which are near the rotation of β-lactose octacetate (—4). The combination of this result with that obtained from the rotations of the sugars themselves, in which gentiobiose was clearly ruled out, gives strong evidence that the common glucose residues of lactose and cellose have identical structure.

WASHINGTON, D. C.

THE ISOMERIC ALPHA AND BETA HEXACETATES OF α-GLUCOHEPTOSE.

BY C. S. HUDSON AND E. YANOVSKY.[1]

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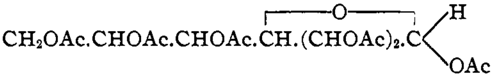
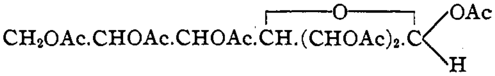
E. Fischer[2] has shown that two isomeric fully acetylated derivatives of α-glucoheptose could be prepared by the action of acetic anhydride on the sugar. When sodium acetate was used to catalyze the reaction, the crystalline product was a hexacetate which melted at 132°, but the use of zinc chloride gave an isomeric hexacetate of m. p. 156°. Fischer has mentioned that these isomeric hexacetates of α-glucoheptose are produced by the same reactions which yield the alpha and beta pentacetates of glucose. Since the isomerism of the glucose pentacetates can be explained, according to Fischer,[3] as due to the existence of the structures that are now generally named the alpha and beta forms, it appears probable that the similarly produced hexacetates of α-glucoheptose have the corresponding structures:



$$\mathrm{CH_2OAc.CHOAc.CHOAc.}\overbrace{\mathrm{CH.(CHOAc)_2.C}}^{\mathrm{O}}\!\left\langle\begin{matrix}\mathrm{H}\\ \mathrm{OAc}\end{matrix}\right.$$

and



$$\mathrm{CH_2OAc.CHOAc.CHOAc.}\overbrace{\mathrm{CH.(CHOAc)_2.C}}^{\mathrm{O}}\!\left\langle\begin{matrix}\mathrm{OAc}\\ \mathrm{H}\end{matrix}\right.$$

in which the asymmetry of the right-hand terminal carbon atom permits the two configurations. If this view is correct, the molecular rotatory power of the alpha form may be written +A + B′, and that of the beta form —A + B′, where A is the rotation of the terminal asymmetric carbon and B′ is that due to the remainder of the structure.[4] It follows then that the difference of the molecular rotations of the two forms is 2A, which is the same as the *difference* in the molecular rotations of the alpha and beta pentacetates of glucose, of rotations +A + B and —A + B, respectively. The rotations of the α-glucoheptose hexacetates are not recorded in Fischer's article, and we have consequently prepared the sub-

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

[2] *Ann.*, 270, 64 (1892); *Ber.*, 26, 2400 (1893).

[3] *Ber.*, *loc. cit.*

[4] Hudson, THIS JOURNAL, 31, 66 (1909).

stances in pure condition and have found the following rotatory powers in chloroform:[1]

α-Hexacetyl α-glucoheptose, $[\alpha]_D^{20} = +87.0$, $[M]_D^{20} = +40{,}200$[2] $= +A + B'$
β-Hexacetyl α-glucoheptose, $[\alpha]_D^{20} = +\ 4.8$, $[M]_D^{20} = +\ 2{,}200 = -A + B'$

Difference $= 38{,}000 = 2A$

The corresponding values for the glucose pentacetates in the same solvent have been found[3] to be

α-Pentacetyl glucose, $[\alpha]_D^{20} = +101.6$, $[M]_D^{20} = +39{,}600$[2] $= +A + B$
β-Pentacetyl glucose, $[\alpha]_D^{20} = +\ 3.8$, $[M]_D^{20} = +\ 1{,}500 = -A + B$

Difference $= 38{,}100 = 2A$

The agreement of the values for 2A is a close one, the discrepancy of 100 amounting to only about 0.25° in specific rotation, which is well within the limits of experimental error. There is thus good evidence that the two hexacetates constitute an alpha and beta pair, and this is supported by the fact, which is described later on, that the lower rotating one may be readily transformed into the other by warming it in acetic anhydride solution with a little zinc chloride, a method which has been found in general to change beta acetates to the corresponding alpha isomers. Since α-glucoheptose is a derivative of *d*-glucose, its more dextrorotatory hexacetate ($[\alpha]_D^{20} = +87°$) is to be named[4] the alpha form, and the other ($[\alpha]_D^{20} = +5$) the beta modification.

Experimental.

Preparation of the Beta Hexacetate of α-Glucoheptose.—A mixture of one part anhydrous sodium acetate, four parts α-glucoheptose, and 16 parts acetic anhydride was heated until the sugar dissolved, and then poured into an excess of cold water. An insoluble sirup precipitated and soon crystallized, crystals also separating from the solution. On recrystallizing the product from hot water a yield equal to 75% of the weight of sugar taken was obtained. Recrystallization from 50% alcohol is a more effective way to obtain the beta hexacetate entirely free from the alpha isomer. After two recrystallizations from this solvent, the material showed the specific rotation of $[\alpha]_D^{20} = +4.8$ in chloroform, a value which did not change with further recrystallization. The substance melted at 135°, uncorrected. Its elementary composition has been established by Fischer. For the acetyl determination, samples of 0.3092 and 0.2680 g. were boiled with 50 cc. 0.25 N H_2SO_4 three hours in a quartz flask with

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[1] *Chloroformum purificatium*, U. S. P., was used in all the measurements of the rotations.

[2] The molecular weight of the hexacetate is taken as 462, that of glucose pentacetate 390.

[3] Hudson and Dale, THIS JOURNAL, **37**, 1264 (1915).

[4] See THIS JOURNAL, **31**, 72 (1909).

a quartz reflux condenser, yielding 55.6 and 56.0% acetyl (CH_3CO) in comparison with 55.8, the calculated value for a heptose hexacetate.

Preparation of the Alpha Hexacetate of **α-Glucoheptose.**—Since it has already been shown by Fischer that this isomer is produced through the acetylation of the sugar with hot acetic anhydride and zinc chloride, we sought to obtain it by a method which has frequently been used in this laboratory to prepare alpha acetates, namely, by heating the acetic anhydride solution of the beta acetate with a little zinc chloride. Ten grams of the beta hexacetate were dissolved in 100 cc. acetic anhydride containing 2 g. $ZnCl_2$. The specific rotation of this solution was —10° to begin with, but after heating it three hours on the steam bath its rotation became constant at +25, indicating that the equilibrium in this solvent between the alpha and beta forms of the hexacetate had been established. On pouring the mixture into cold water an insoluble sirup precipitated and soon crystallized. The aqueous solution was extracted with chloroform, the extract washed with sodium bicarbonate solution and with water, and the crystals which formed when the chloroform was evaporated were united with those from the insoluble mass. One recrystallization from hot water of this product yielded crystals which had a specific rotation of +32, but on recrystallizing then five times from ether, a constant specific dextrorotation of +87.0° in chloroform was found. The pure substance melted at 164°, uncorrected, which is higher than the value found by Fischer, 156°, but our material was probably more nearly free from the beta isomer. Two acetyl estimations gave 55.6 and 55.5% CH_3CO in comparison with the calculated value 55.8.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

TRIPHENYLMETHYL. XXVI. TAUTOMERISM OF TRIARYLCARBINOLS.

BY M. GOMBERG AND N. E. VAN STONE.

Received June 12, 1916.

I. Introduction.

Historical.—The historical development of the application of the tautomeric hypothesis to the triphenylmethane derivatives may be said to fall mainly within the following periods:

(1) The complex dyes were considered as possessing of necessity a radically different constitution from that of the corresponding triarylcarbinols, for the very reason of the striking difference in properties. The dyes were *assumed* to possess a quinonoid constitution (I) in contradistinction from the benzenoid constitution of the carbinols (III). The possible existence of compounds isomeric with the carbinols but themselves colored and quinonoid, or the existence of salts isomeric with the