20. *Butylidene Derivatives of Glucitol.*

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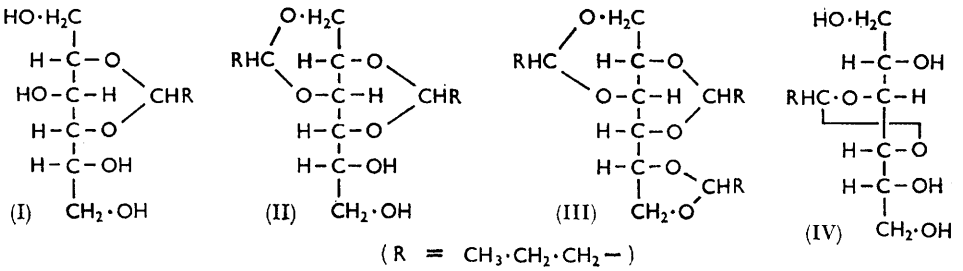
Condensation of D-glucitol with *n*-butyraldehyde in the presence of various catalysts has been studied, and the cyclic 2,4- and 3,4-mono-, 1,3:2,4-di-, and 1,3:2,4:5,6-tri-*O*-butylidene derivatives have been characterised. The structures assigned to the last two compounds are based on the assumption that there is no significant migration of acetal groups during partial hydrolysis. Independent correlation of structure for the acetals was possible using the known but-2′-enylideneglucitols.

D-Glucitol condenses with *n*-butyraldehyde in the presence of aqueous sulphuric acid to yield 2,4-*O*-butylidene-D-glucitol (I) (21%) (cf. preparation of 2,4-*O*-furfurylideneglucitol [1]). This material on acid hydrolysis was proved to be a glucitol derivative (isolation of glucitol as its trisphenylboronate) and an *n*-butyraldehyde derivative (isolation of *n*-butyraldehyde as its bisdimedone). The structure of the monoacetal (I) followed from the facts that it consumed 1 mol. of periodate and liberated 1 mol. of formaldehyde. The 2,4-*O*-butylidene-L-xylose resulting from the oxidation was characterised as its crystalline *p*-nitrophenylhydrazone. Hydrolysis of the xylose acetal gave crystalline L-xylose (7%), which was characterised further as its tetra-acetate. The monoacetal (I) yielded a crystalline tetra-acetate (identical with the product from reduction of tetra-*O*-acetyl-2,4-*O*-but-2′-enylideneglucitol), a bisphenylboronate, and a ditriphenylmethyl ether, thus supporting the presence of four hydroxyl groups, two of which were probably primary. Confirmation of the structure followed when the monoacetal (I) was obtained by reduction of 2,4-*O*-but-2′-enylidene-D-glucitol.[2]

Holst [3] condensed glucitol and *n*-butyraldehyde using concentrated sulphuric acid as the catalyst, and fractionally distilled the product to give two syrupy tributylideneglucitols which he did not characterise. We could not repeat this fractionation, but partial acid hydrolysis of the syrupy distillate gave crystalline 1,3:2,4-di-*O*-butylidene-D-glucitol (II) (15%), 2,4-monoacetal (10%), and an intractable syrup. This result suggests that the triacetal product was indeed a mixture of isomers, one of which was 1,3:2,4:5,6-tri-*O*-butylidene-D-glucitol (III). The same diacetal (II) was obtained by reduction of 1,3:2,4-di-*O*-but-2′-enylideneglucitol, but its structure was proved independently by periodate oxidation in which 1 mol. of oxidant was consumed and 1 mol. of formaldehyde was liberated. The resulting crystalline 2,4:3,5-di-*O*-butylidene-*aldehydo*-L-xylose (42—67%) was characterised

[1] Hockett, U.S.P. 2,584,129 (*Chem. Abs.*, 1952, **46**, 8148); Ruskin and Hockett, U.S.P. 2,853,495 (*Chem. Abs.*, 1959, **53**, 5150).
[2] Bonner, Bourne, and Lewis, *J.*, 1963, 3375.
[3] Holst, U.S.P. 2,355,533 (*Chem. Abs.*, 1945, **39**, 191); U.S.P. 2,387,662 (*Chem. Abs.*, 1946, **40**, 499).

through its crystalline *p*-nitrophenylhydrazone. The dibutylidenexylose, as expected,[4] mutarotated in chloroform, and on crystallisation from ethanol gave an unstable alcoholate. On acid hydrolysis it yielded xylose. The diacetal (II) gave a crystalline diacetate (identical



with the product from reduction of 5,6-di-*O*-acetyl-1,3:2,4-di-*O*-but-2′-enylideneglucitol), a dibenzoate, and a monotriphenylmethyl ether monoacetate, thus substantiating the presence of two hydroxyl groups, of which one is probably primary. Partial acid hydrolysis of the diacetal gave the 2,4-monoacetal (10%), thus indicating that the diacetal was a 1,3:2,4-substituted compound.

Pure, crystalline tributylideneglucitol (III) was obtained by hydrogenation of crystalline 1,3:2,4:5,6-tri-*O*-but-2′-enylideneglucitol. On partial hydrolysis it yielded the crystalline 1,3:2,4-diacetal (II) (41%)—thus proving its structure—and the 2,4-monoacetal (I) (15%). The identity of the diacetal was confirmed further by isolation of its dibenzoate, which was identical with the aforementioned sample.

When glucitol and the aldehyde were condensed using a trace of toluene-*p*-sulphonic acid as catalyst and removing the water of acetalisation by azeotropic distillation with benzene, a different syrupy mixture of triacetals seemed to be formed, since acid hydrolysis, under the same conditions as for the hydrolysis of the triacetal product obtained using concentrated sulphuric acid, now yielded 3,4-*O*-butylidene-D-glucitol (IV) (13%) in addition to the 2,4-monoacetal (8%), but only a trace of the crystalline diacetal (II). The 3,4-monoacetal reduced 2 mol. of periodate and liberated 2 mol. of formaldehyde but no formic acid. The same monoacetal was obtained also by reduction of 3,4-*O*-but-2′-enylidene-D-glucitol, thus confirming its structure. The isolation of a 3,4-monoacetal suggests that, barring ring re-arrangements, the original triacetal contained some 1,2:3,4:5,6-tri-*O*-butylidene-D-glucitol.

It is clear therefore that *n*-butyraldehyde and crotonaldehyde resemble other aldehydes in forming from glucitol a 2,4-monoacetal and a 1,3:2,4:5,6-triacetal, from which the 1,3:2,4-diacetal can be obtained by hydrolysis. However, it seems that the triacetal fraction is a mixture, containing also the 1,2:3,4:5,6-compound.

Experimental

Quantitative periodate oxidations [5] and formaldehyde determinations [6,7] used standard procedures. *n*-Butyraldehyde, present in the formaldehyde determination, does not interfere.[8] Light petroleum refers to the fraction b. p. 60—80°.

Reduction of But-2′-enylideneglucitols to Butylidene Derivatives.—The compound dissolved in ethanol (5—10% w/v), except where stated, was reduced with hydrogen at room temperature and atmospheric pressure in the presence of a palladium catalyst (0·01—0·02 g./g. of compound).

[4] Bourne, Corbett, and Stacey, *J.*, 1952, 2810; Wolfrom, *J. Amer. Chem. Soc.*, 1930, **52**, 2464; 1931, **53**, 2275.
[5] Aspinall and Ferrier, *Chem. and Ind.*, 1957, 1216.
[6] Mitchell, Kolthoff, Proskauser, and Weissberger, "Organic Analysis," Interscience Publ. Inc., New York, 1953, Vol. I, p. 288.
[7] Mitchell and Percival, *J.*, 1954, 1423.
[8] Feigl, "Spot Tests in Organic Analysis," Elsevier Publ. Co., Amsterdam, 5th edn., 1956, p. 331.

Reduction of 2,4-O-*But-2′-enylidene*-D-*glucitol.*—The monoacetal [2] (1·00 g.) in 80% aqueous ethanol, absorbed 1·01 mol. of hydrogen. The 2,4-O-*butylidene*-D-*glucitol* (Found: C, 50·85; H, 8·4. $C_{10}H_{20}O_6$ requires C, 50·8; H, 8·5%) was crystallised from ethanol (10 ml.) as needles (0·86 g., 85%), m. p. 158—159°, $[\alpha]_D^{25}$ −10·1° (*c* 1·9 in H_2O), $[\alpha]_D^{26}$ −9·2° (*c* 1·9 in 1% aqueous boric acid).

Condensation of D-*Glucitol and* n-*Butyraldehyde in the Presence of Aqueous Sulphuric Acid.*—Equimolar amounts of polyol (18 g.) and *n*-butyraldehyde were used, as described for crotonaldehyde; [2] 2,4-*O*-butylidene-D-glucitol was obtained (21%, from ethanol), m. p. and mixed m. p. with the aforementioned 2,4-monoacetal, 157—158°, $[\alpha]_D^{24}$ −9·6° (*c* 1·9 in H_2O), $[\alpha]_D^{25}$ −4·8° [*c* 1·9 in 4% w/v 60% aqueous methanolic $(PhBO)_3$].

Identification of the Products of Acid Hydrolysis of 2,4-O-*Butylidene*-D-*glucitol.*—The compound (0·50 g.), water (20 ml.) and Zeo-Karb 225 ion exchange resin (Permutit Co. Ltd.) in the hydrogen form (0·3 ml.) were heated at 100° for 1 hr.; volatile matter was distilled off at 20 mm. into a trap cooled in liquid nitrogen. Water (20 ml.) was added to the residue, and the procedure was repeated twice. The distillate was added to dimedone (0·6 g.) in water (40 ml.). After 2 days the yield of *n*-butyraldehyde bisdimedone was 0·40 g., m. p. and mixed m. p. with authentic specimen, 127—128°. Recrystallised from ethanol, the material had m. p. 130°. The non-volatile residue was extracted with warm methanol (10 ml.) and the extract was added to phenylboronic anhydride (0·66 g., 1·0 mol.) in methanol (2 ml.). The yield of D-glucitol trisphenylboronate [9] was 0·59 g. (0·62 mol.). Recrystallised from ethanol–light petroleum it had m. p. 193—194°, not depressed in admixture with an authentic specimen.

Periodate Oxidation of 2,4-O-*Butylidene*-D-*glucitol.*—(*a*) *Quantitatively.* The compound consumed 1·09, 0·97, and 0·97 mol. of periodate (2·3 mol. initially present) after 3, 8·5, and 21·5 hr., respectively, and liberated 0·97 mol. of formaldehyde (theory, 1·0). (*b*) *Qualitatively.* Sodium periodate (1·17 g., 1·1 mol.) in water (20 ml.) was added with cooling during 10 min. to the 2,4-monoacetal (1·17 g.) in water (20 ml.) containing sodium hydrogen carbonate (0·1 g.). After a further 1 hr. at room temperature, the solution was evaporated (bath 30—40°). The distillate, collected in a receiver cooled in an acetone-solid carbon dioxide mixture, was treated with dimedone (1·2 g.) in water (total volume then 300 ml.). The yield of formaldehyde bisdimedone was 0·43 g. (0·3 mol.), m. p. and mixed m. p. with an authentic specimen, 187—188·5°. The syrupy 2,4-*O*-butylidene-L-xylose was extracted in 99% yield from the inorganic salts with chloroform. On paper chromatography in butan-1-ol–ethanol–water (40 : 11 : 19 v/v) it had R_F 0·87. Part (0·2 g.) in ethanol (2 ml.) was refluxed with *p*-nitrophenylhydrazine (0·15 g., 1 mol.) for 30 min. to yield 2,4-O-*butylidene*-L-*xylose*-p-*nitrophenylhydrazone* (0·04—0·11 g., 12—33%), m. p. 188—190° (Found: C, 53·3; H, 6·4; N, 12·2. $C_{15}H_{21}N_3O_6$ requires C, 53·1; H, 6·2; N, 12·4%).

Part (0·6 g.) of the remaining butylidenexylose in water (50 ml.) was boiled with Zeo-Karb 225 ion exchange resin in the hydrogen form (a few grains) in an open flask for 15 min. The reaction mixture was evaporated, and the residue was extracted with boiling ethanol. The ethanolic extract yielded crude L-xylose (0·05 g.) on cooling. Recrystallisation gave α-L-xylose (0·03 g., 7%), m. p. and mixed m. p. 144°. This material on acetylation gave tetra-*O*-acetyl-β-L-xylose (47%), m. p. and mixed m. p. 124°, from ethanol.

Derivatives of 2,4-O-*Butylidene*-D-*glucitol.*—(*a*) The monoacetal (0·385 g.), treated with acetic anhydride in pyridine, yielded 1,3,5,6-*tetra*-O-*acetyl*-2,4-O-*butylidene*-D-*glucitol*, 0·40 g. (61%), m. p. 68—69°, $[\alpha]_D^{18}$ −7·9° (*c* 2·2 in $CHCl_3$) (Found: C, 53·6; H, 7·0; N-alkali uptake, 9·72 ml./g. $C_{18}H_{28}O_{10}$ requires C, 53·4; H, 7·0%, uptake, 9·89 ml./g.), as needles from 10 parts 50% aqueous ethanol. Reduction of 1,3,5,6-tetra-*O*-acetyl-2,4-*O*-but-2′-enylidene-D-glucitol [2] also yielded the 2,4-*O*-butylidene acetal tetra-acetate, m. p. and mixed m. p. with the above specimen, 67—69°. (*b*) The acetal (1 g.) gave a *bisphenylboronate* (Found: C, 64·5; H, 6·5; B, 5·1. $C_{22}H_{26}B_2O_6$ requires C, 64·7; H, 6·4; B, 5·3%) by using the same method as described for the preparation of 2,4-*O*-but-2′-enylidene-D-glucitol bisphenylboronate.[2] After crystallisation from light petroleum, the product (needles; 0·85 g., 49%), had m. p. 82—84·5°, $[\alpha]_D^{20}$ −6·1° (*c* 1·4 in $CHCl_3$), $[\alpha]_D^{21}$ −3·8° [*c* 1·5 in 4% w/v $(PhBO)_3$ in $CHCl_3$]. (*c*) The acetal (0·5 g.) gave a *di*-O-*triphenylmethyl derivative* when the same method as described for the preparation of 2,4-*O*-but-2′-enylidene-di-*O*-triphenylmethyl-D-glucitol [2] was used. After crystallisation from methanol, the product (needles; 0·81 g., 53%), $[\alpha]_D^{22}$ +9·5° (*c* 1·7 in $CHCl_3$) melted sharply

[9] Kuivila, Keough, and Soboczenski, *J. Org. Chem.*, 1954, **19**, 780; Bourne, Lees, and Weigel, unpublished results.

within the range 70—80° (effervescence). After some hours at room temperature, the material had m. p. *ca.* 90° (eff.). Analysis [Found (two preparations): C, 80·3, 80·3; H, 6·9, 6·8. $C_{48}H_{48}O_6$ requires C, 80·0; H, 6·7%] showed that the material was not solvated. This melting phenomenon is similar to that observed for the butenylideneditriphenylmethylglucitol.[2] The triphenylmethyl groups are assumed to be at the 1- and the 6-position.

Preparation of the Tributylideneglucitols.—(*a*) 1,3:2,4:5,6-*Tri*-O-*butylidene*-D-*glucitol.* 1,3:2,4:5,6-Tri-*O*-but-2′-enylidene-D-glucitol (8·9 g., m. p. 112—114°) absorbed 2·96 mol. of hydrogen. The product, after removal of the catalyst and ethanol, was distilled at 132—134°/0·05 mm. (bath 185°) to give one main fraction, 6·53 g. (72%), n_D^{25} 1·4618, $[\alpha]_D$ +0·5° (*c* 10·1 or 1·9 in EtOH). After 3 weeks, the fraction partially solidified. A sample was crystallised from 85% aqueous ethanol to yield 1,3:2,4:5,6-*tri*-O-*butylidene*-D-*glucitol* (Found: C, 62·8; H, 9·2. $C_{18}H_{32}O_6$ requires C, 62·8; H, 9·4%), m. p. 31—33°. (*b*) *Holst's method, i.e., by using concentrated sulphuric acid.* By condensing D-glucitol and the aldehyde, Holst [3] obtained two isomeric tributylidene derivatives—one (40%), b. p. 162—167°/4 mm., n_D^{25} 1·462, $[\alpha]_D^{25}$ +10·0° (*c* 10·0 in EtOH), and the other (22%), b. p. 172—177°/4 mm. (not characterised further). In our hands, the method gave products which distilled from 136 to 162°/0·2 mm., with a small forerun at *ca.* 60°. The distillates (yield 50—80%) were redistilled (Found: C, 62·8; H, 9·4. $C_{18}H_{32}O_6$ requires C, 62·8; H, 9·4%), n_D^{25} 1·461—1·463, $[\alpha]_D^{20}$ +2·3° to +7·0° (*c* 1·7 in EtOH), but did not afford a fraction of characteristic b. p. (*c*) *By using toluene*-p-*sulphonic acid.* D-Glucitol (50 g.), *n*-butyraldehyde (100 ml., 4·14 mol.), benzene (100 ml.), and toluene-*p*-sulphonic acid (0·1 g.) were refluxed under a Dean and Stark head on a water-bath for 2 hr. More catalyst (0·1 g.) was then added and after a further 4 hr., 13·8 ml. (93%) of water had been collected. The solution was passed through Biodeminrolit (Permutit Co. Ltd.) to remove the catalyst, and was then evaporated. The residue was distilled at 0·1 mm. A forerun, b. p. 48—60° was discarded; the main fraction (81 g., 86%), had b. p. 143—148°, $[\alpha]_D^{21}$ +7·0° (*c* 10·0 in EtOH), n_D^{25} 1·460.

Partial Acid Hydrolysis of the Triacetals obtained by Holst's Method.—The triacetal fraction (130 g.), suspended in 60% aqueous acetic acid (576 ml.), was kept at 88—90° for 1 hr. The homogeneous solution was evaporated (bath *ca.* 45°) and the cold residue was extracted with light petroleum using first a 200 ml., then a 50 ml. portion. The combined extracts contained unchanged starting material (25—32 g.). The light petroleum-insoluble material was dissolved in hot chloroform–benzene (130 ml. each), and allowed to cool, the 2,4-monoacetal (10—13 g.) crystallising. Recrystallisation from ethanol afforded the pure compound (46—78% recovery), m. p. and mixed m. p. 157—158°. The chloroform–benzene crystallisation liquors were evaporated and the residue (71 g.) was crystallised from a mixture of benzene (71 ml.) and light petroleum (100 ml.) to yield crude 1,3:2,4-diacetal. Crystallisation of this from benzene gave material (10—16 g.), m. p. 128—131°. Recrystallisation from benzene would not improve this value, but crystallisation from water gave material (50% recovery) of m. p. and mixed m. p. with the diacetal prepared below, 132°. The benzene–light petroleum liquors contained an intractable syrup.

Reduction of 1,3:2,4-*Di*-O-*but*-2′-*enylidene*-D-*glucitol.*—The diacetal absorbed 2·01 mol. of hydrogen. The 1,3:2,4-*di*-O-*butylidene*-D-*glucitol* was crystallised from benzene to yield chunky crystals (69—80%), m. p. 130—132°, $[\alpha]_D^{22}$ +1·6° (*c* 1·6 in EtOH) (Found: C, 57·6; H, 9·0. $C_{14}H_{26}O_6$ requires C, 57·9; H, 9·0%).

Periodate Oxidation of 1,3:2,4-*Di*-O-*butylidene*-D-*glucitol.*—(*a*) *Quantitatively.* The compound consumed 0·98, 1·02, and 1·00 mol. of periodate (3·8 mol. initially present) after 1·75, 7·25, and 22 hr. respectively, and liberated 0·98 mol. of formaldehyde (theory, 1·0 mol.). (*b*) *Qualitatively.* Sodium periodate (0·9 g., 1·2 mol.) in water (15 ml.) was added during 12 min. to a fine suspension of the diacetal (1·0 g.) in water (25 ml.) containing sodium hydrogen carbonate (0·1 g.) at such a rate that the pH was $\geqslant$6·9. After a further 1 hr. at 20°, the solution was worked up as described for the 2,4-monoacetal. The distillate yielded formaldehyde bisdimedone (0·82 g., 0·81 mol.), m. p. and mixed m. p. 187—188°. The material in the chloroform extract was thrice crystallised from 15 parts of light petroleum to yield needles of 2,4:3,5-*di*-O-*butylidene-aldehydo*-L-*xylose*, 0·37 g. (42%), m. p. 108—110° (Found: C, 60·6; H, 8·5. $C_{13}H_{22}O_5$ requires C, 60·4; H, 8·6%), $[\alpha]_D^{20}$ −66° ⟶ +0·4° (*c* 1·6 in $CHCl_3$). A molecular weight analysis, by a standard cryoscopic procedure [10] with dry benzene as solvent, indicated that the compound was monomeric (Found: *M*, 256 ± 2. Calc.: *M*, 258·3) over the concentration range studied, *i.e.*, up

[10] Finch and Gardner, *J. Inorg. Nuclear Chem.*, 1963, **25**, 927.

to 0·2M. The compound had a strong carbonyl absorption at 5·75 mμ. Crystallisation of this material from ethanol gave a compound, presumably the hemiacetal, which showed a new strong absorption band at 2·93 mμ and virtually no absorption at 5·75 mμ. This material was unstable —the m. p., at about 80—90°, was not reproducible, and different preparations gave different elemental combustion analysis values. Improved yields (67%) of the dibutylidene acetal were obtained by directly extracting it from the reaction mixture with chloroform.

2,4:3,5-Di-*O*-butylidenealdehydo-L-xylose (0·20 g.), *p*-nitrophenylhydrazine (0·115 g.), and ethanol (3 ml.) were heated at 75—85° for 3 hr. The mixture was filtered, and the filtrate placed in a refrigerator for 3 days. The crude product, 0·22 g. (72%), m. p. 175—176° when recrystallised from ethanol gave the pure p-*nitrophenylhydrazone*, needles (Found: C, 57·8; H, 7·0; N, 10·8. $C_{19}H_{27}N_3O_6$ requires C, 58·0; H, 6·9; N, 10·7%), m. p. 182—184°, $[\alpha]_D^{22}$ −147·2° (*c* 1·5 in EtOH).

The xylose diacetal (0·25 g.), water (5 ml.), and Zeo-Karb 225 resin in the hydrogen form were kept at 100° for 4 hr. The resin was filtered off and washed, and the combined filtrate and washings were evaporated. The residual syrup crystallised from methanol gave L-xylose, 0·09 g. (62%), m. p. and mixed m. p. 142—143°.

Derivatives of 1,3:2,4-*Di*-O-*butylidene*-D-*glucitol*.—(*a*) 5,6-Di-*O*-acetyl-1,3:2,4-di-*O*-but-2′-enylidene-D-glucitol [2] (0·60 g.) absorbed 2·14 mol. of hydrogen, and the 5,6-*di*-O-*acetyl*-1,3:2,4-*di*-O-*butylidene*-D-*glucitol* formed was crystallised from 10 parts of 50% aqueous ethanol as needles (Found: C, 57·8; H, 8·2; N-alkali-uptake, 5·27 ml./g. $C_{18}H_{30}O_8$ requires C, 57·7; H, 8·1%; uptake, 5·34 ml./g.) (0·52 g., 86%), m. p. 94°, $[\alpha]_D^{22}$ +2·8° (*c* 1·8 in EtOH). 1,3:2,4-Di-*O*-butylidene-D-glucitol, treated with acetic anhydride in pyridine, also yielded the diacetate (66%), m. p. and mixed m. p. with the above sample, 93—94°. (*b*) The diacetal (0·20 g.) in pyridine (1·4 ml.) was treated with benzoyl chloride (0·18 ml., 2·2 mol.) for 2 hr. The 5,6-*dibenzoate* crystallised from light petroleum as needles (0·14 g., 41%), m. p. 110°, $[\alpha]_D^{17}$ −30·0° (*c* 1·6 in $CHCl_3$) (Found: C, 67·8; H, 7·05; N-alkali uptake, 3·96 ml./g. $C_{28}H_{34}O_8$ requires C, 67·45; H, 6·9%; uptake, 4·01 ml./g.). (*c*) The diacetal (1·0 g.) in pyridine (6·5 ml.) was treated with triphenylmethyl chloride (1 g., 1 mol.) for 27 hr. at room temperature. After being worked up in the usual way, the product was crystallised from light petroleum (30 ml.) to yield unchanged diacetal (0·2 g.; m. p. and mixed m. p. 131·5°). The crystallisation liquors were evaporated and the syrupy residue was dissolved in pyridine, and treated with acetic anhydride. The product was crystallised twice from light petroleum and then once from 75% aqueous ethanol to yield an O-*acetyl*-1,3:2,4-*di*-O-*butylidene*-O-*triphenylmethyl*-D-*glucitol* (Found: C, 72·9; H, 7·2. $C_{35}H_{42}O_7$ requires C, 73·2; H, 7·4%) (0·55 g., 35% based on the diacetal not recovered), m. p. 126—127°, $[\alpha]_D^{22}$ −23·8° (*c* 1·7 in $CHCl_3$). The triphenylmethyl and acetyl groups are assumed to be at the 6- and the 5-position, respectively.

Partial Acid Hydrolysis of 1,3:2,4-*Di*-O-*butylidene*-D-*glucitol*.—The diacetal (2·0 g.) in 60% aqueous acetic acid (20 ml.) was kept at 90° for 3 hr. The solution was evaporated (bath 40°) and the residue dissolved in chloroform (10 ml.). The crystals (0·3 g.) which separated were thrice crystallised from ethanol to yield the 2,4-monoacetal (0·16 g., 10%), m. p. and mixed m. p. 155—158°. The chloroform-soluble material was a syrup.

Partial Acid Hydrolysis of 1,3:2,4:5,6-*Tri*-O-*butylidene*-D-*glucitol*.—The triacetal (4·45 g. of the semi-solid) was hydrolysed as described for the hydrolysis of the mixed triacetals obtained by Holst's method. The yield of starting material recovered was 1·28 g., that of recrystallised 1,3:2,4-diacetal, m. p. and mixed m. p. 129—130°, 1·1 g. (41% based on the triacetal not recovered) (benzoylation yielded the dibenzoate), and of recrystallised 2,4-monoacetal, m. p. and mixed m. p. 157—158° (0·32 g., 15% based on the triacetal not recovered).

Partial Acid Hydrolysis of the Triacetals obtained using Toluene-p-*sulphonic Acid*.—The triacetal fraction (70·3 g.) was treated as described for the hydrolysis of the triacetals obtained by Holst's method. The yield of starting material recovered was 23·3 g., that of syrupy diacetal, 21·6 g. [which yielded only a trace (0·89 g.) of crude 1,3:2,4-diacetal on crystallisation], and that of monoacetal, 13·8 g. This material was crystallised from ethanol (100 ml.) to yield the 2,4-monoacetal (2·54 g., 8% based on unrecovered triacetal). The crystallisation liquors were concentrated and yielded 3,4-*O*-butylidene-D-glucitol (4·14 g., 13% based on unrecovered triacetal), m. p. 109—110°. A mixed m. p. with 3,4-monoacetal, m. p. 112—113°, described below, showed no depression. Recrystallisation from ethanol yielded a small quantity of material of m. p. 112—113°.

Reduction of 3,4-O-*But*-2′-*enylidene*-D-*glucitol*.—The monoacetal [2] (0·8 g.) in 80% aqueous

ethanol (30 ml.) absorbed 1·14 mol. of hydrogen. Crystallisation of the product from ethanol yielded **3,4-O-*butylidene*-D-*glucitol*** (Found: C, 50·7; H, 8·4. $C_{10}H_{20}O_6$ requires C, 50·8; H, 8·5%) (0·6 g., 74%), m. p. 112—113°, $[\alpha]_D^{21}$ +37·2° (*c* 1·7 in H_2O).

Periodate Oxidation of **3,4-O-*Butylidene*-D-*glucitol***.—The compound consumed 1·97, 1·99, and 2·01 mol. of periodate (4·4 mol. initially present) after 1·5, 7, and 20·5 hr., respectively, and liberated 1·98 mol. of formaldehyde (theory, 2·0); no formic acid was found by volumetric analysis (theory, 0·0).

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