# A NOTE ON THE POLYSACCHARIDES OF WHEAT FLOUR SQUEEGEE[1]

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The isolation of starch in high yield from wheat flour is made difficult by the formation of a sludge, commonly referred to as "squeegee," which retains about 30% of the starch granules (1,2). The highly hydrated quality of this sludge is attributed largely to the presence of pentosan (1), removal of which leads to improved recovery of good-quality starch (1,3). By enzymatically degrading the starch entrapped in squeegee, Simpson (3) isolated the pentosan component as the main constituent (70%) of the enzyme-resistant fraction (A). After further purification, the pentosan was found (4) to be water-soluble and closely related in structure to the pentosan that dissolves in the flour slurry (5). It appeared possible, therefore, that the unidentified, nonpentosan part of fraction A might be involved in the formation of squeegee, perhaps by interacting with soluble pentosan when the flour is dispersed in water.

About half of pentosan-rich material A isolated by Simpson is soluble in 0.5*N* potassium hydroxide (4). It has now been found that a similar proportion (60%) of the material (prepared according to the procedure described by Simpson, 3) can be extracted into water at 50°C., the residue (B) being a highly swollen, firm gel. Extraction of B in turn with 5, 12.5, and 25% potassium hydroxide afforded three fractions, together comprising 25% of A. The acid hydrolysate (1*N* $H_2SO_4$) of each of these alkali-soluble fractions was found by paper chromatography to contain arabinose and xylose as major constituents and a lesser percentage of glucose. Also, the hydrolysate of the latter two fractions contained mannose as a minor constituent sugar.

The alkali-insoluble material (C) (2.0 g. from 50 g. of starting material A), which also was highly swollen and gelatinous, was degraded by acetolysis in the presence of sulfuric acid (6). The acetolysate was deacetylated with sodium methoxide, and paper chromatographic examination of the degradation products showed the presence of glucose, mannose, xylose, and a disaccharide. This mixture (1.0 g.) was fractionated by preparative paper chromatography, affording a) the disaccharide (225 mg.), which was found to be cellobiose (m.p. 226°–228°C.; characterized by its X-ray powder diagram); b) D-man-

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nose (27 mg.), which was converted to the phenylhydrazone (m.p. 198°–200°C., $[\alpha]_D^{27}$ + 32° (eqm. value, c, 1 pyridine); characterized by its X-ray powder diagram).

Fraction C was almost completely soluble in cuprammonium hydroxide solution. Dissolved material was precipitated as a gel by acidification with 6*N* hydrochloric acid, washed thoroughly with the acid, then with water, and dried through ethanol and ether (analysis: C, 41.0%; H, 5.9%; ash, 5.7%). As shown by acetolysis, this recovered material still contained mannose as a minor component sugar and a trace of xylose. On oxidation with sodium metaperiodate at 15°C., it consumed 1.09 moles of oxidant per mole in 120 hr. and yielded only a trace of acid. Sodium borohydride reduction of the oxidized polysaccharide, followed by acid hydrolysis, yielded erythritol as virtually the sole product detectable by paper chromatography. Hence, fraction C consisted mainly of a linear 1,4-bonded hexosan, in accord with the high yield of cellobiose obtained on partial degradation. On acetylation with acetic anhydride and sulfuric acid, material C yielded a triacetate (calc. for $C_6H_{10}O_5(OCOCH_3)_3$: acetyl, 44.8%; found: acetyl, 44.6%), 40% of which was soluble in acetone ($[\alpha]_D^{27}$ 17° (c, 2.4)).

These data show that, in addition to pentosans, wheat flour squeegee contains hexose polysaccharides, the major proportion of which is structurally indistinguishable from cellulose. Another constituent sugar of the hexosan fraction is D-mannose, which does not appear to have been detected previously in wheat endosperm hemicelluloses (7). The highly swollen quality of water-insoluble residue B and alkali-insoluble residue C suggests that these hexosan-rich fractions may contribute to the sludge characteristics of squeegee. Presence of the mannan and cellulosic components may have particular significance in this context, since a low concentration of mannan increases water absorption and interfiber bonding in pulps (8).

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