drazones and the starting materials. In this way it was established that Ia, IIa and IIIa eliminated hydrogen bromide while IVa and Va were recovered unchanged. The constants of the unsaturated hydrazones are included in Table II.

When the above procedure was applied to IIa, a yellow substance m.p. 168° (dec.), $\lambda_{\max}$ 378 mμ, log $\epsilon_{\max}^{\text{chlf}}$ 4.43, was obtained. This substance gave a positive Beilstein test for halogen. When its solution in chloroform was washed with water an equivalent amount of bromide ion was found present in the aqueous layer. The yellow substance was the hydrobromide of the hydrazone Ib which was recovered halogen-free from the chloroform solution. Va was extremely insoluble in glacial acetic acid.

Reaction of Halo Ketones with 2,4-Dinitrophenylhydrazine in Acetic Acid.—To a solution of the halo ketone in glacial acetic acid there was added 1 mole of 2,4-dinitrophenylhydrazine and the solution kept at its boiling point for 5 minutes. The product which precipitated on cooling was characterized by comparison with authentic samples of the dinitrophenylhydrazones of the starting material or the corresponding α,β-unsaturated ketone. Here again the hydrobromide of Ib was obtained from IIa. Under these conditions, the formation of Va from V is sluggish and is accompanied by acetylation of 2,4-dinitrophenylhydrazine.

Reaction of Halo Hydrazones with Methanol.—The halo hydrazone was dissolved in methanol and the solution refluxed for 15–30 minutes. After removal of the solvent the yellow methoxy hydrazone was shown to be halogen-free in the Beilstein test. The constants of the methoxy hydrazones are included in Table II.

Formation of Dinitrophenylosazones.—A mixture of the halo hydrazone or the methoxy hydrazone was refluxed with excess of Brady reagent for 3–4 hours. The bright red osazone precipitated during the reaction. The mixture was cooled and the osazone collected and recrystallized as indicated in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, PURDUE UNIVERSITY]

A Polymer-homologous Series of Crystalline Oligosaccharide Acetates from Xylan Hydrolysate[1]

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The series of crystalline oligosaccharides from xylobiose to xylohexaose is converted to the corresponding series of oligosaccharide acetates, all of which are obtained crystalline in the β-D′-configuration. The melting points and specific rotations of these derivatives are correlated with their degrees of polymerization.

A series of crystalline oligosaccharides composed only of D-xylopyranose units uniformly joined by $(1 \rightarrow 4)$-β-D′-linkages has been isolated from xylan hydrolysate.[2] The series extends from xylobiose to xylohexaose inclusive. These are the first crystalline oligosaccharides to be isolated which are composed solely of pentose sugar units. The series is of special interest since its members are structurally identical to the corresponding members of the series from cellulose, except that the xylo-oligosaccharides lack the projecting primary alcohol group on each ring unit characteristic of the gluco-oligosaccharides. Comparisons between the two series may therefore be expected to indicate the effect of the primary alcohol group on molecular properties. Such comparisons including rates of hydrolysis are now in progress. As a further aid for comparison of the two series and to obtain further characterization of the xylo-oligosaccharides, they were converted to their crystalline acetates. Each member of the series was acetylated in a hot mixture of acetic anhydride and sodium acetate in such a way as to preserve unaltered the general structural arrangement and to esterify free anomeric hydroxyls in the β-D′-configuration. Hence, all anomeric carbon atoms within the structures have the same relative steric configurations.

Optical rotations, melting points and molecular weights of the various β-D′-acetates are shown in Table I. Although the molecular weights determined by Rast method, using the precautions cited by Smith and Young[3] and Meldrum, Saxer and Jones,[4] are in agreement with the expected values, the accuracy of the determination apparently decreases as the molecular weight increases. The melting points increase progressively with degree of polymerization and tend to approach the softening temperature of xylan diacetate. Optical rotations vary uniformly with the degree of polymerization of the oligosaccharide. Freudenberg and coworkers[5] have shown that if the type of linkage in a polymer-homologous series is uniform, the expression $[M]_n/n$ plotted against $(n - 1)/n$ (where $[M]$ is the molecular rotation and n is the degree of polymerization) yields a straight line for $n \geqq 2$. When the molecular rotations of the present series are plotted against the suggested function of degree of polymerization, a linear relation is found to exist as shown in Fig. 1. This finding is further evidence for the presence of uniform linkages in the series members.

TABLE I

PREPARATION AND YIELD OF β-OLIGOSACCHARIDE ACETATES

Sugar, xylo-	G. taken	NaAc, g.	Ac_2O, g.	Reflux, hr.	Yield, g.
Biose	1.50	2.00	20	3.0	2.10
Triose	0.80	0.90	17	4.5	1.32
Tetraose	.80	1.36	17	5.5	1.42
Pentaose	.90	1.41	19	6.5	1.25
Hexaose	.40	0.70	10	7.5	0.46

The acetyl content of the β-D-acetates was deter-

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(1) Journal Paper No. 602 of the Purdue University Agricultural Experiment Station.

(2) R. L. Whistler and C. C. Tu, THIS JOURNAL, in press.

(3) J. H. C. Smith and W. G. Young, *J. Biol. Chem.*, **75**, 289 (1927).

(4) W. B. Meldrum, L. P. Saxer and T. O. Jones, THIS JOURNAL, **65**, 2023 (1943).

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TABLE II

CONSTANTS OF SUGAR ACETATES PREPARED FROM CRYSTALLINE OLIGOSACCHARIDES ISOLATED FROM XYLAN

Sugar acetate	$[\alpha]^{25}D$ in $CHCl_3$	M.p., °C.	Rast molecular weight Calcd.	Found
β-Xylobiose hexaacetate	−74.47 (*c* 0.9)	154–155	534	545, 553, 563
β-Xylotriose octaacetate	−84.26 (*c* 0.6)	109–110	750	726, 740, 742
β-Xylotetraose decaacetate	−93.70 (*c* 0.8)	201–202	966	950, 970, 936
β-Xylopentaose dodecaacetate	−97.50 (*c* 1.1)	248–249	1182	1070, 1190, 1155
β-Xylohexaose tetradecaacetate	−102.00 (*c* 1.5)	260–261	1398	1370, 1377, 1460

mined by the method of Kunz and Hudson[6] and in each case was found to be in agreement with the calculated value provided care was taken to allow sufficient time for completion of the saponification.

A similar homologous series of oligosaccharide acetates was obtained by Dickey and Wolfrom[7] through partial acetolysis of cellulose. These oligosaccharides were produced in the presence of sulfuric acid and acetic anhydride and hence the free anomeric hydroxyls were acetylated in the α-D′-configuration.

Experimental

General Procedure for the Acetylations.—The sugar was mixed with the amount of fused sodium acetate and acetic anhydride indicated in Table I in a two-necked, round-bottomed flask fitted with a reflux condenser and a mercury sealed stirrer. The mixture was heated in a boiling water bath for 3 to 7 hours. At the end of this time, the warm solution was poured, with very vigorous stirring, into 100 ml. of ice–water mixture. The white powder which formed was separated, dried and purified by crystallization. The quantity of each product obtained and the resulting yield are shown in Table I.

Crystallization.—The characteristics of the crystalline acetates are shown in Table II. The individual crystallization procedures are described below.

1. **β-Xylobiose Hexaacetate.**—One gram of the dried powder was dissolved in ethyl alcohol and the solution was concentrated. Distilled water was added dropwise until the solution appeared cloudy. Upon cooling crystallization occurred. The crystals were removed by filtration, washed thoroughly with water and purified by recrystallization from ethanol. The acetate was found to be identical with that reported by Whistler, Bachrach and Tu.[8]

Anal. Calcd. for $C_{10}H_{12}O_9(CH_3CO)_6$: acetyl, 48.32. Found: acetyl, 48.20.

2. **β-Xylotriose Octaacetate.**—One and three-tenths grams of the dried powder was dissolved in 10 ml. of methanol and filtered. Upon cooling long needles crystallized. The separated crystals were purified by recrystallization from methanol; yield 1.0 g.

Anal. Calcd for $C_{15}H_{18}O_{13}(CH_3CO)_8$: acetyl, 45.87. Found: acetyl, 45.65.

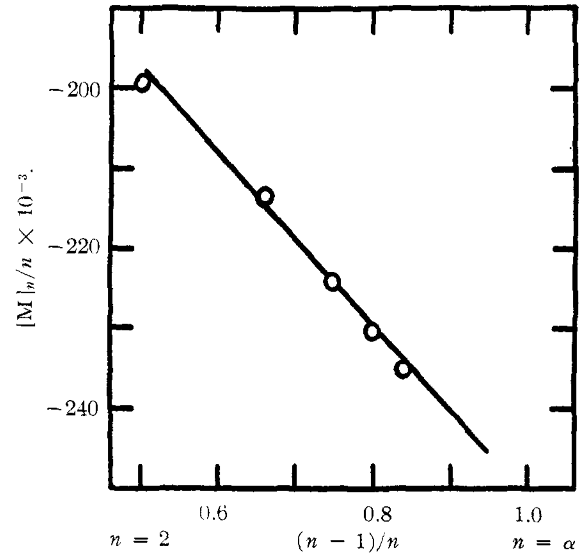

Fig. 1.

3. **β-Xylotetraose Decaacetate.**—Seven-tenths gram of the dried powder was dissolved in dioxane, the solution was filtered and warmed, and 20 ml. of petroleum ether was added. Upon cooling crystallization occurred; yield 0.5 g. The crystals were separated and recrystallized from dioxane and petroleum ether.

Anal. Calcd. for $C_{20}H_{24}O_{17}(CH_3CO)_{10}$: acetyl, 44.50. Found: acetyl, 44.25.

4. **β-Xylopentaose Dodecaacetate.**—One and six-tenths grams of the dried powder was dissolved in 67 ml. of dioxane, warmed and filtered, and 36 ml. of petroleum ether was added. Upon cooling crystallization occurred; yield 0.80 g. The separated crystals were recrystallized from dioxane and petroleum ether.

Anal. Calcd. for $C_{25}H_{30}O_{21}(CH_3CO)_{12}$: acetyl, 43.70. Found: acetyl, 43.90.

5. **β-Xylohexaose Tetradecaacetate.**—Forty-six hundredths gram of the dried powder was dissolved in 35 ml. of dioxane. To the warmed and filtered solution 16 ml. of petroleum ether was added. Upon cooling crystallization occurred; yield 0.38 g. The crystals were separated and recrystallized.

Anal. Calcd. for $C_{30}H_{36}O_{25}(CH_3CO)_{14}$: acetyl, 43.10. Found: acetyl, 43.30.

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(7) E. E. Dickey and M. L. Wolfrom, *ibid.*, **71**, 825 (1949).

(8) R. L. Whistler, J. Bachrach and C. C. Tu, *ibid.*, **74**, 3059 (1952).