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ACID-CATALYSED MONOACETALATION OF SOME 2-DEOXYALDITOLS*

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ABSTRACT

Acid-catalysed monobutylidenation of 2-deoxy-D-*arabino*-hexitol, 2-deoxy-D-*lyxo*-hexitol, and 2-deoxy-D-*erythro*-pentitol yielded a 1,3-monoacetal as a kinetic product in each reaction. The thermodynamic products were 4,6-monoacetals from 2-deoxy-D-*arabino*-hexitol and 2-deoxy-D-*lyxo*-hexitol, and a 3,5-monoacetal from 2-deoxy-D-*erythro*-pentitol. 2-Deoxy-D-*lyxo*-hexitol also yielded diastereoisomeric 4,5-monoacetals.

INTRODUCTION

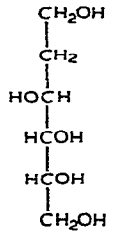
Previous studies of the monobutylidenation of 2-deoxy-D-*arabino*-hexitol postulated the formation of a 1,3-acetal in the kinetic phase and a 3,4-acetal in the thermodynamic phase[1]. This postulation is in contrast with the predictions of the Barker–Bourne rules of acetal formation[2]. The absence of any other detailed, acid-catalysed, monoacetalation studies of non-terminal deoxyalditols prompted a reinvestigation of the original study and an extension to two other non-terminal deoxyalditols.

RESULTS

2-Deoxy-D-*arabino*-hexitol (**1**) reacted with butyraldehyde (equimolar) in aqueous hydrochloric acid to give a product mixture from which three components were isolated, namely, **1**, 1,3-*O*-butylidene-2-deoxy-D-*arabino*-hexitol (**2**) formed in the kinetic phase, and 4,6-*O*-butylidene-2-deoxy-D-*arabino*-hexitol (**3**) formed in the thermodynamic phase.

The reaction was monitored by g.l.c. after trimethylsilylation[3]. Typical chromatograms are shown in Fig. 1, and measurement of peak areas allowed the construction of a plot of concentration versus time (Fig. 2). From this analysis, the initial rate

*Dedicated to Dr. Elizabeth Percival.



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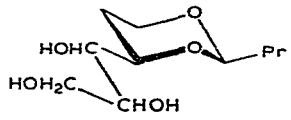

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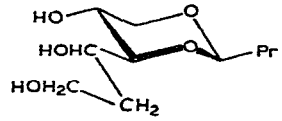

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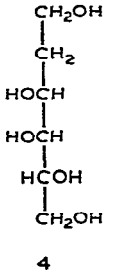
coefficient at 30° for 2-deoxy-D-*arabino*-hexitol was found to be 5.7×10^{-3} l.mol^{-1}.sec^{-1} (*cf.* 5.5×10^{-3} l.mol^{-1}.sec^{-1} at 25° by a spectrophotometric method[1]).

2-Deoxy-D-*lyxo*-hexitol (**4**), when treated with butyraldehyde as described for **1**, gave **4**, 1,3-*O*-butylidene-2-deoxy-D-*lyxo*-hexitol (**5**) formed in the kinetic phase, 4,5-*O*-butylidene-2-deoxy-D-*lyxo*-hexitols (**6**) (thought to be thermodynamic products),



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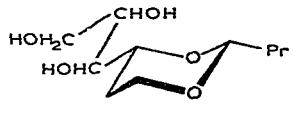

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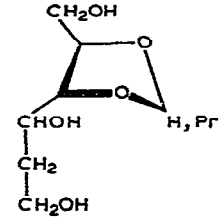

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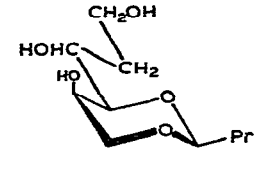

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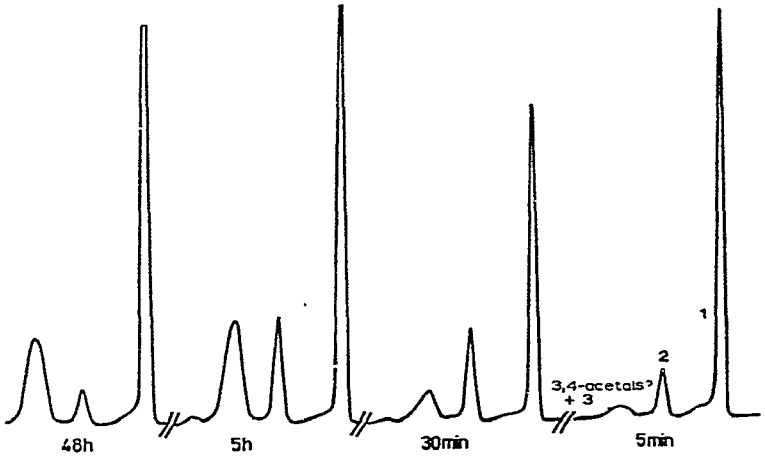


Fig. 1. Chromatograms of products of reaction of butyraldehyde and 2-deoxy-D-*arabino*-hexitol: **1**, 2-deoxy-D-*arabino*-hexitol; **2**, 1,3-acetal; **3**, 4,6-acetal.

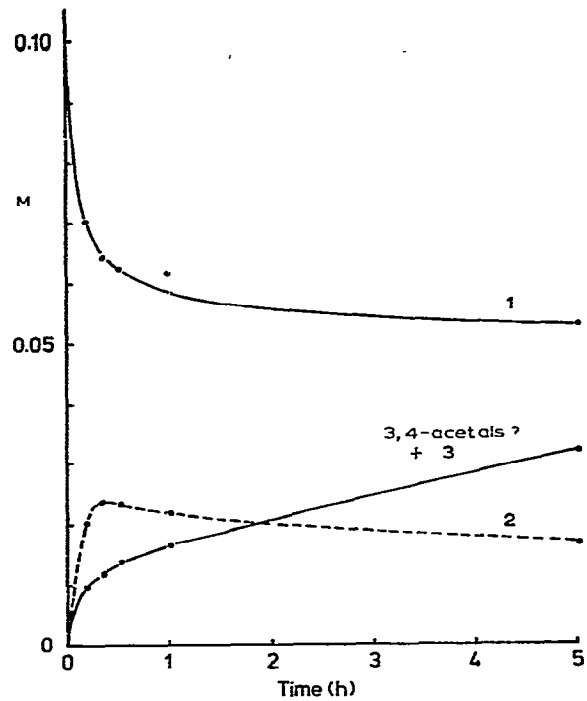
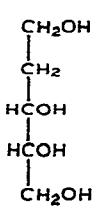


Fig. 2. Concentration (mol.l^{-1}) versus time for 2-deoxy-D-*arabino*-hexitol and its acetals in the reaction with butyraldehyde: **1**, **2**, and **3**, as in Fig. 1.

and 4,6-*O*-butylidene-2-deoxy-D-*lyxo*-hexitol (**7**) also formed in the thermodynamic phase. The chromatograms showed only three peaks, because **6** and **7** had identical retention times, as subsequently established from the properties of the pure products. The initial rate coefficient at 30° for 2-deoxy-D-*lyxo*-hexitol was found to be 5.35×10^{-3} l.mol^{-1}.sec^{-1}.

2-Deoxy-D-*erythro*-pentitol (**8**), when monobutylidenated as described for **1**, gave **8**, 1,3-*O*-butylidene-2-deoxy-D-*erythro*-pentitol (**9**) formed in the kinetic phase, and 3,5-*O*-butylidene-2-deoxy-D-*erythro*-pentitol (**10**) formed in the thermodynamic phase.



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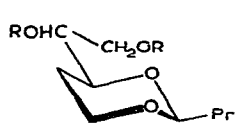

9 R = H
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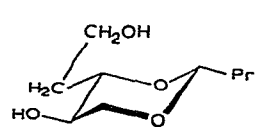

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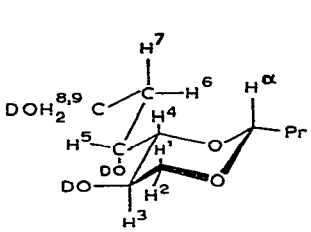

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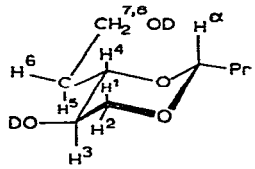

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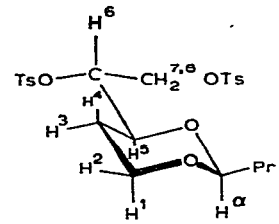

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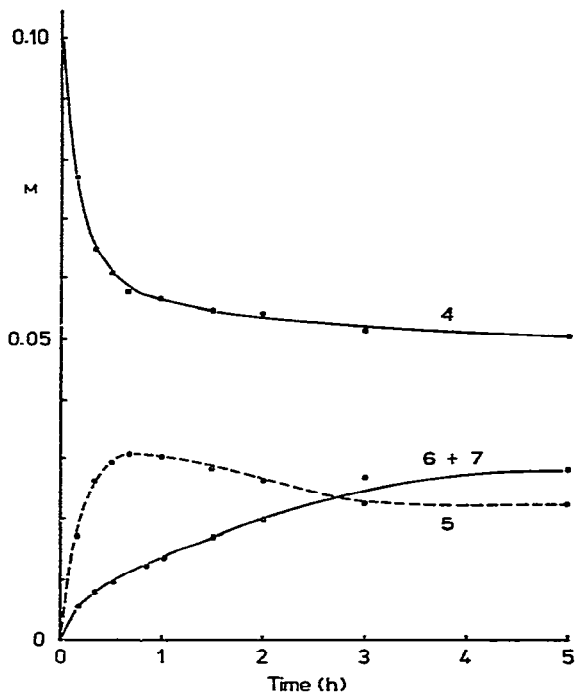

Fig. 3. Concentration (mol.l^{-1}) versus time for 2-deoxy-D-*lyxo*-hexitol and its acetals in the reaction with butyraldehyde: **4**, 2-deoxy-D-*lyxo*-hexitol; **5**, 1,3-acetal; **6**+**7**, 4,5+4,6-acetals.

The structures of the monobutylidene acetals were determined by periodate oxidation in conjunction with n.m.r. spectroscopy. Table I shows the periodate uptake, and the formic acid and formaldehyde liberated per mole of acetal. Information regarding the distribution of the remaining, unsubstituted hydroxyl groups in the acetals is sufficient to make unambiguous assignments of structure for each 1,3-acetal. For the remaining acetals, the information gained from periodate-oxidation experiments narrows the possible structures to three or four.

TABLE I

PERIODATE-OXIDATION RESULTS PER MOLE OF ACETAL

Monobutylidene acetal	*Periodate uptake*	*Formic acid liberated*	*Formaldehyde liberated*	*Possible ring structures*		
2-Deoxy-D-*arabino*-hexitol						
1,3-acetal (2)	2	1	1	1,3		
4,6-acetal (3)	0	0	0	3,5	4,5	4,6
2-Deoxy-D-*lyxo*-hexitol						
1,3-acetal (5)	1.98	0.99	0.98	1,3		
4,5-acetals (6)	0.2	0	0	3,5	4,5	4,6
4,6-acetal (7)	0	0	0	3,5	4,5	4,6
2-Deoxy-D-*erythro*-pentitol						
1,3-acetal (9)	0.97	0	0.92	1,3		
3,5-acetal (10)	0	0	0	1,4 4,5	3,4	3,5

P.m.r. spectroscopy helped to resolve the structural assignments that were unavailable from the periodate-oxidation data, and supported the structure assignments based on such data. Information regarding the size of the acetal ring can be obtained from the chemical shift[4–6] and coupling constant[7] of the acetal proton, *i.e.*, that proton on the carbon atom directly attached to the two ring oxygens. The signals for acetal protons for five-membered rings appear ~0.5 p.p.m. to lower field than those for acetal protons in six-membered rings. The coupling constants of acetal protons in five-membered rings are also smaller than those in the corresponding six-membered rings. Hence, provided that the acetal-proton resonances can be clearly observed, five-membered and six-membered rings can be distinguished. The n.m.r. data in Table II clearly accord with these generalisations.

The hydroxyl-proton resonances are also helpful in structure assignment in this series of acetals, because of the multiplicity shown[8,9] when spectra are recorded for solutions in methyl sulphoxide. For the acetals in Table I where the periodate-oxidation data were inconclusive, the p.m.r. data in Table II for hydroxyl- and acetal-proton resonances allowed the structures to be assigned. For example, the non-consumption of periodate by 4,6-*O*-butylidene-2-deoxy-D-*arabino*-hexitol (3) indicated a 3,5, 4,5, or 4,6 acetal. The acetal proton has δ 4.43 and J 5.1 Hz, indicating a six-membered ring. The presence of one primary and two secondary hydroxyl groups was also detected. Only a 4,6-acetal structure is consistent with these facts.

The six-membered ring acetals are depicted with the carbon atoms of the alditol in a planar zig-zag conformation. Evidence for these conformations comes from detailed analysis of the p.m.r. spectra of the acetals and their derivatives in conjunction with computer simulation[10] of the spectra. The coupling constants (Table III) obtained by computer simulation for three acetals are consistent with a planar zig-zag conformation for the carbon backbone of the alditol and a fixed chair

TABLE II

220-MHz P.M.R. DATA FOR ACETAL- AND HYDROXYL-PROTON RESONANCES IN Me_2SO-d_6

Monobutylidene acetal	*Acetal H* δ (J)	$J_{H,OH}$ (*Hz*)			*Possible structure on the basis of p.m.r. and periodate data*
2-Deoxy-D-*arabino*-hexitol					
1,3-acetal (2)	4.53 (5.0 Hz)	5.3[a]	7.5[b]	5.5[b]	
4,6-acetal (3)	4.43 (5.1 Hz)	5.1[a]	6.0[b]	7.2[b]	4,6
2-Deoxy-D-*lyxo*-hexitol					
1,3-acetal (5)	4.47 (5.0 Hz)	6.0[a]	6.4[b]	7.8[b]	
4,5-acetals (6)	4.95 (4.6 Hz)	5.0[a]	?	?	4,5
4,6-acetal (7)	4.50 (5.2 Hz)	5.3[a]	6.1[b]	6.8[b]	4,6
2-Deoxy-D-*erythro*-pentitol					
1,3-acetal (9)	4.47 (5.5 Hz)	5.6[a]	5.1[b]	—	
3,5-acetal (10)	4.43 (5.1 Hz)	5.1[a]	5.2[b]	—	3,5

[a]Primary hydroxyl. [b]Secondary hydroxyl.

conformation of the acetal ring. The substituents on the acetal ring are such that one would not expect interconversion[11–14]. As the carbon backbone of the parent deoxyalditols would be expected to adopt a planar zig-zag conformation in the absence of any parallel 1,3-interactions[15–21], it seems that acetalation causes no modification of this conformation. The five-membered ring of 4,5-*O*-butylidene-2-deoxy-D-*lyxo*-hexitol (6) is depicted as an envelope conformation, but interconversion with twist-chair and other envelope conformers is possible[22].

DISCUSSION

There are no reported monoacetals of 2-deoxy-D-*lyxo*-hexitol. 2-Deoxy-D-*erythro*-pentitol yielded a monobenzylidene acetal[23] (26%), of unknown structure, by direct reaction. A previous monobutylidenation study[1] of 2-deoxy-D-*arabino*-hexitol assigned the product of the kinetic phase as the 1,3-acetal. The syrupy thermodynamic product was concluded to be mainly the 3,4-acetal(s). The present work confirms that the product of the kinetic phase is the 1,3-acetal, but the thermodynamic phase yielded the 1,3- and 4,6-acetals (total yield, 7%). G.l.c. indicated that, at equilibrium, there was ~50% of unchanged alditol. Therefore, there was considerable loss on work-up. Similar losses also occurred in the other two 2-deoxyalditol systems studied. The previously postulated thermodynamic product, *i.e.*, the 3,4-acetals, was not isolated in the present study, although there is evidence for the existence of the

TABLE III

COUPLING CONSTANTS (Hz) FOR SOME SIX-MEMBERED CYCLIC ACETALS

Acetal	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$	$J_{6,8}$	$J_{7,8}$	$J_{7,9}$	$J_{8,9}$
4,6-*O*-Butylidene-2-deoxy-D-*arabino*-hexitol (3)[a]	−10.3	10.3	0	5.5	0	9.1	0	1.5	0	9.0	4.5	−14.2	6.6	6.6	6.6[d]	−11.0
3,5-*O*-Butylidene-2-deoxy-D-*erythro*-pentitol (10)[a]	−10.9	10.1	0	5.1	0	8.9	0	8.9	3.1	−14.2	5.0[c]	5.0	11.0	−11.0	—	—
1,3-*O*-Butylidene-2-deoxy-4,5-di-*O*-toluene-*p*-sulphonyl-D-*erythro*-pentitol (11)[b]	−11.6	2.8	12.7	1.75	5.1	−12.0	2.8	12.2	0	6.8	0	3.7[e]		?	—	—

[a]Run in Me_2SO-d_6. [b]Run in C_5D_5N. [c]$J_{5,8}$ 5.0 Hz. [d]Average values; $J_{6,9}$ 6.6 Hz. [e]$J_{6,7} + J_{6,8}$.

3,4-acetals from the polarimetric study (Fig. 4). This study indicates the presence, at reaction equilibrium, of an acetal having a high, positive optical rotation. The structurally similar 3,4-acetal of D-glucitol[24] has $[\alpha]_D$ +37°.

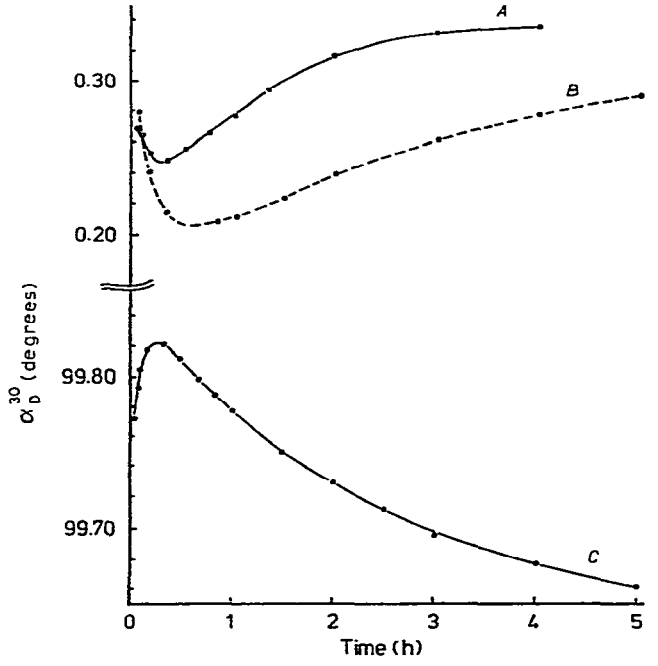

Fig. 4. Plot of α_D^{30} versus time for the reactions between butyraldehyde and some 2-deoxyalditols: *A*, 2-deoxy-D-*arabino*-hexitol+acetals; *B*, 2-deoxy-D-*lyxo*-hexitol+acetals; *C*, 2-deoxy-D-*erythro*-pentitol+acetals.

The shapes of the rotation *vs.* time curves (Fig. 4) for the other two systems studied qualitatively fit the observed rotations of the main components present. For 2-deoxy-D-*lyxo*-hexitol[25], $[\alpha]_D$ +18°, a decrease in rotation occurs during the formation of the 1,3-acetal, $[\alpha]_D$ −12.2°, followed by an increase in rotation as the concentrations of the 4,6-acetal, $[\alpha]_D$ −7.3°, and 4,5-acetals, $[\alpha]_D$ +80.5°, build up. The formation of the 4,5-acetals parallels the formation of such α-*threo* acetals by galactitol[26] and 1-deoxy-D-galactitol[27]. Reaction of 2-deoxy-D-*erythro*-pentitol[28], $[\alpha]_D$ −21°, to yield first the 1,3-acetal, $[\alpha]_D$ +2.8°, causes a rise in rotation, followed by a fall as the 3,5-acetal, $[\alpha]_D$ −57.6°, forms.

Each of the three 2-deoxyalditols gave a kinetic phase, with the acetal having a β-ring carrying no hydroxyl group at C-5 of the dioxane ring as the main product. The 2-deoxy group should enhance the nucleophilicity of O-1 and O-3, and so enhance the rate of acetal formation thereat. The thermodynamic phase in each reaction gave an acetal that had a β-ring with a hydroxyl group at C-5 of the dioxane

ring. Why this unexpected differentiation takes place between β-ring systems is not fully understood.

EXPERIMENTAL

Techniques. — G.l.c. was performed on a Pye-104 instrument with 10% P.P.E. as stationary phase at 163° and 140°, respectively, for 2-deoxy-D-*arabino*-hexitol and 2-deoxy-D-*erythro*-pentitol. For 2-deoxy-D-*lyxo*-hexitol, the stationary phase was 7.5% Apiezon K at 170°. Compounds were injected as their trimethylsilyl ethers in pyridine solution. T.l.c. was performed on Polygram Sil G (Camlab, Cambridge) with butanone saturated with water. Quantitative periodate oxidations and determinations of formic acid and formaldehyde were effected by standard procedures. P.m.r. spectra were recorded by using a Varian HR-220 instrument and solutions in Me_2SO-d_6 alone or admixed with D_2O (internal Me_4Si). The spectrum of 1,3-*O*-butylidene-2-deoxy-4,5-di-*O*-toluene-*p*-sulphonyl-D-*erythro*-pentitol was obtained for a solution in C_5D_5N. 2-Deoxy-D-*arabino*-hexitol, 2-deoxy-D-*lyxo*-hexitol, and 2-deoxy-D-*erythro*-pentitol were prepared by reduction of the commercially available 2-deoxyaldoses with sodium borohydride. Melting points were measured on a Thomas Hoover or Gallenkamp instrument, and are uncorrected. Computer simulation of n.m.r. spectra was performed by using the UEA NMR BASIC and UEA NMR ITERATIVE programmes[29] on the University of London CDC 1700 and CDC 6600 computers, respectively.

Preparation of 1,3- (**2**) *and 4,6-*O*-butylidene-2-deoxy-*D-arabino-*hexitols* (**3**). — A solution of 2-deoxy-D-*arabino*-hexitol[1] (9.15 g) in 0.5M hydrochloric acid (550 ml) was shaken with freshly distilled butyraldehyde (3.97 g). The mixture was left at room temperature for 48 h. neutralised with 4M sodium hydroxide, and then concentrated *in vacuo* to a paste. The organic fraction was extracted with hot ethanol. The extract was filtered, concentrated to a small volume, introduced onto a column of alumina (active, neutral, 1000 g), and eluted with ethanol–water (9:1). T.l.c. of the fractions showed that the two monoacetals had eluted together free from starting material. The monoacetals were fractionated on a column of Dowex 1-X8(HO^-) resin[26] (300 ml) by elution with CO_2-free, deionised water. T.l.c. showed **2** (0.2 g) to have been eluted first, as a chromatographically homogeneous syrup (R_F 0.54) that slowly crystallised; when recrystallised from ethyl acetate, **2** had m.p. and mixture m.p. 61.5–63.5°; lit.[1] m.p. 61.5–63.5°.

Later column fractions gave a syrup (0.66 g) that crystallised from hot ethyl acetate, to give **3**, R_F 0.60, m.p. 89–91°, $[\alpha]_D^{25}$ −12.5° (*c* 0.79, water).

Anal. Calc. for $C_{10}H_{20}O_5$: C, 54.52; H, 9.15. Found: C, 54.50; H, 8.98.

*1,3-*O*-Butylidene-2-deoxy-*D-lyxo-*hexitol* (**5**). — A solution of 2-deoxy-D-*lyxo*-hexitol[25] (3.23 g) in 0.5M hydrochloric acid (195 ml) was shaken with butyraldehyde (1.40 g) and then left at room temperature for 30 min. The organic phase was neutralised, concentrated, and extracted with ethanol as described above. The extract yielded a syrup that slowly crystallised and was then extracted with hot chloroform

(2 × 100 ml). Concentration of the extract gave a syrup that contained (t.l.c.) two monoacetals which were fractionated on a column (100 ml) of Dowex 1-X8(HO^-) resin as described above. The major monoacetal, eluted first, was recrystallised from chloroform–light petroleum (b.p. 60–80°) (1:3) to give **5** (0.09 g), m.p. 60–61°, $[\alpha]_D^{27.5}$ −12° (*c* 0.9, methanol), R_F 0.47.

Anal. Calc. for $C_{10}H_{20}O_5$: C, 54.52; H, 9.15. Found: C, 54.63; H, 9.26.

Preparation of 4,5- (**6**) *and 4,6-*O*-butylidene-2-deoxy-*D-lyxo-*hexitols* (**7**). — 2-Deoxy-D-*lyxo*-hexitol (3.32 g), 0.5M hydrochloric acid (200 ml), and butyraldehyde (1.44 g) were reacted together as described for 2-deoxy-D-*arabino*-hexitol. Fractionation of the product on Dowex 1-X8 (HO^-) resin, with recrystallisation from ethyl acetate of the product eluted first, gave **7** (0.12 g), m.p. 90–91.5°, $[\alpha]_D^{20}$ −7° (*c* 0.78, water), R_F 0.41.

Anal. Calc. for $C_{10}H_{20}O_5$: C, 54.52; H, 9.15. Found: C, 54.2; H, 9.25.

Recrystallisation from chloroform of the monoacetal eluted second gave **6** (0.2 g), m.p. of diastereoisomeric mixtures from three different preparations 76–77°, 78–79°, and 86–87°, $[\alpha]_D^{20}$ +80.5° (*c* 0.8, material of m.p. 78–79°, water), R_F 0.47.

Anal. Found: C, 54.25; H, 9.15 (for material of m.p. 78–79°).

Preparation of 1,3- (**9**) *and 3,5-*O*-butylidene-2-deoxy-*D-erythro-*pentitols* (**10**). — By using a procedure identical to that described for 2-deoxy-D-*arabino*-hexitol, 2-deoxy-D-*erythro*-pentitol[28,30] (18.25 g) was treated with hydrochloric acid (1325 ml) and butyraldehyde (9.5 g). Fractionation of the product mixture on alumina gave, first, **10** (4.7 g), m.p. 84–85° (from ethyl acetate), $[\alpha]_D^{20}$ −58° (*c* 0.84, water), R_F 0.81.

Anal. Calc. for $C_9H_{18}O_4$: C, 56.82; H, 9.54. Found: C, 56.98; H, 9.60.

Eluted second was syrupy, chromatographically homogeneous **9** (2.73 g), $[\alpha]_D^{27.5}$ +3° (*c* 1.25, methanol), R_F 0.70.

Anal. Found: C, 54.38; H, 9.27.

The 4,5-ditoluene-*p*-sulphonate (**11**) of **9**, prepared conventionally (65%), had m.p. 120–121° (from ethanol).

Anal. Calc. for $C_{23}H_{30}O_8S_2$: C, 55.40; H, 6.07; S, 12.86. Found: C, 55.12; H, 6.09; S, 12.24.

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