

hours from the start, fermentation had ceased and the rotation was found to be within  $0.2^\circ$  V. ( $46.8^\circ$ ) of the calculated end point. The solution was then cleared with a slight excess of basic lead acetate, filtered through an asbestos layer in a Büchner funnel, the excess of lead in the filtrate precipitated by  $H_2S$ , a quantity (30-40 g.) of active decolorizing carbon, such as "Eponit" or "Norit," added, and the solution again filtered. The excess of  $H_2S$  was removed from the filtrate with an air current and the solution boiled under reduced pressure to a sirup of approximately 20-25% water content. Alcohol (95%) was then added just below the point of the precipitation of a sirupy phase and some crystals of melibiose were stirred in. We are much indebted to Prof. J. J. Blanksma for a supply of these crystals, because the spontaneous crystallization of melibiose is very difficult to accomplish. After standing four days at a temperature near freezing, the solution had crystallized to a solid mass. The crystals were ground in a mortar with 75% alcohol at room temperature, filtered on a Büchner funnel, washed first with 75% alcohol, then with 95%, and afterwards dried in a desiccator. The melibiose was colorless and gave a correct value for its specific rotation, considering the crystals as  $C_{12}H_{22}O_{11} \cdot 2H_2O$ . It could be recrystallized without difficulty by dissolving to a dilute solution in water, adding decolorizing carbon, filtering, boiling under reduced pressure to a thick sirup, adding EtOH (95%) to saturation, seeding and allowing to crystallize at room temperature. In several experiments the yield has ranged between 175-200 g., as mentioned.

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## A SECOND CRYSTALLINE *d*-FRUCTOSE PENTACETATE. ( $\alpha$ -*d*-FRUCTOSE PENTACETATE.)

BY C. S. HUDSON AND D. H. BRAUNS.

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Recently<sup>1</sup> we described the preparation and properties of a crystalline *d*-fructose pentacetate obtained by the action of acetic anhydride and sulfuric acid on *d*-fructose. We have made different attempts to convert this fructose pentacetate into the other theoretically possible isomeric form by heating with zinc chloride in acetic anhydride solution, but very little change in specific rotation was noticed and from the solution only the original substance could be recovered. On the other hand, the action of zinc chloride in acetic anhydride solution on fructose *tetracetate* caused a considerable change in specific rotation and it seemed that an isomeric fructose *tetracetate* might be obtained. However, the crystalline sub-

<sup>1</sup> THIS JOURNAL, 37, 1283 (1915).

stance which was separated after the rotation had become constant proved to be a *d*-fructose *pentacetate* different from the *d*-fructose *pentacetate* described before. Whereas that fructose *pentacetate* has a melting point of  $108^{\circ}$  and a negative specific rotation  $[\alpha]_{\text{D}}^{20} = -120.9$  (in chloroform solution) the new fructose *pentacetate* has a melting point of  $70^{\circ}$  and rotates positive  $[\alpha]_{\text{D}}^{20} = +34.75$  (in chloroform solution). This new *d*-fructose *pentacetate* shows the same stability to zinc chloride as the other fructose *pentacetate*, therefore the usual method for establishing an equilibrium between the aldose acetates fails in this case of ketose derivatives. We have also obtained the fructose *pentacetate* of m. p.  $108^{\circ}$  from fructose tetracetate by the action of sulfuric acid and acetic anhydride, showing that identical ring formation exists in both *pentacetates*, because both have now been prepared from the same tetracetate. Therefore we would name, according to the rule previously proposed,<sup>1</sup> *d*-fructose *pentacetate* of m. p.  $70^{\circ}$  and  $[\alpha]_{\text{D}}^{20} = +34.75$  the alpha form and *d*-fructose *pentacetate* of m. p.  $108^{\circ}$  and  $[\alpha]_{\text{D}}^{20} = -120.9$  the beta form.  $\alpha$ -Fructose *pentacetate* was also obtained directly from fructose by the action of zinc chloride in acetic anhydride solution and also by the action of pyridine in acetic anhydride solution. The sirups resulting from these reactions crystallized very slowly and it is more advantageous to prepare  $\alpha$ -fructose *pentacetate* from the fructose tetracetate, especially as we have found an easy way to prepare the tetracetate with a fairly good yield. Fructose tetracetate was made the first time by the action of acetyl bromide on fructose at about  $-15^{\circ}$ .<sup>2</sup> The yield of the pure product was small (about 5%) and prevented the further investigation of the substance. Lately a better result has been obtained by the action of a solution of hydrogen bromide in acetic anhydride (a reagent first used by J. K. Dale)<sup>3</sup> on fructose, which gave a yield of 20% of the theory, but the easiest and cheapest way found is the action of a solution of zinc chloride in acetic anhydride at  $0^{\circ}$ , stopping the reaction as soon as the fructose has dissolved. In this way a yield of 30% can be obtained.<sup>4</sup>

By the action of a solution of hydrogen bromide in acetic acid (a reagent first used for this kind of reaction by E. Fischer)<sup>5</sup> on  $\beta$ -fructose *pentacetate*, a considerable change in rotation was observed, indicating that the bromo-tetracetyl fructose was formed. By working up the sirupy reaction product in the usual way, tetracetyl fructose was obtained, evidently as a result of the action of water on the bromoacetyl fructose. The action

<sup>1</sup> THIS JOURNAL, 31, 72 (1909).

<sup>2</sup> Brauns, *Verslag. K. Akad. v. Wetensch.*, Amsterdam, 1908, p. 577.

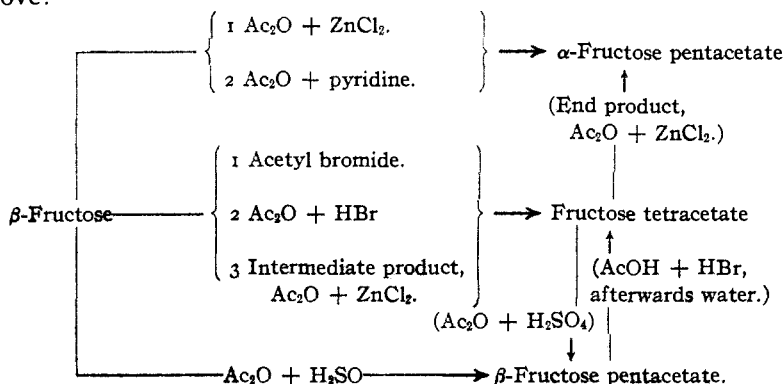
<sup>3</sup> THIS JOURNAL, 37, 2745 (1915).

<sup>4</sup> Starting with the tetracetate of fructose, we have recently prepared crystalline tetracetyl methyl fructoside. Its preparation and properties will be described in a later article.

<sup>5</sup> *Ber.*, 43, 2521 (1910).

of acetyl bromide and of acetic anhydride and HBr on fructose probably also forms bromotetracetyl fructose, and this substance reacts with the water to produce fructose tetracetate. On account of the low temperature at which these reactions have to be carried on, the rotations of the solutions, which might furnish further evidence on this point, are not so easy to follow. The action of hydrogen bromide in acetic acid solution on  $\alpha$ -fructose pentacetate did not give any change in rotatory power and the original  $\alpha$ -fructose pentacetate was recovered.

The following scheme gives a summary of the different reactions stated above:



The pure, powdered crystalline fructose which was used for the reactions must be regarded as the  $\beta$ -fructose, as the initial negative specific rotation of about  $-140^\circ$  in aqueous solution changes towards an equilibrium of about  $-90^\circ$ . The action of zinc chloride in acetic anhydride solution on  $\beta$ -fructose resulted in an  $\alpha$ -derivative and therefore we expected that an  $\alpha$ - and  $\beta$ -fructose tetracetate would be the intermediate products.  $\beta$ -Fructose pentacetate, which may be formed as a by-product in this reaction, cannot be one of the intermediate products leading up to  $\alpha$ -fructose pentacetate, because we have found, as stated above, that  $\beta$ -fructose pentacetate is not changed by a solution of zinc chloride in acetic anhydride. We have been unable to separate another fructose tetracetate from this reaction, though we stopped it at different stages. The formation of the known fructose tetracetate from  $\beta$ -fructose pentacetate by means of hydrogen bromide and acetic acid, followed by the action of water, is an indication by analogy with the aldose sugars that the described fructose tetracetate is a  $\beta$ -derivative. Also its high negative rotation (about  $-91$ ) suggests this view.

#### Experimental.

**Improved Methods for the Preparation of Fructose Tetracetate.**—Instead of acetyl bromide, acetic anhydride saturated with HBr gas, the reagent recently recommended by J. K. Dale, was used. Thirty

grams of pure recrystallized *d*-fructose were added in the form of fine powder to 150 cc. of reagent, containing per 100 g. acetic anhydride about 51 g. hydrogen bromide, and the mixture was cooled by ice water and vigorously stirred by a motor driven glass paddle. After an hour nearly all the fructose had dissolved. The reaction product was vigorously shaken with 400–500 cc. ice water and the solution stirred for a couple of hours with cooling, in order to convert the acetic anhydride into acetic acid. The solution was neutralized in a large dish with sodium bicarbonate, separated from the excess of solid bicarbonate by filtration and the residue on the filter washed with chloroform to dissolve the adhering acetylated sugar. The filtrate was extracted with chloroform for the same purpose. The chloroform solutions were mixed, dried with calcium chloride and distilled *in vacuo* to a small volume, 30–50 cc. This solution was then spread in a thin layer on a flat crystallizing dish and a strong current of air was passed over the yellowish fluid, adding occasionally some ether. The separated crystals were filtered by suction and the mother liquor put aside for further crystallization. In this way a yield of 19–20% of fructose tetracetate was obtained. For recrystallization, fructose tetracetate was dissolved in boiling absolute alcohol and filtered. After cooling, an equal amount of ether was added. If the alcoholic solution was yellow, some eponite or other decolorizing carbon was added before filtering. The alcohol-ether solution was allowed to evaporate in a beaker in the air.

The easiest and cheapest method found for the preparation of tetracetyl fructose was the following: One hundred grams of very pure recrystallized *d*-fructose were added in the form of fine powder with stirring to a solution of 9 g. zinc chloride in 500 cc. acetic anhydride which was cooled to near 0° by an ice bath. When the reaction started a considerable amount of heat was set free and careful cooling according to need with ice was required. After half an hour's stirring of the mixture, the ice bath was taken away and the cooling continued during the next half hour with water at about +10°. Afterward the stirring was continued another half hour at room temperature and then, without further standing, the sugar having nearly completely dissolved, an equal amount of cold water was added and the stirring continued for a couple of hours with cooling in order to convert the acetic anhydride into acetic acid. The reaction product was worked up as described above, yielding about 70 g. of fructose tetracetate or 30% of the theoretical.

**Methods of Preparation and Properties of  $\alpha$ -*d*-Fructose Pentacetate.**—

Forty grams of fructose tetracetate were dissolved in 600 cc. acetic anhydride and 2 g. zinc chloride in small pieces were added and dissolved by shaking. This solution of fructose tetracetate in acetic anhydride had a negative specific rotation of  $-85.6^\circ$ , which changed after the

addition of the  $\text{ZnCl}_2$  and 24 hours' standing at room temperature to the constant value  $+9.5$ . The solution was diluted with an equal amount of cold water and stirred for a couple of hours with cooling in order to convert the excess of acetic anhydride to acetic acid. This solution was worked up as described before and it gave a sirup which, after the addition of a small amount of absolute alcohol and occasional stirring, crystallized. The crystals were separated by suction, yielding about 36 g. of a fairly pure product. This was recrystallized by dissolving in a small amount of chloroform, filtering and evaporating the chloroform solution with a dry current of air to a thick sirup and adding a small amount of absolute alcohol. By rubbing the walls of the vessel with a glass rod crystallization was induced. A second recrystallization did not change the rotatory power and melting point. The substance  $\alpha$ -fructose pentacetate melts at  $70^\circ$ . It is colorless, odorless and has a bitter taste. Its crystallizing power is much less than that of  $\beta$ -fructose pentacetate, though its crystalline form can be easily distinguished without a magnifying glass. It is easily soluble in the usual solvents except in water and petroleum ether.

0.2517 and 0.2850 g. gave 0.4550 and 0.5156 g.  $\text{CO}_2$  and 0.1287 and 0.1437 g.  $\text{H}_2\text{O}$ . Calc. for  $\text{C}_6\text{H}_7\text{O}(\text{C}_2\text{H}_3\text{O}_2)_5$ : C, 49.21%; H, 5.68%. Found: 49.30 and 49.34% C and 5.72 and 5.64% H.

$\alpha$ -Fructose pentacetate was saponified in the same way as  $\beta$ -fructose pentacetate. By shaking 0.4000 g. powdered  $\alpha$ -fructose pentacetate with 70 cc. 0.1 *N* sodium hydroxide during 3 hours at  $0^\circ$  and titrating with 0.1 *N* sulfuric acid and phenolphthalein, the amount of acetic acid produced was found to be 76.88%. In a similar experiment of 5 hours' duration the value 77.26% was found and in a third, also lasting 5 hours, the value was 77.20%. The theoretical quantity for a fructose pentacetate is 76.93%.

Evidently the saponification is complete after 3 hours. The solution was levorotatory after saponification, indicating the regeneration of fructose.

The molecular weight of  $\alpha$ -fructose pentacetate was determined by the lowering of the freezing point of benzene. In three experiments 1.6291, 3.4506 and 4.719 g.  $\alpha$ -fructose pentacetate per 100 g. benzene gave the respective depressions  $0.212^\circ$ ,  $0.435^\circ$  and  $0.575^\circ$  from which the values 389, 398 and 410 are calculated for the molecular weight in comparison with the theoretical value 390.

The specific rotation of  $\alpha$ -fructose pentacetate was measured in chloroform solution. 2.000 g.  $\alpha$ -fructose pentacetate after one recrystallization were made up to 25 cc. with chloroform<sup>1</sup> and the solution polarized in a 1 cm. tube at  $20^\circ$  with sodium light 2.75 circular degrees to the right, hence  $[\alpha]_D^{20} = +34.4^\circ$ . After a second recrystallization from chloroform-alcohol, 2.000 g.  $\alpha$ -fructose pentacetate made up in the same manner rotated 2.78 circular degrees to the right hence  $[\alpha]_D^{20} = +34.75$ , which is taken as the specific rotation of the pure substance.

The mother liquor of the first recrystallization of  $\alpha$ -fructose pentacetate

<sup>1</sup> *Chloroformum purificatum*, U. S. P.

from several preparations, crystallized after standing in a desiccator, yielding about 10 g. of a crystalline substance of m. p. 64–65° and a specific rotation of  $-7.8^\circ$ . The wash fluid and mother liquor of these crystals crystallized again. The new crystalline product had a m. p. of 55–56° and a specific rotation of  $-19^\circ$ . 0.250 g. of this substance was saponified in the usual way by shaking with 0.1 *N* sodium hydroxide for 3½ hours at 0°. Under the same conditions samples of 0.250 g. of fructose tetracetate and  $\alpha$ -fructose pentacetate were saponified, which gave the required figures, whereas the unknown substance gave values for a pentacetate. It is probably a mixture of  $\alpha$ - and  $\beta$ -fructose pentacetate, but the small amount of the sample and the nearly equal solubilities of the fructose pentacetates prevented their separation.

The reaction of a solution of zinc chloride in acetic anhydride on fructose tetracetate, which resulted in the formation of  $\alpha$ -fructose pentacetate, was stopped at different points in order to learn if an intermediate product was formed, possibly the hypothetical  $\alpha$ -fructose tetracetate. In one experiment the reaction was stopped when the specific rotation had reached about  $-30^\circ$ . The only crystalline substance which could be separated in the ordinary way proved to be  $\alpha$ -fructose pentacetate. In a second experiment the reaction was stopped before this point was reached, at a specific rotation of about  $-50$ . Starting from 4 g. fructose tetracetate 1.25 g. of fructose tetracetate was recovered and about 0.4 g. of  $\alpha$ -fructose pentacetate, but no other crystalline substance could be separated.

In attempts to obtain  $\alpha$ -fructose pentacetate directly from fructose by the action of zinc chloride in acetic anhydride solution we obtained a colorless sirup, which only partially crystallized after standing a month in a vacuum desiccator with occasional seeding and stirring. Five grams zinc chloride were dissolved in 250 cc. acetic anhydride and 50 g. powdered pure fructose were added under stirring, keeping the mixture at about  $+10^\circ$ . When the fructose was dissolved, the reaction fluid was put aside for one night in order to convert the fructose tetracetate into  $\alpha$ -fructose pentacetate. The following morning the specific rotation (assuming that all fructose was converted into pentacetates) was found to be  $+10.0$ . The fluid was worked up in the usual way, yielding a colorless sirup which slowly crystallized. From it were obtained about 8 g. of  $\alpha$ -fructose pentacetate and a large amount of mother liquor, which did not crystallize on long standing. Therefore,  $\alpha$ -fructose pentacetate may be prepared directly from fructose but the yield is not so good as that obtained by the acetylation of fructose tetracetate.

$\alpha$ -Fructose pentacetate was also obtained by using pyridine as a catalyst of the acetylation.<sup>1</sup> Ten grams of powdered pure fructose were added to a mixture of 67 cc. pyridine and 50 cc. acetic anhydride, which was

<sup>1</sup> Behrend and Roth, *Annalen*, 331, 364 (1904).

cooled to  $0^{\circ}$  and vigorously stirred by a motor driven glass paddle. After 3 hours the fructose was dissolved and the solution was kept for two days in the ice box. The solution was then poured into 250 cc. ice water, an oil separated, and the supernatant fluid was poured off. The oil was stirred several times with petroleum ether in order to extract the pyridine but the remaining sirup crystallized only after several months' standing. The crystals were separated by pressing between filter paper and amounted to about 1 g. They melted at about  $-62^{\circ}$  and showed a specific rotation of  $+28.1$ . After one recrystallization the m. p. changed to  $70^{\circ}$  and the specific rotation to  $+35.5^{\circ}$ .

0.300 g. of these crystals were saponified by shaking with 70 cc. 0.1 *N* sodium hydroxide at  $0^{\circ}$  during 3 hours. By titrating with 0.1 *N* sulfuric acid and phenolphthalein the amount of acetic acid produced was found to be 76.42%. The theoretical quantity for fructose pentacetate is 76.93%.

These results show that  $\alpha$ -fructose pentacetate is formed by the action of a solution of pyridine in acetic anhydride on fructose.

**Conversion of Fructose Tetracetate into  $\beta$ -Fructose Pentacetate.**—This reaction is important, as it establishes, in combination with the above mentioned results, that the described  $\alpha$ - and  $\beta$ -fructose pentacetates have identical ring formation. Twenty grams of fructose tetracetate were added in the form of fine powder to a mixture of 120 cc. acetic anhydride and 5 cc. concentrated sulfuric acid, which was cooled by an ice and salt bath and vigorously stirred by a motor driven glass paddle. The fructose tetracetate dissolved easily. After three-quarters of an hour, 300 cc. ice water were added and stirring was continued for  $1\frac{1}{2}$  hours under cooling with ice water. The mixture was neutralized in a large dish with sodium bicarbonate and further treated as has been described for the preparation of fructose tetracetate. The yield was 17 g. crystals melting gradually from  $99-105^{\circ}$  and showing a specific rotation of  $-106.3$ . The crystals were washed with ether and the specific rotation rose to  $-114.4^{\circ}$ . After one recrystallization the specific rotation increased to  $-118.6^{\circ}$  and a second recrystallization from ether brought it to  $-120.5^{\circ}$ , a value which was changed only slightly by a further recrystallization. The specific rotation was therefore found to agree with  $\beta$ -fructose pentacetate ( $-120.9^{\circ}$ ) and also the melting point of the recrystallized product,  $108-109^{\circ}$ , was found to be identical with that of the  $\beta$ -pentacetate. The presence of small amounts of unaltered fructose tetracetate is probably the reason that the pure  $\beta$ -fructose pentacetate cannot be obtained as readily by this reaction as by its preparation from fructose, which has been previously described.<sup>1</sup>

**Experiments for Establishing an Equilibrium between the Fructose Pentacetates and for Converting Fructose Tetracetate to an Isomeric Form.**—As has been stated in the introduction, no equilibrium could be

<sup>1</sup> THIS JOURNAL, 37, 1283 (1915).

established between the fructose pentacetates by the usual method of heating with  $\text{ZnCl}_2$  in acetic anhydride solution, and therefore it is concluded that the ketose pentacetates differ in this respect from the aldose pentacetates. Three grams of  $\beta$ -fructose pentacetate were dissolved in 25 cc. acetic anhydride. The specific rotation was found to be  $-121.8^\circ$  and it was not changed by heating the solution for  $\frac{1}{4}$  hour on the steam bath. After dissolving 0.3 g. zinc chloride the specific rotation changed to  $-111.2^\circ$ . After keeping this solution for 2 days at room temperature the specific rotation was  $-107.4^\circ$  and the color yellow. The solution was heated for 10 minutes on the steam bath and the rotation changed to  $-103.6^\circ$ . This rotation did not change further in two subsequent reheatings. The fluid was worked up in the ordinary way and yielded about 1 g. of  $\beta$ -fructose pentacetate, which was identified by the specific rotation.

The next experiment was made with  $\alpha$ -fructose pentacetate. Three grams  $\alpha$ -fructose pentacetate were dissolved in 25 cc. acetic anhydride and the specific rotation was found to be  $+26.5^\circ$ . After dissolving 0.3 g. zinc chloride the specific rotation changed to  $+26.1^\circ$  and remained the same after heating for 10 minutes on the steam bath. A subsequent heating of 30 minutes on the steam bath changed the specific rotation to  $+26.8^\circ$  and turned the solution slightly yellow. From this solution nearly the original amount of  $\alpha$ -fructose pentacetate was recovered, which was identified by the melting point and specific rotation. Therefore zinc chloride does not change  $\alpha$ -fructose pentacetate. The action of sulfuric acid on solutions of  $\alpha$ - and  $\beta$ -fructose pentacetates in acetic anhydride also did not establish an equilibrium between the fructose pentacetates. The solutions gradually became dark brown and no other substance than the respective pentacetate could be recovered from them. Boiling with acetic anhydride (b. p.  $138^\circ$ ) also did not change  $\alpha$ - and  $\beta$ -fructose pentacetate. After  $\frac{1}{4}$  hour boiling the specific rotation of  $\beta$ -fructose pentacetate in acetic anhydride remained the same,  $+26.1^\circ$ , and the specific rotation of  $\beta$ -fructose pentacetate changed only from  $-121.6^\circ$  to  $-118.4^\circ$ . After a subsequent boiling of  $\frac{1}{4}$  hour the specific rotations were, respectively,  $+25.4^\circ$  and  $-117.1^\circ$ . From both solutions nearly all the original substance was recovered.

The tetracetate of fructose shows similar behavior and has not changed in solution to an isomer. Whereas tetracetyl glucose shows mutarotation in alcoholic solution<sup>1</sup> tetracetyl fructose does not show any change in rotation in absolute or 50% alcohol. The addition of a few drops glacial acetic acid did not produce any change. Also a 50% alcoholic solution made up and polarized at  $3-4^\circ$  did not show a change in rotation more than  $0.1^\circ$ , when the solution was gradually changing to a temperature

<sup>1</sup> E. Fischer, *Ber.*, 42, 2778 (1909).



of  $20^{\circ}$ . Further, the action of zinc chloride in glacial acetic acid solution did not materially change the specific rotation. Two grams fructose tetracetate were dissolved in 25 cc. glacial acetic acid. The specific rotation was found to be  $-80.0^{\circ}$ . After dissolving about 50 mg.  $ZnCl_2$  the specific rotation was  $-79.5^{\circ}$  and after  $\frac{1}{4}$  hour heating on the steam bath  $-79.8^{\circ}$ . After dissolving 2 g. zinc chloride on the steam bath in 5 minutes the specific rotation was  $-78.0^{\circ}$ . When small amounts of sulfuric acid or ammonia are added to an acetic anhydride solution of fructose tetracetate a material change in rotation goes hand in hand with a saponification and destruction.

**Action of Hydrogen Bromide in Acetic Acid Solution on  $\alpha$ - and  $\beta$ -Fructose Pentacetate.**—This reagent was first used by E. Fischer<sup>1</sup> for preparing in the most convenient way the bromoacetyl derivatives from the acetates of the aldoses. The following experiments show that the bromotetracetyl fructose is undoubtedly formed by similar action, but it could not be separated on account of its easy decomposition by water.

Seven grams of  $\beta$ -fructose pentacetate were dissolved in a 25 cc. measuring flask in 8 cc. glacial acetic acid and the volume completed with a saturated solution of hydrogen bromide in glacial acetic acid. The rotation was followed during 20 minutes after the addition of the hydrogen bromide reagent. The specific rotations are figured on the basis of 7 g. substance present in 25 cc. solution. The small difference in molecular weight of fructose pentacetate (390) and the bromotetracetyl fructose (411) may allow this assumption. The specific rotation of  $\beta$ -fructose pentacetate in acetic acid solution is  $-121.7$ . After the mixture had stood 20, 30, 45, 65 and 85 minutes the specific rotation had the respective values,  $+45.7$ ,  $+53.6$ ,  $+59.2$ ,  $+60.5$ ,  $+60.0$ , which shows that in only 65 minutes the change in specific rotation amounted to more than  $+180$ .<sup>2</sup> By shaking this reaction product with 200 cc. ice water and working up the mixture in the described way 3.5 g. of tetracetyl fructose were obtained. Further experiments will be made to separate the bromoacetyl fructose in a crystalline state. The action of this reagent on  $\alpha$ -fructose pentacetate was also investigated. Seven grams  $\alpha$ -fructose pentacetate were dissolved in a 25 cc. measuring flask in 8 cc. glacial acetic acid and the volume completed with a saturated solution of hydrogen bromide in glacial acetic acid. The specific rotation of  $\alpha$ -fructose pentacetate in glacial acetic

<sup>1</sup> *Ber.*, 43, 2521 (1910).

<sup>2</sup> The difference between the specific rotations of  $\beta$ -glucose pentacetate and bromotetracetyl glucose is  $+194$ , the difference for the analogous compounds of galactose  $+211$ , for cellose the difference is about  $+110$ , and for milk sugar  $+110$ , showing the great difference in specific rotations between the fully acetylated  $\beta$ -derivatives of the sugars and the bromoacetyl derivatives.

acid is +26.5. Twenty minutes after the reagent had been added the specific rotation was found to be +26.6, a value which did not change during the next thirty minutes. The solution was heated on the steam bath for 5 minutes, the color turning from yellow to a dark yellow. The specific rotation was now found to be +23.9. The solution was shaken with 200 cc. ice water and further worked up in the usual way and yielded 3 grams of a crystalline substance melting at 70° with a specific rotation in chloroform solution of +34.3. Therefore about half of the original  $\alpha$ -fructose pentacetate has been recovered, the rest probably being saponified and destroyed.

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## BROMOACETYLXYLOSE AND BETA-TRIACETYLMETHYLXYLOSIDE.

By J. K. DALB.<sup>1</sup>

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During an investigation of methods for brominating and acetylating the sugars, there was obtained from xylose a crystalline bromoacetyl derivative which is very similar in properties to the acetohalogen derivatives of other sugars. The bromine atom is very active and can be readily replaced by an oxyacetyl group, forming tetracetyl xylose, or by an oxymethyl group forming a triacetylmethylxyloside. This latter compound, on hydrolysis with dilute alkali, yields the well-known  $\beta$ -methylxyloside. This correlation, together with its analysis, low rotation and method of preparation, appears sufficient to justify the naming of this acetylated methyl xyloside,  $\beta$ -triacetylmethylxyloside.

**Preparation of Bromoacetylxylose.**—Émil Fischer<sup>2</sup> has prepared the bromoacetyl derivative of several of the sugars by the action of a saturated solution of hydrobromic acid gas in acetic acid on the corresponding completely acetylated sugar. The action of acetyl bromide directly upon the sugars has also been employed by a number of investigators for the preparation of these compounds. Bodart<sup>3</sup> successfully prepared chloroacetyl lactose by suspending lactose in acetic anhydride and passing gaseous hydrochloric acid into the mixture. From consideration of these results, it appeared probable that a concentrated solution of hydrobromic acid in acetic anhydride would act directly upon the sugars, giving the bromoacetyl derivatives. The following method for the preparation of bromoacetyl xylose has also been employed successfully in the preparation of bromoacetyl lactose, bromoacetyl maltose, and

<sup>1</sup> Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

<sup>2</sup> *Ber.*, 43, 2530 (1901); 44, 2537 (1902).

<sup>3</sup> *Monatsh.*, 23, 1 (1902).