[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

2,4:3,5-Dimethylene-D-sorbitol and Some of its Derivatives

BY RAYMOND M. HANN, J. K. WOLFE AND C. S. HUDSON

In prior communications[1] from this Laboratory a mechanism has been proposed to explain the limited acetolysis by a 1 to 2% sulfuric acid acetolyzing mixture at 0° of the methylene acetals of the sugar alcohols. This mechanism is based upon the premise that the acetal linkages which are formed through secondary hydroxyl groups are relatively stable under experimental conditions which cause a rapid rupture of those formed through primary hydroxyl groups. According to this view the acetolysis of such an acetal as 1,3:2,5:4,6-trimethylene-D-mannitol proceeds through the formation of an assumed intermediate product, namely, 3,4-di-(hydroxymethyl)-2,5-methylene-D-mannitol (a compound in which the cyclic acetal linkage is formed solely through secondary hydroxyl groups), which then undergoes acetylation and forms 1,6-diacetyl-3,4-di-(acetoxymethyl)-2,5-methylene-D-mannitol, the substance which is actually isolated from the reaction mixture. Although study of the structure of the crystalline acetolysis products of the methylene acetals of dulcitol,[1a] xylitol,[1c] D-mannitol,[1a] D-sorbitol[1b] and D-epirhamnitol[1d] has disclosed no exception to the mechanism which has been proposed, the fact that the yield of crystalline acetolysis product from certain acetals is low suggests the possibility that some concurrent rupture and acetylation of the acetal linkages formed through secondary hydroxyl groups may lead to the formation of other acetolysis products. While it is evident that complete rupture of all the acetal and acetoxymethyl ether linkages and subsequent acetylation of the hydroxyl groups so formed will yield the fully acetylated sugar alcohol, it has been found that the acetolysis of 1,3:2,5:4,6-trimethylene-D-mannitol by a 2% sulfuric acid acetolyzing mixture at 20° for five days (when the rotation of the reaction mixture had attained a constant value) gave a yield of only 14% of crystalline D-mannitol hexaacetate; the other reaction products could not be crystallized and it seems plausible to assume that they are acetylacetoxymethyl-D-mannitols which differ in structure and proportion in the reaction mixture depending upon the ease of rupture of the different secondary hydroxyl linkages under the conditions employed. Up to the present time no evidence has been available which would allow a decision regarding relative stability among the secondary alcoholic acetal linkages in any methylene sugar alcohol acetal. Recently, however, we have prepared a dimethylene-D-sorbitol[2] by debenzoylation of the 1,6-dibenzoyldimethylene-D-sorbitol that is obtained through the condensation of the known 1,6-dibenzoyl-D-sorbitol[3] with formaldehyde. The conditions of the synthesis confine the acetal linkages to the secondary hydroxyl groups at positions 2, 3, 4 and 5. In seeking to locate the linkages more precisely, the 1,6-dibenzoyl-2,3,4,5-dimethylene-D-sorbitol was subjected to acetolysis with a sulfuric acid acetolyzing mixture at 0° for fifteen minutes. The crystalline acetolysis product, which melted at 115–116° and rotated $[\alpha]^{20}D$ +9.3° in chloroform and agreed in composition with a dibenzoyl-acetyl-acetoxymethyl-methylene-D-sorbitol, was obtained in a yield of 72%; the isolation of this substance indicated that three of the four acetal linkages are comparable in stability and that the other one is relatively easily ruptured. Upon saponification, the acetolysis product forms the known 2,4-methylene-D-sorbitol (V), a fact which not only proves that the ruptured linkage is at position 3 or 5 but permits the assignment of the structure 2,4:3,5-dimethylene-D-sorbitol (II) to the diacetal and the structure 1,6-dibenzoyl-2,4:3,5-dimethylene-D-sorbitol (I) to the condensation product of 1,6-dibenzoyl-D-sorbitol with formaldehyde. The evidence which has been presented also limits the structure of the acetolysis product to 1,6-dibenzoyl-2,4-methylene-5-acetyl-3-acetoxymethyl-D-sorbitol or 1,6-dibenzoyl-2,4-methylene-3-acetyl-5-acetoxymethyl-D-sorbitol and a decision between these two structures would furnish a proof that the remaining stable linkage was at position 3 or 5, re-

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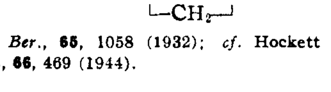
[1] (a) Ness, Hann and Hudson, THIS JOURNAL, **65**, 2215 (1943); (b) Ness, Hann and Hudson, *ibid.*, **66**, 665 (1944); (c) Hann, Ness and Hudson, *ibid.*, **66**, 670 (1944); (d) Ness, Hann and Hudson, *ibid.*, **66**, 1235 (1944).

[2] Haworth and Wiggins [*J. Chem. Soc.*, 58 (1944)] have recently described this new dimethylene-D-sorbitol and several of its derivatives. They have shown that the diacetal is 2,3,4,5-dimethylene-D-sorbitol. Decision among the three possible precise structures (2,3:4,5-, 2,4:3,5- or 2,5:3,4-dimethylene-D-sorbitol) was left open by these authors. The present results prove that the substance is the 2,4:3,5-dimethylene-D-sorbitol, as is explained in the continuation. It follows that the dimethylene-D-glucosaccharic acid which is obtained by its oxidation possesses the structure of 2,4:3,5-dimethylene-D-glucosaccharic acid. The epimerization of this 2,4:/3,5-dimethylene-D-glucosaccharic to dimethylene-L-idosaccharic acid [Haworth, Jones, Stacey and Wiggins, *ibid.*, 61 (1944)] involves a Walden inversion at carbon 5; it is highly improbable that the 2,4-cyclic acetal structure can be changed by this inversion; assuming, therefore, its presence in the dimethylene-L-idosaccharic acid the other cyclic acetal ring must be at 3,5. It appears therefore that the Walden inversion at carbon 5 represents a change in configuration, but not in structure, and we conclude that the dimethylene-L-idosaccharic acid is 2,4:3,5-dimethylene-L-idosaccharic acid as indicated by the formula

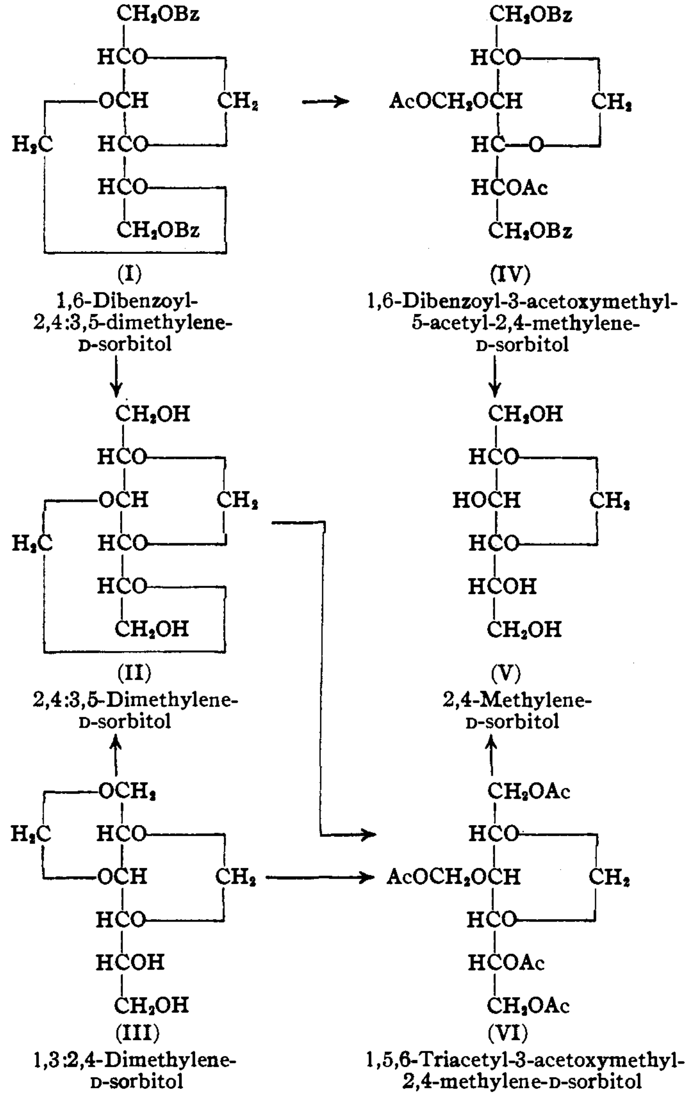


[3] Müller, *Ber.*, **65**, 1058 (1932); *cf.* Hockett and Fletcher, THIS JOURNAL, **66**, 469 (1944).

spectively. Because of the experimental difficulties involved in the conversion of such mixed esters to substances suitable for structural study[1a] recourse was taken to a study of the limited acetolysis of the 2,4:3,5-dimethylene-D-sorbitol (II), the structure of which has just been shown. The acetolysis of this diacetal at 0° for thirty minutes gave a 79% yield of the 1,5,6-triacetyl-3-acetoxymethyl-2,4-methylene-D-sorbitol (VI) which has previously been obtained by the limited acetolysis of the isomeric 1,3:2,4-dimethylene-D-sorbitol (III).[1b] The isolation of this substance in such good yield is evidence that rupture of the acetal linkage at position 5 occurred at a much more rapid rate than that at position 3; had the rupture occurred more rapidly at the latter position the predominant acetolysis product would have been the unknown 1,3,6-triacetyl-5-acetoxymethyl-2,4-methylene-D-sorbitol. This establishment of the relative instability of the linkage at position 5 in 2,4:3,5-dimethylene-D-sorbitol makes it highly probable that the previously described dibenzoylacetyl-acetoxymethyl-methylene-D-sorbitol, melting at 115–116°, is 1,6-dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol (IV). The structural relationships among the acetals and their derivatives are shown by the diagram.

Recently we have extended our investigations of methylene acetals of the sugar alcohols to some of those of the desoxyhexitols and in this connection it was desired to obtain 1,6-didesoxy-2,4:3,5-dimethylene-D-sorbitol. In the course of the preparation of the latter substance 1,6-ditosyl-2,4:3,5-dimethylene-D-sorbitol was heated in acetone solution with sodium iodide for two hours at 100°; the reaction product was not the expected 1,6-didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-D-sorbitol, but a 1-tosyl-6-desoxy-6-iodo-2,4:3,5-dimethylene-D-sorbitol (m. p. 128–129°; $[\alpha]^{20}_{D}$ $-8.5°$ in chloroform), the structure of which is proved in the accompanying article. The replacement of both tosyloxy groups by iodine was readily effected by refluxing the 1,6-ditosylated diacetal and sodium iodide in acetic anhydride solution[4] for two hours; the reduction with hydrogen and Raney nickel of the 1,6-didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-D-sorbitol so obtained yields the desired 1,6-didesoxy-2,4:3,5-dimethylene-D-sorbitol.

We express our appreciation to Dr. A. T. Ness for performing the microchemical analyses and to Mr. Harry W. Diehl for assistance in preparing some of the diacetal derivatives.



(I) 1,6-Dibenzoyl-2,4:3,5-dimethylene-D-sorbitol

(IV) 1,6-Dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol

(II) 2,4:3,5-Dimethylene-D-sorbitol

(V) 2,4-Methylene-D-sorbitol

(III) 1,3:2,4-Dimethylene-D-sorbitol

(VI) 1,5,6-Triacetyl-3-acetoxymethyl-2,4-methylene-D-sorbitol

Experimental

1,6-Dibenzoyl-2,4:3,5-dimethylene-D-sorbitol (I).—A suspension of 20.0 g. of 1,6-dibenzoyl-D-sorbitol[3] in a mixture of 40 cc. of dioxane and 20 cc. of 37% aqueous formaldehyde was cooled to 0° and saturated with gaseous hydrochloric acid; the alcohol dibenzoate dissolved and the dibenzoate of the diacetal was gradually deposited from the clear solution. The reaction mixture was allowed to stand at 5° for eighteen hours and the mass of crystals which had formed was thinned with 100 cc. of cold alcohol and filtered. The product (13.2 g.) was recrystallized from 50 parts of alcohol and gave 12.3 g. (58%) of slender needles which melted at 158–159° and rotated $[\alpha]^{20}_{D}$ $+18.7°$ in chloroform (*c*, 0.62). The substance is readily soluble in acetone, ethyl acetate and acetic acid, and insoluble in water. Haworth and Wiggins[3] recorded a melting point of 160° and a specific rotation $[\alpha]^{19}_{D}$ $+22.7°$ in chloroform (*c*, 1.545) for their 1,6-dibenzoyl-dimethylene-sorbitol.

Anal. Calcd. for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35; C_6H_5CO, 50.7. Found: C, 63.81; H, 5.29; C_6H_5CO, 50.5.

1,6-Dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol (IV) from 1,6-Dibenzoyl-2,4:3,5-dimethylene-D-sorbitol (I).—A solution of 5.0 g. of 1,6-dibenzoyl-2,4:3,5-

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[4] Haskins, Hann and Hudson, This Journal, 64, 139 (1942).

dimethylene-D-sorbitol in 50 cc. of an acetolyzing solution, prepared by adding 1 cc. of concentrated sulfuric acid dropwise to an ice-cold mixture of 35 cc. of acetic anhydride and 15 cc. of acetic acid, was allowed to stand at 25° for fifteen minutes and then poured upon crushed ice; the precipitated acetolysis product was separated by filtration and upon recrystallization from 5 parts of alcohol it formed thin elongated platelets which sintered at 113° and melted at 115–116°. The compound is nearly insoluble in water, but readily soluble in acetone, ethyl acetate and chloroform; in the last solvent it shows a specific rotation $[\alpha]^{20}\text{D}$ +9.3° (*c*, 1.11). The yield was 4.5 g. (72%).

Anal. Calcd. for $C_{26}H_{28}O_{11}$: C, 60.46; H, 5.46; saponification, 0.1507 g. substance requires 11.67 cc. 0.1 *N* alkali (four saponifiable groups). Found: C, 60.49; H, 5.65; saponification, 0.1507 g. substance consumed 11.50 cc. 0.1 *N* NaOH.

2,4-Methylene-D-sorbitol (V) from 1,6-Dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol (IV).—To an ice-cold solution of 3.2 g. of 1,6-dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol in 30 cc. of chloroform a 0.2 *N* sodium methylate solution (3 cc.) was added and the reaction mixture was allowed to stand at 5° for eighteen hours. The precipitate of 2,4-methylene-D-sorbitol (1.2 g.; quantitative) which had deposited was recrystallized from 20 cc. of alcohol; the 0.8 g. of product so obtained showed a specific rotation $[\alpha]^{20}\text{D}$ −9.8° in chloroform (*c*, 1.14) and a melting point of 163–164° in agreement with the known values[1b] for 2,4-methylene-D-sorbitol. A mixed melting point determination with authentic 2,4-methylene-D-sorbitol, m. p. 163–164°, showed no depression.

2,4:3,5-Dimethylene-D-sorbitol (II) from 1,6-Dibenzoyl-2,4:3,5-dimethylene-D-sorbitol (I).—A solution of 14.0 g. of 1,6-dibenzoyl-2,4:3,5-dimethylene-D-sorbitol in 100 cc. of chloroform was cooled to 0° and 10 cc. of 0.2 *N* sodium methylate solution was added. The next day the precipitate of diacetal which had deposited was separated by filtration and recrystallized from 20 parts of alcohol. The yield was 6.5 g. (93%). The compound, which melted at 192–193° and rotated $[\alpha]^{20}\text{D}$ + 44.3° in pyridine (*c*, 1.0) and +41.5° in water (*c*, 1.40), forms plates which are readily soluble in water, pyridine and warm methyl and ethyl alcohols, and nearly insoluble in cold ethyl alcohol, acetone, benzene and chloroform. Haworth and Wiggins[2] found a melting point of 192–193° and a specific rotation $[\alpha]^{18}\text{D}$ +42.5° in water (*c*, 1.412) for the diacetal.

Anal. Calcd. for $C_8H_{14}O_6$: C, 46.60; H, 6.84. Found: C, 46.54; H, 6.83.

1,5,6-Triacetyl-3-acetoxymethyl-2,4-methylene-D-sorbitol (VI) from 2,4:3,5-Dimethylene-D-sorbitol (II).—A solution of 1.0 g. of 2,4:3,5-dimethylene-D-sorbitol in 10 cc. of the previously mentioned acetolyzing solution was allowed to stand at 0° for thirty minutes and then poured into 300 cc. of ice-cold water; after partial neutralization of the acids by the addition of 15 g. of sodium bicarbonate, the reaction mixture was extracted with chloroform and the extract was concentrated *in vacuo* to dryness. The crystalline reaction product, which weighed 1.5 g. (79%), after a single recrystallization from 8 parts of alcohol gave a product which melted at 93–95° and rotated $[\alpha]^{20}\text{D}$ +11.3°; these constants are in agreement with the values of 94–95° and +11.0°, respectively, which have been recorded[1b] for 1,5,6-triacetyl-3-acetoxymethyl-2,4-methylene-D-sorbitol and a mixed melting point determination with an authentic sample of the latter compound prepared by the limited acetolysis of 1,3:2,4-dimethylene-D-sorbitol (III) showed no depression. The formation of this acetolysis product from 2,4:3,5-dimethylene-D-sorbitol (II) could occur only through a rupture of the acetal linkage at position 5 and its isolation in such high yield may be taken as an indication that in this diacetal the acetal linkage at position 3 is comparable in stability with those at positions 2 and 4.

1,6-Diacetyl-2,4:3,5-dimethylene-D-sorbitol.—This compound was prepared by the acetylation of 2,4:3,5-dimethylene-D-sorbitol in pyridine solution by acetic anhydride. The yield was quantitative. It was recrystallized from 10 parts of alcohol and formed glistening plates which melted at 114–115° and rotated $[\alpha]^{20}\text{D}$ +6.6° in chloroform (*c*, 1.28); it is soluble in acetone, ethyl acetate, carbon tetrachloride and pyridine, and nearly insoluble in water.

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.24; CH_3CO, 29.7. Found: C, 49.76; H, 6.08; CH_3CO, 29.4.

1,6-Ditosyl-2,4:3,5-dimethylene-D-sorbitol.—To a solution of 1.0 g. of 2,4:3,5-dimethylene-D-sorbitol in 10 cc. of pyridine, 2.3 g. (2.5 molecular equivalents) of *p*-toluenesulfonyl chloride was added; the reaction mixture cooled perceptibly and then gradually warmed to a temperature of about 30°. The next day ice was added and the crystalline precipitate (2.5 g.; quantitative) which deposited was recrystallized from 50 parts of alcohol, forming the silky needles of the diacetal ditosylate melting at 97–98° and rotating $[\alpha]^{20}\text{D}$ +4.6° in chloroform (*c*, 1.18). The compound is readily soluble in cold carbon tetrachloride, acetone, benzene and ethyl acetate, hot methyl and ethyl alcohols, sparingly soluble in cold methyl and ethyl alcohols, and nearly insoluble in water. Haworth and Wiggins[2] record a melting point of 102–103° and a specific rotation $[\alpha]^{23}\text{D}$ +5.4° in chloroform (*c*, 1.28) for this substance. The melting point of our compound was not raised by repeated recrystallization.

Anal. Calcd. for $C_{22}H_{26}O_{10}S_2$: C, 51.35; H, 5.09; S, 12.46. Found: C, 51.36; H, 5.16; S, 12.31.

1,6-Didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-D-sorbitol.—A mixture of 4.0 g. of 1,6-ditosyl-2,4:3,5-dimethylene-D-sorbitol, 3.4 g. (3 molecular equivalents) of sodium iodide and 40 cc. of acetic anhydride was refluxed for two hours. The cooled reaction mixture was poured into ice water and the suspension was agitated by an air current; as the conversion of the anhydride to acetic acid progressed the didesoxy-di-iodo-dimethylene-D-sorbitol crystallized. The yield was 3.0 g. (91%). The compound was recrystallized from 20 parts of alcohol in the form of needles which melted at 151–152° and rotated $[\alpha]^{20}\text{D}$ +17.0° in chloroform (*c*, 1.23); it is readily soluble in ethyl acetate, acetone, pyridine, hot methyl and ethyl alcohols, sparingly soluble in cold methyl and ethyl alcohols, and nearly insoluble in water.

Anal. Calcd. for $C_8H_{12}O_4I_2$: C, 22.55; H, 2.84; I, 59.58. Found: C, 22.72; H, 2.92; I, 59.39.

1,6-Didesoxy-2,4:3,5-dimethylene-D-sorbitol.—A solution of 1.0 g. of 1,6-didesoxy-1,6-di-iodo-2,4:3,5-dimethylene-D-sorbitol in a mixture of 100 cc. of methyl alcohol and 10 cc. of 4% methyl alcoholic potassium hydroxide was agitated with 0.3 g. of Raney nickel and hydrogen under slight positive pressure. Within thirty minutes 113 cc. of hydrogen, measured at 25° and 760 mm. (calcd., 115 cc.), had been absorbed and no further absorption was noted in the following thirty minutes. The solutions from the reduction of a total of 3.2 g. of didesoxy-di-iodo-diacetal were combined, filtered to remove the catalyst, and the filtrate was concentrated *in vacuo* to dryness; the residue was extracted with cold chloroform and the extract was evaporated to crystallization by an air current; the crystalline residue, which was somewhat volatile at room temperature, was recrystallized from 25 cc. of boiling isopentane. The yield was 0.5 g. (45%). The didesoxy-diacetal formed plates which melted at 73–74° and rotated $[\alpha]^{20}\text{D}$ +34.3° in chloroform (*c*, 0.36); it is soluble in cold chloroform, ether, acetone, methyl and ethyl alcohols and water.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.35; H, 8.13.

Summary

The limited acetolysis of the dimethylene-D-sorbitol which results by debenzoylation of the condensation product of 1,6-dibenzoyl-D-sorbitol and formaldehyde yields the known 1,3,5-triacetyl - 3 - acetoxymethyl - 2,4 - methylene - D-

sorbitol. This fact is a proof that the diacetal, known previously only as 2,3,4,5-dimethylene-D-sorbitol,[2] is 2,4:3,5-dimethylene-D-sorbitol. It also indicates that in the D-sorbitol methylene acetals the acetal linkage which is formed through the secondary hydroxyl group at position 3 is more stable to acetolysis than that at position 5, an inference which allows assignment of the structure of 1,6-dibenzoyl-3-acetoxymethyl-5-acetyl-2,4-methylene-D-sorbitol to the acetolysis product of 1,6-dibenzoyl-2,4:3,5-dimethylene-D-sorbitol.

The 2,4:3,5-dimethylene-D-sorbitol has been converted to 1,6-didesoxy-2,4:3,5-dimethylene-D-sorbitol by known reactions.

BETHESDA, MARYLAND RECEIVED AUGUST 19, 1944

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Selective Exchange of Tosyloxy for Iodo Groups in Certain Cyclic Acetals of 1,6-Ditosyl-D-sorbitol. 2,4:3,5-Dimethylene-D-epirhamnitol

BY A. T. NESS, RAYMOND M. HANN AND C. S. HUDSON

In 1932 Oldham and Rutherford[1] heated methyl 2,3-diacetyl-4,6-ditosyl-β-D-glucoside and methyl 2,3,4,6-tetratosyl-β-D-glucoside with sodium iodide in acetone solution at 100° for two hours. They found that under these experimental conditions the tosyloxy group ($(p)CH_3C_6H_4SO_2O—$ = TsO—) which was attached to the primary carbon atom at position 6 was *the only one to be replaced by iodine*, according to the equation $H_2\overset{|}{C}—OSO_2C_6H_4CH_3(p) + NaI = H_2\overset{|}{C}—I + NaOSO_2C_6H_4CH_3(p)$. Although the discoverers of the selectivity of this reaction proposed it, cautiously and specifically, as "a method for the identification and estimation of the 6-hydroxyl group in glucose," it has subsequently been designated under the name of the "Oldham–Rutherford rule" as offering the possibility of distinguishing primary from secondary hydroxyl groups in the carbohydrate series. The extent of its applicability can of course only be determined by experiments on various types of carbohydrate derivatives. It has been pointed out,[2] for instance, that the presence of tosyl groups on both a primary and an adjacent secondary hydroxyl group, as in 5,6-ditosyl-1,3:2,4-dibenzylidene-D-sorbitol and certain completely tosylated polyhydroxy alcohols (tetratosyl erythritol and tritosyl glycerol), can lead to the formation of an unsaturated compound rather than the iodo derivative. Such types of structure were not present in the substances which Oldham and Rutherford studied. Recently, in connection with studies on the acetals of the sugar alcohols, we have encountered an interesting two-stage variation of the reaction, which appears to be based on the influence of the D-sorbitol configuration; the present communication reports the anomalous results which were obtained when several 1,6-ditosylated derivatives of D-sorbitol were subjected to iodination under the usual conditions of the Oldham–Rutherford technique.

Further study of the recently described 2,4-methylene-D-sorbitol[3] has shown that, upon tosylation in pyridine solution with about two molecular equivalents of *p*-toluenesulfonyl chloride, it yields the expected 1,6-ditosyl-2,4-methylene-D-sorbitol (I). Attempts to convert this ditosyl derivative to a 1,6-didesoxy-1,6-di-iodo-2,4-methylene-D-sorbitol (III) by heating it at 100° for two hours in an acetone solution with sodium iodide (the usual conditions employed by Oldham and Rutherford[1]) resulted in the formation of a product (m. p. 195–196°; $[\alpha]^{20}D$ −13.4° in acetone), the analysis of which indicated that it is a desoxy-iodo-tosyl-2,4-methylene-D-sorbitol.[4] Confirmation of this composition was obtained when it was found that this product as well as the 1,6-ditosyl-2,4-methylene-D-sorbitol (I) could be partially converted to the 1,6-didesoxy-1,6-dihalogenated acetal (III) by extending the reaction period to five hours. As pointed out by Oldham and Rutherford, such prolongation of the time of heating may lead to side reactions of undetermined nature; in the present experiments some free iodine was formed and the yield of 1,6-didesoxy-1,6-di-iodo-2,4-methylene-D-sorbitol was low, namely, 19% from the ditosylate (I) and 31% from the desoxy-iodo-tosyl-2,4-methylene-D-sorbitol. In reviewing the factors which might be responsible for this low yield, the possibility of anhydro formation was considered and it was recalled that 2,3,7-tritosyl-D-gluco-D-*gulo*-heptosan <1,5>β<1,6> upon being heated in acetonylacetone solution with sodium iodide, formed 2,3-ditosyl-4,7-anhydro-D-gluco-D-*gulo*-heptosan <1,5>β<1,6>,[5] while similar treatment of its 4-

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(1) Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

(2) Tipson and Cretcher, *J. Org. Chem.*, **8**, 95 (1943); Hann, Ness and Hudson, THIS JOURNAL, **66**, 73 (1944).

(3) Ness, Hann and Hudson, *ibid.*, **66**, 665 (1944).

(4) A similar partial iodination has been observed by Dr. John K. Wolfe of this Laboratory. 1,6-Ditosyl-2,4:3,5-dibenzylidene-D-sorbitol (m. p. 123–124°; $[\alpha]^{20}D$ +7.8° in chloroform) yielded a desoxy-iodo-tosyl-2,4:3,5-dibenzylidene-D-sorbitol melting at 143–144° and rotating $[\alpha]^{20}D$ +17.3° in chloroform, when subjected to iodination by the usual Oldham–Rutherford procedure. The definitive structure of this desoxy-iodo-tosyl-dibenzylidene-D-sorbitol is under investigation.

(5) Montgomery, Richtmyer and Hudson, THIS JOURNAL, **65**, 1848 (1943).