Note on the Reaction of Gaseous Chlorine with a Wheat Flour Hemicellulose[1]

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When wheat flour is bleached with gaseous chlorine, the starch and the hemicelluloses are among the various fractions that can be affected (1,2). Detailed studies have been made on the effect of chlorine on wheat-flour starch by Ingle and Whistler (2) and on a wheat-straw hemicellulose by Whistler and Pyler (3). The latter workers did not include the hemicelluloses of wheat flour in their studies but predicted that because of similarities in structure, these polysaccharides would react with chlorine in the same way as the wheat-straw hemicellulose. The results in this Note tend to confirm their prediction. Gaseous chlorine reacted rapidly with a hemicellulose isolated from the "tailings" fraction to produce pronounced physical and chemical changes that may be of importance in the interpretation of chlorine bleaching of flour. Preliminary results described in this Note also indicate that chlorine reacts with the hemicellulose in agreement with the mechanism proposed by Whistler and Pyler (3).

The material used in this work was a hemicellulose isolated from the "tailings"

[1]Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

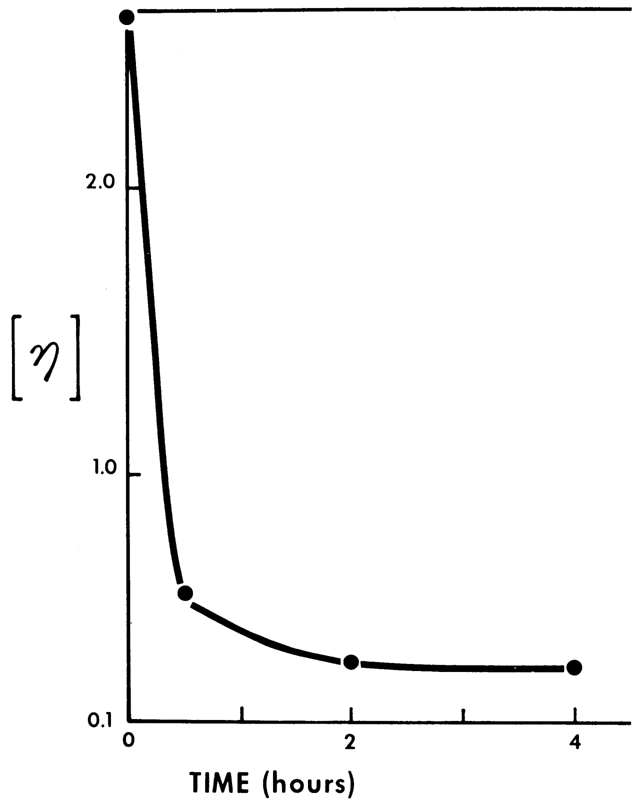

Fig. 1. Changes in intrinsic viscosity of a wheat-flour hemicellulose exposed to chlorine gas for various time periods. Values of [η] are expressed in dl./g.

fraction of a HRW wheat flour. This polysaccharide did not complex with borate and was eluted with water from a diethylaminoethyl cellulose column (4). Chlorine was used as received in cylinders from Matheson Co., Inc. Generally, oxidations were conducted according to the procedure of Ingle and Whistler (2). Lyophilized hemicellulose solids (containing 10% moisture) and chlorine in a weight ratio of 1:1 were treated in sealed bottles (250-ml. capacity) at room temperature, in daylight, for periods ranging from 0.5 to 4 hr. Aldehyde groups were determined on the hemicellulose solids by the procedure of Martin and co-workers (5), and total carbonyl groups by the cyanohydrin method of Schmorak and Lewin (6). Intrinsic viscosities were measured in aqueous cadmium ethylenediamine ("Cadoxen") containing 4% cadmium (7). Paper chromatography was performed according to a method described previously (4), and paper electrophoresis by a procedure described by Foster (8).

Gaseous chlorine depolymerized the hemicellulose rapidly, as evidenced by a drop in intrinsic viscosity of solutions of the chlorine-treated hemicellulose (Fig. 1); most of the change occurred within 30 min. With increase in time of exposure to

TABLE I. FUNCTIONAL GROUPS PRESENT IN HEMICELLULOSE TREATED WITH GASEOUS CHLORINE

Time hr.	Reducing Groups	Total Carbonyl Groups
	μmol. carbonyl/g. hemmicellulose solids	
0	0.035	0.17
0.6	0.073	...
2.0	0.28	1.00
4.0	0.32	1.25

chlorine there was an increase in aldehyde groups (Table I). Also, nonreducing carbonyl groups increased, indicating the presence of compounds that contained keto or carboxyl groups, or both. The hemicellulose solids resulting from chlorine treatment for 1 hr. did not dissolve completely in water. Analysis of the water-soluble portion showed the presence of arabinose with small quantities of xylose, whereas the insoluble portion contained xylose in polymeric form. The origin of the compounds in the chlorine-treated hemicellulose can be explained by the mechanism proposed by Whistler and Pyler (3) for the action of chlorine (chlorinolysis) on polysaccharides in general. The hemicellulose studied here consists of a linear polymer of 1,4-linked D-xylopyranose units with L-arabofuranose side-chain residues attached to certain D-xylose units of the framework, principally through position-3 (9,10,11). According to the above mechanism, chlorine first forms a chlorooxonium cation with the C-1 and C-3 glycosidic oxygen bond on the hemicellulose. This cation complex can undergo cleavage through attack by whatever anions may be present. In this case the attack was preferentially directed at the C-3 oxygen bond connecting the labile arabofuranose branch to the xylan chain, since all of the arabinose was split off in the early stages of the reaction, leaving behind the insoluble xylan. Since the undegraded hemicellulose contained only pentoses and no carbon C-6 hydroxyl groups were present, no stable levoglucosans could be formed (as is the case when polymers of hexoses are exposed to chlorine). Therefore, depolymerization of this hemicellulose was accompanied by an increase in reducing groups. The nonreducing groups in the chlorine-treated hemicellulose could have originated in two ways. First, when the cation complex is split, a hypochlorite ester is always formed. This ester could undergo dehydrochlorination in the presence of moisture to produce a carbonyl group (3). Secondly, since excess chlorine is present, some of the reducing-sugar units could undergo secondary oxidation to form carboxylic acids. Paper electrophoresis showed that acidic components were formed in the hemicellulose treated with chlorine for 2 and 4 hr. (Fig. 2), and that a secondary oxidation did occur during these periods. No attempt was made to determine the concentrations of the acidic groups.

In conclusion, past studies on the chlorine bleaching of wheat flours have been concerned with the effect of chlorine on the starch fraction, with little attention given to the hemicelluloses. The results in this study show that the wheat-flour hemicelluloses, mainly xylan with arabinose side chains, are affected by chlorine bleaching. The arabinose side chains are split off in the early stages of the reaction, leaving a stable insoluble xylan. As the result of this reaction, the rheological and water-absorbing capacity of a wheat flour should be altered.

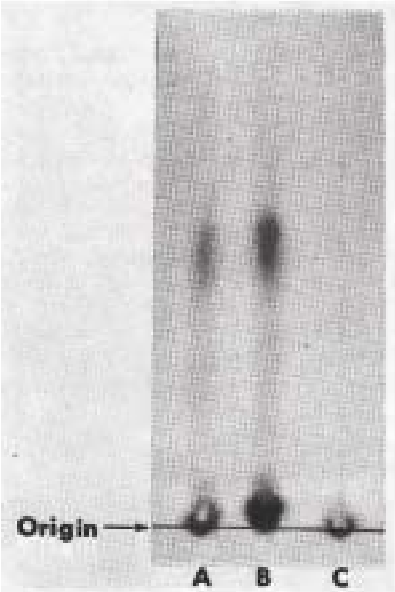

Fig. 2. Paper electropherogram of wheat-flour hemicellulose treated with gaseous chlorine for: A, 4 hr.; B, 2 hr.; and C, 0.5 hr. Acidic components are shown migrating from the origin.

Literature Cited

1. UCHINO, N., and WHISTLER, R. L. Oxidation of wheat starch with chlorine. Cereal Chem. 39: 477 (1962).

2. INGLE, T. R., and WHISTLER, R. L. Action of chlorine on semidry starch. Cereal Chem. 41: 474 (1964).

3. WHISTLER, R. L., and PYLER, R. E. Action of chlorine on wheat flour polysaccharides. Cereal Chem. 45: 183 (1968).

4. COLE, E. W. Isolation and chromatographic fractionation of hemicelluloses from wheat flour. Cereal Chem. 44: 411 (1967).

5. MARTIN, A. R., SMITH, L., WHISTLER, R. L., and HARRIS, M. Estimation of aldehyde groups in hydrocellulose from cotton. J. Res. Natl. Bur. Std. 27: 449 (1942).

6. SCHMORAK, J., and LEWIN, M. The determination of small concentrations of carbonyl groups in starch by the cyanohydrin method. Anal. Chem. 33(10): 1403 (1961).

7. SWENSON, H. In: Methods in carbohydrate chemistry, ed. by R. L. Whistler; vol. III, p. 89. Academic Press: New York (1963).

8. FOSTER, A. B. Zone electrophoresis. In: Methods in carbohydrate chemistry, ed. by R. L. Whistler and M. L. Wolfrom; vol. I, p. 51. Academic Press: New York (1962).

9. MONTGOMERY, R., and SMITH, F. The carbohydrates of Gramineae. I. The constitution of a hemicellulose of the endosperm of wheat (*Triticum vulgare*). J. Am. Chem. Soc. 77: 2834 (1955).

10. MARCHESSAULT, R. H., HOLAVA, H., and TIMELL, T. E. Correlation of chemical composition and optical rotation of native xylans. Can. J. Chem. 41: 1612 (1963).

11. GOLDSCHMID, H. R., and PERLIN, A. S. Interbranch sequences in the wheat arabino-xylan selective enzymolosis studies. Can. J. Chem. 41: 2272 (1963).

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