valuable since it involves no alteration of the kerogen—it is absolutely certain that the products obtained existed as such in the original shale.

By the action of benzene in a sealed tube at 200°, the amount of extract obtainable from pyrobituminous shale is more than trebled. As this amounts to 20% of the kerogen, it will be very interesting to find its constitution, and evidently this can best be done by the method described above.

By the action of nitric acid the kerogen may be completely removed from the shale, though in a highly altered condition. The products obtained are humins.

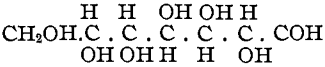
MONTREAL, CANADA

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. IV. TWO ISOMERIC CRYSTALLINE HEXA-ACETATES OF DEXTRO-ALPHA-MANNOHEPTOSE

BY C. S. HUDSON AND K. P. MONROE[1]

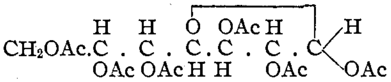
RECEIVED NOVEMBER 28, 1923

Fischer and Passmore[2] prepared from *d*-mannose by the cyanohydrin synthesis a sugar, *d*-α-mannoheptose, the configuration of which was established later by Peirce[3] to be



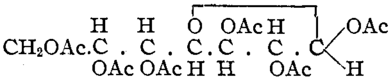
$$\begin{array}{lcccccl} & \text{H} & \text{H} & \text{OH} & \text{OH} & \text{H} & \\ \text{CH}_2\text{OH.} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{.COH}\\ & \text{OH} & \text{OH} & \text{H} & \text{H} & \text{OH} & \end{array}$$

It is to be expected that a sugar of this structure will yield, like glucose, two fully acetylated derivatives of configurations



$$\begin{array}{lccccccl} & \text{H} & \text{H} & \text{O} & \text{OAc} & \text{H} & & \text{H}\\ \text{CH}_2\text{OAc.} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \\ & \text{OAc} & \text{OAc} & \text{H} & \text{H} & \text{OAc} & & \text{OAc}\end{array}$$

and



$$\begin{array}{lccccccl} & \text{H} & \text{H} & \text{O} & \text{OAc} & \text{H} & & \text{OAc}\\ \text{CH}_2\text{OAc.} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \\ & \text{OAc} & \text{OAc} & \text{H} & \text{H} & \text{OAc} & & \text{H}\end{array}$$

(Ac = $CH_3.CO$)

We attempted to prepare these compounds by the usual methods, with the result that we have crystallized two isomeric hexa-acetates and have obtained good evidence of the existence of a third form in an amorphous state. The *first hexa-acetate of d-α-mannoheptose* was prepared by acetylating the sugar with boiling acetic anhydride and sodium acetate. The melting point of the pure crystalline substance is 106° and its rotation in chloroform solution is to the right, $[\alpha]_D^{20} = +24.2°$. When a solution of this hexa-acetate in acetic anhydride containing a small quantity of

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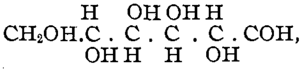
[1] This work was done in 1918 in the Carbohydrate Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture. Part 3 of this series was published in THIS JOURNAL, **46**, 483 (1924).

[2] Fischer and Passmore, *Ber.*, **23**, 2226 (1890).

[3] Peirce, *J. Biol. Chem.*, **23**, 327 (1915). The proof of the configuration consists in Peirce's demonstration that *d*-α-mannoheptitol is antipodal to *d*-α-galaheptitol and that the same relation holds between the corresponding heptaric acids.

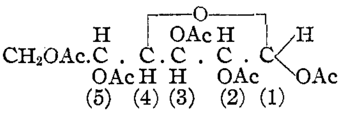
zinc chloride was warmed on the steam-bath, the specific rotation changed slowly during the course of an hour from an initial value of +22° to a final constant rotation of +80°. This large increase in rotation towards the right indicates that the first hexa-acetate is a beta form corresponding, for example, to β-glucose penta-acetate ($[\alpha]_D^{20} = +4°$), and that it changes in large measure in a solution of acetic anhydride and zinc chloride to a more dextrorotatory hexa-acetate, an alpha form similar, for example to α-glucose penta-acetate ($[\alpha]_D^{20} = +102°$). This transformation of the first hexa-acetate yielded a sirupy product which crystallized only in small part. The crystals are those of a pure substance which will be designated the *second hexa-acetate of d-α-mannoheptose*, m. p. 139–140°, of levorotation $[\alpha]_D^{20} = -31°$ in chloroform. Since the substance rotates to the left it cannot be the expected alpha form. We infer that the strongly dextrorotatory amorphous acetate which constitutes the main portion of the product of the transformation of the first hexa-acetate consists largely of the predicted alpha form and that the crystalline second hexa-acetate differs in structure from the first in having its internal oxygen ring on some other than the gamma carbon atom.

It has been shown[4] that four isomeric crystalline penta-acetates of galactose exist, which may be divided into two pairs, one pair probably possessing the usual gamma or butylene ring, while the other pair is presumed to have its ring on some other carbon atom. Because of the close similarity between the configuration of *d*-galactose,



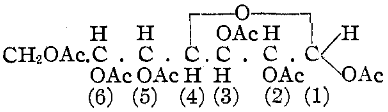
$$\mathrm{CH_2OH.}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\mathrm{COH},$$

and that of *d*-α-mannoheptose, which differ solely by the asymmetric carbon atom 6 present in the latter, it is probable that the molecular rotations of corresponding derivatives of the two sugars will be nearly alike. This view may be given quantitative expression as follows. Consider a β-penta-acetate of galactose and a β-hexa-acetate of *d*-α-mannoheptose and assume that both substances are of the butylene ring type. Their structures are



$$\mathrm{CH_2OAc.}\underset{(5)}{\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\mathrm{C}}}}\,.\,\underset{(4)}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\underset{(3)}{\overset{\mathrm{OAc}}{\underset{\mathrm{H}}{\mathrm{C}}}}\,.\,\underset{(2)}{\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\mathrm{C}}}}\,.\,\underset{(1)}{\mathrm{C}}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OAc}\end{smallmatrix}$$

and



$$\mathrm{CH_2OAc.}\underset{(6)}{\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\mathrm{C}}}}\,.\,\underset{(5)}{\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\mathrm{C}}}}\,.\,\underset{(4)}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\underset{(3)}{\overset{\mathrm{OAc}}{\underset{\mathrm{H}}{\mathrm{C}}}}\,.\,\underset{(2)}{\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\mathrm{C}}}}\,.\,\underset{(1)}{\mathrm{C}}\begin{smallmatrix}\mathrm{H}\\ \mathrm{OAc}\end{smallmatrix}$$

If the molecular rotation of the galactose derivative is P and that of the mannoheptose compound Q, the difference $Q - P$ equals the rotation of the asymmetric carbon atom 6 (or, less probably, atom 5), R_6.

Consider now that the common ring for a similar pair of acetates of the two sugars is on some other carbon atom, for example, Carbon 5. The

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[4] Hudson and Johnson, This Journal, **38**, 1223 (1916).

rotation of the new galactose derivative is now P' and that of the new mannoheptose compound Q', but since the two structures still differ only by the presence of asymmetric Carbon 6 in one of them, the difference $Q' - P'$ still equals R_6, if the principle of additive optical superposition holds in such cases. Assuming that the principle does hold, it may be expected that *a constant difference* $Q - P = Q' - P'$ *holds between the molecular rotations of derivatives of mannoheptose and those of similar derivatives of galactose, provided the respective derivatives that are compared have like ring structures.*

This deduction permits the establishment of a correspondence in ring type between the known acetates of these two sugars as follows. Let it be assumed that the first mannoheptose hexa-acetate is the beta form of the butylene ring structure, corresponding to the first penta-acetate of galactose, an assumption which appears justified from the fact that the two substances are produced by the same method in large yield and that each passes in acetic anhydride solution under the catalyzing action of zinc chloride to its more dextrorotatory isomer. Their molecular rotations, $[M]_D$, in chloroform solution are

First *d*-galactose penta-acetate (mol. wt., 390)	$[\alpha]^{20}_{D} = +23°$,	$[M]^{20}_{D} = +8,970°$
First *d*-α-mannoheptose hexa-acetate (mol. wt., 462)	$[\alpha]^{20}_{D} = +24°$,	$[M]^{20}_{D} = +11,100°$
		Difference = —2,130

Now the second mannoheptose hexa-acetate cannot correspond in configuration to the second galactose penta-acetate because the latter is the alpha form of the first galactose penta-acetate. Its structure may correspond, however, to that of the third or fourth galactose penta-acetate. Its molecular rotation in comparison with that of the third galactose penta-acetate is

Third *d*-galactose penta-acetate	$[\alpha]^{20}_{D} = -42°$,	$[M]^{20}_{D} = -16,400°$
Second *d*-α-mannoheptose hexa-acetate	$[\alpha]^{20}_{D} = -31°$,	$[M]^{20}_{D} = -14,300°$
		Difference = —2,100°

It is evident that the difference between these molecular rotations is the same as the difference found in the case of the beta forms of the butylene ring structure previously tabulated, a fact which indicates that the third penta-acetate and second hexa-acetate have a like ring structure. Whether the second hexa-acetate can be transformed to an isomer corresponding to the fourth galactose penta-acetate remains to be determined, as our experimental work was interrupted at this point.

The method that is here used to correlate types of ring structure among similar derivatives of different sugars by a comparison of their molecular rotatory powers is probably capable of extensive application. In a later article the method will be extended to a similar comparison of various derivatives of mannose and rhamnose.

Experimental Part

Preparation of the First Hexa-acetate of *d*-α-Mannoheptose.—Pure crystalline *d*-α-mannoheptose was acetylated by adding four parts of sugar in small portions to 16 parts of acetic anhydride containing one part of sodium acetate, at a gentle boil. The solution was poured into water and neutralized with sodium bicarbonate. The acetylated sugar separated as an insoluble phase, sometimes sirupy, sometimes crystallizing immediately after the pouring into water or after the neutralization. In some instances the sirup crystallized only after several days' standing. The crude crystalline product was recrystallized from hot water or 50% alcohol; yield, about 75% of the weight of the sugar. After three recrystallizations from water the melting point and specific rotation became constant; m. p., 106°.

Rotation. Subs., 0.721, 1.397 in *chloroformum purificatum, U.S.P.* to make 25 cc.: rotation, 1.39° and 2.74° to the right, respectively (2dm. tube, sodium light). $[\alpha]_{20}^{D}$ = +24.1, +24.4.

Acetyl determinations were made by boiling the substance with 50 cc. of 0.2 *N* sulfuric acid for three hours in a quartz flask with a quartz reflux condenser.

Analyses. Subs., 0.3234, 0.3167. Calc. for heptose hexa-acetate: acetyl, 55.8. Found: 56.0, 55.7. Subs., 0.0953: CO_2, 0.1698; H_2O, 0.0479. Calc. for heptose hexa-acetate: C, 49.4; H, 5.6. Found: C, 49.7; H, 5.6.

Transformation of the First and Preparation of the Second Hexa-acetate.—A solution of 10 g. of the first hexa-acetate in 100 cc. of acetic anhydride containing 2 g. of zinc chloride showed a specific rotation of about +22°. When the solution was warmed on the steam-bath for an hour the rotation increased steadily and became constant at about +80°. The solution was then poured into water and neutralized with sodium bicarbonate. The resulting brown, insoluble gum did not crystallize from alcoholic solution but when it was dissolved in ether and the solution allowed to evaporate slowly a low yield, about 10%, of small hard prismatic crystals was obtained. These were recrystallized from ether until the rotation showed a constant value. The melting point of the pure substance was 139–140°.

Analyses. Subs., 0.5036, 0.5373. Found: acetyl, 55.7, 55.9. Subs., 0.1095: CO_2, 0.1975; H_2O, 0.0551. Found: C, 49.2; H, 5.6.

Rotation. Subs., 0.282 in *chloroformum purificatum, U.S.P.*, to make 25 cc.: rotation, 0.70° to the left (2dm. tube, sodium light); $[\alpha]_{D}^{20}$ = —31°.

Summary

The fully acetylated derivatives of *d*-galactose and of *d*-α-mannoheptose appear to correspond in their structures as follows.

Derivatives of *d*-galactose	Corresponding derivatives of *d*-α-mannoheptose	Type of structure
First penta-acetate m. p., 142°; $[\alpha]_D$ = +23	First hexa-acetate m. p., 106°; $[\alpha]_D$ = +24	Both are beta forms of probably the butylene ring type.
Second penta-acetate m. p., 96°; $[\alpha]_D$ = +107	Amorphous acetate of high dextrorotation	Probably the alpha forms of the butylene ring type.

Third penta-acetate m. p., 98°; $[\alpha]_D$ = —42°	Second hexa-acetate m. p., 139–40°; $[\alpha]_D$ =—31	The beta forms of some other than the butylene ring type.
Fourth penta-acetate m. p., 87°; $[\alpha]_D$ = +61°	Not yet known	The alpha forms of this second ring type.

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[Contribution from the Department of Chemistry, Yale University]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. VIII. THE ELECTROLYTIC REDUCTION OF CARBONYL DERIVATIVES[1,2]

By Harold Hibbert and Roland R. Read

Received December 31, 1923

Theoretical Discussion

One of the outstanding, fundamental problems in organic chemistry is that of the laws dictating and governing the phenomena of "polymerization," and to the student of carbohydrate and polysaccharide chemistry the factors giving rise to the polymerization of anhydro-sugars and polysaccharides present a subject of absorbing interest.

A correct interpretation of these factors would be of considerable value, not only in enabling us to obtain a clearer insight into the changes occurring in plant growth but also in connection with the manufacture of cellulose and allied products, and their industrial application.

There would seem to be little or no doubt but that the polymerization of anhydro-sugars and polysaccharides is intimately related to the "residual valence" of the carbonyl (CO) group, so that a determination of the relative magnitude of this, in derivatives containing the carbonyl radical (either active or latent), might be expected to yield valuable data regarding the tendency of a particular substance to undergo polymerization.

Up to the present time, attempts made to define the reactivity of the carbonyl group have been concerned with reactions involving the use of a second complex component and under conditions where the energy changes involved are of considerable magnitude.

Thus Stewart[3] has shown that when hydrogen attached to a carbon atom adjacent to the carbonyl group of a ketone is replaced by methyl, there results a decrease in the additive capacity of the carbonyl group for sodium bisulfite. The conclusion drawn from his experiments was that the reactivity of the carbonyl group is not peculiar to itself

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[1] This paper is constructed from a dissertation presented by Roland R. Read in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Communicated to the Organic Division, American Chemical Society, Birmingham, Alabama, April 1922.

[3] Stewart, *J. Chem. Soc.*, **87,** 185 (1905).