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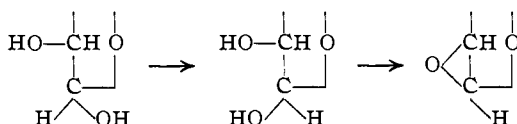
PENTOSE REACTIONS. II. DERIVATIVES OF XYLOSE

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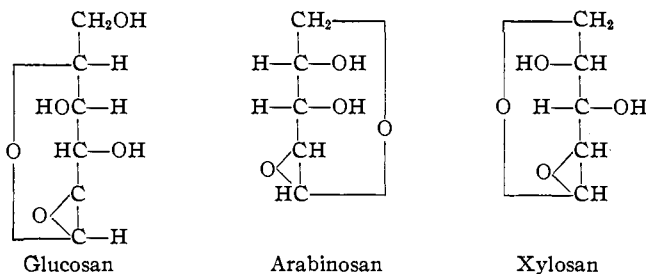
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The transformation of xylose into furfural is a dehydration of an entirely different type from the one which xylose undergoes when it is heated alone. Only about 1% of furfural is formed in the latter case and the major product is xylosan: $C_5H_{10}O_5 \rightarrow C_5H_8O_4 + H_2O$. This synthesis of xylosan from α -*D*-xylose is comparable to the production of glucosan from α -*D*-glucose¹ or arabinosan from β -*L*-arabinose.² All three of these sugars have adjacent hydroxyls on carbon atoms 1 and 2. Evidently this is essential, for α -*L*-arabinose, which does not, rearranges into the β -isomer before dehydration occurs



The ethylene oxide structure has been assumed in the case of glucosan and arabinosan. The same is assumed in the present paper for xylosan.



From these structures, it would appear that the properties of xylosan and glucosan should be comparable. Xylosan showed the normal molecular weight in cold glacial acetic acid, but in water it was trimolecular. Warming the acetic acid solution to the boiling point of water caused polymerization, which changed the colorless solution to brown. Accordingly the best way to isolate the xylosan is to precipitate it from cold glacial acetic acid solution with ether. Attempts were made to crystallize it from acetic acid by evaporating at a low temperature, but the polymer was obtained in every case. The latter is a brown, wax-like substance. Xylosan yielded furfural when it was distilled with 12% hydrochloric acid, but only three-fourths of the theoretical amount was formed in twenty-four hours. Xy-

¹ Pictet and Castan, *Helv. Chim. Acta*, **3**, 645 (1920); Cramer and Cox, *ibid.*, **5**, 884 (1922); Pictet and Vogel, *ibid.*, **9**, 806 (1926).

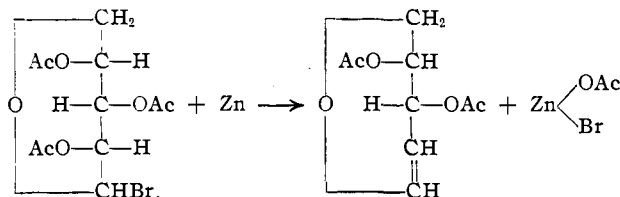
² Vogel, *ibid.*, **11**, 1210 (1928).

losan was easily oxidized. These properties of xylosan differ somewhat from the properties of glucosan as recorded by Pictet and Castan. They reported glucosan to be crystalline, deliquescent and soluble in water, evidently to a colorless solution. Since α -glucosan is so much more stable than 3,4,6-triacetylglucose anhydride, of which it would be the parent, Hickinbottom³ has questioned the $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$ ring in the former. Furthermore,

Brigl and Schinle⁴ were unable to synthesize glucosan in a crystalline state. Glucosan was prepared in this investigation and its properties were found to be very similar to those of xylosan. Both were deliquescent solids. Both dissolved in water giving a brown colored solution and both gave colorless solutions in acetic acid. Like xylosan, glucosan reduced Fehling's solution readily and dilute neutral potassium permanganate solution instantly.

Diacetylxylosan.—Acetylation of xylosan by a cold mixture of acetic anhydride and pyridine yielded diacetylxylosan. This compound is precipitated by dilution with water as an amorphous white solid. A brown solution is obtained in benzene or chloroform just as when xylosan is dissolved in water. Cryoscopic molecular weight determination in benzene showed that polymerization into a trimer, $\left(\begin{array}{c} \text{CH}_2-(\text{CHOAc})_2-\text{CH}-\text{CH} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \right)_3$, had occurred.

Diacetylxylyl.—Bromoacetylxylose was synthesized from xylose and acetyl bromide and on reduction with zinc dust yielded diacetylxylyl, a synthesis which has recently been described by Levene and Mori.⁵



Benzoyl hydrogen peroxide is known to convert a carbon-to-carbon double bond into an ethylene oxide derivative. The same reaction takes place with unsaturated carbohydrate derivatives as, for example, with such compounds⁶ as glucal, rhamnal and cellobial. With diacetylxylyl, oxidation of this type should yield diacetylxylosan or diacetylxyloxan, or a mixture of both. Actually, perbenzoic acid reacted with diacetylxylyl to give

³ Hickinbottom, *J. Chem. Soc.*, 3143 (1928).

⁴ Brigl and Schinle, *Ber.*, **62**, 1716 (1929).

⁵ Levene and Mori, *J. Biol. Chem.*, **83**, 803 (1929).

⁶ Bergmann and Schotte, *Ber.*, **54**, 440, 1564 (1921); Tanaka, *Bull. Chem. Soc. Japan*, **5**, 214 (1930).

a white solid possessing many of the characteristics of the diacetylxylosan. Thus the material dissolved in acetic acid to form a colorless solution, while in chloroform or benzene it dissolved with production of a brown coloration. This color interfered with polarimetric readings, but it is certain that the observed rotation was lower than that of diacetylxylosan. Both substances on heating in a capillary tube polymerize to give a brown substance. There is a shrinkage in volume but no apparent melting. Differing from this, a mixture of the two melts as it polymerizes. Thus, it seems evident that other products than diacetylxylosan are also present. These could include diacetylxylosan or even 1-benzoyl-3,4-diacetylxylose. Due to the small quantity available, this point could not be established with certainty. The material on hydrolysis gives a product which, with phenylhydrazine, yields phenylxylosazone, a change typical of either xylose or lyxose.

Experimental Part

Xylosan.—Twelve grams of xylose was heated in a boiling xylene vapor-bath under 2 mm. pressure. Water was immediately liberated as shown by the heat generated in a phosphorus pentoxide trap. After one hour the mass started to melt and at the end of one and one-half hours the whole was bubbling vigorously. This continued for about twenty hours, after which period the xylose had acquired a dark caramel color. A loss in weight of 1.4 g. or 12% of the weight of the sugar occurred, corresponding to slightly more than one equivalent of water. Traces of furfural were detectable in the distillate by colorimetric methods.

The residue in the reaction tube was dissolved by boiling with several portions of glacial acetic acid. Although only a small amount of hot acetic acid was required to effect complete solution of xylosan, a gummy precipitate resulted if such a solution was cooled. To prevent this, the hot solution was poured into enough additional cold glacial acetic acid (500 cc.) to hold the xylosan in solution. An amorphous, cream-colored precipitate formed. On settling overnight, a gummy mass which was discarded formed in the bottom of the container. When the solution was decanted into two volumes of ether a flocculent, white precipitate separated which settled rapidly. The product was filtered in a dry atmosphere to prevent polymerization. This was accomplished by covering the Buchner funnel filtration system with a bell jar at the bottom of which calcium chloride was spread. The suspension to be filtered was added through the top of the jar by means of a separatory funnel.

The xylosan was washed on the filter with a little alcohol, then with an alcohol-ether mixture, and finally with 100 cc. of dry ether. It was dried in a vacuum desiccator over phosphoric anhydride. The yield of white, granular solid was 5.5 g., or 52% of the theoretical.

The product is very soluble in water, giving a brown colored solution. Xylosan is very soluble also in glacial acetic acid. This solution is colorless, but turns brown at 100°. It dissolves appreciably in ethylene glycol, hot ethyl alcohol, methyl alcohol, acetone and cold acetic acid and is insoluble in ether and chloroform. Xylosan reduces cold, neutral potassium permanganate solution instantly.

Rotation. Subs., 0.5138, in water to make 100 cc., 0.6804 g.; rotation +0.35, +0.47° (1-dm. tube, sodium light); $[\alpha]_D^{20}$ +68.1, +68.3°. After three weeks, the rotation of the second was +0.48, $[\alpha]_D^{20}$ +68.4°, showing an absence of mutarotation.

Mol. wt. in water: Subs., 0.1945 in 30 g. of water; f. p. lowering, 0.031°. Calcd.

for $(C_6H_8O_4)_3$: 396. Found: 398. *Mol. wt.* in acetic acid: Subs., 0.1059 in 30 g. of glacial acetic acid; f. p. lowering, 0.110° . Calcd. for $C_6H_8O_4$: 132. Found: 124.

Anal. (By F. D. Pilgrim) Subs., 0.1673, 0.1561; CO_2 , 0.2764, 0.2512; H_2O , 0.1008, 0.0923. Calcd. for $C_6H_8O_4$: C, 45.2; H, 6.1. Found: C, 44.3, 44.0; H, 6.65, 6.59. Xylosan is very hygroscopic, making it difficult to obtain an accurate analysis.

Furfural Formation.—A solution of 0.1945 g. of xylosan was steam distilled for twenty-four hours with 12% hydrochloric acid. At the end of that time furfural was coming over in very small amounts. A colorimetric analysis⁷ of the distillate showed 0.1067 g. of furfural formed. The theoretical yield was 0.1411 g. This slow formation of furfural indicates that the xylosan hydrolyzes very slowly.

Melting Point Determination.—At $95-97^\circ$ and atmospheric pressure, the white, unimolecular form of xylosan changed to a dark brown solid with a definite shrinkage in volume, the latter at $205-210^\circ$ being converted into another form without melting. A special melting point tube was then made by drawing one end of a 5-mm. tube to a capillary, which was sealed off. On heating the product under these conditions, at 0.3 mm. there was a slight darkening and shrinkage in volume at $119-20^\circ$, with apparent conversion into a new product at $163-165^\circ$. This last material was similar in appearance to that obtained at 95° under atmospheric pressure.

Diacetylxylan.—Four grams of xylosan was dissolved in 20 cc. of cold pyridine and 20 g. of cold acetic anhydride added and the mixture kept in a refrigerator for seventy-two hours at -3° and then poured into ice water: It was stirred with ice, filtered, dissolved in cold acetic acid and again filtered into ice water. It was then filtered by suction and washed with water, yielding a somewhat gummy solid which after standing for a few days in a vacuum desiccator over sulfuric acid became white and powdery. The solutions of diacetylxylan in chloroform or benzene were brown in color and in acetic acid, colorless. This suggested, as with xylosan, that the brown solution contained a polymeric modification and that the colorless solution in acetic acid held unpolymerized diacetylxylan.

Rotation. Subs., 1.000, in chloroform (U. S. P.) to make 10 cc.; rotation, $+3.8^\circ$ (1-dm. tube, sodium light); $[\alpha]_D +38.0^\circ$.

Mol. wt. Subs., 0.1603 in 10 g. of benzene; f. p. lowering, 0.126° . Calcd. for $(C_9H_{12}O_6)_3$: 648. Found: 651.

Anal. Subs., 0.3000: cc. of 0.1 N NaOH \approx acetic acid formed by hydrolysis, 27.8. Calcd. for $C_9H_{12}O_6$: acetyl, 39.81. Found: 39.85.

Diacetylxylan darkened at $88-89$ and at $95-100^\circ$ became much darker and underwent a shrinkage in volume, polymerization apparently occurring at this point.

Bromotriacetylxylan was prepared from xylose essentially by Dale's⁸ method. This was converted into diacetylxylan by reduction with zinc dust, using 50% acetic acid at -15° as the solvent. Since our preparation of diacetylxylan, Levene and Mori's⁹ record of its synthesis has appeared.

Anal. Subs., 0.3520: cc. of 0.1 N NaOH, 35.1. Calcd. for $C_9H_{12}O_5$: acetyl, 43.0. Found: 42.9.

Oxidation of Diacetylxylan with Perbenzoic Acid.—Into a thoroughly dried suction flask was placed 1.5 g. of diacetylxylan. A chloroform solution of perbenzoic acid, prepared by the method of Hibbert and Burt¹⁰ was filtered into the flask with suction.

⁷ Youngburg and Pucher, *J. Biol. Chem.*, **61**, 741 (1924).

⁸ Dale, *THIS JOURNAL*, **37**, 2745 (1915).

⁹ Levene and Mori, *J. Biol. Chem.*, **83**, 803 (1929).

¹⁰ Hibbert and Burt, *THIS JOURNAL*, **47**, 2240 (1925).

The suction was stopped before the last portion of the solution went through the filter to avoid drawing any moist air into the flask. The flask was tightly stoppered and shaken for a few minutes. When the diacetylxytal had completely dissolved, the mixture was left for twenty-four hours at 0°. It was then washed with ice water, followed by ice-cold sodium bicarbonate solution, and finally twice more with ice water. The chloroform solution was dried with calcium chloride, after which the solvent was removed *in vacuo*. The residue was taken up in 10 cc. of glacial acetic acid and the solution poured into 500 cc. of ice water. The white precipitate which formed was collected on a filter, washed with water, and dried in a vacuum desiccator over phosphoric anhydride. This product weighed 0.3382 g. An attempted melting point determination showed that it polymerized at 93–94°, uncorr.

The optical rotation in chloroform could not be measured because the solution was too brown to permit of observation. With a one decimeter tube the possible rotation was less than the error of observation.

Anal. Subs., 0.2755: cc. of 0.1 N alkali equivalent to the acetic acid formed, 12.5. Calcd. for $C_9H_{12}O_8$ (diacetylxylosan or diacetyllyxosan): acetyl, 20.0; calcd. for diacetylxylose: acetyl, 18.5. Found: 19.5.

Xylosazone Formation.—The residual solution from the acetyl determination was made neutral to litmus with sodium carbonate, and was then evaporated *in vacuo* to 10 cc. Two grams of sodium acetate and 1 g. of phenylhydrazine hydrochloride were added. The solution was allowed to stand for forty-five minutes at room temperature and was then heated in a boiling water-bath for two hours. After being left to cool overnight, 0.095 g. of yellow crystals formed which were carefully collected, washed with water and dried. The melting point of 153.4° (uncorr.) identified the substance as xylosazone. A mixed melting point with xylosazone also gave a value of 153°.

Glucosan.—Glucose (28.50 g.) was pyrolyzed in a 100-cc. round-bottomed flask according to the directions of Pictet and Castan.¹ The flask was evacuated to 13–15 mm. pressure and was then placed in an oil-bath which was adjusted to a temperature of 152–155°. The glucose melted and then began to bubble vigorously, giving off vapor. After three hours all reaction had ceased. The loss in weight, corresponding to one molecule of glucose minus one molecule of water, was 4.52 g. The residue was a slightly brown, wax-like substance. Attempts to crystallize it from absolute methanol were unsuccessful, but no extended efforts in this direction were carried out. The glucosan was very soluble in water and acetic acid, giving a brown colored solution in the former. It was slightly soluble in alcohol, giving a brown solution. It reduced Fehling's solution readily and dilute, neutral potassium permanganate solution instantly. Its water solution decolorized bromine water instantly. Pouring a cold acetic acid solution into ether gave a flocculent, white precipitate. Cooling a hot, saturated solution in acetic acid caused a brown, gummy mass to separate. When left in the open air the product rapidly absorbed moisture. In all these characteristics, the glucosan was identical with the similarly prepared xylosan.

Summary

Xylosan is formed by the pyrolysis of xylose. It is easily oxidizable. It polymerizes to a brown-colored trimer in aqueous solution, but in acetic acid solution it remains in the unpolymerized, colorless state. Diacetylxylosan shows the same tendency to polymerize in solvents other than acetic acid. Diacetyllyxosan, or a mixture of it with diacetylxylosan, is formed by the action of benzoyl hydrogen peroxide on diacetylxytal.

Glucosan, prepared in the manner of xylosan, has properties which closely resemble xylosan.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. XV.¹ THE BEHAVIOR OF 3-GLUCOSIDO-ARABINOSE HEPTA-ACETATE TOWARD AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE

BY WM. LLOYD EVANS AND CHARLES C. CLARK

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It has been shown recently that there is a marked difference in the behavior of the 4-hexosido-glucoses and the 6-hexosido-glucoses toward aqueous solutions of potassium hydroxide.¹ These differences were attributed principally to the following general causes: (a) the chemical character of the hexosido section of the disaccharide molecule; and (b) the point of the hexosidic attachment. When maltose and cellobiose are acted upon by aqueous solutions of potassium hydroxide, it is found that the yields of lactic acid from these two disaccharides are about one-half as much as one would expect from an equivalent solution of glucose. In seeking an explanation for this latter fact through the application of the enediol theory of chemical behavior in the carbohydrates, it was shown that maltose and cellobiose should form a 3-glucosido-arabinose and formaldehyde as their first decomposition products in each case. Therefore, it becomes evident that these intermediate 3-glucosido-arabinoses obtained from maltose and cellobiose should be expected to show the same general reaction toward aqueous solutions of potassium hydroxide as did the original disaccharides under the same experimental conditions. If this assumption is correct, then in the alkaline decomposition of the 3-glucosido-arabinoses one should obtain pyruvic aldehyde, lactic and formic acids in yields of approximately the same order of magnitude as those obtained from cellobiose and maltose. To establish these points experimentally was the principal objective in this work.

Experimental Part

Cellobiose Octa-acetate.—The method used for the preparation of cellobiose octa-acetate was essentially that described by Zemplén.² If the heat of reaction was insufficient to cause the temperature to rise to 100°, the mixture was heated on an electric hot-plate to that point. Our experience coincided with that of Haworth and Hirst,^{3,4} who found that it was better to judge the progress of the reaction by the color of the

¹ Contribution XIV of this series, *THIS JOURNAL*, **53**, 4384 (1931).

² Zemplén, *Ber.*, **59**, 1254 (1926).

³ Haworth and Hirst, *J. Chem. Soc.*, 2809 (1927).

⁴ Cf. Haworth, Hirst, Streight, Thomas and Well, *ibid.*, 2636 (1930).