

257. *The isoPropylidene Derivatives of Hexahydric Alcohols.*
Part II. isoPropylidene Derivatives of Sorbitol.*

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Graded acidic hydrolysis of triisopropylidene sorbitol is shown to give 3 : 4-5 : 6-diisopropylidene sorbitol, 3 : 4-isopropylidene sorbitol, and sorbitol. This proves the triketal to be 1 : 2-3 : 4-5 : 6-triisopropylidene sorbitol. Some new derivatives of 2 : 3-4 : 5-diisopropylidene aldehydo-D-arabinose are described.

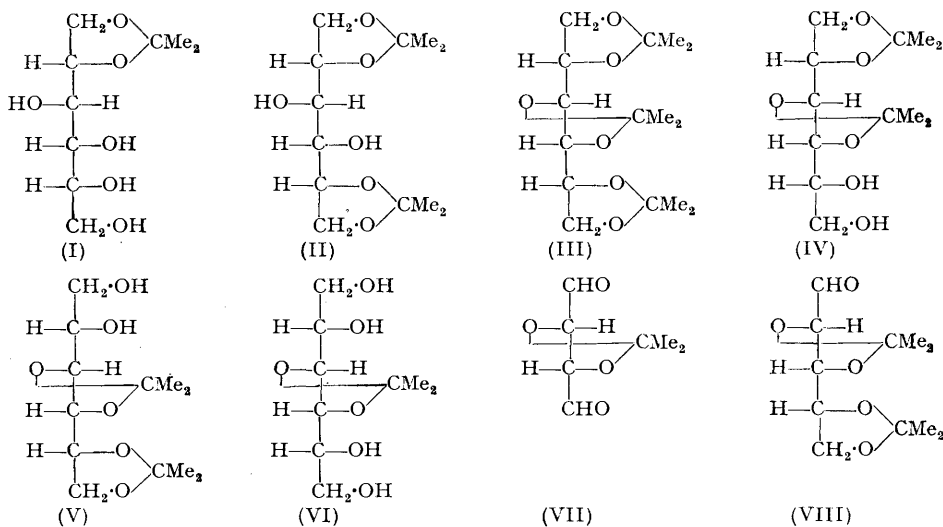
THE early claim by Speier (*Ber.*, 1895, **28**, 2531) that a crystalline triisopropylidene sorbitol results from the condensation of sorbitol (D-glucitol) with excess of acetone in the presence of 1% hydrogen chloride has since been verified by Asahina and Shinoda (*J. Pharm. Soc. Japan*, 1930, **50**, 1; *Chem. Abs.*, 1930, **24**, 1704) and by Strain (*J. Amer. Chem. Soc.*, 1934, **56**, 1756). Recently, Pressman, Anderson, and Lardy (*ibid.*, 1950, **72**, 2404) reported that they had prepared the 1 : 2- (I) and the 1 : 2-5 : 6-isopropylidene derivative (II) by treating sorbitol with acetone in the presence of zinc chloride, and had converted the diisopropylidene compound into triisopropylidene sorbitol with acetone and concentrated sulphuric acid. This evidence did not permit a precise structure to be assigned to the triketal because of the possibility of rearrangement of the isopropylidene groups in the presence of concentrated sulphuric acid. We have now proved that triisopropylidene sorbitol possesses the 1 : 2-3 : 4-5 : 6-structure (III) by showing that it can be converted, by partial acidic hydrolysis, into 3 : 4-5 : 6-diisopropylidene sorbitol (V) and 3 : 4-isopropylidene sorbitol (VI), compounds which were not encountered by Pressman, Anderson, and Lardy (*loc. cit.*).

After triisopropylidene sorbitol had been submitted to mild acid hydrolysis, the products were separated, by fractional crystallisation and fractional distillation, into unchanged triisopropylidene sorbitol (46%), a crystalline diisopropylidene sorbitol (10%), a syrupy mixture (A) of diisopropylidene sorbitols (14%), and a crystalline monoisopropylidene sorbitol (8%). The two new crystalline compounds were shown to be derivatives of sorbitol by conversion into triisopropylidene sorbitol and sorbitol hexa-acetate, this step being necessary because they had been prepared in small yields from a sorbitol sample which had not been specially purified (cf. Bourne and Wiggins, *J.*, 1948, 1933; Barker and Bourne, *J.*, 1952, 905).

The crystalline monoisopropylidene sorbitol gave syrupy tetramethyl, tetra-acetyl, and tetramethanesulphonyl derivatives. Acidic hydrolysis of the tetramethyl ether yielded a syrupy tetramethyl hexitol; this syrup rapidly consumed one mol. of lead tetra-acetate, and so must have possessed an α -glycol group. It followed that a five-membered ketal ring must

* Part I, *J.*, 1946, 13.

have been present in the *isopropylidene sorbitol* and, since this compound readily formed crystalline ditrityl and diacetyl ditrityl derivatives, it was probable that the ring did not involve either of the primary positions of the hexitol molecule (cf. Helferich, *Adv. Carbohydrate Chem.*, 1948, **3**, 88); thus the *isopropylidene* group most probably engaged the 2 : 3-, 3 : 4-, or 4 : 5-positions. The second of these three possibilities would have explained why the tetramethanesulphonyl ester of the *isopropylidene sorbitol* yielded iodine and



3.3 mols. of sodium methanesulphonate when heated with sodium iodide in acetone at 100° , for in this case the methanesulphonyloxy-groups would have been arranged in vicinal pairs at the primary and adjacent secondary positions (cf. Bladon and Owen, *J.*, 1950, 598). Nevertheless, in view of the fact that 3 : 4-dimethanesulphonyl 1 : 2-5 : 6-diisopropylidene mannitol undergoes the same exchange reaction (Bladon and Owen, *loc. cit.*), this conversion could not be used as a basis for the unequivocal elimination of the alternative 2 : 3- and 4 : 5-structures.

Proof that the *isopropylidene sorbitol* was in fact the 3 : 4-compound (VI) was obtained from a completely independent approach, namely, from an examination of its behaviour when treated with sodium metaperiodate. The consumption of 1.93 mols. resulted in the production of 2 mols. of formaldehyde, but no formic acid. In conformity with this conclusion, the larger fragment resulting from the oxidation was identified as 2 : 3-*isopropylidene D-threodihydroxysuccindialdehyde* (VII) by conversion into 2 : 3-*isopropylidene D-threodihydroxysuccindialdehyde bisphenylhydrazone* and dibenzylidene *D-threitol*, both known compounds.

The structure of the crystalline *diisopropylidene sorbitol* was established in a similar manner. Since the compound rapidly consumed 0.99 mol. of sodium metaperiodate and gave 0.86 mol. of formaldehyde, it must have carried an α -glycol group at either the 1 : 2- or the 5 : 6-position. In the former case the major oxidation product should have been a *diisopropylidene aldehydo-D-arabinose* and, in the latter, a *diisopropylidene aldehydo-L-xylose*. A syrupy *diisopropylidene pentose* was isolated and had physical constants similar to those reported by Wiggins (*J.*, 1946, 13) and by English and Griswold (*J. Amer. Chem. Soc.*, 1948, **70**, 1390) for 2 : 3-4 : 5-*diisopropylidene aldehydo-D-arabinose* (VIII). Moreover, *D-arabinose dibenzyl mercaptal* and α -*D-arabinose tetra-acetate* were isolated when the product of the hydrolysis of the syrup was treated with the appropriate reagents. Thus the crystalline *diisopropylidene sorbitol* must have been one of the three possible isomers possessing the 3 : 4 : 5 : 6-structure. The fact that its ditoluene-*p*-sulphonate gave iodine and 1.84 mols. of sodium toluene-*p*-sulphonate, when treated with sodium iodide in acetone at 100° , was in agreement with this view.

The definite assignment of the 3 : 4-5 : 6-structure (V) to the crystalline *diisopropyl-*

idene sorbitol became possible when it was converted into the above 3:4-*isopropylidene* sorbitol by acidic hydrolysis. It followed that the triketal from which both were derived initially was 1:2-3:4-5:6-*triisopropylidene* sorbitol (III) and that the *diisopropylidene aldehydo*-D-arabinose aforementioned carried the acetone residues in the 2:3- and the 4:5-positions (VIII).

Two new crystalline derivatives of 2:3-4:5-*diisopropylidene aldehydo*-D-arabinose were prepared during this work; they were the semicarbazone and the bisdimezone compound. The latter was insoluble in water, a fact which explained why the dimezone derivative of formaldehyde could be isolated in pure form from the periodate oxidation products of 3:4-5:6-*diisopropylidene* sorbitol only after the formaldehyde had been separated by distillation in steam.

These results and those described in Part I of this series (*loc. cit.*) show that there is a close parallel between mannitol and sorbitol inasmuch as each condenses with acetone to give a triketal possessing the 1:2-3:4-5:6-structure; moreover, during acidic hydrolysis of the *triisopropylidene* derivatives, the ketal groups engaged at the primary positions are the least stable in each case. One might expect that two *diisopropylidene* sorbitols would be formed when 1:2-3:4-5:6-*triisopropylidene* sorbitol is hydrolysed, *i.e.*, that the 3:4-5:6-*diisopropylidene* sorbitol described should have been accompanied by its 1:2-3:4-isomer (IV). Evidence in support of this was obtained when the above syrupy mixture (A) of *diisopropylidene* sorbitols was oxidised with sodium metaperiodate and then hydrolysed to give a syrup, which was identified as a mixture of arabinose and xylose by chromatographic analysis.

The similarity of the behaviour of the two hexitols towards acetone is still further emphasised when it is recalled that Pressman, Anderson, and Lardy (*loc. cit.*) were able to prepare both 1:2-*isopropylidene* and 1:2-5:6-*diisopropylidene* sorbitol by much the same procedure as Baer and Fischer (*J. Biol. Chem.*, 1939, **123**, 463) used to prepare 1:2-5:6-*diisopropylidene* mannitol.

EXPERIMENTAL

1:2-3:4-5:6-*Triisopropylidene Sorbitol from Sorbitol*.—A mixture of sorbitol (80 g.), acetone (1 l.), and concentrated sulphuric acid (8 c.c.) was shaken for 18 hours, neutralised with concentrated aqueous ammonia (*d* 0.880; 28 c.c.) and sodium carbonate (50 g.), and filtered. The filtrate and acetone washings were combined, concentrated at 12 mm., in the presence of a small amount of sodium carbonate, to *ca.* 150 c.c., and poured into ice-water (2.5 l.). Recrystallisation of the precipitate, from aqueous acetone containing a trace of ammonia, gave colourless needles of *triisopropylidene* sorbitol (51.2 g.), m. p. 46°, $[\alpha]_D^{18} + 13.8^\circ$ (*c.* 6.1 in methyl alcohol); reported constants are m. p. 45–48°, $[\alpha]_D + 12.7^\circ$, $+14.3^\circ$ (in ethyl alcohol) (Asahina and Shinoda, *loc. cit.*; Strain, *loc. cit.*; Pressman, Anderson, and Lardy, *loc. cit.*).

Graded Hydrolysis of 1:2-3:4-5:6-Triisopropylidene Sorbitol.—A solution of *triisopropylidene* sorbitol (32.3 g.) in absolute ethyl alcohol (792 c.c.), containing 5*N*-hydrochloric acid (16.2 c.c.), was kept at 18–20° for 105 minutes, cooled to 0°, neutralised with barium carbonate, and filtered. The filtrate and alcohol washings were combined and evaporated at 40°, leaving a syrup, which was extracted exhaustively with cold acetone. Evaporation of the acetone solution gave a syrup, which was dissolved in ethyl alcohol (30 c.c.) and poured into ice-water containing a trace of ammonia. Recrystallised from aqueous acetone, the precipitate gave *triisopropylidene* sorbitol (15 g.), m. p. 45° alone or on admixture with the above specimen.

Evaporation of the aqueous alcoholic solution yielded a syrup, which was extracted exhaustively with cold benzene, leaving a solid residue; several crystallisations of the solid from dry acetone gave 3:4-*isopropylidene sorbitol* (2.0 g.), m. p. 89–90°, $[\alpha]_D^{20} + 31.0^\circ$ (*c.* 4.9 in methyl alcohol) (Found: C, 48.8; H, 8.0. $C_8H_{18}O_6$ requires C, 48.6; H, 8.2%).

The benzene solution was evaporated and the residue was distilled at 0.015 mm., a fraction which had b. p. 138° (bath-temp.) being collected as a colourless syrup (6.6 g.), having $n_D^{25} 1.4650$ (Found: C, 55.0; H, 8.3. Calc. for $C_{12}H_{22}O_6$: C, 55.0; H, 8.5%). Crystallisation of this fraction from ether-light petroleum (b. p. 40–60°) gave 3:4-5:6-*diisopropylidene sorbitol* (2.8 g.), m. p. 55–56°, $[\alpha]_D^{25} + 25.2^\circ$ (*c.* 1.4 in ethyl alcohol). This compound gave correct analytical data for a hemihydrate, even after being dried at 25°/0.01 mm. over phosphoric anhydride [Found (on samples from three separate experiments): C, 53.0, 52.9, 53.0; H, 8.4,

8·7, 8·5. $C_{12}H_{22}O_6 \cdot \frac{1}{2}H_2O$ requires C, 53·1; H, 8·5%]. A syrupy residue (A) resulted from evaporation of the ether–light petroleum mother-liquors; its examination is reported on p. 1414.

1 : 2 : 3 : 4 : 5 : 6-*Triisopropylidene Sorbitol from 3 : 4-isoPropylidene Sorbitol*.—3 : 4-*iso*-Propylidene sorbitol (1·0 g.), condensed with acetone, as described above, yielded 1 : 2 : 3 : 4 : 5 : 6-*triisopropylidene sorbitol* (0·55 g.), m. p. 46° alone or on admixture with a specimen prepared directly from sorbitol.

1 : 2 : 3 : 4 : 5 : 6-*Triisopropylidene Sorbitol from 3 : 4-5 : 6-Diisopropylidene Sorbitol*.—Treatment of 3 : 4-5 : 6-*diisopropylidene sorbitol* (0·50 g.) with acetone and concentrated sulphuric acid, as described above, gave 1 : 2 : 3 : 4 : 5 : 6-*triisopropylidene sorbitol* (0·29 g.), m. p. 45–46° alone or on admixture with a specimen prepared directly from sorbitol.

Sorbitol Hexa-acetate from 3 : 4-isoPropylidene Sorbitol.—The *isopropylidene* compound (0·30 g.) was heated at 100° for 2 hours with *n*-sulphuric acid (5 c.c.). The solution was diluted with water (20 c.c.), neutralised with barium carbonate, filtered, and concentrated to a syrup, which, when acetylated, gave sorbitol hexa-acetate (0·35 g.), m. p. and mixed m. p. 99–100°.

Sorbitol Hexa-acetate from 3 : 4-5 : 6-Diisopropylidene Sorbitol.—When hydrolysed and then acetylated (see above), 3 : 4-5 : 6-*diisopropylidene sorbitol* (0·30 g.) gave sorbitol hexa-acetate (0·25 g.), m. p. and mixed m. p. 100°.

1 : 2 : 5 : 6-*Tetra-acetyl 3 : 4-isoPropylidene Sorbitol*.—A mixture of 3 : 4-*iso*propylidene sorbitol (1·00 g.), acetic anhydride (2·7 c.c.), and pyridine (15 c.c.) was kept at 25° for three days, poured into excess of sodium hydrogen carbonate solution, and extracted with chloroform. The extracts were washed successively with dilute sulphuric acid, sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), filtered, and concentrated to a syrup, which was then distilled. The main fraction (1·32 g.) of the *tetra-acetate* had b. p. 160–164° (bath-temp.)/0·04 mm., $[\alpha]_D^{20} + 8\cdot0^\circ$ (*c*, 2·3 in chloroform), n_D^{19} 1·4475 (Found : C, 52·5; H, 6·7; Ac, 44·2. $C_{17}H_{26}O_{10}$ requires C, 52·3; H, 6·7; Ac, 44·1%).

1 : 2 : 5 : 6-*Tetramethanesulphonyl 3 : 4-isoPropylidene Sorbitol*.—A solution of 3 : 4-*iso*propylidene sorbitol (0·50 g.) and methanesulphonyl chloride (4 mols.) in dry pyridine (4·0 c.c.) was kept at 0° for 20 hours, poured into water (30 c.c.), and extracted with chloroform. The extracts were washed successively with ice-cold dilute sulphuric acid, sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), filtered, and evaporated at 30°, leaving a syrup, which was dried at 30°/0·01 mm. to give 1 : 2 : 5 : 6-*tetramethanesulphonyl 3 : 4-iso*propylidene sorbitol (1·08 g.) as a glass, $[\alpha]_D^{18} - 2\cdot7^\circ$ (*c*, 3·7 in chloroform) (Found : C, 28·9; H, 5·0; S, 24·5. $C_{13}H_{26}O_{14}S_4$ requires C, 29·2; H, 4·9; S, 24·0%).

Treatment of 1 : 2 : 5 : 6-Tetramethanesulphonyl 3 : 4-isoPropylidene Sorbitol with Sodium Iodide.—The methanesulphonate (1·068 g.) was heated in a sealed tube with sodium iodide (1·30 g.) and dry acetone (15 c.c.) for 4 hours at 100°, during which an intense iodine colour developed. The resulting precipitate was collected, washed with acetone (45 c.c.), and dried at 100°, to give sodium methanesulphonate (0·776 g., representing an exchange of 3·28 methanesulphonyloxy-groups per molecule of the ketal).

1 : 2 : 5 : 6-*Tetramethyl 3 : 4-isoPropylidene Sorbitol*.—An anhydrous solution of 3 : 4-*iso*propylidene sorbitol (2·00 g.) in acetone (10 c.c.) was refluxed for 20 hours with methyl iodide (5 c.c.) and silver oxide (10 g.). The solvents were removed by distillation and the residue was extracted exhaustively with hot chloroform. The methylation was repeated twice with acetone as the solvent and twice without acetone. The final syrup was distilled at 90–110° (bath-temp.)/0·2 mm. and then refractionated. The bulk of the product distilled at 90–92° (bath-temp.)/0·015 mm., giving the *tetramethyl ether* as a colourless, mobile syrup (0·90 g.), $[\alpha]_D^{17} + 23\cdot7^\circ$ (*c*, 1·3 in methyl alcohol), n_D^{17} 1·4425 (Found : C, 55·8; H, 9·1. $C_{13}H_{26}O_6$ requires C, 56·1; H, 9·4%).

1 : 2 : 5 : 6-*Tetramethyl Sorbitol*.—A solution of 1 : 2 : 5 : 6-*tetramethyl 3 : 4-iso*propylidene sorbitol (0·66 g.) in methyl alcohol (24·5 c.c.) and 5*N*-hydrochloric acid (0·5 c.c.) was kept at 18° for 26 hours, neutralised with silver carbonate, and filtered. The filtrate and methanolic washings were combined and concentrated, the colloidal silver which separated being removed by filtration through "Celite." Complete removal of the solvent left a syrup, which was fractionally distilled at 0·015 mm. The main fraction, a colourless, mobile syrup (0·46 g.), b. p. 113–120° (bath-temp.)/0·015 mm., $[\alpha]_D^{16} - 4\cdot0^\circ$ (*c*, 5·5 in methyl alcohol), n_D^{23} 1·4540, was the *tetramethyl sorbitol* (Found : C, 50·3; H, 9·0. $C_{10}H_{22}O_6$ requires C, 50·4; H, 9·3%).

Treatment of 1 : 2 : 5 : 6-Tetramethyl Sorbitol with Lead Tetra-acetate.—The *tetramethyl sorbitol* (0·0486 g.) was oxidised with lead tetra-acetate in glacial acetic acid, and the excess of the oxidising agent was determined by Hockett and McClenahan's method (*J. Amer. Chem. Soc.*, 1939, 61, 1667). The number of moles of lead tetra-acetate consumed per mole of tetra-

methyl sorbitol was: 1.03 (2 minutes), 1.06 (9 minutes), 1.06 (46 minutes), 1.11 (71 minutes), and 1.16 (325 minutes).

3 : 4-isoPropylidene 1 : 6-Ditrityl Sorbitol.—A solution of triphenylmethyl chloride (1.20 g.) and **3 : 4-iso**propylidene sorbitol (0.50 g.) in dry pyridine (4.0 c.c.) was kept at room temperature for 24 hours and poured into ice-water (90 c.c.). The resulting oil was separated by decantation, washed with cold aqueous alcohol, and then crystallised from aqueous alcohol, to give **3 : 4-iso**propylidene 1 : 6-ditrityl sorbitol hydrate (0.80 g.) as small prisms, m. p. 79–83°, $[\alpha]_D^{20} +1.0^\circ$ (*c*, 2.2 in pyridine) (Found: C, 78.0; H, 6.9. $C_{47}H_{146}O_8 \cdot H_2O$ requires C, 77.9; H, 6.7%).

2 : 5-Diacetyl 3 : 4-isoPropylidene 1 : 6-Ditrityl Sorbitol.—A solution of triphenylmethyl chloride (1.20 g.) and **3 : 4-iso**propylidene sorbitol (0.50 g.) in dry pyridine (10 c.c.) was kept at room temperature for 36 hours before acetic anhydride (0.50 c.c.) was added. After another 48 hours, the solution was poured into ice-water (70 c.c.) giving a white precipitate, which, when crystallised from ethyl alcohol, afforded **2 : 5-diacetyl 3 : 4-iso**propylidene 1 : 6-ditrityl sorbitol (1.30 g.), m. p. 103–105°, $[\alpha]_D^{17} +6.6^\circ$ (*c*, 2.4 in pyridine) (Found: C, 77.7; H, 6.4. $C_{51}H_{50}O_8$ requires C, 77.5; H, 6.4%).

Oxidation of 3 : 4-isoPropylidene Sorbitol with Sodium Metaperiodate.—(a) *Amount of periodate consumed.* An aqueous solution of **3 : 4-iso**propylidene sorbitol (0.050 g.) was mixed with 0.28M-sodium metaperiodate (10 c.c.), and the whole was diluted to 50 c.c. The sorbitol derivative was omitted from a similar control solution. Portions (2 c.c.) of the reaction mixture and of the control solution were withdrawn at intervals; each portion was added immediately to a solution of sodium hydrogen carbonate (0.50 g.) and potassium iodide (1.0 g.) in water (50 c.c.), and the iodine liberated was titrated against sodium arsenite solution (cf. Jackson, *Org. Reactions*, 1944, 2, 341). From the results, the number of moles of periodate consumed per mole of **3 : 4-iso**propylidene sorbitol was calculated to be: 1.82 (2 minutes), 1.88 (4 minutes), 1.93 (63 minutes), and 1.93 (36 hours).

(b) *Determination of formic acid produced.* To **3 : 4-iso**propylidene sorbitol (0.0146 g.) in water (15 c.c.), 0.25M-sodium metaperiodate (10 c.c.) was added and the mixture was kept at 20° for 1 hour (cf. Hirst and Jones, *J.*, 1949, 1659). A portion (5 c.c.) of the solution was mixed with ethylene glycol (0.2 c.c.) to destroy excess of periodate and titrated against 0.01N-sodium hydroxide, methyl-red being used as the indicator. No formic acid was produced, because the slightly acid solution required the same volume of alkali for neutralisation as did a control from which the *iso*propylidene sorbitol was omitted.

(c) *Determination of formaldehyde produced.* **3 : 4-iso**Propylidene sorbitol (1.2×10^{-4} mole) was oxidised with sodium metaperiodate and the formaldehyde produced was isolated as its dimedone derivative (m. p. 188°), as described by Reeves (*J. Amer. Chem. Soc.*, 1941, 63, 1476). Two independent experiments showed, respectively, 1.94 and 2.00 moles of formaldehyde to be liberated from each mole of **3 : 4-iso**propylidene sorbitol.

2 : 3-isoPropylidene D-threoDihydroxysuccindialdehyde.—An aqueous solution (35 c.c.) of **3 : 4-iso**propylidene sorbitol (4.00 g.) and sodium metaperiodate (2 mols.) was kept at room temperature for 20 hours, before being evaporated at 12 mm. in the presence of sodium hydrogen carbonate. The residue was extracted exhaustively with chloroform and the dried extracts were evaporated to give a syrup (2.58 g.), which was dried at 40°/0.01 mm. and was essentially **2 : 3-iso**propylidene *D-threo*dihydroxysuccindialdehyde.

A solution of the dialdehyde (0.20 g.) in ethyl alcohol (5 c.c.) was heated for 90 minutes with phenylhydrazine (0.30 g.), and then water was added until a faint turbidity was produced. On cooling, buff-coloured needles (0.11 g.) of the phenylhydrazone were deposited. Recrystallised twice from ethyl alcohol, they had m. p. 143°, $[\alpha]_D^{14} -236^\circ$ (*c*, 0.9 in chloroform). Fischer and Appel (*Helv. Chim. Acta*, 1934, 17, 1574) gave m. p. 145°, $[\alpha]_D^{20} -239^\circ$ (in ethyl alcohol), for this compound.

Dibenzylidene D-Threitol.—A solution of **2 : 3-iso**propylidene *D-threo*dihydroxysuccindialdehyde (1.0 g.) in *N*-sulphuric acid (8 c.c.) was kept at 100° for 3 hours, neutralised with barium carbonate, and centrifuged. The supernatant liquid was evaporated at 35°; an aqueous solution (20 c.c.) of the residue was stirred with sodium amalgam for 5 hours, neutralised with sulphuric acid, and evaporated at 12 mm., the residue being extracted with hot dry methyl alcohol. The extract was concentrated to 25 c.c., saturated with dry hydrogen chloride, shaken for 20 hours with benzaldehyde (10 c.c.), neutralised with sodium hydrogen carbonate, and filtered. The filtrate and methanolic washings were concentrated at 12 mm.; water was added during the distillation to aid the removal of the excess of benzaldehyde. The syrup which was extracted with chloroform from the residue was crystallised thrice from ethyl alcohol and once from dioxan, to give dibenzylidene *D-threitol*, m. p. 228°, alone or on admixture with

a specimen prepared from 3:4-cyclohexylidene D-mannitol (Bourne, Corbett, and Erilinne, *J.*, 1950, 786).

3:4-5:6-Diisopropylidene 1:2-Ditoluene-*p*-sulphonyl Sorbitol.—A solution of 3:4-5:6-diisopropylidene sorbitol (0.40 g.) and toluene-*p*-sulphonyl chloride (0.64 g.) in dry pyridine (2 c.c.) was kept at room temperature for 20 hours, poured into ice-water (120 c.c.), and extracted with chloroform. The extracts were washed successively with ice-cold dilute sulphuric acid, sodium hydrogen carbonate solution, and water, dried (MgSO_4), filtered, and evaporated to a syrupy ester (0.65 g.), which was dried at $30^\circ/0.01$ mm.; it had $[\alpha]_D^{20} +11.8^\circ$ (*c.* 4.4 in chloroform) (Found: C, 54.4; H, 6.1; S, 11.1. $\text{C}_{26}\text{H}_{34}\text{O}_{10}\text{S}_2$ requires C, 54.7; H, 6.0; S, 11.2%).

Treatment of 3:4-5:6-Diisopropylidene 1:2-Ditoluene-*p*-sulphonyl Sorbitol with Sodium Iodide.—The ditoluene-*p*-sulphonate (0.5867 g.) was heated in a sealed tube at 100° for 6 hours with sodium iodide (0.70 g.) and dry acetone (15 c.c.), an intense iodine colour developing. The precipitated sodium toluene-*p*-sulphonate, after being washed with dry acetone (15 c.c.) and dried at 100° , weighed 0.3646 g., which represented an exchange of 1.84 toluene-*p*-sulphonyloxy-groups per molecule of the diketal.

Oxidation of 3:4-5:6-Diisopropylidene Sorbitol with Sodium Metaperiodate.—(a) *Amount of periodate consumed.* A solution (35 c.c.) of 3:4-5:6-diisopropylidene sorbitol (0.0478 g.) in water was mixed with 0.3M-sodium metaperiodate (5 c.c.), and the whole was diluted to 50 c.c. The excess of periodate was determined at intervals by the method already described. The number of moles of periodate consumed per mole of diisopropylidene sorbitol was: 0.93 (2 minutes), 0.96 (5 minutes), 0.99 (10 minutes), and 0.99 (30 minutes).

(b) *Determination of formaldehyde produced.* (i) 3:4-5:6-Diisopropylidene sorbitol (0.0333 g.) was oxidised with sodium metaperiodate and an attempt was made to isolate the resulting formaldehyde as its dimedone derivative, according to Reeves's method (*loc. cit.*). However, the product (0.0788 g.), which corresponded in weight to 2.1 moles of formaldehyde per mole of diisopropylidene sorbitol, had m. p. $136\text{--}162^\circ$, compared with m. p. 189° for the dimedone derivative of formaldehyde; it was most probably a mixture of the water-insoluble dimedone derivatives of formaldehyde and 2:3-4:5-diisopropylidene aldehydo-D-arabinose (see later).

(ii) An aqueous solution (2.0 c.c.) of the diisopropylidene sorbitol (0.0144 g.) was mixed with 0.1M-sodium metaperiodate (5.0 c.c.), kept at room temperature for 2 hours, and distilled in steam under diminished pressure. The distillate, treated with a solution of dimedone in ethyl alcohol, gave 0.86 mol. of the dimedone derivative of formaldehyde, m. p. and mixed m. p. $187\text{--}188^\circ$.

2:3-4:5-Diisopropylidene aldehydo-D-Arabinose.—A solution of sodium metaperiodate (3.10 g.) and 3:4-5:6-diisopropylidene sorbitol (3.10 g.) in water (40 c.c.) was kept at room temperature for 5 hours, saturated with sodium chloride, and extracted exhaustively with chloroform. The extracts were dried (MgSO_4), filtered, and evaporated to a syrup, which was fractionally distilled. The major fraction was a mobile syrup (2.1 g.), which had b. p. $85\text{--}90^\circ$ (bath-temp.)/0.04 mm., $[\alpha]_D^{17} -17.1^\circ$ (*c.* 7.2 in chloroform), $n_D^{16} 1.4480$. Wiggins (*loc. cit.*) gave b. p. 80° (bath-temp.)/0.03 mm., $[\alpha]_D^{17} -14.4^\circ$ (in chloroform), $n_D^{25} 1.4421$, for 2:3-4:5-diisopropylidene aldehydo-D-arabinose; English and Griswold (*loc. cit.*) recorded b. p. $60\text{--}65^\circ/0.08$ mm., $[\alpha]_D^{22} -18.2^\circ$ (in chloroform).

D-Arabinose Dibenzyl Mercaptal.—The diisopropylidene aldehydo-D-arabinose (0.10 g.) was shaken with toluene- ω -thiol (0.20 g.) and concentrated hydrochloric acid (0.10 c.c.) for 9 hours. Ice-water was added, giving an oil; addition of ether extracted the excess of thiol and left a white solid, which was recrystallised from absolute ethyl alcohol, to yield silky needles of D-arabinose dibenzyl mercaptal (0.05 g.), $[\alpha]_D^{18} +19.0^\circ$ (*c.* 2.8 in pyridine), m. p. $148\text{--}149^\circ$ alone or on admixture with an authentic specimen (Found: C, 60.0; H, 6.2; S, 16.7. Calc. for $\text{C}_{18}\text{H}_{24}\text{O}_4\text{S}_2$: C, 60.0; H, 6.35; S, 16.85%).

α -D-Arabinose Tetra-acetate.—A solution of diisopropylidene aldehydo-D-arabinose (1.0 g.) in N-sulphuric acid (10 c.c.) was kept at 100° for 1 hour, neutralised with barium carbonate, and filtered. The filtrate and aqueous washings were combined and evaporated at 12 mm. to a syrup (0.50 g.). Examination by filter-paper chromatography showed arabinose to be the only sugar component. The syrup was treated with acetic anhydride (2.5 c.c.) and fused sodium acetate (0.4 g.) at 100° for 1 hour, cooled, and poured into water, from which the ester was extracted with chloroform. The syrupy product had partly crystallised after several days. The crystals, separated by trituration with aqueous ethyl alcohol, had m. p. 94° alone or on admixture with an authentic specimen of α -D-arabinose tetra-acetate, and showed $[\alpha]_D^{19} -41.2^\circ$ (*c.* 3.2 in chloroform).

Bisdimedone Derivative of 2 : 3-4 : 5-Diisopropylidene aldehydo-D-Arabinose.—A solution of dimedone (0.72 g.) in 50% aqueous alcohol (16 c.c.) was added to a solution of 2 : 3-4 : 5-diisopropylidene aldehydo-D-arabinose (0.20 g.) in the same solvent (5 c.c.), and the mixture was kept at room temperature for 40 hours before being heated to 70° for 2 hours. Water (10 c.c.) was added and the solution cooled. Recrystallised twice from aqueous ethyl alcohol, the precipitate gave stout prisms of the *bisdimedone* derivative (0.30 g.), m. p. 147—148°, depressed on admixture with dimedone itself, $[\alpha]_D^{20} - 34.8^\circ$ (*c*, 2.7 in chloroform) (Found : C, 66.0; H, 8.0. $C_{27}H_{40}O_8$ requires C, 65.8; H, 8.2%).

2 : 3-4 : 5-Diisopropylidene aldehydo-D-Arabinose Semicarbazone.—Diisopropylidene aldehydo-D-arabinose (0.20 g.) was treated with an aqueous solution (0.5 c.c.) of sodium acetate (0.3 g.) and semicarbazide hydrochloride (0.20 g.). After 24 hours, water (3 c.c.) was added; the precipitate, crystallised from benzene–light petroleum (b. p. 60—80°), gave needles of 2 : 3-4 : 5-diisopropylidene aldehydo-D-arabinose semicarbazone, m. p. 144—145°, $[\alpha]_D^{20} + 7.6^\circ$ (*c*, 2.9 in ethyl alcohol) (Found : C, 50.2; H, 7.3; N, 14.6. $C_{15}H_{21}O_5N_3$ requires C, 50.2; H, 7.4; N, 14.6%).

3 : 4-isoPropylidene Sorbitol from 3 : 4-5 : 6-Diisopropylidene Sorbitol.—A solution of 3 : 4-5 : 6-diisopropylidene sorbitol (1.253 g.) in ethyl alcohol (28.3 c.c.) and *n*-hydrochloric acid (3.1 c.c.) was kept at 19.5° for 49 minutes, cooled to 0°, neutralised with lead carbonate, and filtered. The filtrate and alcohol washings were combined and evaporated to a syrup, which was extracted with acetone. The syrup obtained when the extracts were evaporated was stirred with hot benzene and then allowed to cool. Recrystallisation of the solid product from acetone gave 3 : 4-isoisopropylidene sorbitol (0.36 g.), m. p. 89—90°, alone or on admixture with the sample described above.

Examination of the Syrupy Mixture (A) of Diisopropylidene Sorbitols.—The syrup (A) (p. 1411) was treated with sodium metaperiodate, and the resulting mixture of pentose derivatives was hydrolysed, under conditions similar to those already described for the conversion of 3 : 4-5 : 6-diisopropylidene sorbitol into *D*-arabinose. An aqueous solution (3%) of the syrupy product was analysed by filter-paper chromatography, the developing solvent being the upper phase of a mixture of butanol (40%), ethanol (10%), water (49%), and ammonia (1%) (Partridge, *Nature*, 1946, 158, 270). An aniline hydrogen phthalate spray revealed two components; these had R_F values identical with those of xylose and arabinose, used as standards on the same chromatogram.

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