedures, provided a di-*O*-methyl sugar that had $[\alpha]_D^{29}$ −10.3° (water). On demethylation, it gave galactose, and was homogeneous in paper chromatography and paper electrophoresis. None of the di-*O*-methyl-D-galactopyranoses shows a negative rotation[2]; the $[\alpha]_D$ values for 2,3- and 3,5-dimethyl ethers of D-galactose, isolated in the present work, were +94° and −25.3°, respectively. The di-*O*-methylgalactose gave an R_G value (0.42) in solvent *A* that was much higher than is to be expected for the known di-*O*-methylgalacto-

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**Tosyl=toluene-*p*-sulphonyl.

pyranoses. The comparative R_G values for 2,3- and 3,5-di-*O*-methyl-D-galactose were 0.22 and 0.40, respectively. The low M_G value (0.23) of the di-*O*-methylgalactose in borate, compared to that (0.65) for 3,5-di-*O*-methylgalactose, suggested that position 2 was substituted. Oxidation of the di-*O*-methyl-D-galactose with bromine water afforded a syrupy lactone that showed a strong C=O absorption at 1785 cm^{-1} in its infrared spectrum, indicating[3] that it was a γ-lactone. The foregoing evidence indicates that the dimethyl ether was 2,5-di-*O*-methyl-D-galactose, and, hence, the partially tosylated compound **2** was methyl 3-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside. The sugar was characterized as the crystalline 2,5-di-*O*-methyl-D-galactonamide.

The partially tosylated compound **3**, on similar methylation, detosylation, detritylation, and hydrolysis, yielded a dimethyl ether that was identical with authentic 3,5-di-*O*-methyl-D-galactose in paper chromatography and paper electrophoresis. The $[\alpha]_D$ value for the free sugar and the $[\alpha]_D$ value and m.p. for the derived hexitol were the same as for authentic samples of 3,5-di-*O*-methyl-D-galactose and 3,5-di-*O*-methyl-D-galactitol. The partially tosylated compound **3**, therefore, was methyl 2-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside.

When detritylation was performed with dry hydrogen chloride in dry chloroform, slight cleavage of the glycosidic bond invariably occurred. In order to prepare pure samples of methyl 2,3-, 2,5-, and 3,5-di-*O*-methyl-β-D-galactofuranosides, detritylations were performed with 50% aqueous acetic acid, and the glycosides were obtained as clear syrups that were chromatographically homogeneous.

The fourth, partially tosylated, compound (**4**) was identified as methyl 2,5-di-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside as follows. Compound **4**, on methylation and detosylation, yielded a methylated, tritylated glycoside that was resolved by column chromatography on silica gel, giving two crystalline fractions (4A, 4B). Fraction 4A, on detritylation, afforded a mono-*O*-methylhexofuranoside, which, on hydrolysis, was converted into a mono-*O*-methyl sugar that was identified by comparison with an authentic sample of 3-*O*-methyl-D-galactose (paper chromatography, paper electrophoresis, $[\alpha]_D$, m.p., and mixed m.p.). A freshly detritylated sample of the faster-moving fraction (4B), on immediate hydrolysis, also appeared to give mainly 3-*O*-methylgalactose. However, a sample of the detritylated sugar that had been kept in a vacuum desiccator failed to give 3-*O*-methylgalactose on hydrolysis; instead, 3 spots were observed on paper chromatography, and a single, non-complexing spot in borate electrophoresis was detected. The fastest-moving spot in paper chromatography appeared to be a hydroxymethyl-2-furaldehyde derivative. On the basis of these observations (which suggested the presence of a hydrofuranol type of ring), and on the reported behavior of 3,6-anhydro derivatives of D-galactose[4-6] and D-glucose[7], and of 2,5-anhydro-L-arabinose[8], fraction 4B is provisionally identified as a methyl 2,5-anhydro-3-*O*-methyl-6-*O*-trityl-β-D-hexofuranoside.

EXPERIMENTAL

Analytical methods. — The organic phase of the following solvent systems (v/v)

was used for paper chromatography: (*A*) butanone, saturated with water containing 2% ammonia; (*B*) ethyl acetate–pyridine–water (8:2:1). Sugars, as their borate complexes, were separated by electrophoresis[9] in 0.2M buffer (pH 10) at 800 volts for 2–3 h. Whatman No. 1 paper was used for all paper-chromatographic work, and Whatman No. 3 MM for all electrophoretic separations. R_G values refer to rates of movement relative to that of 2,3,4,6-tetra-*O*-methyl-D-glucose. Thin-layer chromatography (t.l.c.) was performed on glass plates (20 × 20 × 0.37 cm) coated with a uniform layer (250 microns) of silica gel G[10], with detection by 5% sulphuric acid in ethanol. Reactions were monitored by t.l.c. on microscope slides coated with silica gel G. Column chromatography was performed on silica gel[11]. Reducing sugars were detected on paper chromatograms and electrophoretograms with aniline hydrogen phthalate[12]. (*A*), and non-reducing sugars (glycosides) with the naphthoresorcinol reagent[13] (*B*). Evaporations were carried out at 35° on a rotary film evaporator. Melting points are corrected, and rotations are equilibrium values.

Methyl 6-O-trityl-β-D-galactofuranoside. — Methyl β-D-galactofuranoside (2.5 g, m.p. 63–65°, $[\alpha]_D$ −108°)[14] was dissolved in dry pyridine (50 ml), and chlorotriphenylmethane (3.6 g) was added. After the solution had been kept for 48 h at room temperature, the product[15] was isolated as a syrup (5.3 g, 95%). Crystallization from cold isopropyl ether containing a few drops of ethanol gave methyl 6-*O*-trityl-β-D-galactofuranoside, m.p. 91–92.5°, $[\alpha]_D^{25}$ −46.3° (*c* 3.0, chloroform).

Anal. Calc. for $C_{26}H_{28}O_6 \cdot 0.5\ C_2H_5OH$: C, 70.57; H, 6.80. Found: C, 70.51; H, 6.50.

Tosylation of Methyl 6-O-trityl-β-D-galactofuranoside. — Methyl 6-*O*-trityl β-D-galactofuranoside (5.0 g) in dry pyridine (100 ml) was tosylated by the dropwise addition of a solution of tosyl chloride (3.0 g) in dry pyridine (20 ml) at 100° during 2 h. After a further period of 8 h at 100°, the solution was cooled to room temperature and poured into a mixture of ice and water. The product was extracted with chloroform (3 × 100 ml), and the combined extracts were washed successively with water, 10% cupric sulfate solution, and water, and finally dried over sodium sulfate. Removal of chloroform gave a syrup (5.3 g) that showed, in addition to the starting material (R_F 0.20), four products when examined by t.l.c. in chloroform–acetone (85:15). The syrupy material was fractionated by column chromatography on silica gel with the same solvent. The following Table summarizes the results.

Fraction No.[a]	*Yield (g)*	$[\alpha]_D^{25}$, *degrees* (c *2-4, chloroform*)	R_F	*Found (%)* C	H	S	*Formula*	*Calc. (%)* C	H	S
1	1.1	−36.8	0.34	66.76	5.87	5.36	$C_{33}H_{34}O_8S$	67.11	5.80	5.42
2	0.6	−27.2	0.58	66 85	6.37	5.03	$C_{33}H_{34}O_8S$	67.11	5.80	5.42
3	0.7	−42.2	0.72	66.36	5.55	5.15	$C_{33}H_{34}O_8S$	67.11	5.80	5.42
4	1.2	−29	0.86	64.30	5.64	8.24	$C_{40}H_{40}O_{10}S_2$	64.50	5.41	8.61

[a] **1**, Methyl 5-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside; **2**, Methyl 3-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside; **3**, Methyl 2-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside; **4**, Methyl 2,5-di-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside.

Methyl 2,3-di-O-methyl-5-O-tosyl-6-O-trityl-β-D-galactofuranoside. — Methyl 5-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (1.0 g) was methylated with methyl iodide (20 ml) and silver oxide (2 g). Filtration and evaporation gave a product that still contained some unmethylated material (t.l.c., chloroform–acetone, 15:1). A second methylation yielded a product (1.0 g, 95%) that was chromatographically pure and crystallized readily. Recrystallization from isopropyl ether gave the title compound, m.p. 106.5–107°, $[\alpha]_D^{25}$ −41.5° (*c* 3.3, chloroform).

Anal. Calc. for $C_{35}H_{38}O_8S$: C, 67.94; H, 6.19; S, 5.18; OCH_3, 15.05. Found: C, 67.51; H, 6.13; S, 5.14; OCH_3, 15.00.

Methyl 2,5-di-O-methyl-3-O-tosyl-6-O-trityl-β-D-galactofuranoside. — Methyl 3-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (0.5 g) was methylated as above, yielding the title compound as a homogeneous (t.l.c.) syrup (0.5 g, 95%), $[\alpha]_D^{27}$ −42.7° (*c* 3.0, chloroform).

Found: C, 67.66; H, 5.74; S, 5.03; OCH_3, 14.82.

Methyl 3,5-di-O-methyl-2-O-tosyl-6-O-trityl-β-D-galactofuranoside. — Fraction 3 (0.5 g), on similar methylation, yielded the title compound (0.5 g, 95%), which, after crystallization from isopropyl ether, had m.p. 135–136°, $[\alpha]_D^{26}$ −51.6° (*c* 2.0, chloroform).

Found: C, 67.58; H, 5.99; S, 5.01; OCH_3, 15.20.

Methyl 3-O-methyl-2,5-di-O-tosyl-6-O-trityl-β-D-galactofuranoside. — The title compound (1 g, 95%) was prepared from Fraction 4 (1 g) by methylation as above, and, after crystallization from isopropyl ether, had m.p. 134.5°, $[\alpha]_D^{27}$ −38.4° (*c* 2.6, chloroform).

Anal. Calc. for $C_{41}H_{42}O_{10}S_2$: C, 64.89; H, 5.58; S, 8.45; OCH_3, 8.18. Found: C, 64.60; H, 5.72; S, 8.12; OCH_3, 8.46.

Methyl 2,3-di-O-methyl-6-O-trityl-β-D-galactofuranoside. — Solutions of methyl 2,3-di-*O*-methyl-5-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (0.745 g) in benzene (10 ml) and sodium methoxide (from 1 g of sodium) in methanol (20 ml) were mixed and boiled for 7 h under reflux[16]. The mixture was cooled to room temperature, water (20 ml) was added, organic solvents were removed by aeration, and the suspension was extracted with chloroform (5 × 25 ml). The chloroform extract was dried with sodium sulfate, and the solution evaporated to a syrup (0.618 g). The product contained traces of two components besides the main product (t.l.c.), and these were removed by chromatography on a column of silica gel by using ethyl acetate–light petroleum (b.p. 65–110°) (30:70), giving the product as a homogeneous syrup (0.540 g, 96%), $[\alpha]_D^{29}$ −62.5° (*c* 2.3, chloroform).

Anal. Calc. for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94; OCH_3, 20.04. Found: C, 72.06; H, 7.19; OCH_3, 19.7.

Methyl 2,5-di-O-methyl-6-O-trityl-β-D-galactofuranoside. — Methyl 2,5-di-*O*-methyl-3-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (0.646 g) was similarly detosylated, isolated, and fractionated as above, to give a syrupy product (0.452 g, 93%), $[\alpha]_D^{29}$ −38.7° (*c* 2.57, chloroform).

Found: C, 72.13; H, 6.89; OCH_3, 19.56.

Methyl 3,5-di-O-methyl-6-O-trityl-β-D-galactofuranoside. — Methyl 3,5-di-*O*-methyl-2-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (0.271 g) on detosylation, isolation, and fractionation as above gave the title compound as a syrup (0.20 g, *ca.* 100%), $[\alpha]_D^{27}$ −51.6° (*c* 2.015, chloroform).

Found: C, 72.64; H, 7.21; OCH_3, 19.52.

Methyl 3-O-methyl-6-O-trityl-β-D-galactofuranoside and the corresponding 2,5-anhydro derivative. — Methyl 3-*O*-methyl-2,5-di-*O*-tosyl-6-*O*-trityl-β-D-galactofuranoside (0.827 g) was detosylated as above to yield a syrup (0.510 g) that showed two components (t.l.c.). The syrup was fractionated on a column of silica gel by using acetone–chloroform (1:15). The faster-moving component (0.36 g, 76%) crystallized on trituration with ether. Recrystallization from ether–light petroleum (b.p. 65–110°) gave a product provisionally identified as a methyl 2,5-anhydro-3-*O*-methyl-6-*O*-trityl-β-D-hexofuranoside, m.p. 112–113°, $[\alpha]_D^{28}$ −63.1° (*c* 3.04, chloroform).

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 75.02; H, 6.54.

The slower-moving fraction (0.101 g, 20%) crystallized on evaporation of the solvent. Recrystallization from isopropyl ether gave methyl 3-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside, m.p. 123–124°, $[\alpha]_D^{27}$ −46.1° (*c* 1.84, chloroform).

Anal. Calc. for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 72.24; H, 6.47.

2,3-Di-O-methyl-β-D-galactose. — Methyl 2,3-di-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside (0.510 g) was dissolved in dry chloroform (20 ml), and dry hydrogen chloride was bubbled through the solution under anhydrous conditions for 10 min at 0°. After 1 h at room temperature, the reaction mixture was neutralized with silver carbonate, filtered, and evaporated to a syrup that was triturated with light petroleum (b.p. 65–110°) to remove most of the triphenylmethane. The residue was dissolved in water, and the solution was filtered and evaporated to a syrup (0.227 g).

The syrup (0.223 g) was heated with 0.5N sulphuric acid (3 ml) at 100°, and the hydrolysis, which was followed by t.l.c. (chloroform–acetone, 1:1), was complete in 6 h. The hydrolysate was neutralized with barium carbonate and filtered, and the filtrate (4 ml) was extracted with chloroform (10 × 4 ml) to remove traces of a fast-moving impurity. The aqueous layer, on concentration, gave the product as a syrup (0.180 g, 82%), $[\alpha]_D^{27}$ +94° (*c* 3.05, water); lit., $[\alpha]_D$ + 80.9° (ref. 18*a*), + 116° (ref. 18*b*). Paper chromatography (solvent *A*) and paper electrophoresis showed a single component having R_F, R_G, and M_G values of 0.18, 0.22, and 0.22, respectively. (Found: OCH_3, 28.7. Di-*O*-methylhexose calc.: 29.8%). Demethylation[17] with boron trichloride gave only galactose.

2,5-Di-O-methyl-D-galactose. — Methyl 2,5-di-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside (0.430 g) was detritylated, isolated, hydrolyzed, and recovered, as described above, but with hydrolysis by 0.2N sulphuric acid (3 ml) for 4.5 h at 100°. The final syrup (0.16 g, 83%), $[\alpha]_D^{27}$ −10.3° (*c* 2.46, water), on paper chromatographic (solvent *A*) and ionophoretic examination showed a single component having R_F, R_G, and M_G values of 0.32, 0.42, and 0.23, respectively. Demethylation gave galactose.

3,5-Di-O-methyl-D-galactose. — Methyl 3,5-di-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside (0.271 g) was detritylated, isolated, hydrolyzed, and recovered, essentially

as described above. The product was a syrup (0.055 g, 42%), $[\alpha]_D^{29}$ −25.3° (*c* 3.75, water); lit.[1], $[\alpha]_D$ −24.8° ±0.5°, water; which showed a single component on paper chromatography and paper electrophoresis, having R_F, R_G, and M_G values of 0.31, 0.40, and 0.65, respectively. Demethylation gave galactose.

Methyl 2,3-, 2,5-, and 3,5-di-O-methyl-β-D-galactofuranosides. — Detritylation with dry hydrogen chloride produced slight cleavage of the glycosides. To overcome this difficulty, further detritylations were performed in 50% acetic acid. Methyl 2,3-di-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside (0.49 g) was stirred magnetically, at room temperature, with 50% aqueous acetic acid (15 ml). After 6 h, the precipitate was removed by filtration, the solution was evaporated, and water was distilled several times from the residue. Finally, the aqueous solution was extracted once with light petroleum (b.p. 65–110°) and concentrated to give syrupy methyl 2,3-di-*O*-methyl-β-D-galactofuranoside (0.231 g, 95%), $[\alpha]_D^{28}$ −122.1° (*c* 2.12, methanol). Paper chromatography of the glycoside produced a single component R_F 0.69 (solvent *A*; a bluish red stain with spray *B*). (Found: OCH_3, 41.95. Di-*O*-methylhexoside calc.: 41.9%).
Methyl 2,5- and 3,5-di-*O*-methyl-β-D-galactofuranosides were similarly prepared in yields of 90%. The former glycoside had an R_F value of 0.71 and a bluish red stain (spray *B*); $[\alpha]_D^{29}$ −104.7° (*c* 1.6, methanol) (Found: OCH_3, 41.6). The latter had R_F (0.67, blue stain); $[\alpha]_D^{29}$ −110.8° (*c* 1.59, methanol) (Found: OCH_3, 41.9).

Methyl 3-O-methyl-β-D-galactofuranoside. — Methyl 3-*O*-methyl-6-*O*-trityl-β-D-galactofuranoside (0.090 g) was detritylated in 50% acetic acid, as described above. The syrupy product (0.038 g, 92%) showed a single component (R_F 0.43, solvent *A*) and a blue colour with spray reagent *B*. It had $[\alpha]_D^{28}$ −142.8° (*c* 1.18, methanol) (Found: OCH_3, 29.81. Mono-*O*-methylhexoside calc.: 29.66%).

2,3-Di-O-methyl-N-phenyl-D-galactosylamine. — 2,3-Di-*O*-methyl-D-galactose (0.05 g) in ethanol (2 ml) was heated under reflux with freshly distilled aniline (26 mg) for 5 h. Removal of ethanol left a syrup that crystallized from acetone at −10°, giving a product that had m.p. 151–153°, $[\alpha]_D^{27}$ −66→−13° (4 days; *c* 1.38, ethanol); lit.[19] m.p. 154–155°, $[\alpha]_D$ −56.8→+12.1° in ethanol; and[20] m.p. 152–154°, $[\alpha]_D$ −69→−13° in ethanol.

2,5-Di-O-methyl-D-galactonamide. — 2,5-Di-*O*-methyl-D-galactose (0.050 g) in water (3 ml) was oxidized in the dark for 72 h with bromine (7 drops) in the presence of barium carbonate (0.060 g). Bromine was removed by aeration, and the aqueous solution was acidified with hydrochloric acid and extracted continuously with chloroform for 24 h. Only traces of a syrup were recovered; consequently, the aqueous layer was evaporated by aeration, and the residue was extracted with chloroform–acetone (1:1). The soluble portion was fractionated on a small column of silica gel by using the same solvent. The syrup (0.020 g) thus recovered was homogeneous, as shown by t.l.c. in chloroform–acetone (1:1). It was distilled (bath temperature 150–160°/0.01 mm) to give the syrupy lactone, $\nu_{max}^{CHCl_3}$ 1785 cm^{-1}, which was dissolved in methanol saturated with ammonia. The solution was kept for 48 h at 0°, and evaporation of the solvent, with recrystallization of the residue from ethanol, gave 2,5-di-*O*-methyl-D-galactonamide, m.p. 184–186°, $[\alpha]_D^{27}$ +41.7° (*c* 1.33, water).

Anal. Calc. for $C_8H_{17}NO_6$: C, 43.04; H, 7.68; N, 6.28. Found: C, 43.40; H, 7.48; N, 6.21.

3,5-Di-O-methyl-D-galactitol. — 3,5-Di-*O*-methyl-D-galactose (0.035 g) in water (2 ml) was mixed with aqueous sodium borohydride[21] (0.07 g in 1 ml). The resulting hexitol, isolated and crystallized in the usual way[2], had m.p. and mixed m.p. 135–136°, $[\alpha]_D^{27}$ −23.7° (*c* 1.18, methanol); lit.[1], m.p. 134–135°, $[\alpha]_D^{26}$ −23.7 ± 1° (*c* 1.01, methanol).

3-O-Methyl-D-galactose. — Methyl 3-*O*-methyl-β-D-galactofuranoside (0.027 g) was hydrolyzed with 0.2N sulphuric acid (1 ml) for 6 h at 100°. Neutralization ($BaCO_3$), filtration, and evaporation of the solution gave a syrup (0.018 g). Paper chromatography and electrophoresis of this syrup showed a single component having R_F, R_G (solvent *A*), and M_G values of 0.04, 0.055, and 0.69, respectively. Demethylation[17] gave galactose. A solution of the syrupy material in absolute ethanol crystallized on seeding, and recrystallization from ethanol gave a product with m.p. 138–140° alone or in admixture with an authentic sample of 3-*O*-methyl-D-galactose; lit.[22], m.p. 144–147°.

Methyl 2,5-anhydro-3-O-methyl-β-D-hexofuranoside. — Methyl 2,5-anhydro-3-*O*-methyl-6-*O*-trityl-β-D-hexofuranoside (0.360 g) was detritylated in 50% aqueous acetic acid, and the product was recovered by the usual method. A portion (0.010 g) of the freshly detritylated material was hydrolyzed with 0.2N sulphuric acid for 6 h at 100°. Neutralization and evaporation gave a syrup that was examined by paper chromatography and electrophoresis. In addition to 3-*O*-methyl-D-galactose (R_F 0.04, R_G 0.055, M_G 0.69), appreciable proportions of a second component (R_F 0.88 and M_G 0.00) and faint traces of a third component 0.21 (R_F) were also detected. The remainder of the detritylated, unhydrolyzed material was dried overnight *in vacuo* and, when examined by paper chromatography (solvent *A*), showed a strongly reducing streak originating at the starting line. The same material, on hydrolysis (0.2N sulphuric) and examination by paper chromatography, showed 3 components [R_F 0.87, 0.208, and 0.09 (solvent *A*); and 0.79, 0.44, 0.27 (solvent *B*)]. All three spots were non-complexing on borate electrophoresis. Prolonged hydrolysis with 0.2N sulphuric acid or 50% aqueous acetic acid showed that the spot having R_F 0.87 was formed at the expense of the spot having R_F 0.09. Scarcity of material precluded further work on this fraction.

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SUMMARY

Partial toluene-*p*-sulphonylation of methyl 6-*O*-trityl-β-D-galactofuranoside produced a mixture of three mono-*O*-toluene-*p*-sulphonyl derivatives and a di-*O*-toluene-*p*-sulphonyl derivative. Successive methylation, desulphonylation, detrityl-

ation, and hydrolysis of these compounds have yielded 2,3-, 2,5-, and 3,5-dimethyl and 3-methyl ethers of D-galactose. The di-*O*-toluene-*p*-sulphonyl derivative, in addition, gave a crystalline anhydro sugar that was tentatively identified as a methyl 2,5-anhydro-3-*O*-methyl-6-*O*-trityl-β-D-hexofuranoside. A proof of structure of these methylated sugars is presented.

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