985. *Aspects of Stereochemistry. Part VIII.* Determination of the Configuration at the Benzylidene Acetal Carbon Atoms in* 4,6-O-*Benzylidene*-D-*glucose and* 1,3-O-*Benzylidene*-L-*arabinitol by Nuclear Magnetic Resonance Spectroscopy.*

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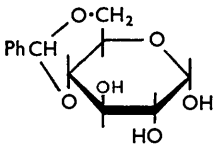
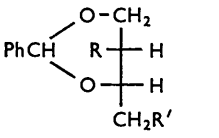
4,6-*O*-Benzylidene-D-glucose and 1,3-*O*-benzylidene-L-arabinitol have been degraded to 1,3-*O*-benzylidene-L-erythritol and 1,3-*O*-benzylidene-L-threitol, respectively. It has been shown that the latter two compounds differ only in the configuration at $C_{(2)}$. From the nuclear magnetic resonance spectra of the acetates of the tetritol derivatives and of related compounds the configuration of the phenyl group relative to the other substituents of the 1,3-dioxan rings has been deduced.

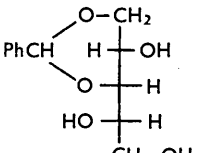
In the reaction of aldehydes, other than formaldehyde, with polyhydric alcohols to yield cyclic acetals, the formation of diastereoisomers is theoretically possible. Since the acid-catalysed reaction which yields cyclic acetals is reversible,[1] the products formed should be those of greatest thermodynamic stability. When five-membered cyclic acetals (1,3-dioxolan derivatives) are produced there is no reason to expect *a priori* the preferential formation of one diastereoisomer and various pairs of diastereoisomers are known.[2] A different situation exists when six-membered cyclic acetals (1,3-dioxan derivatives) are formed. If, as is probable, the 1,3-dioxan ring assumes a chair conformation,[1] then the diastereoisomers will have respectively an equatorial and an axial substituent at the acetal carbon atom. Because of adverse non-bonded interactions, the latter configuration will be relatively unstable and it has been predicted [3] that such a diastereoisomer is unlikely to be formed. Certain benzylidene derivatives described in the literature,[4] which were



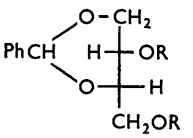
(I)



(II) R = R′ = OH
(III) R = OH, R′ = H
(IV) R = R′ = AcO
(V) R = R′ = BzO



(VI)



(VII) R = H
(VIII) R = Ac
(IX) R = Me·SO$_2$

considered to be examples of diastereoisomers, have been shown to be dimorphs.[2] There is no substantiated example of the formation of diastereoisomers in the reaction of benzaldehyde with tetritols and higher polyhydric alcohols to yield six-membered cyclic acetals. Moreover, in no case has experimental evidence been recorded which would indicate the configuration of the benzylidene acetal carbon atoms. The 5-hydroxy-2-phenyl-1,3-dioxans [5] (1,3-*O*-benzylideneglycerols) and their *p*-nitrophenyl analogues [6] are anomalous in that they may be considered as diastereoisomeric at $C_{(2)}$ or $C_{(5)}$. We now record direct experimental evidence of the configuration at the benzylidene acetal carbon atoms in 4,6-*O*-benzylidene-D-glucose and 1,3-*O*-benzylidene-L-arabinitol.

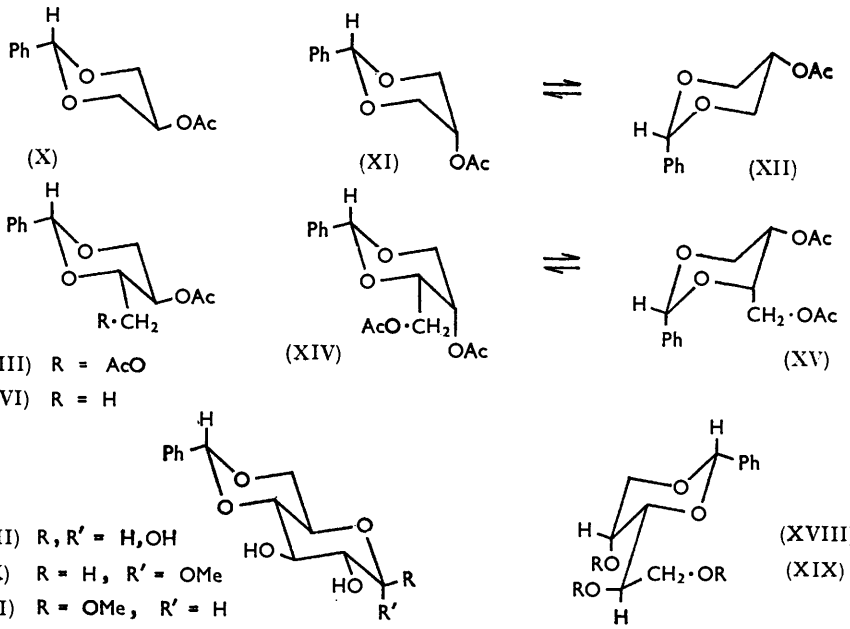
* Part VII, *J.*, 1961, 3633.

[1] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.
[2] Dobinson, Foster, and Stacey, *Tetrahedron Letters*, 1959, No. 1, p. 1.
[3] Angyal and Mills, *Rev. Pure Appl. Chem.* (*Australia*), 1952, **2**, 185.
[4] Fischer, *Annalen*, 1892, **270**, 64; *Ber.*, 1894, **27**, 1524; Hann, Ness, and Hudson, *J. Amer. Chem. Soc.*, 1946, **68**, 1769; Ness, Hann, and Hudson, *ibid.*, 1948, **70**, 765.
[5] Baggett, Brimacombe, Foster, Stacey, and Whiffen, *J.*, 1960, 2574.
[6] Dobinson and Foster, *J.*, 1961, 2338.

4,6-*O*-Benzylidene-D-glucose (I), the structure of which other than at the acetal carbon atom has been proved,[7] was oxidised with sodium metaperiodate and the resultant 2,4-*O*-benzylidene-D-erythrose[8] was smoothly reduced with sodium borohydride to 1,3-*O*-benzylidene-L-erythritol (II). The diol (II) gave a crystalline di-*O*-acetate, di-*O*-benzoate, and di-*O*-toluene-*p*-sulphonate; the di-*O*-methanesulphonate was amorphous. Reduction of the di-*O*-toluene-*p*-sulphonate with lithium aluminium hydride afforded 1,3-*O*-benzylidene-4-deoxy-L-erythritol (III).

In the presence of acid, D-arabinitol reacts[9] with benzaldehyde to yield a 1,3-*O*-benzylidene derivative (m. p. 151—152°, $[\alpha]_D$ −7·6° in pyridine), for which the location of the cyclic acetal residue has been fully proved.[9] We have used the corresponding derivative (VI) (m. p. 149—151°, $[\alpha]_D$ +7·2° in pyridine) of L-arabinitol the structure of which is confirmed by the physical constants. Application, in sequence, of periodate oxidation and borohydride reduction to 1,3-*O*-benzylidene-L-arabinitol, afforded 1,3-*O*-benzylidene-L-threitol (VII) which gave a crystalline di-*O*-toluene-*p*-sulphonate, di-*O*-methanesulphonate, and di-*O*-acetate. Reduction of the dimethanesulphonate with lithium aluminium hydride yielded 1,3-*O*-benzylidene-L-threitol as the only identifiable product. Under similar conditions the analogous di-*O*-toluene-*p*-sulphonate afforded only a small yield of a product tentatively identified as 1,3-*O*-benzylidene-4-deoxy-L-threitol which was isolated by way of the *p*-phenylazobenzoate.

The structural relationship of 1,3-*O*-benzylidene-L-threitol (VII) and 1,3-*O*-benzylidene-L-erythritol (II) was shown by the conversion of the di-*O*-methanesulphonate (IX) of the former compound into the di-*O*-benzoate (V) of the latter by treatment with sodium



benzoate in dimethylformamide. The nucleophilic displacement of a sulphonyloxy-group by this reagent was first described by Reist *et al.*,[10] who converted methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-toluene-*p*-sulphonyl-α-D-galactopyranoside into methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside. Methanesulphonyloxy-groups are displaced with equal

[7] Freudenberg, Toepffer, and Andersen, *Ber.*, 1928, **61**, 1750.
[8] MacDonald, Fischer, and Ballou, *J. Amer. Chem. Soc.*, 1956, **78**, 3720; Sowden, *ibid.*, 1950, **72**, 808.
[9] Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 1663.
[10] Reist, Spencer, and Baker, *J. Org. Chem.*, 1959, **24**, 1618.

facility: for example, *cis*- and *trans*-5-methanesulphonyloxy-2-phenyl-1,3-dioxan are converted, respectively, into *trans*- and *cis*-5-benzoyloxy-2-phenyl-1,3-dioxan.[11] Thus 1,3-*O*-benzylidene-L-threitol and 1,3-*O*-benzylidene-L-erythritol differ only in the configuration at $C_{(2)}$. The location of the cyclic acetal residue and the stereochemistry of the tetritol moiety ensure that the 2-hydroxyl group and the hydroxymethyl group in 1,3-*O*-benzylidene-L-erythritol are *trans*-substituents in the 1,3-dioxan ring and likewise the corresponding groups in 1,3-*O*-benzylidene-L-threitol are *cis*-disposed. The configuration of the phenyl group at the acetal carbon atom relative to the other substituents of the 1,3-dioxan rings in these compounds may be deduced from the proton magnetic resonance spectra of their acetates and of related compounds, the relevant signals for which are recorded in the Table. A full analysis of the spectra of these compounds is reserved for a separate communication. A preliminary report has been made.[12]

It has been found[12] that *trans*-5-acetoxy-2-phenyl-1,3-dioxan (1,3-*O*-benzylideneglycerol) gave a type *X* * proton magnetic resonance spectrum showing a complex coupling pattern for the ring protons indicative of molecular rigidity and existence in conformation (X). The ring substituents may therefore be assigned to definite equatorial or axial positions. The *cis*-isomer, however, gave a simpler, type *Y* * spectrum which contained a single broad absorption for the protons at positions 4 and 6, indicating conformational instability and a relatively rapid interconversion between different conformations. The ring substituents therefore cannot be assigned to specific axial or equatorial positions but must occupy an average or intermediate position. The interconversion has, for convenience, been represented by the formulæ (XI) ⇌ (XII) although it is recognised that the extreme positions in the interconversion may not necessarily involve the perfect

Selected shielding values from the nuclear magnetic resonance spectra of certain 1,3-dioxan derivatives.

Compound	Spectrum type	Conformn.	Shielding value [a] A	B	C
trans-5-Acetoxy-2-phenyl-1,3-dioxan	*X*	(X)	4·61	8·00	
2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol	*X*	(XIII)	4·54	7·97	7·97
2-*O*-Acetyl-1,3-*O*-benzylidene-4-deoxy-L-erythritol	*X*	(XVI)	4·56	7·99	
Me 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside	*X*	(XX)	4·54		7·97 (2)
Me 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside	*X*	(XXI)	4·54		7·97 (2)
cis-5-Acetoxy-2-phenyl-1,3-dioxan	*Y*	(XI) ⇌ (XII)	4·51	7·88	
2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-threitol	*Y*	(XIV) ⇌ (XV)	4·47	7·90	7·99
2,4,5-Tri-*O*-acetyl-1,3-*O*-benzylidene-L-arabinitol	*Y*	(XIX) [b]	4·45	7·91	7·98 (2)

[a] A, proton at benzylidene acetal carbon atom; B, acetyl protons in CH_3·CO·O groups attached to dioxan ring; C, protons in side chain and other acetyl group(s). Relative intensity in parentheses if other than unity. [b] Only one conformation is shown although the molecule is conformationally unstable.

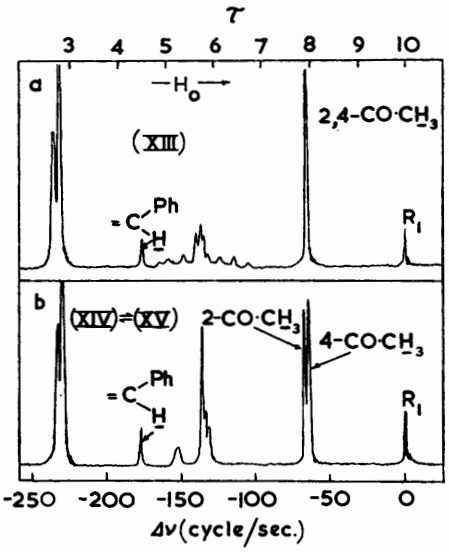
chair forms shown. Non-bonded interactions may cause deformation of the perfect chair forms but the extent is difficult to assess. For *trans*-5-acetoxy-2-phenyl-1,3-dioxan (X) the shielding value (τ 4·61) for the axial proton on the acetal carbon atom was higher than that (τ 4·51) for the corresponding proton in the *cis*-isomer (XI) ⇌ (XII), which is intermediate between axial and equatorial. Further, the equatorial acetyl group in the *trans*-isomer (X) had a higher shielding value (τ 8·00) for the protons than that (τ 7·88) for the protons of the acetyl group in the *cis*-isomer which again must be intermediate between

* The terms type *X* and *Y* have been introduced[12] solely for convenience of discussion. It is not intended that they should be of general application.

[11] Bukhari, Foster, and Lehmann, unpublished results.
[12] Baggett, Dobinson, Foster, Homer, and Thomas, *Chem. and Ind.*, 1961, 106.

axial and equatorial. These observations are consistent with those recorded by Lemieux *et al.*[13] for certain acetylated pyranose sugar derivatives.

2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (IV) gave a type *X* spectrum (see Figure) with a complex coupling pattern (τ 5—7) indicative of molecular rigidity, whereas the L-threitol isomer (VIII) gave a type *Y* spectrum (see Figure) suggestive of conformational instability. By analogy with the results for the 5-acetoxy-2-phenyl-1,3-dioxans, the proton on the benzylidene acetal carbon atom in 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (IV) may be assigned an axial position since its shielding value (τ 4·54) is higher than that (τ 4·47) for the corresponding proton in the conformationally unstable L-threitol analogue (VIII). Hence, the phenyl group in the L-erythritol derivative (IV) must be equatorial. Further, the L-erythritol compound (IV) gave a single peak (τ 7·97) for both the groups of acetyl protons. That the acetoxy-group in this derivative (IV) (and hence the acetoxymethyl group also) is equatorial to the 1,3-dioxan ring is suggested by the similarity of the shielding value (τ 7·97) for its protons to that (τ 8·00) for the acetyl protons in *trans*-5-acetoxy-2-phenyl-1,3-dioxan (X) which has the



Nuclear magnetic resonance spectra of (a) 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (type X) and (b) 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-threitol (type Y).

acetoxyl group equatorial. 2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-threitol (VIII) gave two peaks (τ 7·90 and 7·99) for the two groups of acetyl protons. The absorption at τ 7·90 corresponds well with that (τ 7·88) for the acetyl protons in *cis*-5-acetoxy-2-phenyl-1,3-dioxan (XI) $\rightleftharpoons$ (XII) and hence may be assigned to the protons in the 2-acetyl group in the conformationally unstable L-threitol derivative (VIII). Since the shielding value (τ 7·97) for the 2-acetyl protons in 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (IV) is higher than that (τ 7·90) for the protons in the corresponding acetyl group in the L-threitol analogue (VIII) the equatorial location of the former acetyl group is substantiated. The shielding values (τ 7·99, 7·97 respectively) for the acetyl protons in the acetoxymethyl groups in 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (IV) and the L-threitol analogue (VIII) are similar. Since the former cyclic acetal is a rigid molecule and the latter is conformationally unstable the signal for the acetyl protons in the acetoxymethyl group appears to be independent of the conformation of the 1,3-dioxan ring.

It follows that if the 2-acetoxy-group in 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol is equatorial, then the acetoxymethyl group is also equatorial and since the phenyl group is similarly located the structure of the cyclic acetal is completely defined by formula

[13] Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

(XIII). Further, since it has been shown that 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol (IV) and its L-threitol analogue differ only in the configuration at $C_{(2)}$, the latter compound must have the structure represented by the equilibrium (XIV) $\rightleftharpoons$ (XV).

Replacement of the acetoxymethyl group in the L-erythritol compound (XIII) by methyl to give 2-*O*-acetyl-1,3-*O*-benzylidene-4-deoxy-L-erythritol (XVI) does not affect significantly the shielding values for the proton on the benzylidene acetal carbon atom and for the 2-acetyl protons.

Since 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol has the structure (XIII), the configuration of the parent compound, 4,6-*O*-benzylidene-D-glucose, may be defined as in formula (XVII) which contains a *trans*-decalin type ring system with the phenyl group equatorial to the 1,3-dioxan ring. This is the predicted [3] structure. It is noteworthy that 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol and methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α- and -β-D-glucopyranoside exhibit the same shielding value (τ 4·54) for the protons at the benzylidene acetal carbon atoms and for the acetyl protons (τ 7·97). The structures (XX) and (XXI) may therefore be allocated to the glucosides.

2,4,5-Tri-*O*-acetyl-1,3-*O*-benzylidene-L-arabinitol (XIX) also gave a type *Y* spectrum indicative of conformational instability. There is a close correspondence (see Table) between the shielding values for the protons on the benzylidene acetal carbon atoms and for the various groups of acetyl protons in the L-arabinitol derivative (XIX) and in 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-threitol (XIV) $\rightleftharpoons$ (XV). The shielding value at τ 7·98 for the former compound was twice the intensity of that at τ 7·99 in the latter since it arises from both the side-chain acetyl groups. The larger side chain in the former compound than in the latter is not sufficient to confer molecular rigidity. Although 2,4,5-tri-*O*-acetyl-1,3-*O*-benzylidene-L-arabinitol is conformationally unstable it is possible that this is not the case for the parent compound 1,3-*O*-benzylidene-L-arabinitol. The reaction of L-arabinitol with benzaldehyde to yield a 1,3- but not a 3,5-*O*-benzylidene derivative has been attributed [5,14] to an intramolecular hydrogen-bonding effect which would be operative only in the conformation (XVIII).

Experimental

1,3-O-*Benzylidene-L-erythritol.*—4,6-*O*-Benzylidene-D-glucose [7] (40 g.) was oxidised with periodate, and the product reduced with sodium borohydride by essentially the method of MacDonald *et al.*[8] After destruction of the excess of borohydride with acetic acid, the neutral solution was added to a column (3 × 20 cm.) of Ultrasorb,[15] and inorganic material was eluted with water. Subsequent elution with aqueous alcohol (1 : 4 v/v), concentration of the eluate, and recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave 1,3-*O*-benzylidene-L-erythritol (22·5 g., 75%), m. p. 135—137° $[\alpha]_D$ −14° (*c* 0·5 in $CHCl_3$), $[M]$ −29°, $[\alpha]_D$ −41° (*c* 0·8 in MeOH), $[M]_D$ −86°. MacDonald *et al.*[8] record m. p. 135—136°, $[\alpha]_D$ −43° in MeOH.

Sulphonylation of the product in the usual way gave 1,3-O-*benzylidene*-2,4-*di*-O-*toluene*-p-*sulphonyl*-L-*erythritol*, m. p. 184° (decomp.) (from benzene–chloroform), $[\alpha]_D$ −49° (*c* 1·0 in $CHCl_3$), $[M]_D$ −210° (Found: C, 57·7; H, 5·0; S, 12·4. $C_{25}H_{26}O_8S_2$ requires C, 57·9; H, 5·05; S, 12·4%). The *di*-O-*methanesulphonate* was amorphous (Found: C, 42·6; H, 4·9; S, 18·0. $C_{13}H_{18}O_8S_2$ requires C, 42·6; H, 5·0; S, 17·5%).

Likewise acylation in the usual manner gave 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol,[16] m. p. 81—83·5°, $[\alpha]_D$ −40° (*c* 0·27 in $CHCl_3$), $[M]_D$ −118°, and 2,4-*di*-O-*benzoyl*-1,3-O-*benzylidene*-L-*erythritol* (33%), m. p. 84—85°, $[\alpha]_{5461}$ −89° (*c* 0·5 in $CHCl_3$), $[M]_{5461}$ −372° (Found: C, 71·75; H, 5·3. $C_{25}H_{22}O_6$ requires C, 71·7; H, 5·3%).

1,3-O-*Benzylidene*-4-*deoxy*-L-*erythritol.*—A suspension of 1,3-*O*-benzylidene-2,4-di-*O*-toluene-*p*-sulphonyl-L-erythritol (24 g.) in tetrahydrofuran (150 ml.) was treated slowly with a slurry of lithium aluminium hydride (9 g.) in tetrahydrofuran (50 ml.), and the mixture was boiled under reflux for 10 hr. A further amount (2 g.) of reductant was added and heating

[14] Brimacombe, Foster, and Stacey, *Chem. and Ind.*, 1958, 1228.
[15] Hughes and Whelan, *Chem. and Ind.*, 1958, 884.
[16] Foster, Haines, and Lehmann, *J.*, 1961, 5011.

was continued for a further 50 hr. The cooled mixture was diluted with ether (200 ml.), the excess of reductant was decomposed with ethyl acetate, and subsequently the alcoholates by addition of water (15—20 ml.). Insoluble inorganic material was collected and washed with ether, and the combined and dried (Na_2SO_4) filtrate and washings were concentrated. The oily residue crystallised from ether–light petroleum (b. p. 40—60°), to yield 1,3-O-*benzylidene*-4-*deoxy*-L-*erythritol* (5·2 g., 58%), m. p. 84—85°, $[\alpha]_D^{18}$ −18° (*c* 1·0 in $CHCl_3$), $[M]_D$ −35° (Found: C, 68·25; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%). Acetylation in the usual manner gave the O-*acetate* (74%), m. p. 51—52°, $[\alpha]_{5461}$ −50° (*c* 0·1 in $CHCl_3$), $[M]_{5461}$ −118° (Found: C, 66·85; H, 7·1. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

1,3-O-*Benzylidene*-L-*arabinitol*.—A rapid stream of hydrogen chloride was passed for 20 min. into a mixture of L-arabinitol (1·5 g.) and benzaldehyde (1·0 g.), and the mixture was stored at room temperature overnight. The hydrogen chloride was then removed as far as possible at room temperature and 0·1 mm. and final traces were removed by storage *in vacuo* over P_2O_5 and KOH. The residue was dissolved in aqueous ammonia containing sodium carbonate (0·5 g.), and the solution was extracted with light petroleum (b. p. 60—80°) to remove benzaldehyde. The product (1·66 g., 66%; m. p. 131—136°) which separated on concentration of the aqueous solution recrystallised from ethanol containing a trace of ammonia to yield 1,3-*O*-benzylidene-L-arabinitol (0·86 g.) m. p. 149—151°, $[\alpha]_D$ +7·2° (*c* 1·38 in pyridine). A further amount (0·25 g., m. p. 147—150°) was obtained from the mother liquor. Haskins *et al.*[9] record m. p. 151—152° and $[\alpha]_D$ −7·6° in pyridine for the D-isomer.

The product was readily converted by the conventional method into 2,4,5-*tri*-O-*acetyl*-1,3-O-*benzylidene*-L-*arabinitol*, m. p. 123—125°, $[\alpha]_D$ +24° (*c* 1·04 in $CHCl_3$), $[M]_D$ +88° (Found: C, 58·9; H, 6·0. $C_{18}H_{22}O_8$ requires C, 59·0; H, 6·1%).

1,3-O-*Benzylidene*-L-*threitol*.—A solution of 1,3-*O*-benzylidene-L-arabinitol (1·1 g.), sodium metaperiodate (1·1 g., 1·1 mol.) and sodium hydrogen carbonate (0·3 g.) in water was stored at room temperature for 2 hr. The solution was then extracted continuously with chloroform overnight, the extract was concentrated, yielding a syrupy residue which was dissolved in aqueous ethanol and treated with sodium borohydride (0·4 g.). After 2 hr. the solution was extracted with chloroform (6 × 30 ml.), and the extract was dried (Na_2SO_4) and concentrated. The residue (m. p. 123—127°) recrystallised from ethyl acetate–light petroleum (b. p. 60—80°), to yield 1,3-O-*benzylidene*-L-*threitol* (0·45 g.), m. p. 133—134°, $[\alpha]_D$ +8° (*c* 1·2 in pyridine), $[M]_D$ +17° (Found: C, 62·85; H, 6·85. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%).

The compound was readily converted by the conventional methods into its 2,4-*di*-O-*acetate*, m. p. 74—76°, $[\alpha]_D$ +43° (*c* 0·9 in $CHCl_3$), $[M]_D$ +126° (Found: C, 61·4; H, 6·2. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2%), 2,4-*di*-O-*toluene*-p-*sulphonate* (88%), m. p. 116—118°, $[\alpha]_D$ +37° (*c* 0·6 in $CHCl_3$), $[M]_D$ +192° (Found: C, 57·9; H, 4·9; S, 12·3. $C_{25}H_{26}O_8S_2$ requires C, 57·9; H, 5·1; S, 12·4%), and 2,4-*di*-O-*methanesulphonate* (85%), m. p. 155—157°, $[\alpha]_D$ +31° (*c* 1·7 in $CHCl_3$), $[M]_D$ +113° (Found: C, 42·5; H, 5·0. $C_{13}H_{18}O_8S_2$ requires C, 42·6; H, 5·0%).

Action of Lithium Aluminium Hydride on Sulphonyl Derivatives of 1,3-O-*Benzylidene*-L-*threitol*.—(*a*) Treatment of 1,3-*O*-benzylidene-2,4-di-*O*-methanesulphonyl-L-threitol (4·4 g.) with lithium aluminium hydride (3 g.) in tetrahydrofuran (250 ml.) by essentially the method described above for the erythritol analogue gave 1,3-*O*-benzylidene-L-threitol (0·5 g., 20%), m. p. 131—133°, as the only identifiable product.

(*b*) To a stirred suspension of lithium aluminium hydride (10 g.) in tetrahydrofuran (250 ml.) was added a solution of 1,3-*O*-benzylidene-2,4-di-*O*-toluene-*p*-sulphonyl-L-threitol (14 g.) in the same solvent (50 ml.), and the mixture was boiled under reflux for 336 hr. The syrupy product (1·1 g.), isolated in the usual way, was esterified with *p*-phenylazobenzoyl chloride (3·5 g.) and pyridine (20 ml.) at 100° for 3 hr. The product, isolated in the usual manner,[17] was chromatographed on alumina. Elution with benzene–light petroleum (1 : 4 v/v) gave several zones, and the product (0·63 g.) from the main zone on rechromatography was found to contain two components of similar mobility. The leading portion of the zone gave a product of m. p. 140—155°, and the trailing portion a compound which after recrystallisation from ethanol–benzene and then benzene–light petroleum had m. p. 158—159° (Found: C, 71·5; H, 5·6; N, 7·3. $C_{24}H_{22}O_4N_2$ requires C, 71·6; H, 5·5; N, 7·0%). This compound is probably 1,3-O-*benzylidene*-4-*deoxy*-2-O-p-*phenylazobenzoyl*-L-*threitol*.

The *p*-phenylazobenzoate (50 mg.) with sodium methoxide in chloroform–methanol gave a

[17] Baggett, Foster, Haines, and Stacey, *J.*, 1960, 3528.

product (21 mg.), m. p. 69—70° (from light petroleum) (Found: C, 67·9; H, 7·25. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%). The compound is probably 1,3-O-*benzylidene*-4-*deoxy*-L-*threitol*.

A solution (0·005M) of the alcohol in CCl_4 showed $\nu_{max.}$ at 3590 cm.$^{-1}$ (ε 102) for bonded hydroxyl group.[6]

Action of Sodium Benzoate in Dimethylformamide on 1,3-O-*Benzylidene*-2,4-*di*-O-*methanesulphonyl*-L-*threitol*.—A mixture of 1,3-*O*-benzylidene-2,4-di-*O*-methanesulphonyl-L-threitol (2 g.), sodium benzoate (8 g.), and dimethylformamide (100 ml.) was boiled under reflux for 6 hr., then diluted with water (100 ml.) and extracted with ether (3 × 100 ml.). The combined extracts were washed with aqueous sodium hydrogen carbonate and then water and dried (Na_2SO_4). After evaporation the residue crystallised with difficulty from aqueous ethanol. Repeated recrystallisation from this solvent mixture and finally from benzene–light petroleum gave 2,4-di-*O*-benzoyl-1,3-*O*-benzylidene-L-erythritol (76 mg., 3·5%), m. p. 85—86° alone and in admixture with the authentic compound.

Nuclear Magnetic Resonance Spectra.—The spectra were obtained at 33° from 1—1·5M-solutions in chloroform with a Mullard SL 44 mark I spectrometer at 32 Mc./sec. Peak positions were measured relative to added tetramethylsilane by graphical interpolation on a side-band " ladder " produced with a Muirhead-Wigan D 695 A decade oscillator; each shift value recorded is the mean of several measurements and is accurate to ±0·5 cycle/sec. (±0·02 p.p.m.).

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