THE ISOMERIC ALPHA AND BETA OCTACETATES OF MALTOSE AND OF CELLOSE.

By C. S. Hudson and J. M. Johnson.[1]

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In continuation of the work which we recently described[2] regarding the preparation of the new alpha lactose octacetate by heating the well-known beta octacetate in acetic anhydride solution with a small amount of zinc chloride, we have applied the method to the octacetate of maltose which is described in the literature and have transformed it likewise to an isomeric crystalline octacetate. The new maltose octacetate rotates to the right in chloroform solution +122°, in comparison with the value +63° for the octacetate from which it was prepared, and on this account we have chosen to designate the new substance as the alpha form, and the earlier discovered octacetate as the beta isomer.

Preparation of β-Maltose Octacetate.—By acetylating maltose with acetic anhydride and sodium acetate, Herzfeld[3] first prepared crystals of this substance, but the earliest accurate description of it was given some years later by Ling and Baker,[4] who found it to melt at 158–9°, and to show a specific rotation of +62 in chloroform solution. We prepared from pure maltose without difficulty a considerable quantity of this octacetate by the Liebermann method and recrystallized it until the specific rotation became constant. The substance melted at 159–60° corr. and exhibited the specific rotations which are recorded in a part of Table I.

Preparation and Description of the New Isomeric α-Maltose Octacetate.—One hundred grams of β-maltose octacetate, of m. p. 159°, were dissolved in 250 cc. of acetic anhydride containing 5 g. of zinc chloride, and the solution was heated on the steam bath until its rotation became constant, which required about eleven minutes only. During this heating the specific rotation changed from the initial value of +59.8° to +110.4°, and it was concluded that this large increase in dextrorotation indicated that most of the original β-octacetate had changed to the hypothetical alpha form. Repeated attempts were made to crystallize the new isomer and this was at last accomplished by the following procedure: The solution which had reached constant rotation was poured into cold water and allowed to stand with an occasional renewal of the water until the viscous insoluble mass of acetylated sugar became hard. After drying and powdering the solid mass, it was dissolved in a very small amount of 95% alcohol so as to form a thick sirup. After standing for some weeks

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

[2] This Journal, 37, 1270 (1915).

[3] *Ber.*, 13, 267 (1880); *Ann.*, 220, 215 (1883).

[4] *J. Chem. Soc.*, 67, 212 (1895); *Ber.*, 28, 1019 (1895); cf. Herzfeld, *Ibid.*, 28, 440 (1895).

at room temperature, this sirup crystallized and by seeding with this material freshly prepared sirups could be brought to rapid crystallization. The new compound was recrystallized from alcohol until the rotatory power reached a constant value. The pure crystals melted at 125° corr. after thorough drying at 70° in a vacuum oven.

0.2112 and 0.2073 g. subs. yielded 0.3832 and 0.3755 g. CO_2, and 0.1098 and 0.1065 g. H_2O, corresponding to 49.54 and 49.40% C, 5.82 and 5.75% H, respectively. Calc. for maltose octacetate: 49.54% C and 5.65% H.

An acetyl estimation was made by boiling in a quartz flask with reflux quartz condenser 0.5 g. substance with 100 cc. 0.25 *N* sulfuric acid during six hours and it indicated 50.62% acetyl (CH_3CO), and duplicate experiments in which the boiling lasted only three hours gave 50.68 and 50.72% acetyl, respectively. These three values agree with the theoretical 50.74% for a maltose octacetate.

The molecular weight of the compound was determined from the lowering of the freezing point of its solutions in benzene. Six experiments with different concentrations showed depressions between 0.090 and 0.235°, which indicated values for the molecular weight ranging between 664 and 694, in comparison with 678, the theoretical value for maltose octacetate. Ling and Baker (*l. c.*) have found 633 in a measurement of the molecular weight of β-maltose octacetate in benzene by the freezing-point method.

Table I records the specific rotatory power of the new octacetate in several solvents, in comparison with the rotation of the β-octacetate. The tube length in all cases is 4 dcm., the readings are expressed in circular degrees for sodium light, and the concentration in grams per 100 cc. of solution, the weighings being made in air with brass weights. The chloroform used was *chloroformum purificatum, U. S. P.*

TABLE I.—THE SPECIFIC ROTATIONS OF THE MALTOSE OCTACETATES.

Substance.	Solvent.	Concentration.	Reading.	$[\alpha]_D^{20}$.
α-Maltose octacetate	Chloroform	5.01	+24.60	+122.77
	Chloroform	9.94	+48.50	+121.94
	Benzene	5.00	+24.80	+124.05
	Benzene	9.93	+48.90	+123.11
	99.5% acetic acid	3.95	+19.63	+124.30
	99.5% acetic acid	10.12	+50.30	+124.25
	Methyl alcohol	5.06	+24.55	+121.24
	Methyl alcohol	10.07	+48.43	+120.25
β-Maltose octacetate	Chloroform	5.09	+12.75	+ 62.59
	Chloroform	10.61	+26.95	+ 62.91
	Benzene	5.20	+15.55	+ 74.83
	Benzene	10.26	+30.70	+ 74.52
	99.5% acetic acid	5.45	+11.95	+ 54.80
	99.5% acetic acid	10.43	+23.95	+ 57.40

The Rotatory Powers of the Alpha and Beta Forms of Cellose Octacetate.—It has been mentioned by Hudson and Dale[1] that the difference between the molecular rotations of the two isomeric octacetates of cellose as given in the literature does not accord with the difference for the two

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

glucose pentacetates. We have investigated this disagreement and find that the recorded value of the specific rotation of β-cellose octacetate is too small and that the correct values for the two octacetates agree well with those of the glucose pentacetates. Skraup and Geinsperger[1] found the specific rotation of α-cellose octacetate to be +43.6 and the value —30 was found for the beta form, both in chloroform solution. Hardt-Stremayr[2] working later in the same laboratory, found +42.7° and +42.9° for the alpha octacetate in chloroform, and expressed the opinion[3] that Geinsperger's value —30 should read +30 and that it really referred to an impure sample of the alpha form. Schliemann[4] has purified the alpha form by numerous recrystallizations from alcohol and from benzene and has found the value +41.5 for its rotation. He found the value —8° for the β-octacetate in chloroform.

We have prepared α-cellose octacetate by the usual method of treating filter paper with acetic anhydride and a small amount of concentrated sulfuric acid. The acetate was recrystallized from hot 95% alcohol until the specific rotation became constant and the following values were found: 9.85 g. per 100 cc. in chloroform $[\alpha]_D^{20} = +41.95°$, 5.85 g. per 100 cc., +40.87°, the chloroform used being *chloroformum purificatum*, U. S. P. The melting point of the compound was 229.5° corr. From this acetate cellose was regenerated by saponification with alcoholic potash, and the crystalline sugar was then acetylated with acetic anhydride in the presence of anhydrous sodium acetate. The product was poured into cold water and soon crystallized. It was found that sixteen successive recrystallizations, first from alcohol and then from mixtures of chloroform and alcohol and of chloroform and ether, were required in order to fully purify the octacetate and obtain material which did not change in rotatory power after further recrystallization. From 75 g. of cellose, 111 g. of octacetate were obtained as the first product. Its rotation was —7.5° in chloroform, which agrees with Schliemann's observation. After the sixteen recrystallizations, 19 g. of pure material, of melting point 202° corr., were in hand. 10.88 g. of this β-octacetate per 100 cc. of its chloroform (*chloroformum purificatum*, U. S. P.) solution rotated to the left, $[\alpha]_D^{20} = -14.48$, and 5.10 g. per 100 cc. gave the value —14.74°.

Transformation of β-Cellose Octacetate to the Alpha Isomer.—Maquenne and Goodwin[5] mention that β-cellose octacetate can be changed to the alpha isomer by heating in acetic anhydride solution with a small quantity of sulfuric acid. We have carried out this transformation by

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[1] *Monatsh.*, **26**, 1471 (1905).

[2] *Ibid.*, **28**, 73 (1907).

[3] *Loc. cit.*, p. 68.

[4] *Ann.*, **378**, 366 (1910).

[5] *Bull. soc. chim.*, [3] **31**, 856 (1904).

heating an acetic anhydride solution of the beta form with a small amount of zinc chloride. 2.96 g. of the β-acetate dissolved in the cold in 50 cc. acetic anhydride containing a trace of zinc chloride read $[\alpha]_D^{20} = -4.8°$, and after fifteen minutes' heating on the steam bath, its rotation became constant at +44.9°. From this solution, by pouring into water and recrystallizing, there were obtained 1.9 g. of α-cellose octacetate of m. p. 221–3° and specific rotation +40.5 in chloroform. Likewise, the beta form was transferred to the alpha by heating with acetic anhydride containing some sulfuric acid, as mentioned by Maquenne and Goodwin, but the yield was very much smaller, due probably to the hydrolyzing action of the acid. Hardt-Stremayr[1] sought to transform the α-octacetate to the beta by the same methods but without success. Evidently the equilibrium in acetic anhydride solution between the two isomers is so far towards the side of the alpha form that it alone has been obtained from the mixture. The recorded rotatory power of the transformed solution also indicates that the point of equilibrium is far towards the side of the α-octacetate. This transformation of the β- to the α-octacetate makes it clear that the production of α-cellose octacetate by the acetolysis[2] of cellulose with acetic anhydride and sulfuric acid does not throw any light upon the question whether cellulose is a condensation product from α-cellose or β-cellose, because either form of the sugar must yield the same α-octacetate in the presence of the reagent mentioned.

Comparison of the Rotations of the Pentacetates of Glucose and the Octacetates of Lactose, Maltose and Cellose.—We have previously shown that the difference between the molecular rotations of the α- and β-glucose pentacetates in chloroform solution agrees with the difference for the α- and β-lactose octacetates, as is suggested by theoretical considerations. The data are now at hand for an extension of this comparison to the octacetates of maltose and of cellose. Since these have the same molecular weight as lactose octacetate, it is sufficient to compare the specific rotations of the substances. In chloroform solution α- and β-lactose octacetates rotate +53 and −4, respectively, the difference being 57°, α- and β-maltose octacetates rotate +122° and +63°, with a difference of 59°, and α- and β-cellose octacetates rotate +41 and −15, giving the difference 56°. These differences agree closely and also, as may be understood from what precedes, agree with the value which can be calculated from the observed difference between the rotations of the α- and β-glucose pentacetates, which have the values +102 and +4, respectively. Their specific rotation difference is thus 98° and since their molecular weight

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[1] *Loc. cit.*

[2] The term acetolysis is coming into use to designate the splitting and simultaneous acetylation of polysaccharides, in the same sense that hydrolysis indicates the splitting and simultaneous hydration.

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.

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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).