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BUTYLIDENE ACETALS OF GALACTITOL

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ABSTRACT

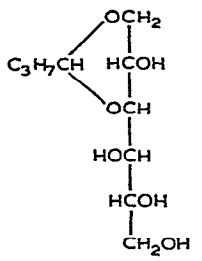
The acid-catalysed reaction of galactitol with butyraldehyde yields the 1,3- and 2,3-mono- and 1,3:4,6-di-acetals, the structures of which were proved by chemical methods. The separation of acetals on an anion-exchange resin is described. Mass spectrometry and n.m.r. spectroscopy were used for characterisation of the methylated acetals and certain partially methylated derivatives of galactitol derived therefrom.

RESULTS AND DISCUSSION

The reaction of approximately equimolar quantities of galactitol and butyraldehyde in 0.5M hydrochloric acid at room temperature gave an optically inactive, mixed monoacetal fraction after 48 h. This mixture could not be fractionated by chromatography on silica gel or by fractional crystallisation, although it was possible to recrystallise it as a mixture.

The monoacetal mixture was fractionated (95%) on a strongly basic ion-exchange resin, Dowex-1(HO^-), to give 1,3-*O*-butylidene-DL-galactitol (**1**) and 2,3-*O*-butylidene-DL-galactitol (**2**), both of which were crystalline. Although two diastereoisomers of the 2,3-monoacetal are possible, only one isomer was detected. Compounds **1** and **2** appear to be the first monoacetals of galactitol to be obtained directly from the reaction of galactitol with an aldehyde. The separation of the acetals on Dowex-1(HO^-) resin is novel, although the same resin has been widely used for the fractionation of anomeric mixtures of glycosides[1,2]. It has been suggested[1] that the pH on the surface of the resin particles is high enough to facilitate the ionisation of the hydroxyl groups of non-reducing carbohydrates. The 1,3-monoacetal was eluted first from the column, suggesting that HO-2 of this acetal is less acidic than HO-1 of the 2,3-monoacetal. Indeed, the hydrogen bonding of HO-2 to the ring oxygen atoms of the 1,3-monoacetal (**3**) makes the ionisation of this hydroxyl proton more difficult, whereas free rotation about the C-1–C-2 bond may weaken the hydrogen bonding of HO-1 to O-2 to a certain degree in the 2,3-monoacetal.

Monitoring of the reaction of galactitol with butyraldehyde by g.l.c. and paper chromatography showed the initial formation of the monoacetals. After 48 h, the reaction mixture also contained two other products, one of which was isolated crystalline and identified as 1,3:4,6-di-*O*-butylidenegalactitol (**4**).



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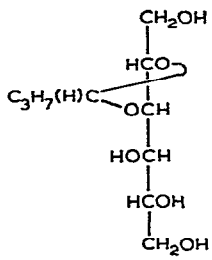

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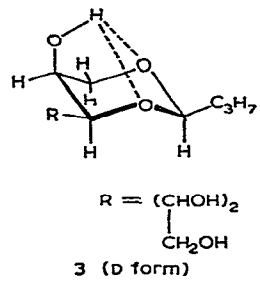

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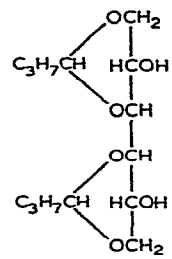

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The structure of the 1,3-acetal (**1**), which was characterised as the tetra-acetate and tetra-benzoate, was proved as follows. It consumed 2.04 mol. of periodate ion and liberated 1.12 mol. of formaldehyde and 0.91 mol. of formic acid. Methylation of **1** gave crystalline tetra- and tri-methyl ethers. Hydrolysis of the acetal group of the fully methylated 1,3-acetal by an acidic resin afforded a crystalline tetra-*O*-methylhexitol, demethylation[3] of which gave galactitol. The tetra-*O*-methylgalactitol did not consume periodate ion, thus showing the absence of vicinal hydroxyl groups. Tritylation gave a crystalline monotrityl derivative, showing the probable presence of one free primary hydroxyl group. These results show the structure of this compound to be 2,4,5,6-tetra-*O*-methyl-DL-galactitol, and the original acetal ring thus occupied the 1,3-positions.

The 2,3-monoacetal (**2**) consumed 2.05 mol. of periodate and liberated 1.08 mol. of formaldehyde and 1.00 mol. of formic acid. It gave a crystalline tetra-acetate and a syrupy tetramethyl ether. Acidic hydrolysis of the latter product yielded a syrupy tetra-*O*-methylhexitol, which, with boron trichloride, gave galactitol. The tetra-*O*-methylgalactitol consumed 1.06 mol. of periodate, to give methoxyacetaldehyde (isolated as the *p*-nitrophenylhydrazone[4] in 75% yield) and tri-*O*-methyl-DL-threose (88%). These facts establish the structure of **2**.

The 1,3:4,6-diacetal (**4**) was characterised as the crystalline diacetate. Methylation of **4** afforded a crystalline dimethyl derivative. A dilute solution of **4** in carbon tetrachloride showed a single, sharp i.r. absorption band at 3580 cm^{-1} in the hydroxyl stretching region, which is characteristic for secondary, intramolecularly bonded, hydroxyl groups[5]. On dilution of the solution to concentrations less than 0.005M, the position of the peak did not change.

Acid hydrolysis of the dimethyl ether of **4** gave a crystalline di-*O*-methylhexitol, which on demethylation gave galactitol. The di-*O*-methylgalactitol consumed 1.07 mol. of periodate ion (after 24 h) but liberated no formaldehyde or formic acid. The reported[6] m.p. of 2,5-di-*O*-methylgalactitol is 183.5°. In our hands, the m.p. could only be raised to 176–177.5° and the tetra-acetate of this compound had m.p. 148° (reported[6] by Painter as 88.5°). It is possible that 2,5-di-*O*-methylgalactitol and its tetra-acetate are each dimorphic. Periodate oxidation of the di-*O*-methylgalactitol and then borohydride reduction of the products, using Painter's method,

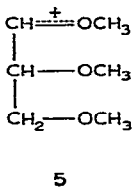
gave 2-*O*-methylglycerol, characterised as the known[6] crystalline di-*p*-nitrobenzoate. The 2,5-di-*O*-methylgalactitol also gave a crystalline ditrityl derivative, thus showing the probable presence of two unsubstituted, primary hydroxyl groups in the molecule. Thus, the structure of **4** is established.

P.m.r. spectroscopy has been used to confirm the ring size of various acetals[7,8]. The ring sizes of the methylated butylidene acetals of galactitol were characterised by the chemical shifts of their acetal-proton signals, the assignments of which were confirmed by double-resonance techniques. The spectra of the monoacetals were complicated and only partial interpretation was possible, but the acetal-proton region was free from other signals. Thus, the spectra of the fully methylated 1,3-monoacetal and the tri-*O*-methyl-1,3-monoacetal showed one-proton triplets (J 5 Hz) at τ 5.42 and 5.41, respectively, characteristic of a six-membered cyclic butylidene acetal. Each spectrum also showed a low-field quartet ($J_{1,1}$ 12.8, $J_{1,2}$ 1.5 Hz) associated with the equatorial proton at C-1. These signals were centred at τ 5.56 and 5.69 for the fully methylated 1,3-monoacetal, and at τ 5.55 and 5.68 for the trimethylated 1,3-monoacetal. The spectrum of the methylated 2,3-monoacetal showed a low-field, one-proton triplet at τ 4.95 (J 5 Hz), as expected for a five-membered acetal ring[8]. The spectrum of the 1,3:4,6-diacetal dimethyl ether showed a two-proton triplet at τ 5.40 (J 5 Hz).

The following signals for methoxyl groups were observed: 1,3:4,6-diacetal dimethyl ether τ 6.57 (2 MeO); 1,3-monoacetal tetramethyl ether τ 6.54, 6.56 (2 MeO), 6.62; 1,3-monoacetal trimethyl ether τ 6.50, 6.51, and 6.54; 2,3-monoacetal tetramethyl ether τ 6.50, 6.52, 6.60, and 6.61; 2,4,5,6-tetra-*O*-methylgalactitol τ 6.49, 6.50, 6.54, 6.61; 1,4,5,6-tetra-*O*-methylgalactitol τ 6.50, 6.51, 6.60, 6.61. These results are in good agreement with those of Rathbone *et al.*[9]. The spectra of 1,3:4,6-di-*O*-butylidenegalactitol and its dimethyl ether are being further investigated.

In the mass spectra of the methylated acetals, the characteristic $(M-1)^+$ peaks were easily detectable[10], at *m/e* 291 for the monoacetals and 317 for the diacetal. Other characteristic, primary fragments, at *m/e* 249 for the monoacetals and 275 for the diacetal dimethyl ether, were formed by the loss of a propyl radical from the molecules[10]. All the spectra also contained peaks at *m/e* 159, which were probably formed by fission of the C-3–C-4 bond[11].

The spectra of the methylated monoacetals contained peaks at *m/e* 133 (**5**) for the methylated side-chains of the acetal rings and at *m/e* 89 (**6**). These fragments were also observed for the tetra-*O*-methylgalactitol diacetates and tri-*O*-methyl-DL-threose, *m/e* $(M-CHO)^+$ (*cf.* ref. 10). The secondary fragments derived from **5**,



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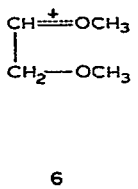

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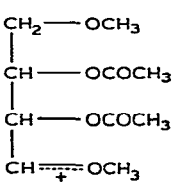

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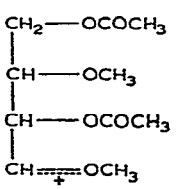

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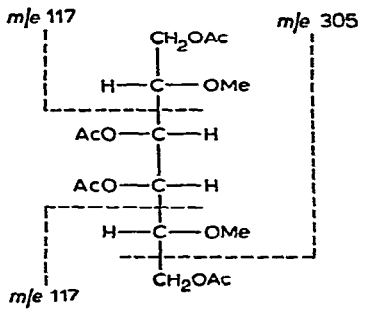
which appeared at *m/e* 102, 71, and 101, were formed by the loss of methoxyl groups and methanol[10]. The fragment *m/e* 59 was formed by the elimination[12] of formaldehyde from **6**.

The primary fragment **7**, *m/e* 233, and the secondary fragment *m/e* 113 were observed in the spectrum of 1,4,5,6-tetra-*O*-methylgalactitol diacetate, as expected[13] for alditols methylated at positions 1 and 4.

The spectrum of 2,4,5,6-tetra-*O*-methylgalactitol diacetate also contained a peak at *m/e* 233, which is probably the fragment **8**. This compound gave a peak at *m/e* 117, which is obtained when C-1 is acetylated and C-2 methylated[13]. Another signal in the spectra of the tetra-*O*-methyl diacetates is *m/e* 277, which is probably formed by the loss of a $-CH_2-O-CH_3$ group from the molecule.

The most-intense signal in the spectrum of 2,5-di-*O*-methylgalactitol tetra-acetate (**9**) is *m/e* 117 (*cf.* ref. 13). The signal at *m/e* 305 must be formed by the loss of an acetoxymethyl radical.



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The spectrum of 2,5-di-*O*-methylgalactitol tetra-acetate did not show any signal at *m/e* 45. This result is to be expected[13] for partially methylated alditol acetates which contain no primary methoxyl group.

EXPERIMENTAL

Standard procedures were used for quantitative determinations of periodate[14], formaldehyde[15], and formic acid[16]. T.l.c. was performed on silica gel, using *A* butanone saturated with water and *B* benzene–methanol (9:1) and detection with 5% ethanolic sulphuric acid at 120°. G.l.c. was effected with a modified Pye 104 instrument, using 7.5% Apiezon K on Celite at 180°. Hydroxy-compounds were injected as their *O*-trimethylsilyl (TMS) ethers, and retention times are relative to that of the TMS derivative of galactitol. P.m.r. spectra were recorded with a Varian HA-100 for solutions in $CDCl_3$, using tetramethylsilane as an internal reference. Mass spectra were recorded on an A.E.I. MS-902 instrument, using the direct-insertion mode and an ionization potential of 70 eV. Light petroleum refers to the fraction having b.p. 60–80° unless otherwise stated.

Reaction between galactitol and butyraldehyde. — A solution of galactitol (15 g) in 0.5M hydrochloric acid (500 ml) was mixed with butyraldehyde (6 ml; 0.9 mol.) and shaken until dissolution occurred. The solution was left at room temperature for 48 h, neutralised with M sodium hydroxide (250 ml) and evaporated under vacuum to 150 ml. The resulting crystals of 1,3:4,6-di-*O*-butylidenegalactitol (**4**) were collected and washed with a little water. The filtrate was extracted with chloroform (2 × 75 ml). Evaporation of the combined and dried extracts and crystallisation of the residue from ether gave a further crop of **4** (total yield, 1.8 g), m.p. 131–133°, R_V 2.20, R_F 0.70 (solvent *A*). After recrystallisation from methanol, **4** had m.p. 133–135° (Found: C, 57.99; H, 8.84. $C_{14}H_{26}O_6$ calc.: C, 57.91; H, 9.03%). The di-acetate of **4** had m.p. 200–202° (from carbon tetrachloride) (Found: C, 57.58; H, 7.92. $C_{18}H_{30}O_8$ calc.: C, 57.74; H, 8.08%).

The filtrate from the above reaction was evaporated under vacuum to give a solid which was extracted with ethanol (3 × 75 ml). Concentration of the combined extracts yielded a syrup (12.5 g), which gave spots, R_F 0.27 and 0.38, on t.l.c. (solvent *A*).

A column of Dowex 1-x8(Cl^-) resin (200–400 mesh, 300 g) was washed with M sodium hydroxide (3 l) and then with deionised and CO_2-free water (3 l). The mixture of monoacetals (4 g) was dissolved in water (5 ml) and applied to the column which was eluted with deionised and CO_2-free water. Fractions (25 ml) were collected and analysed by t.l.c. 1,3-*O*-Butylidene-DL-galactitol (**1**, 2.4 g), eluted first, crystallised on standing at 5° overnight. After recrystallisation from ethanol–ether (5:1), **1** had m.p. 73–75°, R_F 0.27 (solvent *A*), R_V 1.58 (Found: C, 50.94; H, 8.62. $C_{10}H_{20}O_6$ calc.: C, 50.83; H, 8.53%).

The tetra-acetate of **1** had m.p. 111–112° (from ethanol) (Found: C, 53.56; H, 6.85. $C_{18}H_{28}O_{10}$ calc.: C, 53.46; H, 6.98%); the tetrabenzoate had m.p. 89–91° (from ethanol) (Found: C, 70.07; H, 5.52. $C_{38}H_{36}O_{10}$ calc.: C, 69.93; H, 5.55%).

Further fractions, on evaporation under vacuum, gave syrupy 2,3-*O*-butylidene-DL-galactitol (**2**, 1.3 g) which crystallised on standing. The recrystallised acetal (ethanol–ether, 5:1) had m.p. 83–85°, R_F 0.38 (solvent *A*), R_V 1.46 (Found: C, 50.66; H, 8.57. $C_{10}H_{20}O_6$ calc.: C, 50.83; H, 8.53%).

The tetra-acetate of **2** had m.p. 46–48° (from ethanol–light petroleum) (Found: C, 53.33; H, 6.77. $C_{18}H_{28}O_{10}$ calc.: C, 53.46, H, 6.98%).

Methylation of 1,3-O-butylidene-DL-galactitol. — A solution of the 1,3-acetal **1** (3 g) in *N,N*-dimethylformamide (25 ml) was stirred with silver oxide (10 g) and methyl iodide (10 ml) at room temperature for 24 h and then filtered. The residue was washed with *N,N*-dimethylformamide. The combined filtrate and washings were evaporated, and the methylation and work-up were repeated on the residue. The *N,N*-dimethylformamide was then removed completely under high vacuum, giving a white solid which was extracted with light petroleum. The concentrated extract deposited a syrup overnight at −5° which, after separation from the supernatant, crystallised from ethanol–light petroleum. The i.r. spectrum of this compound (Nujol mull) showed hydroxyl absorption, and the n.m.r. spectrum contained three

methoxyl signals which indicated that the compound was a 1,3-*O*-butylidene-tri-*O*-methyl-DL-galactitol (0.16 g, 4.5%), m.p. 91–93°, R_F 0.24 (solvent *B*) (Found: C, 56.53; H, 9.21; OMe, 33.18. $C_{13}H_{26}O_6$ calc.: C, 56.10; H, 9.42; OMe, 33.45%).

T.l.c. of the supernatant gave a single spot, R_F 0.49 (solvent *B*), and evaporation gave a colourless syrup which crystallised on standing at −5°. The tetramethyl ether (2.6 g, 69%) had m.p. 22–24°, gave a single peak on g.l.c., and had no i.r. absorption for hydroxyl (Found: C, 57.73; H, 9.71; OMe, 42.21. $C_{14}H_{28}O_6$ calc.: C, 57.51; H, 9.65; OMe, 42.46%).

2,4,5,6-Tetra-O-*methyl*-DL-*galactitol.* — A solution of 1,3-*O*-butylidene-tetra-*O*-methyl-DL-galactitol (2.1 g) in ethanol–water (7:3; 50 ml) was refluxed and stirred for 3 h with Amberlite IR-120(H^+) resin (50 ml). The reaction mixture was shown to contain one main product, R_F 0.16 (solvent *B*), and a small amount of unhydrolysed acetal (R_F 0.49). The ethanol solution was evaporated to give a syrup which was extracted with light petroleum (b.p. 40–60°) to remove the unreacted acetal. The remaining syrup was crystallised from ether–light petroleum to give 2,4,5,6-tetra-*O*-methyl-DL-galactitol (0.74 g, 43.5%), m.p. 72–74° (Found: C, 50.31; H, 9.12; OMe, 51.73. $C_{10}H_{22}O_6$ calc.: C, 50.41; H, 9.31; OMe, 52.10%). The di-acetate was syrupy (Found: C, 51.81; H, 8.20. $C_{14}H_{26}O_8$ calc.: C, 52.16; H, 8.13%).

The tetra-*O*-methylgalactitol (40 mg) dissolved in dichloromethane (3 ml) was treated with boron trichloride (4 ml) at −75° for 1 h. After the usual working-up procedure, galactitol (78%) was obtained, m.p. and m.m.p. 187–188°.

2,4,5,6-Tetra-O-*methyl-1*-O-*trityl*-DL-*galactitol.* — A solution of the foregoing tetra-*O*-methylgalactitol (100 mg) in dry pyridine (3 ml) was treated with trityl chloride (200 mg). After 5 days, the reaction mixture was poured into water. The product was collected, dried, and recrystallised from ethanol to give the title compound (0.11 g, 55%), m.p. 134–136° (Found: C, 72.36; H, 7.37; OMe, 25.50. $C_{29}H_{36}O_6$ calc.: C, 72.47; H, 7.55; OMe, 25.83%).

2,3-O-*Butylidene-1,4,5,6-tetra*-O-*methyl*-DL-*galactitol.* — A solution of the 2,3-acetal **2** (3 g) in *N*,*N*-dimethylformamide (20 ml) was treated with silver oxide (10 g) and methyl iodide (10 ml) for 24 h, and the product was remethylated as described above.

The final residue was extracted with light petroleum, and evaporation of the extract gave the title compound as a syrup (2.7 g, 71%), b.p. 113–116°/0.4 mmHg, for which g.l.c. showed a single peak and t.l.c. gave a single spot, R_F 0.42 (solvent *B*). (Found: C, 57.35; H, 9.49; OMe, 42.16. $C_{14}H_{28}O_6$ calc.: C, 57.51; H, 9.65; OMe, 42.46%).

1,4,5,6-Tetra-O-*methyl*-DL-*galactitol.* — A solution of the 2,3-monoacetal tetramethyl ether (2.5 g) in ethanol–water (7:3, 25 ml) was refluxed and stirred with Amberlite IR-120(H^+) resin (25 ml) for 3 h. After filtration, the solvent was evaporated to give a syrup, for which t.l.c. showed one main product (R_F 0.19) together with a small amount of unhydrolysed acetal. The syrup was purified by elution from silica gel with benzene–methanol (9:1) to give the title compound as a pale-yellow syrup (1.5 g, 74%) (Found: C, 50.57; H, 9.10; OMe, 51.88. $C_{10}H_{22}O_6$ calc.: C, 50.41;

H, 9.31; OMe, 52.10%). The di-acetate was syrupy and had R_F 0.47 (solvent *B*) (Found: C, 51.96; H, 8.23; OMe, 38.17. $C_{14}H_{26}O_8$ calc.: C, 52.16; H, 8.13; OMe, 38.50%).

The tetramethyl ether (26 mg) was demethylated with boron trichloride (2 ml) at −75°, giving galactitol (70%), m.p. and m.m.p. 187–189°.

*Periodate oxidation of 1,4,5,6-tetra-*O*-methyl-*DL*-galactitol.* — A solution of tetra-*O*-methylgalactitol (250 mg) and sodium metaperiodate (0.25 g) in water (5 ml) was left at room temperature for 1.5 h. More water (3 ml) was added and the solution was distilled. The distillate (3 ml) was treated with a warm solution of *p*-nitrophenylhydrazine. Crystallisation of the precipitate from aqueous ethanol gave orange needles of methoxyacetaldehyde *p*-nitrophenylhydrazone (0.165 g, 75%), m.p. and m.m.p. 113–116°.

The remaining solution was extracted with chloroform (10 × 15 ml). The combined, dried, and evaporated extracts gave a syrupy tri-*O*-methyl-DL-threose (0.15 g, 88%), which gave a single spot, R_F 0.26, on t.l.c. (solvent *B*) and showed n.m.r. signals for an aldehyde proton and three methoxyl groups (Found: C, 51.57; H, 8.64; OMe, 57.01. $C_7H_{14}O_4$ calc.: C, 51.84; H, 8.70; OMe, 57.40%).

*1,3:4,6-Di-*O*-butylidene-2,5-di-*O*-methylgalactitol.* — A solution of the diacetal (1.1 g) in *N,N*-dimethylformamide (20 ml) was stirred with silver oxide (5 g) and methyl iodide (5 ml) at room temperature for 23 h and then filtered, and the residue was washed with *N,N*-dimethylformamide.

The combined filtrate and washings were evaporated under vacuum to give a solid, which was extracted with hot ether. On cooling of the extract, the title compound (0.95 g, 79%) separated, m.p. 162–164° (from ether or methanol) (Found: C, 60.25; H, 9.33; OMe, 19.41. $C_{16}H_{30}O_6$ calc.: C, 60.35; H, 9.50; OMe, 19.50%). The i.r. spectrum showed no hydroxyl absorption, and t.l.c. gave a single spot, R_F 0.55 (solvent *B*).

*2,5-Di-*O*-methylgalactitol.* — A solution of the foregoing diacetal dimethyl ether (0.7 g) in ethanol–water (7:3, 25 ml) was stirred and refluxed with Amberlite IR-120(H^+) resin (25 ml) for 2 h. The resin was filtered off and washed with hot ethanol. The filtrate and the washings were evaporated to give a solid which was crystallised several times from ethanol to give the title dimethyl ether (0.2 g, 43.5%), m.p. 176–177.5°. The compound gave a single spot on t.l.c., R_F 0.03 (solvent *B*) and 0.12 (benzene–methanol, 9.2) (Found: C, 45.54; H, 8.52; OMe, 29.78. $C_8H_{18}O_6$ calc.: C, 45.70; H, 8.63; OMe, 29.52%).

The dimethyl ether (40 mg) was acetylated with pyridine (3 ml) and acetic anhydride (4 ml), to give a tetra-acetate (90%), m.p. 148°. The compound gave one spot on t.l.c., R_F 0.42 (solvent *B*) (Found: C, 50.81; H, 6.79; OMe, 16.33. $C_{16}H_{26}O_{10}$ calc.: C, 50.79; H, 6.93; OMe, 16.40%).

The dimethyl ether (28 mg) was demethylated in dichloromethane (2 ml) with boron trichloride (2 ml) at −75°. The usual working-up procedure gave galactitol (70%), m.p. and m.m.p. 187–188°.

*2,5-Di-*O*-methyl-1,6-di-*O*-tritylgalactitol.* — A solution of 2,5-di-*O*-methyl-

galactitol (50 mg) in pyridine (5 ml) was treated with trityl chloride (150 mg). After five days, the reaction mixture was poured into water, and the product (42%) which separated on cooling at 5° was recrystallised from ethanol to give the title compound, m.p. 202–204° (Found: C, 79.54; H, 6.56; OMe, 9.07. $C_{46}H_{46}O_6$ calc.: C, 79.51; H, 6.67; OMe, 8.93%).

Periodate oxidation of 2,5-di-O-methylgalactitol. — The dimethyl ether (62 mg) was dissolved in 15mM sodium metaperiodate (200 ml). Aliquots (2 ml) were used for the determination of periodate uptake. After 2 h, the remaining solution was extracted continuously with chloroform. The extract on evaporation gave a syrup (58 mg) which, after borohydride reduction, yielded 2-*O*-methylglycerol (57 mg), characterised as the di-*p*-nitrobenzoate, m.p. 158–160°; lit.[6] m.p. 159.5–160.5°.

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