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 α-fructose pentacetate has been recovered, the rest probably being saponified and destroyed.

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BROMOACETYLXYLOSE AND BETA-TRIACETYLMETHYLXYLOSIDE.

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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 β-methylxyloside. This correlation, together with its analysis, low rotation and method of preparation, appears sufficient to justify the naming of this acetylated methyl xyloside, β-triacetylmethylxyloside.

Preparation of Bromoacetylxylose.—Emil Fischer[2] 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[3] 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

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

[2] *Ber.*, 43, 2530 (1901); 44, 2537 (1902).

[3] *Monatsh.*, 23, 1 (1902).

bromoacetyl glucose, with yields of from 55–70% of the theoretical amount. Mannose and galactose have not given, by this method, crystalline compounds.

Twenty-five grams of finely ground xylose were treated in an Erlenmeyer flask at room temperature with 150 cc. of a saturated solution of hydrobromic acid in acetic anhydride. A very violent reaction followed. The resulting straw-colored sirup was cooled, mixed with 300 cc. of chloroform and the solution shaken with ice-water, sodium bicarbonate solution, and again three or four times with water. After drying with calcium chloride the chloroform solution was evaporated at 50° under diminished pressure to a thick sirup. This was dissolved in a little dry ether and on rapid evaporation beautiful crystals formed spontaneously. The substance thus obtained was evidently somewhat impure, because it decomposed in the air in a very short time with the evolution of hydrobromic acid fumes. On purification by recrystallization from dry ether the compound became more stable and could be kept for several hours without appreciable signs of decomposition.

For analysis 0.4405 g. of the pure, dry substance was dissolved in methyl alcohol, a drop of strong nitric acid added and the bromine precipitated as silver bromide by an aqueous solution of silver nitrate.

Obtained, 0.2407 g. silver bromide, corresponding to 23.25% bromine.

Calc. for $C_5H_6O_4(C_2H_3O)_3Br$: bromine, 23.57%. Found, 23.25.

Triacetyl bromoxylose is very soluble in chloroform, benzene and acetone, rather soluble in ether and almost insoluble in ligroin. It was recrystallized from dry ether until its specific rotation became constant. The melting point of the pure substance dried in a vacuum desiccator was 102° (uncorr.). In chloroform[1] solution, 0.6360 g. of the compound per 25 cc. of the solution gave a reading to the right, +10.8°, in a two decimeter tube, using sodium light, hence $[\alpha]_{20}^{D} = +212.2°$. A duplicate measurement, in which 0.7930 g. of the compound were used, gave $[\alpha]_{20}^{D} = +212.1°$. The identification of this compound was confirmed by converting it into β-tetracetylxylose and into β-triacetylmethylxyloside, using the methods by which Koenigs and Knorr[2] prepared β-pentacetyl glucose and β-tetracetylmethylglucoside from bromoacetyl glucose.

Preparation of β-Triacetylmethylxyloside.—For the preparation of this compound, it is not necessary to have the bromoacetylxylose in a very pure condition. If the syrup obtained by evaporating the chloroform extract is stirred well with petroleum ether, it soon hardens to a semicrystalline mass, which can be used without further purification. This product is dissolved in ten times its weight of methyl alcohol and a

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[1] *Chloroformum Purificatum*, U. S. P., was used throughout this work.

[2] *Ber.*, 34, 970 (1901).

solution of silver nitrate in 80% methyl alcohol is added until complete precipitation of the silver bromide is effected. The filtrate from the silver bromide is treated with hydrogen sulfide and shaken with barium carbonate. The filtrate from this is evaporated to a thick sirup on the steam bath under diminished pressure. This sirup is dissolved in a little hot water which, on cooling, deposits thin plate-like crystals, which analysis and conversion into β-methylxyloside show to be β-triacetylmethylxyloside. The crystalline substance is very soluble in chloroform, alcohol, ether and hot water. It was purified by recrystallization from water until its specific rotation became constant. The melting point of the pure substance dried in a vacuum desiccator over calcium chloride was 115° (uncorr.). With chloroform as solvent, 0.5785 g. of this compound per 25 cc. of the solution gave a reading to the left, —2.8° in a two decimeter tube, with sodium light, hence $[\alpha]^{\mathrm{D}}_{20} = -60.5^\circ$. After another recrystallization, a duplicate measure, in which 0.6751 g. of the compound was used, gave $[\alpha]^{\mathrm{D}}_{20} = -60.8^\circ$.

0.2274 g. and 0.2078 g. gave 0.4149 and 0.3800 g. CO_2 and 0.1272 and 0.1163 g. H_2O, corresponding to 49.76 and 49.87% C and 6.26 and 6.26% H.

Calc. for $(C_5H_6O_4)(CH_3O)(C_2H_3O)_3$: 49.63% C and 6.25% H.

Two acetyl determinations, made by shaking 0.25 g. of the substance with 70 cc. 0.1 *N* NaOH for two hours in a glass-stoppered bottle at 0°, gave 61.94 and 62.27% acetic acid, which agree with the theoretical value for triacetylmethylxyloside, 62.07%.

Conversion of β-Triacetylmethylxyloside into β-Methylxyloside.—0.4575 g. of the first-named compound was shaken with about 50 cc. 0.1 *N* NaOH for two hours. The solution was then neutralized with H_2SO_4 and evaporated to dryness. The residue was extracted with hot ethyl acetate which on evaporation deposited crystals that melted at 155–156° and had a specific rotation $[\alpha]^{\mathrm{D}}_{20} = -65.3^\circ$. Obtained 0.13 g. Fischer[1] gives for β-methylxyloside, m. p. 156–157° and $[\alpha]^{\mathrm{D}}_{20} = -65.8^\circ$.

Conversion of Bromoacetylxylose into β-Tetracetylxylose.—Four grams of crude bromoacetylxylose were dissolved in 75 cc. of galcial acetic acid. This solution was shaken a few minutes with 5 g. of silver acetate. The filtrate from the silver bromide precipitate was neutralized with sodium bicarbonate and extracted with chloroform. This extract was concentrated to a thick sirup under diminished pressure and the sirup dissolved in a little ether. Crystals soon appeared of m. p. 126–127° (corr.) and $[\alpha]^{\mathrm{D}}_{20} = -24.9^\circ$ in chloroform solution.

Hudson and Johnson[2] found for β-tetracetylxylose $[\alpha]^{\mathrm{D}}_{20} = -25.1^\circ$ (chloroform solution) and m. p. 128° (corr.).

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[1] *Ber.*, 28, 1158 (1895).

[2] Following article by Hudson and Johnson.