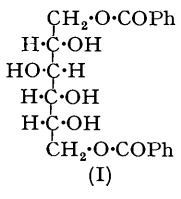
23. *The Dibenzoates of Sorbitol and Mannitol and their Methylene Derivatives.*

By W. N. Haworth and L. F. Wiggins.

Dibenzoyl sorbitol and dibenzoyl mannitol have been converted into the corresponding dimethylene derivatives. Debenzoylation of the dibenzoyl dimethylene hexitols yielded the two stereoisomeric dimethylene hexitols, both of which gave well-crystalline ditosyl,* dityityl,* dichloro-, and dimethyl derivatives. Oxidation of dimethylene sorbitol and dimethylene mannitol gave the corresponding dimethylene saccharic acids. Proof was thus obtained that the benzoyl groups in dibenzoyl sorbitol and dibenzoyl mannitol were attached to the primary alcoholic groups and consequently that the methylene groups in both compounds involved linkage with the four central carbon atoms.

Dibenzoyl sorbitol (I) was first prepared by Müller (*Ber.*, **1932**, **65**, 1055), and has now been converted into the crystalline dimethylene derivative (II) by treatment with paraformaldehyde and concentrated sulphuric acid. Debenzoylation of the *dibenzoyl dimethylene sorbitol* was effected by means of a trace of sodium in methyl-alcoholic solution. The *dimethylene sorbitol* so obtained readily gave crystalline *dityityl dimethylene sorbitol.* It is well known that trityl chloride reacts preferentially with primary alcoholic groups, and most often with primary alcoholic groups only, so that formation of ditrityl dimethylene sorbitol gave a strong indication that in dimethylene sorbitol the methylene groups are not linked with primary alcoholic hydroxyl groups.

Oxidation of dimethylene sorbitol with chromic anhydride in glacial acetic acid solution gave rise to two products, dimethylene glucosaccharic acid (IV) and a dimethylene hexonic acid, both compounds being isolated as their methyl esters. The former compound was identical with the product obtained by methylenation of potassium hydrogen saccharate (Haworth, Jones, Stacey, and Wiggins, following paper). The isolation of this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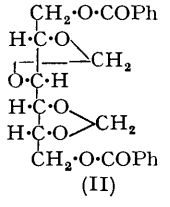
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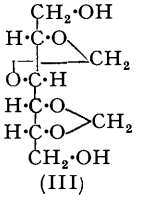
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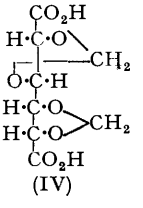
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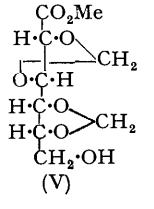
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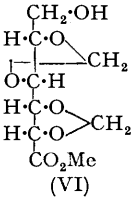
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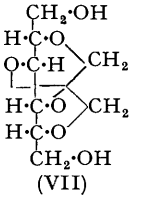
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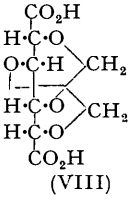
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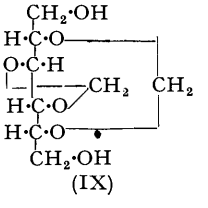
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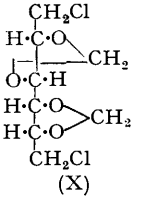
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dibasic acid containing the six carbon atom chain provided rigorous proof that the two methylene groups in dimethylene sorbitol and in the corresponding dibenzoyl dimethylene sorbitol involved linkage with the four central carbon atoms and that the two free hydroxyl groups in dimethylene sorbitol were the two primary alcoholic hydroxyl groups. This also proves that the benzoyl groups in dibenzoyl sorbitol are attached to carbon atoms C_1 and C_6. The methyl dimethylene hexonate isolated from the oxidation products of dimethyl-

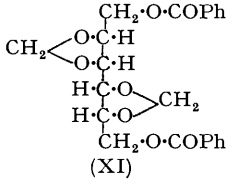
* The contractions "tosyl" for "toluene-*p*-sulphonyl" and "trityl" for "triphenylmethyl" have been used throughout.

ene sorbitol might be a derivative of gluconic acid (V) or *l*-gulonic acid (VI) according to whether oxidation had occurred at carbon atom C_1 or C_6 respectively. From 2 : 3 : 4 : 5-dimethylene sorbitol there were prepared : (i) 1 : 6-*dichloro dimethylene sorbitol*, by the action of thionyl chloride in pyridine ; (ii) a 1 : 6-*dimethyl* derivative, by two treatments with methyl iodide and silver oxide ; and (iii) a *ditosyl* derivative by treatment with tosyl chloride in pyridine.

In all these dimethylene derivatives of sorbitol and those of mannitol described below, the formaldehyde might be involved in acetal formation with either the hydroxyl groups attached to adjacent carbon atoms or with those attached to alternate carbon atoms. Thus 2 : 3 : 4 : 5-dimethylene sorbitol might be portrayed as (III) or (VII) and accordingly dimethylene glucosaccharic acid might be written as (IV) or (VIII). Still another possibility is that the formaldehyde may condense with the hydroxyl groups on carbon atoms C_3 and C_4 and with those on carbon atoms C_2 and C_5. Thus, dimethylene sorbitol could be formulated by (IX). A study of the atomic models of these structures shows that all are possible, but we regard the last-mentioned possibility as the least probable. We have formulated all the methylene derivatives of sorbitol and mannitol here described on the basis that the methylene groups involve linkage with adjacent carbon atoms, but it must be remembered that the other types of structure are equally possible and we leave this question quite open. We hope later to publish experiments showing the true method of linkage.

A similar series of derivatives has been prepared from mannitol. When mannitol is treated with two molecular proportions of benzoyl chloride in pyridine solution, it gives a dibenzoate in good yield (Einhorn and Hollandt, *Annalen*, 1898, **301**, 95). We have methylenated this compound by two methods : (1) with a 38% solution of formalin saturated with hydrogen chloride and (2) with paraformaldehyde and concentrated sulphuric acid. By method (1) we isolated dibenzoyl dimethylene mannitol in 26% yield together with a *dibenzoyl monomethylene mannitol* in 12·5% yield, the structure of which has not yet been determined. By method (2) we obtained the dimethylene derivative only, in a yield 60% of the theoretical. The benzoyl groups in the dimethylene derivative were removed catalytically by means of a small amount of sodium methoxide and dimethylene mannitol was isolated in almost quantitative yield. The dimethylene mannitol gave a crystalline *dimethyl* derivative on treatment with methyl iodide and silver oxide and also a ditosyl derivative on treatment with toluene-*p*-sulphonyl chloride in pyridine solution. Treatment with triphenylmethyl chloride gave a crystalline *ditrityl* derivative, providing strong evidence that in dimethylene mannitol it is the secondary alcoholic groups that are engaged in acetal formation with formaldehyde. Dimethylene mannitol has been oxidised by means of chromic anhydride in glacial acetic acid solution and a small amount of *dimethyl dimethylene mannosaccharate* obtained. The isolation of this dibasic acid containing the original six carbon atom chain provides complete proof that in dimethylene mannitol the formaldehyde residues are not attached to the primary alcoholic hydroxyl groups which are free to undergo oxidation with formation of carboxyl groups. It follows that the benzoyl groups in dibenzoyl mannitol must be attached to carbon atoms C1 and C6. We have also been able to convert dimethylene mannitol, by treatment with thionyl chloride in pyridine solution, into dichloro dimethylene mannitol, identical with the compound prepared from dichloro mannitol by Micheel (*Annalen*, 1932, **496**, 77). Since we have established that dimethylene mannitol has two free primary alcoholic hydroxyl groups, it follows that this dichloro-derivative must be 1 : 6-dichloro 2 : 3 : 4 : 5-dimethylene mannitol.

Hudson, Hann, and Haskins (*J. Amer. Chem. Soc.*, 1943, **65**, 67) have recently prepared the dimethylene derivative of dibenzoyl mannitol by a method slightly different from those described here. These authors have also obtained the dimethylene mannitol and several of its derivatives and the constants they have recorded agree closely with those we have found for our preparations. Hudson *et al.* (*loc. cit.*) converted ditosyl dimethylene mannitol, by treatment with sodium iodide in acetone, into the same di-iodo dimethylene mannitol that was obtained by Micheel (*loc. cit.*) by methylenation of dichloro mannitol and subsequent treatment with sodium iodide in acetone.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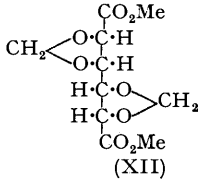
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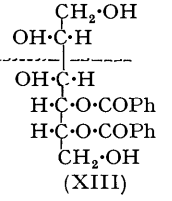
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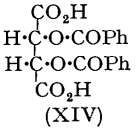
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The conversion of the ditosyl derivative into the di-iodo-derivative was in itself a good indication that the tosyl groups were attached to the primary alcoholic hydroxyl groups, as it has been found that only tosyl groups so attached could be exchanged for iodine atoms by treatment with sodium iodide in acetone.

The structure of dibenzoyl mannitol has been the object of much controversy in the past. Ohle, Erlbach, Hepp, and Toussaint (*Ber.*, 1929, **62**, 2982) described it as the 2 : 3- or 4 : 5-dibenzoyl derivative of mannitol (XIII). This conclusion was based on the result of the oxidation of dibenzoyl mannitol with potassium permanganate and the isolation of what was believed to be dibenzoyl *meso*-tartaric acid (XIV). Brigl and Gruner (*Ber.*, 1932, **65**, 642) showed, however, that this so-called dibenzoyl *meso*-tartaric acid was in fact benzoyl glycollic acid and they suggested that the dibenzoyl derivative of mannitol was most probably 1 : 6-dibenzoyl mannitol. Further evidence that the benzoyl groups in this compound must occupy the primary alcoholic hydroxyl groups was given by Muller (*Ber.*, 1932, **65**, 1055), who had obtained a tritosyl derivative from di-

benzoyl mannitol. For on treatment of this compound with sodium iodide in acetone solution no iodine atoms were introduced into the mannitol molecule, which indicated that the primary alcohol groups must be occupied by benzoyl, and not by tosyl groups. Otherwise reaction with sodium iodide would have occurred. The experiments described herein confirm the view that the structure of the mannitol dibenzoate of Einhorn and Hollandt is that of 1 : 6-dibenzoyl mannitol.

It is opportune to mention here the striking difference which exists in the ease of formation of the 1 : 6-dibenzoates of mannitol and sorbitol. Whereas mannitol dibenzoate is readily obtained in 80% yield, the yield of sorbitol dibenzoate has never been found to exceed 25%. The reason for this difference is not obvious but would seem to be associated in some way with the *cis*-orientation of hydroxyls on C2 and C3 in mannitol and their *trans*-orientation in sorbitol.

Experimental.

1 : 6-*Dibenzoyl Sorbitol.*—This compound was prepared according to the instructions given by Muller (*loc. cit.*). Yield, 25% of the theoretical; m. p. 140° (Found : C, 61·7; H, 5·5. Calc. for $C_{20}H_{22}O_8$: C, 61·5; H, 5·6%).

1 : 6-*Dibenzoyl Dimethylene Sorbitol.*—1 : 6-Dibenzoyl sorbitol (8 g.), paraformaldehyde (8 g.), and concentrated sulphuric acid (3 c.c.) were thoroughly mixed; the mixture warmed to 60° during the reaction. After cooling, the mixture was shaken with chloroform overnight. The chloroform extract was decanted, a further amount of chloroform added, and the mixture shaken for an hour; the chloroform layer was then again decanted. This extraction process was repeated twice more and the combined chloroform extracts were washed successively with sodium bicarbonate solution and water. After the extract had been dried over anhydrous magnesium sulphate and evaporated to dryness, a crystalline residue was obtained which, recrystallised from alcohol, formed long needles (6 g.), m. p. 160°, $[\alpha]_D^{19°}$ + 22·7° (*c*, 1·545 in chloroform) (Found : C, 63·9; H, 5·4. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·3%).

2 : 3 : 4 : 5-*Dimethylene Sorbitol.*—1 : 6-Dibenzoyl dimethylene sorbitol (3·5 g.) was suspended in dry methyl alcohol (100 c.c.), sodium (50 mg.) added, and the mixture shaken overnight. The solution thus obtained was evaporated to dryness under diminished pressure, and the residue extracted with ether in order to remove methyl benzoate. The final residue was recrystallised from 95% alcohol. Yield, 1·25 g.; m. p. 192—193°; $[\alpha]_D^{18°}$ + 42·5° (*c*, 1·412 in water) (Found : C, 46·9; H, 6·6. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8%).

1 : 6-*Dichloro Dimethylene Sorbitol.*—To a solution of dimethylene sorbitol (0·18 g.) in dry pyridine (1·5 g.) at 0°, thionyl chloride (1·5 g.) was carefully added, When the mixture was heated to 100°, evolution of sulphur dioxide occurred. After ½ hour's heating the mixture was poured into water, chloroform added, the solution filtered through charcoal, and the insoluble material washed with more chloroform. The washings were added to the main filtrate, and the chloroform layer separated. The aqueous layer was extracted twice with chloroform and the combined chloroform extracts were washed with sodium bicarbonate solution and with water and dried over anhydrous magnesium sulphate. After filtration with charcoal the solution was evaporated to dryness; the solid crystallised from alcohol in needles (0·12 g.), m. p. 116—118°, $[\alpha]_D^{15°}$ +20·0° (*c*, 2·596 in chloroform) (Found : C, 39·7; H, 5·4; Cl, 29·3. $C_8H_{12}O_4Cl_2$ requires C, 39·5; H, 5·0; Cl, 29·2%).

1 : 6-*Ditrityl Dimethylene Sorbitol.*—Dimethylene sorbitol (0·3 g.) was dissolved in anhydrous pyridine (5 c.c.), trityl chloride (0·85 g.) added, and the mixture set aside for 24 hours. When the solution, which contained crystals of pyridine hydrochloride and the *ditrityl* derivative of dimethylene sorbitol, was poured into ice-water, a syrupy product separated which rapidly solidified. After filtration and washing with water, this material, recrystallised from acetone–chloroform–alcohol, formed prismatic crystals (0·45 g.), m. p. 209—210°, $[\alpha]_D^{18°}$ + 12·0° (*c*, 2·16 in chloroform) (Found : C, 79·7; H, 5·9. $C_{46}H_{42}O_6$ requires C, 80·0; H, 6·1%).

1 : 6-*Ditosyl Dimethylene Sorbitol.*—Dimethylene sorbitol (0·2 g.) was dissolved in dry pyridine (5 c.c.), tosyl chloride (0·4 g.; 2·2 mols.) added, the mixture poured into water after 24 hours, and the solution extracted four times with chloroform. The extract was washed with 5% sulphuric acid, sodium bicarbonate solution, and with water and evaporated to dryness. The product was a syrup (0·31 g.), which rapidly crystallised on treatment with alcohol. Recrystallisation from alcohol gave light feathery needles (0·23 g.), m. p. 102—103°, $[\alpha]_D^{23°}$ + 5·4° (*c*, 1·28 in chloroform) (Found : C, 51·8; H, 5·2. $C_{22}H_{26}O_{10}S_2$ requires C, 51·4; H, 5·1%).

1 : 6-*Dimethyl Dimethylene Sorbitol.*—Dimethylene sorbitol (1 g.) was methylated by three treatments with methyl iodide and silver oxide, the product being extracted after each treatment with boiling chloroform. In this way was obtained a syrup which distilled at 115—120° (bath temp.)/0·03 mm. and crystallised on cooling. Recrystallisation from ether–petrol gave clusters of small needles (0·7 g.), m. p. 43°, $[\alpha]_D^{17°}$ + 9·4° (*c*, 3·205 in chloroform) (Found : C, 51·7; H, 7·6; OMe, 25·9. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7; OMe, 26·5%).

Oxidation of 2 : 3 : 4 : 5-*Dimethylene Sorbitol.*—Dimethylene sorbitol (2 g.), suspended in glacial acetic acid (100 c.c.), was stirred while a solution of chromic anhydride (2·8 g., 4·5 atoms of oxygen, whereas 4 atoms are required theoretically) in glacial acetic acid (200 c.c.) was added during 1½ hours. Stirring was continued overnight, and the green solution evaporated to dryness. The acetic acid was removed as completely as possible by evaporation with water. The residue was dissolved in water, and hydrated barium hydroxide (16 g.) dissolved in water added. After an hour the precipitated chromium hydroxide was removed by centrifuging, and the gelatinous precipitate washed with water. The clear liquid was freed from barium with dilute sulphuric acid, care being taken that no excess of sulphuric acid was present. The barium sulphate was removed by centrifuging and washed with water, and the clear liquid evaporated to dryness. The residue was refluxed with 2% methyl-alcoholic hydrogen chloride (300 c.c.) for 6 hours, the acid neutralised with silver carbonate, and the solution filtered and evaporated to a syrup (1·3 g.). The syrup rapidly crystallised and was recrystallised from ethyl alcohol in two fractions : (1) Dimethyl dimethylene glucosaccharate (0·8 g.), m. p. and mixed m. p. with a specimen obtained from potassium glucosaccharate 157° (Haworth, Jones, Stacey, and Wiggins, *loc. cit.*), $[\alpha]_D^{18°}$ + 38·7° (*c*, 1·5 in chloroform); (2) *methyl dimethylene gluconate* or l-*gulonate* (0·07 g.), m. p. 147—148°, $[\alpha]_D^{18°}$ + 55·3° (*c*, 0·833 in chloroform) (Found : C, 46·1; H, 6·1; OMe, 12·6. $C_9H_{14}O_7$ requires C, 46·1; H, 6·0; OMe, 13·2%).

Methylenation of 1 : 6-*Dibenzoyl Mannitol.*—(*a*) Into a suspension of dibenzoyl mannitol (Brigl and Grüner, *Ber.*, 1932, **65**, 641) (20 g.) in 38% formalin (140 c.c.) at 0°, hydrogen chloride was passed until the solution was saturated; the solid dissolved and a syrupy layer separated. The mixture was extracted three times with chloroform, and the extract washed successively with water, aqueous ammonia, and water and dried over anhydrous magnesium sulphate. After evaporation in the presence of a small amount of barium carbonate a syrup (20 g.) was obtained, which was dissolved in ethyl alcohol–acetone. On cooling, a crystalline material (9 g.) separated, m. p. 112—120°. Fractional crystallisation from ethyl alcohol gave 1 : 6-dibenzoyl dimethylene mannitol (5·5 g.), m. p. 121°, $[\alpha]_D^{16°}$ + 51·2° (*c*, 1·916 in chloroform) (Found : C, 64·1; H, 5·3. Calc. for $C_{22}H_{22}O_8$: C, 63·8; H, 5·3%), and 1 : 6-*dibenzoyl monomethylene mannitol*, the latter forming feathery needles (2·6 g.), m. p. 154°, $[\alpha]_D^{17°}$ + 25·0° (*c*, 1·44 in chloroform) (Found : C, 62·7; H, 5·3. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%).

(*b*) 1 : 6-Dibenzoyl mannitol (20 g.), paraformaldehyde (20 g.), and concentrated sulphuric acid (15 c.c.) were stirred together, the temperature rising to 60°; after cooling, the mixture was shaken for 3 hours with chloroform (300 c.c.), which was then decanted. This extraction process was repeated twice more and the combined chloroform extracts were washed with dilute aqueous ammonia and with water, dried over anhydrous magnesium sulphate, filtered, and evaporated to give a syrup, which rapidly crystallised. Recrystallisation from alcohol gave the product in prismatic crystals (13 g.; 60% of the theoretical), m. p. 121°. Hudson, Hann, and Haskins (*J. Amer. Chem. Soc.*, 1943, **65**, 67) record m. p. 120—122° and $[\alpha]_D$ + 47·5° in chloroform (*c*, 0·8) for 1 : 6-dibenzoyl dimethylene mannitol.

2 : 3 : 4 : 5-*Dimethylene Mannitol.*—1 : 6-Dibenzoyl dimethylene mannitol (16 g.), dissolved in dry methyl alcohol (500 c.c.), was shaken overnight with a piece of clean sodium. Evaporation of the solution obtained gave methyl benzoate and crystals of dimethylene mannitol. The former was removed in ether, and the latter recrystallised from ethyl alcohol, forming prismatic crystals (6·1 g.; 95% of the theoretical), m. p. 138—139°, $[\alpha]_D^{16°}$ + 70·5° (*c*, 1·42 in water) (Found : C, 47·0; H, 6·6. Calc. for $C_8H_{14}O_6$: C, 46·6; H, 6·8%). Hudson *et al.* (*loc. cit.*) record m. p. 139° (corr.) and $[\alpha]_D^{20°}$ + 71·1° in water (*c*, 0·9) for this substance.

Chlorination of Dimethylene Mannitol.—To a solution of dimethylene mannitol (1 g.) in dry pyridine (4 g.) at 0°, thionyl chloride (4 g.) was added. Smooth evolution of sulphur dioxide occurred when the mixture was heated on a boiling water-bath. After 2 hours' heating, it was poured into ice-water, chloroform added, the liquid filtered, the residue washed with chloroform, and the chloroform-layer separated. The aqueous layer was re-extracted twice with chloroform and the combined extracts were washed with a solution of sodium bicarbonate and water and dried over anhydrous magnesium sulphate. On evaporation of the solvent crystals of 1 : 6-dichloro dimethylene mannitol separated; recrystallised from ethyl alcohol, these formed prismatic crystals (0·7 g.; 60% of the theoretical), m. p. 156°, not depressed by a specimen prepared by Micheel's method (*Annalen*, 1932, **496**, 77).

1 : 6-*Ditosyl Dimethylene Mannitol.*—Dimethylene mannitol (0·5 g.), dissolved in dry pyridine (5 c.c.), was treated with tosyl chloride (1 g.; 2 mols.). The mixture was kept overnight and then poured into ice-water. Crystals immediately separated; recrystallised from ethyl alcohol, they formed short needles (1 g.; 90% of the theoretical), m. p. 166—167°, $[\alpha]_D^{22°}$ +68·6° (*c*, 1·1 in chloroform) (Found : C, 51·4; H, 5·7. Calc. : C, 51·4; H, 5·1%). Hudson *et al.* (*loc. cit.*) record m. p. 164—165° and $[\alpha]_D$ + 68·1° in chloroform (*c*, 0·8) for 1 : 6-ditosyl 2 : 3 : 4 : 5-dimethylene mannitol.

1 : 6-*Dimethyl Dimethylene Mannitol.*—Dimethylene mannitol (0·8 g.) was methylated smoothly as the result of two treatments with silver oxide and methyl iodide. The product was extracted each time with chloroform. Evaporation of the chloroform extract from the second methylation gave a mass of crystals which, recrystallised from ether–petrol, formed thin lustrous plates (0·65 g.), m. p. 65·5°, $[\alpha]_D^{19°}$ + 74·9° (*c*, 2·11 in chloroform) (Found : C, 51·4; H, 7·6; OMe, 26·4. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7; OMe, 26·5%).

1 : 6-*Ditrityl Dimethylene Mannitol.*—The treatment of dimethylene mannitol with trityl chloride (1·4 g.; 2 mols.) was the same as that with tosyl chloride (above). The syrupy product which separated on pouring into ice-water soon crystallised. It was washed with water and recrystallised from acetone–alcohol–chloroform, forming small prisms (0·9 g.), m. p. 210°, $[\alpha]_D^{18°}$ + 24·0° (*c*, 1·25 in chloroform) (Found : C, 79·7; H, 6·1. $C_{46}H_{42}O_6$ requires C, 80·0; H, 6·1%).

Oxidation of 2 : 3 : 4 : 5-*Dimethylene Mannitol.*—Dimethylene mannitol (5 g.), dissolved in glacial acetic acid (50 c.c.), was stirred while a solution of chromic anhydride (6·8 g.) in glacial acetic acid (300 c.c.) was added during 2 hours. Stirring was continued overnight, and the green solution then evaporated to dryness. Chromium in a solution of the residue in water was removed as chromium hydroxide by addition of a small excess of cold barium hydroxide solution. The gelatinous precipitate was centrifuged and washed with water, and barium removed from the filtrate by the addition of the required amount of dilute sulphuric acid. After centrifuging, the clear supernatant liquid was evaporated to dryness, and the residue refluxed with 2% methyl-alcoholic hydrogen chloride (300 c.c.) for 6 hours. Neutralisation with silver carbonate, filtration and evaporation gave a syrup (1·3 g.) which, from its solution in methyl alcohol, deposited crystals (0·5 g.). These were recrystallised from methyl alcohol and showed m. p. 109°, $[\alpha]_D^{15°}$ + 99·2° (*c*, 1·653 in chloroform) (Found : C, 46·0; H, 4·9; OMe, 22·7. $C_{10}H_{14}O_8$ requires C, 45·8; H, 5·3; OMe, 23·6%). After the separation of the last traces of the crystalline material evaporation of the mother-liquor gave a syrup which could not be crystallised; $[\alpha]_D^{18°}$ + 56·0° (*c*, 2·143 in chloroform) (Found : OMe, 17·5. Methyl dimethylene hexonate requires OMe, 13·2% and dimethyl dimethylene mannosaccharate requires 22·7%). This product is being investigated further.

Dimethylene Mannosaccharodimethylamide.—Dimethyl dimethylene mannosaccharate (50 mg.) was dissolved in dry methyl alcohol (3 c.c.) containing 33% methylamine, and the solution cooled to 0° and left thereat for 24 hours. Evaporation of the solvent in a vacuum gave a crystalline solid, which, recrystallised from alcohol, formed short needles, m. p. 278° (Found : C, 46·1; H, 6·2. $C_{10}H_{16}O_6N_2$ requires C, 46·2; H, 6·2%)

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