is 390, in comparison with 678 for the biose octacetates, the calculated difference for the latter becomes 98 × (390/678) = 56°. As has been shown from theory, the value of this difference is a measure of the rotatory power of that end asymmetric carbon atom which is common to all the acetylated aldose sugars. The close numerical agreement, among the four acetylated sugars here described, may be interpreted to mean that the differences in structure which distinguish them do not appreciably affect the rotatory power of this end asymmetric carbon atom. Possibly this may be due somewhat to the fact that the three bioses are derivatives of glucose, and have much of their structure in common with that sugar.[1]

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THE ISOMERIC PENTACETATES OF MANNOSE.

BY C. S. HUDSON AND J. K. DALE.[2]

Received March 12, 1915.

The possibility of the existence of two isomeric pentacetates of *d*-mannose has been foreshadowed by Franchimont's[3] recognition of the two pentacetates of glucose, the beta form of which was discovered by him[4] in 1879 and the alpha form by Erwig and Koenigs[5] in 1889. Mannose may be readily acetylated by any of the customary reagents but it is only within the last two years that methods have been applied which result in a crystallization of the acetylated sugar. E. Fischer and Oetker[6] have prepared crystalline mannose pentacetate by acetylating β-mannose at low temperature (0°) with a mixture of acetic anhydride and pyridine (Behrend's method), and have regarded the substance, which they found to melt at 117.5° and to have a specific rotation of —24.9 in chloroform solution, as the β-pentacetate because of its preparation from β-mannose by the above mentioned method and its levorotation. Shortly before the appearance of Fischer and Oetker's description of the β-pentacetate, our colleague, Mr. H. L. Sawyer, succeeded in crystallizing from the products of the action of acetic anhydride and zinc chloride on β-mannose at 0° a mannose pentacetate which he found to melt at 117–118° and

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[1] The transformation of galactose pentacetate of m. p. 142° by heating with acetic anhydride and zinc chloride has yielded an isomeric crystalline pentacetate, of m. p. about 96°, which is being examined further. The expected isomeric form of xylose tetracetate has also been crystallized, found to melt at 59° and to have the specific rotation to the right of +88 in chloroform. This work will be published in detail later.—C. S. Hudson.

[2] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

[3] *Rec. trav. chim. Pays Bas*, 11, 106 (1892)

[4] *Ber.*, 12, 1940 (1879).

[5] *Ibid.*, 22, 1464 (1889).

[6] *Ibid.*, 46, 4029 (1913).

to show a specific rotation of —25.3 in chloroform.[1] The substance is evidently the same as that which Fischer and Oetker have prepared, and the fact that it may be obtained from β-mannose at 0° by acetylation with acetic anhydride mixed with $ZnCl_2$, as well as with pyridine as a catalyst, increases the probability that the substance is the beta form. Recently we have transformed this pentacetate into the isomeric alpha form by heating it in acetic anhydride solution with a small amount of $ZnCl_2$. Although the spontaneous crystallization of the new pentacetate was very difficult to accomplish, an examination of the solubilities of the first crystals which were obtained suggested a method of operation by which the substance may be prepared with ease as beautiful crystals.

Preparation of the β-Pentacetate of Mannose by the Action of Acetic Anhydride and $ZnCl_2$.[2]—Four grams of fused zinc chloride were dissolved in 40 g. of acetic anhydride, the solution was cooled to zero and 10 g. of very pure β-mannose were added a little at a time, the mixture being kept at zero with occasional shaking until all the sugar went into solution, which required about twenty-four hours. Ice water was then added and after a time the insoluble viscous phase crystallized. On recrystallization from 95% alcohol, β-mannose pentacetate was obtained in a yield of 45–50% of the theoretical. The substance was successively recrystallized from 95% alcohol until the specific rotation became constant. A solution consisting of 2.1073 g. pentacetate made up to 25 cc. with chloroform (*chloroformum purificatum,* U. S. P.) gave a negative rotation, —4.26 circular degrees, in a 200 mm. tube, hence $[\alpha]_D^{20} = -25.3°$. A similar solution containing 4.534 g. pentacetate gave a specific rotation of —25.1°. The melting point of the substance was 117–8° corr. These values agree with those found by Fischer and Oetker. An acetyl estimation, which was made by boiling in a quartz flask with reflux condenser half a gram of the pentacetate with 100 cc. of 0.25 *N* sulfuric acid during three hours, indicated 76.78% acetic acid, and in duplicate 77.22%, against 76.93% as the theoretical value for a mannose pentacetate.

Transformation of β-Mannose Pentacetate to the New Isomeric Alpha Form.—When the β-pentacetate was dissolved in acetic anhydride containing a small amount of $ZnCl_2$, the rotation was found to change towards the right very slowly at room temperature but rapidly on the steam bath. After a constant value was reached, the solution was poured into cold water and the oily substance which separated was then thoroughly washed with cold water. The material was found to be soluble in hot water and such a solution on cooling and long standing slowly deposited crystals which proved to be the isomeric α-pentacetate. Further experiments have

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[1] Unpublished communication.

[2] The directions for this preparation are based upon hitherto unpublished work by Mr. H. L. Sawyer and myself.—C. S. Hudson.

shown the following to be a more convenient method for the preparation of the substance. Twenty grams of β-pentacetate are dissolved in 30 cc. of acetic anhydride containing about 1 g. of fused zinc chloride and the solution is heated on the steam bath until no further change in the rotation is noticed, which requires about thirty minutes. The solution is cooled, mixed with 500 cc. of ice water, and the acid is neutralized with sodium bicarbonate. A thick, gummy substance separates and is removed, washed in cold water, and dissolved in boiling water. On cooling, the solution slowly deposits about 7 g. of crystals of the α-pentacetate in nearly pure condition. The substance has been recrystallized from water until the specific rotation became constant. The melting point of the pure material, dried in a vacuum desiccator over $CaCl_2$ and KOH, is 64° corr.

0.2246 and 0.3149 g. subs. yielded 0.4044 and 0.5681 g. CO_2 and 0.1164 and 0.1623 g. H_2O, in duplicate corresponding to 49.10 and 49.20% C and 5.79 and 5.77% H, respectively. Calc. for a mannose pentacetate 49.21% C and 5.68% H.

Acetyl determinations, made by boiling in a quartz flask with a reflux condenser 0.5 g. substance with 100 cc. 0.25 H_2SO_4 during three hours gave 77.11 and 77.18% acetic acid, which agree with the theoretical value for a mannose pentacetate, 76.93%.

In chloroform (*chloroformum purificatum* U. S. P.) solution 0.9197 g. of the α-pentacetate per 25 cc. of the solution gave a reading to the right, +4.04 circular degrees, in a 2 dcm. tube with sodium light, or $[\alpha]_D^{20} = +54.9°$. A duplicate measurement, in which 1.2007 g. pentacetate were used, gave $[\alpha]_D^{20} = +55.1°$.

Comparison of the Rotatory Powers of the Alpha and Beta Forms of Mannose Pentacetate with those of the Glucose Pentacetates.—If the molecular rotations of the α- and β-pentacetates of glucose are written (+A + B) and (—A + B), respectively, those of the corresponding mannose pentacetates may be considered, as a first approximation, to be (+A + B′) and (—A + B′), where B and B′ have different values. It follows that the difference of the rotations of the mannose pentacetate pair is 2A, which is equal to the difference for the glucose pentacetates. We have previously[1] found the molecular rotations of the glucose pentacetates in chloroform solution to be +39,600 for the alpha form and +1,500 for the beta, hence the difference is 38,100. The difference in the specific rotations of the mannose pentacetates in the same solvent is (55.0 + 25.2) = 80.2°, which corresponds to a molecular rotation difference of +31,300, since the molecular weight of the pentacetate is 390. There is thus some lack of agreement between these values, corresponding to 17° in specific rotation, which suggests that the change from the glucose chain, of rotation B, to the mannose chain, of rotation B′, may somewhat change the value of A. On the other hand, the agreement with theory appears sufficient to justify the nomenclature which has been adopted for the two pentacetates of mannose.

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[1] THIS JOURNAL, 37, 1264 (1915).