1364. *The* 4,6-O-*Butylidene Acetals of* D-*Glucose and* D-*Glucitol*

By T. G. Bonner, E. J. Bourne, and D. Lewis

n-Butyraldehyde and D-glucose condensed to give 4,6-*O*-butylidene-D-glucose, which on reduction yielded 4,6-*O*-butylidene-D-glucitol (1,3-*O*-butylidene-L-gulitol). Periodate oxidation of either the glucose or glucitol acetal gave 2,4-*O*-butylidene-D-erythrose, and thence on reduction 1,3-*O*-butylidene-L-erythritol.

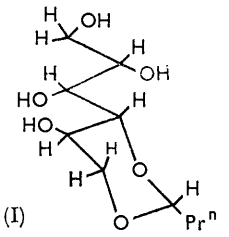
This Paper describes the synthesis and proof of structure of 4,6-*O*-butylidene-D-glucitol (I) (1,3-*O*-butylidene-L-gulitol), an acetal which, as expected, was not obtained as an end-product by direct butylidenation [1] of D-glucitol.

n-Butyraldehyde and D-glucose condense in the presence of a trace of concentrated sulphuric acid to yield the expected 4,6-*O*-butylidene-D-glucose (24—38%). This acetal appears to be dimorphic, one form melting at 150° and the other at 168°; but in chemical reactions or physical properties (infrared spectra in a Nujol mull, paper chromatography and specific rotation) other than melting point the two forms are identical. Both the dimorphs would be expected to have the same conformation as 4,6-*O*-benzylidene-D-glucose,[2] and from the high initial positive rotation which exhibits a downward directed mutarotation, we would infer that the solid dimorphs are both α-glucoses. The α-configuration was also tentatively assigned to them for their infrared spectra [3] in Nujol mulls. The acetal was characterised through its crystalline *p*-nitrophenylhydrazone, the formation of which indicates that C-1 is not involved in the acetal linkage.

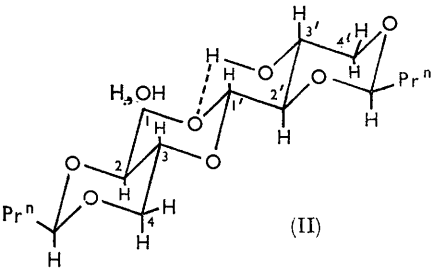
The acetal consumed 2 mol. of periodate in a slightly acid solution, and liberated 2 mol. of formic acid but no formaldehyde. The major periodate oxidation product was solid 2,4-*O*-butylidene-D-erythrose. Evidence that the erythrose acetal was not monomeric was (*a*) that a Nujol mull of the compound showed no carbonyl absorption in the infrared, (*b*) that the acetal mutarotated in solution, and (*c*) that a cryoscopic determination of the molecular weight using dry benzene as solvent showed that the acetal was a dimer at infinite dilution. The material became increasingly associated with increase in concentration. The association was rapidly reversed on dilution. Using dry acetic acid as solvent again showed that the solute was associated. Schaffer [4] found that 2,4-*O*-ethylidene-D-erythrose in formamide has a molecular weight corresponding to 2·16 monomer units (no concentration of solute was stated), and he proposed that two monomer units link together through a 1,3-dioxan ring. A similar structure could exist for the butylidene acetal, for which structure (II) could presumably be a favoured conformation, since the large substituents on all three rings are equatorial.

[1] T. G. Bonner, E. J. Bourne, S. E. Harwood, and D. Lewis, *J.*, 1965, 121.
[2] A. B. Foster, A. H. Haines, J. Homer, J. Lehmann, and L. F. Thomas, *J.*, 1961, 5005.
[3] W. B. Neely, *Adv. Carbohydrate Chem.*, 1957, **12**, 26.
[4] R. Schaffer, *J. Amer. Chem. Soc.*, 1959, **81**, 2838.

The 1,3-*O*-benzylideneglycerols (*M* of monomer 180) are associated [5] to about 1·1 monomer units at a concentration of about 0·15M (calculated on the monomer) in benzene solution. The corresponding value for the erythrose acetal (*M* of monomer 174) is about 6·6 monomer units. Assuming that the benzylidene acetals are associating through hydrogen

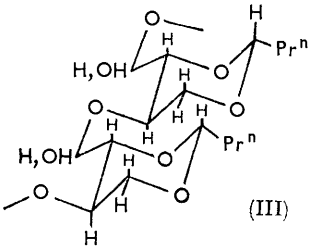


(I)



(II)

bonding [they cannot form dimers of type (II)], then the dimeric erythrose acetal is forming much stronger hydrogen bonds, and possibly hemi-acetals of type (III) are also present. The infrared spectrum of a carbon tetrachloride solution of the butylidene acetal showed a broad intermolecular hydrogen bond band which is presumably due to the C-1-reducing hydroxyl group of the dimer, and which decreased in intensity with increasing dilution of the solute, and a strong intramolecular hydrogen-bond band which is presumably due to the hydroxyl hydrogen of C-3′ bonding to an oxygen of C-1′.



(III)

The n.m.r. spectrum of the acetal in deuterochloroform was inconclusive. The specific rotation of the acetal depended greatly on the solvent used. The acetal could be recovered unchanged from the solution. The specific rotation in benzene varied in a complex manner with the concentration.

The dimer persisted on acetylation for the acetate in dry benzene was strictly dimeric up to the highest concentration of solute studied. Schaffer found that the acetate of ethylidene erythrose was also dimeric. On the other hand, as would be expected, the acetal reacted as the monomer to give a 2,5-dichlorophenylhydrazone, an oxime, and a dimedone anhydride.

Proof that the acetal was in fact an erythrose derivative followed when reduction by borohydride gave 1,3-*O*-butylidene-L-erythritol, which on mild acid hydrolysis gave crystalline erythritol (94%) and n-butyraldehyde which was characterised as its bisdimedone (58%).

The conformation of 1,3-*O*-butylidene-L-erythritol would be expected to be the same as that of 2,4-di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol.[2] The butylidene acetal gave a crystalline monophenylboronate, a di(toluene-*p*-sulphonate), and a monotriphenylmethyl ether monoacetate, thus revealing the presence of two hydroxyl groups, one of which was probably primary.

Reduction of 4,6-*O*-butylideneglucose by borohydride gave 4,6-*O*-butylidene-D-glucitol (I). The structure of the acetal was confirmed in the following way. On mild acid hydrolysis it was proved to be (i) a glucitol derivative through isolation of glucitol as its hexa-acetate (78%) and (ii) an n-butyraldehyde derivative through isolation of butyraldehyde as its bisdimedone (73%). The acetal (I) gave a crystalline tetra-acetate, a tetrabenzoate, and a monotriphenylmethyl ether triacetate, thus revealing the presence of four hydroxyl groups, one of which is probably primary. The acetal (I) consumed 2 mol. of periodate and liberated 1 mol. each of formic acid and formaldehyde. The major oxidation product was

[5] P. E. Verkade and J. D. van Roon, *Rec. Trav. chim.*, 1942, **61**, 831.

proved to be 2,4-*O*-butylidene-D-erythrose when it gave a dimedone anhydride identical with 2,4-*O*-butylideneerythrose dimedone anhydride obtained above. The acetal (I) did not migrate on molybdate ionophoresis.[6]

Experimental

Paper Chromatography.—Whatman No. 1 paper was used with the following solvents: (A) butan-1-ol–ethanol–water (40 : 11 : 19, v/v); (B) ethyl acetate–acetic acid–water (9 : 2 : 2, v/v); (C) ethyl methyl ketone–water (9 : 1, v/v); (D) di-isopropyl ether, the stationary phase in the paper being dimethyl sulphoxide.[7] A silver nitrate–sodium hydroxide spray was used. For non-reducing compounds, an initial potassium periodate spray is advantageous.

Light petroleum refers to the fraction b. p. 60—80°.

Acetylations. The compound (1 part) was treated with a mixture of pyridine and acetic anhydride (2 : 1, v/v; 10 parts) for 1 hr. at room temperature.

Quantitative periodate oxidations [8] and formaldehyde [9,10] and formic acid [11] determinations used standard procedures. n-Butyraldehyde, present in the formaldehyde determination, does not interfere.[12]

4,6-O-*Butylidene*-D-*glucose.*—The acetal was synthesised using a method similar to that for the synthesis [13] of 4,6-*O*-ethylideneglucose. Concentrated sulphuric acid (0·2 ml.) was added to n-butyraldehyde (44 ml., 2 mol.) and this solution was added immediately to anhydrous D-glucose (45 g., 1 mol.). The mixture was kept at 35—40° for 2—3 days after which a sample was completely, or almost completely, soluble in hot ethanol. The mixture was crystallised from a solution of ethanol (80 ml.) and ethyl acetate (50 ml.), or from ethanol alone (50 ml.) containing aqueous ammonia (2 ml.), to yield the crude product (35 g.). No satisfactory solvent for crystallising the acetal was found. Ethanol–ethyl acetate mixtures or the minimum volume of ethanol gave 60% recoveries of 4,6-O-*butylidene*-D-*glucose* (14—22 g., 24—38%) (Found: C, 51·4; H, 7·5. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%), $[\alpha]_D^{17}$ +38° (6 min.) ⟶ +1·1° (Final, 1·7 hr.) (*c* 1·8 in H_2O), effervescing between 150° and 157° to give a brown melt. Occasionally the acetal had m. p. 165—168° (no decomp.), and this material (Found: C, 50·9; H, 7·5%), $[\alpha]_D^{17}$ +41° (9 min.) ⟶ +0·8° (Final, 3 hr.) (*c* 1·8 in H_2O) appeared to be identical (infrared spectrum of a Nujol mull; R_F in solvent A was 0·83, and in solvent B was 0·74—0·79; periodate oxidation; and reduction) with the lower-melting material. Presumably dimorphic forms were present, but inoculating a solution of one form with seeds of the other did not give the other form. The infrared spectra of Nujol mulls indicated α-glucoses,[3] but were not conclusive owing to the existence of several absorption bands near 900 cm.$^{-1}$ and to uncertainty of the position of the methylene rock of the acetal ring.

Periodate Oxidation of 4,6-O-*Butylidene*-D-*glucose.*—(*a*) *Quantitatively.* The acetal (1 mol.), m. p. *ca.* 150°, consumed 1·55, 1·92, and 1·96 mol. of periodate (3·9 mol. initially present) (theor. 2·0) after 1·6, 8·2, and 20·25 hr., respectively, and gave 0·02 mol. of formaldehyde (theor. 0·0) and 1·88 mol. of formic acid (theor. 2·0). The material, m. p. 165—168°, consumed 1·64, 1·89, and 1·97 mol. of periodate (4·15 mol. initially present) after 1·3, 4·0, and 20·5 hr., respectively, and gave 0·03 mol. of formaldehyde and 1·90 mol. of formic acid.

(*b*) *Qualitatively.* The oxidation was based on the method used for the oxidation [14] of 4,6-*O*-ethylideneglucose. The acetal (11·8 g., 1 mol.), suspended in water (50 ml.), was treated during 0·5 hr. at about 20°, with a solution of sodium periodate (23 g., 2·13 mol.) in water (175 ml.) and with sufficient 2N-sodium hydroxide (40 ml.) to maintain the pH at about 4·5 (pH meter). After a further 2·5 hr. the pH was raised to 7·5 with 2N-sodium hydroxide (5 ml.),

[6] E. J. Bourne, D. H. Hutson, and H. Weigel, *J.*, 1960, 4252; H. Weigel, *Adv. Carbohydrate Chem.*, 1963, **18**, 61.
[7] B. Wickberg, *Acta Chem. Scand.*, 1958, **12**, 615.
[8] G. O. Aspinall and R. J. Ferrier, *Chem. and Ind.*, 1957, 1216.
[9] J. Mitchell, I. M. Kolthoff, E. S. Proskauser, and A. Weissberger, "Organic Analysis," vol. I, Interscience Publ. Inc., New York, 1953, p. 288.
[10] W. E. A. Mitchell and E. Percival, *J.*, 1954, 1423.
[11] E. L. Hirst and J. K. N. Jones, *J.*, 1949, 1659.
[12] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publ. Co. Amsterdam, 6th edn., 1960, p. 350.
[13] R. C. Hockett, D. V. Collins, and A. Scattergood, *J. Amer. Chem. Soc.*, 1951, **73**, 599.
[14] R. Barker and D. L. MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 2301.

and the suspension was freeze-dried. The residue was extracted with ethyl acetate (two 200-ml. portions, then one 50-ml. portion). The combined extracts were evaporated, the residue was dissolved in benzene (100 ml.), and the solution was freeze-dried to yield 2,4-O-*butylidene*-D-*erythrose* (Found: C, 55·1; H, 8·2. $C_8H_{14}O_4$ requires C, 55·2; H, 8·1%), 7·8 g., (89%), m. p. 99—100°. The compound did not crystallise from solution satisfactorily. R_F (one spot only) in solvent A was 0·93 and in solvent D was 0·78. The specific rotation of the compound depended on the solvent.

Solvent	Concn. (%)	$[\alpha]_D$	Temp.
Chloroform	1·7	+13·4° (9 min.) ⟶ +10·5° (equil. 19 hr.)	20°
Absolute ethanol	0·8	−12·6° (5 min.) ⟶ −16·3° (equil. 2 hr.)	22
Dry pyridine	0·8	−44·2° (no mutarotation)	21
Dry benzene	0·8	−26·7° (7 min.) ⟶ −19·3° (equil. 1·3 hr.)	18
" Ordinary " benzene ...	0·8	−24·5° (9 min.) ⟶ −17·4° (equil. 14 hr.)	22

The material recovered from the above solutions was in each case unchanged acetal. When water (0·2 v/v) was added to the pyridine solution, the solution had the expected rotation. The following specific rotations were obtained using ordinary benzene:

Concn. (g./100 ml.)	2·95	2·09	1·47	0·74	0·37
$[\alpha]^{20}_{5461}$	−27·0°	−26·0°	−24·1°	−21·4°	−20·4°

In a Unicam S.P. 100 spectrophotometer and a 4-cm. cell a saturated solution of the acetal in dry carbon tetrachloride gave a broad shoulder between 3280 and 3505 $cm.^{-1}$ which virtually disappeared on half-dilution of the solution, and a sharp peak at 3570 $cm.^{-1}$, which remained after dilution. A molecular-weight analysis of the acetal using a standard cryoscopic technique,[15] and dry benzene as solvent, gave M as 1·94 monomer units at infinite dilution. The apparent molecular weight increased progressively with increasing concentration of solute and corresponded to 6·55 monomer units at a concentration, calculated on the monomer, of 0·149M. The association was readily reversible as shown by the fact that a half-dilution of a 0·174M solution gave a resistance reading corresponding to a 0·082M solution. Using dry acetic acid as solvent gave M as 1·50 and 2·66 monomer units at infinite dilution, and at a concentration calculated on the monomer, of 0·158M, respectively. The material recovered from this experiment was unchanged acetal.

4,6-O-*Butylidene*-D-*glucose*-p-*nitrophenylhydrazone*.—The acetal (0·5 g., 1 mol.), *p*-nitrophenylhydrazine (0·32 g. 1 mol.), and ethanol were refluxed for 5 min. Light petroleum (3·5 ml.) was added to the cooled solution, and the product (0·59 g., m. p. 147—150°) crystallised. Two recrystallisations from 10 parts of ethanol gave needles of the p-*nitrophenylhydrazone* (0·3 g., 38%) (Found: C, 51·9; H, 6·6; N, 11·1. $C_{16}H_{23}N_3O_7$ requires C, 52·0; H, 6·3; N, 11·4%), $[\alpha]_D^{20}$ −31·0° (*c* 1·2 in EtOH), m. p. 158—158·5°. If placed in the bath above 120°, the sample melted with effervescence, resolidified, and remelted at 158°. A mixed m. p. with *p*-nitrophenylhydrazine showed depression.

Derivatives of 2,4-O-*Butylidene*-D-*erythrose*.—(*a*) The acetal (0·6 g.) gave an *acetate* (Found: C, 55·4; H, 7·4; Ac, 19·8. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·5; Ac, 19·9%), 0·5 g. (67%), m. p. 154—156°, $[\alpha]_D^{24}$ −39·0° (*c* 1·8 in $CHCl_3$), as needles from 10 parts of ethanol. A molecular-weight analysis, using a standard cryoscopic procedure, and dry benzene as solvent, indicated that the compound was dimeric (M, found, 427; M, required for dimer, 432·5) over the concentration range studied, *i.e.*, up to 0·09M.

(*b*) The acetal (0·4 g., 1 mol.), 2,5-dichlorophenylhydrazine (0·4 g., 1 mol., m. p. 102°), and ethanol (3 ml.) were warmed into solution. The ethanol was evaporated at a water-pump and the residue crystallised from 20 ml. and then 10 ml. of light petroleum to yield the off-white 2,5-*dichlorophenylhydrazone* (Found: C, 50·3; H, 5·5; Cl, 21·0; N, 8·5. $C_{14}H_{18}Cl_2N_2O_3$ requires C, 50·5; H, 5·4; Cl, 21·3; N, 8·4%), needles, 0·49 g. (64%), m. p. 104—106°, $[\alpha]_D^{24}$ +28·8° (*c* 1·6 in $CHCl_3$). A mixed m. p. with either of the starting materials showed depression.

(*c*) The acetal (0·2 g.), hydroxylamine hydrochloride (0·14 g., 1·8 mol.), and anhydrous sodium acetate (0·14 g.) were refluxed for 10 min. in a mixture of water (3 ml.) and methanol (1 ml.). The solution was evaporated and the residue crystallised from water (1 ml.), and then from

[15] A. Finch and P. J. Gardner, *J. Inorg. Nuclear Chem.*, 1963, **25**, 927.

benzene (4 ml.) to yield blades of the *oxime* (Found: C, 51·0; H, 8·1; N, 7·3. $C_8H_{15}NO_4$ requires C, 50·8; H, 8·0; N, 7·4%), 0·13 g. (60%), m. p. 93—95°, $[\alpha]_D^{21}$ +6·3° (*c* 0·8 in $CHCl_3$).

(*d*) The acetal (0·4 g., 1 mol.) in ethanol (*ca.* 5 ml.) was poured into a warm solution of dimedone (0·64 g., 2 mol.) in water (100 ml.). After 1 day at room temperature, the precipitate was filtered off, and crystallised from 10 parts of ethanol to yield granular crystals of the *dimedone anhydride* (Found: C, 69·1, 68·9; H, 8·3, 8·3. $C_{24}H_{34}O_6$ requires C, 68·9; H, 8·2%. The bis-dimedone, $C_{24}H_{36}O_7$, requires C, 66·0; H, 8·3%), 0·38 g. (40%), m. p. 232—234·5°, $[\alpha]_D^{24}$ −80·6° (*c* 1·8 in $CHCl_3$).

4,6-O-*Butylidene*-D-*glucitol*.—4,6-*O*-Butylidene-D-glucose (2·34 g., 1 mol.) in water (234 ml.) was treated with potassium borohydride (0·30 g., 0·56 mol.) in water 30 (ml.) overnight, after which time the solution was non-reducing to Fehling's solution. Amberlite IR-120 resin (B.D.H.) in the hydrogen form (15 ml.) was added and, when the solution had pH 6·6, it was filtered and the resin washed with water. The combined filtrates were evaporated (bath 40°) and the residue was dissolved in methanol (a few ml.) and re-evaporated under reduced pressure. This methanol treatment was repeated twice more with ordinary methanol and then once with dry methanol, after which a sample showed a negative boron-flame test. The solid was crystallised from ethyl acetate or from 20 parts of chloroform to yield 4,6-O-*butylidene*-D-*glucitol* (Found: C, 50·8; H, 8·3. $C_{10}H_{20}O_6$ requires C, 50·8; H, 8·5%), plates, m. p. 103—104·5°, $[\alpha]_D^{20}$ −26·8° (*c* 1·7 in H_2O), 1·7 g. (72%), R_F in solvent A, 0·70. The compound did not migrate on molybdate ionophoresis,[6] and in this respect it thus behaved as 4,6-*O*-ethylidene-D-glucitol [16] and not as 4,6-di-*O*-(α-D-glucosyl)-D-glucitol.[17]

Periodate Oxidation of 4,6-O-*Butylidene*-D-*glucitol*.—(*a*) *Quantitatively*. The acetal (1 mol.) consumed 2·06, 1·96, and 1·98 mol. of periodate (3·96 mol. initially present) after 0·9, 3·3, and 8 hr., respectively (theor. 2·0), and gave 0·95 mol. of formaldehyde (theor. 1·0) and 1·00 mol. of formic acid (theor. 1·0).

(*b*) *Qualitatively*. The acetal (1 g., 1 mol.) was oxidised by sodium periodate (2 g., 2·21 mol.) as described for 4,6-*O*-butylideneglucose. The product was proved to be 2,4-*O*-butylidene-D-erythrose when part (0·3 g.) of it was converted into its dimedone anhydride, 0·41 g. (57%), m. p. 231—235°. A mixed m. p. with the authentic dimedone anhydride, prepared above, showed no depression. In a repeat oxidation, using sodium hydrogen carbonate instead of 2N-sodium hydroxide, the reaction mixture was evaporated (bath 30—40°) at a water pump after the oxidation. The distillate was collected in a flask cooled in a mixture of acetone and solid carbon dioxide. A warm solution of dimedone (1·13 g.) in water was added to the distillate, and the total volume made up to 300 ml. The yield of formaldehyde bisdimedone was 0·87 g. (70%), m. p. 184—186°. A mixed m. p. with authentic formaldehyde bisdimedone, m. p. 188°, showed no depression.

Derivatives of 4,6-O-*Butylidene*-D-*glucitol*.—(*a*) The acetal (0·5 g.) gave a *tetra-acetate* (Found: C, 53·4; H, 6·8; Ac, 42·3. $C_{18}H_{28}O_{10}$ requires C, 53·5; H, 7·0; Ac, 42·6%), 0·65 g. (76%), m. p. 63—65°, $[\alpha]_D^{23}$ +4·3° (*c* 1·85 in $CHCl_3$) as plates after two crystallisations from 13 parts of light petroleum.

(*b*) The acetal (0·5 g.) in pyridine (4·5 ml.) was benzoylated with benzoyl chloride (1·08 ml., 4·4 mol.) for 4·5 hr. The product was crystallised from methanol (3 ml.) and then from 15 parts of methanol to yield the 1,2,3,5-*tetrabenzoate* (Found: C, 69·7; H, 5·6; Bz, 65·2. $C_{38}H_{36}O_{10}$ requires C, 69·9; H, 5·6; Bz, 64·4%) as a voluminous crystalline mass, 1·0 g. (72%), m. p. 99—104°, $[\alpha]_D^{23}$ +5·2° (*c* 1·8 in $CHCl_3$). Two further crystallisations did not sharpen this m. p.

(*c*) The acetal (0·5 g., 1 mol.) in pyridine (3·5 ml.) was treated with triphenylmethyl chloride (0·6 g., 1 mol.) for 34 hr. at room temperature. This product did not crystallise and was therefore acetylated and yielded a *tri*-O-*acetyltriphenylmethyl ether* (Found: C, 69·4; H, 6·8. $C_{35}H_{40}O_9$ requires C, 69·5; H, 6·7%) 0·4 g. (31%), m. p. 148—149°, $[\alpha]_D^{23}$ +23·6° (*c* 1·8 in $CHCl_3$) as needles from 40 parts of light petroleum. The triphenylmethyl group is assumed to be at the 1-position.

Acid Hydrolysis of 4,6-O-*Butylidene*-D-*glucitol*.—The acetal (0·3 g.) was gently boiled at atmospheric pressure for 20 min. with 0·4N-hydrochloric acid (15 ml.) with a stream of nitrogen bubbling through. The distillate (*ca.* 5 ml.) was collected in a receiver cooled in a mixture of acetone

[16] T. G. Bonner, E. J. Bourne, and D. Lewis, unpublished results.
[17] D. Abbott, E. J. Bourne, and H. Weigel, unpublished results.

and solid carbon dioxide. Sodium hydrogen carbonate (0·5 g.) was added to the cooled reaction mixture, and the remaining volatile material was collected in the receiver by distillation at a water pump. Dimedone (0·36 g.) dissolved in warm water (*ca.* 50 ml.) was added to the distillate and the whole was made up to 80 ml. with water. Butyraldehyde bisdimedone, 0·31 g. (73%), m. p. and mixed m. p. 132—134°, crystallised.

The dry glucitol–sodium chloride residue in the distillation flask was acetylated, and when it was poured into water glucitol hexa-acetate, 0·43 g. (78%), m. p. and mixed m. p. 98—99°, crystallised.

1,3-O-*Butylidene*-L-*erythritol*.—2,4-*O*-Butylidene-D-erythrose (3 g.) was reduced by borohydride using a similar method to that described for the reduction of 4,6-*O*-butylideneglucose. The 1,3-O-*butylidene*-L-*erythritol* (Found: C, 54·45; H, 9·2. $C_8H_{16}O_4$ requires C, 54·5; H, 9·15%), 2·86 g. (94%), m. p. 84—87°, $[\alpha]_D^{21\cdot5}$ −17·8° (*c* 1·8 in $CHCl_3$) crystallised from carbon tetrachloride (40 ml.) as plates or needles. The compound is readily soluble in water.

Derivatives of 1,3-O-*Butylidene*-L-*erythritol*.—(*a*) The acetal (0·5 g., 1 mol.), triphenylmethyl chloride (0·79 g., 1 mol.), and pyridine (2 ml.) were kept at room temperature for 1 day. The triphenylmethyl ether was isolated, but did not crystallise, and was acetylated. The product was crystallised from light petroleum (10 ml.) and then from 4 parts of ethanol to yield a *mono-O-acetyl triphenylmethyl ether* (Found: C, 75·6; H, 7·1. $C_{29}H_{32}O_5$ requires C, 75·6; H, 7·0%), granular crystals, 0·72 g. (55%), m. p. 83—86°, $[\alpha]_D^{28\cdot5}$ −33·3° (*c* 1·7 in $CHCl_3$). The acetyl and triphenylmethyl groups are assumed to be at the 2- and 4-positions, respectively.

(*b*) The acetal (0·3 g., 1 mol.), toluene-*p*-sulphonyl chloride (0·72 g., 2·2 mol.), and pyridine (1·2 ml.) were kept at room temperature for 1 day and then poured into water. The precipitate (0·74 g., melting up to 150°) was crystallised once from ethanol (35 ml.) to yield the 2,4-*di*-(*toluene*-p-*sulphonate*) (Found: C, 54·3; H, 5·8; S, 13·05. $C_{22}H_{28}O_8S_2$ requires C, 54·5; H, 5·8; S, 13·2%), 0·62 g. (75%), m. p. 155—156°, $[\alpha]_D^{22\cdot5}$ −32·6° (*c* 1·8 in $CHCl_3$).

(*c*) The pure *monophenylboronate* was prepared by allowing a hot solution of the acetal (0·5 g., 1 mol.) and phenylboronic anhydride (0·27 g., 0·31 mol.) in 90% aqueous methanol to crystallise (Found: C, 64·15; H, 7·4; B, 4·15. $C_{14}H_{19}BO_4$ requires C, 64·15; H, 7·3; B, 4·1%), 0·51 g. (68%), m. p. 60·5—62°, $[\alpha]_D^{22\cdot5}$ +28·0° (*c* 1·2 in $CHCl_3$).

Acid Hydrolysis of 1,3-O-*Butylidene*-L-*erythritol*.—The acetal (0·4 g.) was hydrolysed as described for the hydrolysis of 4,6-*O*-butylideneglucitol, but using only 0·3N-hydrochloric acid (15 ml.). The yield of butyraldehyde bisdimedone was 0·44 g. (58%), m. p. and mixed m. p. 133—134°. The dry erythritol–sodium chloride residue was extracted with boiling absolute ethanol (a 7-ml. and then a 3-ml. portion). The combined extracts deposited erythritol, 0·26 g. (94%), m. p. 116—120°, at −20°. A mixed m. p. with authentic erythritol, m. p. 118—120°, showed no depression, and the product co-chromatographed with erythritol in solvent A, R_F 0·40 (the m. p. of L-threitol is 88°).

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