142. *The Constitution of Trimethylene Sorbitol.*

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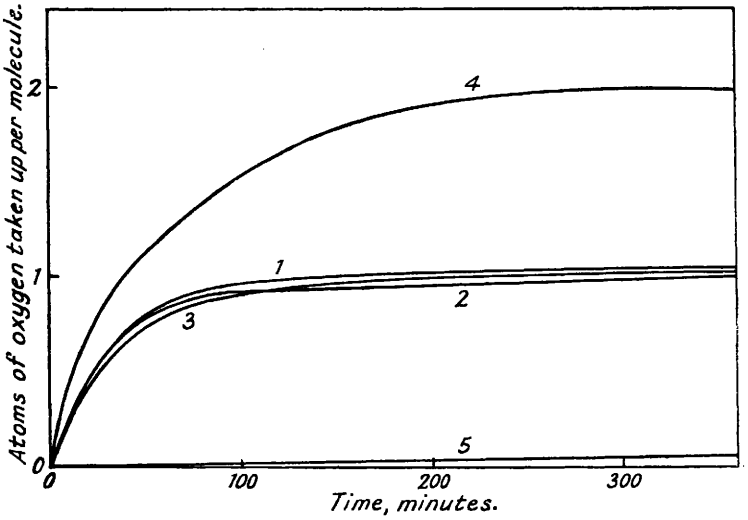
Trimethylene sorbitol is progressively hydrolysed by dilute acid to give a di- and a mono-methylene sorbitol. Evidence is presented which shows that these compounds are 1 : 3-2 : 4-5 : 6-trimethylene sorbitol, 1 : 3-2 : 4-dimethylene sorbitol, and 2 : 4-monomethylene sorbitol, respectively.

Although trimethylene sorbitol was first described by Schultz and Tollens in 1896 (*Annalen*, **289**, 23), yet the precise orientation of the formaldehyde residues has apparently not been determined. This we have now been able to do as a result of a study of the products of the graded hydrolysis of the trimethylene compound. In the course of this and other work concerned with the methylene derivatives of hexitols and saccharic acids (see, *e.g.*, Haworth and Wiggins, this vol., pp. 58, 155), we have observed that cyclic acetal formation with formaldehyde gives much more stable structures than with other aldehydes such as benzaldehyde or

acetaldehyde. For instance, 70% acetic acid at 100° failed to effect hydrolysis of the methylene groups, whereas the same reagent rapidly removes one acetaldehyde residue from triethylidene sorbitol (Appel, J., 1935, 425). Trimethylene sorbitol is hydrolysed, however, by 0·1N-sulphuric acid in 40 hours and by N-sulphuric acid in 2 hours, the time being that required for the attainment of a constant rotation. From the hydrolysate a *dimethylene sorbitol* (soluble in chloroform) and a *monomethylene sorbitol* (insoluble in chloroform but soluble in methyl alcohol) were separated, by virtue of these solubility differences, in yields of 31% and 14% respectively. Treatment of either of these with paraformaldehyde and concentrated sulphuric acid gave trimethylene sorbitol (m. p. 213°), identical with the original material.

The dimethylene sorbitol formed a crystalline *monotrityl* derivative, a fact strongly indicating the presence of one primary hydroxyl group. It also formed a *monobenzoate*, a *dibenzoate*, a *dimethyl* derivative, and a *diacetate*, all crystalline. Evidence of the presence of two free hydroxyl groups at adjacent carbon atoms was obtained by oxidation with lead tetra-acetate solution according to the procedure of Hockett and McClenahan (*J. Amer. Chem. Soc.*, 1939, **61**, 1667), whereby it was found that the initial rapid reaction ceased after one atomic proportion of oxygen per molecule of dimethylene sorbitol had been consumed. A comparative experiment was carried out with diethylidene sorbitol in which it was known that hydroxyl groups were present on C_5 and C_6 (Appel, *loc. cit.*). The graph of the rate of oxidation follows almost exactly that for dimethylene sorbitol (see figure).

Rates of oxidation of hexitol derivatives with lead tetra-acetate.



1. 1 : 3-2 : 4-*Dimethylene sorbitol.*
2. 1 : 2-3 : 4-*Diethylidene sorbitol.*
3. 2 : 4-*Monomethylene sorbitol.*
4. 3 : 4-*Monoacetone mannitol.*
5. 1 : 6-*Ditosyl* 2 : 4-*monomethylene sorbitol.*

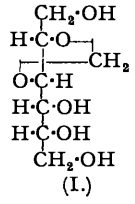
Thus dimethylene sorbitol possesses one of two structures: (*a*) that in which the methylene groups are attached to C_1, C_2, C_3, and C_4, or (*b*) that in which they are attached to C_3, C_4, C_5, and C_6 of sorbitol. The third possible structure, that with free hydroxyl groups at C_2 and C_4 is unlikely because of the formation of a triphenylmethyl derivative.

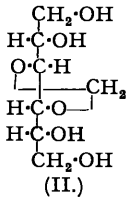
Diethylidene sorbitol, which is known to have free hydroxyl groups on C_5 and C_6 (Appel, *loc. cit.*), was methylated, and 5 : 6-*dimethyl diethylidene sorbitol* obtained. When this was treated with paraformaldehyde and concentrated sulphuric acid simultaneous hydrolysis of the acetaldehyde groups and methylenation occurred, and there was obtained a crystalline 5 : 6-dimethyl dimethylene sorbitol. The dimethylene sorbitol under discussion was now methylated, and the dimethyl derivative so obtained had the same m. p. and specific rotation as the 5 : 6-dimethyl dimethylene sorbitol prepared as just described. Moreover, a mixture of the two substances showed no depression of m. p. It is clear, therefore, that in dimethylene sorbitol the hydroxyl groups on C_1, C_2, C_3, and C_4 are involved in acetal formation with two residues of formaldehyde.

The actual orientation of the methylene linkages in dimethylene sorbitol was ascertained from a study of the monomethylene sorbitol produced at the same time by the hydrolysis of trimethylene sorbitol. In view of the fact that both the mono- and the di-methylene sorbitol yield the original trimethylene compound when methylenated, it is reasonable to assume that the hydrolysis of the trimethylene compound is progressive and that monomethylene sorbitol arises through dimethylene sorbitol.

Monomethylene sorbitol contains two primary alcohol groups inasmuch as it yields a *dityrityl* and a *ditosyl* derivative, the latter compound being converted by sodium iodide in acetone into a crystalline *di-iodo monomethylene sorbitol*. We have seen that in the dimethylene sorbitol, C_5 and C_6 are not involved in acetal formation, and this must also be true of the monomethylene compound. It follows from these observations that

the formaldehyde residue in monomethylene sorbitol must be attached to one of the following pairs of atoms: C_2 and C_3 (I); C_3 and C_4 (II); C_2 and C_4 (III).


(I.)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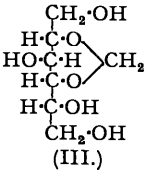
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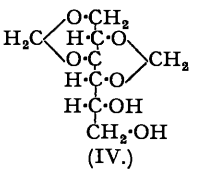
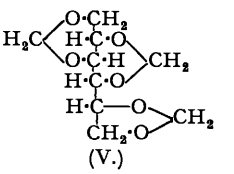

(IV.)


(V.)

A decision has been reached between these possibilities by studying the rates of oxidation of monomethylene sorbitol and of its ditosyl derivative with lead tetra-acetate: 1 mol. of monomethylene sorbitol used up one atom of oxygen, indicating the presence of one glycol group only (*i.e.*, a group with free hydroxyls on adjacent carbon atoms). Inspection of (II) shows the presence of two glycol groups, and therefore two atoms of oxygen would be consumed, as was indeed the case in a comparative experiment with 3 : 4-monoacetone mannitol (see figure). Treatment of the 1 : 6-ditosyl derivative of monomethylene sorbitol with lead tetra-acetate showed that no glycol group was present in this compound, an observation which eliminates (I) as a possible structure. Thus the methylene group in monomethylene sorbitol must be attached to C_2 and C_4 and the substance is represented by (III).

Since 2 : 4-monomethylene sorbitol arises from 1 : 2-3 : 4-dimethylene sorbitol it follows that the latter substance is 1 : 3-2 : 4-dimethylene sorbitol (IV) and that the original trimethylene compound is 1 : 3-2 : 4-5 : 6-trimethylene sorbitol (V).

Pentonic acid derivative.	M. p.	$[\alpha]_D$ in chloroform.	M. p. of amide.
Dimethylene pentonic acid methyl ester from dimethylene sorbitol ...	200°	−33·0°	267°
Methyl dimethylene d-*arabonate* (high melting)	200—201	−31·1	268
Methyl dimethylene l-*arabonate*	200—201	+34·1	268
Methyl dimethylene d-*xylonate*	200	+32·0	267

An alternative method of establishing the constitution of dimethylene sorbitol consisted in its oxidation first with lead tetra-acetate and then with bromine water, and an examination of the carboxylic acid so produced. Analysis of the product obtained corresponded with its being a dimethylene pentonic acid, and clearly this pentonic acid would have the configuration either of *l*-xylose or of *d*-arabinose according as the glycol group in the dimethylene sorbitol was at the 5 : 6- or at the 1 : 2-position. The method was not diagnostic, however, and had to be abandoned because the physical properties (*i.e.*, m. p. and specific rotation) of the derivatives of xylonic acid and arabonic acids under consideration were not sufficiently different. This similarity of properties is shown in the above table. For the purpose of this comparison the dimethylene derivatives of *d*- and *l*-arabonic acid and *d*-xylonic acid were synthesised from *d*-arabinose, *l*-arabinose, and *d*-xylose, respectively.

Experimental.

Preparation of Trimethylene Sorbitol.—(*a*) *By using hydrochloric acid and* 38% *formalin solution.* (i) Sorbitol (20 g.), 38% formalin solution (20 c.c.), and fuming hydrochloric acid (20 c.c.) were heated together under reflux for 1½ hours. The solution was cooled, and extracted with 20-c.c. portions of chloroform until all the chloroform-soluble material was removed. The combined chloroform extracts were washed successively with water, 0·5N-sodium hydroxide, and again with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. Crystallisation of the residue three times from ethyl alcohol gave a mass of colourless needles (1·1 g.; 4·6%), m. p. 206°. Schultz and Tollens (*loc. cit.*) record m. p. 206° for trimethylene sorbitol.

(ii) 38% Formalin solution (20 c.c.) containing sorbitol (20 g.) was saturated with hydrogen chloride, and the solution shaken overnight with chloroform (20 c.c.). The mixture was extracted with successive quantities of chloroform, the extracts combined, washed with water, 0·5N-sodium hydroxide, and again with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. After recrystallisation from ethyl alcohol the trimethylene sorbitol (2·5 g.; 10·5%) had m. p. 206°.

(*b*) *By using concentrated sulphuric acid and paraformaldehyde.* Sorbitol (10 g.). paraformaldehyde (10 g.), and concentrated sulphuric acid (10 c.c.) were stirred together. The mixture became quite warm and, after it had cooled to room temperature again, chloroform (100 c.c.) was added and the mixture shaken for 4 hours. The chloroform was decanted and the extraction process repeated several times. The combined chloroform extracts were washed with dilute ammonia solution and with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. The residue, after recrystallisation from ethyl alcohol (yield 5·9 g.; 49%), showed m. p. 206°, $[\alpha]_D^{18°}$ −28·9° in chloroform (*c*, 1·73). Schultz and Tollens (*loc. cit.*) record m. p. 206°, and $[\alpha]_D$ −29·3° (in chloroform) for trimethylene sorbitol.

The substance prepared in the above experiments was repeatedly recrystallised from ethyl alcohol and eventually showed m. p. 212—213°, $[\alpha]_D^{12°}$ −28·2° in chloroform (*c*, 6·32); it was therefore pure trimethylene sorbitol (Found: C, 50·0; H, 6·4. Calc. for $C_9H_{14}O_6$: C, 49·5; H, 6·4%).

Hydrolysis of Trimethylene Sorbitol.—(*a*) *By* 70% *acetic acid.* Trimethylene sorbitol (0·34 g.) (m. p. 206°) was heated with 20 c.c. of 70% acetic acid for 2½ hours at 100° without there being any perceptible change in the specific rotation of the solution. On evaporation, unchanged starting material was recovered.

(*b*) *By* N-*sulphuric acid.* Trimethylene sorbitol (1·818 g.) (m. p. 206°) was boiled with 30 c.c. of N-sulphuric acid for 2 hours, the specific rotation changing from $[\alpha]_D$ −30·0° to $[\alpha]_D$ −18·2° (constant value). The solution was neutralised with barium carbonate, filtered, and evaporated to dryness. The crystalline residue was extracted three times with hot chloroform, and the extract evaporated to dryness and recrystallised, forming feathery needles from

chloroform (0·53 g.). This substance was 1 : 3-2 : 4-*dimethylene sorbitol* and showed m. p. 173°, $[\alpha]_D^{18°}$ −25·6° in water (*c*, 6·33) (Found: C, 46·4; H, 6·7. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8%). The material was extremely soluble in ethyl alcohol and water but not very soluble in chloroform.

The residue, after chloroform extraction, was extracted with hot ethyl alcohol. This extract was evaporated to 2 c.c. and a little ether added, whereupon feathery crystals of 2 : 4-*monomethylene sorbitol* separated and were recrystallised from ethyl alcohol–ether (yield 0·11 g.), m. p. 162°, $[\alpha]_D^{21°}$ −9·1° in water (*c*, 3·632) (Found: C, 43·7; H, 7·6. $C_7H_{14}O_6$ requires C, 43·3; H, 7·3%).

Remethylenation of 2 : 4-*Monomethylene Sorbitol.*—2 : 4-Monomethylene sorbitol (0·066 g.) was mixed with paraformaldehyde (0·15 g.), and the mixture warmed with concentrated sulphuric acid (0·2 c.c.) until a clear solution was obtained; it was then shaken for several hours with chloroform, the chloroform extract decanted, and the extraction process repeated twice more. The combined extracts were washed with dilute ammonia solution and with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. The residue recrystallised from methyl alcohol in the form of needles, m. p. 209—210°, mixed m. p. with authentic pure trimethylene sorbitol 210—212°.

Remethylenation of 1 : 3-2 : 4-*Dimethylene Sorbitol.*—1 : 3-2 : 4-Dimethylene sorbitol (0·735 g.) was warmed with paraformaldehyde (1·5 g.) and concentrated sulphuric acid (1·0 c.c.) until a clear solution was obtained; this was then extracted several times with chloroform, the chloroform extract washed with dilute ammonia solution and with water, and evaporated to dryness. The residue, recrystallised from methyl alcohol (yield 0·230 g.), had m. p. 209—210°, undepressed on admixture with trimethylene sorbitol (m. p. 210—212°).

Monobenzoyl 1 : 3-2 : 4-*Dimethylene Sorbitol.*—1 : 3-2 : 4-Dimethylene sorbitol (1 g.) was dissolved in 5N-sodium hydroxide solution (10 c.c.), benzoyl chloride (2·5 c.c.) added, and the mixture shaken for several hours. The solid which separated was filtered off, washed with water, and recrystallised from alcohol. It was probably 6-*benzoyl* 1 : 3-2 : 4-*dimethylene sorbitol*. Yield, 0·6 g., m. p. 195—197°, $[\alpha]_D$ −15·9° in chloroform (*c*, 0·877) (Found: C, 58·4; H, 5·5. $C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%).

5 : 6-*Dibenzoyl* 1 : 3-2 : 4-*Dimethylene Sorbitol.*—1 : 3-2 : 4-Dimethylene sorbitol (1 g.) was dissolved in dry pyridine (20 c.c.), and benzoyl chloride (3·5 c.c.) added. The mixture became warm and pyridine hydrochloride separated; after being kept overnight, it was poured into ice-water, whereupon a syrupy precipitate separated, which crystallised after being washed with water and triturated with alcohol; recrystallised from alcohol, it formed plates (0·55 g.), m. p. 135—137° $[\alpha]_D^{18°}$ −56·3° in chloroform (*c*, 1·135) (Found: C, 63·7; H, 5·2. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·3%).

6-*Trityl* 1 : 3-2 : 4-*Dimethylene Sorbitol.*—1 : 3-2 : 4-Dimethylene sorbitol (0·27 g.) was dissolved in dry pyridine (3 c.c.), trityl chloride (1·1 mols.) added, and the mixture kept for 4 days at room temperature. On pouring this into water, a crystalline precipitate separated, which, after being washed with water, was recrystallised from alcohol (0·32 g.), m. p. 194°, $[\alpha]_D^{20°}$ −8·0° in chloroform (*c*, 2·0) (Found: C, 72·9; H, 6·2. $C_{27}H_{28}O_6$ requires C, 72·3; H, 6·3%).

5 : 6-*Diacetyl Dimethylene Sorbitol.*—Dimethylene sorbitol (0·3 g.) was boiled with acetic anhydride (5 c.c.) and fused sodium acetate (0·4 g.) for 5 minutes. The product was poured into ice-water, and after several hours the solution was neutralised with sodium hydrogen carbonate and extracted with chloroform. After being dried over magnesium sulphate, the extract was evaporated to dryness and the residue recrystallised from alcohol (0·33 g.), m. p. 135—136°, $[\alpha]_D^{18°}$ −15·4° in chloroform (*c*, 1·69) (Found: C, 49·4; H, 6·4; Ac, 30·1. $C_{12}H_{18}O_8$ requires C, 49·5; H, 6·2; Ac, 29·6%).

5 : 6-*Dimethyl* 1 : 3-2 : 4-*Dimethylene Sorbitol.*—Dimethylene sorbitol (1 g.) was methylated by means of silver oxide and methyl iodide in the usual manner. After three treatments the product was recrystallised from ethyl alcohol, forming lustrous needles (0·24 g.), m. p. 193—194°, $[\alpha]_D^{20°}$ −23·8° in chloroform (*c*, 0·587) (Found: C, 51·4; H, 7·7. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%).

5 : 6-*Dimethyl Dimethylene Sorbitol from* 1 : 2-3 : 4-*Diethylidene Sorbitol.*—5 : 6-*Dimethyl* 1 : 2-3 : 4-*diethylidene sorbitol*. Diethylidene sorbitol (3 g.), prepared by Appel's method (*loc. cit.*), was methylated by five treatments with silver oxide and methyl iodide, the product being extracted after each treatment with boiling chloroform. The methylation was difficult owing to the insolubility of diethylidene sorbitol. Finally a syrup was obtained which distilled at 140° (bath temp.)/0·03 mm. (1·25 g.), $n_D^{21°}$ 1·4616, $[\alpha]_D^{18°}$ −9·8° in chloroform (*c*, 2·555) (Found: C, 54·6; H, 8·1. $C_{12}H_{22}O_6$ requires C, 54·9; H, 8·4%).

Methylenation of 5 : 6-*dimethyl diethylidene sorbitol.* The foregoing 5 : 6-*dimethyl diethylidene sorbitol* (1·2 g.) was warmed for 20 minutes with paraformaldehyde (1·2 g.) and concentrated sulphuric acid (1 c.c.) during which the evolution of acetaldehyde occurred. The mixture was then shaken with chloroform for 3 hours, the chloroform decanted, and the operation repeated. The combined chloroform extracts were washed with sodium bicarbonate solution and with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. The residue recrystallised from alcohol in lustrous needles of 5 : 6-dimethyl 1 : 3-2 : 4-dimethylene sorbitol (0·25 g.), m. p. 193—194°, $[\alpha]_D$ −22·2° in chloroform (*c*, 0·678) (Found: C, 51·6; H, 8·0%); the mixed m. p. with the specimen prepared as above showed no depression.

1 : 6-*Ditosyl* 2 : 4-*Monomethylene Sorbitol.*—2 : 4-Monomethylene sorbitol (0·3 g.) was dissolved in dry pyridine (3 c.c.), and tosyl chloride (0·6 g.) added in small portions at 0°. The solution was allowed to warm to room temperature, and kept thereat for 24 hours. On pouring into ice-water a syrup was precipitated which rapidly crystallised. The crystals were collected, washed with water, and recrystallised from alcohol, affording feathery needles (0·31 g.), m. p. 129—130°, $[\alpha]_D^{18°}$ −2·0° in chloroform (*c*, 2·0) (Found: C, 49·7; H, 5·2. $C_{21}H_{26}O_{10}S_2$ requires C, 50·2; H, 5·2%).

Treatment of 1 : 6-*Ditosyl* 2 : 4-*Monomethylene Sorbitol with Sodium Iodide in Acetone Solution.*—A solution of this 1 : 6-*ditosyl* 2 : 4-*monomethylene sorbitol* (0·3 g.) and dry sodium iodide (0·7 g.) in dry acetone (50 c.c.) was heated in a sealed tube at 110° for 8 hours. Crystals of sodium *p*-toluenesulphonate separated during the reaction. When the tube had cooled, these crystals were filtered off and weighed (0·205 g.; 80%). The acetone filtrate was evaporated, and the residue treated with a chloroform–water mixture. A little sodium thiosulphate was added, and the mixture shaken in a separating funnel. Some material would not dissolve in either layer; this was collected and recrystallised from alcohol, forming plates (0·12 g.), m. p. 210° (Found: C, 20·9; H, 3·4; I, 59·3. $C_7H_{12}O_4I_2$ requires C, 20·4; H, 3·0; I, 61·3%). It was 1 : 6-*di-iodo monomethylene sorbitol.* The chloroform layer of the filtrate from these crystals was separated, washed with water, dried over anhydrous magnesium sulphate, and evaporated to dryness. The residue recrystallised from alcohol in feathery needles (0·18 g.), m. p. 185° (Found: C, 32·2; H, 4·1; I, 36·4%). This substance has not been identified.

Benzoylation of 2 : 4-*Monomethylene Sorbitol.*—2 : 4-Monomethylene sorbitol (0·18 g.) was dissolved in dilute sodium hydroxide solution, benzoyl chloride (0·44 c.c.) added, and the mixture shaken for several hours and diluted with ice-water. The precipitate was filtered off and recrystallised twice from ethyl alcohol (0·03 g.), m. p. 154°, $[\alpha]_D^{20°}$ −10·0° in chloroform (*c*, 0·4) (Found: C, 66·5; H, 5·2. $C_{28}H_{26}O_9$ requires C, 66·4; H, 5·2%); it was *tribenzoyl monomethylene sorbitol.* Benzoylation in pyridine solution gave only a syrupy product which resisted attempts at crystallisation.

1 : 6-*Ditrityl* 2 : 4-*Monomethylene Sorbitol.*—2 : 4-Monomethylene sorbitol (0·49 g.) was dissolved in dry pyridine (5 c.c.), trityl chloride (2·2 mols.) added, and the mixture set aside for 24 hours. On pouring this into water, a syrupy precipitate separated which was triturated with water and then dissolved in chloroform. The chloroform extract was washed with 5% sulphuric acid, with dilute sodium bicarbonate, and with water, dried over anhydrous magnesium

sulphate, and evaporated. A syrup was left which crystallised after several weeks. It was recrystallised with difficulty from pyridine; m. p. 112—115° (Found: C, 79·9; H, 6·5. $C_{45}H_{40}O_6$ requires C, 79·8; H, 6·0%). An attempt to tritylate and then acetylate monomethylene sorbitol in the same pyridine solution gave only *tetra-acetyl* 2 : 4-*monomethylene sorbitol*, m. p. 152°, $[\alpha]_D$ −4·0° in chloroform (*c*, 1·5) (Found: C, 50·1; H, 6·2; Ac, 48·4. $C_{15}H_{22}O_{10}$ requires C, 49·7; H, 6·1; Ac, 47·5%).

Oxidation of Dimethylene Sorbitol with Lead Tetra-acetate and with Bromine.—Dimethylene sorbitol (1·84 g.) was dissolved in glacial acetic acid (40 c.c.), lead tetra-acetate (1·2 mols.) added, and the mixture shaken for 24 hours. After evaporating it to dryness at 30°/15 mm., water was added, and the mixture again evaporated in order to remove the last traces of acetic acid. The residue was dissolved in water (20 c.c.), excess of bromine (4 c.c.) added, and the mixture kept at 30° for 4 days. The excess bromine was removed by aeration, and the lead bromide precipitate (A) filtered off. The filtrate was neutralised with lead carbonate and filtered, the residue (B) was washed well with water, and the combined filtrate and washings evaporated to a syrup which was refluxed with 5% methyl-alcoholic hydrogen chloride (200 c.c.) for 6 hours. The alcoholic solution was neutralised with lead carbonate, filtered, and evaporated to dryness; the residue recrystallised from methyl alcohol in small needles (0·042 g.), m. p. 195°. A further amount was obtained from the lead carbonate residue (B) by repeated extraction with boiling water (the lead salt of the dimethylene pentonic acid was only slightly soluble in water). The aqueous extract was evaporated to dryness, the lead bromide precipitate (A) added to the product, and the mixture refluxed with 4% methyl-alcoholic hydrogen chloride (300 c.c.) for 6 hours. After neutralisation with lead carbonate, filtration, and evaporation, the residue was recrystallised twice from methyl alcohol. Total yield, 0·432 g. (23·5%), m. p. 200°, $[\alpha]_D^{18°}$ −33·0° in chloroform (*c*, 1·076) (Found: C, 46·8; H, 6·0. $C_8H_{12}O_6$ requires C, 47·1; H, 5·9%). This substance was *methyl dimethylene* l-*xylonate*.

Dimethylene l-*Xylonamide*.—The foregoing ester (45 mg.) was dissolved in dry methyl alcohol (5 c.c.), the solution saturated with ammonia at 0°, and kept for 24 hours. Evaporation in a vacuum gave a mass of crystals which was recrystallised from methyl alcohol (30 mg.), m. p. 267° (Found: C, 44·7; H, 5·6. $C_7H_{11}O_5N$ requires C, 44·4; H, 5·8%).

Methyl Dimethylene d-*Arabonate*.—*d*-Arabinose was oxidised by means of bromine water in the usual way, and the resulting syrupy arabonic acid–lactone mixture (1 g.) methylenated by gentle warming with paraformaldehyde (1 g.) and concentrated sulphuric acid (0·8 c.c.) for 15 minutes. The mixture was then refluxed for 6 hours with methyl alcohol (100 c.c.), and after neutralisation of the sulphuric acid with barium carbonate, the filtered solution was evaporated to dryness. Upon extraction with chloroform and subsequent removal of the solvent, a syrup was obtained which partly crystallised. This was recrystallised to give *methyl dimethylene* d-*arabonate* (0·10 g.), m. p. 200—201°, $[\alpha]_D$ −31·1° in chloroform (*c*, 3·540) (Found: C, 47·0; H, 6·2. $C_8H_{12}O_6$ requires C, 47·1; H, 5·9%). From the mother-liquors was isolated 0·06 g. of an isomeric *ester*, m. p. 99—100°, $[\alpha]_D^{16°}$ −75·2° in chloroform (*c*, 1·01) (Found: C, 47·4; H, 6·2%). In a second preparation, however, we failed to obtain any of this isomer.

Dimethylene d-*Arabonamide*.—Methyl dimethylene *d*-arabonate (0·13 g.) was suspended in dry methyl alcohol (5 c.c.), the mixture saturated with ammonia at 0°, and the solution kept at 0° for 24 hours, during which time some feathery needles crystallised. The mixture was evaporated in a vacuum, and the residue recrystallised from methyl alcohol (90 mg.); m. p. 268° (Found: C, 43·9; H, 5·6. $C_7H_{11}O_5N$ requires C, 44·4; H, 5·8%).

Methyl Dimethylene l-*Arabonate*.—This *ester* was prepared from *l*-arabinose in the same way as the enantiomorphic compound from *d*-arabinose. It had m. p. 200—201°; $[\alpha]_D^{16°}$ +34·1° in chloroform (*c*, 1·35) (Found: C, 47·2; H, 5·8. $C_8H_{12}O_6$ requires C, 47·0; H, 5·9%). No isomeric ester was found.

Dimethylene l-*Arabonamide*.—This *amide* was prepared in the same way as its enantiomorph and had m. p. 268° (Found: C, 44·7; H, 5·9. $C_7H_{11}O_5N$ requires C, 44·4; H, 5·8%).

Methyl Dimethylene d-*Xylonate*.—*d*-Xylose was oxidised by means of bromine water in the usual way. The syrupy xylonic acid–lactone mixture (1·02 g.) was methylenated by warming with paraformaldehyde (1 g.) and concentrated sulphuric acid (3 c.c.) until a clear solution was obtained. Methyl alcohol (80 c.c.) was then added, and the solution boiled for 6 hours. Thereafter it was neutralised with barium carbonate, filtered, evaporated to dryness, and the residue extracted with chloroform. This extract, on evaporation, gave a crystalline residue which recrystallised from methyl alcohol in long feathery needles (0·11 g.), m. p. 200°, $[\alpha]_D^{22°}$ +32·0° in chloroform (*c*, 3·0) (Found: C, 47·1; H, 5·7. $C_8H_{12}O_6$ requires C, 47·0; H, 5·9%).

Dimethylene d-*Xylonamide*.—The foregoing *ester* (30 mg.) was dissolved in dry methyl alcohol (5 c.c.), the solution saturated with ammonia gas at 0°, and kept at that temperature for 24 hours; the solvent and the ammonia were removed in a vacuum, and the residue recrystallised from methyl alcohol, forming feathery needles (15 mg.), m. p. 267° (Found: C, 44·0; H, 5·6. $C_7H_{11}O_5N$ requires C, 44·4; H, 5·8%).

Oxidation-rate Determinations with Lead Tetra-acetate.—The procedure used was that of Hockett and McClenahan (*loc. cit.*). 0·0005 Mol. of the substance to be oxidised was dissolved in glacial acetic acid (49 c.c.) in a 100-c.c. flask, and lead tetra-acetate solution (50 c.c.) (15 g. in 500 c.c. of glacial acetic acid) rapidly run in; the volume was made up to 100 c.c. with glacial acetic acid, and the solution thoroughly shaken. A 10-c.c. sample was withdrawn as quickly as possible after the oxidising agent had been added, and run into potassium iodide–sodium acetate solution (20 c.c.) [potassium iodide (10 g.) and crystalline sodium acetate (125 g.) in water (500 c.c.)], the liberated iodine being titrated with 0·02N-sodium thiosulphate. At intervals, further 10-c.c. portions were withdrawn, and the amount of oxidising agent consumed estimated. A blank titration was carried out with 5 c.c. of the standard lead tetra-acetate just beforehand. From these data the number of g.-atoms of oxygen taken up by 1 g.-mol. of the compound used could be calculated:

(*a*) Dimethylene sorbitol (0·1021 g.); 0·11 (3 mins.); 0·38 (15 mins.); 0·78 (48 mins.); 0·94 (84 mins.); 0·98 (112 mins.); 1·02 (156 mins.). (*b*) Diethylidene sorbitol (0·108 g.): 0·13 (4 mins.); 0·56 (25 mins.); 0·74 (41 mins.); 0·87 (65 mins.); 0·93 (108 mins.); 1·02 (720 mins.). (*c*) 2 : 4-Monomethylene sorbitol (0·095 g.): 0·10 (3 mins.); 0·51 (23 mins.); 0·78 (56 mins.); 0·86 (78 mins.); 0·95 (130 mins.); 1·12 (750 mins.). (*d*) 3 : 4-Monoacetone mannitol (0·111 g.): 0·20 (3 mins.); 0·96 (35 mins.); 1·46 (88 mins.); 1·98 (247 mins.). (*e*) 1 : 6-Ditosyl 2 : 4-monomethylene sorbitol (0·260 g.): 0·06 (3 mins.); 0·03 (21 mins.); 0·04 (60 mins.); 0·05 (111 mins.); 0·10 (230 mins.).

These results are shown graphically in the figure.

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