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ACID-CATALYSED FORMATION OF DIACETALS FROM BUTYRALDEHYDE AND CERTAIN D-GLUCITOL DERIVATIVES*

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ABSTRACT

Acid-catalysed dibutylidenation of 1-deoxy-D-glucitol and 3-*O*-methyl-D-glucitol yields the 2,4:5,6-diacetals as the main, thermodynamically controlled products, and 2-deoxy-D-*arabino*-hexitol (*i.e.*, 2-deoxy-D-glucitol) yields the 1,3:4,6-diacetal as the main, thermodynamically controlled product.

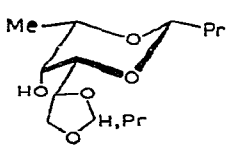
INTRODUCTION

The presence or absence of a kinetic phase in the monobutylidenation of 1- and 2-deoxy-D-glucitol and 3-*O*-methyl-D-glucitol, and the main acetals formed, have been reported[1]. This paper extends these studies to the diacetalation of these alditols.

RESULTS

1-Deoxy-D-glucitol. The alditol (1 mol.) reacted with butyraldehyde (1.9 mol.) in the presence of conc. hydrobromic acid to produce a complex mixture of diacetals at all stages of the reaction, as shown by g.l.c. and p.m.r. analysis. After reaction for 2.5 h, a mixture of unknown, kinetically controlled diacetals (4%, m.p. 67–69°) was obtained, but at equilibrium (2 days), the main product was the syrupy 2,4:5,6-diacetal (**1**), consisting of a mixture of isomers differing in the configuration of the acetal carbon of the five-membered ring. The mixed 2,4:5,6-isomers were isolated in 20% yield by fractionation of the product on neutral alumina, and a very small amount of one of the isomers was obtained pure. The p.m.r. spectrum showed that it was the isomer having the propyl group and C-4 *trans* with respect to the 5,6-ring, since this acetal has the more-deshielded[2], dioxolane-acetal proton.

*Dedicated to the memory of Professor Edward J. Bourne. Professor Bourne took an active part in the work described in this paper and, had it not been for his untimely death, he would have been a co-author on this paper. In addition to dedicating this paper to his memory, the authors also wish to put on record their gratitude for the part he has played in their researches.



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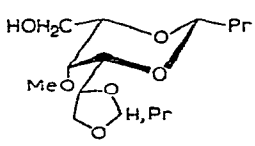

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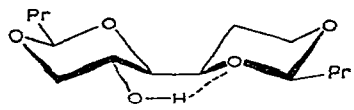

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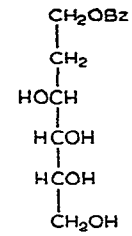

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The mixed 2,4:5,6-diacetal (**1**) was very soluble in all organic solvents, and could not be crystallised. However its purity was assessed from its elemental analysis, as well as from g.l.c. and t.l.c. data. It yielded a monoacetate and a monomethyl ether, both of which were syrupy. The acetal groups were removed from the methyl ether by acid hydrolysis, and the resulting, syrupy *O*-methyldeoxyhexitol consumed 2.3 mol. of periodate and released 1.10 mol. of formaldehyde and 1.05 mol. of formic acid, showing unambiguously that it was 1-deoxy-3-*O*-methyl-D-glucitol. The diacetals therefore had the 2,4:5,6-structure. Further evidence for this structure was given by the p.m.r. spectrum of the parent diacetals which showed acetal protons having chemical shifts[3] corresponding to five- (τ 5.1 and 5.05) and six- (τ 5.40) membered rings*, and the infrared spectrum of a solution (0.7mM) in carbon tetrachloride showed a single, sharp absorption at 3580 cm^{-1}, characteristic[4] of a hydroxyl group involved in hydrogen bonding in a five-membered ring. High-abundance peaks at *m/e* 261 and 131 in the mass spectrum of the syrupy 1-deoxy-3-*O*-methyl-D-glucitol tetra-acetate (M, 348) are believed[5] to arise from the fragmentation between C-2–C-3 and C-3–C-4.

3-O-Methyl-D-glucitol. This alditol (1 mol.) reacted with butyraldehyde (3.7 mol.) in the presence of 5M hydrochloric acid to yield a syrupy mixture of 2,4:5,6-diacetals (**2**, 65%) after 6 h. The mixture gave an unresolved peak on g.l.c., and the p.m.r. spectrum showed acetal protons at τ 5.42 (6-membered ring) and τ 5.11 and 5.04 (5-membered rings having the propyl groups *cis* and *trans* to C-4, respectively). Methylation of the mixture, which gave the expected elemental analysis, yielded a syrupy product which showed two methoxyl signals (τ 6.46 and 6.60) and acetal-proton triplets at τ 5.43 (dioxane ring) and τ 5.11 and 5.06 (dioxolane ring having the propyl groups *cis* and *trans* to C-4, respectively). The acetal-proton signals showed that the ratio of the stereoisomers was unchanged after methylation. The mass spectrum gave high-abundance peaks corresponding to fragments of *m/e* 275 (M − Pr) and 203 (loss of C-5 and C-6). The diacetal dimethyl ether was hydrolysed with a cation-exchange resin to yield a syrupy di-*O*-methylhexitol, the tetra-acetate of

*A referee has commented that the evidence for the structure of the thermodynamically controlled diacetals is also consistent with a 2,5:4,6-arrangement of rings, if the acetal protons have similar shifts[2] in seven- and five-membered rings. We acknowledge this point, but believe that a 2,5:4,6-diacetal is unlikely, as it contains an unfavoured *y-erythro* ring[14].

which was also syrupy. The di-*O*-methylhexitol consumed 2.15 mol. of periodate and released 1.08 mol. of formaldehyde and 1.10 mol. of formic acid. Since the starting material had a methoxyl group at C-3, these data limit the structure of the dimethyl ether to the 1,3 or 2,3 isomers. The mass spectrum of the tetra-acetate indicated[5] that the ether links were at C-1 and C-3, as high-abundance peaks corresponding to fragments of *m/e* 45, 161, and 261 were obtained, corresponding to fission between C-1 and C-2, C-3 and C-4, and C-2 and C-3, respectively. Thus, the diacetals have the 2,4:5,6-structure. This conclusion was confirmed by the following reaction sequence. Tosylation of **2** followed by reduction of the syrupy product with lithium aluminium hydride gave a syrupy 1-deoxy derivative. This product could not be obtained analytically pure, but the p.m.r. spectrum showed a doublet at τ 8.69 (J 6.2 Hz) consistent with the presence of a MeCH group.

1,3-Di-*O*-methyl-D-glucitol was also synthesised from the known[6] 2,4-*O*-benzylidene-5,6-*O*-isopropylidene-D-glucitol by sequential methylation and acid hydrolysis. The product showed the same chromatographic behaviour as the material obtained from the di-*O*-butylidene-3-*O*-methylglucitols. Partial, acid hydrolysis of the dibutylidene methyl ethers yielded the known[1], crystalline 2,4-*O*-butylidene-3-*O*-methyl-D-glucitol (37%), which was further characterised as its crystalline benzeneboronate.

2-Deoxy-D-arabino-*hexitol.* The reaction of this alditol (1 mol.) with butyraldehyde (2 mol.) in the presence of conc. hydrobromic acid was monitored by g.l.c. (Fig. 1). The chromatograms showed that the diacetalation occurred rapidly, compared to the conditions used for monoacetalation[1], and that the uncharacterised, kinetically controlled diacetals soon yielded the thermodynamically controlled 1,3:4,6-diacetal. When the reaction was stopped after 0.5 min, the kinetically controlled diacetals were isolated in good yield as a syrupy mixture. The p.m.r. spectrum showed overlapping acetal-triplets at τ ~4.95, suggesting the presence of five-membered rings.

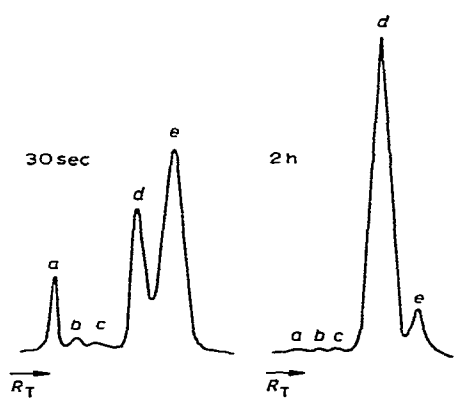


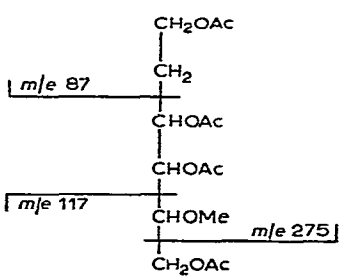
Fig. 1. Gas chromatograms of 2-deoxy-D-*arabino*-hexitol and butyraldehyde (2 mol.) in hydrobromic acid: *a*, 2-deoxy-D-*arabino*-hexitol; *b*, 1,3-acetal; *c*, 4,6-acetal; *d*, 1,3:4,6-diacetal; *e*, unknown diacetals.

The complexity of the acetal-proton region implied that the unidentified product was a mixture, most probably of stereoisomers. Attempts to fractionate this diacetal mixture on neutral or basic alumina, silica gel, and an anion-exchange resin[7] were unsuccessful.

After 3 h, the condensation yielded the crystalline 1,3:4,6-diacetal (**3**, 36%) as the main product. The p.m.r. spectrum of the diacetal showed overlapping acetal-proton triplets at τ 5.51 and 5.46 (J 5.0 Hz), corresponding to acetal protons in six-membered rings. The proton of the free hydroxyl group gave a doublet signal (τ 2.98) which showed that the hydroxyl group was at a secondary carbon. Thus, the evidence limits the structure to the 1,3:4,6 isomer, and the small $^3J_{HCOH}$ coupling[8] (1.5 Hz) confirmed that the hydroxyl group was equatorial. Only a limited amount of double-resonance analysis of a 220-MHz spectrum was possible, but a computer simulation of the spectrum[9] gave coupling values (see Experimental) consistent with data[10] for 1,3-dioxanes.

The infrared spectrum of the diacetal **3** (0.5mM solution in carbon tetrachloride) showed a single absorbance (3540 cm^{-1}) for the hydroxyl-stretching vibration. This is likely to be due[4] to the six-membered ring formed by hydrogen bonding of HO-5 to O-3. The mass spectrum had a strong abundance peak at *m/e* 231 (M−Pr).

The diacetal **3** yielded a monoacetate, a monobenzoate, and a monomethyl ether, each of which was syrupy. Hydrolysis of the monomethyl ether with a cation-exchange resin yielded a syrupy, chromatographically homogeneous 2-deoxy-*O*-methylhexitol, which consumed 1.1 mol. of periodate but yielded no formaldehyde or formic acid. These data limit its structure to the 5-methyl ether. The ether yielded a syrupy tetra-acetate. The fragmentations[11] leading to high-abundance peaks in the mass spectrum of the tetra-acetate (M, 348) are shown below. Abundant fission of the C-2–C-3 bond would not be expected[12], so the ion of *m/e* 87 may have been another species.



Hence, the parent diacetal **3** has HO-5 free. The syrupy 5-*O*-benzoyl diacetal, when treated with a cation-exchange resin, gave crystalline 1-*O*-benzoyl-2-deoxy-D-*arabino*-hexitol (**4**), which was further characterised as the crystalline tetra-acetate. The position of the benzoyl group in **4** was indicated by the consumption of 3.3 mol. of periodate, with release of 1.2 mol. of formaldehyde and 2.1 mol. of formic acid.

Also, the ester **4** migrated in molybdate ionophoresis. The only monosubstituted 2-deoxy-*arabino*-hexitols which would migrate[12] in this buffer have the substituent at C-1 or C-6. The predicted mobilities for the C-1 and C-6 substituted compounds are ~0.8 and ~0.5, relative to 2-deoxy-*arabino*-hexitol; the observed mobility was 0.76.

DISCUSSION

A dimethylene acetal of unknown structure has been obtained[13] directly from 1-deoxy-D-glucitol. The predicted[14], thermodynamically favoured diacetal should have either a 2,4:3,5 structure, *i.e.*, a *cis*-fused ring system with C-6 axial (as given in methylenation[15] of gluconic acid), or a 2,4:5,6-ring structure (**1**); the diacetals isolated had the structure **1**.

Benzylidenation[16] of 3-*O*-methyl-D-glucitol yielded the predicted, thermodynamically favoured, two 2,4:5,6-diacetals, differing only in the configuration of the acetal carbon atom of the five-membered ring. The present work therefore conforms to this pattern. The direct methylenation [17] of the alditol yields a diacetal of unknown structure.

2-Deoxy-D-*arabino*-hexitol yielded a dimethylene[18] and a di-(*m*-nitrobenzylidene)[19] acetal, both of undetermined structure. The predicted, thermodynamically favoured, ring pattern is the observed 1,3:4,6-arrangement (**3**).

The acid hydrolysis of 5-*O*-benzoyl-1,3:4,6-di-*O*-butylidene-2-deoxy-D-*arabino*-hexitol to yield 1-*O*-benzoyl-2-deoxy-D-*arabino*-hexitol (**4**) is an example of the well-known acyl migration towards a primary position[20]. The interest here is that the migration is to the further (C-1) position rather than to C-6. In general, the same considerations apply to the formation of the cyclic ortho-acid intermediate in acyl migration as apply in the formation of cyclic acetal derivatives[21]. This may mean that the reaction sequence involves the following cyclic intermediates: 5,6→4,6→3,4→1,3.

EXPERIMENTAL

Techniques. — G.l.c. was performed on a Pye-104 instrument, usually with an Apiezon K (7.5%) stationary phase at 182°. Hydroxy compounds were injected as their trimethylsilyl ethers[22]. T.l.c. was performed on silica gel-coated glass or precoated plastic plates, with *A* butanone saturated with water, or *B* benzene–methanol (9:1). Quantitative periodate oxidations[23], and formaldehyde[24] and formic acid[25] determinations were effected by standard procedures. The mass spectra were measured on an A.E.I. MS-902 instrument at an ionising energy of 70 eV, with the direct-insertion mode and a source temperature of 200–220°. P.m.r. spectra were recorded with a Varian HR-220 or a modified Varian HA-100 instrument for solutions in deuteriochloroform with tetramethylsilane as internal standard. The infrared spectra were recorded on a Perkin–Elmer 325 spectrophotometer. Light petroleum refers to the fraction having b.p. 60–80°.

Kinetically controlled di-O-butylidene-1-deoxy-D-glucitols. — A solution of 1-deoxy-D-glucitol[1] (0.5 g) in conc. hydrobromic acid (47%, 0.2 ml) was shaken with butyraldehyde (0.4 ml). After 2.5 h, the acid was neutralised with aqueous sodium hydroxide and the solution was evaporated to give a syrup which was extracted at room temperature with light petroleum. The concentrated extract gave a mixture of diacetals (0.03 g), m.p. 67–69° (Found: C, 61.5; H, 9.5. $C_{14}H_{26}O_5$ calc.: C, 61.3; H, 9.55%).

2,4:5,6-Di-O-butylidene-1-deoxy-D-glucitols. — 1-Deoxy-D-glucitol (3 g), butyraldehyde (3 ml), and conc. hydrobromic acid (47%, 1 ml) were shaken overnight at room temperature and then extracted with light petroleum at room temperature. The extract was washed with aqueous sodium hydrogen carbonate and water, and dried over sodium sulphate. Evaporation gave a syrup (3.5 g), for which t.l.c. (solvent *B*) showed a major, fast-moving product and several minor products. The syrup was fractionated in neutral alumina (200 g) with ethyl ether. The first 300 ml contained polymeric butyraldehydes, and the next 1000 ml contained the syrupy 2,4:5,6-diacetals (1 g) (Found: C, 61.3; H, 9.4%).

(*a*) With acetic anhydride–pyridine, the diacetals (0.2 g) yielded the syrupy 3-acetates (0.25 g) (Found: C, 60.6; H, 8.8. $C_{16}H_{28}O_6$ calc.: C, 60.7; H, 8.9%).

(*b*) The diacetals (0.4 g) in dry *N,N*-dimethylformamide (10 ml) were stirred at room temperature with silver oxide (6 g) and methyl iodide (6 ml) for 15 h to yield, in the usual way, the syrupy 3-methyl ethers (0.3 g) (Found: C, 63.5; H, 9.9; OMe, 12.1. $C_{15}H_{28}O_5$ calc.: C, 62.5; H, 9.8; OMe, 10.8%).

1-Deoxy-3-O-methyl-D-glucitol. — The foregoing 3-*O*-methyl diacetals (0.25 g) were treated with refluxing 0.1M hydrochloric acid (10 ml) for 5 h. The cooled reaction mixture was poured into water (25 ml), whereupon a brown oil separated, which was removed by extraction with a little chloroform. Evaporation of the water layer gave the syrupy title compound (0.15 g) (Found: C, 47.0; H, 8.8; OMe, 17.0. $C_7H_{16}O_5$ calc.: C, 46.7; H, 8.9; OMe, 17.2%).

2,4:5,6-Di-O-butylidene-3-O-methyl-D-glucitols. — A solution of 3-*O*-methyl-D-glucitol[1] (3 g) in 5M hydrochloric acid was shaken vigorously with freshly distilled butyraldehyde (5 ml) for 6 h at room temperature. The mixture was extracted with light petroleum, and the extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated. The resulting syrup was chromatographed on neutral alumina with light petroleum. Polymeric butyraldehydes were eluted first, followed by the syrupy diacetals (3 g), $[\alpha]_D^{25}$ −2.9° (*c* 0.85, carbon tetrachloride). The Me_3Si derivative gave an unresolved peak on g.l.c.: *T* 2.15 relative to Me_3Si-D-glucitol, and 2.60 relative to Me_3Si-3-*O*-methyl-D-glucitol (Found: C, 60.1; H, 9.3; OMe, 10.1. $C_{15}H_{28}O_6$ calc.: C, 59.2; H, 9.3; OMe, 10.2%).

2,4:5,6-Di-O-butylidene-1,3-di-O-methyl-D-glucitols. — A solution of the 3-*O*-methyl diacetals (1.3 g) in *N,N*-dimethylformamide (25 ml) was stirred with methyl iodide (5 ml) and silver oxide (5 g) for 22 h at room temperature to yield the syrupy 1,3-di-*O*-methyl diacetals (0.8 g), R_F 0.51 (solvent *B*) [Found (2 samples): C, 61.6; H, 9.6; OMe, 18.8. $C_{16}H_{30}O_6$ calc.: C, 60.35; H, 9.5; OMe, 19.5%].

1,3-Di-O-methyl-D-glucitol. — A solution of the 1,3-di-*O*-methyl diacetals (0.7 g) in ethanol (20 ml) and water (20 ml) was boiled under reflux with Amberlite IR-120 (H^+) resin (30 ml) for 2 h. The resin was filtered off and washed well with hot methanol. The combined filtrate and washings were evaporated, the resulting syrup was extracted with ethyl ether, and the extract was evaporated to a syrup (0.2 g). Paper chromatography showed some impurity, and therefore part of the product was purified by preparative paper chromatography with 1-butanol–ethanol–water (40:11:19). The purified syrup was acetylated in pyridine with acetic anhydride to give the syrupy tetra-acetate, which was pure by t.l.c., R_F 0.41 (solvent *B*).

2,4:5,6-Di-O-butylidene-3-O-methyl-1-O-toluene-p-sulphonyl-D-glucitols. — A solution of the 2,4:5,6-di-*O*-butylidene-3-*O*-methyl-D-glucitols (0.5 g) and toluene-*p*-sulphonyl chloride (0.36 g) in pyridine (5 ml) was stored overnight at room temperature. A small amount of water was added, the mixture was poured into aqueous sodium hydrogen carbonate, and the mixture was extracted with chloroform. Evaporation of the extract gave the syrupy 1-tosylates (Found: C, 57.8; H, 8.0. $C_{22}H_{34}O_8S$ calc.: C, 57.6; H, 7.5%).

2,4:5,6-Di-O-butylidene-1-deoxy-3-O-methyl-D-glucitols. — Lithium aluminium hydride (0.3 g) was added to a solution of the foregoing 1-tosylates (0.3 g) in ether (30 ml), which was then boiled under reflux for 12 h. The excess reductant was destroyed with ethyl acetate, and the alcoholates with water. Evaporation of the ether gave the crude, syrupy 1-deoxy-3-*O*-methyl derivatives.

Partial, acid hydrolysis of 2,4:5,6-di-O-butylidene-3-O-methyl-D-glucitols. — A mixture of the diacetals (0.3 g) in aqueous hydrobromic acid (~24%, 10 ml) was boiled under reflux for 30 min. After neutralisation with sodium hydroxide, the solution was evaporated and the residue was extracted with hot, light petroleum. 2,4-*O*-Butylidene-3-*O*-methyl-D-glucitol (0.1 g), m.p. and mixture m.p.[1] 155–156°, crystallised from the extract.

The 3-*O*-methyl-2,4-acetal (70 mg) in methanol was treated with benzeneboronic anhydride (90 mg). The methanol was evaporated and the residue was crystallised from carbon tetrachloride to yield the benzeneboronate (70 mg), m.p. 105–107°.

Kinetically controlled di-O-butylidene-2-deoxy-D-arabino-hexitols. — 2-Deoxy-D-*arabino*-hexitol[1] (2 g) was dissolved in conc. hydrobromic acid (1 ml) and mixed with butyraldehyde (2.5 ml). The exothermic reaction was stopped after 0.5 min by neutralising with aqueous sodium hydroxide, the mixture was evaporated, and the residue was extracted with light petroleum at room temperature. The extract was evaporated to yield the syrupy, unknown diacetals (3.5 g), R_F 0.50, admixed with some 1,3:4,6-diacetal, R_F 0.42 (solvent *B*). The Me_3Si derivative of the unknown diacetals had *T* 2.22 (relative to Me_3Si-D-glucitol), 3.15 (relative to Me_3Si-2-deoxy-D-*arabino*-hexitol); *cf.* 1,3:4,6-diacetal: *T* 1.82 and 2.60, respectively.

1,3:4,6-Di-O-butylidene-2-deoxy-D-arabino-hexitol. — 2-Deoxy-D-*arabino*-hexitol (3 g) was dissolved in conc. hydrobromic acid (47%, 2 ml) and shaken with freshly distilled butyraldehyde (3.2 ml). An exothermic reaction started soon after

the addition of the aldehyde. The reaction flask was cooled by dipping into cold water for a few minutes, and was then left at room temperature for 3 h. The mixture was neutralised by the addition of aqueous sodium hydroxide and evaporated. The residue was extracted with light petroleum at room temperature. The concentrated extract at −5° gave the 1,3:4,6-diacetal (1.8 g), R_F 0.42 (solvent *B*), $[\alpha]_D^{25}$ +16° (*c* 1, carbon tetrachloride), m.p. 64–66°, after recrystallisation; a mixture m.p. with 1,3-*O*-butylidene-2-deoxy-D-*arabino*-hexitol, m.p. 61–63°, showed depression (Found: C, 61.1; H, 9.4%). N.m.r. data: H-1e, τ 4.17; H-1a, 3.75; H-2e, ~1.45; H-2a, 2.05; H-3, 4.08; H-4, 3.51; H-5, 3.91; H-6e, 4.16; H-6a, 3.36; $J_{1e,1a}$ −11.4, $J_{1e,2e}$ 1.1, $J_{1e,2a}$ 5.1, $J_{1a,2e}$ 2.4, $J_{1a,2a}$ 12.1, $J_{2e,2a}$ −13.1, $J_{2e,3}$ 2.3, $J_{2a,3}$ 12.0, $J_{3,4}$ 4.2, $J_{4,5}$ 9.2, $J_{5,6e}$ 5.3, $J_{5,6a}$ 10.2, and $J_{6e,6a}$ −10.5 Hz.

*Derivatives of 1,3:4,6-di-O-butylidene-2-deoxy-*D-arabino-*hexitol.* — (*a*) The diacetal (0.1 g) was acetylated to yield the syrupy 5-acetate.

(*b*) The diacetal (2 g) in pyridine (20 ml) was treated with benzoyl chloride (4 ml) to yield the syrupy 2-deoxy-5-benzoate (2 g) (Found: C, 66.6; H, 7.15. $C_{21}H_{30}O_6$ calc.: C, 66.6; H, 8.0%).

(*c*) The diacetal (0.9 g) in dry *N*,*N*-dimethylformamide (15 ml) was stirred with silver oxide (2.5 g) and methyl iodide (3 ml) for 24 h at room temperature, to yield the syrupy 5-methyl ether (0.5 g), b.p. 172–178°/8 mmHg, *T* 1.37 (relative to Me_3Si-glucitol) (Found: C, 62.3; H, 10.0; OMe, 10.5).

*2-Deoxy-5-*O-*methyl-*D-arabino-*hexitol.* — A solution of 1,3:4,6-di-*O*-butylidene-2-deoxy-5-*O*-methyl-D-*arabino*-hexitol (0.45 g) in ethanol–water (70:30) was boiled under reflux in the presence of Amberlite IR-120 (H^+) resin (25 ml) for 3 h. The resin was filtered off and was washed well with hot methanol. The combined filtrate and washings were evaporated to yield a syrup which showed three spots on t.l.c. The syrup was dissolved in ethyl acetate, and kept at −5°, whereupon syrupy 2-deoxy-5-*O*-methyl-D-*arabino*-hexitol separated (0.1 g), R_F 0.03 (one spot only, solvent *B*). The 5-methyl ether (0.06 g) in pyridine was treated with acetic anhydride to yield the syrupy tetra-acetate (0.075 g) (Found: C, 51.6; H, 6.85; OMe, 8.9. $C_{15}H_{24}O_9$ calc.: C, 51.7; H, 6.9; OMe, 8.9%).

*1-*O-*Benzoyl-2-deoxy-*D-arabino-*hexitol.* — A solution of 5-*O*-benzoyl-1,3:4,6-di-*O*-butylidene-2-deoxy-D-*arabino*-hexitol (1.9 g) in ethanol–water (70:30, 30 ml) was boiled under reflux in the presence of Amberlite IR-120 (H^+) resin (25 ml) for 3 h. The resin was filtered off and washed well with hot ethanol, and the combined filtrate and washings were concentrated. Crystallisation of the residue yielded the title compound, m.p. 161–163.5°, *M* 0.76 (in molybdate buffer[12], relative to 2-deoxy-D-*arabino*-hexitol), R_F 0.68 (solvent *A*) (Found: C, 57.4; H, 6.75. $C_{13}H_{18}O_6$ calc.: C, 57.8; H, 6.7%).

*Periodate oxidation of 1-*O-*benzoyl-2-deoxy-*D-arabino-*hexitol.* — The benzoate (1 mol.) consumed 3.06, 3.30, and 3.30 mol. of periodate (9.57 mol. initially present) after 0.25, 1.33, and 9 h, respectively (calc. 3.0). Due allowance was made for the absorption of the compound (ε at 223 nm, 1270 $m^2 . mol^{-1}$). The oxidation liberated 1.2 mol. of formaldehyde (calc. 1.0) and 2.1 mol. of formic acid (calc. 2.0).

3,4,5,6-Tetra-O-*acetyl-1*-O-*benzoyl-2-deoxy*-D-arabino-*hexitol.* — The 2-deoxy-1-benzoate (0.05 g) in pyridine was treated with acetic anhydride to yield the tetra-acetate (0.05 g), m.p. 69–71° (Found: C, 58.1; H, 5.7. $C_{21}H_{26}H_{10}$ calc.: C, 57.5; H, 6.0%).

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