THE HEMICELLULOSES OF MAIZE COBS AND RYE STRAW [1]

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INTRODUCTION

The carbohydrates of the cereal straws and products represent a type of raw material that can be obtained in large amounts and that might be of great commercial value. Of these carbohydrates the most important are hemicelluloses and cellulose. The term "hemicellulose" includes polyoses, polyuronides, and cellulosans. Their chemical relationship to other constituents in the plant is not known definitely nor is the nature of their origin.

This report presents the results of a partial qualitative study of the sugars in the hemicelluloses of maize cobs and rye straw as well as a determination of their chain length and number of functional groups.

REVIEW OF THE LITERATURE

In 1930, Preece (*13*)[2] fractionated the hemicelluloses of maize cobs into four groups. The products of hydrolysis consisted principally of xylose, a methyl pentose, arabinose, and a uronic acid. One fraction corresponded to the formula

$$(C_5H_8O_4)_{43}\cdot(C_6H_{10}O_4)_3\cdot(C_6H_8O_6)_2$$

with a molecular weight of approximately 6,466. In 1936, Angell and Norris (*2*) found that the maximum yield of fraction A from this source depended upon the pH at which the precipitation was brought about; the isoelectric zone was found to be pH 4.0–4.1. These authors were unable to confirm the presence of the methyl pentose.

The hemicellulose of rye straw have been less well studied. Norman (*12*) indicates that they contain at least two fractions, A and B; the nature of the sugars present was not determined. Fraction A contained 5 percent of uronic acids, 60 percent of an anhydropentose, and 35 percent of an anhydrohexose; fraction B was made up of 29 percent of uronic anhydrides, 60 percent of anhydropentose, and 11 percent of anhydrohexose.

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[2] Italic numbers in parentheses refer to Literature Cited, p. 46.

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EXPERIMENTAL METHODS

White maize cobs and rye straw were both grown on college land which consisted of Merrimac fine sandy loam. The materials were ground to pass a 1-mm. sieve, and were freed of contaminating substances in the manner usually employed in such studies.

The hemicelluloses were removed from the prepared material by extractions with 4-percent sodium hydroxide. Four 22-hour extractions were made in the cold; a final extraction was made for 6 hours in a bath of boiling water. The extracts were mixed and the hemicelluloses precipitated completely by means of acetic acid and 95-percent alcohol, due attention being paid to the isoelectric points. No attempts were made to fractionate the precipitate. On the extracted basis, the yield was about 33 and 18 percent respectively. Purification was effected by the method of Anderson et al. (*1*) and by electrodialysis. The sodium sulfite test indicated the presence of a trace of lignin after purification.

The methods employed for characterization were those cited previously (*3*) and those now to be described. The iodine and alkali numbers and R_{Cu} values were determined by the methods of Kline and Acree (*10*), Schoch and Jensen (*14*), and Farley and Hixon (*6*) respectively. The iodine number, defined as the number of cubic centimeters of 0.1 N iodine in alkaline solution which will react with 1 gm. of carbohydrate material, is a measure of the aldehyde group (*4*). On the assumption that the aldehyde group is a terminal unit, the molecular weight of the carbohydrate may be calculated by the use of equation

$$RCHO + I_2 + 3NaOH \rightarrow RCOONa + 2NaI + 2H_2O \qquad (1)$$

By inspection it may be seen that 20,000 cc. of 0.1 N iodine will be necessary to oxidize the aldehyde group of 1 gm. molecular weight of the polysaccharide to the carboxyl group. Hence, the average molecular weight of heterogeneous polysaccharide may be calculated from the formula

$$20{,}000/\text{iodine number} = \text{molecular weight} \qquad (A)$$

In a manner similar to that described above, the R_{Cu} number may also be used to estimate the molecular weight (*7*). The values obtained, however, are extremely low because the reaction does not appear to be stoichiometric. A calculation by formula B (*11*) is a more suitable procedure.

$$132 \times R_{Cu}\ (\text{xylose})\ /R_{Cu}\ (\text{hemicellulose}) = \text{molecular weight} \qquad (B)$$

Analytical data not included here seem to indicate that the R_{Cu} for xylose is approximately 2,247.

Acetylations were conducted according to the method of Haworth and coworkers (*9*). In order to obtain a successful acetylation of hemicelluloses from rye straw, it was necessary to hydrate the material and then to dehydrate it without allowing it to become dry. Acetyl values were determined by the procedure of Bryant and Smith (*5*).

Specific rotations were calculated from data obtained from a Schmidt and Haensch saccharimeter.

Hydrolyses were effected by a 4-percent solution of sulfuric acid during about 4 hours' time in a boiling water bath. The ratio of sample to acid was 1 to 50.

ANALYTICAL DATA

A résumé of the data obtained is given in table 1. Fermentation tests on the hydrolytic products indicated the presence of a very small amount of hexose sugars. Gas was not produced until after 6 hours of incubation; no gas whatever was produced in the blanks for the same period of time. The saccharic and mucic acid test were not wholly conclusive. Mannose was not present. By means of benzylphenylhydrazine, *l*-arabinose was found in the hemicellulose from maize cobs, but not in that of rye straw. The presence of xylose was established by the xylonobromide test.

TABLE 1.—*A partial chemical analysis of hemicelluloses from maize cobs and eye straw on an ash- and moisture-free basis*

Determination	Hemicellulose	
	Maize cobs	Rye straw
Hexose	Trace	Trace
Uronic acid anhydride ....percent	3.75	3.67
Anhydroxylose ....percent	81.2	85.8
Arabinose	Trace	Not detected
Alkali number	11.98	11.78
Iodine number	3.43	1.14
Molecular weight	5,831	17,543
R_{Cu} value (milligrams of copper per gram of polysaccharide)	73.00	50.00
Molecular weight (from formula B)	4,063	5,932
Molar ratio of uronic acid anhydride to anhydroxylose	1:29	1:31
Molecular weight	4,004	4,268
Specific rotation $[\alpha]_D^{20}$		
Before hydrolysis ....degrees	−93.8	−94.2
After hydrolysis ....degrees	+35.1	+27.5
Acetyl value:		
Calculated (for xylan diacetate, $C_9H_{12}O_6$) ....percent	39.8	39.8
Found ....percent	40.2	39.7

The residue after hydrolysis amounted to 2.5 and 0.7 percent respectively for maize cobs and rye straw. Only a trace of furfural was detected in the residue from the maize cobs. It need not necessarily be assumed that the reacting compound came from the sugars of unhydrolyzed hemicellulose. Preliminary tests on the rate and procedure of the hydrolysis indicated that a maximum of reducing power was obtained in 4 hours. The initial slope of the curves was similar to that obtained from starch when treated in the same way. The positive optical rotation of the hydrolyzed hemicellulose and the strong negative rotation prior to hydrolysis, together with the rate of hydrolysis, strongly suggest that a beta linkage is present and that a pyranoside structure is predominant. Haworth and coworkers (*8*) found that xylan from esparto cellulose of different origin contains xylopyranose residues and a constant proportion of combined *l*-arabinose in the furanose form.

It should be emphasized that the preparations used for the analyses were considered to be heterogeneous; hence the molecular weights reported represent the average or the mean of the different fractions. As indicated by the iodine number and the R_{Cu} values, the average molecular weights differ considerably. These variations for either product are due in part to differences in the sensitivity of the methods. The iodine method is believed to yield fairly accurate data for substances composed of relatively short chains (*10*). The values obtained by this method for rye straw hemicelluloses, however, appear to be too high.

The molecular weights determined from the ratio of uronic acid anhydride to anhydroxylose are in fair agreement with those obtained from formula B, and probably represent the more reliable data. The ratios refer to a chain consisting of 29 and 31 anhydroxylose units respectively, each having a hexuronic acid anhydride terminal unit. On this bases the molecular weights are approximately 4,004 and 4,268 respectively for the 30 and 32 unit chains. The hexose and arabinose are constituents of a chain, but their position and amount are not known; hence they have not been considered in these calculations. Anhydroxylose and a hexuronic acid anhydride appear to account for approximately 85 and 90 percent of the hemicelluloses of maize cobs and rye straw respectively.

The two hemicelluloses are similar to each other and to commercial cornstarch in their degree of alkali liability.

The carbon and hydrogen content of the acetate of maize-cob hemicellulose was 49.5 and 5.9 percent respectively. The theoretical percentage content of carbon and hydrogen in xylan diacetate, $C_9H_{12}O_6$, is 49.98 and 5.60 respectively.

The data presented strongly suggests that the hemicelluloses of maize cobs have a beta linkage and have the pyranose structure. The hemicellulose appears to consist of 81.2 percent of anhydroxylose, 3.75 percent of uronic acid anhydride, and a trace of both a hexose and arabinose. The hemicellulose of rye straw appears to possess the same type of linkage and structure and to consist of 85.8 percent of anhydroxylose, 3.67 percent uronic acid anhydride, and a trace of hexose; arabinose was not detected.

SUMMARY

The total hemicelluloses of maize cobs and rye straw were isolated and purified. Data for both strongly suggest that the beta linkage is present and that the pyranose structure is predominant. Determinations of the average molecular weights of the hemicelluloses by reducing methods and by calculations based on the ratio of uronic acid anhydride to anhydroxylose indicate a considerable variation, but the most probable values are believed to be between four and six thousand.

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