626. *But-2-enylidene Derivatives of Glucitol.*

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

Condensation of D-glucitol with crotonaldehyde in the presence of various catalysts has been studied, and the 2,4- and 3,4-mono-, 1,3:2,4-di-, and 1,3:2,4:5,6-tri-*O*-but-2′-enylidene derivatives have been characterised. Evidence is presented for ring migration during the syntheses, leading to formation of an isomeric triacetal suspected of being a 1,2:3,4:5,6-tri-*O*-but-2′-enylidene derivative. The structures assigned to the di- and tri-acetals are based on the assumption that there is no significant migration of acetal groups under the mild conditions of partial hydrolysis employed.

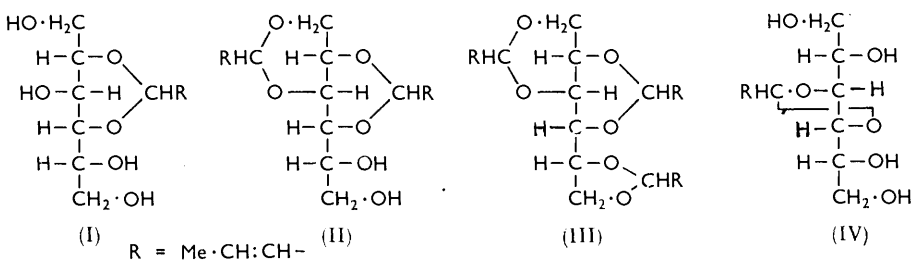
There appears to be no reference in the literature to the reaction between glucitol and crotonaldehyde. The present paper describes the cyclic acetals obtained from this reaction.

Commercial D-glucitol condenses with the aldehyde in the presence of anhydrous zinc chloride, to yield 2,4-*O*-but-2′-enylidene- (I) (6%), 1,3:2,4-di-*O*-but-2′-enylidene- (II) (4%), 1,3:2,4:5,6-tri-*O*-but-2′-enylidene- (III) (3%), and a syrupy tri-*O*-but-2′-enylidene-D-glucitol (*ca.* 15%), and a tri-*O*-but-2′-enylidene-D-mannitol (0·03%). The last compound probably arose from D-mannitol present as impurity in the commercial glucitol employed.

The 2,4-monoacetal (I) was obtained more easily and in better yield by using as catalyst either a trace of concentrated sulphuric acid or aqueous sulphuric acid (compare the preparation of 2,4-*O*-furfurylidene-D-glucitol [1]). This method also gave a trace (0·04%) of 3,4-acetal (IV).

The tri-*O*-but-2′-enylideneglucitols were also obtained by condensing crotonaldehyde with (*a*) glucitol in the presence of a trace of toluene-*p*-sulphonic acid or phosphoryl chloride [2] as catalyst, or (*b*) the 2,4-monoacetal (I) in the presence of phosphoryl chloride; in both methods the water formed was removed by azeotropic distillation with benzene.

The structure of the 2,4-monoacetal (I) followed from the facts that it consumed one mol. of periodate and liberated one mol. of formaldehyde. Paper chromatography of the neutralised solution revealed the presence of xylose, which had been presumably liberated by hydrolysis of the acetal (see below). Also the monoacetal (I) readily yielded a bis-



phenylboronate, a tetra-acetate, and a dityl ether, thus revealing the presence of four hydroxyl groups, two of which were probably primary.

The 3,4-*O*-but-2′-enylideneglucitol (IV) consumed two mol. of periodate and liberated two mol. of formaldehyde, but no formic acid. As the compound was obtained in low yield it was proved to be (i) a glucitol derivative by acid hydrolysis to the hexitol which on ionophoresis in sodium metavanadate buffer [3,4] ran as glucitol, and (ii) a monobut-enylidene derivative by quantitative conversion into crotonaldehyde 2,4-dinitrophenylhydrazone.

[1] Hockett, U.S.P. 2,584,129; *Chem. Abs.*, 1952, **46**, 8148.
[2] Bonner, Bourne, and Harwood, unpublished work.
[3] Frahn and Mills, *Austral. J. Chem.*, 1959, **12**, 65.
[4] Angus, Bourne, and Weigel, unpublished work.

The crystalline diacetal (II) was shown to have rings at the 1,3:2,4-positions because it consumed one mol. of periodate and liberated one mol. of formaldehyde, gave xylose after removal of the acetal rings by hydrolysis (paper-chromatographic evidence), and on partial acid hydrolysis yielded the 2,4-monoacetal (39%).

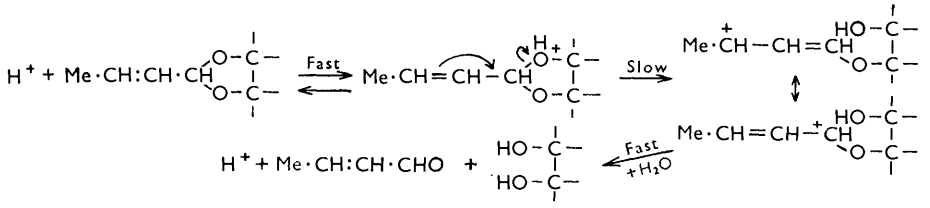
The structure of the 1,3:2,4:5,6-triacetal (III) followed from partial acid hydrolysis to the 1,3:2,4-diacetal (83%) and the monoacetal (I) (5%). Again, as the triacetal was obtained only in low yield, it was shown to be a glucitol derivative and to contain three butenylidene groups, as above.

The crystalline tri-*O*-butenylidene-D-mannitol was proved to be a mannitol derivative and to contain three butenylidene groups. Additional evidence was that the same material was isolated on condensation of D-mannitol and crotonaldehyde with phosphoryl chloride as catalyst.

When the syrupy tri-*O*-butenylideneglucitol was hydrolysed in the conditions used for hydrolysis of the crystalline triacetal of glucitol, the 3,4-monoacetal (IV) (7%) was the only crystalline material obtained. It is possible that, barring ring re-arrangements during hydrolysis, this material was derived from 1,2:3,4:5,6-tri-*O*-but-2′-enylidene-D-glucitol. A 1,5:2,6:3,4- (*i.e.*, two eight-membered rings) or a 1,6:2,5:3,4-structure (*i.e.*, a nine- and a seven-membered ring) is improbable.

The precise composition of the syrupy triacetal could not be determined. Irrespective of whether it was prepared by method (*a*) or by the zinc chloride method, the yield was much greater than that of the crystalline 1,3:2,4:5,6-triacetal. It distilled as one main fraction and behaved as a triacetal on paper chromatography. Elemental combustion analyses consistently gave a slightly low carbon value, but the material had a satisfactory butenylidene content (2·86 rings per mole of hexitol). Since acid hydrolyses of the material under different conditions did not yield any 1,3:2,4-diacetal and only a trace (2%) of 2,4-monoacetal, which could have arisen from the known trace of 1,3:2,4:5,6-triacetal present in the sample, these rings are probably absent from the material.

Further, the 2,4-monoacetal (I), free from 3,4-monoacetal, was converted into the triacetal by method (*b*) above. The yield of crystalline triacetal was again low (12—17%). The main product was once more a syrupy triacetal, which yielded 3,4-*O*-but-2′-enylidene-glucitol (10%) on hydrolysis. This result is taken as evidence for ring migration, which is more likely to have occurred during synthesis of the material than during the milder conditions and more dilute solutions used for the hydrolysis. Ring migration is of course well established.[5,6] The lability of the butenylidene ring in an acidic environment may itself be a factor facilitating this migration. Indeed attempts to measure the uptake of periodate by the usual ultraviolet spectrophotometric method[7] gave anomalous results



with the monoacetals because even dilute (0·015M) aqueous sodium periodate was acid enough[8,9] (pH 5·3) to hydrolyse the acetal rings. Scission of the rings is to be expected if this process is one which requires rupture of a carbon–oxygen bond in the protonated

[5] Fletcher and Diehl, *J. Amer. Chem. Soc.*, 1952, **74**, 3799.
[6] Reeves, *J. Amer. Chem. Soc.*, 1949, **71**, 2868.
[7] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.
[8] Crouthamel, Hayes, and Martin, *J. Amer. Chem. Soc.*, 1951, **73**, 82.
[9] Crouthamel, Meek, Martin, and Banks, *J. Amer. Chem. Soc.*, 1949, **71**, 3031.

species (as in the case of acyclic acetals [10]), since this step would be facilitated by the olefinic bond of the butenylidene group which supplements the effect due to the oxygen atom.

Since the butenylidene ring can be removed so smoothly by dilute acid, it may find applications for use as a blocking group during synthesis.

When zinc chloride is used as catalyst for the condensation of crotonaldehyde and glucitol, the cyclic acetals produced show little tendency to polymerise. This behaviour is in marked contrast with that of the products from acraldehyde, which readily yields polymeric material of unknown composition with glucitol or sucrose in the presence of zinc chloride.[11]

Generalisations have been formulated by which the structure of favoured acetals of polyols may be predicted from the configuration of the alcohol,[12] or the conformation of the rings themselves.[13] For glucitol, the main monoacetal obtained had the predicted 2,4(*i.e.*, βC)-ring. The second isomer, having the 3,4(αT)-ring would not have been predicted. This is the first substantiated example where glucitol forms such an acetal ring, though it is known [14] to do so in ketal formation (*O*-methylenation of mannitol is also known [5] to yield, in addition to the predicted 1,3-compound, *i.e.*, a β-ring, some 3,4-monoacetal, *i.e.*, an αT-ring).

In this work the only pure di- and tri-butenylidene derivatives which have been isolated have the expected 1,3:2,4- and 1,3:2,4:5,6-rings.

Although the crystalline triacetal gave a high yield of pure diacetal on hydrolysis, chromatography and a varying melting point indicated a mixture, possibly due to an asymmetric acetal carbon atom [13] or, less probably, to *cis-trans*-C=C isomerism. Infrared spectra did not solve the problem.[15]

As will be reported later, all the structures of the acetals assigned above were further confirmed when reduction yielded the corresponding butylidene compounds, which were correlated with those obtained by condensing butyraldehyde with D-glucitol and whose structures had been independently determined.[2]

Experimental

Materials.—Crotonaldehyde was redistilled and the fraction having b. p. 100—104° was used. D-Glucitol (B.D.H.) was used without purification. Paper ionophoresis of this glucitol in sodium metavanadate buffer,[3] prepared [4] by dropwise addition of concentrated sulphuric acid, to a 1·5% aqueous solution of the metavanadate until the pH was 6·0 (on storage the pH rises to 6·5), indicated the presence of appreciable amounts of mannitol, revealed as a blue spot ($R_{glucitol}$ between 0·38 and 0·65), as well as glucitol (a brownish spot).

Paper Chromatography.—Whatman No. 1 paper was used with the following solvents: (*a*) butan-1-ol–ethanol–water (40 : 11 : 19, v/v); (*b*) light petroleum (b. p. 60—80°), the stationary phase in the paper being dimethyl sulphoxide [16] (with this solvent, the paper was dipped in a freshly prepared 20% solution of the sulphoxide in benzene and immediately placed between two sheets of Whatman No. 3 paper to minimise absorption of moisture while chloroform solutions of the compounds to be chromatographed were being applied to the paper); (*c*) as for (*b*) but with dimethylformamide as the stationary phase; (*d*) as for (*c*) but with di-isopropyl ether as the moving phase. R_F values for systems (*b*)—(*d*) were variable. A 2,4-dinitrophenylhydrazine spray [17] was used to detect the butenylidene derivatives.

[10] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, p. 334.
[11] Bonner, Bourne, and Ruszkiewicz, unpublished work.
[12] Barker, Bourne, and Whiffen, *J.*, 1952, 3865.
[13] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 2.
[14] Bourne, McSweeney, Stacey, and Wiggins, *J.*, 1952, 1408.
[15] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 45.
[16] Wickberg, *Acta Chem. Scand.*, 1958, **12**, 615.
[17] Bland, *Nature*, 1949, **164**, 1093.

Condensation of D-*Glucitol and Crotonaldehyde in the Presence of Zinc Chloride.*—Powdered D-glucitol (25 g.), powdered freshly fused zinc chloride (50 g.), and crotonaldehyde (250 ml.) were stirred for 1 hr. at 50°, and the solution was then set aside for 5 hr. at room temperature (20°) before being concentrated at 40° at a water pump until the solvent was being removed only slowly. Water (30—40 ml.) was added and the solution was extracted with chloroform (200—400 ml.). The aqueous (lower) layer (X) was re-extracted with chloroform. The extracts were combined and washed with sufficient aqueous sodium carbonate solution (Y) to precipitate any zinc salt. The mixture was filtered, and the organic layer was separated and evaporated to dryness to leave a residue which was extracted with water (3 × 35 ml.). Evaporation of the water left a residue (6—11·5 g.) which was crystallised from benzene to yield material which was digested with 10 parts of boiling benzene. An insoluble portion (0·25 g.; impure 2,4-monoacetal) was filtered off. The filtrate deposited impure 1,3:2,4-*di*-O-*but*-2′-*enylidene*-D-*glucitol*, which after two recrystallisations from 15 parts of ethanol–light petroleum (b. p. 60—80°) (1 : 4) yielded the pure diacetal (0·3—2·2 g., 0·8—6%), m. p. 154—155°, $[\alpha]_D^{22}$ +23·5° (*c* 2·1 in EtOH) (Found: C, 58·8; H, 7·8. $C_{14}H_{22}O_6$ requires C, 58·7; H, 7·7%). R_F values in solvents (*a*), (*c*), and (*d*) were 0·85, 0·00, and 0·05, respectively. Some preparations partially melted at 130° and remained in this state until they gave a clear melt at 154°. On other occasions, samples were prepared which melted normally at 154—155° if placed in the bath below 129°. If placed in the bath above 129°, effervescence occurred and the sample partially melted, the melt resolidifying and melting again sharply at 154° (drying such material over phosphorus pentoxide for 2·5 days did not affect this phenomenon). Very occasionally the compound had a sharp m. p. of 122°; this material (possibly an unstable dimorphic form) gave material of m. p. 154° on recrystallisation. The compound crystallised as a voluminous mass though on two occasions, discrete crystals separated which were a mixture of fine needles and thin plates, both forms having m. p. 154°.

The water-insoluble part of the chloroform extract was extracted with light petroleum (b. p. 60—80°) (40—100 ml.). The extract contained material which crystallised from 10 parts of 60% aqueous ethanol, to yield 1,3:2,4:5,6-*tri*-O-*but*-2′-*enylidene*-D-*glucitol* (0·2—2·4 g., 0·4—5%) (Found: C, 63·6; H, 7·6. $C_{18}H_{26}O_6$ requires C, 63·9; H, 7·7%), m. p. 108—110°. On two occasions the m. p. was raised to 114—116° with shrinking from 110°. The specific rotation, $[\alpha]_D^{22}$, depended on the particular sample and was within the range +11·3° to +16·0° (*c* 1·7 in EtOH). The R_F values in solvents (*a*), (*b*), and (*d*) were 0·92, 0·90, and 0·80, respectively. With solvent (*c*) in favourable cases, the material showed as two overlapping spots, with R_F 0·6—0·7. The light petroleum extract after removal of the crude 1,3:2,4:5,6-triacetal contained a syrupy tri-*O*-butenylidene-D-glucitol (*ca.* 7 g., 15%).

The aqueous layer (X) and the sodium carbonate washings (Y) were combined, and concentrated aqueous sodium carbonate was added until the mixture was alkaline. The zinc salts were removed by filtration and were washed with water. The filtrate and washings were evaporated almost to dryness and extracted with hot ethanol (2 × 40 ml.). The combined extracts were concentrated and deposited crude 2,4-O-*but*-2′-*enylidene*-D-*glucitol* on cooling. Two recrystallisations from 15—20 parts of ethanol gave the pure monoacetal as needles (1·4—2·5 g., 4—8%), m. p. 169—170°, $[\alpha]_D^{26}$ +0·2° (*c* 2·1 in H_2O), $[\alpha]_D^{27}$ −0·9° (*c* 2·0 in 1% aqueous boric acid), $[\alpha]_D^{23}$ +29·3° (*c* 2·2 in 4% ethanolic phenylboronic acid), $[\alpha]_D^{16}$ +44·8° [*c* 1·1 in 4% ethanolic $(PhBO)_3$] (Found: C, 51·7; H, 7·85. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%). The R_F value in solvent (*a*) was 0·61.

Condensation of D-*Glucitol and Crotonaldehyde in the Presence of Concentrated Sulphuric Acid.*—To a cold suspension of D-glucitol (2 g.) in crotonaldehyde (4 ml., 4·4 mol.), concentrated sulphuric acid (3 small drops) was carefully added. Within a few minutes most of the glucitol had passed into solution, and soon a heavy precipitate was formed. After 9 hr. the mixture was made alkaline with aqueous sodium hydrogen carbonate. The 2,4-*O*-but-2′-enylidene-D-glucitol (0·8 g., 31%) m. p. 166—168°, was filtered off. No diacetal was formed (paper-chromatographic evidence). Attempts to force the reaction to the di- and tri-acetal stage by using larger amounts of concentrated sulphuric acid were unsuccessful.

Condensation of D-*Glucitol and Crotonaldehyde in the Presence of Aqueous Sulphuric Acid.*—To a solution of D-glucitol (18 g.) in 3N-sulphuric acid (5 ml.) was added crotonaldehyde (8 ml., 1 mol.). After 7 and 14 min. further aldehyde (1 mol. each time) was added. After 7·5 hr., sodium hydrogen carbonate (1·7 g.) in water (4 ml.) was added, followed by ethanol (30 ml.). After 20 hr. the crude product (13·6 g.; m. p. 161—164°) was filtered off and crystallised from

ethanol, to yield 2,4-*O*-but-2′-enylidene-D-glucitol (10·6 g., 46%), m. p. 167—169°. Paper chromatography indicated the presence of a small amount of diacetal in the reaction liquors.

Use of a 1 : 1 mol. ratio (cf. ref. 1) of hexitol (182 g.) to aldehyde gave a 31% yield of crystallised 2,4-monoacetal. The ethanolic mother-liquors of the reaction mixture were diluted with more ethanol and deposited crude D-glucitol (15% recovery) at −20°. Concentration of the liquors then gave 3,4-*O*-but-2′-enylidene-D-glucitol (0·1 g., 0·04%), m. p. 148—151°. A mixed m. p. with pure 3,4-monoacetal, m. p. 150—151°, described below, showed no depression. In solvent (*a*) the compound had the same R_F value (0·61) as the 2,4-monoacetal, and attempts to distinguish these two compounds by using an ethyl acetate–acetic acid–water solvent (9 : 2 : 2, v/v) containing phenylboronic acid [18] (0·38% w/v) were also unsuccessful.

Preparation of the Trialkylideneglucitols.—(*a*) *From D-glucitol.* D-Glucitol (90 g., 1 mol.), crotonaldehyde (3—5 mol.), benzene (310—400 ml.) and, as catalyst, phosphoryl chloride [2] (3 drops) or toluene-*p*-sulphonic acid (0·05 g.) were refluxed together under a Dean and Stark head. After about 1 hr., more catalyst (about equal to that initially present) was added and the reaction proceeded further until a total of 10—16 ml. of water had been collected (27ml. ≡ 100% of triacetal). The reaction could not be forced past this stage. The benzene–crotonaldehyde solution was decanted from the paste and was evaporated to a syrup; this was dissolved in ethanol (80—110 ml.), and enough aqueous ammonia was added to destroy any catalyst. Water was added until a turbidity appeared; the mixture was clarified with more ethanol and set aside at 5°; it then deposited crude triacetal. This was recrystallised from 50% aqueous ethanol until the m. p. was 105—108°. The yield of 1,3:2,4:5,6-tri-*O*-but-2′-enylidene-D-glucitol was then 2—7 g. (1—4%). One experiment gave a yield of 8%. The first aqueous-ethanolic crystallisation liquors were evaporated to dryness and the residue was extracted at room temperature with light petroleum (b. p. 60—80°) (2 × 150 ml.). The extract was concentrated and the residue distilled, to yield the syrupy *tri*-O-*butenylidene*-D-*glucitol* (34 g., 20%) [Found (two preparations): C, 63·0, 62·4; H, 7·5, 7·7. $C_{18}H_{26}O_6$ requires C, 63·9; H, 7·7%], n_D^{25} 1·4911, 1·4907, $[\alpha]_D^{23}$ +17·7°, +15·4° (*c* 1·8 in EtOH). In solvents (*a*)—(*d*) the R_F values were 0·92, 0·96, 0·83, and 0·90, respectively.

(*b*) *From pure* 2,4-*monoacetal.* Recrystallised 2,4-*O*-but-2′-enylidene-D-glucitol (11·7 g., 1 mol.), crotonaldehyde (12 ml., 2·9 mol.), benzene (50 ml.), and phosphoryl chloride (1 drop) were refluxed together. A homogeneous solution was obtained [see method (*a*) above] and 92—94% of the water expected from complete triacetalisation was collected. The solution was evaporated, and the crystalline 1,3:2,4:5,6-triacetal (12—17%) and the syrupy triacetal [40%; n_D^{25} 1·4928; $[\alpha]_D^{22}$ +18·4° (*c* 1·8 in EtOH)] were isolated as described in method (*a*).

Periodate Oxidation of 2,4-O-*But-2′-enylidene*-D-*glucitol.*—Attempts to measure the uptake of periodate by the usual ultraviolet spectrophotometric method [7] gave anomalous results. Presumably the periodate solution (0·015M; pH 5·3) was sufficiently acid to hydrolyse the acetal rings. After 1·5 days a sample of the reaction mixture was neutralised and run in solvent (*a*). It gave a single spot corresponding to xylose, but not arabinose (*p*-anisidine or silver nitrate spray). Crotonaldehyde formed from the hydrolysis has a strong absorption peak [19] (ε 15,000) at 223 mμ, the wavelength used in the experiment, and so would interfere with the determination. It was shown that the 2,4-monoacetal itself had an insignificant absorption at 223 mμ (ε 44). The periodate oxidations were then performed in nearly neutral solution (pH 7·3), prepared by addition of 0·1N-sodium hydroxide (9·0 ml.) to 0·01527M-sodium periodate (250 ml.). After reaction for 1·5 days, the solution had pH 7·6. The 2,4-monoacetal (1 mol.) had consumed 0·95, 0·95, and 1·03 mol. of the 2·4 mol. of periodate initially present after 2·25, 6, and 13·5 hr., respectively. The formaldehyde liberated was determined within 2 hr. of adding the periodate by a standard procedure,[20,21] and gave 0·99 mol. of compound (theory 1·0). Crotonaldehyde, present in the reaction mixture, does not interfere.[22]

Sodium periodate (1·27 g., 1·2 mol.) in water (50 ml.) was added (1 hr.) dropwise to the monoacetal (1·17 g., 1 mol.) in water (30 ml.) containing sodium hydrogen carbonate (0·2 g.) at such a rate that the pH was 7·0—7·2. After a further 1·25 hr. at room temperature, the

[18] Bourne, Lees, and Weigel, *J. Chromatog.*, in the press.
[19] Bayliss and McRae, *J. Phys. Chem.*, 1954, **58**, 1006.
[20] Mitchell, Kolthoff, Proskauer, and Weissberger, "Organic Analysis," Vol. I, Interscience Publ. Inc., New York, 1953, p. 288.
[21] Mitchell and Percival, *J.*, 1954, 1423.
[22] Feigl, "Spot Tests in Organic Analysis," Elsevier Publ. Co., Amsterdam, 5th edn., 1956, p. 331.

solution was evaporated to dryness (bath 30—40°). The distillate was collected in a receiver cooled in acetone–solid carbon dioxide and was treated with dimedone (1 g.) in ethanol (7 ml.) and glacial acetic acid (5 drops), and was left at room temperature overnight. The yield of formaldehyde bisdimedone was 0·20 mol., m. p. 185—188°. A mixture with authentic formaldehyde bisdimedone, m. p. 189°, melted at 186—189°.

Derivatives of 2,4-O-*But*-2′-*enylidene*-D-*glucitol*.—(*a*) The monoacetal, treated with acetic anhydride in pyridine, yielded the 1,3,5,6-*tetra-acetate* (23%), m. p. 75—76°, $[\alpha]_D^{18}$ −8·4° (*c* 1·1 in $CHCl_3$) (Found: C, 53·9; H, 6·8%; N-alkali uptake, 9·75 ml./g. $C_{18}H_{26}O_{10}$ requires C, 53·7; H, 6·5%; uptake, 9·94 ml./g.), as needles from 10 parts of 50% aqueous ethanol.

(*b*) Hot solutions of the monoacetal (0·2 g., 1 mol.) in water (1·6 ml.) and phenylboronic anhydride (0·16 g., 0·6 mol.) in methanol (1 ml.) were mixed.[23] On cooling, the crude product (0·30 g.; m. p. 127—128°) crystallised. Recrystallisation from 50 parts of light petroleum (b. p. 60—80°) gave a 2,4-O-*but*-2′-*enylidene*-D-*glucitol bisphenylboronate* (0·18 g., 52%), m. p. 129—131°, $[\alpha]_D^{16}$ +18·6° (*c* 1·1 in $CHCl_3$), $[\alpha]_D^{16}$ +9·6° (*c* 1·2 in EtOH), $[\alpha]_D^{15}$ +31·0° [*c* 1·1 in 4% w/v ethanolic $(PhBO)_3$] (Found: C, 64·9; H, 6·2; B, 5·25. $C_{22}H_{24}B_2O_6$ requires C, 65·1; H, 6·0; B, 5·3%). The phenylboronate groups are assumed to span the 1,3- and 5,6-positions.

(*c*) The monoacetal (1 g., 1 mol.), triphenylmethyl chloride (2·385 g., 2 mol.), and pyridine (9 ml.) were kept at 100° for 1 hr. The cooled solution was poured into water and extracted with chloroform. The extract was washed twice with water and evaporated to dryness. The residue crystallised from methanol (20 ml.) at −20° to yield the crude product (1 g.), which was thrice crystallised from 5 : 16 benzene–light petroleum (b. p. 60—80°), to yield the pure 2,4-O-*but*-2′-*enylidene*-*di*-O-*trityl*-D-*glucitol* as rosettes (0·5 g., 16%), $[\alpha]_D^{23}$ +9·3° (*c* 1·7 in $CHCl_3$), m. p. 127—129° (effervescence) (Found: C, 80·3, 80·0; H, 6·7, 6·4. $C_{48}H_{46}O_6$ requires C, 80·2; H, 6·35%). When the product was melted in a sublimation apparatus, no material condensed on the cold (−78°) finger. These results may mean that the compound was occluding a gas, *e.g.*, air. It is assumed that the trityl groups are at positions 1 and 6.

Periodate Oxidation of 3,4-O-*But*-2′-*enylidene*-D-*glucitol*.—An attempt to measure the periodate uptake in the usual manner [7] gave anomalous results, but with the neutral conditions described for the 2,4-monoacetal there was an uptake of 1·99, 2·01, and 2·05 mol. (3·6 mol. initially present) after 1·75, 5·5, and 13 hr., respectively (theory 2·0). The formaldehyde liberated was determined within 2 hr. of adding the periodate, by a standard procedure,[20,21] as 1·92 mol. (theory 2·0). The formic acid produced simultaneously was found to be 0·007 mol. (theory 0·0).

Periodate Oxidation of 1,3:2,4-*Di*-O-*but*-2′-*enylidene*-D-*glucitol*.—The uptake of periodate was determined in the usual manner; [7] the compound (1 mol.) had consumed 0·96 and 0·98 mol. of periodate (3·2 mol. initially present) after 2 and 6 hr., respectively. The formaldehyde produced was determined [20,21] (0·97 mol.). The diacetal (1 g.) was treated with sodium periodate as described for the 2,4-monoacetal. The yield of formaldehyde bisdimedone, after crystallisation from ethanol, was 0·34 mol. (m. p. 184—187°; mixed m. p. 187—188°). When sodium hydrogen carbonate was omitted from the oxidation, chromatography of the reaction mixture in solvent (*a*) gave a spot running as xylose (but not arabinose).

Derivatives of 1,3:2,4-*Di*-O-*but*-2′-*enylidene*-D-*glucitol*.—(*a*) The diacetal, treated with acetic anhydride in pyridine, yielded 5,6-*di*-O-*acetyl*-1,3:2,4-*di*-O-*but*-2′-*enylidene*-D-*glucitol* (79%), m. p. 144·5—146°, $[\alpha]_D^{20}$ + 10·7° (*c* 1·5 in $CHCl_3$) (Found: C, 58·7; H, 7·1%; N-alkali uptake, 5·42 ml./g. $C_{18}H_{26}O_8$ requires C, 58·4; H, 7·1%; uptake, 5·40 ml./g.), as plates from 5 parts of ethanol. (*b*) The diacetal (1 g., 1 mol.), benzoyl chloride (0·9 ml., 2·2 mol.), and pyridine (10 ml.) were kept at room temperature for 44 hr. The product was worked up as described for the dityrityl ether of 2,4-butenylideneglucitol. Crystallisation from methanol (50 ml.) and then ethanol (35 ml.) gave needles of the 5,6-*dibenzoate* (0·98 g., 57%), m. p. 179·5—180·5° $[\alpha]_D^{23}$ −27·5° (*c* 1·7 in $CHCl_3$) (Found: C, 67·6; H, 6·3%; N-alkali uptake, 4·04 ml./g. $C_{28}H_{30}O_8$ requires C, 68·0; H, 6·1%; uptake, 4·05 ml./g.).

Partial Acid Hydrolysis of 1,3:2,4-*Di*-O-*but*-2′-*enylidene*-D-*glucitol*.—0·01N-Hydrochloric acid (107 ml.) was poured with cooling into a swirled cold solution of the diacetal (4·0 g.) in ethanol (160 ml.). After 5 hr. at 20—21°, sodium hydrogen carbonate (0·16 g.) in water was added and the solution evaporated to dryness. A small amount of ethanol was added to the residue, and the whole was re-evaporated. This process was repeated with chloroform. The residue was dissolved in hot chloroform (40 ml.). The solution was set aside overnight to allow

[23] Kuivila, Keough, and Soboczenski, *J. Org. Chem.*, 1954, **19**, 780.

the monoacetal and inorganic salts to be precipitated. These were collected and recrystallised from ethanol, to give 2,4-*O*-butenylidene-D-glucitol (0·74 g., 39% based on the diacetal not recovered), m. p. and mixed m. p. 167—168°. The chloroform-soluble material, after two crystallisations from ethanol–light petroleum (b. p. 60—80°) gave the diacetal (1·68 g.), m. p. 152°.

Partial Acid Hydrolysis of 1,3:2,4:5,6-*Tri*-O-*but*-2′-*enylidene*-D-*glucitol*.—The triacetal (15 g., m. p. up to 108°) was treated as described for the hydrolysis of the diacetal above, except that the reaction time was 1 hr. The chloroform-insoluble part of the reaction mixture gave the 2.4-monoacetal (0·5 g., 5%), m. p. 164—167°. The chloroform filtrate was evaporated. Unchanged starting material (1·3 g.) was extracted from the residue with light petroleum (b. p. 60—80°) (2 × 50 ml.). Crystallisation of the material from light petroleum extract from a mixture of ethanol (10 ml.) and light petroleum (b. p. 60—80°) (2 ml.) and then thrice from 50 parts of light petroleum gave a pure *tri*-O-*butenylidene*-D-*mannitol* (Found: C, 63·5; H, 7·6. $C_{18}H_{26}O_6$ requires C, 63·9; H, 7·7%) (0·14 g., 1%), m. p. 166·5—167·5°, $[\alpha]_D^{22}$ −3·1° (*c* 1·4 in $CHCl_3$). A mixed m. p. with a tri-*O*-butenylidene-D-mannitol (prepared [24] by condensing mannitol with the aldehyde), m. p. 165—166°, $[\alpha]_D^{22}$ − 5·1° (*c* 1·5 in $CHCl_3$), showed no depression. In solvents (*a*), (*c*), and (*d*) the compound had R_F values of 0·94, 0·90, and 0·91, respectively. The light petroleum-insoluble part (12 g.) of the chloroform extract was crystallised once from benzene (120 ml.), to yield 1,3:2,4-di-*O*-but-2′-enylidene-D-glucitol (9·6 g., 83% based on unrecovered starting material), m. p. 149—152°. A mixed m. p. with pure diacetal, m. p. 154—155°, showed no depression.

Partial Acid Hydrolysis of the Syrupy Tributenylideneglucitol.—(i) The syrupy triacetal (13·3 g.) prepared by method (*a*) was hydrolysed as described for the 1,3:2,4:5,6-triacetal. The weight of unchanged starting material recovered was 1·0 g.; that of a syrupy fraction which did not crystallise and was presumed to be a diacetal was 5·7 g.; and that of monoacetal and inorganic salts was 1·1 g. The last fraction was twice crystallised from 15 parts of ethanol to give 3,4-*O*-*but*-2′-*enylidene*-D-*glucitol* (0·6 g., 7% based on unrecovered triacetal), m. p. 150—151°, $[\alpha]_D^{21}$ +23·6° (*c* 1·8 in H_2O) (Found: C, 51·3; H, 7·4. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%). (ii) A similar hydrolysis for 2·5 hr. gave a similar (6%) yield of the 3,4-monoacetal. The diacetal fraction from this experiment was hydrolysed in the conditions described for the hydrolysis of the 1,3:2,4-diacetal. The only crystalline product was a trace (2%) of the 2,4-monoacetal. (iii) The syrupy triacetal obtained by method (*b*), when hydrolysed according to the details for hydrolysis of the 1,3:2,4:5,6-triacetal, gave a similar result to that in (i) above, *i.e.*, no material containing a 2,4-ring was isolated and the yield of crystallised 3,4-monoacetal was 10%.

Identification of the Polyol and Determination of Crotonaldehyde in the Acetals.—The acetal (*ca.* 0·004 g.) in ethanol (0·3 ml.) was hydrolysed with N-hydrochloric acid (0·3 ml.) for 10 min. at 100°. Sodium hydrogen carbonate (0·04 g.) was added to the solution, and the whole evaporated to dryness. The residue was extracted with hot absolute ethanol, and the extract was concentrated. The concentrate was examined by ionophoresis in sodium metavanadate buffer (see above under " Materials ").

The compound (0·02—0·2 g.) in water or ethanol was added to a 0·25% solution of 2,4-dinitrophenylhydrazine (10% excess) in 2N-hydrochloric acid. The precipitated crotonaldehyde 2,4-dinitrophenylhydrazone was weighed. A mixed m. p. with authentic hydrazone, m. p. 188°, showed no depression. Results are tabulated.

Compound	Ionophoresis: hydrolysate moves as	Crotonaldehyde 2,4-dinitrophenylhydrazone (mole/mole of acetal)
3,4-*O*-But-2′-enylideneglucitol	Glucitol	0·96, m. p. 184—187°
1,3:2,4:5,6-Tri-*O*-but-2′-enylideneglucitol	Glucitol [a]	2·90, m. p. 182—184°
Syrupy tri-*O*-but-2′-enylideneglucitol	Glucitol [b] *	2·86, m. p. 183—185°
Tri-*O*-but-2′-enylidenemannitol	Mannitol	2·74, m. p. 184—186°

* With borate buffer, pH 9·2 (Frahn and Mills, *Chem. and Ind.*, 1956, 578). [a, b] Acetylation gave (*a*) 53% and (*b*) 37% of crystallised glucitol hexa-acetate, m. p. and mixed m. p. 97—98°.

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ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY. [*Received, January 15th*, 1963.]

[24] Bonner, Bourne, and Lewis, unpublished work.