WATER-INSOLUBLE PENTOSANS: THEIR EFFECTS ON DOUGH RHEOLOGICAL PROPERTIES AND ROLES IN BREAD BAKING AND STALENESS

by

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TO MY PARENTS

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

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INTRODUCTION

Pentosans of wheat endosperm are classified as hemicelluloses. Certain authors have utilized different methods in nomenclature of hemicelluloses and pentosans. Aspinall (3) classified pentosans and hemicelluloses by differences in solubility. However, such a classification lacks precision in both chemical structure and biological function. The term hemicellulose has been used to refer to the water-insoluble, non-starchy polysaccharides and the term pentosan to the water-soluble polysaccharides (20). In this study, the term water-soluble pentosans was utilized to describe the pentosans extracted by water and the term water-insoluble pentosans for those pentosans not extracted by water.

The pentosans derived from cereals and grasses are characterized by the presence of single-unit side chains of L-arabinofuranose residues linked to a backbone of D-xylopyranose residues. Besides D-xylose and L-arabinose, certain hexose sugars and their derivatives, such as D-galactose, D-glucose, D-glucuronic acid and 4-O-methyl-D-glucuronic acid, also appear to be involved in their compositions (30, 51). Pentosans represent very large molecules, with intrinsic viscosities some 15 to 20 times greater than those of flour protein. Their minimum molecular weight is about 15,000, although the actual value appears to depend on the method of isolation and purification. Some of the water-insoluble pentosans possess pronounced hydration swelling capacities,

without actually entering solution (59).

In the last three decades, efforts have been made to study the chemical structure, physical properties of water-soluble pentosans (44, 48, 57), the role of water-soluble pentosans in bread baking (17, 65) and the mechanism of gelation on the addition of oxidizing agents to water-soluble pentosans(60,73). However, few studies dealt with water-insoluble pentosans, in spite of their constituting a large portion of the pentosans. In Europe some investigators (14, 15, 16, 24, 35) have investigated the water-insoluble pentosans from wheat flour, as well as from other sources.

In this study, a series of experiments was conducted to examin effects of water-insoluble pentosans from hard red winter wheat, barley, rye, and oats on rheological properties of dough, and on baking and keeping qualities.

LITERATURE REVIEW

Occurrence

Pentosans, composed largely of D-xylose units are widely distributed in the plant kingdom as a cellular component and help to form the framework of the cell wall. Bran contains the most pentosans in the wheat kernel and is also the portion which is highest in water-insoluble pentosans (30%) (29). Wheat flour contains 2-3% of total pentosans of which 20-25% are readily soluble in cold water as water-soluble pentosans. Water-insoluble pentosans are found in the tailings fraction of flour (4, 70). Recently a small portion of pentosans was found with gluten (21).

Montgomery and Smith (52), and Medcalf and Gilles (51) reported that the building units of water-insoluble pentosans were similar to those of water-soluble pentosans. The main difference was that water-insoluble pentosans were less linear. Water-insoluble pentosans found in corn and oats hulls were similar to those in wheat bran (52). The water-insoluble pentosans, extracted with dilute alkali, from pericarp of corn are composed of arabinose, xylose, galactose, and glucuronic acid and form gummy solutions in water. The framework of corn pericarp water-insoluble pentosans, like that of wheat bran, is composed principally of 1,4-linked D-xylopyranose residues with L-arabinofuranosyl side chains.

Determination of Pentosan Content

Analytical methods for pentosan content are based on acid hydrolysis of pentosans to pentoses, dehydration of the pentoses to furfural, and determination of the furfural.

The most common acid used is 12% hydrochloric acid (HCl). However, Davidek et al. (23) decreased the analysis time 50% by substituting 20.3% (w/v) HCl for the normally used 12% (w/v). Bethge (10) claimed that substitution of hydrobromic acid for HCl eliminated the interference from hydroxymethylfurfural during colorimetry.

A volumetric bromine method was approved by the American Association of Cereal Chemists (A.A.C.C., 52-10) (1) using 12% HCl with distillation at 150°C. at a rate of 30 ml. per 10 min. The distilled furfural reacted with bromine and excess bromine was back-titrated with potassium iodide and thiosulfate. The reaction with bromine should be at 0°C. or lower to minimize the competition of methylfurfural with furfural to consume a second mole of bromine (36, 37).

The phenol-sulfuric acid method for polysaccharide determination was developed by Dubois et al. (25) and is commonly adopted due to its reproducibility and convenience. The phenol-sulfuric reagent forms a stable yellow-orange color with carbohydrates capable of being dehydrated to a furfural. Absorption is measured at 480 nm. for pentoses, uronic acids and at 490 nm. for furfural and hexoses.

An xylene-partition method, approved by A.A.C.C. (52-11) (1), involved the partition ratio of furfural in xylene and water (61). The furfural in a xylene extract was measured colorimetrically after reaction with aniline-acetate (1). The pink aniline-furfural color faded very rapidly under strong light sources. However, stability of aniline-furfural color was improved by use of a buffer solution prepared from stannous chloride, stannic chloride, and ammonium acetate in acetic acid. The buffer stabilized the color reaction for at least 45 min. (18). The influence of glucuronic acid and hydroxymethylfurfural on the absorbance was very small.

Hampl (32) and Hampl and Prihoda (33) determined pentosan content by polarography of furfural in a weak alkaline solution buffered at pH 7.5. Pentosans were hydrolyzed by distilling with 13.5% HCl. The distillate was neutralized with 30% NaOH (sodium hydroxide) and titrated with 0.2N NaOH potentiometrically to pH 7.5. Borate buffer (pH7.5) was added to this solution, and nitrogen was passed through the solution for 5 min. After 30 min., the sample was polarographed. The curve fell within the range of 1-1.8 volts.

Mathers and Beck (49) proposed a method for determining pentosans by measuring the absorption of the furfural solution at 277 nm. Only about 80-81% of the theoretical amount of furfural was recovered by distillation.

Fraser and Holmes (27) used an orcinol-iron reagent to react with a furfural solution and measured the absorption of the resulting compound at 670 nm. They suggested that the xylose equivalent of the sample analyzed multiplied by 0.97 gave a quantitative measurement of the pentosans present (28).

The official method approved by the Association of Official Agricultural Chemists (A.O.A.C.) for pentosans involved gravimetric determination of the furfural phloroglucide from reaction of furfural and phloroglucin (2).

Isolation of Water-Insoluble Pentosans

The first step in isolating water-insoluble pentosans involves removal of gluten, starch, and water-solubles from flour (21, 22, 47). This can be done by the dough process (56), by alkaline fractionation (5), or by extraction of flour with water followed by removal of gluten by solublization with dilute acetic, formic, lactic, oxalic or citric acid solutions (9). A batter method can be used for direct separation of tailings, gluten, and prime starch from flour. Yamazaki (70) washed the crude tailings over a 400-mesh stainless-steel sieve with distilled water to remove starch. After the solid residue was suspended in water and centrifuged, it deposited in two layers: the lower layer was prime starch and the upper layer was mucilaginous material, i.e., flour tailings which contained small starch granules, damaged starch, protein, and pentosans.

If isolation was started from whole grain, an intermediate layer, mostly bran powder and also rich in pentosans, was obtained in addition to the two layers described above (4).

Different methods have been utilized to extract pentosans from the pentosan-rich flour tailings fraction. Simpson (64) used pancreatin to remove protein and starch. Pancreatin, which contains both protolytic and amylolytic enzymes, can be used as an amylase at pH 7.4 and as a protease at pH 8 (50). After the enzyme digestion, an equal amount of 95% ethanol was added to precipitate the pancreatin product. The precipitate was isolated, washed with ethanol and ether, and dried under vacuum at 40°C. The pancreatin product was then suspended in oxygen-free 0.5N sodium hydroxide and stirred under nitrogen for 3 hrs. The mixture was filtered through cloth and neutralized with 50% acetic acid. Pentosans were precipitated with 2 volumes of 95% ethanol. Further purification was done by acetylation (52). After being dissolved in aceton, the solution was fractionally precipitated with petroleum ether (57). Four pentosan fractions were obtained and deacetylation was followed (53).

Cole (19) used alpha-amylase to remove starch from the tailings fraction of flour according to the procedure described by Kuendig et al. (44). Flour tailings were suspended in 0.02M phosphate buffer (pH 7.2) and alpha-amylase was added, followed by dialysis against phosphate buffer. The dialysate was extracted with 0.5N sodium hydroxide under nitrogen, followed by centrifugation. The supernatant solution was removed and neutralyzed. The pentosans were precipitated by adding ethanol

(4 volumes of absolute ethanol to 1 volume of polysaccharide solution). The precipitate was removed, dissolved in water, treated with alpha-amylase, and dialyzed once more by the procedure described above to remove any residual starch. After dialysis, the solution was concentrated. The water-insoluble pentosans were fractionated on a column of DEAE-cellulose in the borate form prepared according to a method proposed by Neukom et al. (55). The elution was accomplished stepwise with distilled water, sodium borate solutions, and 0.2M sodium hydroxide. The corresponding fractions were combined, evaporated to a volume of 100 ml., dialyzed against water and freeze-dried.

Cartano and Juliano (13) followed the method of Cole (19) with minor modifications. The protein in the solution after sodium hydroxide extraction was removed by adjusting pH to 3 with trichloroactic acid (TCA).

Jelaca and Hlynka (38) used amyloglucosidase to remove occluded starch from flour tailing, and then washed over a 400-mesh sieve, freeze-dried and finely ground.

Upton and Hester (68) were able to separate the tailings of flour into three subfractions by centrifugation. Compositions of the three subfractions were studied.

L-arabinose, D-xylose, D-glucose and traces of galactose are present in isolated pentosans. Ratios vary with the sources and methods used for isolation. D'Appolonia and MacArthur (22) reported that pentosans fractions with different viscosities and carbohydrate compositions could be obtained from

sludge using various methods of treatment. Most results showed that D-xylose and L-arabinose were the primary hydrolytic products from the pentosans isolated from flour tailings (13, 22, 38, 42, 51). The carbohydrate compositions reported are summarized in Table 1.

TABLE 1. CARBOHYDRATE COMPOSITION OF WATER-INSOLUBLE PENTOSANS

Source	Relative Ratio			Reference
	Arabinose	Xylose	Glucose	
Sorghum				
whole grain	1.56	1		(42)
endosperm	1.79	1		
pericarp	1.28	1		
Milled rice	1.09	1	0.35	(13)
Hard red spring wheat				
Canadian	0.64	1	0.10	(39)
No. 5 Canada Western	0.59	1	0.15	(39)
Selkirk	0.71	1	0.93	(50)
Durum				
2CWAD	0.68	1	0.19	(39)
Weel	0.83	1	0.50	(50)

Properties of Water-Insoluble Pentosans

Water-soluble and insoluble pentosans can absorb several times their dry weights of water. Yamazaki (70) found that purified tailings (pentosan content 30-65%) absorbed 10-16 times their weight of dilute bicarbonate solution. Sandstedt et al. (63) reported that crude tailing had a much greater water

absorption than the starch. Kulp and Bechtel (45) demonstrated the effect of pentosans on water-absorption utilizing the farinograph. They reported, when 1% of 55% water-insoluble pentosans were added to flour, the water absorption was raised 5.0 to 5.6% above that of the control flour, or 9.1 to 10.0% on the basis of pentosan content by constant-flour farinograph method. Using the constant-dough farinograph method, Jelaca and Hlynka (38) confirmed the results obtained by Kulp and Bechtel (45). They also reported that the water-insoluble pentosans absorbed eight times their weight of water.

When a dry mix of flour and freeze-dried pentosans fraction was tested on the farinograph, erratic and abnormal farinograms were obtained, indicating poor rehydration of pentosans. This difficulty was overcome by rehydrating the pentosans fraction overnight with a portion of water at refrigerator temperature. Kulp and Bechtel (45), and Jelaca and Hlynka (38) also found that mixing time and dough stability were affected by the addition of pentosans when these properties were compared at an equal consistency (500 Brabender Unit, B.U.). Without adjustment of the water absorption, pentosans increased the consistency from 500 to 700 B.U., and shortened the mixing time considerably.

Kulp and Bechtel (45) reported that there were no significant effects on the amylogram characteristics and on the extensimetric properties of doughs when wheat water-insoluble pentosans were added to the flour. Drews (24) reported that amylograms were dependent on the properties of pentosans,

alpha-amylase, and starch. Kulp and Bechtel (45, 46) concluded that the pentosans supported the flour-dough structure since they increased the water-carrying capacity of the dough without altering its physical properties. Also, pentosans did not cause any changes in gas evolution and retention.

Effects of Water-Insoluble Pentosans on Baking Performance

Casier and Soenen's (14) studies showed that addition of 1% water-insoluble rye pentosans to soft wheat dough considerably increased water absorption as well as resistance to kneading, and improved the dough stability. Addition of 1% of water-insoluble pentosans from soft wheat increased bread volume by 6% and improved crumb structure, color, and retention of freshness. This was contrary to results obtained by Kulp and Bechtel (45, 46) who reported that bread with added pentosans was inferior in volume, grain, and texture to control bread, and also lacked the characteristic silkiness.

Casier et al. (15,16) reported that addition of 2% of water-insoluble wheat or rye pentosans to European wheat flour or starch brought about better dough consistency and expansion as monitored by the farinograph and the alveograph. Pentosans could further improve bread size and bread quality, e.g., porosity, and excellence of crumb and crust and longer-lasting freshness.

Jelaca and Hlynka (39) reported that addition of 1% water-insoluble pentosans from Canadian hard red spring wheat (CHRS) to CHRS flour, decreased loaf volume. An increase

in loaf volume was observed when pentosans from durum wheat and a low-grade red spring wheat were added. In most instances, water-insoluble pentosans resulted in a deterioration of other loaf characteristics, e.g., texture, color, and coarseness of grain.

Effects of Tailings Fraction on Staling of Bread

Staling is a term which indicates decreasing consumer acceptance of bakery products due to progressive changes in the crumb, other than those resulting from spoilage of organisms. During staling there are changes in flavor, crumb firmness, texture, and mouth feel (7). This phenomenon could be considered as a partial redistribution of moisture between the principal components (69). When staling occurs, moisture moves from crumb to crust and results in soft, leathery crust (58)

A series of experiments with normal and decrusted bread was performed (11) to determine whether moisture migration from crumb to crust had any effect upon compressibility or crumbliness tests which were employed to follow the progress of crumb staling. Although moisture determinations revealed a loss of moisture from the normal crumb and a relatively constant moisture in the decrusted crumb, the rate and extent of changes in crumbliness and compressibility of the intact and decrusted bread were not appreciably different.

Similar work was done by Bechtel et al. (8). Besides the

physical laboratory tests described in the previous paragraph, sensory perception judgements of freshness of bread were made. Two batches of bread were prepared in the same way, except for the amount of water used in the dough which was adjusted so that one batch had a loaf moisture of approximately 38% and a crumb moisture slightly more than 2% higher than the other. After the same storage time, the bread of higher crumb moisture was judged to be definitely fresher than the bread 2% lower in crumb moisture. The physical tests had little significance as a measure of the bread staling process. During a period from 44 to 440 hours of storage, the sensory test panel did note an increasing difference in the freshness of bread with or without crust. Even though the physical tests revealed no difference in compressibility, crumbliness, and swelling power between the intact and decrusted crumbs, the sensory perception panel judged that the decrusted crumb was fresher. This revealed that the difference in moisture in crumb affected bread staling.

Bechtel and Meisner (6) found that the tailings fraction in flour, with its high moisture-sorbing capacity, permitted making bread of high moisture content. The bread was judged to be significantly fresher than bread of lower moisture content. Then, the tailings fraction may be of importance in the staling of bread.

EXPERIMENTAL - MATERIALS AND METHODS

Determination of Pentosan Content in Cereals

Various cereals including soft wheat and soft wheat shorts, hard red winter (HRW) wheat and HRW wheat shorts, barley, rye, oats, bulgur wheat, long-grain and medium-grain rice, red and white sorghum, African millets, yellow and white corn, and soy grits were used for analyzing the pentosan content.

The method for determination of pentosan content in cereals and cereal products reported by Cerning and Guilbot (18) was adopted. Steam distillation was performed on an apparatus developed by Duffau (26), which was connected with a Graham condenser (Fig. 1). The distillate was collected in a 250-ml. volumetric flask.

Sample (0.1 to 0.15 g.) was introduced into part 'a' of the distillation apparatus. Hydrochloric acid (30 ml. of 4.20N) was added into the same part to wash down particles adhering to the sides of the tubes, and then a glass stopper was inserted. The same acid (300 ml.) was introduced into part 'b'. The system was heated gently and regulated carefully so as to distill 250 ml. distillate into the volumetric flask within $1\frac{1}{4}$ to $1\frac{1}{2}$ hour. An aliquot (5 ml.) of the distillate, or distillate which had been diluted with HCl to give a furfural concentration of 40-120 µg/5 ml., was pipetted into a 50-ml. volumetric flask.

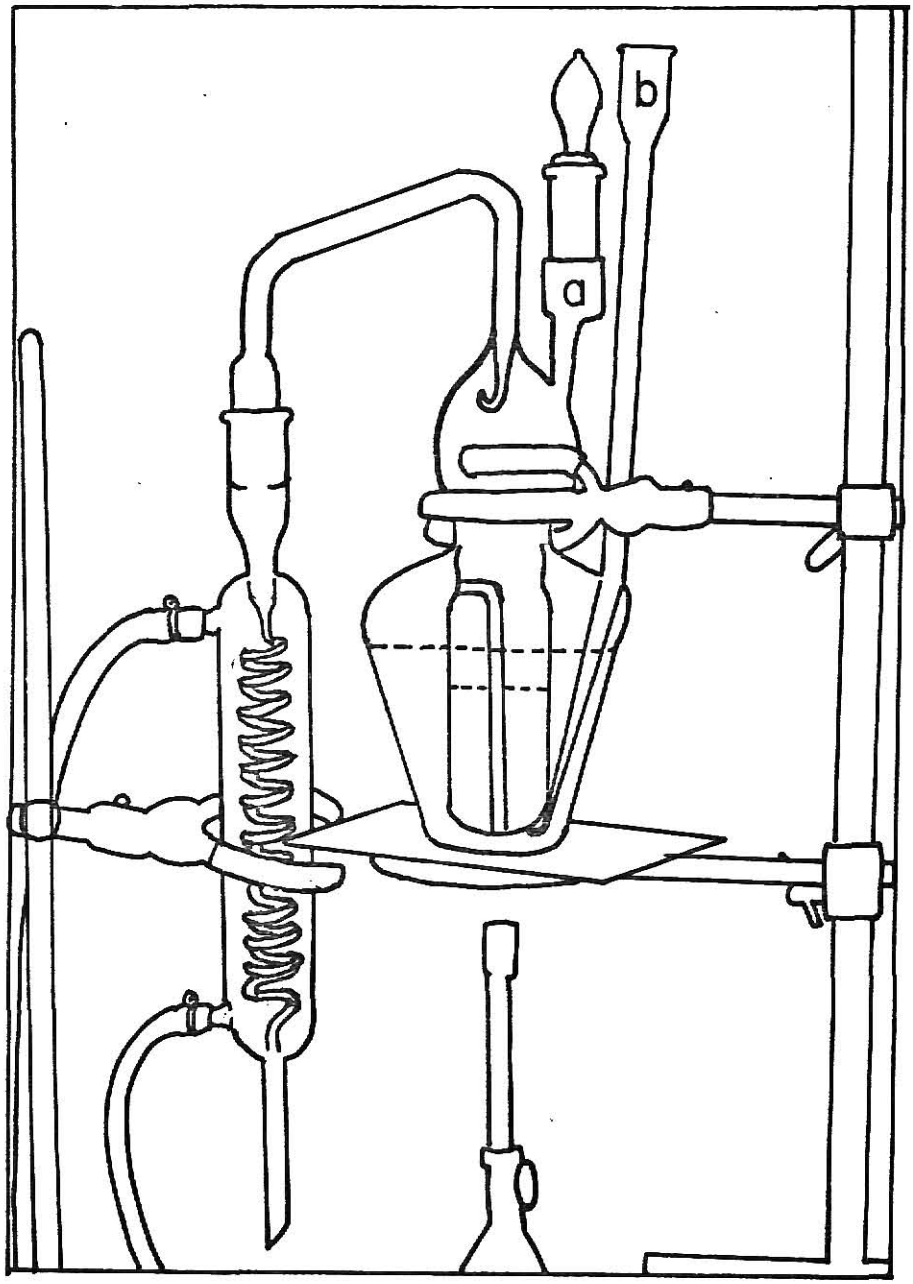


Fig.1. Apparatus for steam distillation

A buffered aniline reagent used to react with furfural. Aniline solution was prepared by diluting 5 ml. of freshly distilled aniline to 500 ml. with 95% ethanol. Buffer solution was made by dissolving 40 g. anhydrous ammonium acetate ($NH_4C_2H_3O_2$, Mallinckrodt Chemical Works, St. Louis, Mo.), 2.7 g. stannous chloride ($SnCl_2 \cdot 2H_2O$, General Chemical Division, Morristown, N. J.), and 4.2 g. stannic chloride ($SnCl_4 \cdot 5H_2O$, Baker Chemical Co., Phillipsburg, N. J.) in 133 ml. glacial acetic acid and diluting to 240 ml. with distilled water. One volume of buffer solution and two volumes of aniline solution were mixed just prior to use.

After 5 ml. of the distilled furfural solution was pipetted into a 50-ml. volumetric flask, the flask was filled to volume with aniline-buffer solution. The rose color was developed, while protecting the flask from sunlight, for exactly 45 min. at room temperature. The absorbance was determined at 530 nm.

A calibration curve was made by steam distilling 100 mg. of xylose in 4.20N HCl in the manner described above. The distillate was diluted 1/50, 1/25, 3/50 times to give a concentration of 8, 16, and 24 µg. xylose/ml, respectively.

Isolation of Water-Insoluble Pentosans

Water-insoluble pentosans were isolated from barley, rye, oats, and HRW wheat. A schematic diagram of the preparation and purification is shown in Fig. 2.

Dehulled rye, whole barley, oats, and HRW wheat (Proximate analyses are shown in Table 2) were ground in a pulverizer and separated on a sifter constructed with 20W, 34W, 50GG, 70GG, and pan for 2 min. The thrus from 20W sieve and overs from the 34W and 50GG sieves were collected for further separation of pentosans.

The overs were washed on a 340-mesh sieve to remove starch and water solubles as much as possible, followed by washing with water in a cloth bag until the water coming out was clear. The material was removed and oven dried at 50°C. Dry material (100 g.) was suspended in 3000 ml. 0.5N NaOH under nitrogen to minimize any possible oxidation that occurs during solubilization of water-insoluble pentosans in alkaline solution. After three hours at room temperature, the suspension was filtered through a cloth bag, squeezed dry by hand, the residue was extracted with 3000 ml. of 0.5N NaOH again. The filtrates were combined, neutralyzed with glacial acetic acid to pH 7, and heated to coagulate any precipitated protein. After cooling to room temperature, the solution was centrifuged (3000rpm, 5 min.). The precipitate was discarded.

TABLE 2. PROXIMATE ANALYSES OF HRW WHEAT, BARLEY, RYE, AND OATS USED FOR ISOLATION OF WATER-INSOLUBLE PENTOSANS

	Moisture %	Protein %	Fat %	Ash %	Fiber %
HRW Wheat	12.0	10.0	1.5	1.7	2.2
Barley	10.8	10.2	1.7	2.5	5.4
Rye	11.5	11.4	1.6	1.8	2.1
Oats	9.0	9.9	4.0	3.8	13.9

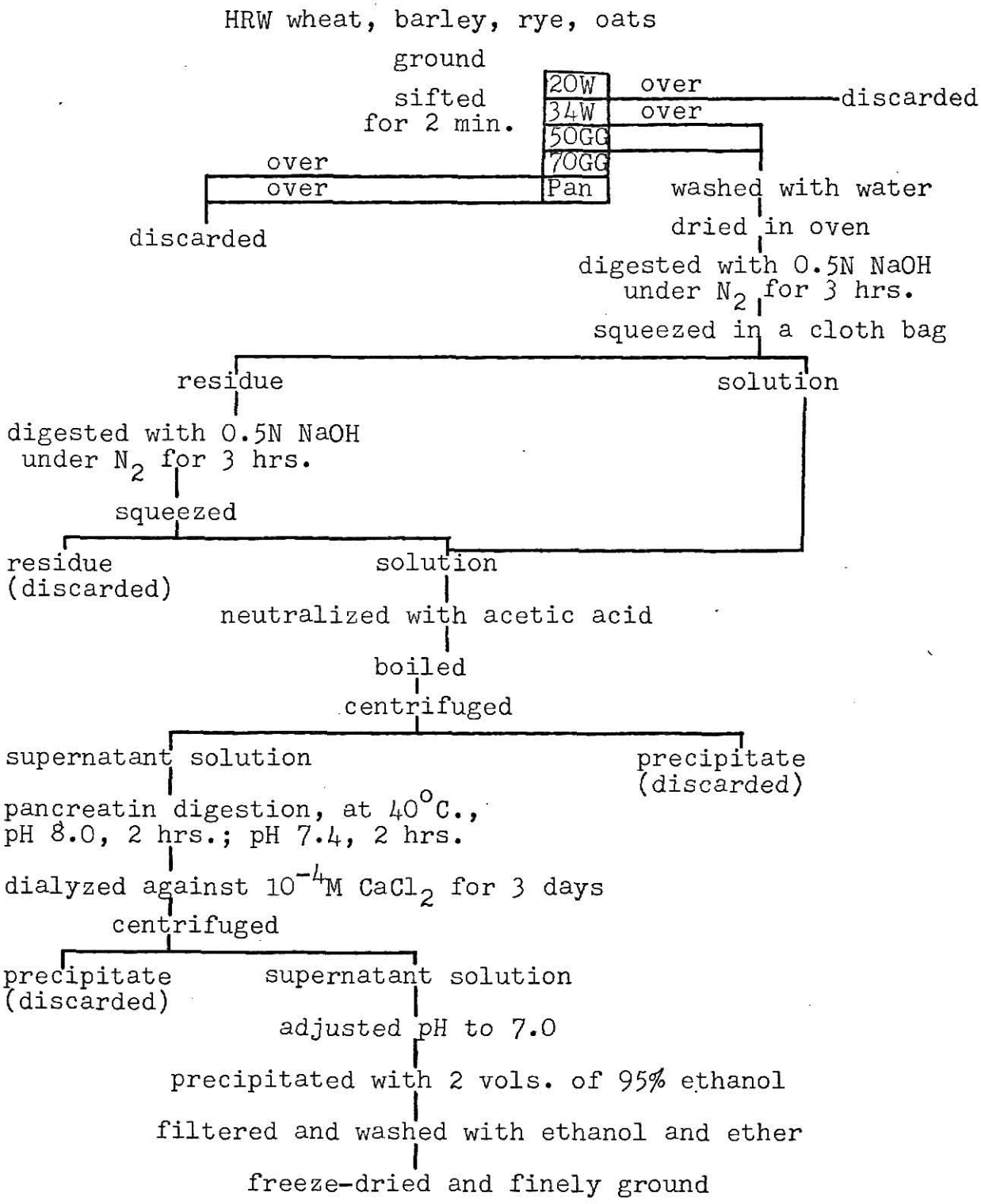


FIG. 2. PREPARATION AND PURIFICATION OF WATER-INSOLUBLE PENTOSANS

About 0.01% (w/v) pancreatin, previously dissolved in 0.01 M NaCl solution and clarified by filtering, and a few crystals of calcium chloride were added to the solution and the pH was adjusted to 8.0. After 2 hrs. digestion at 40°C., the solution was adjusted to pH 7.4 with diluted HCl solution, followed by another 2 hrs. digestion. The solution was then dialyzed at room temperature against 10^{-4}M calcium chloride for 3 days. Pentosans were recovered by precipitation with 2 volumes of 95% ethanol at 4°C. The precipitate was collected, filtered, washed (ethanol and ethyl ether), freeze-dried, and finely ground.

The following analyses were performed on the water-insoluble pentosans obtained: Moisture content by vacuum-oven method (1), protein content by micro-Kjeldahl method (1), ash content by a rapid method (1), pentosan content by the method by Cerning and Guilbot (18), and crude fat content by extraction with petroleum ether on a Goldfish extractor for 12 hours (2).

Freeze-dried samples (20 mg.) of the pentosans from wheat, rye, barley, and oats were weighed in glass tubes. After 5 ml. of 1N H_2SO_4 were added, the suspensions were stirred and placed in a beaker containing dry ice and methyl alcohol. The tubes were sealed after the sample had frozen and were placed in an oven at 110°C. for 24 hours. The sealed tubes were removed cooled, and opened. The solutions were neutralized with barium carbonate ($BaCO_3$) and desalted with AG 3-X4 resin (OH^-

form, Bio-Rad Laboratories, Richmond, Calif.). The resin and any precipitate were removed by centrifuging and filtering and were washed thoroughly with distilled water. The filtrates were dried in a vacuum oven at 40°C. Distilled water (2 ml.) was added to each dried sample and an aliquot of the solution was chromatographed on thin-layer plates.

Thin-layer plates were prepared as follows. Glass plates (20 x 20 cm.) were coated with a 250-μ layer of silica gel G in 0.1M sodium dihydrogen phosphate buffer (pH 5). The plates were dried in oven at 110°C. for 30 min. The plates were allowed to cool to 50 to 60°C. and transferred to a desiccator. The solvent used for one-dimensional ascending chromatography was a mixture of n-butyl alcohol-acetone-phosphate buffer (pH 5) (40:50:10 v/v/v) (71). The chromatographic chamber was lined with filter paper to insure saturation with solvent vapor. The solvent was allowed to advance 16.5 cm. above the base line before the plates were removed and air dried. Spots were visualized by spraying the plate with concentrated sulfuric acid, followed by heating the plate at 150°C. for 5 to 10 min.

A densitometer (Photovolt multiplier photometer, Model 520-A) with a scanning stage (Model 52-C) and variable response recorder (Varicord Model 42-B) (Photovolt Corp., N. Y.) was used to quantitatively measure the sugars separated by thin-layer chromatograph. Peak areas on the recording chart were measured by weights of the paper under the peak.

Areas were converted to the weights of sugar components using a linear regression equation of the corresponding standard compounds.

Each standard (8 to 40 ug. of D-xylose, L-arabinose, D-glucose, or D-galactose) was spotted to give six spots on the plate. Peak areas were measured as described above, and a linear regression of peak area and weight of sugar spotted was drawn.

Physical Dough Tests

Commercial wheat flour was used throughout these studies. The flour contained 13.2% moisture, 11.9% protein, and 0.44% ash. Water-insoluble pentosans isolated from wheat, barley, rye, and oats were used in varying amounts to replace the flour. Their water-absorption, effects on resistance, extensibility, and ratio of resistance to extension were studied.

Water absorption was measured for each sample on a Brabender farinograph (C.W. Brabender Instruments Inc., South Hackensack, N. J.) using a 50-g. bowl and the constant-dough weight method described by A.A.C.C. (1) on a 14% moisture basis. Titration was conducted with a small buret to give a consistency of 500 Brabender Units (B.U.) at maximum, i.e., at maximum consistency, the center of the curve reached the 500-B.U. line. Flour and pentosans were mixed for five min. before titration with water. Addition of water was completed within 25 sec. after opening the buret stopcock. The farinograph was

operated until the top of the curve again crossed the 500-B.U. line after attaining peak consistency. The increase in water-absorption in the presence of added water-insoluble pentosans was considered to be the water absorption of the added pentosans.

The extensigraph (Extensimeter, C.W. Brabender Instrument Inc., South Hackensack, N. J.) was operated according to A.A.C.C. Method (1) using 300 g. of flour and 6-g. of salt. The salt was dissolved in part of the water prior to addition. The amount of water used was equal to farinograph absorption, less roughly 2% to compensate for the effect of salt. Dough was mixed 1 minute, rested 5 min. and mixing resumed to full development time according to the farinograph. Water absorption was corrected to give 500-B.U. consistency at the maximum.

When mixing was completed, 150.0 ± 0.1 g. of dough was scaled off, rounded and shaped. Then the dough was clamped tightly in a greased dough holder and stored on the dough holder in a humidified chamber until required for testing.

The first stretching operation was performed exactly 45 min. from the end of shaping. The stretching hook was stopped when the test piece was broken. Dough was removed from the holder, reshaped, allowed another 45-minute rest, and then stretched again. The third test on the same dough was performed after another 45-minute rest as described above.

Four measurements were made on each extensigram:

resistances to extension (heights of curve, in cm., at 5 cm. extension on the kymograph chart and at maximum extension), extensibility (total length of curve in cm.), and area under curve (sq. cm.). The ratio of resistance at-5cm. extension to extensibility was calculated.

Baking Process

Commercial flour was used for making bread. Isolated water-insoluble pentosans from wheat, barley, rye, and oats were added (1 and 2%) to replace flour. Pretreatment of isolated freeze-dried pentosans (rehydrated with part of the water and kept in refrigerator overnight) was employed to avoid the probable occurrence of under- or over-mixing of dough.

The following baking formula was employed (67).

	gram	flour basis (%)
flour (14% m.b.)	400.0	100
water	variable	variable
yeast	12.0	3.0
salt	8.0	2.0
granulated sugar	20.0	5.0
bromate	90 ppm	---

Two level of water were added to prepare pentosan-supplemented bread. In batch 1, the amount of water used was the same as that used for the control bread, i.e., 100% flour. In batch 2, the optimum amount of water measured from the

farinograph was added. To prepare the control bread, an optimum amount of water was used.

All ingredients were combined at room temperature in a vertical mixer, with a MacDuffee-type bowl and fork, and were mixed at first speed (low)for 1 min. and then at second speed (medium) to optimum dough development. The dough was scaled into 125-g. pieces, rounded, and rested for 40 min. at 86°F. and 85% relative humidity (R.H.) in a fermentation cabinet. The pieces of dough were then molded in a moulder (Moline Company, Duluth, Minn.) with the first press at 15 cm., second press at 0.5 cm., and board height at 1.8 cm. The dough was panned and proofed at 96°F. and 92% R.H. in a proofing cabinet to a height of 1.5 cm. over the pan. Pup loaves were baked at 425°F. for 20 min.

Loaf volume was measured by rapeseed displacement immediately after the loaf was removed from oven. The weight was also determined to calculate specific volume.

Staling Test

The staling test was performed 2 hrs. after the bread had been removed from the oven and after storage at 30°C. for 1, 2, 3, and 4 days. Two central pieces, each 1-inch thick, were sliced and used for the test.

A freshly cut slice of bread was placed on the platform of a Bloom Gelometer (Precision Scientific Co., Chicago, Ill.)

which can be vertically adjusted so that the slice just touched the bottom surface of plunger. Lead shot was then released into a cup that depressed the plunger into the slice. The degree of crumb firmness was expressed in terms of the weight of shot required to compress the slice by 4 mm.

After measurement of the degree of crumb firmness, the crust was removed from one of the two slices. Both slices (with and without crust) were then weighed, using a scale sensitive to at least 0.2 g. Their moisture contents were determined by a 2-stage air-oven method (1) and calculated using the following equation:

$$T.M. = A + \frac{(100 - A)\ B}{100}$$

where T.M. = % total moisture;

A = % moisture lost in air-drying; and

B = % moisture in air-dried sample as determined by oven-drying.

RESULTS AND DISCUSSION

Determination of Pentosan Content of Cereals

The pentosan contents of various cereals are shown in Table 3. The method by Cerning and Guilbot (18) was adopted due to its accuracy in determining pentosan content. Aniline should be distilled at 184°C. and stored at 4°C. in a brown bottle protected from light. In this way, aniline could be kept for about 6 months without the necessity of redistillation. The buffer should be prepared just prior to use since there was no way to keep it without changing its color. The buffer turned light yellow about one hour after preparation. It was necessary to check the amount of time required to reach maximum absorbance. The maximum color development was reached within 30 to 50 min. Although the resultant rose color was easily destroyed by sunlight, the effect of laboratory light on the color was found to be minor.

Pentosan contents reported by other investigators were 3.72% in sorghum (41), 8.03% in rye (31), 3.06-3.31% in barley (62). The inconsistency between the reported values and the results obtained in this study was attributed to the different methods or treatment used. Salum and Rukosuer (62) reported that water-heat treatment could reduce the pentosan content, where Bulgokov (12) claimed that pretreatment with water increased the amount of furfural formed after hydrolysis in hydrochloric acid.

TABLE 3. PENTOSAN CONTENTS OF CEREALS

Cereal	Pentosan Content(%)[a]	Cereal	Pentosan Content (%)[a]
HRW wheat	6.73	Long-grain rice	5.11
HRW wheat shorts	19.02	Medium-grain rice	5.05
Soft wheat	6.12	Red sorghum	2.94
Soft wheat shorts	19.66	White sorghum	3.04
Barley	11.42	African millets	3.80
Rye	9.30	Yellow corn	4.91
Oats	12.21	White corn	4.08
Bulgur wheat	7.96	Soy grits	5.04

[a] Values are averages of duplicate or triplicate analyses and reported on a dry basis.

Isolation of Water-Insoluble Pentosans from HRW Wheat, Barley, Rye, and Oats

The proximate analyses and carbohydrate compositions of water-insoluble pentosans isolated from HRW Wheat, barley, rye, and oats are shown in Tables 4 and 5, respectively.

Water-insoluble pentosans were weighed after freeze-drying to calculate the yield. Average yields (Table 4), based on the amount of grain used, were 1.20%, 1.04%, 0.69%, and 1.31% for pentosans from wheat, barley, rye, and oats, respectively. If based on the "overs" from the 34W and 50GG sieves and "thrus" from 20W sieve after two minutes sifting, the yields would be 9.86% for wheat, 8.35% for barley, 6.24% for rye, and 7.55% for oats. The "overs" were mainly bran and shorts. When yields (6.24 to 9.86%) were compared with the pentosan content in bran (29), only 1/4 to 1/3 of the pentosans were actually isolated and purified. The rest remained in the bran and were difficult to extract even with prolonged extraction.

Oats pentosans were lowest in protein content (Table 4) and highest in pentosans while wheat pentosans were highest in protein and lowest in pentosans. The material used for isolation of oats pentosans was partly husk and oats dust. Oats dust contains about 16% by weight of groat hairs, 11% of husk fragments, and about 10% of proteins (43). Containing about 16.4% protein, wheat shorts is richer in protein than oats dust. The protein contents are 11.8-14.9% in barley bran and dust

and 15.0-17.8% in rye bran (43). Therefore, the protein contents of isolated pentosans were dependent on the materials used for isolation.

The carbohydrate compositions of pentosans varied with the sources. There was a trace of galactose present in barley and oats pentosans, but no galactose found in HRW wheat and rye pentosans. Oats pentosans were high in xylose content and barley pentosans were high in glucose.

TABLE 4. PROXIMATE ANALYSES AND YIELDS OF WATER-INSOLUBLE PENTOSANS ISOLATED FROM HRW WHEAT, BARLEY, RYE, AND OATS

Source	Yield[a] %	Moisture %	Protein[b] %	Fat %	Ash %	Pentosan %
HRW wheat	1.20	7.79	9.23	0.30	2.01	62.80
Barley	1.04	9.36	6.51	0.24	2.32	64.92
Rye	0.69	8.32	6.08	0.35	2.23	65.46
Oats	1.31	8.64	3.69	0.31	3.49	74.84

[a] Yield based on the weight of grain used

[b] N x 5.7 = Protein

TABLE 5. CARBOHYDRATE COMPOSITION OF WATER-INSOLUBLE PENTOSANS ISOLATED FROM HRW WHEAT, BARLEY, RYE, AND OATS

Source	Relative Ratio		
	Arabinose	: Xylose	: Glucose
HRW wheat	0.95	: 1	: 1.28
Barley	0.42	: 1	: 0.95[a]
Rye	0.60	: 1	: 1.10
Oats	0.17	: 1	: 0.21[a]

[a] Traces of galactose

Effect of Water-Insoluble Pentosans on Farinographic Properties

Farinograms with or without added water-insoluble pentosans are shown in Figure 3. The farinographic properties are summarized in Table 6.

Addition of water-insoluble pentosans to flour resulted in changing the farinographic dough properties. Arrival times and developing times were increased and departure times were decreased. The longer arrival times into a homogeneous mass due to the high water absorption and slow hydration rate of freeze-dried water-insoluble pentosans. A longer time was required to form the maximum gluten network due to the retarding effect of pentosans on the formation of dough structure. Dough stability was reduced by adding pentosans. As more pentosans were added, dough stability was reduced in most instances. The tolerance index was not greatly affected; when more than 3% of wheat pentosans were added, the tolerance index was increased to 80 B.U./5 min. This showed that the dough could not tolerate over-mixing.

Water-insoluble pentosans from HRW wheat absorbed 5.24 to 6.48 times their dry weight of water. Barley pentosans absorbed 6.49 to 10.04; rye pentosans, 7.68 to 8.40; and oats pentosans, 5.33 to 5.92 times their dry weights of water. With increasing amounts of pentosans added, the protein content of the flours was reduced, which in turn indicates that the water absorption of the flour itself was reduced. This explained why water

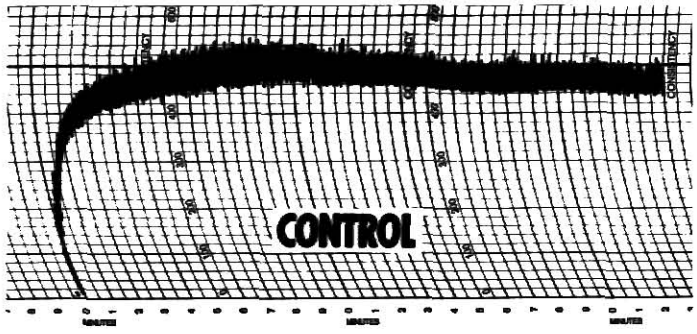
absorption did not increase linearly with the amount of pentosans added.

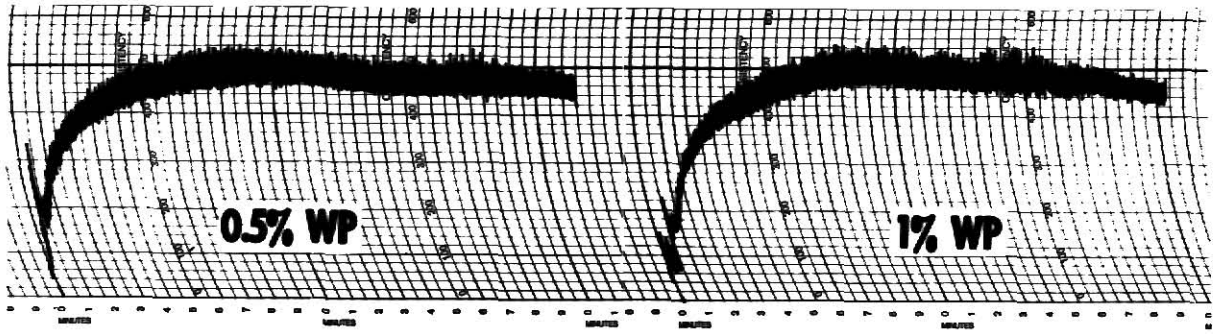
The results can be summarized as follows. Barley pentosans were superior in water absorption, followed by rye pentosans. Oats pentosans absorbed the least amount of water. In this study, 1% of isolated wheat pentosans which contained 62.8% pentosans were found to raise the absorption 6.48% above that of the control flour on a dry basis, or 10.3% on the basis of pentosan content. The corresponding increases for barley, rye, and oats pentosans were 9.59%, 8.40%, and 5.91% on a dry weight basis, respectively, and 14.87%, 12.83%, and 7.90% on the basis of pentosan content, respectively.

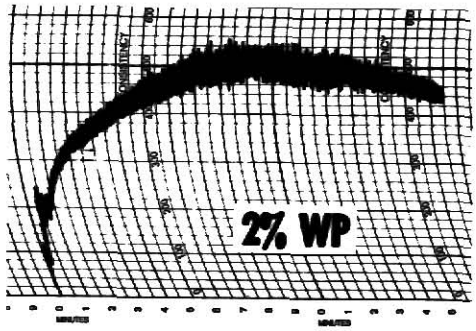
FIG. 3. FARINOGRAMS OF DOUGH PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE(RP), AND OATS (OP).

FARINOGRAPH

WATER INSOLUBLE PENTOSANS







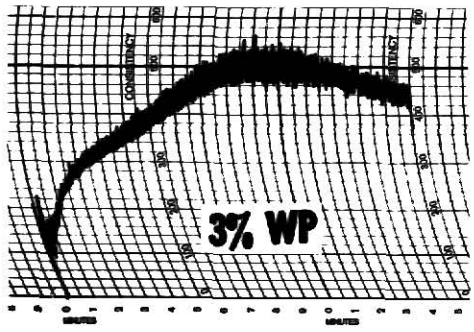
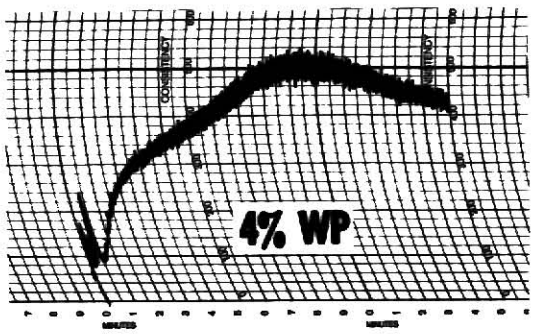
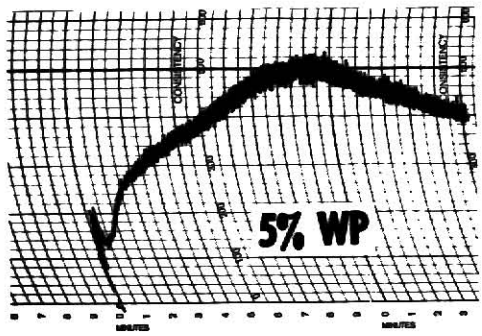
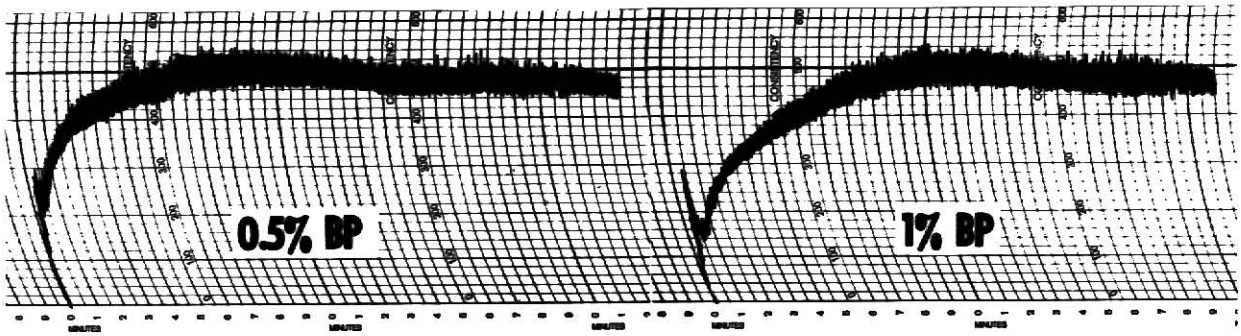
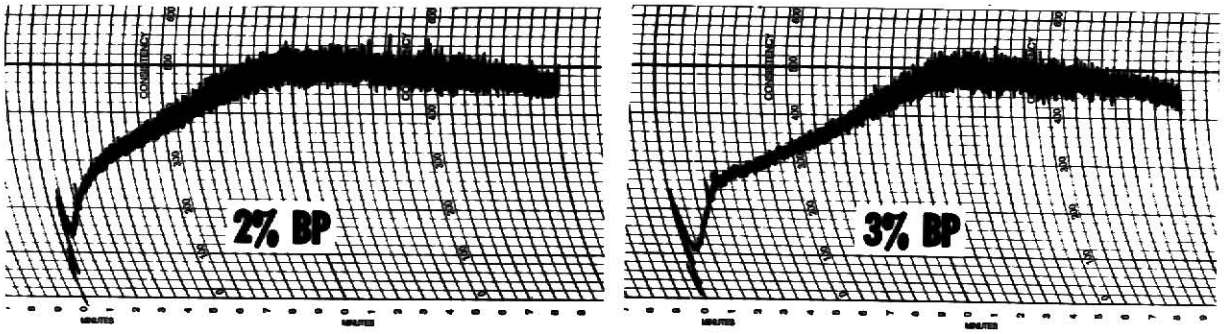


FIG. 3. FARINOGRAMS OF DOUGH PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP) (CONTINUED).


4% WP


5% WP


0.5% BP
1% BP


2% BP
3% BP

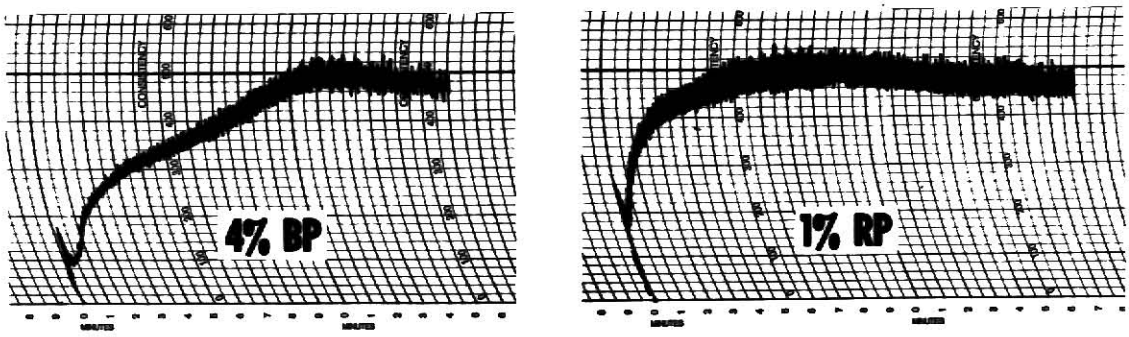
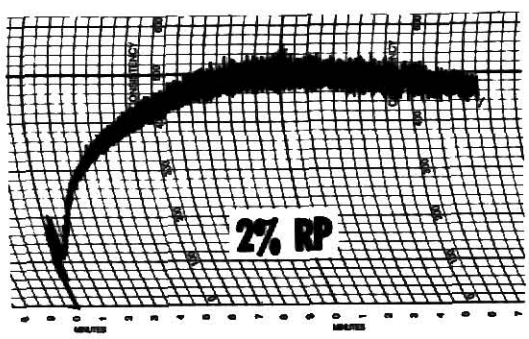
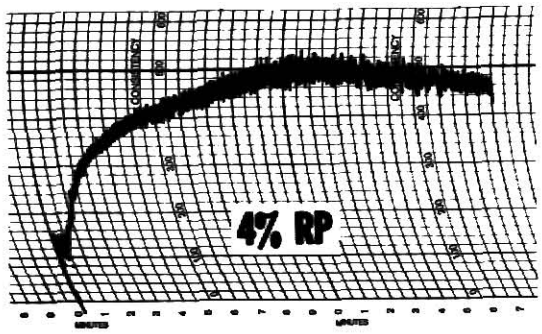
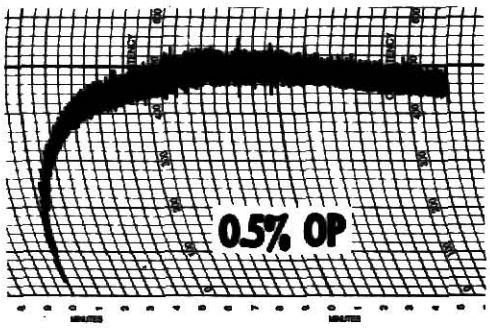
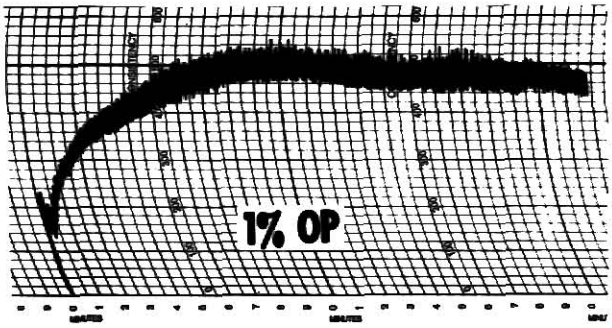

4% BP
1% RP

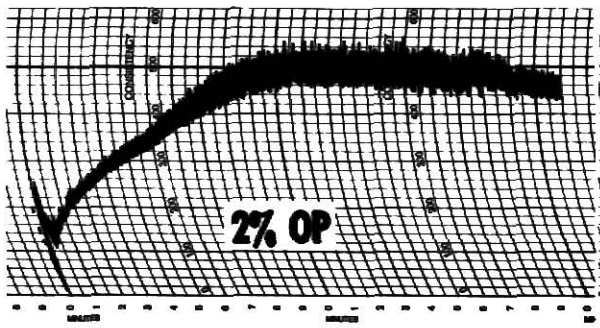
FIG. 3. FARINOGRAMS OF DOUGH PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP). (CONTINUED)


2% RP


4% RP


0.5% OP


1% OP


2% OP

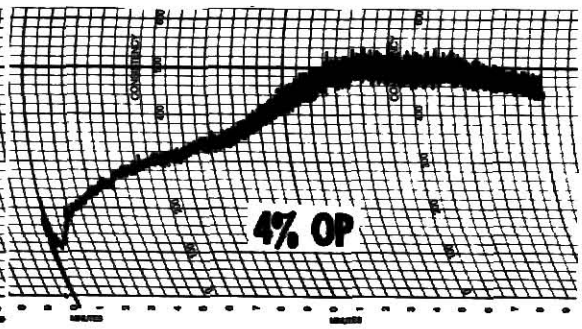

4% OP

TABLE 6. FARINOGRAPHIC PROPERTIES OF DOUGHS PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS ISOLATED FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP)

	Water Absorption %	Arrival Time min.	Developing Time min.	Departure Time min.	Dough Stability min.	Tolerance Index B.U./5 min	Increase in Water Absorption[a] %/g.
100% Wheat flour	68.6	4.25	8.75	21.0	16.75	20	
0.5% WP	70.6	5.50	8.25	19.5	14.0	26	6.37
1% WP	72.7	5.5	8.50	18.0	12.5	24	6.48
2% WP	76.1	6.0	8.50	14.25	7.75	32	5.92
3% WP	79.6	7.25	9.0	12.25	5.0	80	5.78
4% WP	84.3	7.75	9.5	12.0	4.25	80	5.74
5% WP	85.2	7.5	9.0	10.25	2.75	100	5.24
0.5% BP	72.0	4.5	9.0	21.5	17.0	25	10.04
1% BP	75.1	7.5	11.75	20.75	13.25	30	9.59
2% BP	79.6	8.0	11.5	18.75	10.75	25	8.10

[a] Compared to control (100% wheat flour)

TABLE 6. FARINOGRAPHIC PROPERTIES OF DOUGHS PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS ISOLATED FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP) (CONTINUED)

	Water Absorption %	Arrival Time min.	Developing Time min.	Departure Time min.	Dough Stability min.	Tolerance Index B.U./5 min.	Increase in Water Absorption[a] %/g.
3% BP	84.6	10.0	11.75	17.25	7.25	34	7.88
4% BP	87.4	10.0	11.5	14.0	4.0	30	6.94
1% RP	74.1	4.5	8.75	17.0	12.5	30	8.40
2% RP	79.6	6.5	10.0	17.0	10.5	24	8.40
4% RP	88.7	8.75	10.25	15.5	6.75	22	7.6
0.5% OP	70.5	5.25	7.25	15.0	9.75	22	5.92
1% OP	73.2	6.0	10.25	20.0	14.0	26	5.91
2% OP	76.9	8.25	12.0	19.5	11.25	18	5.33
4% OP	84.6	11.0	13.0	18.5	7.5	32	5.77

[a] Compared to control (100% wheat flour)

Effect of Water-Insoluble Pentosans on Extensimetric Properties

Extensigrams with or without added water-insoluble pentosans are shown in Figures 4 and 5. The extensimetric properties are summarized in Table 7.

Two measurements of resistance to stretching were taken from the extensigrams: maximum height of the curve in Brabender Units, and the height of the curve after 5 cm. of stretching. In most instances, the higher the maximum resistance, the higher the resistance at 5-cm. extension.

Measurement of resistance at constant dough extension was selected instead of measurement of maximum resistance, since the lengths of extension of two identical dough pieces occasionally were different due to differences in dimensions of the test samples. In such instances, the maximum may be shifted over a wide range of extensibilities (34).

The control dough had the highest maximum resistance and resistance at 5-cm. extension.

There were significant differences when the extensibilities of the control dough were compared with those of the pentosans-supplemented dough. However, lower extensibilities were found for the dough supplemented with 2% barley pentosans.

The area under the curve indicates the total force used in stretching the dough. It is difficult to characterize doughs by simply comparing the area under the curve. There are

occasions when doughs with quite different characteristics give the same area. For example, one dough might be very resistant to stretching with short extensibility, while another might be very extensible with little resistance.

The extensigram of the control dough had the largest area under the curve. The area under curve decreased with the amount of pentosans added.

The ratio of resistance at 5-cm. extension to extensibility (designated as ratio) was used to eliminate confusion encountered when using the area under the curve. A flour with greater resistance to stretching would have a high ratio value, while one with little resistance would have a low ratio value. Combined with the area under the curve, the ratio indicates distinctly the stability of the dough during fermentation. Flours with low ratio values are mostly very extensible, considering their resistance to stretching, and their doughs, on fermenting, quickly become soft and flowy. This kind of dough is also weak, slack and not machinable. If the ratio is too high, it indicates that the resistance to stretching compared with extensibility is too great and, on fermenting, the dough tends to be tough, resistant, and difficult to machine (65).

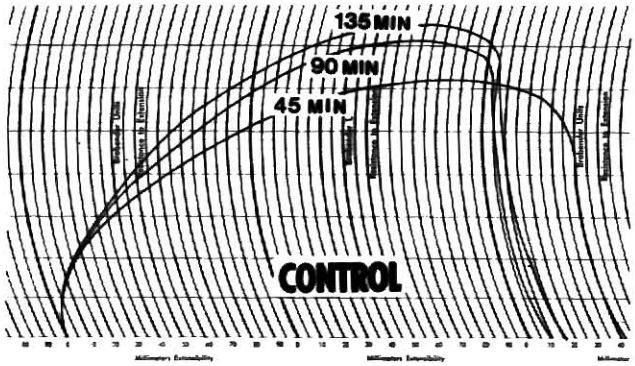
In this experiment the control dough had highest ratio, with one exception. In general the addition of pentosans made the doughs slack, weak and sticky. Doughs containing oats

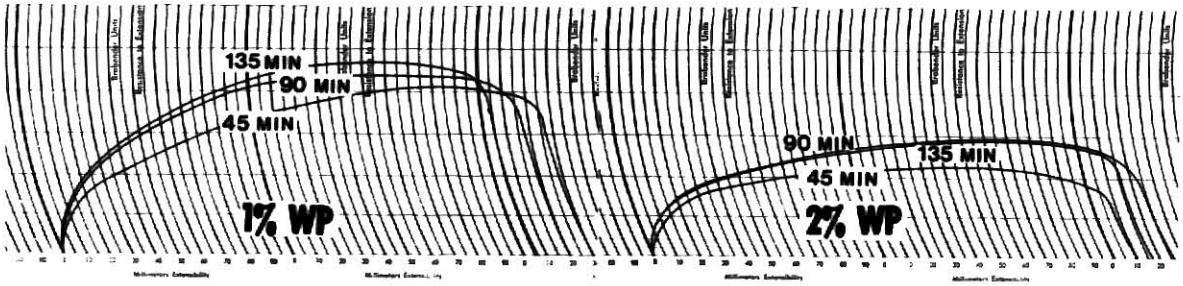
pentosans were high in maximum resistance and extensibility and relatively low in resistance at 5-cm. extension. These observations indicated that oats pentosans reduced the resistance of the dough to stretching, and, at the same time, made the dough more extensible. Differences in the effects of adding pentosans from wheat, barley, and rye were not marked. However, the pentosans did lower the ratio and made the dough difficult to handle. The doughs were slightly sticky and weak as judged by "hand feeling". Addition of 2% of wheat pentosans produced very different extensigrams; the dough had the lowest resistances, areas under curve and ratio values.

FIG. 4. EXTENSIGRAMS OF DOUGH PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP) AND BARLEY (BP).

EXTENSIGRAPH

WATER INSOLUBLE PENTOSANS





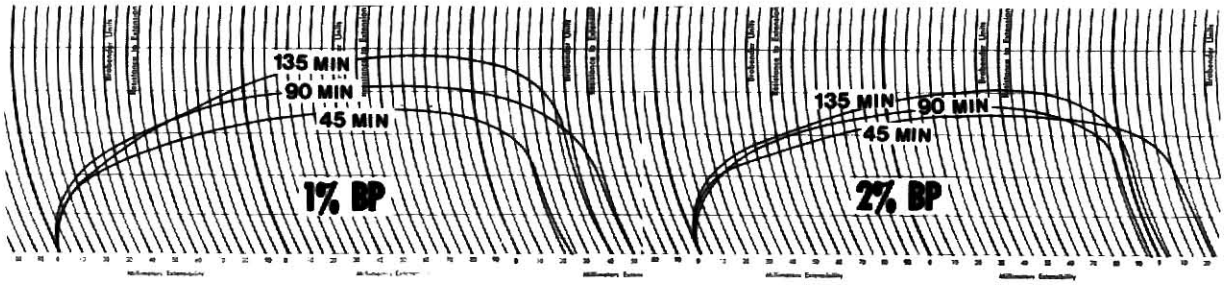
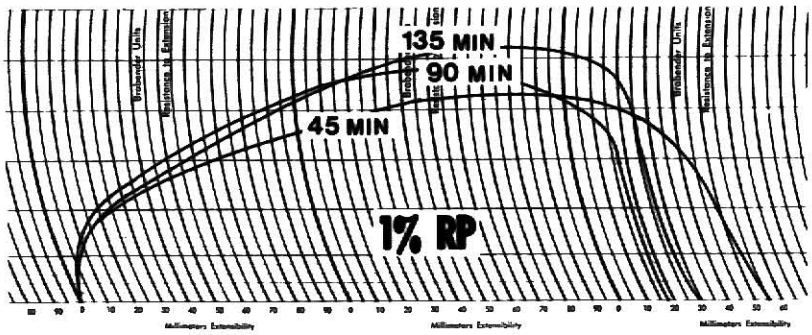
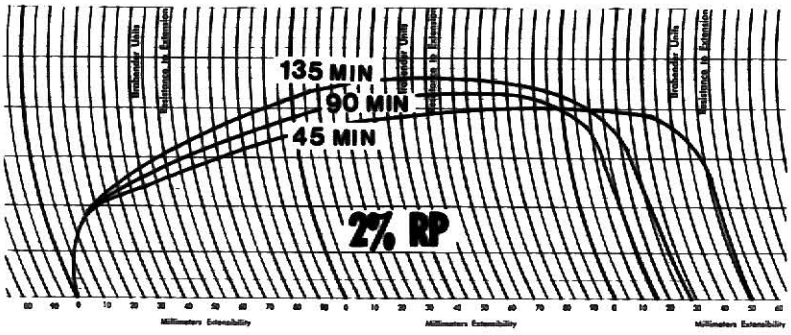
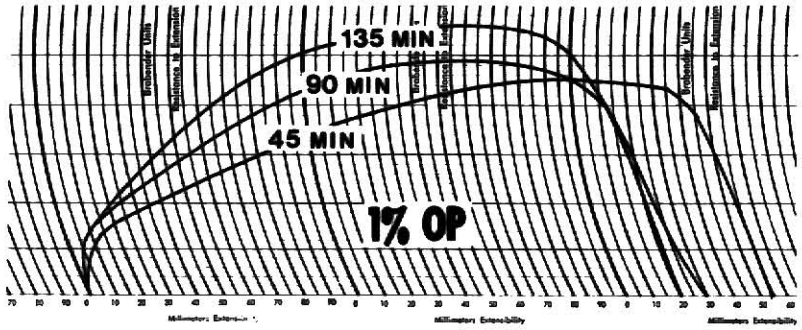


FIG. 5. EXTENSIGRAMS OF DOUGHS PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM RYE (RP), AND OATS (OP).


135 MIN
90 MIN
45 MIN
1% RP


135 MIN
90 MIN
45 MIN
2% RP


135 MIN
90 MIN
45 MIN
1% OP

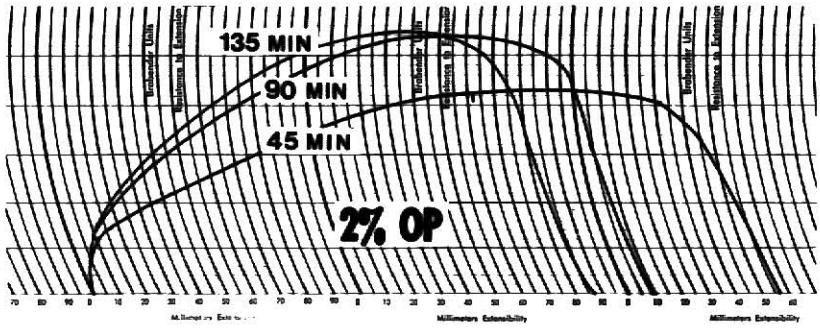

135 MIN
90 MIN
45 MIN
2% OP

TABLE 7. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP) ON THE EXTENSIMETRIC PROPERTIES OF FLOUR DOUGH

	Maximum Resistance B.U.			Extensibility mm.			Area Under Curve cm^2			Resistance at 5-cm Extn. B.U.			Resistance at 5-cm Extensibility B.U./mm.		
	Rest Period min.			Rest Period min.			Rest Period min.			Rest Period min.			Rest Period min.		
	45	90	135	45	90	135	45	90	135	45	90	135	45	90	135
100% Wheat flour	620	710	750	242	210	218	203.5	197.8	215.7	350	388	410	1.45	1.65	1.90
1% WP	400	434	460	229	220	207	124.5	127.1	130.3	238	290	320	2.04	1.32	1.46
2% WP	250	240	195	240	211	231	85.1	74.3	65.5	155	172	146	0.65	0.82	0.63
1% BP	345	398	480	223	250	241	110.1	144.1	157.8	240	288	272	1.08	1.15	1.13
2% BP	350	360	404	219	197	209	111.6	104.8	120.0	260	282	292	1.19	1.43	1.40
1% RP	424	470	516	256	218	230	147.5	143.0	159.0	260	300	280	1.02	1.38	1.22
2% RP	400	426	456	249	219	228	143.6	128.3	145.4	252	280	300	1.01	1.28	1.32
1% OP	450	484	558	253	228	219	149.6	148.3	165.4	220	284	334	0.87	1.25	1.53
2% OP	428	535	540	255	208	191	145.6	146.3	132.2	230	312	322	0.90	1.50	1.69

Effects of Water-Insoluble Pentosans on Baking Performance

Breads were prepared from flour, with or without added pentosans, at different absorptions. Water absorption of batch 1 pentosan breads was the same as that of the control bread. The control bread and batch 2 pentosan breads were prepared with an optimum amount of water measured from farinograph.

Specific loaf volumes of breads prepared with constant water absorption or with optimum water absorption are shown in Tables 8 and 9, respectively. Batch 1 bread containing 1% pentosans showed an increase in specific volume over that of the control bread. When 2% of pentosans were added, the breads were smaller than the control bread and specific volumes were reduced. Only the bread with 2% oats pentosans showed an increase in specific volume over the control bread, but its specific volume was less than that of bread with 1% oats pentosans.

In batch 2, the specific volumes of breads containing wheat and barley pentosans decreased with the increasing amounts of the pentosans. The oats and rye pentosans improved the specific volumes of breads. It is likely that further additions of the pentosans to the flour would tend to reduce the specific volumes and finally might decrease the specific volumes below that of the control bread. Although the

addition of pentosans up to 2% improved the bread volume, bread containing added pentosans was coarser in grain, darker in color, and lacked silkiness. The rehydrated pentosans were brown in color; therefore, they gave the bread a dark color somewhat like that of whole wheat bread. The darkness of bread increased as more pentosans were added.

Comparing breads containing equal amounts of added pentosans, batch 1 breads had lower specific volume than those in batch 2. In batch 1 breads, the amount of water supplied for flour hydration was less than optimum, while, in batch 2 bread, the optimum amounts of water were used. When the optimum amount of water is used, the physical conditions of the dough were at an optimum and, consequently, the loaf expanded to its maximum volume.

The increase in specific volumes of the breads, when up to 2% of water-insoluble pentosans were added, might be due to a binding between pentosans and gluten similar to the binding between water-soluble pentosans and gluten suggested by Cawley, (17), Jelaca and Hlynka (39), Johansson et al. (40), and Geissmann and Neukom (73). When larger amounts of pentosans were added, more 'free' pentosans were present which might become an obstacle to the formation of the gluten network.

Moisture contents of whole bread and crumb during four days of storage are shown in Tables 10 and 11. There were no marked differences in moisture contents between batch 1 breads and the control bread. However, batch 1 breads were generally

lower in moisture content by 1 or 2% than batch 2 breads. Less water was added when preparing the doughs for the batch 1 breads. Therefore, baked under the same conditions, the bread was lower in moisture content. This is consistent with results reported by Bechtel et al. (8) who prepared breads differing in crumb moisture by adjusting the amounts of water used in the doughs. The moisture contents of the crumb of batch 2 breads were raised with increasing addition of water-insoluble pentosans (1 or 2%).

The degree of crumb firmness as a function of storage time is shown in Tables 12 and 13. The degree of crumb firmness is one measure of the freshness of bread; the bread with softer crumb is usually judged to be fresher.

The crumb of batch 1 bread supplemented with 1% pentosans was found to be softer than that of the control bread at all storage times. In batch 1 breads, crumb firmness increased with increasing amounts of added pentosans. The relationship between crumb firmness and the amount of pentosans added (Tables 10, 11, 12, and 13) revealed that crumb could be softened by adding a suitable amount of pentosans. The degree of crumb firmness of bread varied with the source of the pentosans. Bread containing 1% oats pentosans was lower in crumb firmness, followed by those containing 1% wheat, rye, and barley pentosans in that order (see Table 12). Interestingly, the order matched the water absorptions. As previously

described, the water absorptions for wheat, barley, rye, and oats pentosans were 6.48, 9.59, 8.40, and 5.91 times their weights of water, respectively. These observations can be explained as follows. If breads were prepared with a constant amount of water, the amount of water available for flour hydration was less when the added pentosans were themselves higher in water absorption. Consequently, the crumb of the resultant bread was toughened.

The crumb firmness of pentosan-containing bread was further improved when an optimum amount of water was used in preparing the dough. Bread containing wheat pentosans had the softest crumb, followed by that containing barley pentosans. There was no strict relationship observed between crumb firmness and water absorption of the pentosans. Differences in the crumb firmness were therefore not due to the water absorptions of the pentosans, but due to the pentosans themselves. The marked differences in crumb firmness may result from characteristic differences in the isolated pentosans and the actual amounts of pentosans present in the isolated pentosans.

Tables 10 through 13 revealed that the higher the moisture content in the crumb, the lower the crumb firmness. The results are consistent with results reported by Bechtel and Meisner (7). They concluded that differences in crumb moisture had a marked effect on the apparent freshness of bread and bread with high crumb moisture was judged to be one day fresher than bread with low moisture content.

TABLE 8. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON THE SPECIFIC VOLUMES OF BREAD WITH A CONSTANT AMOUNT OF WATER (BATCH 1)

	Weight g.	Volume c.c.	Specific Volume g./c.c.	Increase in Specific Volume[a] %
100% Wheat flour	102.0	674.0	6.61	
1% HRW wheat pentosans	101.5	808.0	7.96	+20.4
2% HRW wheat pentosans	103.5	634.5	6.13	- 7.3
100% Wheat flour	104.0	684.0	6.58	
1% Barley pentosans	104.0	713.5	6.87	+ 4.4
2% Barley pentosans	105.0	654.0	6.23	- 5.3
100% Wheat flour	101.0	684.0	6.58	
1% Rye pentosans	100.5	752.0	7.48	+ 6.6
2% Rye Pentosans	102.0	683.0	6.71	- 4.4
100% Wheat flour	106.5	699.5	6.56	
1% Oats pentosans	105.0	755.0	7.18	+ 9.5
2% Oats pentosans	106.5	749.0	7.04	+ 7.3

[a] Compared to control (100% wheat flour)

TABLE 9. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON THE SPECIFIC VOLUME OF BREAD WITH AN OPTIMUM AMOUNT OF WATER (BATCH 2)

	Weight g.	Volume c.c.	Specific Volume g./c.c.	Increase in Specific Volume[a] %
100% Wheat flour	102.0	674.0	6.61	
1% HRW wheat pentosans	102.0	795.0	7.78	+17.7
2% HRW wheat pentosans	102.0	709.0	6.95	+ 5.2
4% HRW wheat pentosans	103.0	645.0	6.27	- 5.1
100% Wheat flour	104.0	684.2	6.58	
1% Barley pentosans	103.0	744.0	7.22	+ 9.7
2% Barley pentosans	103.0	734.0	7.12	+ 8.2
100% Wheat flour	101.2	684.2	6.58	
1% Rye pentosans	101.2	790.0	7.81	+11.3
2% Rye pentosans	99.5	841.0	8.45	+18.9
100% Wheat flour	106.5	699.5	6.56	
1% Oats pentosans	107.0	765.0	7.15	+ 9.0
2% Oats pentosans	105.8	771.5	7.29	+11.1

[a] Compared to control (100% wheat flour)

TABLE 10. CHANGES IN MOISTURE CONTENTS OF CRUMB AND BREAD PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP) DURING FOUR DAYS STORAGE -- BREAD PREPARED WITH A CONSTANT AMOUNT OF WATER (BATCH 1)

		Moisture Content (%) Storage Time (days)				
		0	1	2	3	4
Control[a]	whole bread	35.08	34.00	33.93	34.96	34.84
	crumb	44.56	41.21	---[b]	37.50	37.54
1% WP	whole bread	33.68	33.38	---	35.14	35.04
	crumb	45.72	42.04	---	40.79	39.87
2% WP	whole bread	36.58	33.83	34.92	35.54	34.90
	crumb	44.17	42.08	40.53	40.01	39.41
Control	whole bread	35.25	35.09	34.37	35.14	35.14
	crumb	43.00	41.53	39.27	39.10	37.57
1% BP	whole bread	---	34.35	34.76	35.03	35.03
	crumb	44.29	41.76	39.33	38.29	37.43
2% BP	whole bread	35.15	34.93	34.38	35.76	35.04
	crumb	43.98	41.56	39.43	38.53	37.74
Control	whole bread	35.63	34.69	34.09	34.27	30.66
	crumb	36.10	40.89	39.19	39.33	37.49
1% RP	whole bread	36.04	34.44	34.87	34.48	34.77
	crumb	45.82	41.86	38.66	38.87	38.17
2% RP	whole bread	35.84	34.46	35.03	34.07	34.50
	crumb	46.45	41.28	39.64	---	37.98
Control	whole bread	34.56	34.86	---	34.28	34.82
	crumb	44.26	40.73	39.95	38.70	37.99
1% OP	whole bread	37.16	---	34.14	---	34.23
	crumb	44.26	40.73	39.43	39.56	37.78
2% OP	whole bread	35.77	34.30	34.55	35.01	34.69
	crumb	43.81	42.31	39.35	39.42	37.76

[a] 100% Wheat flour

[b] Data were not available.

TABLE 11. CHANGES IN MOISTURE CONTENTS OF CRUMB AND BREAD PREPARED FROM FLOUR SUPPLEMENTED WITH WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT (WP), BARLEY (BP), RYE (RP), AND OATS (OP) DURING FOUR DAYS STORAGE -- BREAD PREPARED WITH AN OPTIMUM AMOUNT OF WATER (BATCH 2)

		Moisture Content (%) Storage Time (days)				
		0	1	2	3	4
Control	whole bread	35.08[a]	34.00	33.93	34.96	34.85
	crumb	44.56	41.21	---[b]	37.50	37.54
1% WP	whole bread	36.23	35.48[a]	37.30	---	35.45
	crumb	45.72	42.45	42.09	42.48[a]	40.89
4% WP	whole bread	40.37	34.25	---	---	---
	crumb	45.93	42.28[a]	---	42.09	---
Control	whole bread	35.25	35.09	34.37	35.14	35.14
	crumb	43.00	41.53	39.27	39.10	37.57
1% BP	whole bread	37.07	36.07	35.96	---	35.88[a]
	crumb	45.98[a]	43.83[a]	41.23	---	39.09
2% BP	whole bread	37.92	37.15	37.84	37.70	37.22
	crumb	47.16	---	43.53	43.20	41.02
Control	whole bread	35.63	34.69	34.09	34.27	30.66
	crumb	36.10	40.89	39.19	39.33	37.49
1% RP	whole bread	36.44	---	36.67	33.93	31.97
	crumb	47.00	43.98[a]	41.85	40.06	38.95
2% RP	whole bread	---	37.20	36.65	36.87	36.57
	crumb	47.18[a]	46.39	42.28[a]	41.84	40.41
Control	whole bread	34.56	34.86	---	34.28[a]	34.82[a]
	crumb	44.26	40.73	39.95	38.70	37.99
1% OP	whole bread	36.12	35.65	35.83	35.64	35.59
	crumb	43.81	44.45	41.83	40.48[a]	39.83
2% OP	whole bread	---	38.28[a]	36.09	33.01	36.69
	crumb	44.00	---	43.06	41.11	40.71

[a] 100% wheat flour
[b] Data were not available.

TABLE 12. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON CRUMB FIRMNESS DURING FOUR DAYS STORAGE -- BREAD PREPARED WITH A CONSTANT AMOUNT OF WATER (BATCH 1)

	Crumb Firmness (g.) Storage Time (days)				
	0	1	2	3	4
100% Wheat flour	71.93	156.15	202.41	254.44	313.58
1% HRW Wheat pentosans	52.26	117.73	149.30	180.89	212.13
2% HRW Wheat pentosans	67.59	158.99	195.81	252.54	304.12
1% Barley pentosans	67.00	157.33	195.29	287.20	312.09
2% Barley pentosans	73.38	169.90	225.73	308.72	343.24
1% Rye pentosans	66.55	118.72	197.71	225.36	299.92
2% Rye pentosans	80.42	136.52	194.20	224.68	310.52
1% Oats pentosans	46.12	123.88	169.65	190.02	251.72
2% Oats pentosans	51.38	125.08	158.01	224.49	275.36

TABLE 13. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON CRUMB FIRMNESS DURING FOUR DAYS STORAGE -- BREAD PREPARED WITH AN OPTIMUM AMOUNT OF WATER (BATCH 2)

	Crumb Firmness (g.) Storage Time (days)				
	0	1	2	3	4
100% Wheat flour	71.93	156.15	202.41	245.44	313.58
1% HRW wheat pentosans	49.31	90.97	126.88	195.42	216.52
2% HRW wheat pentosans	39.39	85.54	112.21	150.58	189.08
4% HRW wheat pentosans	47.83	114.11	130.53	----[a]	202.12
1% Barley pentosans	49.02	117.25	180.06	----	----
2% Barley pentosans	50.11	80.06	146.71	192.75	236.00
1% Rye pentosans	59.06	112.28	154.57	190.78	212.89
2% Rye pentosans	60.90	79.15	145.41	130.80	195.67
1% Oats pentosans	70.21	104.65	135.58	210.36	275.05
2% Oats pentosans	58.62	143.03	175.49	223.62	283.32

[a] Data not available

Effects of Water-Insoluble Pentosans on Staleness of Bread

A linear regression equation was derived from the data for crumb firmness and storage time. With crumb firmness represented by Y and storage time by X, the regression was expressed by $Y = A + BX$. The value of B, i.e., the slope of the straight line, was used as a factor to evaluate the staling rate. The regression relationships were summarized in Tables 14 and 15.

When compared with the control bread, the breads from batch 1 and batch 2 containing added wheat, rye, or oats pentosans had smaller values of B, i.e., lower staling rates. The staling rate was also affected by the amount of pentosans added. In batch 1, this rate increased as the amount of added pentosans increased, except from rye. In batch 2, the results were reversed. The rate decreased as the amount of added pentosans increased, except from oats. With 1% of wheat, barley, or oats pentosans added to flour, the staling rates of the breads in batch 1 were lower than those of the breads in batch 2. However, with 2% added pentosans, the results were reversed. The breads prepared in batch 2 with 2% added pentosans had smaller values of B, and staled more slowly.

Efforts were made to compare the effects of different pentosans on the staling rates. Bread containing rye pentosans had the lowest B values (see Table 15). Wheat pentosans also showed a satisfactory retardation effect on staling of bread,

followed in order of apparent effectiveness by oats and barley pentosans.

It is concluded that, when optimum amounts of water are used in preparing the dough, staling rates could be slowed to some extent with increasing amount of added pentosans.

TABLE 14. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON THE STALING RATE OF BREAD PREPARED WITH A CONSTANT AMOUNT OF WATER (BATCH 1)

	Regression $Y = A + BX$	Staling Rate of Bread B
100% Wheat flour	$Y = 83.38 + 58.16X$	58.16
1% HRW wheat pentosans	$Y = 67.28 + 36.49X$	36.49
2% HRW wheat pentosans	$Y = 82.49 + 56.66X$	56.66
1% Barley pentosans	$Y = 79.77 + 58.95X$	58.05
2% Barley pentosans	$Y = 88.49 + 67.85X$	67.85
1% Rye pentosans	$Y = 66.97 + 57.34X$	57.34
2% Rye pentosans	$Y = 79.60 + 54.83X$	54.83
1% Oats pentosans	$Y = 60.81 + 47.73X$	47.73
2% Oats pentosans	$Y = 57.38 + 54.74X$	54.74

TABLE 15. EFFECTS OF WATER-INSOLUBLE PENTOSANS FROM HRW WHEAT, BARLEY, RYE, AND OATS ON THE STALING RATE OF BREAD PREPARED WITH AN OPTIMUM AMOUNT OF WATER (BATCH 2)

	Regression $Y = A + BX$	Staling Rate of Bread B
100% Wheat flour	$Y = 83.38 + 58.16X$	58.16
1% HRW wheat pentosans	$Y = 48.03 + 43.89X$	43.89
2% HRW wheat pentosans	$Y = 42.54 + 36.42X$	36.42
4% HRW wheat pentosans	$Y = 60.02 + 36.36X$	36.36
1% Barley pentosans	$Y = 50.09 + 65.42X$	65.42
2% Barley pentosans	$Y = 44.10 + 48.58X$	48.58
1% Rye pentosans	$Y = 68.64 + 38.63X$	38.63
2% Rye pentosans	$Y = 56.95 + 32.42X$	32.42
1% Oats pentosans	$Y = 56.02 + 51.54X$	51.54
2% Oats pentosans	$Y = 70.82 + 53.00X$	53.00

GENERAL CONCLUSION

Pentosan contents in various cereals were determined by the method of Cerning and Guilbot (18). Water-insoluble pentosans were isolated from HRW wheat, barley, rye, and oats which contain 6.73%, 11.42%, 9.30%, and 12.2% of total pentosans, respectively. The water absorptions of the isolated water-insoluble pentosans were measured by a constant-dough farinograph method and were found to be 6.48, 9.59, 8.40, and 5.91 times their weights of water, respectively, on the basis of dry weight, and 10.3, 14.87, 12.83, and 7.90 times their weights of water, respectively, on the basis of pentosan content. The differences were attributed to differences in chemical compositions, such as the content of various carbohydrates in pentosans.

The addition of freeze-dried water-insoluble pentosans to flour resulted in changes in the farinographic properties of dough. The arrival times and developing times were delayed and the departure times were shortened. These revealed that dough stabilities were reduced by addition of pentosans. Presumably, the high water absorption and slow hydration rate of freeze-dried water-insoluble pentosans could delay dough development.

So far as extensimetric properties were concerned, doughs containing water-insoluble pentosans were found to have less maximum resistances, less areas under the curve, and smaller

ratios of resistance at 5-cm. extension to extensibility than the control dough. Such supplemented doughs would be softer and flow more quickly upon fermentation. There was no marked difference in the extensimetric properties when pentosans isolated from HRW wheat, barley, and rye were added, but dough containing oats pentosans was found to be higher in extensibility and lower in resistance to extension than the other doughs containing pentosans. These observations indicated that oats pentosans reduced the resistance of dough to stretching and made the dough more extensible.

When bread was prepared with the same amount of water as used for the control bread, the volume of bread with 1% added pentosans was always greater than that of the control bread. However, when 2% pentosans were added, only oats pentosans caused an increase in volume. The volumes of bread with 2% wheat, barley, and rye pentosans were inferior to that of the control bread. It is most likely that there exists an optimum level for each pentosans to improve the baking performance of wheat flour.

When breads were prepared with optimum amounts of water (farinograph), the volume of bread supplemented with 1 or 2% pentosans was improved by 5.2% (with 2% wheat pentosans) to 18.9% (with 2% rye pentosans). However, the breads were coarser in grain and darker in color. The darkness of the pentosan bread was due to the brown color of rehydrated water-insoluble pentosans.

Crumb firmness was related to the water-insoluble pentosans as well as to the moisture content of crumb. The crumb of bread which was higher in moisture or was supplemented with a suitable amount of pentosans was usually softer than that of control bread. Pentosans isolated from different sources affected crumb firmness differently. Both the characteristics of the pentosans and the actual amount of pentosans present in the isolated pentosans are probably different.

Staling was retarded and therefore the keeping quality of bread was improved when a suitable amount of pentosans were added. The effect was enhanced when bread was prepared with an optimum amount of water. Rye pentosans were superior to the other pentosans tested in retarding staling. Wheat pentosans also showed a satisfactory effect on staling rate.

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WATER-INSOLUBLE PENTOSANS: THEIR EFFECTS ON DOUGH RHEOLOGICAL PROPERTIES AND ROLES IN BREAD BAKING AND STALENESS

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A series of studies was conducted to examine the effect of water-insoluble pentosans on the physical properties of dough, and the baking and keeping qualities of bread.

Water-insoluble pentosans were isolated from HRW wheat, barley, rye, and oats, which contain 6.73%, 11.42%, 9.30%, and 12.21% of total pentosans, respectively. The water-absorption of the isolated water-insoluble pentosans were measured by a constant-dough farinograph method and were found to be 6.48, 9.59, 8.40, and 5.91 times their weight of water, respectively, on the basis of dry weight, and 10.3, 14.87, 12.83, and 7.90 times their weight of water, respectively, on the basis of pentosan content.

Added freeze-dried water-insoluble pentosans affected both the farinographic and extensimetric properties of dough. They increased the arrival and developing times while decreasing the departure time and dough stability. These affects were presumably due to high water absorption of the pentosans which could delay dough development. Pentosans reduced the resistance to extension, the area under the curve, and the ratio of resistance at 5-cm. extension to extensibility on the extensigram. Consequently, a pentosans supplemented dough was weak and slack during processing.

Specific loaf volumes were improved by 4.4% to 20.4% by supplementing flour with 1 and 2% of water-insoluble pentosans. The degree of improvement was also related to the amount of

water used in preparing the dough.

Crumb firmness of bread was related to the amount of water-insoluble pentosans as well as to the moisture content of the crumb. The crumb of bread which was higher in moisture or was supplemented with 1 and 2% of pentosans was usually softer than that of control bread. Pentosans isolated from different sources affected crumb firmness differently. This is probably due both the characteristics of the pentosans and the actual amount of pentosans present in the isolated pentosans are different.

Staling was retarded and therefore the keeping quality of the bread was improved with pentosan supplementation. After four days storage, crumb firmness values were 313.5 g. for the control bread and 202.13 g., 312.12 g., 299.92 g., and 251.72 g., respectively, for bread containing 1% of HRW wheat, barley, rye, and oats pentosans, if the same amount of water was used. The effect was enhanced when the bread was prepared with an optimum amount of water. Rye pentosans were superior to the other water-insoluble pentosans in retarding staling.