methyl arabinosides only in respect to the terminal asymmetric carbon atom which has an acetyl instead of a methyl group, the rotation of the 2 forms of the tetracetate may be expressed as $(-A'-B)$ and $(A'-B)$, and their sum, $-2B$, from the values of the molecular rotations of the α- and β-arabinose tetracetates given earlier in this article, is +60,200 or $-B = 30{,}100$. Hence, the specific rotation of α-triacetyl-methyl-*l*-arabinoside (M. W. 290) is calculated to be $(-A - B)/290 = (-26{,}950 + 30{,}100)/290 = +11°$, and that of the β-form $(26{,}950 + 30{,}100)/290 = +197°$. The calculated value for the β-form, +197°, is near enough to the specific rotation (+182°) of the triacetyl-methyl-*l*-arabinoside that we have described to justify its classification in the β-series.

WASHINGTON, D. C.

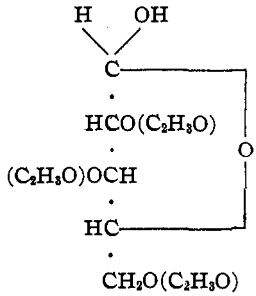
[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

TRIACETYL-*d*-XYLOSE AND ALPHA TRIACETYLMETHYL-*d*-XYLOSIDE.

BY C. S. HUDSON AND J. K. DALE.

Received March 28, 1918.

In a recent article one of the authors[1] described the preparation from *d*-xylose ($[\alpha]_D = +19°$) of bromoacetyl-*d*-xylose, a crystalline compound which was found to be very similar in its reactions to bromoacetyl-glucose. The bromine atom could be replaced by an oxymethyl or an oxyacetyl group by reactions that are quite analogous to those by which tetracetyl-methyl-glucoside and pentacetyl-glucose are prepared from bromoacetyl-glucose. An incompletely acetylated derivative of glucose, tetracetyl-glucose, can also be prepared from bromoacetyl-glucose by the substitution of an hydroxyl group in place of the bromine atom.[2] In analogy with this reaction a partially acetylated derivative of xylose, *triacetyl-d-xylose*, has been prepared from bromoacetyl-xylose. On the assumption that it is a γ-cyclo derivative its structure is



This triacetate showed mutarotation in both chloroform and water

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[1] Dale, THIS JOURNAL, 37, 2745 (1915).

[2] Fischer and Kurt, *Ber.*, 45, 912 (1912).

solution. In the former the specific rotation changed from an initial value of $[\alpha]_D^{23} = +70.11°$ to a constant value of $[\alpha]_D^{21} = +40.8°$ in about 10 days, the temperature being 20°. The mutarotation of the substance is to be expected because tetracetyl-glucose exhibits mutarotation; in both cases the mobility of the H and OH groups on the end asymmetric carbon atom can give rise to α- and β-forms which can establish an equilibrium in solution. The direction of the mutarotation indicates that the crystalline form of triacetyl-*d*-xylose that we have had in hand belongs to the α-series. It is true that by the acetylation of this triacetate the β-form of tetracetyl-xylose has been isolated as crystals (see below), but this fact does not alter the conclusion because the triacetate doubtless mutarotates very rapidly in hot acetic anhydride containing sodium acetate and thus yields the β-tetracetate, just as both α- and β-glucose yield β-glucose pentacetate by this method of acetylation.[1]

Optical Superposition among the Acetylated Derivatives of Xylose.—From a comparison of the molecular structures of the α- and β-pentacetates of glucose and the α- and β-tetracetyl-methyl-glucosides the authors[2] drew the conclusion that the sum of the molecular rotations of the two pentacetates is presumably equal to the sum of the molecular rotations of the 2 tetracetyl-methyl-glucosides, and this deduction was well verified by measurements of the specific rotations of the 4 compounds. A similar relation exists between the molecular structures of the α- and β-tetracetates of xylose and the α- and β-triacetylmethyl-xylosides, hence, it is to be expected that the sum of the molecular rotations of the α- and β-tetracetates of xylose is equal to that of the α- and β-triacetyl-methyl-xylosides. The preparation and properties of α-triacetyl-methyl-xyloside are described below, those of the other 3 compounds having been recorded in previous contributions[3] from this laboratory. In Table I are recorded the specific and molecular rotations of these compounds in chloroform (U. S. P.) solution, while in the last column the sums of the molecular rotations of the 2 pairs are shown.

TABLE I.

Compound.	Specific rotation.	Molecular rotation.	Sum of molecular rotation of each pair.
α-Xylose tetracetate	+ 89.1	+28,300	+20,400
β-Xylose tetracetate	— 24.9	— 7,900	
α-Triacetyl-methyl-xyloside	+119.6	+34,700	+17,100
β-Triacetyl-methyl-xyloside	— 60.7	—17,600	

The agreement is not so good as it was in the case of the similar derivatives of glucose.

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[1] Hudson, *J. Ind. Eng. Chem.*, 8, 379 (1916).

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

[3] Dale, *Ibid.*, 37, 2745 (1915); Hudson and Johnson, *Ibid.*, 37, 2748 (1915).

A comparison can also be made between the 2 triacetyl-methyl-xylosides, the corresponding 2 tetracetyl-methyl-glucosides and the tetracetyl-methyl-galactosides. If $(A + B)$[1] represents the molecular rotation of α-triacetyl-methyl-xyloside where A is the rotation of the end asymmetric carbon atom and B that of the remainder of the molecule, the molecular rotation of β-triacetyl-methyl-xyloside may be represented by $(-A + B)$. In similar manner let $(A + B')$ and $(-A + B')$ represent the molecular rotations of the α- and β-tetracetyl-methyl-glucosides and $(A + B'')$ and $(-A + B'')$ those of the α- and β-tetracetyl-methyl-galactosides. The difference between the rotations of each of these pairs is the same quantity, $2A$. This conclusion is tested in Table II, the rotations referring to chloroform (U. S. P.) solutions.

TABLE II.

Compound.	Specific rotation.	Molecular rotation.	Difference of molecular rotation for each pair (2*A*).
α-Triacetyl-methyl-*d*-xyloside	+119.6	+34,700	+52,300
β-Triacetyl-methyl-*d*-xyloside	— 60.7	—17,600	
α-Tetracetyl-methyl-*d*-glucoside	+130.5	+47,300	+53,900
β-Tetracetyl-methyl-*d*-glucoside	— 18.3	— 6,600	
α-Tetracetyl-methyl-*d*-galactoside	+133.0	+48,400	+53,100
β-Tetracetyl-methyl-*d*-galactoside	— 13.0	— 4,700	

The agreement of the values in the last column is satisfactory. Since the acetylated xylosides thus fit in with the similar derivatives of two other sugars, it seems probable that the lack of better agreement between the two sums in Table I is referable to some abnormal condition affecting the tetracetates of xylose, or one of them.

Experimental.

Preparation of Triacetyl-*d*-xylose.—Twenty g. of bromoacetyl-xylose was dissolved in 60 cc. of acetone to which had been added 2 cc. of water, and the solution was shaken with freshly prepared silver carbonate until carbon dioxide ceased to be evolved and a few drops showed no reaction for halogen with silver nitrate. After the mixture of silver carbonate and silver bromide had been filtered off, the filtrate was evaporated to a sirup which slowly deposited crystals on standing. The mixture of crystals and sirup was thinned with ether and the crystals separated by filtering on a Büchner funnel. The yield of this product after one recrystallization from ether was between 2 and 3 g. A total quantity of about 10 g. was prepared by this method. Triacetyl-*d*-xylose is easily soluble in chloroform and in acetone, somewhat soluble in water and in alcohol and only slightly soluble in ether. It readily reduces Fehling's solution on warming. The pure compound melted gradually at 138–141° (corr.).

Calc. for $C_{11}H_{16}O_8$: C, 47.8; H, 5.84. Found: C, 47.80; H, 5.93.

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[1] THIS JOURNAL, 31, 66 (1909).

Two acetyl determinations made by boiling 0.30 g. in a quartz flask with a reflux condenser with 50 cc. 0.25 *N* sulfuric acid for 2 and 3 hours, respectively, gave 65.17% and 64.99% acetic acid, which results agree with the theoretical value for triacetyl-xylose, 65.22%.

After several recrystallizations from ether, 0.4540 g. of the substance made up to 25 cc. solution with chloroform (*Chloroformum purificatum*, U. S. P.) showed an initial reading to the right of 2.56 circular degrees in a 2 dcm. tube, using sodium light, hence $[\alpha]_D^{21} = +70.45°$. After another recrystallization from ether a duplicate measurement in which 0.8041 g. of the compound were used gave as the initial specific rotation $[\alpha]_D^{23} = +70.11°$. As mentioned before, the reading slowly changed from this value to become constant in about 10 days at +40.8°.

β-Tetracetyl-*d*-xylose from Triacetyl-*d*-xylose.—Two g. of triacetyl-*d*-xylose was acetylated by boiling with 10 cc. of acetic anhydride and 0.5 g. of anhydrous sodium acetate. The solution was poured into water and the insoluble phase which at first separated as a thick sirup soon hardened into a crystalline mass. The crystals were filtered off and twice recrystallized from alcohol. There was obtained of the purified material 0.6 g. Its melting point was 126–128° (corr.), and its specific rotation in chloroform (U. S. P.) solution was $[\alpha]_D^{21} = -24.4°$. This melting point and specific rotation agree with those of β-tetracetyl-*d*-xylose.[1]

Preparation of α-Triacetylmethyl-*d*-xyloside.—To a boiling solution of 5 g. of anhydrous sodium acetate in 100 cc. of acetic anhydride 25 g. of α-methyl-*d*-xyloside was gradually added. The boiling was continued 2 or 3 minutes, the reaction mixture was then poured into about 800 cc. of cold water, and an insoluble sirup separated and soon crystallized. This was filtered off and recrystallized from alcohol. The yield was 19 g. It was further recrystallized from alcohol several times until its specific rotation became constant.

The pure substance melted at 86° (corr.). In chloroform (U. S. P.) solution 1.0116 g. of the compound in 25 cc. of the solution gave a reading to the right, 9.67° in a 2 dcm. tube, with sodium light, hence $[\alpha]_D^{20} = +119.5°$. After another recrystallization a similar measurement gave a specific rotation of $[\alpha]_D^{20} = +119.6°$.

Two acetyl determinations made by shaking 0.3 g. of the compound with 100 cc. 0.1 *N* sodium hydroxide for 2 and 4 hours, respectively, in glass stoppered bottles, at 0°, gave 62.08% and 62.12% acetic acid, which agree with the theoretical value for triacetyl-methyl-xyloside, 62.07%.

Calc. for $C_{12}H_{17}O_8$: C, 49.63; H, 6.25. Found: C, 49.40; H, 6.28.

Preparation of β-Triacetyl-methyl-*d*-xyloside by Direct Acetylation.—By the action of a solution of silver nitrate in 80% methyl alcohol upon bromoacetyl-xylose, one of the authors[2] has prepared β-triacetyl-methyl-*d*-xyloside. We have also succeeded in preparing it by acetylating β-

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[1] Hudson and Johnson, This Journal, **37**, 2748 (1915).

[2] Dale, *Loc. cit.*

methyl-*d*-xyloside. Fifteen g. of this substance was gradually added to a boiling solution of 6 g. of anhydrous sodium acetate in about 60 cc. acetic anhydride. After boiling for a few minutes the reaction mixture was cooled, mixed with 800 cc. of cold water, and an insoluble sirupy phase separated and crystallized almost immediately. After one recrystallization of the substance from water its specific rotation was found to be $[\alpha]_D^{22} = -60.9°$, and the melting point 115° (uncorr.). These values, which remained the same after another recrystallization, agree with those previously found for β-triacetyl-methyl-*d*-xyloside that had been prepared from bromoacetyl-xylose.

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[CONTRIBUTION FROM THE LABORATORIES OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

BY-PRODUCTS OF THE FERMENTATION OF CABBAGE.

BY V. E. NELSON AND A. J. BECK.

Received April 1, 1918.

The results of this investigation are merely the outgrowth of some work which was planned in this laboratory to shed further light upon the chemical changes taking place in silage and the direct cause of these transformations.

In the fermentation of green plant tissue two dominant factors contribute to the production of the various chemical by-products, namely enzymes and bacteria. To what extent enzymes are a factor to the exclusion of bacteria is a very debatable question requiring considerable experimental investigation before a solution can be made, and one which our experiments were planned to answer. For certain specific reasons we chose the cabbage instead of the corn plant as a method of solving this problem. Before any progress could be made, it was necessary to determine the by-products resulting from the fermentation of cabbage or sauerkraut, as it is commonly called.

As far as the authors are aware no systematic quantitative study of this product has been made.

Experimental.

For the estimation of acids, alcohols and esters of fermented products, certain methods were employed which have been little utilized by biological chemists. A detailed description of the methods will not be given here as it is the intention of one of the authors to discuss these methods in a forthcoming paper on the volatile by-products of certain soft cheeses, and a determination of the volatile fatty acids, esters and alcohols resulting from the growth of certain microörganisms on synthetic media. However, a very brief summary may not be out of place. For information more in detail, it is necessary to consult Suzuki, Hastings and Hart[1] on the volatile

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[1] *J. Biol. Chem.*, **7**, 431–458 (1910).