STRUCTURE AND PROPERTIES OF WATER-SOLUBLE ARABINOXYLANS FROM FLOURS OF CANADA WESTERN RED SPRING (CWRS) WHEATS

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by

Onkar S. Rattan

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TO MY PARENTS

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ABSTRACT

Ten flours from eight different varieties of the Canadian Western Red Spring (CWRS) wheat class (Neepawa, Katepwa, Roblin, Columbus, Benito, Laura, Lancer, and Selkirk) were used to isolate arabinoxylans (AX), the main constituent of water-soluble pentosans. Preliminary technological tests on the flours of these varieties have shown that the water-soluble pentosan content was significantly correlated to the ash content and starch damage ($r = 0.79$ and $r = 0.68$, $p \leq 0.05$, respectively).

Chemical analysis has shown that the amount of bound phenolics (ferulic acid) varied among the AX of various flours; the highest amounts were detected in the varieties Neepawa and Roblin while the lowest amount was found for the preparation of Columbus. A small variation in the ratio of xylose/arabinose was found among the Ax, while gel filtration on Sepharose CL-2B has indicated substantial differences in the molecular size among these polymers. These results were consistent with the intrinsic viscosity values which ranged between 3.69-5.48 dl/g.

Oxidative gelation (H_2O_2/peroxidase system) studies (as probed by dynamic rheometry) have shown that a certain minimum amount of oxidant was needed for effective gel network

formation. Furthermore, the high molecular weight (HMW) AX samples (e.g. Katepwa B) formed rigid gels at lower concentrations than their low molecular weight (LMW) counterparts (e.g. Columbus). In addition to the molecular size, the ferulic acid content was found to play a role in determining the rigidity of the gel network. Purified AX also exhibited substantial surface activity as evidenced by the low surface tension values of their solutions.

Fortification studies using two arabinoxylan preparations (a high, HMW and a low molecular weight, LMW, sample) and flours of diverse breadmaking quality (a composite sample 2CW of CWRS class and HY368 of the Canadian Prairie Spring wheat class) indicated that these polymers increased the water absorption and the dough development time. Significant correlations were found between farinograph absorption and amount of AX added ($r = 0.90\text{-}0.99$, $p \leq 0.05$ for HMW- and LMW-supplemented flours of 2CW and HY368) Both HMW and LMW arabinoxylans, when added at different levels, were found to effect the loaf volume of breads baked from the two flours. The HMW arabinoxylan increased the loaf volume up to a level of fortification of 0.5% (w/w) for both flours. The LMW arabinoxylan increased the volume up to a fortification level of 0.7% in the case of 2CW flour. In contrast, for the HY368 flour there was a continuous increase in loaf volume with

added LMW arabinoxylan up to a level of 1.1% (w/w).

Fortified breads of both flours had higher moisture content and higher A_w values than those of control samples when stored at 7°C for a period of seven days. Moreover, fortified bread crumbs (both 2CW and HY368) were found to be less firm than control samples when compressed to a constant deformation in a Ottawa Texture Measuring System. The bread staling process of control and fortified (with LMW AX at 0.5% and 0.9% levels) bread crumbs of the 2CW and HY368 flours was also studied by monitoring the increments in the melting enthalpy of recrystallized amylopectin during storage (7°C up to 7 days). The enthalpy values of AX-fortified breads were found to be higher than the control bread samples. The enthalpy values obtained at 0.9% (w/w) fortification level exceeded those of 0.5% (w/w) for any given storage period.

1. INTRODUCTION

Wheat flour primarily consists of two major components, starch and proteins. These two components not only contribute towards the nutritional quality of bread but also possess unique functional properties which permit the flour to be converted into dough and subsequently into bread. Since the wheat flour is primarily made of ground endosperm, it contains several other minor constituents, such as lipids, ash and pentosans. Pentosans make up 2-3% of a baker's patent flour and out of this about one third is water-soluble pentosans. This water-soluble fraction mainly consists of polymeric pentose-containing carbohydrates.

In spite of being relatively minor constituents of the wheat flour, pentosans are considered to have an impact on dough rheology and subsequently on the bread quality parameters, such as loaf volume, crumb, texture and staling characteristics (Jankiewicz and Michniewicz, 1987; Kim and D'Appolonia, 1977a). Many studies in the past have dealt with the characterization of these constituents from various cereals. More specifically, their physicochemical properties in solution (Fincher and Stone, 1974; Andrewartha et al, 1979) as well as their functional role in the bread system have been examined (Jelaca and Hlynka, 1972; McCleary, 1986; Michniewicz et al, 1992). Izydorczyk et al (1990,1991a&b) have recently

examined the structural and physicochemical properties of pentosans and their purified constituents (arabinoxylan and arabinogalactan) from flours of various wheat cultivars belonging to several Canadian wheat classes. Their findings suggested that most of the functional properties attributed to pentosans in dough and bread systems are contributed mainly by the arabinoxylan component.

The objective of the present study was to further elaborate on the chemical, physical and functional properties of water-soluble arabinoxylans derived from flours of several Canada Western Red Spring (CWRS) wheat cultivars. Following the technological characterization of the flours two specific objectives were addressed:

I. Isolation, fractionation and characterization of water-soluble arabinoxylans from ten varieties belonging to the CWRS class. Characterization of these polysaccharides included:

(a) Molecular size distributions

(b) Covalently bound phenolics

(c) Monosaccharide composition

(d) Viscosity

(e) Oxidative-gelation potential

II. Fortification of wheat flours of diverse bread making quality with purified arabinoxylans to assess their impact on the baking characteristics of the base flours.

2. REVIEW OF LITERATURE

Different statements can be found in the literature regarding the definition of pentosans. According to Hoseney (1984), pentosans are polymers which are mainly composed of pentose sugars, such as arabinose and xylose, along with hexoses and proteins. These polysaccharides are considered as an integral part of plant cell walls and as such are found in the endosperm of cereal grains, e.g. wheat, oat, barley and rye. Pentosans are classified as water-soluble and water-insoluble depending on their solubility in an aqueous medium. It has been also found that water soluble pentosans can be further divided into two components (Neukom and Markwalder, 1975; Neukom, 1976): 1) a high molecular weight arabinoxylan component and 2) a low molecular, highly branched, arabinogalactan which is covalently bound to peptide moieties. Water-insoluble pentosans have a highly branched structure and a large molecular size. Two unique properties associated with water-soluble pentosans are: 1) they form highly viscous solutions and 2) they can undergo intermolecular cross-linking in the presence of certain oxidants. These two properties of water-soluble pentosans have been considered functionally relevant in dough and bread making. Therefore, the following literature review will focus on the structure, chemical composition and functional role of wheat flour pentosans in breadmaking.

2.1 Wheat flour pentosans origin and isolation

Pentosans present in wheat flour (2-3%) mainly originate from the thin cell walls of the endospermic tissue of wheat kernel. Water-insoluble pentosans which make-up about two thirds of the total wheat flour pentosans are considered to be joined to the cellulose microfibrils of cell walls via ester linkages. According to Neukom et al (1962), water-soluble pentosans constitute about 30-40% of the total pentosan content of wheat flour. These water-soluble pentosans are thought to be held on the surface of cell walls by non-covalent forces.

Several methods have been developed for isolation, purification, and fractionation of water-soluble pentosans from wheat flour. In the early studies, half-saturated ammonium sulphate solution and copper reagents were employed to isolate these gum-like substances from flour (Baker et al, 1943; Freemar & Gortner, 1932). Such preparations, however, were crude and were contaminated with large amounts of starch and proteins. Relatively purified preparations of pentosans can be obtained by the use of enzymes. Hydrolytic enzymes not only remove the contaminating proteins (Simpson ,1954) but also help in removing water-soluble starch (Fincher and Stone, 1974; Howard, 1957; Kündig et al, 1961). Additional methods available to remove the proteins include heat treatment as well as adsorption on Filtrol or other clays (Crowe and

Rasper, 1988a; Izydorczyk et al, 1990; Lin and Pomeranz, 1968; Pence et al, 1950). It was initially thought that arabinoxylan was the main constituent of water-soluble pentosans. However, the studies of Perlin (1951) have suggested an association between proteins with pentosans. Later, the work of Kündig et al (1961), and Neukom et al (1962) had shown that in addition to arabinose and xylose, water-soluble pentosans also contain galactose and proteins which could not be separated without disrupting the polymeric nature of pentosans. As a result, in addition to polymers of xylose and arabinose, water-soluble pentosans were also considered to contain other polymeric species of galactose and proteins.

Different techniques have been applied to fractionate water-soluble pentosans. In most of the previous studies DEAE-Cellulose chromatography has been used to fractionate the water-soluble pentosans (D'Appolonia et al, 1970; Kim & D'Appolonia, 1976; Kündig et al, 1961; Lineback et al, 1977). However, in these studies some inconsistencies were reported which partially arise from the variation in sample composition and partially from the fact that DEAE-cellulose chromatography yields heterogeneous fractions. Fincher and Stone (1974) were able to fractionate water-soluble pentosans into two distinct fractions: (a) a high molecular weight arabinoxylan and, (b) a low molecular weight arabinogalactan-

peptide by $(NH_4)_2SO_4$ precipitation. The same workers also used ethanol (80%) for fractionation of water-soluble pentosans. Recently, a modified scheme for the isolation and purification of water-soluble pentosans was developed by Izydorczyk et al (1990). This method includes the use of α-amylase from human saliva to remove water-soluble starch. The application of heat along with adsorption on vega clay were shown to eliminate most of the proteinaceous contaminants. By employing this scheme, these researchers were able to isolate pentosan preparations with an improved purity.

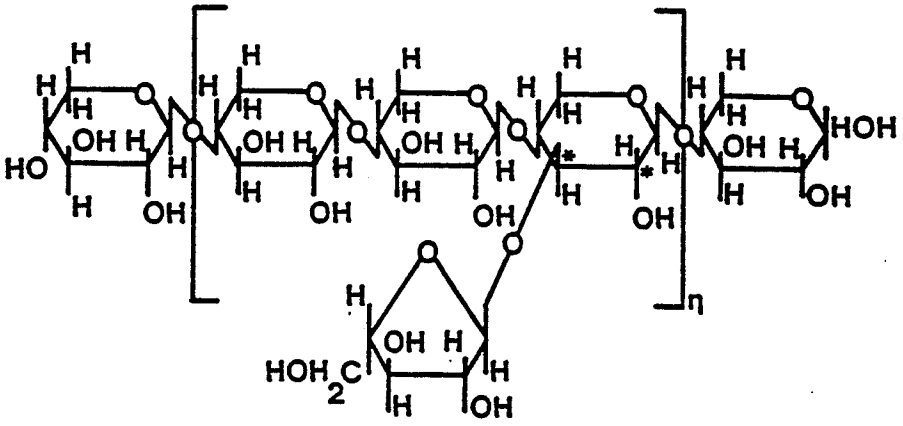
2.2 Chemistry of water-soluble pentosan constituents

2.2.1 Arabinoxylan

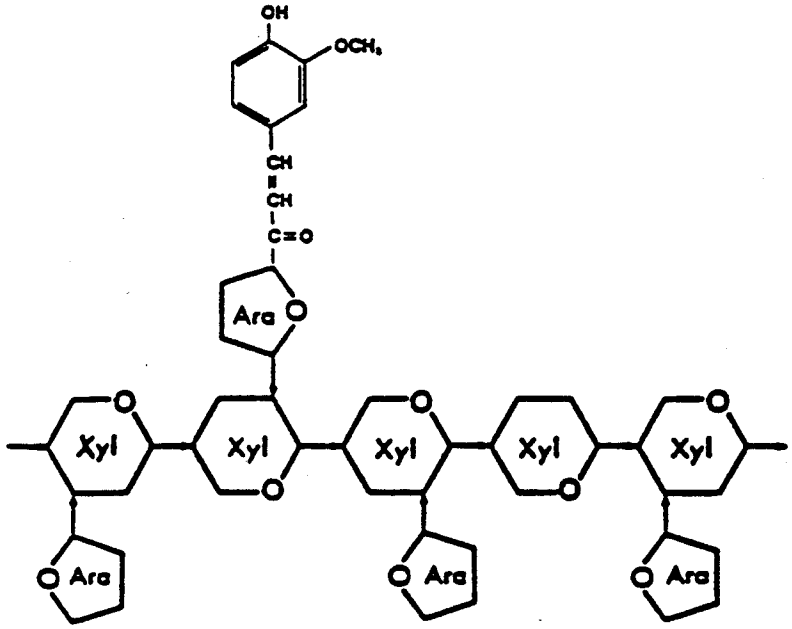
Arabinoxylan constitutes the bulk of water-soluble pentosans (Montgomery & Smith, 1955; Perlin, 1951). It is made up of a linear chain backbone of β(1-4) glycosidically linked D-xylose residues. To this xylan backbone, α,L-arabinose residues are attached randomly at the C_2 or C_3 carbons of xylose residues (Fig. 1). These arabinose side chains are considered to be responsible for the solubility of this polymeric carbohydrate in an aqueous medium (Neukom et al, 1967). Although the exact distribution of arabinose along the xylan backbone is not exactly known, it has been suggested that there are certain

Figure 1. Structure of arabinoxylan with possible branching points as shown by *(a) and ferulic acid linkage to O_5 of arabinose residue (b),(Shelton & D'Appolonia, 1985; Neukom,1976)

a

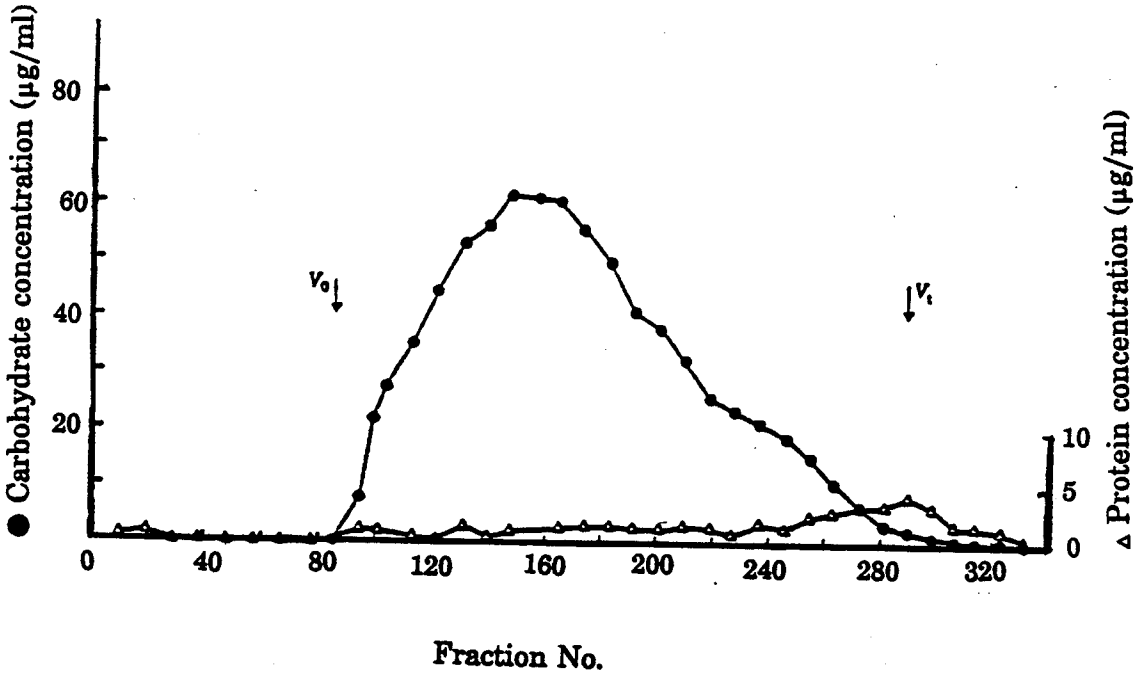


b



areas along the xylan chain which remain unsubstituted and are called smooth regions. Such regions of two to five xylose residues were found to be free from arabinose side chains (Goldschmid & Perlin, 1963; Ewald & Perlin, 1959). Furthermore, it has been found that the degree of substitution in arabinoxylan varies among flours of different origin. For example, arabinoxylans from durum wheat flours had a more branched structure than those of hard red spring wheat flours (Medcalf et al, 1968). Later studies on conventional-height and semi-dwarf wheat varieties have also shown variations in the degree of branching of arabinoxylans (D'Appolonia & MacArthur,1975). Similarly, arabinoxylan from hard red winter and spring wheats were found to be more branched than those from soft wheats (Ciacco & D'Appolonia, 1982). Elution profiles of arabinoxylans on Sepharose 4B columns (Fig. 2) indicate that these polymers have a broad distribution of molecular size (Fincher and Stone, 1974). The molecular weight values reported for arabinoxylans vary depending on the method applied. For example, Mares and Stones (1973) found that the molecular weight of arabinoxylan ranges from $5x10^5$ to $8x10^5$ by gel filtration. Andrewartha et al (1979) and Girhammar et al (1986) used a sedimentation technique for molecular weight determination of arabinoxylan and reported much lower values (65,000-66,000). One of the unique structural features of

Figure 2. Chromatography of water-soluble arabinoxylan on Sepharose-4B: • Carbohydrate, ▵ Protein. (Fincher & Stone, 1974).


● Carbohydrate concentration (μg/ml)
80
60
40
20
0
40
80
120
160
200
240
280
320
V_0
V_t
10
5
0
△ Protein concentration (μg/ml)
Fraction No.

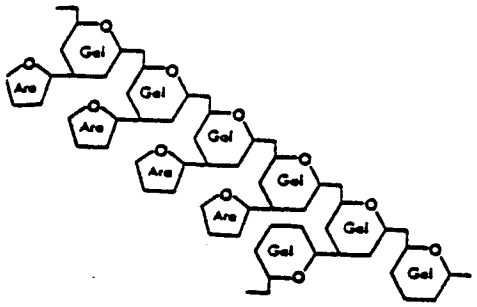
arabinoxylans is the presence of ferulic acid. This phenolic acid is covalently linked to the O_5 atom of arabinose residues via ester linkages (Fausch et al, 1963; Smith & Hartley, 1983), as shown in Figure 1. Ferulic acid plays an important role in the functional properties of arabinoxylans especially with respect to their gel forming capacity.

2.2.2 Arabinogalactan

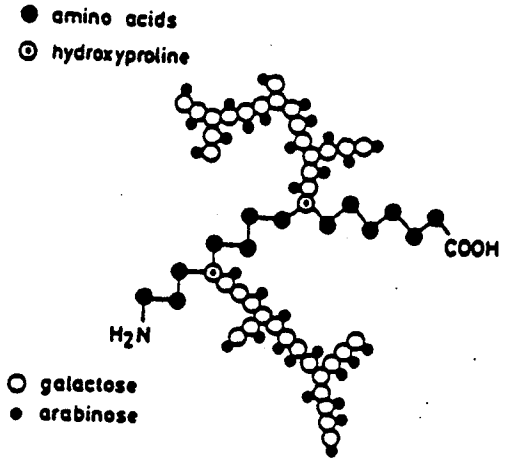
The structure of the arabinogalactan-peptide constituent of water soluble pentosans was independently studied by two groups (Fincher and Stone, 1974; Neukom et al, 1975). In both studies it was found that arabinogalactan has a highly branched structure in which galactopyranosyl units are glycosidically linked to each other through β(1-3) and β(1-6) linkages. Single arabinose residues are also linked to galactose units glycosidically, as shown in Figure 3a. Arabinogalactan is the low molecular weight component of the water-soluble pentosans. Average molecular weights reported for this polymer are 22,000 (Fincher and Stone, 1974) and 30,000-32,000 dalton (Straham et al, 1981). A peptide moiety is also attached to the carbohydrate chains of arabinogalactan (Fincher and Stone, 1974). It has been established that covalent linkages between the amino acid residue hydroxyproline of the peptide component and a

Figure 3. Structure of arabinogalactan: (a) Neukom (1973) (b) Straham *et al* (1981).

a


Gal
Ara
Gal
Ara
Gal
Ara
Gal
Ara
Gal
Gal
Gal

b


amino acids
hydroxyproline
COOH
H_2N
galactose
arabinose

galactose residue of the polysaccharide chain exists. (Straham et al, 1981), as shown in Figure 3b. In a recent study Izydorczyk et al (1991a) have reported high contents (8.4-13.7% on a molar basis) of hydroxyproline for purified arabinogalactan-peptides isolated from various wheat flours.

2.3 Physical properties of water-soluble pentosans

The most important physical properties exhibited by water-soluble pentosans are:

1) Ability to form highly viscous solutions in small polymer concentrations.
2) Formation of a viscoelastic gel network when their aqueous solutions are treated with an oxidizing agent such as hydrogen peroxide in the presence of peroxidase.

These properties are considered to play a major role in dough development and finally in the breadmaking process.

2.3.1.Viscosity

The intrinsic viscosity of isolated water-soluble pentosans was studied by many researchers (D'Appolonia and MacArthur, 1975; Medcalf et al, 1968) who concurred that the arabinoxylan fraction is the main contributor to the viscosity of water-soluble pentosan solutions. A more recent study has shown a

variation in intrinsic viscosity values of water-soluble pentosans isolated from various wheat varieties of different Canadian Wheats (Izydorczyk et al, 1991b). The higher viscosity value reported in this study was found for pentosans belonging to a Canadian Western Red Spring wheat, variety Katepwa (Table 1). Also, in the same study, the intrinsic viscosities of arabinoxylans (2.75-4.23 dl/g) were found to be considerably higher than those of arabinogalactan fractions (0.045-0.060 dl/g). This is in agreement with the view that arabinoxylan is the constituent responsible for the viscous character of pentosan solutions.

2.3.2 Oxidative Gelation

Oxidative gelation of water-soluble extracts from wheat flour was first observed by Durhum (1925). This unique property was later traced back to the pentosans by Baker et al (1943) and Udy (1956). The gelation reaction has been studied extensively (Fausch et al, 1963; Geissmann & Neukom, 1973; Markwalder & Neukom, 1976, Neukom & Markwalder, 1976) and it has been shown that reagents which generate free radicals are more effective in enhancing gel formation (Hoseney & Faubion, 1981). Therefore, the effect of various oxidizing agents such as ammonium persulphate, ferric chloride, linoleic acid in the presence of the enzyme lipoxygenase, and hydrogen peroxide in the

Table 1. Limiting viscosities of pentosans and their fractions(dl/g), Izydorczyk *et al* (1991b).

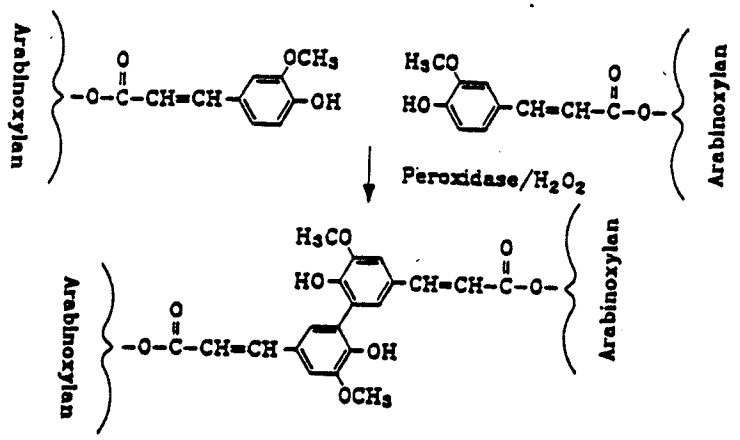
Variety	Pentosan	Arabinoxylan	Arabinogalactan
HY 355	2.78	3.98	0.047
HY 320	2.76	3.40	0.045
Oslo	2.07	3.15	0.062
Glenlea	2.00	3.12	0.053
Fielder	2.37	2.75	0.050
Norstar	2.08	3.14	0.060
Marshall	1.47	2.81	0.058
Katepwa	3.11	4.23	0.057

presence of peroxidase were investigated in relation to pentosan gelation (Crowe & Rasper, 1988a; Izydorczyk et al, 1990). These studies have clearly indicated that the hydrogen peroxide/peroxidase system was the most effective in promoting gel formation (Izydorczyk et al, 1990). In contrast, commonly used oxidizing agents in promoting flour maturation such as bromate and iodate were found to be ineffective in gel formation (Crowe & Rasper 1988b; Izydorczyk et al, 1990).

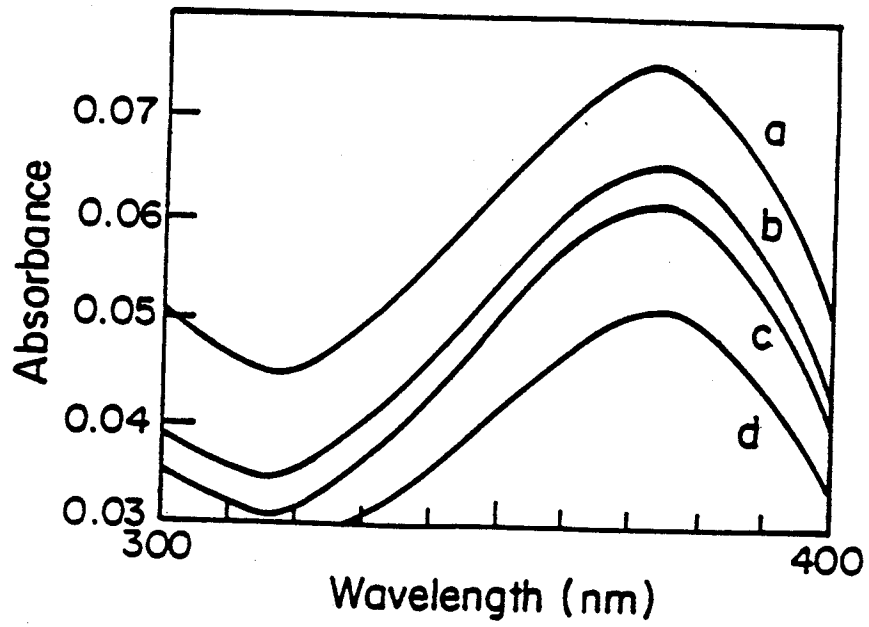
The mechanism of oxidative gelation has been a subject of several investigations in the past (Panter and Neukom, 1968; Neukom and Markwalder, 1978). Ferulic acid associated with the arabinoxylan fraction of water-soluble pentosans is thought to be involved in gel formation. This was supported by the identification of diferulic acid in addition to ferulic acid in pentosan gels (Neukom and Markwalder, 1978); the former being absent from solutions of arabinoxylan before oxidation. Therefore, it has been suggested that oxidative coupling of ferulic acid residues from adjacent arabinoxylan chains takes place during gel network formation (Geissmann & Neukom, 1973; Izydorczyk et al, 1990), as illustrated in Figure 4A. The involvement of ferulic acid was further evidenced by the disappearance of the peak at 375 nm in the uv spectrum of pentosan solutions, Figure 4B (Izydorczyk et al, 1990); the peak at 375 nm is attributed to

Figure 4. A. Mechanism for oxidative phenolic coupling of two ferulic acid residues present on arabinoxylan molecules. (Neukom & Markwalder, 1978).
B. Time dependent changes in the uv spectra of 0.5% (w/v) pentosan solution after addition of peroxidase (0.11 PU/ml)and H_2O_2 (0.2 ppm); pentosan solutions (0.5 ml) were mixed with 3.0 ml of 0.07M glycine-NaOH (pH 10.0) and the spectra were recorded immediately: (a) control, 0 time; (b) 45s; (c) 100s; (d) 180s (Izydorczyk et al ,1991a).

A


Arabinoxylan
Arabinoxylan
Peroxidase/H_2O_2
Arabinoxylan
Arabinoxylan

B


Absorbance
0.07
0.06
0.05
0.04
0.03
300
400
Wavelength (nm)
a
b
c
d

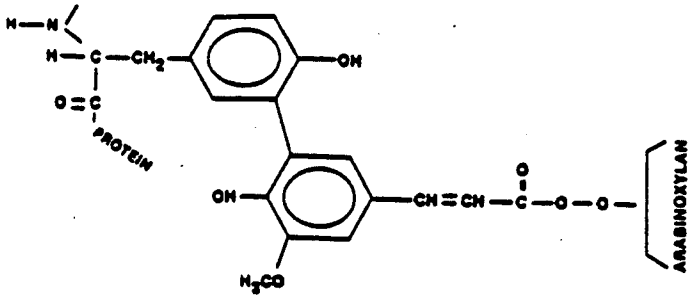
ferulic acid. Previous studies have also indicated that pentosan gels can be liquified by proteolytic enzymes (Neukom, 1976). It was, therefore thought that in addition to diferulic crosslinking, proteins may also play a role in gel network formation. Two possible mechanisms have been postulated for the involvement of proteins in pentosans gels as shown in Figures 5a and 5b. In the first case (Fig. 5a), cross linking between the amino acid tyrosine of protein and the ferulic acid residue of arabinoxylan has been implicated (Neukom & Markwalder,1978). Secondly, crosslinking between the activated double bond of ferulic acid of arabinoxylan and a sulphydryl group of protein has been suggested, Figure 5b (Hoseney & Faubion, 1981; Sidhu et al, 1980). However, both these two postulates have not been experimentally confirmed yet.

2.4 Functional properties of water-soluble pentosans

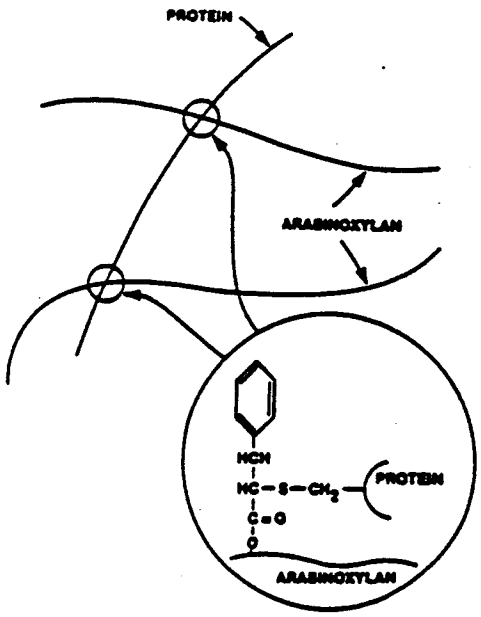
Water-soluble pentosans represent only a small fraction of the wheat flour, but are considered to be important constituents in the bread making technology. Their functionality in bread is linked to their hydrophilic nature and the ability of forming viscous solutions or cross-linked gel networks upon oxidation. These properties are thought to be important in dough or batter development, particularly with respect to

Figure 5. Mechanism for gelation via protein and ferulic acid (a) Cross-linking between tyrosine and ferulic acid (Neukom & Markwalder, 1978); (b) cross-linking through an -SH group of protein and the propenyl group of ferulic acid (Hoseney and Faubion, 1981).

a


PROTEIN
OH
OH
CH=CH
ARABINOXYLAN
H_3CO

b


PROTEIN
ARABINOXYLAN
PROTEIN
ARABINOXYLAN

water content and moisture distribution, and thus have an effect on quality of the final product.

2.4.1 Water absorption

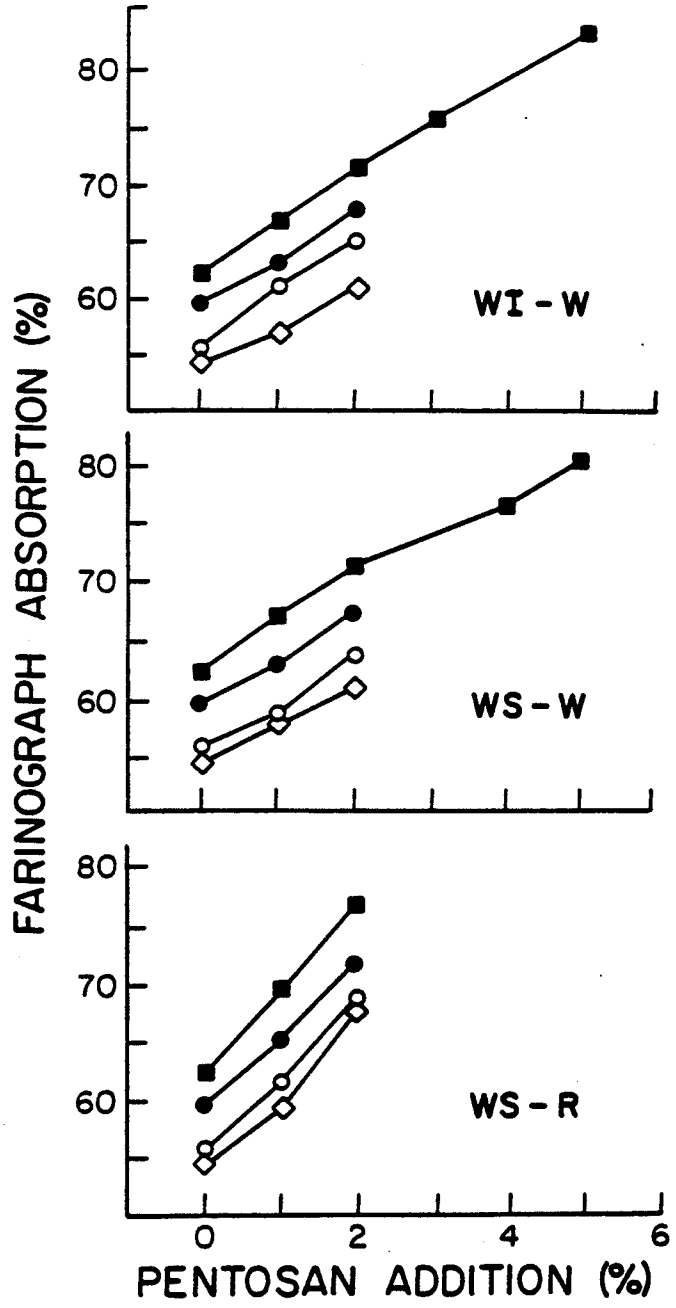
Inspite of the fact that the extent of water absorption by the flour is dependent primarily on the protein content, degree of starch damage, pentosans because of their hydrophillic nature are important contributors to the water absorption properties of flour during dough mixing. Bushuk (1966) has stated that water-soluble pentosans are responsible for holding approximately 23% of the water in dough. Considering the relatively small amounts of pentosans present in flour (2-3%), this value is of great magnitude. According to Tao and Pomeranz (1967), water soluble pentosans from hard red winter, hard red spring and soft red winter wheats increased the water absorption when added to wheat flour. The work of Jelaca and Hlynka (1971) showed that water-insoluble and water-soluble pentosans can absorb 6.3 and 6.7 times their weight of water, respectively. However, in later studies by Kim and D'Appolonia (1977a) it was found that the water absorption capacity of water-soluble pentosans is not of specific value, but is dependent upon many factors, such as availability of water in dough, speed of mixing and presence of other constituents. Moreover, it depends on the method of evaluation. Jankiewicz and Michnie-

wicz (1987) observed an increase in the farinograph absorption and dough development time when water-soluble rye pentosans were added at a level of 1.5% and 3.0% to wheat flour. Recent work of Michniewicz et al (1991) also confirmed that farinograph absorption increased when water-soluble, water-insoluble wheat pentosans and water-soluble rye pentosans were added to wheat flours at different levels. These researchers also found a positive correlation between farinograph absorption and amount of added pentosans (Fig. 6).

2.4.2 Role of pentosans in dough rheology

The effect of pentosans on the viscoelastic properties of a dough system is not fully understood yet. Many contradictory results have been reported in the literature. Neukom and Deuel (1958) have demonstrated by using the extensigraph that water-soluble pentosans have an improving effect on the viscoelastic properties of dough. On the other hand, Kulp and Bechtel (1963) showed that water-insoluble pentosans have no effect on the extensigraph properties of dough. The work of Jelaca and Hlynka (1972) demonstrated an increase in resistance to extension when a crude preparation of water-soluble pentosans was added to flours at 1.0% level. Furthermore, in a reconstitution study of gluten-starch admixtures, pentosans increased the dough rigidity in the presence of bromate (Patil et al,

Figure 6. Farinograph water absorption of wheat flours supplemented with pentosan preparations for wheat or rye: WI-W= water-insoluble wheat, WS-W= water-soluble wheat, WS-R= water-soluble rye; base flours ■ =Katepwa, • =Marshall, ○ =HY320, ◇ =Fielder. (Michniewicz et al, 1991).


FARINOGRAPH ABSORPTION (%)
80
70
60
WI - W
80
70
60
WS - W
80
70
60
WS - R
0
2
4
6
PENTOSAN ADDITION (%)

1976). Hanh and Rasper (1974) also observed a slight strengthening of the elastic response of dough supplemented with water-soluble pentosans from hard red spring wheat flours.

2.4.3 Role of pentosans in bread making

Two major approaches have been adopted in the past years to elucidate the role of pentosans in the breadmaking process. One includes the fortification of wheat flour with pentosans and examination of their effect on product quality such as bread loaf volume, crumb structure, etc. The other is to depolymerize the native pentosans in flour using specific pentosan degrading enzymes and study the effect of the degraded polymer on product quality. Early studies by Pence et al (1950) showed an increase in bread loaf volume when wheat flour was reconstituted with water-soluble extracts of flours. These workers, however, have attributed this effect to the protein present in water-soluble extracts. In contrast, Hoseney and co-workers (1969) showed that water-soluble pentosans rather than protein are mainly responsible for the increase in the bread loaf volume. Using the second approach, Tracey (1964) depolymerized the pentosans in situ and observed a decrease in loaf volume. This effect of pentosans was later confirmed by Cawley (1964). Furthermore, Casier and Soenen

(1967) found that pentosans when added at a level of 2% not only improve the loaf volume but also the bread crumb characteristics. In an another study, Tao and Pomeranz (1967) also reached to similar conclusions. D'Appolonia et al (1970), reported an increase in loaf volume of gluten-starch loaves with added pentosans. Finally, Jelaca and Hlynka (1972), reported an improvement in loaf volume when water-soluble pentosans were added to wheat flour of a hard red spring cultivar.

Recently, McCleary (1986) elegantly demonstrated the role of pentosans in bread baking. In his studies, pentosans and particularly arabinoxylans were degraded in situ with a purified xylanase preparation. The enzyme-treated flours yielded sticky doughs with poor bread making qualities (low loaf volume and a soggy texture). Delcour et al (1991) also observed that water-soluble pentosans from wheat and rye can increase the volume of gluten-starch loaves. Similarly, the work of Michniewicz et al (1992) indicated an increase in loaf volume when water-soluble wheat and rye pentosans were added to a wheat flour at a level of 2%.

2.4.4 Role of pentosans in retarding bread staling

Bread staling is manifested by increases in firmness of bread crumb. This is considered to be primarily due to starch

retrogradation. Kim and D'Appolonia (1977b) using starch gel model systems have suggested that pentosans decrease the extent of retrogradation by forming hydrogen bonds with amylopectin. In this course of action, pentosans reduce the available sites for intermolecular bonding between starch molecules upon storage. Furthermore, a reconstitution study has shown a reduction in crumb firming rate in the presence of pentosans (Kim and D'Appolonia, 1977a). Prentice et al (1954) have also observed a lower crumb firmness on adding tailings to the wheat flour. They postulated that the reduced firmness was due to the higher hydration capacity of tailings. Moreover, Jankiewicz and Michniewicz (1987) have examined the effect of added water-soluble pentosans (isolated from rye) on bread firmness using the Baker Compressimeter. They found that breads supplemented with pentosans were less firm than controls over a period of six days.

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Wheat cultivars

Eight different wheat varieties and a total of 10 samples belonging to the Canadian Hard Red Spring (CWRS) wheat class were obtained from different seed growers in Manitoba, as shown in Table 2. These samples were used for the preparation of water-soluble pentosans and their arabinoxylan fractions from the respective flours.

3.1.2 Wheat flours

Two additional wheat flours belonging to two separate wheat classes, a composite flour of CWRS (2CW) and a CPS wheat flour (HY368), were used in the fortification study and were provided by the baking laboratory of the Department of Plant Science, University of Manitoba. The extraction rate, protein and ash contents of these two flours were: 72%, 13.0%, 0.46% (14% m.b.) for 2CW and 67%, 11.5%, 0.35% for HY368, respectively. The total and water-soluble pentosan contents of these flours were 1.98±0.04%,0.74±0.04% (2CW) and 1.79±0.05%, 0.65±0.03% (HY368), respectively.

Table 2. Wheat varieties of the Canadian Western Red Spring (CWRS) wheat class used in this study.

Variety
1. Neepawa
2. Roblin A (Seine River Seeds)
3. Roblin B (Boissevain Select Seeds)
4. Katepwa A (Boissevain Select Seeds)
5. Katepwa B (Seine River Seeds)
6. Columbus
7. Benito
8. Laura
9. Lancer
10. Selkirk

3.1.3 Reagents and Chemicals

Enzymes such as , α-amylase from porcine pancreas,type I-A, EC 3.2.1.1, (1,260 units/mg of protein) and horseradish peroxidase type II, EC 1.11.1.7, (220 purpurogallin units, PU, per mg of solid) were purchased from Sigma Chemical Comp. Ferulic acid (4-hydroxy-3-methoxycinnamic acid) was obtained from Aldrich Chemical Co. Inc., Milwaukee, WI. Monosaccharide standards (arabinose, glucose, galactose and xylose) were obtained from Attech Associates, Dearfield, IL. Reagent grade H_2O_2 (30%) was a product of Mallinkcrodt, Inc. Paris, KY. Vega clay was a product of Pembina Mountain Clays, Winnipeg, Manitoba. All other chemicals used were of analytical reagent grade.

3.2 Methods

3.2.1 Milling and Technological Tests

3.2.1a Milling

All wheat samples were tempered to 15.5% moisture content by adding appropriate amounts of water and allowing the kernels to stand for 24 hrs at 21°C. They were then milled into straight grade flours on a Buhler pneumatic laboratory mill.

3.2.1b Test Weight

Test weight of each wheat sample was determined using an Ohaus Test Weight apparatus with a 0.5 litre container. Total weight of two 0.5L containers was determined and multiplied with 100 to obtained the equivalent kilograms per hectolitre. The average of three measurements was reported on an "as is" moisture basis.

3.2.1c Protein Content

Protein content of flours and whole wheat flours was determined according to AACC approved method (method 39-11, AACC 1983) using the Dickey-John near infrared analyzer (Dickey-John Corp, Auburn, IL). The instrument was calibrated for protein content using values obtained from the Kjeldhal method.

3.2.1d Moisture Content of Grain and Flour

The moisture content of whole grain samples was determined by using an electronic moisture meter (Canadian Aviation Electronics Ltd., model CAE 919) according to the AACC approved method (method 44-11, AACC 1983). The moisture content of flours was determined by using the Brabender Rapid Moisture Tester according to the AACC approved method (method 44-15A, AACC 1983).

3.2.1e Ash Content of Flour

The ash content of flour was determined according to the AACC approved method (method 08-01, AACC 1983) in which the flour sample was incinerated at 560°C.

3.2.1f Falling Number Value

The falling number value was determined according to the AACC approved method (method 56-81B, AACC 1983) using the single sample apparatus from the Falling Number Co. (Sweden).

3.2.1g Zeleny-Sedimention Volume

The sedimentation test value was determined according to the AACC approved method (method 56-60, AACC 1983).

3.2.1h Damaged Starch

Starch damage was determined by the AACC approved method (method 76-30A, AACC 1983).

3.2.1i Amylograph

Amylograms of wheat flours were obtained using a Brabender Visco-amylograph with a 65 g flour sample, according to the AACC approved (method 22-10, AACC 1983).

3.2.1j Flour wet gluten

Percent wet gluten in flour was determined according to the I.C.C. standard method 137 (ICC,1982) using the Falling Number Co. Glutamatic 2100 apparatus.

3.2.1k Farinograph

Macro-farinograms were obtained by the AACC approved method (method 54-21, AACC 1983) using a 50 g flour weight.

3.2.1l Extensigraph

Extensigrams were obtained according to the method of Holas and Tipples (1978) using a Barbender Extensigraph. The flours were mixed with water, equivalent to the farinograph water absorption value into a farinograph mixer, for a period of farinograph dough development time. Doughs were then stretched after a 45 min and a 135 min rest period. The reported data (Table 3) belong to the 135 min curves. Areas under the curves were measured by using a polar compensation planimeter (Sokkiska Ltd., Tokyo).

3.2.1m Baking

The GRL remix baking test (Kilborn and Tipples, 1981) was used to evaluate the baking performance of each flour using 100g of flour. Volumes of the resulting loaves were measured with a pup loaf volumeter (National Mfg. Co.) using wheat grain. The

baking strength index was determined according to Tipples and Kilborn (1974).

3.2.2 Wheat cultivar identification

Gliadin Gel Electrophoresis (PAGE) was performed on each variety, according to the procedures described by Sapirstein and Bushuk (1985).

3.2.3 Determination of total and water-soluble pentosans.

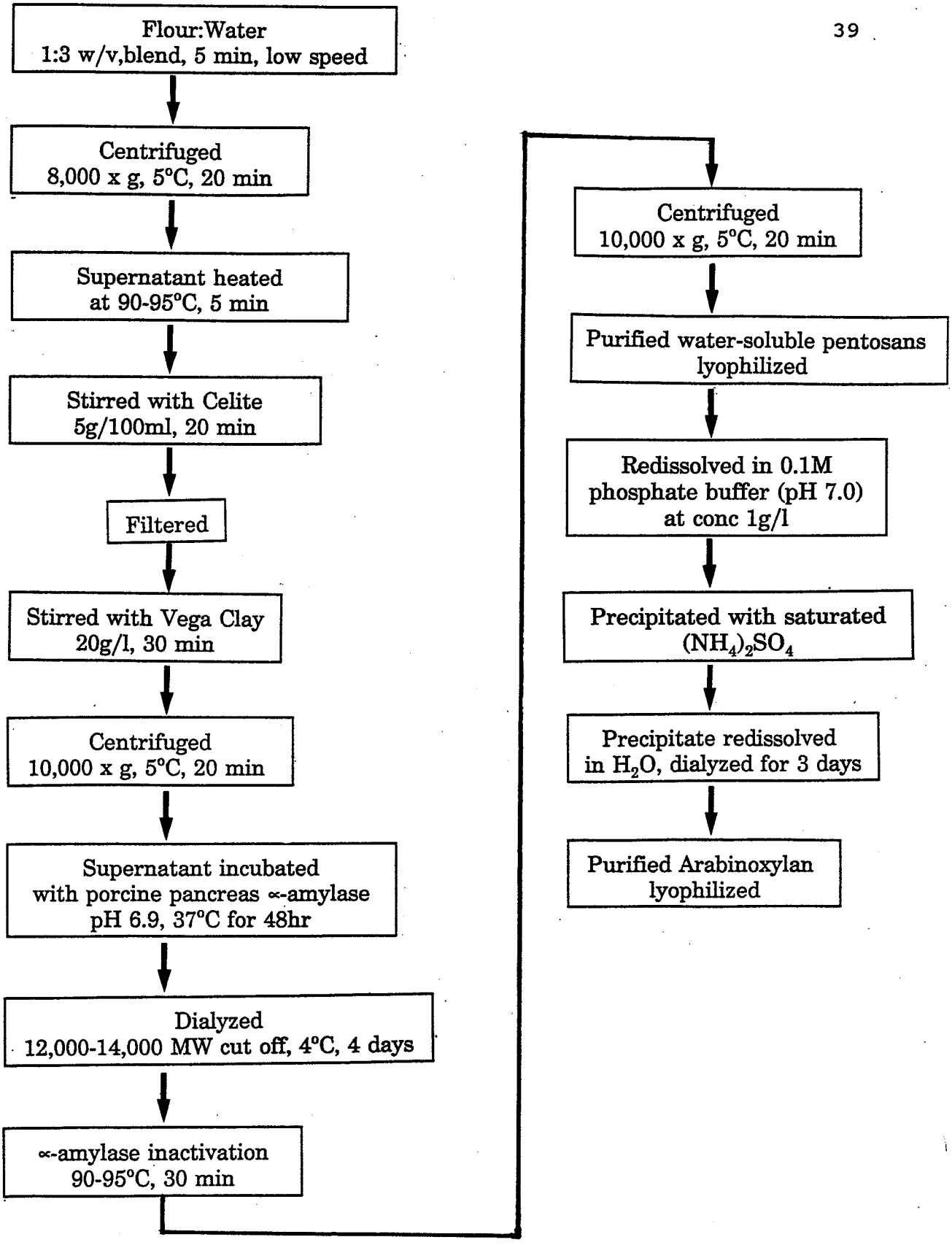
The content of total and water-soluble pentosans in wheat flours were determined by the phloroglucinol method described by Douglas (1981). A typical standard curve of this assay is given in appendix 1.

3.2.4 Extraction, purification and fractionation of water-soluble pentosans.

3.2.4a Extraction and purification of water-soluble pentosans

Water-soluble pentosans were extracted and purified according to the method described by Izydorczyk et al (1990), with some minor modifications (Fig. 7,page 39). Flours were blended with three volumes of water and stirred in a commercial blender for five minutes at room temperature. The slurry thus formed was then centrifuged at 8000xg for 20 minutes at 5°C. The

Figure 7. Procedure for extraction and purification of water-soluble arabinoxylans from wheat flours.


Flour:Water
1:3 w/v,blend, 5 min, low speed
Centrifuged
8,000 x g, 5°C, 20 min
Supernatant heated
at 90-95°C, 5 min
Stirred with Celite
5g/100ml, 20 min
Filtered
Stirred with Vega Clay
20g/l, 30 min
Centrifuged
10,000 x g, 5°C, 20 min
Supernatant incubated
with porcine pancreas ∝-amylase
pH 6.9, 37°C for 48hr
Dialyzed
12,000-14,000 MW cut off, 4°C, 4 days
∝-amylase inactivation
90-95°C, 30 min
Centrifuged
10,000 x g, 5°C, 20 min
Purified water-soluble pentosans
lyophilized
Redissolved in 0.1M
phosphate buffer (pH 7.0)
at conc 1g/l
Precipitated with saturated
$(NH_4)_2SO_4$
Precipitate redissolved
in H_2O, dialyzed for 3 days
Purified Arabinoxylan
lyophilized

supernatant was heated at 95°C for five minutes. Following this treatment, the coagulated proteins were removed by centrifugation. The centrifuged and filtered extracts were then stirred with vega clay (20 g/L of extract) three times for 30 min each. The pH of the extract was adjusted to 6.0 after each treatment with vega clay. The extracts were then incubated twice with α-amylase from porcine pancreas, at 37°C for 48 hr at pH 6.9. After incubation the extracts were dialyzed against distilled water in 12,000-14,000 MW cut off cellulose tubes, until no sugars were detectable (by the phenol-sulphuric method, Dubois et al, 1956) in the dialysis water. Following dialysis the enzyme was inactivated by heating the solution at 95°C for 30 min and then removed by centrifugation at 10,000xg. The supernatants were finally lyophilized.

3.2.4b Fractionation of the water-soluble pentosans

The arabinoxylan fraction of water-soluble pentosans was obtained by selective precipitation with saturated ammonium sulphate according to the method of Fincher and Stone (1974). The purified pentosans were dissolved (at conc. of 1.0 g/l) in 0.1M phosphate buffer at pH 7.0 and $(NH_4)_2SO_4$ was added slowly until saturation. The precipitated arabinoxylan was recovered after 24 hr by filtration on a fibreglass filter paper. The

arabinoxylan was subsequently redissolved in distilled water and exhaustively dialyzed to remove $(NH_4)_2SO_4$. The extract was finally lyophilized.

3.2.5 Protein content of water-soluble pentosans

The protein content of water-soluble pentosans and their arabinoxylan fractions was determined by the method of Lowry et al (1951) using bovine serum albumin as standard.

3.2.6 Gel filtration chromatography

Two separate columns, packed with Sepharose CL-2B (2.5 x 90 cm) and Sepharose CL-4B (2.5 x 91 cm), were employed to determine the molecular size distribution of pentosans and their arabinoxylan fractions. Filtered and degassed solution of NaCl (0.3% w/v) containing sodium azide (0.05% w/v) were used as eluent at a flow rate of 35 ml/hr. Samples of water-soluble pentosans and arabinoxylans (10 mg) were dissolved in the eluent solution (3-5 ml), and applied to the columns. All runs were carried out at room temperature. Fractions of 5 ml were collected in each case. The total and void volumes of the two columns were determined with xylose and Blue Dextran 2000, respectively. Each fraction was used to analyze for carbohydrates (phenol-sulphuric acid method), proteins (Lowry et al, 1951), and feruloyl groups; the latter were determined

by measuring the absorbance of fractions at 375 nm after adjusting the pH to 10.0 with 1M NaOH (Thibault and Rombouts, 1986).

3.2.7 Chemical analyses of arabinoxylans

3.2.7a Phenolics

3.2.7a (i) Method 1

Arabinoxylan solutions (0.25% w/v) were made in 0.07M glycine-sodium hydroxide buffer of pH 10.0. The concentration of feruloyl in these solutions was determined by direct absorbance readings at 375 nm. The molar extinction coefficient for ferulic acid was taken as 31,600 (Fry, 1982)

3.2.7a (ii) Method 2

Phenolic acids were also determined by HPLC as described by Izydorczyk et al (1991a) with minor modifications. Samples of arabinoxylans (150-200 mg) were treated with 10 ml of 2M NaOH at 60°C for 2 hr under N_2 atmosphere. The hydrolysates were then acidified with HCL to pH 2.0. The resulting solutions were treated once with a mixture of hexane (HPLC grade) and water at a ratio 1:1. The aqueous phase with free phenolics was further treated three times (at ratio 1:1) with diethyl ether-ethyl acetate (1:1, HPLC grade). All the organic phases

were pooled together and dehydrated with anhydrous sodium sulphate. The resulting solution was filtered and evaporated to dryness under vacuum at 30°C. The residue was then dissolved in known amounts of methanol and subjected to HPLC using a Supercosil LC-18 column (3.3 cm x 4.6 mm, 3 μm diameter particles) at 37°C. An absorbance detector (Water Associates, Model 441) was employed at 280 nm to detect the peaks. The separation of phenolics was programmed isocratically with 5% methanol for the first five min at a rate of 1ml/min. This was followed by a 5 minute linear gradient to 15% methanol. The eluent with this composition was run isocratically for the next five minutes, followed by ten minutes linear gradient up to 30% methanol, and finally by a ten minutes isocratic elution (30% methanol). Retention times of standards and peak area integrations of standards and samples were obtained using a chromatopac C-R3A data processor (Shimadzu Corporation, Japan) attached to the HPLC. Hydroxybenzoic acid was used as an internal standard.

3.2.7b Monosaccharide analysis

The relative amounts of component monosaccharides in the arabinoxylan fractions were measured by a Water Associates HPLC system, equipped with a model 441 refracting index detector, using the procedures of Izydorczyk et al (1991a).

Samples of arabinoxylans were hydrolysed with 1M H_2SO_4 for 2 hr at 100°C. The hydrolysates were then neutralized with $BaSO_4$ before injection. All standards and samples were run isocratically at a flow rate of 0.6 ml/min at 85°C through an Aminex HPX-87P (300 x 7.8 mm) column, in conjunction with a guard column. Deionised-degassed water was used as a mobile phase. Retention times and peak heights were obtained with the Maxima 820 software associated with the HPLC system.

3.2.8 Rheological measurements

3.2.8a Intrinsic viscosity

Viscosities of aqueous arabinoxylan solutions were measured by Ubbelohde viscometers (International Research Glassware, Kenilworth, NJ) in the concentration range of 0.02 to 0.1% (w/v) at constant temperature (25.0 ± 0.5°C). The reduced viscosity values of arabinoxylans at various concentrations were calculated using distilled water as a solvent. The reduced viscosity values were then plotted against polymer concentration and the curves were extrapolated to zero concentration using the Huggins equation (Huggins, 1942), to obtain the intrinsic viscosities (see appendix 2).

3.2.8b Viscosity as a function of shear rate

Apparent viscosities of arabinoxylans solutions (2.0% w/v) were determined using a Bohlin VOR Rheometer (Bohlin Reologi, Edison, NJ) as a function of shear rate, at a temperature of 25.0 ± 0.1°C. A concentric cylinder geometry was used for the shear rate sweeps. The radii of inner rotor and outer cylinder were 7 and 7.7 mm, respectively. The length of rotor was 21 mm. The samples were subjected to shear sweeps between 5 and 924 s^{-1}. All measurements were done at least in triplicate and the average is reported.

3.2.8c Gelation studies of arabinoxylans

The formation of gel networks of arabinoxylans in solution were studied in three parts using small amplitude shear stress measurements on the Bohlin VOR Rheometer operated in the oscillatory mode. A parallel plate geometry (30 mm diameter) and a torsion bar of 19.3 g was used to follow the gelation process. Immediately after adding the oxidant and the enzyme to the arabinoxylan solution, the reaction mixture was placed between the parallel plates and the gap was adjusted to 1.0 mm. The whole setup (parallel plates with reaction mixture) was covered by a thin layer of light mineral oil (Mallinckrodt, Inc. Paris, KE) to prevent water losses due to evaporation. Data were continuously taken at one minute

intervals for a period of 80 minutes at a frequency of 1.0 Hz and 4.0% strain. Constant temperature was maintained throughout the course of the measurements (15.0 ± 0.1°C). Triplicate samples were tested and values for the storage modulus (G'), loss modulus (G"), and tan δ were obtained using the software package of the Bohlin Rheometer.

In the first part of the studies on gelation behaviour of arabinoxylan solutions (polymer concentration 1.0% w/v) the rigidity development was monitored at different concentrations of oxidant (1.0-100 ppm H_2O_2) in the presence of peroxidase (0.11 PU/ml). Secondly, gel formation was followed in arabinoxylan solutions of two different preparations (a low limiting viscosity arabinoxylan from the cultivar Columbus, and a high limiting viscosity arabinoxylan from Katepwa B) by employing a constant amount of oxidant (3 ppm H_2O_2 and 0.11 PU/ml peroxidase) at different polymer concentrations. Finally, for comparative intervarietal measurements, the formation of gel networks was monitored at a polymer concentration of 1.0% w/v and 3.0 ppm H_2O_2 in the presence of peroxidase (0.11 PU/ml).

3.2.9 Surface tension measurements

A Fisher's Surface Tensiomat (Model 21, Fisher Scientific, Winnipeg, MB) apparatus was used to measure the decrease in

surface tension of water by arabinoxylan at a concentration of 0.5% (w/v). The solutions were placed in a dish of 5.5 cm in diameter with 4.0 cm depth, and changes in surface tension were recorded at five minute intervals for 120 minutes at 23.0±0.2°C.

3.2.10 Fortification studies of flours with added arabinoxylans

3.2.10a Arabinoxylans and base flours

Two arabinoxylan preparations, differing in their limiting viscosity values and molecular weights (from two different flours), were obtained according to the procedure described in section 3.2.4: one with high [η] value (5.48 dl/g, MW 201,623 from Katepwa B) and one of low [η] value (3.69 dl/g, MW 134,673 Columbus). The base flours used for the baking studies belonged to two different classes of wheat, the CWRS (2CW) and the CPS (HY368).

3.2.10b Farinograph absorption

A microfarinograph was used to determine the water absorption of the above two flours with added arabinoxylans (at levels of 0.5-1.3%) according to the approved AACC method (method 54-21, AACC 1983). Arabinoxylans were mixed with 10 g of flour in a

dry form prior to the test.

3.2.10c Bread baking procedures with added arabinoxylans

The GRL remix method (Kilborn and Tipples,1981) was employed for the fortification study with some minor modifications. The bread formula used is given below:-

Flour (14% m.b.)	100.0 g
Yeast	3.0 g
Salt	1.0 g
Sucrose	2.5 g
Potassium bromate	15 ppm
Ammonium phosphate (monobasic)	0.1%
Malt syrup	0.6%
Arabinoxylan	amount varied depending on the nature of the base flour used.
Water	Micro farinograph absorption

Arabinoxylans (pulverized dried form) were mixed with the flours (CPS & CWRS) at different levels (0.3-1.1% of the weight of flour taken) and doughs were made by adding water equivalent to the farinograph absorption value (i.e. to obtain equivalent dough consistency of 500 B.U.). These doughs were

then allowed to ferment for 2 hr and 45 min, remixed and allowed to set again for additional 25 min. Following this, the doughs were sheeted, moulded and cut into two halves of equal weight. Each half was then placed into a separate baking pan (8 cm x 3.5 cm x 4.7 cm) for proofing (55 min). Baking was done for 25 minutes at 430°F (312°C). Loaf volumes were measured after 25 minutes of cooling, as described earlier in section 3.2.1. The loaves were then vacuum-packed in plastic bags using a commercial vacuum sealer (Decosonic, Decosonic Inc., Montreal) and stored at 7°C.

3.2.11 Water activity measurements

Water activity (a_w) of the bread crumbs was measured after 1,3,5 and 7 days of storage (at 7°C) using a CX-1 water activity measuring system (Decagon Devices, Pullman, WA) according to the procedures described by Czuchajowska and Pomeranz (1989).

3.2.12 Moisture content determination

The moisture content of control and arabinoxylan-supplemented (at different levels) bread crumbs stored for 1,3,5 and 7 days (at 7°C) were determined according to the AACC approved method (method 44-15A).

3.2.13 Bread staling studies

3.2.13a Bread Firmness Measurements

The Ottawa Texture Measuring system (OTMS, Engineering and Statistical Research Institute, Ottawa) equipped with Apple software (Personal Computer Products Inc, San Diego, California, USA) was used to follow bread firmness of control and arabinoxylan fortified bread crumbs. Bread crumb slices with a 12 mm thickness were cut out from the centre of the loaves with a commercial bread cutter (TEFAL,model 220, West Germany). These slices were compressed to a 40% compression (4.8 mm) using a 28 mm (area 6.15 x 10^{-2} m^2) diameter plunger with a load cell of 11.36 Kg and cross head speed of 100 mm/min. The compression curves (time in sec vs force in Newtons) were plotted using the apple software. Using these curves, the force readings at 25% compression were taken for comparison purposes. Typical compression curves for control and fortified bread crumbs obtained in these experiments are shown in appendix 3.

3.2.13b Differential Scanning Calorimetry

The staling (recrystallization) process of starch in bread was assessed by calorimetry following storage of the bread crumb at 7°C for a designated time period. The crumb samples were

freeze dried and analyzed with a DuPont 9900 Thermal Analyzer equipped with a DuPont 910 cell base and a low pressure Differential Scanning Calorimeter (DSC) cell , according to the method of Biliaderis et al (1985). Triplicate measurements were performed on samples weighing 3 to 3.5 mg (30% aqueous suspensions of freeze dried crumb)and the average is reported. The samples were heated in the calorimeter at a rate of 10°C/min. Staling endotherm peak temperature and apparent enthalpy values (ΔH; J/g) were determined using the DuPont software. Some typical DSC thermal profiles obtained are given in appendix 4.

3.2.14 Statistical analysis

Analysis of variance (ANOVA) and multiple regression analysis was performed on the data where applicable using the Number Cruncher Statistical System (NCSS, 1987; Kaysville, Utah). Differences among samples and treatments were revealed by the Duncan's multiple range test.

4. RESULTS AND DISCUSSION

The present research study was carried out in three phases.

In the first phase, following the confirmation of purity of the ten wheat varieties employed in this work, technological tests were performed on grains and their flours, doughs and breads. The results of these tests were intercorrelated and correlated to the total and water-soluble pentosan contents found in these flours.

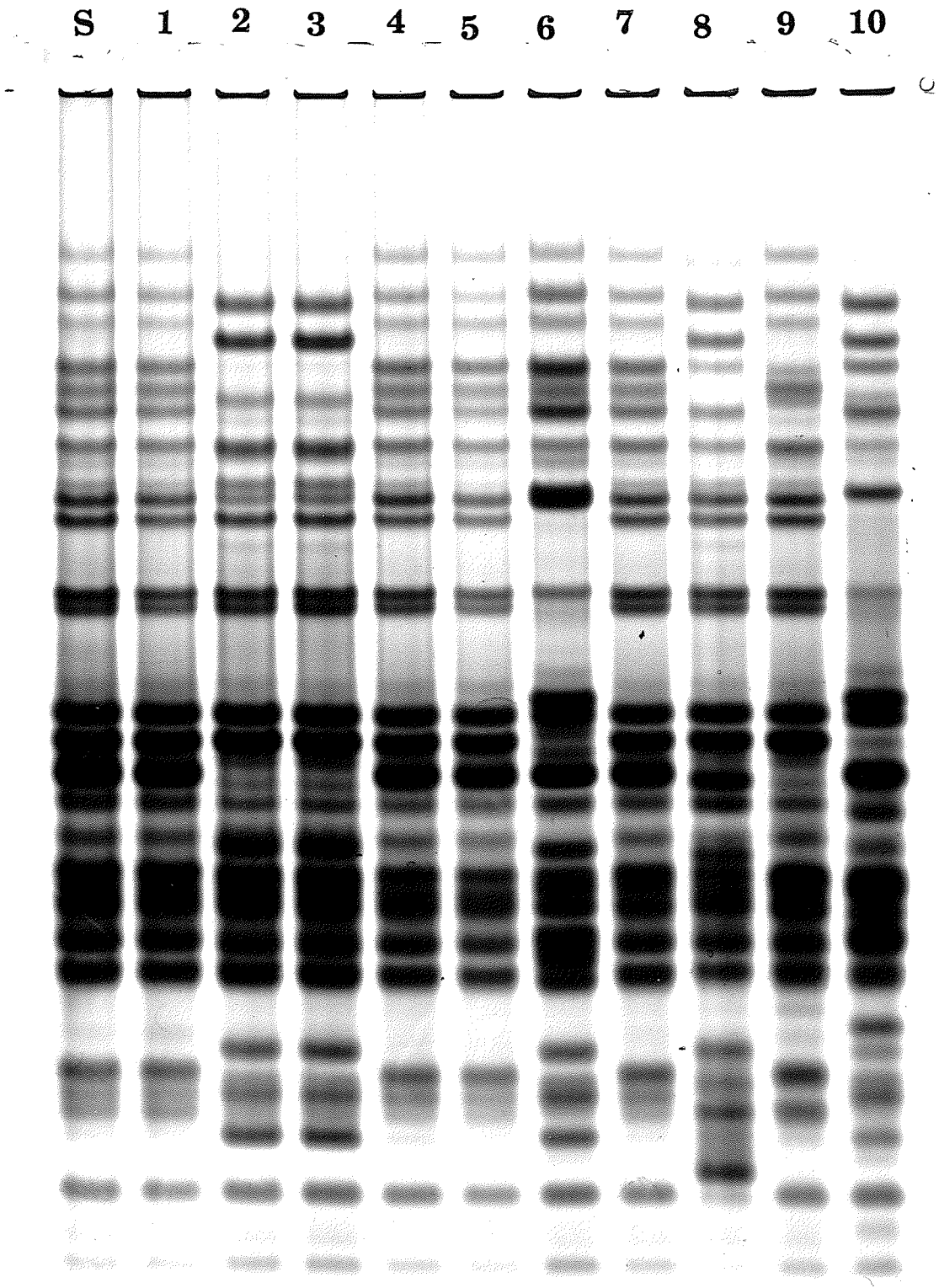
In phase two, water-soluble arabinoxylans (the main fraction of water-soluble pentosans) from the flours of ten varieties were isolated, characterized and their physicochemical properties were studied in solution.

In the final phase of these studies, arabinoxylans extracted from the above flours were added to two base flours of diverse bread making qualities (belonging to two different classes; CWRS and CPS) and their effect on the dough and bread quality parameters were examined.

4.1 Variety Identification

The purity of the wheat varieties in this study was assessed by gel electrophoresis (PAGE) of their gliadin proteins, according to the method of Sapirstein and Bushuk (1985). The patterns obtained are shown in Figure 8. Each cultivar has a band pattern (electrophoregram) that is characteristic of the

Figure 8. Gliadin PAGE patterns of different CWRS wheat cultivars : S= Standard variety Neepawa, Lane # 1 Neepawa, 2 Roblin A, 3 Roblin B, 4 Katepwa A, 5 Katepwa B, 6 Columbus, 7 Benito, 8 Laura, 9 Lancer, 10, Selkirk.


S
1
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genotype and is independent of growth conditions. The patterns obtained for the gliadin proteins of flours used in this study (Fig. 8) were compared with those compiled by Bushuk and co-workers (Sapirstein and Bushuk, 1985; Ng et al , 1988) for a number of Canadian wheat cultivars and were found typical of the designated varieties.

4.2 Technological Tests

In this section the results of different standard tests performed on grain, flour, dough and bread of the cultivars used in this study are discussed under the following subsections.

4.2.1 Grain

Wheat cultivars with hectolitre weight 80 kg or more are generally considered to be of excellent quality. However, this characteristic is highly dependent on the environmental conditions which are essential for optimum development of the wheat kernel and thus in turn contribute to a high hectolitre weight. In contrast, poor environmental conditions lead to low hectolitre weight. The hectolitre weights (HWT) of the ten cultivars in this study ranged from 75.6 to 83.3 kg/hl, (Table 3).

The protein contents of the grain samples of these varieties

Table 3. Grain & Flour quality analyses of CWRS wheat varieties.

	Grain				Flour					
Sample	HWT	WPro	FN	Yld	FPro	Ash	Sed	SD	FWG	AMYL
Neepawa	75.6	14.3	438	73.1	13.6	0.46	67	25	40.6	710
Roblin A	83.3	15.4	404	74.4	14.7	0.49	72	21	43.1	810
Roblin B	77.5	16.3	410	73	16.1	0.47	70	21	49.1	720
Katepwa A	78.5	15.1	450	71.5	14.3	0.48	65	29	44	810
Katepwa B	75.9	10.7	357	69.8	10.1	0.5	41	31	26.8	650
Columbus	76.1	16.7	462	71.3	15.9	0.45	65	23	48.4	790
Benito	78.7	14.7	519	69.8	13.7	0.46	55	27	41.5	720
Laura	78.2	14.5	423	70.7	13.4	0.42	71	25	38	760
Lancer	78.1	12.9	502	74.5	12.6	0.41	62	24	33.7	1000
Selkirk	76.9	14.2	384	74.3	13.3	0.39	72	20	38.7	840

HWt = Hectoliter weight in Kg/hl; WPro = Grain protein content (14 % m.b.)
FN = Hagberg falling number (sec); Yld = % flour yield; Ash = % ash content,
14% m.b.; FPro = % Flour protein content (14 % m.b.); Sed = Zeleny sedimentation Value (cc)
SD = starch damage; FWG = % Flour wet gluten content; Amyl = Amylograph peak viscosity
(B.U.)

covered a wide range (10.7-16.7%), as shown in Table 3. The protein content of wheat grain is dependent on the environmental factors during grain development and strongly influences its breadmaking potential. The Falling Number values obtained for the ten varieties of CWRS wheats ranged from 357-519 (Table 3), indicating that the grain samples had not suffered any significant damage due to pre-harvest sprouting (i.e. they do not have high α-amylase activity).

4.2.2 Wheat flour

The flour yield ranged between 69.8-74.5% for the ten varieties of wheat grain milled in the Buhler pneumatic laboratory mill (Table 3). The flour protein and ash content values were within 10.1-16.1% and 0.39-0.51%, respectively. Ash content of a flour does not affects its bread making performance, but breads baked from flours with high ash content tend to be darker in color, and thereby affects the consumer's acceptability of the product (Pratt, 1977). Commercial straight grade hard wheat flours are considered to contain ash content in the range of 0.41-0.49% (Ziegler and Greer, 1971).

The sedimentation test (sed), which measures the volume of flour particles which have been allowed to swell in an aqueous lactic acid solution and then allowed to settle down

for a given period of time, is used to provide information on the baking strength of wheat flours (Zeleny, 1947). Sedimentation values falling above 60 cc or more are indicative of very strong flours, while values falling below 20 cc are typical of very weak flours with poor baking quality (Pinckney et al, 1957). The sedimentation test generally reveals differences in both protein content and protein quality among flours. Fowler and De La Roche (1975) reported a highly significant correlation between the sedimentation value and the protein content for a group of similar varieties of bread wheats. On the other hand, Orth et al (1972), did not find any correlation between protein content and sedimentation value. However, in a different study, Orth and Bushuk (1972) found a positive correlation between the amount of insoluble glutenin proteins (residue proteins) and the sedimentation value. In the present study, the sedimentation values obtained for the ten varieties ranged between 41 to 72 cc and they were significantly correlated with flour protein content (r=0.704*) and flour wet gluten (r=0.642**) as shown in Table 5.

The results of starch damage for the wheat flours are shown in Table 3. The flour of Katepwa B had the highest starch damage, in agreement with a low amylograph peak viscosity and with a low falling number value. The flour wet gluten (FWG), the gluten mass that remains after washing the

flour with 2% NaCl, ranged among the ten varieties between 26.8-48.4% (Table 3). The FWG was highly correlated with the flour protein content (r=0.985**).

The Amylograph viscosity (AMY) values, also indicative of α-amylase activity in the flours, are given in Table 3.

4.2.3 Dough Rheology

Water absorption is an important factor to the baker because of the dual role played by water in the baking process (Bushuk, 1966). First, when water is mixed with flour it yields a unique composite system (dough) that can be transformed into the final product upon baking (bread). Second, water imparts texture and other quality attributes to bread. Farinograph is an instrument which determines the resistance of dough to mixing and gives the following information :

(1) Water absorption (FAbs), is the amount of water that must be added to 50 g (14% moisture basis) of flour to give a dough with a fixed maximum consistency of 500 Brabender Units. The range of FAbs for the flours obtained in this study was 61.7-70.3% (Table 4). These absorption values were significantly correlated to flour protein (r=0.726*) and flour wet gluten content (r=0.750*). Similar relationships have been reported by Kunerth and D'Appolonia (1985) and Flower and De La Roche (1975).

Table 4. Dough & Bread quality analyses of CWRS wheat varieties.

	Farinograph			Extensograph				Bread	
Sample	FAbs	DDT	MTI	E	Rm	Rm/E	A	RLV	BSI
Neepawa	64.3	6.5	25	185	570	3	146	870	97
Roblin A	67	11.5	10	200	1080	5.4	232	1025	104
Roblin B	70.3	12	5	180	1000	5.5	226	1150	107
Katepwa A	68.4	7	5	162	820	5.1	172	975	103
Katepwa B	64.2	1.5	45	128	820	6.4	141	555	86
Columbus	69.4	8	25	189	690	3.6	155	1170	110
Benito	65.9	8.5	10	156	770	4.9	156	885	97
Laura	66.7	10	20	179	990	5.5	205	930	105
Lancer	61.9	7	30	172	830	4.8	166	810	97
Selkirk	61.7	6	25	194	635	3.3	144	865	98

FAbs = % Farinograph absorption; DDT = Dough development time (min); MTI = Mixing tolerance index (B.U.); E = Extensigraph extensibility (cm); Rm = Resistance to extension at maximum (B.U.); Rm/E = Ratio of resistance to extensibility ; A = Area under the curve (cm^2); RLV = Remix loaf volume (cc); BSI = Baking strength index (%).

Table 5. Correlation coefficients between technological data[1], and pentosans (total & water-soluble) for CWRS wheat varieties.

	HWT	WPro	FN	Yld	FPro	Ash	SED	SD	FWG	AMYL	FAbs	DDT	MTI	E	Rm	Rm/E	A	RLV	BSI	TP	WSP
HWT	1																				
WPro	256	1																			
FN	-209	264	1																		
Yld	310	180	-082	1																	
FPro	862**	986**	263	256	1																
ASH	216	-031	-231	-376	-180	1															
SED	339	716*	015	-632*	704*	-432	1														
SD	-275	-580	157	-745*	-610	134	-794	1													
FWG	197	982**	260	157	985**	080	642**	-516	1												
AMYL	280	057	332	648	095	-602	375	-384	-016	1											
FAbs	172	714*	139	-368	726*	535	216	-040	750*	-365	1										
DDT	595	865**	241	300	807*	-032	-727*	-630	740*	143	577	1									
MTI	-548	-763*	-306	-113	-754*	-158	-571	304	-784**	-027	-617	-794**	1								
E	324	690*	-042	703*	681*	-415	127	-892**	607	388	116	644	382	1							
Rm	712*	138	-172	038	174	310	169	-296	095	027	432	773**	-399	036	1						
Rm/E	366	-348	-235	-387	-896**	514	-440	435	127	-229**	268	041	-037	-585	782*	1					
A	-618	477	-131	274	517	214	-582	-437	439	049	553	-842**	0	406	895**	459	1				
RLV	258	980**	239	230	990**	-023	711*	-608	962**	122	746*	810**	-716*	686*	233	-358	553	1			
BSI	293	931**	220	197	906**	-13	787*	-573	875**	204	761*	805**	-656*	695*	302	-211	603	963**	1		
TP	-152	-03	-126	-507	-200	584	-385	663*	-166	-376	573	-202	053	-496	205	474	026	016	096	1	
WSP	0	-200	-257	-500	-190	789**	-362	685*	-110	-632	452	-136	-103	-530	261	527	159	-203	-206	697*	1

[1] Decimals omitted, except for those with perfect correlations (i.e. r = 1 or r = -1)

*, ** Significantly correlated at 5% and 1% level respectively.

(2) Dough development time (DDT), is the time in minutes required for the dough to reach a maximum consistency (500 B.U.). It indicates the strength of the flour, i.e. the longer the dough development time, the stronger the flour is. In this study the DDTs ranged from 1.5 to 11.5 minutes, indicating the presence of weak and strong flours among the cultivars. The dough development time of these cultivars was significantly correlated to flour protein content (r=0.807**), sedimentation value (r=0.727*) and flour wet gluten (r=0.740*). These findings are consistent with the observations made by Kunerth and D'Appolonia (1985).

(3) Mixing Tolerance Index, (MTI), is the difference in consistency between peak value and 5 minutes past the peak (in B.U.). This parameter is related to the stability of dough towards overmixing. Doughs with low MTI values can withstand overmixing, while doughs with high MTI values cannot tolerate the excessive mixing and must be handled with care. As expected, significant negative correlations were obtained between MTI and DDT (r=-0.794**), FPro (r=-0.754*),and FWG (r=-0.784**).

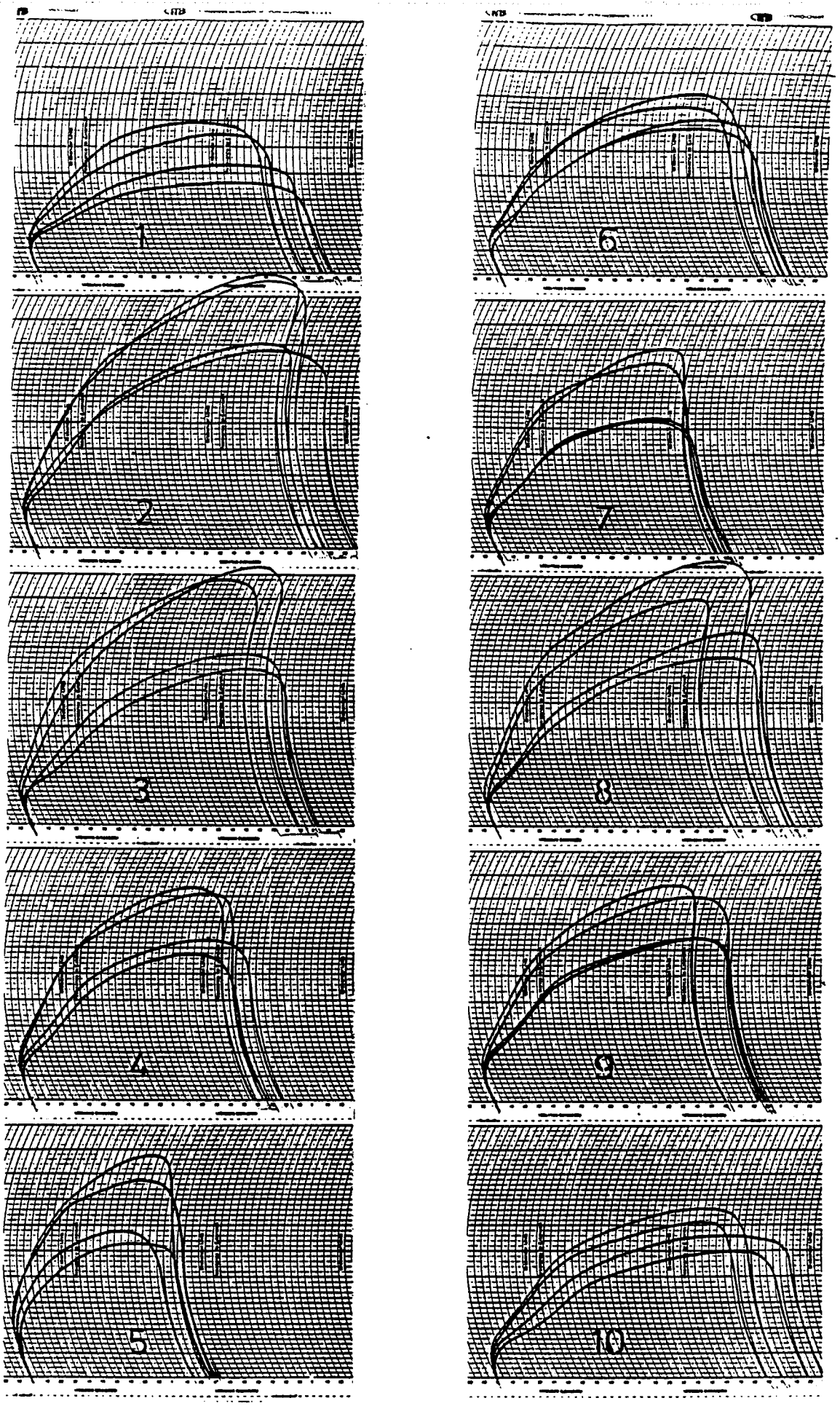
The constantly changing physical properties of dough makes the system dynamic. It is thus important to monitor the rheological properties of dough after mixing in order to predict the quality of the final product. The most common

instrument used for such measurements is the Brabender Extensigraph. This instrument gives information about the resistance to stretching and extensibility of dough in the form of a curve called extensigram (Fig. 9). The two parameters derived from the extensigram are first, the extensibility (E), which is the length of curve in millimetres from the start of stretching until the dough breaks, and second, the maximum height of the curve in Barbender Units, representing the resistance to extension (Rm). Since resistance to extension (Rm) is related to the elastic properties of the viscoelastic dough, and extensibility (E) is related to the viscous component, the ratio of the two Rm/E gives an indication of the balance of elastic and viscous components in the dough. Another parameter (A) represents the energy required to stretch a piece of dough to its breaking point, which can be calculated from the area under the extensigraph curve. The values of these parameters obtained in this study for the ten samples are given in Table 4. The elasticity (Rm) values were positively correlated with the ratio Rm/E (r=0.782*) and area A (r=0.895**).

4.2.4 Bread baking test

The commonly used baking procedure to test Canadian bread wheats is the GRL Remix Method, (Kilborn and Tipples, 1981)

Figure 9. Extesigrams for flours of the ten varieties; (1) Neepawa, (2) Roblin A, (3) Roblin B, (4) Katepwa A, (5) Katepwa B, (6) Columbus, (7) Benito, (8) Laura, (9) Lancer, (10) Selkirk. The upper lines (duplicate dough samples) correspond to a resting period of 135 min and lower lines (duplicate dough samples) correspond to a resting period of 45 min.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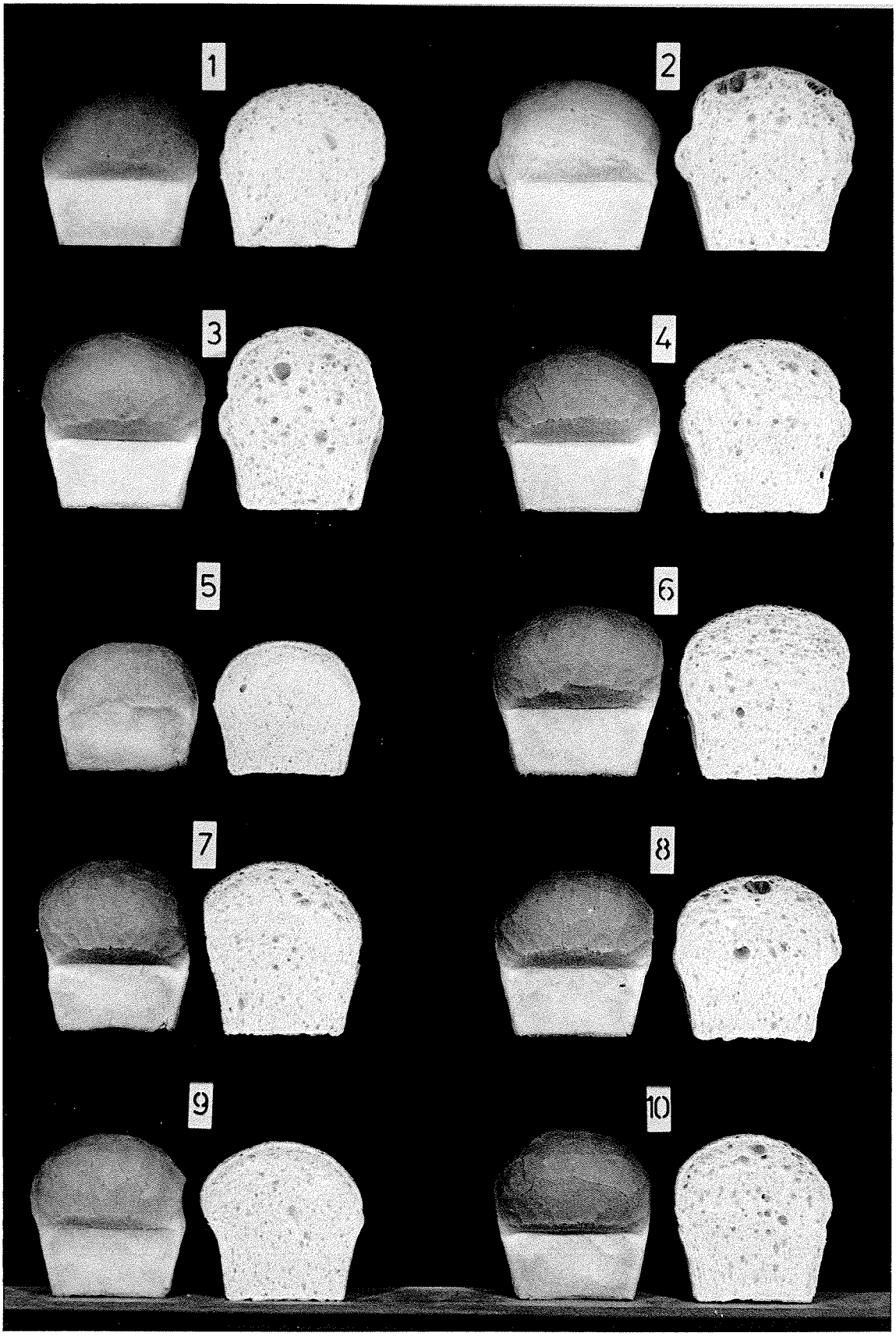
which is originally based on the method described by Irvine and McMullan (1960). This method was adopted in the present study and the results obtained for loaf volume of bread for each individual variety are given in Table 4. The obtained loaf volume values ranged between 555 and 1170 cc. The external and internal quality characteristics of breads are also shown in Figure 10. Statistical analysis (Table 5) showed that Remix loaf volume (RLV) is positively related to FPro (r=0.990**), SED (r=0.711*), FWG (r=0.962**), FAbs (r=0.746*), DDT (r=0.810**), E (r=0.686*) and negatively correlated to MTI (r=-0.716*). It is well documented that the loaf volume is directly related to protein content, but protein quality also plays a major role in determining the final quality of the product. In order to include the protein quality, Tipples and Kilborn (1974) normalized the RLV to a constant protein content. These workers introduced a parameter called "Baking Strength Index" (BSI). According to these researchers the BSI is a protein quality parameter that expresses loaf volume, by the Remix baking method, as a percentage of the volume normally expected for a Canada hard red spring wheat flour of the same protein content. This parameter is calculated as:

$$BSI = \text{loaf volume} \times 100 / (FPro \times 70) - 58$$

Tipples and Kilborn (1974) have developed this parameter from linear regression analysis of 116 wheat samples for their

Figure 10. Bread loaves for the flours of different wheat cultivars; loaf #, (1) Neepawa, (2) Roblin A, (3) Roblin B, (4) Katepwa A, (5) Katepwa B, (6) Columbus, (7) Benito, (8) Laura, (9) Lancer, (10), Selkirk.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protein content and loaf volume values. The slope of the regression line obtained was 70 and the intercept was 58; BSI is expressed as a percentage value. For the flours examined in this study, statistical analysis showed that BSI was significantly correlated to loaf volume (r=0.963**), FPro (r=0.906**),FWG (r=0.875**), FAbs (r=0.761*), DDT (r=0.805*), MTI (r=-0.656*) and E (r=0.695*).

4.2.5 Total and water-soluble pentosans in flours

The contents of total and water-soluble pentosans of flours for the ten wheat samples are given in Table 6. The total pentosan (TP) and water-soluble pentosan (WSP) contents ranged within 1.44-2.19% and 0.45-0.68%, respectively. The highest amounts of both TP and WSP were found for the two Katepwa (A & B) flours. A significant correlation was found between total and water-soluble pentosans (r=0.697*), Table 5. A similar relationship between the two has been reported by Shogren et al (1987). Both total and water-soluble pentosans were also found to be significantly correlated to starch damage, (r= 0.662* and 0.685*, respectively). Furthermore, a positive correlation was found between WSP and ash content of flours (r= 0.789*). These observations are consistent with the findings of Hasimato et al (1987) who reported linear relationships between ash content and total pentosan contents

TABLE 6. Total and Water-soluble pentosans content of wheat flours.

Variety	Total pentosans(%)[a]	WSP(%)[a,b]
Neepawa	1.72±.09	0.64±.02
Roblin A	1.74±.12	0.59±.02
Roblin B	1.81±.07	0.61±.01
Katepwa A	2.19±.18	0.68±.03
Katepwa B	2.13±.06	0.68±.05
Columbus	2.06±.09	0.52±.02
Benito	1.70±.04	0.57±.03
Laura	1.98±.07	0.61±.02
Lancer	1.65±.08	0.50±.01
Selkirk	1.44±.05	0.45±.02

[a]n=3±SD
[b]water-soluble pentosans

of different grains including wheat. Among the samples of the present study no relationships were found between loaf volume and total pentosans or water-soluble pentosans. However, using a large number of samples (n=24) Shogren et al (1987) have shown (through multiple regression analysis) that, in addition to protein content, pentosans also effect the bread-making quality parameters, such as bake absorption, dough mixing time and loaf volume.

4.3 Extraction and purification of water-soluble arabinoxylans

The isolation of arabinoxylans from wheat flours was accomplished in two stages. First, water-soluble pentosans were extracted and purified according to the procedure described in section 3.2.4. In order to remove most of the contaminating proteins, flour extracts were extensively treated with vega clay. The amount of residual proteinaceous material found in the freeze dried water-soluble pentosans is given in Table 7. Among the ten different preparations, protein contents ranged within 1.99-3.12%. The pentosans prepared in this study were of much lower protein content than those reported in earlier studies (Ciacco and D'Appolonia,1982; D'Appolonia and MacArthur,1975; Izydorczyk et al ,1991a; Lin and Pomeranz, 1968; Lineback et al, 1977;

Table 7. Protein content of water-soluble pentosans and their arabinoxylan fractions from different wheat varieties.

Variety	WSP[a]	AX[b]
Neepawa	2.27±.02[c]	1.23±.01[c]
Roblin A	2.37±.01	1.49±.02
Roblin B	3.12±.01	2.20±.01
Katapwa A	2.12±.05	1.21±.01
Katapwa B	2.38±.04	1.35±.01
Columbus	1.99±.01	0.93±.02
Benito	2.27±.02	1.11±.01
Laura	2.26±.01	1.14±.02
Lancer	2.45±.05	1.18±.01
Selkrik	2.55±.03	1.03±.02

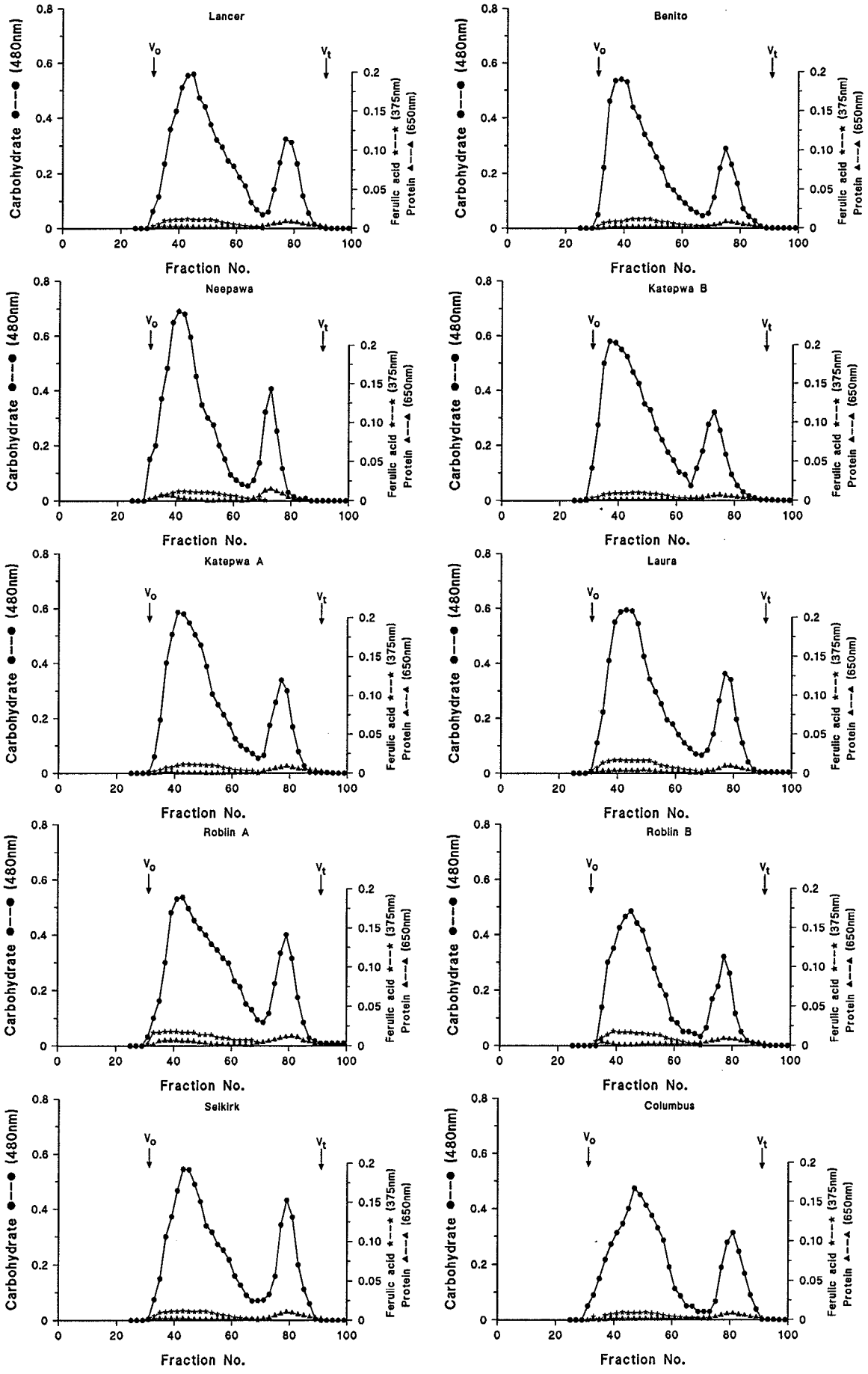
[a]Water-soluble pentosans

[b]Arabinoxylans

[c]% (w/w); means ± SD (n=3)

Patil et al, 1976 and Yeh et al,1980). A preparation of α-amylase from porcine pancreas was employed to remove water-soluble starch. To attain maximum purity, incubation of crude pentosan extracts with this enzyme was repeated twice. Following each incubation, the extracts were subjected to extensive dialysis in order to remove all small molecular weight α-D-glucans. The gel permeation chromatography (Sepharose CL-2B) profiles of pentosan extracts after treatment with the porcine pancreatic α-amylase were identical to those of pentosan preparations treated with a salivary α-amylase preparation according to the method of Izydorczyk et al (1991a). This finding suggested that the porcine pancreatic α-amylase did not have any pentosanase activity. Each preparation of water-soluble pentosans revealed two major peaks upon elution on a Sepharose CL-2B column (Fig. 11). The first asymmetric peak, which elutes in the vicinity of the void volume, corresponds to the high molecular weight component, arabinoxylan (Izydorczyk et al, 1991a). The second symmetrical peak (Fig. 11) corresponds to the low molecular weight component of water-soluble pentosans, arabinogalactan. Very small amounts of proteinaceous material was detected in the eluted fractions of the arabinoxylan peak region. A small but distinctive peak of proteinaceous material co-eluting with carbohydrates in the region of arabinogalactan peak is due to

Figure 11. Gel filtration profiles of water-soluble pentosans on Sepharose CL-2B column, (2.5x90 cm) eluted with 0.3% NaCl and 0.05% NaN_3, at a flow rate of 35 ml/h, at 22°C. Absorbance readings at 480 nm (•),375 nm (*) and 650 nm (▲) correspond to eluting carbohydrates, ferulic acid, and proteins, respectively.

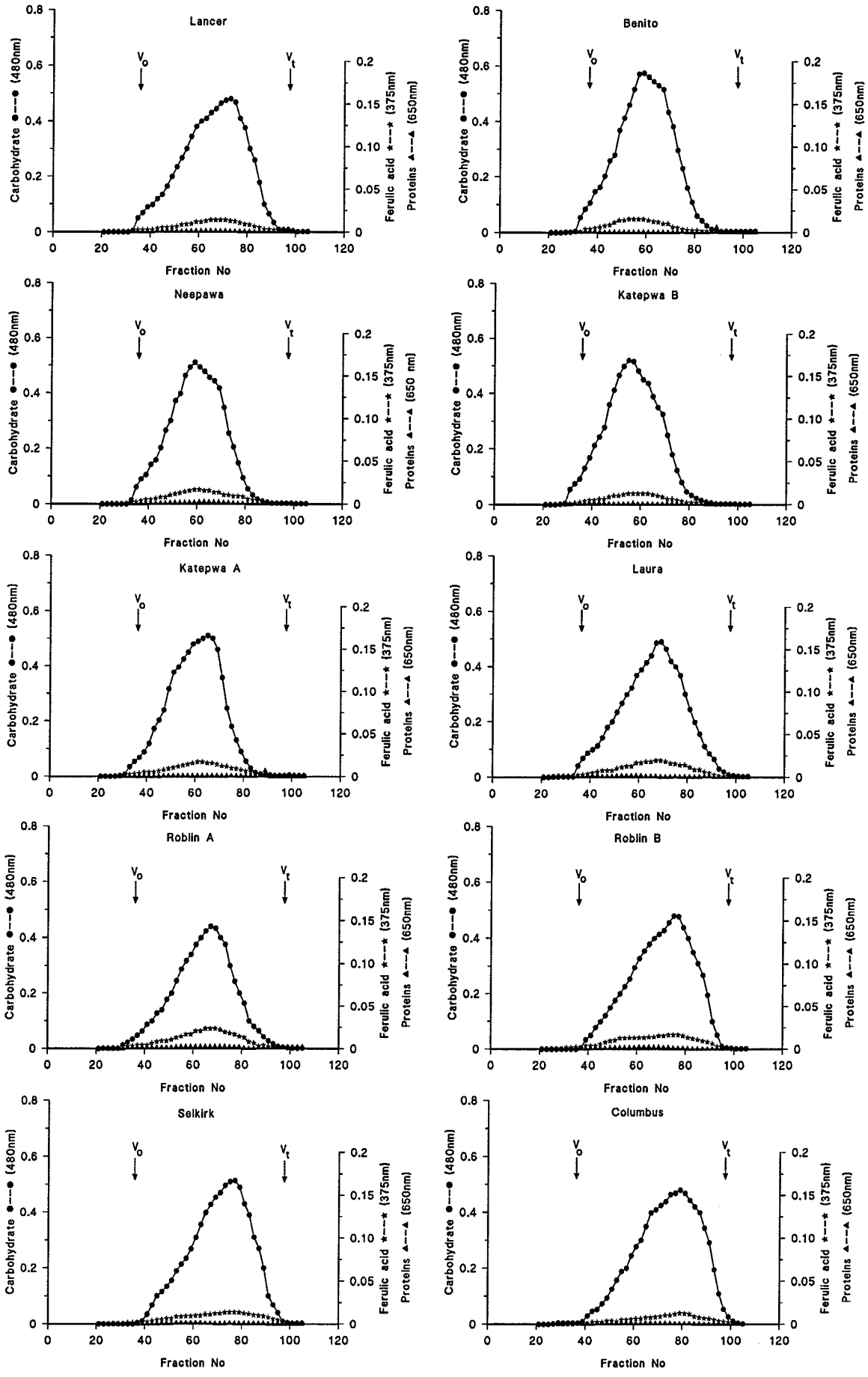

Lancer
Benito
Neepawa
Katepwa B
Katepwa A
Laura
Roblin A
Roblin B
Selkirk
Columbus
Carbohydrate ●--● (480nm)
Ferulic acid *--* (375nm)
Protein ▲--▲ (650nm)
Fraction No.
Vo
Vt

the covalently bound peptide moiety to this constituent (Fincher et al, 1974). The distribution of ferulic acid in the eluted fractions was confined to the high molecular weight arabinoxylan region indicating that feruloyl groups are associated with this polydisperse polysaccharide fraction. These observations are in support of the findings of previous studies (Fincher and Stone, 1974; Izydorczyk et al, 1991a). The arabinoxylan component of water-soluble pentosans of the ten varieties were obtained by ammonium sulphate precipitation. The residual amount of proteinaceous material found associated with arabinoxylan preparations ranged within 1.0-2.2% (Table 7). The gel filtration profiles of these preparations on a Sepharose CL-4B column are shown in Figure 12. Each arabinoxylan eluted as a broad asymmetric peak indicating a broad molecular weight distribution. Also, there were differences in the elution volumes among samples, indicating variability in the molecular size of these polysaccharides (Fig. 12).

4.4 Chemical analysis of arabinoxylans

In addition to molecular weight distribution, arabinoxylans were chemically characterized with respect to their ferulic acid content and component monosaccharides.

Figure 12. Gel filtration profiles of arabinoxylans on Sepharose CL-4B column, (2.5x91 cm) eluted with 0.3% NaCl and 0.05% NaN_3, at a flow rate of 35 ml/h, at 22°C. Absorbance readings at 480 nm (•),375 nm (*) and 650 nm (▲) correspond to eluting carbohydrates, ferulic acid, and proteins, respectively.


Lancer
Benito
Neepawa
Katepwa B
Katepwa A
Laura
Roblin A
Roblin B
Selkirk
Columbus
Carbohydrate ●--● (480nm)
Ferulic acid *--* (375nm)
Proteins ▲--▲ (650nm)
Fraction No
Vo
Vt

4.4.1 Phenolic compounds

Phenolic compounds such as ferulic (4-hydroxy-3-methoxy cinnamic) and p-coumaric (4-hydroxy cinnamic) acids are covalently bound to cell walls of several members of the Graminaeae family (Harris and Hartley, 1976). Ferulic acid, in particular, is known to be bound to the arabinoxylan fraction of water-soluble pentosans of wheat (Kündig et al,1961; Neukom,1976; Smith and Hartley, 1983). Feruloyl groups play an important role in the functional properties (in a isolated system) of arabinoxylans; i.e. they are involved in formation of diferulic bridges between two separate arabinoxylan chains (Geissmann and Neukom, 1973; Neukom, 1976; Izydorczyk et al, 1990). In this study, two methods, HPLC and Spectrophotometry, have been applied to determine the amount of bound phenolics in arabinoxylans. The data obtained by both methods were comparable (Table 8). The HPLC chromatograms also revealed the presence of both cis- and trans-isomers of ferulic acid (Fig. 13) in all preparations. This observation supports the findings of Izydorczyk et al (1991a), who showed the presence of these two isomers of ferulic acid in arabinoxylans of several varieties of wheats belonging to different classes. Significant differences in ferulic acid content were found among the arabinoxylan preparations. The highest amounts of ferulic acid were found for the arabinoxylans from the

TABLE 8. Phenolic Acid content of arabinoxylans from different wheat varieties.

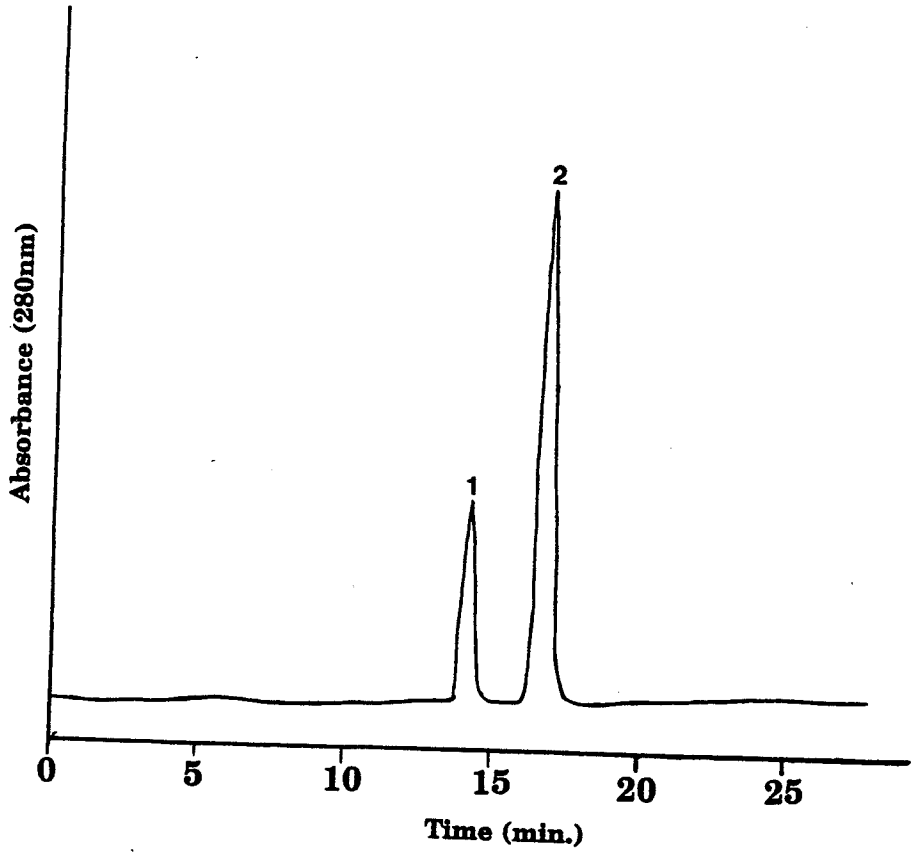
Variety	Total Phenolics (mg/g)[a]	
	1[b]	2[c]
Neepawa	1.35±0.07	1.45±0.02
Roblin A	1.50±0.04	1.61±0.02
Roblin B	1.52±0.02	1.49±0.01
Katepwa A	1.06±0.05	1.02±0.02
Katepwa B	1.11±0.02	1.07±0.04
Columbus	0.93±0.01	0.90±0.03
Benito	1.10±0.03	1.05±0.01
Laura	1.27±0.04	1.24±0.03
Lancer	1.07±0.02	1.10±0.05
Selkirk	1.04±0.06	1.07±0.04

[a]Expressed as ferulic acid, (n=3±SD).

[b]Spectrophotometric measurements of solutions after adjustment of pH to 10.0 with 0.07M glycine-NaOH at 375 nm; extinction coefficient 31,000 (Fry, 1982).

[c]HPLC method; numbers represent the sum of cis-and trans-ferulic acids.

Figure 13. HPLC chromatogram of deesterified phenolic acids from a purified arabinoxylan (cv. Neepawa); (1) cis-ferulic acid, (2) trans-ferulic acid.


Absorbance (280nm)
1
2
0
5
10
15
20
25
Time (min.)

cultivars Roblin (A & B) and Neepawa, while the lowest amount was observed for the arabinoxylan of Columbus.

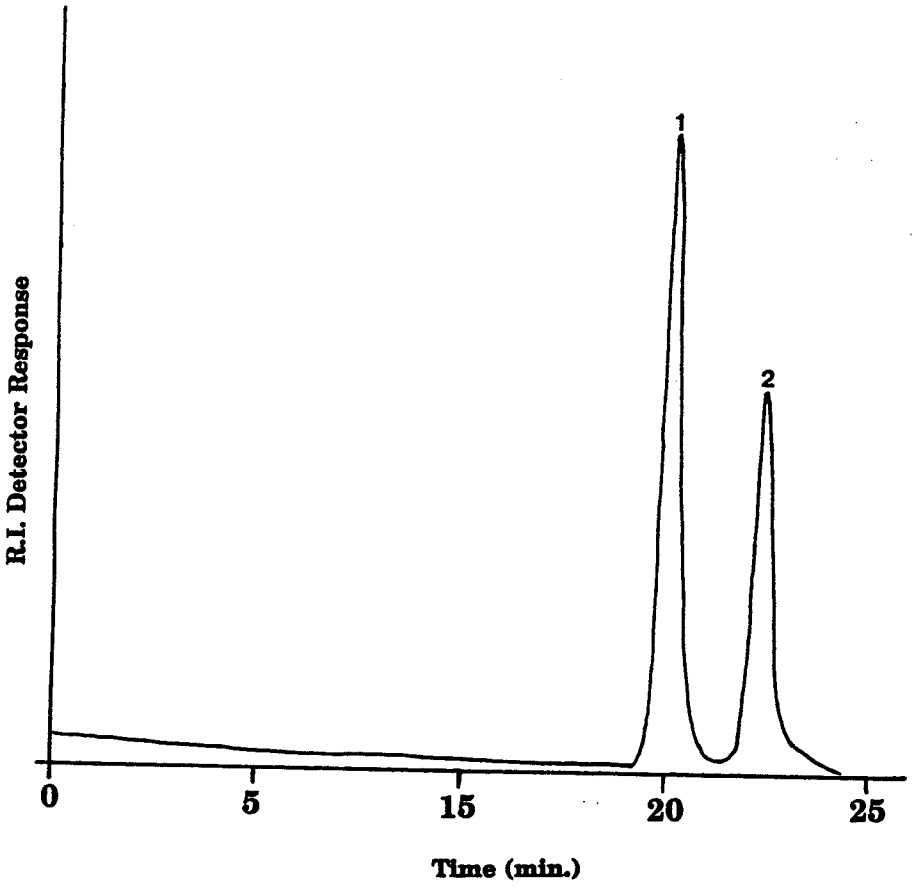
4.4.2 Monosaccharide composition

The ratio of component sugars of arabinoxylan is an indicator of the degree of branching for this polysaccharide. In addition to branching, the ratio of the two constituent sugars has been suggested to influence the solubility and conformation of arabinoxylan in aqueous solutions (Andrewartha et al, 1979). Table 9 shows the ratios of component monosaccharides (determined by HPLC) found in the arabinoxylan preparations. Only two sugars arabinose and xylose were detected in the arabinoxylan hydrolyzates (Fig. 14), indicating that a high degree of purity was achieved upon isolation of these polysaccharides. A relatively small variation in the ratios of xylose to arabinose was observed among the samples (1:1.47-1:1.62). A much broader variation in Ara/Xyl ratios (1:1.41-1:1.89) was reported earlier by Izydorczyk et al (1991a) for arabinoxylans isolated from cultivars belonging to different wheat classes. Arabinoxylans from Selkirk and Columbus had the most branched structure compared to the rest of the samples. Previous studies have indicated that the degree of branching of this polysaccharide varies with the botanical source, cultivar and growth location

Table 9. Ratio of component sugars in Arabinoxylans

Variety	Arabinose:Xylose
Neepawa	1.00:1.56
Roblin A	1.00:1.53
Roblin B	1.00:1.54
Katepwa A	1.00:1.61
Katepwa B	1.00:1.56
Columbus	1.00:1.49
Benito	1.00:1.56
Laura	1.00:1.62
Lancer	1.00:1.60
Selkrik	1.00:1.47

Figure 14. HPLC chromatogram of monosaccharides from a purified arabinoxylan hydrolyzate (cv. Columbus); (1) xylose, (2) arabinose.


R.I. Detector Response
1
2
0
5
15
20
25
Time (min.)

of the grain (Ciacco and D'Appolonia, 1982; D'Appolonia and MacArthur, 1975; Izydorczyk et al, 1991a; Medcalf et al, 1968).

4.5 Physical and functional properties of arabinoxylans

The physical properties of arabinoxylans in aqueous solutions were studied with respect to their viscosity, gelation and interfacial properties.

4.5.1 Intrinsic viscosity

The arabinoxylan fraction of water-soluble pentosans is considered to play a functional role in dough and batters because of its ability to form viscous solutions or cross-linked hydrated networks. Substantial differences in limiting viscosity values were observed among the arabinoxylans from various cultivars (3.69-5.48 dl/g, Table 10). The highest value was for the arabinoxylan Katepwa B, and the lowest viscosity value was found in the case of Columbus. These data were in general agreement with the peak elution volumes on Sepharose CL-4B of these polysaccharides (Fig. 12). It is known that limiting viscosity of polysaccharides is a measure of the hydrodynamic volume of macromolecules and this is related to their molecular size and chain conformation. As a whole class (CWRS), the intrinsic viscosity values of wheat

Table 10. Limiting viscosities and apparent molecular weights[1] of arabinoxylans from different wheat varieties.

Variety	Limiting viscosity (dl/g)	Apparent MW
Neepawa	4.77	175,000
Roblin A	4.37	160.043
Roblin B	4.03	147,347
Katepwa A	4.45	163,033
Katepwa B	5.48	201,623
Columbus	3.69	134,673
Benito	4.67	171,261
Laura	4.39	160,790
Lancer	4.17	152,572
Selkirk	4.07	148,839

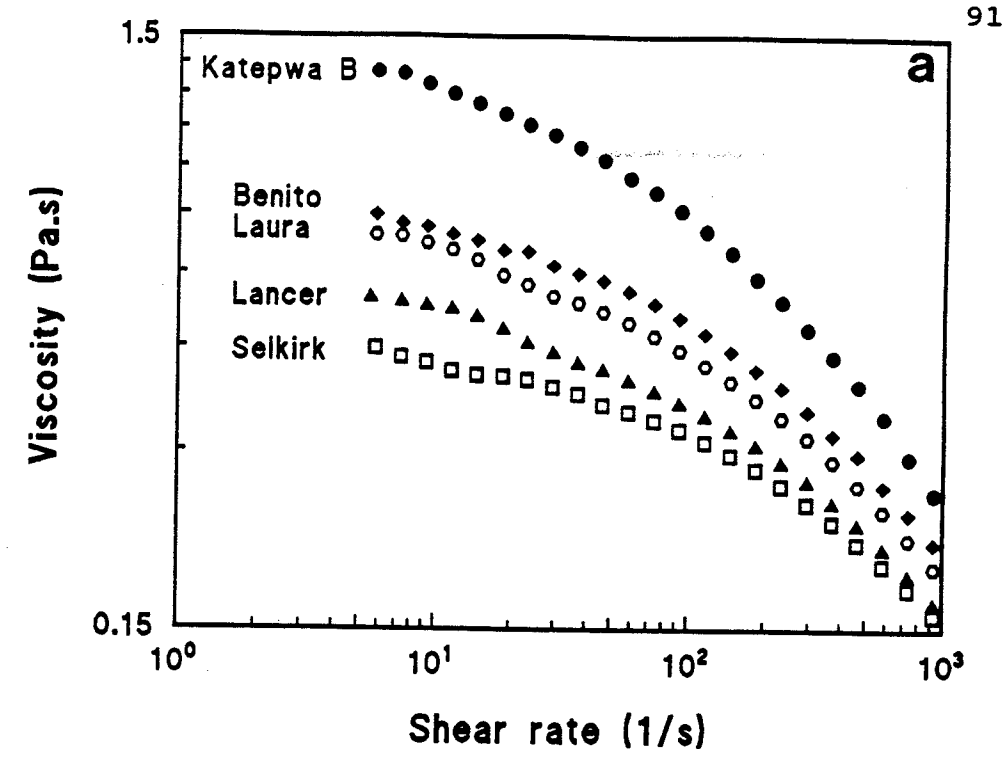
[1]Calucated from equation $[\eta] = 3.47 \times 10^{-3}\ MW^{0.98}$, derived by Anger *et al* (1986).

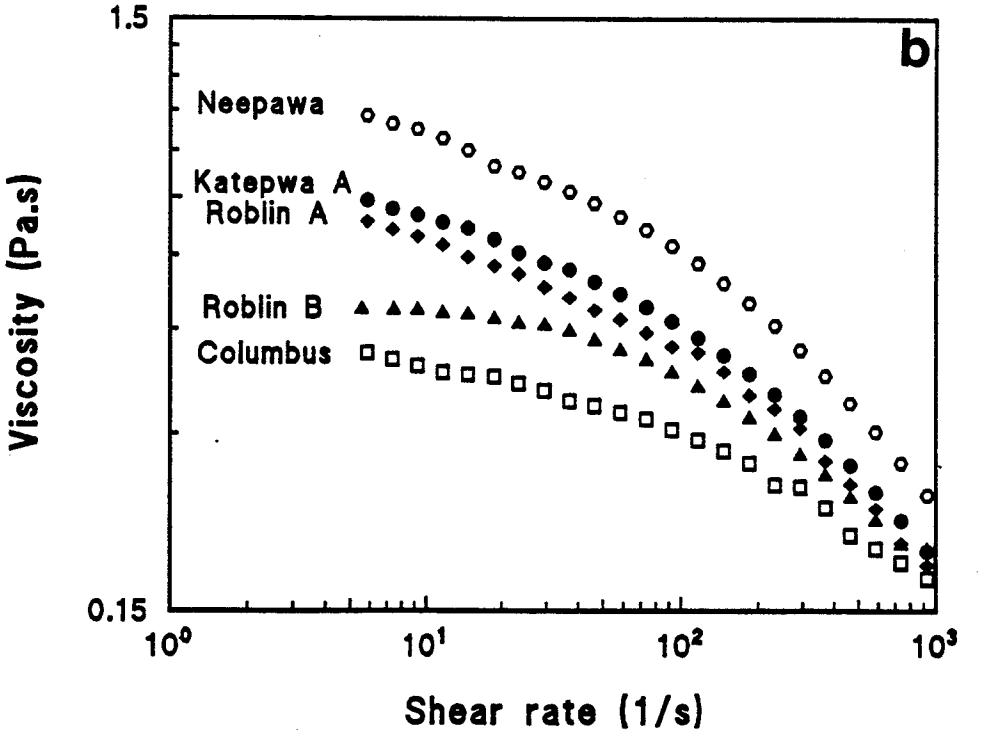
arabinoxylans in the present study were generally found to exceed the values reported earlier by Izydorczyk et al (1991b) for arabinoxylans from flours of different classes of Canadian wheats (2.75-4.23 dl/g). Apparent molecular weights were also calculated from the limiting viscosity number using the equation given by Anger et al (1986), $[\eta] = 3.47 \times 10^{-3} MW^{0.98}$. The molecular weight range for the ten arabinoxylans was 134,674-201,623 (Table 10). Arabinoxylans from cv. Columbus exhibited the lowest molecular weight (134,673), whereas that from cv. Katepwa B the highest (201,623), Table 10.

4.5.2 Effect of shear rate on apparent viscosity of arabinoxylans

The effect of shear rate on the apparent viscosity of arabinoxylan solutions (2.0% w/v) is shown in Figure 15. Each curve is characterized by a slow decrease in apparent viscosity at the low shear rate, followed by a rapid fall in viscosity (shear thinning) at higher shear rates. This type of behaviour is typical for pseudoplastic materials. Differences in apparent viscosities at different shear rates were observed among samples, indicating differences in molecular size and/or conformation of the polymeric species present in these materials. These results further support the differences in intrinsic viscosity values (Table 10) and gel filtration

Figure 15. Steady shear flow curves of arabinoxylan solutions (2.0%, w/v) at 25°C.


1.5
0.15
Viscosity (Pa.s)
Katepwa B
a
Benito
Laura
Lancer
Selkirk
10^0
10^1
10^2
10^3
Shear rate (1/s)


1.5
0.15
Viscosity (Pa.s)
b
Neepawa
Katepwa A
Roblin A
Roblin B
Columbus
10^0
10^1
10^2
10^3
Shear rate (1/s)

profiles (Fig. 12).

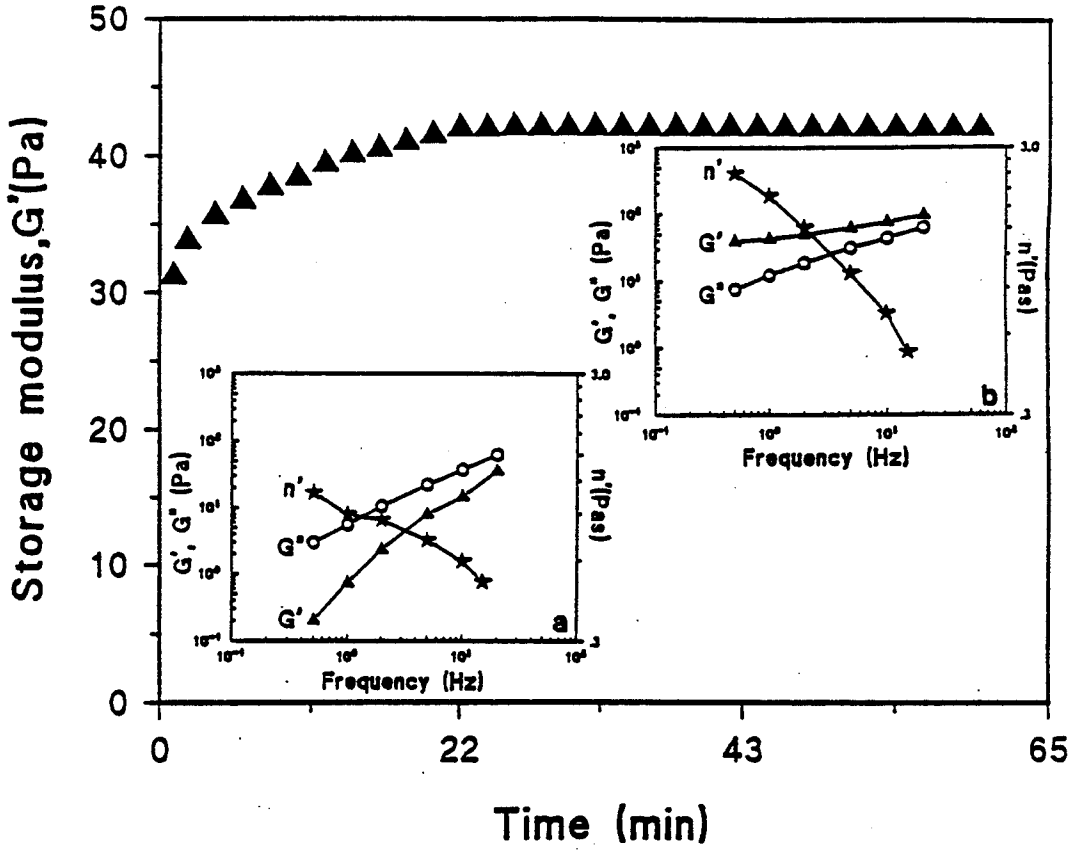
4.5.3 Gelation

It has been shown that pentosans and particularly arabinoxylans undergo gelation in the presence of oxidising agents such as H_2O_2/peroxidase (Baker et al, 1943; Udy, 1956). The mechanism of oxidative gelation involves the formation of covalent cross-linkages between arabinoxylan molecules via diferulic bridges (Geissmann and Neukom, 1973; Izydorczyk et al, 1990; Markwalder, 1975; Neukom, 1976).

In the present studies, the gel network formation of arabinoxylans was monitored by small-amplitude shear stress oscillatory measurements. First, the effects of oxidant and polymer concentration were investigated. Second, the gel forming behaviour of different arabinoxylans at a particular concentration of polymer and oxidant (H_2O_2/peroxidase) were compared.

Figure 16 illustrates the rheological responses of a viscous arabinoxylan solution undergoing oxidative gelation. The inset (a) shows the mechanical spectrum of the arabinoxylan solution (polymer concentration 2.3%, w/v) before the addition of the oxidant (H_2O_2/peroxidase). In this spectrum the viscous component, loss modulus (G") predominates over the elastic modulus (G') in the range of frequencies

Figure 16. Development of storage modulus, G', with time of a typical arabinoxylan (cv. Columbus) solution (2.3%, w/v) treated with horseradish peroxidase (0.11 PU/ml) and H_2O_2 (3.0 ppm). Data were collected at a frequency of 1.0 Hz and strain of 4.0% at 15°C. Insets represent the mechanical spectra of the arabinoxylan solution before the addition of the oxidant (a) and after gel network development (b).


Storage modulus,G'(Pa)
50
40
30
20
10
0
0
22
43
65
Time (min)
G', G" (Pa)
n'(Pas)
n'
G"
G'
Frequency (Hz)
a
b

tested. This behaviour is typical of a viscous solution. Following oxidative gelation, the storage modulus prevails over the viscous modulus and the mechanical spectrum (inset b) becomes typical of a solid-like material.

The effect of different levels of an oxidant (H_2O_2/peroxidase) on gel network formation, as manifested by the storage modulus G', at a constant concentration of arabinoxylan (1.0% w/v) is shown in Figure 17. An increase in the storage modulus, G', was observed with increasing concentration of oxidant up to a level of 3.0 ppm. Further increases in oxidant concentration did not influence the storage modulus, indicating that a certain minimum level of oxidant is required to form an effective gel network.

Two different arabinoxylan samples, one of high molecular weight, (i.e. high intrinsic viscosity; Katepwa B) and the other of low molecular weight (i.e. low intrinsic viscosity; Columbus) were selected to study the effect of polymer concentration on storage modulus (at a constant level of H_2O_2, 3.0 ppm). As shown in Figure 18, linear relationships between the storage modulus, G'(plateau value) of the gel network and polymer concentration were observed for both arabinoxylan samples (Katepwa B, $r=0.997$, $p \leq 0.01$ for a concentration range 0.6-1.4%, w/v; Columbus, $r=0.987$, $p \leq 0.01$ for a concentration range 1.0-2.3%, w/v). The results of these

Figure 17. Effect of H_2O_2 concentration (1.0-100 ppm) on storage modulus (G') of arabinoxylan (cv. Roblin A, 1.0%, w/v) in the presence of horseradish peroxidase (0.11 PU/ml). Data were collected at a frequency of 1.0 Hz and strain of 4.0% at 15°C. The inset shows development of storage modulus at three different concentrations of H_2O_2 (ppm) with time.

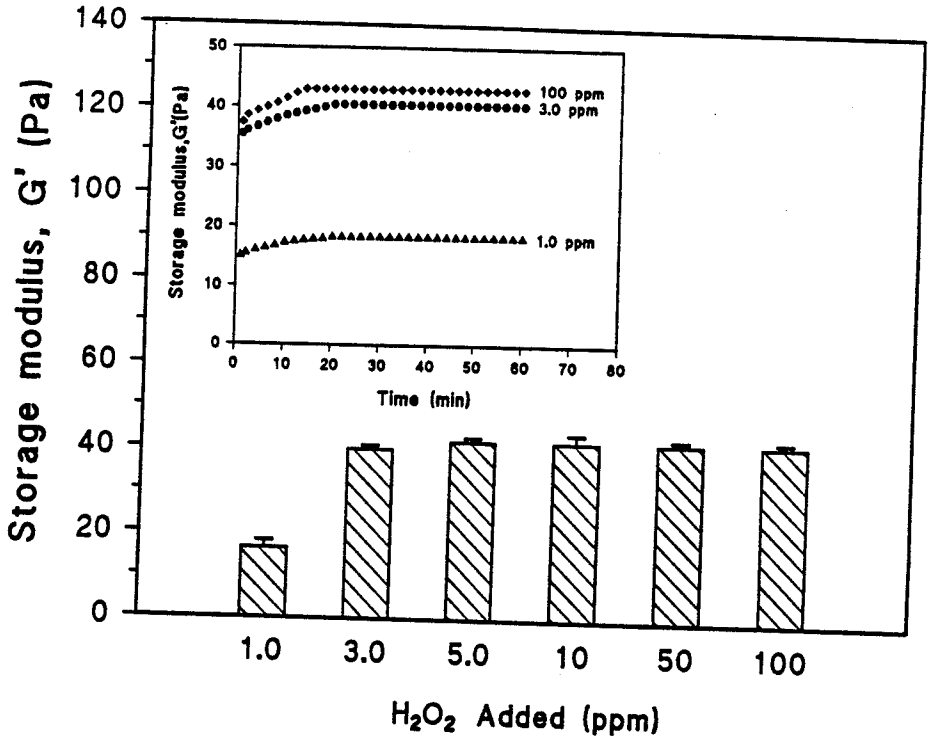
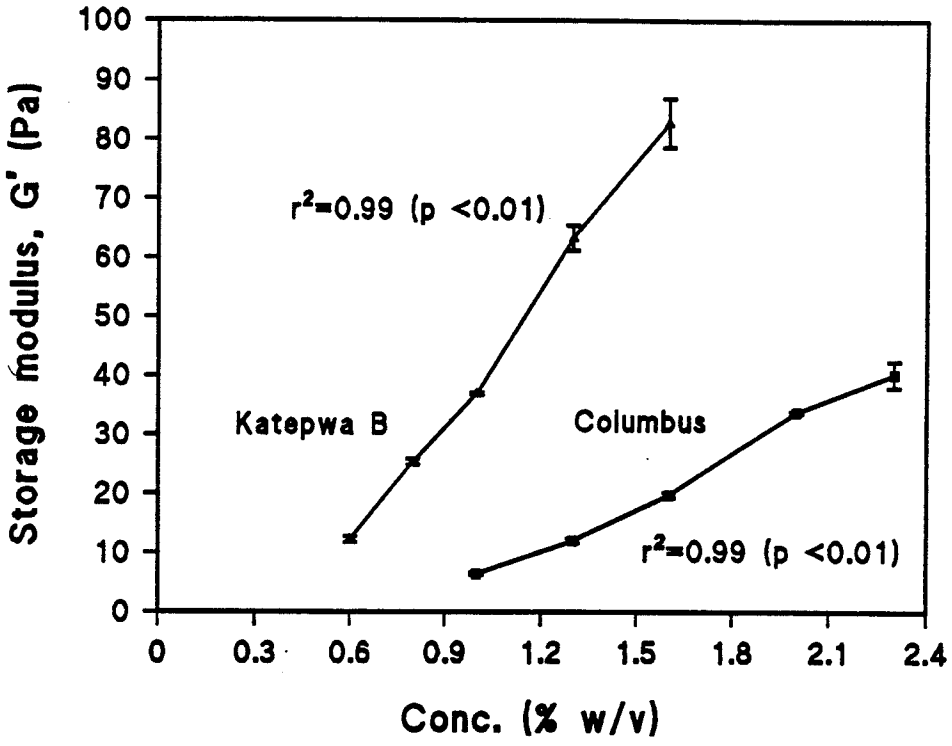
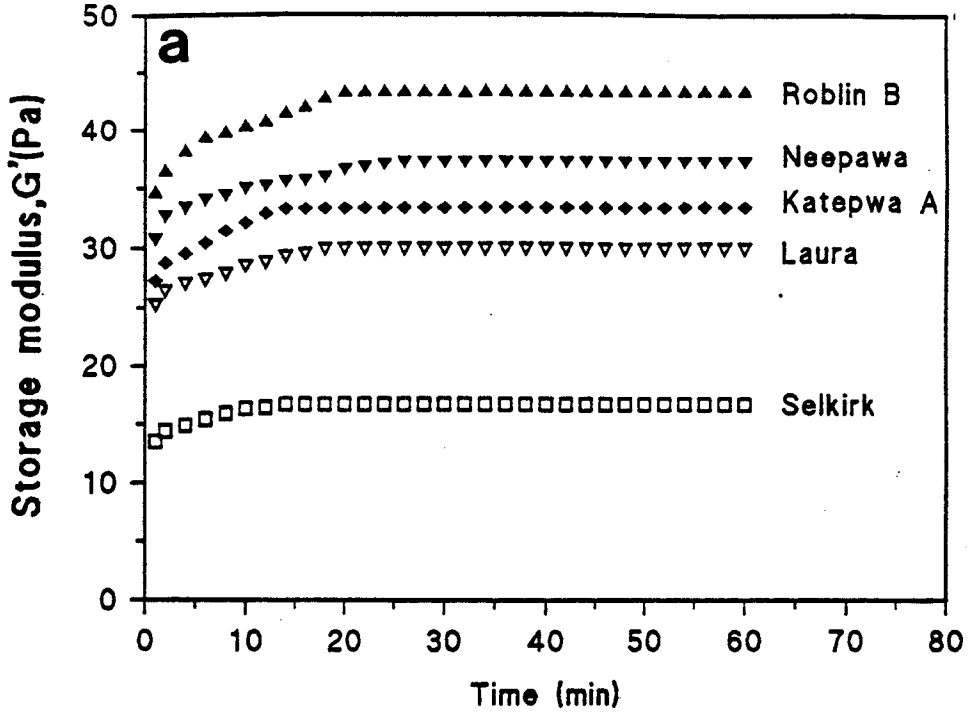

Storage modulus, G' (Pa)
140
120
100
80
60
40
20
0
1.0
3.0
5.0
10
50
100
H2O2 Added (ppm)
Storage modulus,G'(Pa)
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
Time (min)
100 ppm
3.0 ppm
1.0 ppm

Figure 18. Effect of arabinoxylan concentration on storage modulus (G') at a constant level of oxidant (H_2O_2= 3.0 ppm) and horseradish peroxidase (0.11 PU/ml). Data were collected at a frequency of 1.0 Hz and strain of 4.0% at 15°C after 2h of reaction with the oxidant. Katepwa B = high intrinsic viscosity; Columbus = low intrinsic viscosity.


Storage modulus, G' (Pa)
100
90
80
70
60
50
40
30
20
10
0
0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
Conc. (% w/v)
r²=0.99 (p <0.01)
Katepwa B
Columbus
r²=0.99 (p <0.01)

studies clearly indicate the impact of molecular size of the polymer on the plateau modulus values. The gel network development in different arabinoxylan solutions (at a concentration of 1.0%, w/v) after addition of peroxidase (0.11 PU/ml) and H_2O_2 (3.0 ppm) is shown in Figure 19 (a & b). For each arabinoxylan, the kinetics of gel network development were characterized by an initial rapid rise in storage modulus which was followed by a plateau region. This type of behaviour can be interpreted as reflecting an initial formation of covalent linkages between ferulic acid residues of adjacent arabinoxylan chains (giving rise to a rapid increase in G'). Once the first crosslinks have formed, they impede the further movement of chains and thus prevent formation of additional cross linkages among the arabinoxylan chains. The values of G' at the plateau region did not change even when the samples were run for 24 hr. The rheological parameters of the cross-linked arabinoxylan gels in terms of storage modulus, loss modulus and their ratio (tan δ) are summarized in Table 11. Significant differences (at $p \leq 0.05$) in values of G'and G" were observed among the ten arabinoxylan samples. The most rigid gels were formed by the two Roblin samples (A and B) as indicated by their low tan δ values, showing a predominant elastic character for the gel network structure. A comparatively weaker gel (higher ratio tan δ, low G' value)

Figure 19. Storage modulus (G') vs time for 1.0% (w/v) solutions of various arabinoxylans treated with H_2O_2 (3.0 ppm) and horseradish peroxidase (0.11 PU/ml). Data were collected at a frequency of 1.0 Hz and strain of 4.0% at 15°C.


a
Storage modulus,G'(Pa)
Time (min)
Roblin B
Neepawa
Katepwa A
Laura
Selkirk
0
10
20
30
40
50
60
70
80

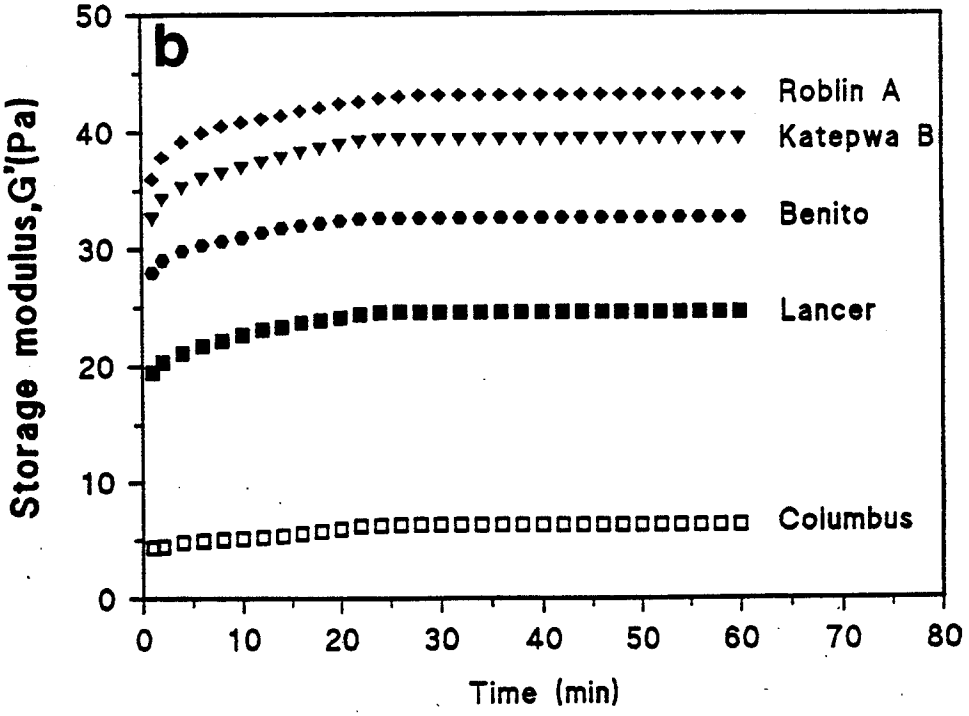

b
Storage modulus,G'(Pa)
Time (min)
Roblin A
Katepwa B
Benito
Lancer
Columbus
0
10
20
30
40
50
60
70
80

Table 11. Storage modulus (G'), loss modulus (G") and tan δ for cross-linked arabinoxylan gels[1].

Variety	G' (Pa)	G" (Pa)	tan δ
Neepawa	38.3±1.3^{f}	0.73±0.04^{b}	0.02
Roblin A	43.0±5.5^{fg}	0.75±0.02^{b}	0.02
Roblin B	43.0±1.0^{g}	0.64±0.07^{ab}	0.01
Katepwa A	33.1±1.2^{e}	1.19±0.12^{d}	0.03
Katepwa B	39.4±1.0^{f}	0.62±0.04^{a}	0.02
Columbus	5.8±0.1^{a}	0.98±0.05^{c}	0.17
Benito	32.6±0.1^{e}	1.64±0.06^{e}	0.05
Laura	30.1±0.7^{d}	1.15±0.07^{d}	0.04
Lancer	24.6±1.2^{c}	1.19±0.07^{d}	0.05
Selkirk	16.8±1.6^{b}	1.50±0.08^{e}	0.09

[1]Arabinoxylan solutions (1.0% w/v) were treated with horseradish peroxidase (0.11 PU/ml) and H_2O_2 (3.0 ppm); reported values are those at 1.0 hr of reaction time and represent means ± S.D. of triplicate measurements. Values followed by the same letter in each column are not significantly different ($p \leq 0.05$).

was obtained by the arabinoxylan of Columbus. A positive relationship ($r=0.594$) was found between the storage modulus, and intrinsic viscosity for all arabinoxylan preparations. A much stronger correlation ($r=0.85$ $p \leq 0.01$) between these two parameters was previously reported by Izydorczyk et al (1991b). In the present study, stronger gels were formed by arabinoxylans having higher amounts of feruloyl groups (Table 8, $r= 0.780$, $p \leq 0.05$). Furthermore, multiple correlations of storage modulus, versus intrinsic viscosity and ferulic acid content of arabinoxylan have indicated an improvement in the correlation coefficient, $r= 0.946$ ($p \leq 0.05$), as shown in Table 12. These data clearly showed that in addition to molecular size, the amount of feruloyl groups in arabinoxylan is also an important determinant of the gelling behaviour of this polysaccharide. As the concentration of bound feruloyl residues increases, the probability of more ferulic acid residues to react with the oxidant in solution also increases and this in turn increases the number of cross-links and hence gel rigidity. In comparing the plateau values of G' of the cross-linked arabinoxylans (Table 11), it is also apparent that the weaker gels correspond to the more branched polysaccharides of the cultivars Columbus and Selkirk. These observations are in agreement with the findings of Izydorczyk et al (1991b).

Table 12. Simple and Multiple Regression intercepts, Coefficients and Correlation coefficients of Storage modulus (G',Pa) of arabinoxylan gels versus limiting viscosity ([η], dl/g) and Ferulic acid content (F, mg/g) of arabinoxylans from different wheat cultivars (CWRS class).

Dependent Variable	Independent Variable	Regression Equation			
		Intercept	Coefficients		Correlation Coefficient
			[η]	F[a]	
G'	[η]	-33.2	14.5		0.594
G'	F	-24.3		46.0	0.780**
G'	[η], F	-78.9	13.0	43.6	0.946**

[a]Data taken from spectrophotometric analysis.

**Indicates significance at $p \leq 0.05$.

4.5.4 Interfacial properties

The results of Table 13 showed that arabinoxylans isolated from different wheat varieties lower the surface tension of water (at a concentration of 0.5%, w/v), implying that these polysaccharide preparations are surface active. Other polysaccharides have been known to possess similar properties and thus to act as emulsifiers and / or stabilizers (Yalpani, 1988). Arabinoxylans are thought to stabilize foams by impeding gas diffusion by virtue of the viscous nature of their solutions or by forming thin elastic films around the gas bubbles, thereby preventing them from coalescence (Prins, 1988). The studies carried out by Izydorczyk et al (1991b) in model systems had shown that arabinoxylans can stabilize protein foams even upon heating. On the basis of their experimental data these authors have also suggested that arabinoxylans, along with gluten, can play a role in the retention of CO_2 in dough systems during the initial stages of baking (Izydorczyk et al, 1991b), and thereby influence the quality characteristics of the final product. Furthermore, McCleary (1986) has shown the importance of arabinoxylans in maintaining a uniform structure in bread crumb.

Table 13. Surface activity of Arabinoxylans[a] in solution (23.0±0.2°C).

Variety	Surface tension (dynes/cm)
Neepawa	60.0±0.3[b]
Roblin A	61.1±0.5
Roblin B	53.7±0.9
Katepwa A	54.2±0.8
Katepwa B	59.1±0.7
Columbus	60.2±0.1
Benito	59.9±0.4
Laura	56.0±0.1
Lancer	59.6±0.3
Selkirk	59.0±0.6

[a]Arabinoxylan concentration, 0.5% (w/v); surface tension of water was 72.6±0.2 at 23.0±0.2°C.

[b]n=3±S.D.

4.6 Bread fortification studies using arabinoxylans: effect on dough and bread properties.

Two base flours of diverse breadmaking qualities, a composite flour of CWRS (2CW) and a CPS flour (HY368), were selected to study the effect of adding arabinoxylans (two different preparations, one of high molecular weight, HMW, $[\eta]$ = 5.48 dl/g, MW = 201,623 and another of low molecular weight, LMW, $[\eta]$ = 3.69 dl/g, MW = 134,673) on their dough and bread properties.

4.6.1 Farinograph absorption (FAbs) and dough development time (DDT)

The effect of adding arabinoxylans into flour (at different levels, see section 3.2.10) into the two base flours was initially examined by a microfarinograph to determine changes in water absorption properties of the base flours. Both preparations (HMW and LMW) increased the farinograph water absorption at a fixed dough consistency (500 B.U.), as shown in Table 14. Significant correlations were found between farinograph absorption and the amount of arabinoxylan (HMW and LMW) added, ($r=0.99$ and $r=0.90$, $p \leq 0.05$, for the HMW Ax in CWRS and CPS flours, respectively; $r=0.98$ and $r=0.97$, $p \leq 0.05$, for the LMW Ax in CWRS and CPS, respectively). Similar relationships have been reported previously by Michniewicz et

Table 14. Farinograph absorption and Dough development time of Control and Arabinoxylan-supplemented CWRS (2CW) and CPS (HY368) wheat flours.

Sample	Farinograph Absorption (%)				Dough Development Time (min)	
	2CW		HY368		2CW	HY368
Control	60.0[a]	(±0.2)	58.0[a]	(±0.1)	5.0	4.0
+0.5% AX (HMW)	62.5	(±0.1)	60.0	(±0.2)	5.5	5.0
+0.9% AX (HMW)	65.0	(±0.2)	63.0	(±0.2)	6.0	6.0
+1.3% AX (HMW)	67.0	(±0.2)	65.6	(±0.3)	8.5	7.0
+0.5% AX (LMW)	62.0	(±0.3)	59.5	(±0.1)	5.5	4.5
+0.9% AX (LMW)	64.6	(±0.2)	63.0	(±0.2)	6.5	6.5
+1.3% AX (LMW)	66.5	(±0.3)	65.0	(±0.4)	8.5	7.0

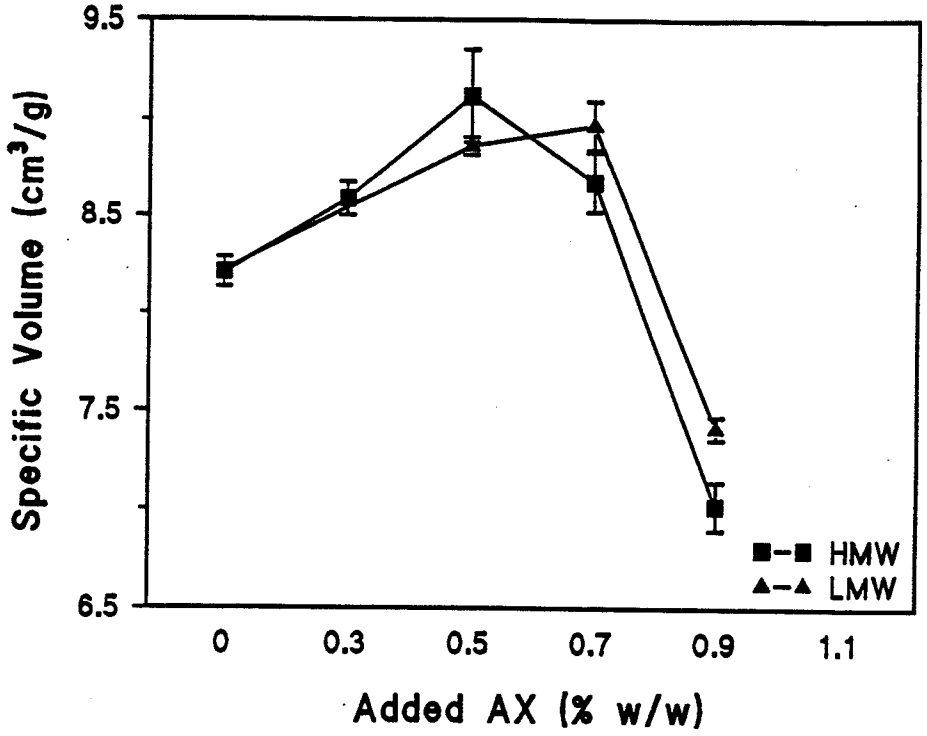
[a]means of triplicate determinations; numbers in the parentheses are standard deviations.

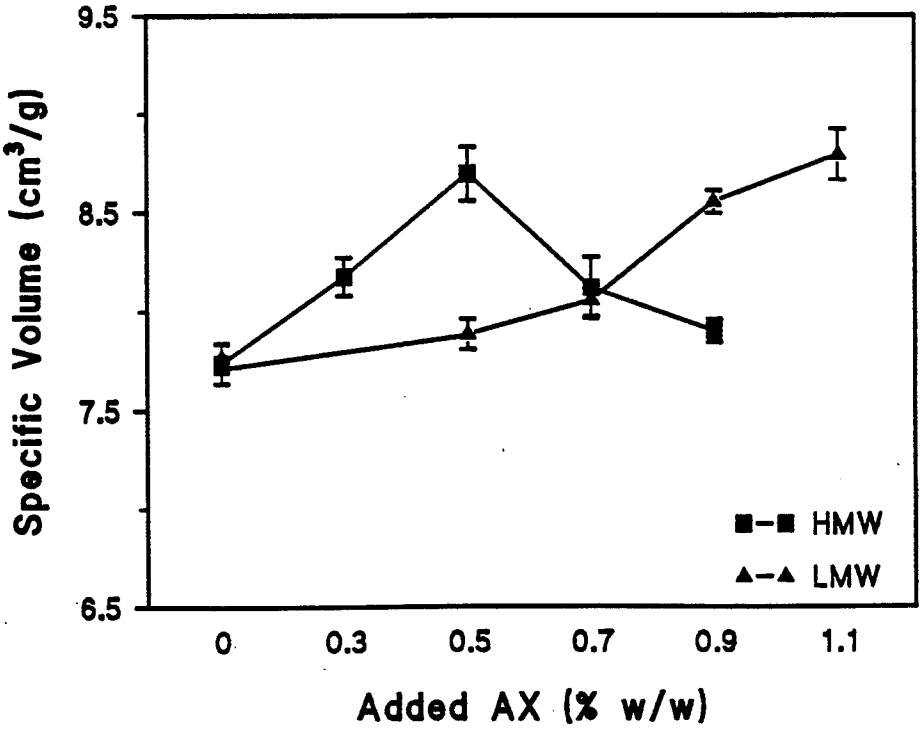
al (1991) for the addition water-soluble wheat and rye as well water-insoluble wheat pentosans to various wheat flours.
It is also evident from Table 14, that arabinoxylans added to the base flours also increased the dough development time. At lower levels (0.5% and 0.9%) of supplementation, both HMW and LMW preparations have increased the dough development time to almost the same extent for the 2CW and HY368 flours. However, at higher levels of supplementation (1.3%, with both preparations), the DDTs were found to be higher in the case of 2CW than the HY368 flours. These findings are consistent with the work of Jelaca and Hlynka (1971) and Michniewicz et al (1991) who also observed an increase in DDT when water-soluble pentosans of different origin were added to different flours.

4.6.2 Effect of added Arabinoxylans on bread loaf volume.

The impact of adding different levels of the two arabinoxylans (HMW and LMW) on bread loaf volumes of 2CW and HY368 wheat flours is seen in Figure 20. Both arabinoxylan preparations have brought about similar effects on the loaf of bread made from the 2CW flour, (Fig. 20a). For example, when HMW arabinoxylan was added to the base flour up to a level of 0.5% (w/w) an increase in loaf volume was observed. However, upon further addition of arabinoxylan a decrease in loaf volume was noticed. Similar responses were also shown for the LMW

Figure 20. Effect of added arabinoxylan (high and low molecular weight, HMW and LMW, preparations) on the specific volume of bread baked from 2CW (a) and HY368 (b) flours.

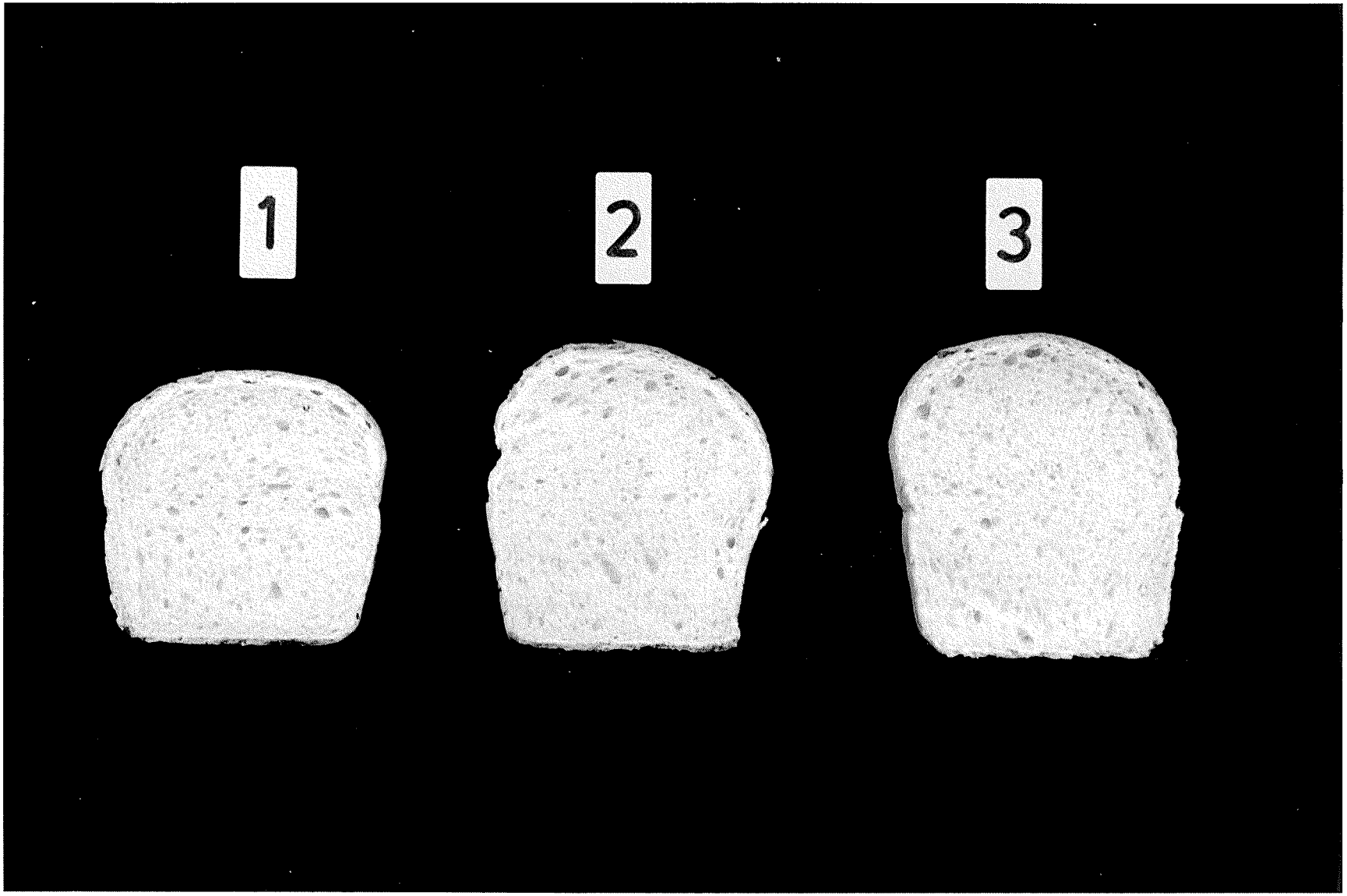

9.5
8.5
7.5
6.5
Specific Volume (cm³/g)
0
0.3
0.5
0.7
0.9
1.1
Added AX (% w/w)
HMW
LMW


9.5
8.5
7.5
6.5
Specific Volume (cm³/g)
0
0.3
0.5
0.7
0.9
1.1
Added AX (% w/w)
HMW
LMW

arabinoxylan-supplemented 2CW flour, except that the maximum loaf volume enhancement took place at a slightly higher concentration (0.7%, w/w). Figure 20b shows the influence of HMW and LMW arabinoxylans on the loaf volume of breads baked from the HY368 flour (CPS). In this case the two arabinoxylan preparations behaved differently from each other. The maximum effect on loaf volume with HMW arabinoxylan was noted at a level of 0.5% (w/w). In contrast, for the LMW arabinoxylan a continuous increase in loaf volume was observed over the entire range of arabinoxylan concentrations tested.

In comparing the results obtained for the two arabinoxylan preparations, an inference can be made that, in addition to the nature of the base flour, differences in the molecular weight of these polysaccharides have a pronounced effect on the characteristics of the final product. It appears that the concentration at which a maximum effect on loaf volume is observed depends on the molecular weight of the arabinoxylan. For example, as shown in Figure 21, a low concentration of added HMW arabinoxylan (0.5%, w/w) have similar effect on loaf volume and crumb texture as 1.1%, (w/w) of LMW. Studies done in the past had shown an increase in the loaf volume with the addition of water-soluble pentosans at a fixed concentration of 1-2%, (D'Appolonia et al, 1970; Jelaca and Hlynka, 1972; Michniewicz et al, 1992; Tao and Pomeranz,

Figure 21 Breads baked from HY368 flour; (1) control, (2) with 0.5% added HMW arabinoxylan (3) with 1.1% added LMW arabinoxylan.


1
2
3

1967). In a different study, Delcour et al (1991) had plotted the effect of different levels of water-soluble pentosans (mainly arabinoxylan) from rye on gluten-starch loaves. They concluded that an optimum concentration of these polymers at 2-3% was effective in enhancing the loaf volume. Between the two polysaccharide fractions of the water-soluble pentosans, arabinoxylan seems to influence the rheological characteristics of the dough system and thereby the properties of bread. The work of Jelaca and Hlynka (1972) has shown that pentosans increase the resistance of dough to extension. Furthermore, the studies of Michniewicz et al (1991) have also suggested that pentosans may interact with flour proteins in the dough system and therefore could indirectly influence the quality of the final product.

4.6.3 Water activity and moisture content of bread crumbs

The texture of bread crumb, the most important quality indicator of baked products, is related to the mechanical properties of bread and is governed by the amount of water present after baking. The moisture content of control and fortified (with both LMW and HMW) bread crumbs belonging to the two base flours were determined and are given in Tables 15 to 18. In each case, the moisture content of control bread crumbs was found to be lower than those supplemented with

Table 15. Moisture content (%) of control and fortified (with HMW arabinoxylan at different levels) bread crumbs made from the 2CW flour, stored at 7°C, over a period of seven days.

Level Added	Moisture Content(%)[x]			
	Day 1	Day 3	Day 5	Day 7
0%	35.4^{a1}	33.1^{b1}	30.8^{c1}	29.4^{d1}
0.3%	36.8^{a2}	34.2^{b2}	33.3^{c2}	31.3^{d2}
0.5%	39.5^{a3}	37.5^{b3}	36.0^{c3}	35.4^{d3}
0.7%	41.0^{a4}	38.0^{b3}	36.6^{c3}	35.6^{c3}
0.9%	44.7^{a5}	41.0^{b4}	39.4^{c4}	38.2^{c4}

Table 16. Moisture content (%) of control and fortified (with LMW arabinoxylan at different levels) bread crumbs made from the 2CW flour, stored at 7°C, over a period of seven days.

Level Added	Moisture Content (%)[x]			
	Day 1	Day 3	Day 5	Day 7
0%	35.8^{a1}	33.0^{b1}	30.8^{c1}	29.6^{d1}
0.5%	37.8^{a2}	35.4^{b2}	32.4^{c2}	31.8^{c2}
0.7%	40.1^{a3}	36.7^{b3}	34.1^{c3}	33.0^{d3}
0.9%	42.3^{a4}	37.3^{b3}	34.9^{c3}	33.6^{d3}

[x]Means of triplicate measurements; values followed by the same letter (row) or numeral (column) are not significantly different ($p \leq 0.05$).

Table 17. Moisture content (%) of control and fortified (with HMW arabinoxylan at different levels) bread crumbs made from the HY368 flour, stored at 7°C, over a period of seven days.

Level Added	Moisture Content (%)[x]			
	Day 1	Day 3	Day 5	Day 7
0%	33.0^{a1}	31.0^{b1}	30.1^{c1}	28.4^{d1}
0.3%	34.2^{a2}	31.2^{b1}	29.6^{c1}	28.8^{d1}
0.5%	35.1^{a3}	33.3^{b2}	32.1^{b2}	30.4^{c2}
0.7%	39.6^{a4}	37.5^{b3}	36.4^{c3}	34.8^{d3}
0.9%	42.6^{a5}	39.4^{b4}	37.4^{c3}	36.1^{c3}

Table 18. Moisture content (%) of control and fortified (with LMW arabinoxylan at different levels) bread crumbs made from the HY368 flour, stored at 7°C, over a period of seven days.

Level Added	Moisture Content (%)[x]			
	Day 1	Day 3	Day 5	Day 7
0%	32.8^{a1}	31.3^{b1}	30.3^{c1}	28.5^{d1}
0.5%	34.6^{a2}	32.4^{b2}	31.0^{c1}	29.3^{d1}
0.7%	36.2^{a3}	33.2^{b2}	32.0^{c2}	30.5^{d2}
0.9%	38.0^{a4}	36.5^{b3}	34.5^{c3}	33.4^{d3}
1.1%	41.9^{a5}	39.1^{b4}	35.6^{c4}	34.6^{d4}

[x]Means of triplicate measurements; values followed by the same letter (row) or numeral (column) are not significantly different ($p \leq 0.05$).

arabinoxylans over the entire storage period. This obviously reflects the higher water absorption values of the arabinoxylan-fortified flours. Moreover, with increasing level of added arabinoxylans the water retained in the crumb also increased. The arabinoxylans increased the water absorption of dough, which in turn increased the moisture content of bread crumbs. Generally, there was a continuous loss of moisture with time of storage although the rate of moisture loss slowed as storage time progressed.

Water activity (a_w) is an important predictor of the rate of microbial spoilage of foods including baked products. The water activity of control and arabinoxylan-fortified bread crumbs were also measured and are given in Tables 19 to 22. In each case there was a continuous decrease in a_w of both control and fortified bread crumbs with increasing storage time. However, the a_w of fortified bread crumbs were always found to be higher than the controls over the same period of storage, presumably due to their higher moisture content (Tables 15-18). In general, the trends of change in a_w paralleled the changes in moisture content.

4.6.4 Crumb firmness

The increase in bread crumb firmness has been used by many researchers to follow the bread staling process. In this study

Table 19. A_w of control and fortified (with HMW arabinoxylan at different levels) bread crumbs made from the 2CW flour, stored at 7°C, over a period of seven days.

Level Added	A_w[x]			
	Day 1	Day 3	Day 5	Day 7
0%	0.962^{a1}	0.956^{b1}	0.953^{c1}	0.948^{d1}
0.3%	0.966^{a2}	0.962^{b2}	0.959^{c2}	0.954^{d2}
0.5%	0.972^{a3}	0.965^{b3}	0.962^{c3}	0.957^{d3}
0.7%	0.973^{a3}	0.966^{b3}	0.964^{b4}	0.958^{c3}
0.9%	0.979^{a4}	0.974^{b4}	0.969^{c5}	0.964^{d4}

Table 20. A_w of control and fortified (with LMW arabinoxylan at different levels) bread crumbs made from the 2CW flour, stored at 7°C, over a period of seven days.

Level Added	A_w[x]			
	Day 1	Day 3	Day 5	Day 7
0%	0.962^{a1}	0.956^{b1}	0.953^{c1}	0.948^{d1}
0.5%	0.967^{a2}	0.962^{b2}	0.956^{c2}	0.952^{d2}
0.7%	0.971^{a3}	0.965^{b3}	0.960^{c3}	0.958^{c3}
0.8%	0.976^{a4}	0.970^{b4}	0.964^{c4}	0.961^{d3}

[x]Means of triplicate measurements; values followed by the same letter (row) or numeral (column) are not significantly different ($p \leq 0.05$).

Table 21. A_w of control and fortified (with HMW arabinoxylan at different levels) bread crumbs made from the HY368 flour, stored at 7°C, over a period of seven days.

Level Added	A_w[x]			
	Day 1	Day 3	Day 5	Day 7
0%	0.961^{a1}	0.954^{b1}	0.949^{c1}	0.944^{d1}
0.5%	0.965^{a2}	0.958^{b2}	0.952^{c2}	0.948^{d2}
0.7%	0.968^{a3}	0.962^{b3}	0.960^{c3}	0.958^{d4}
0.9%	0.968^{a3}	0.963^{b3}	0.960^{c3}	0.955^{d3}
1.1%	0.972^{a4}	0.965^{b4}	0.961^{c3}	0.959^{d4}

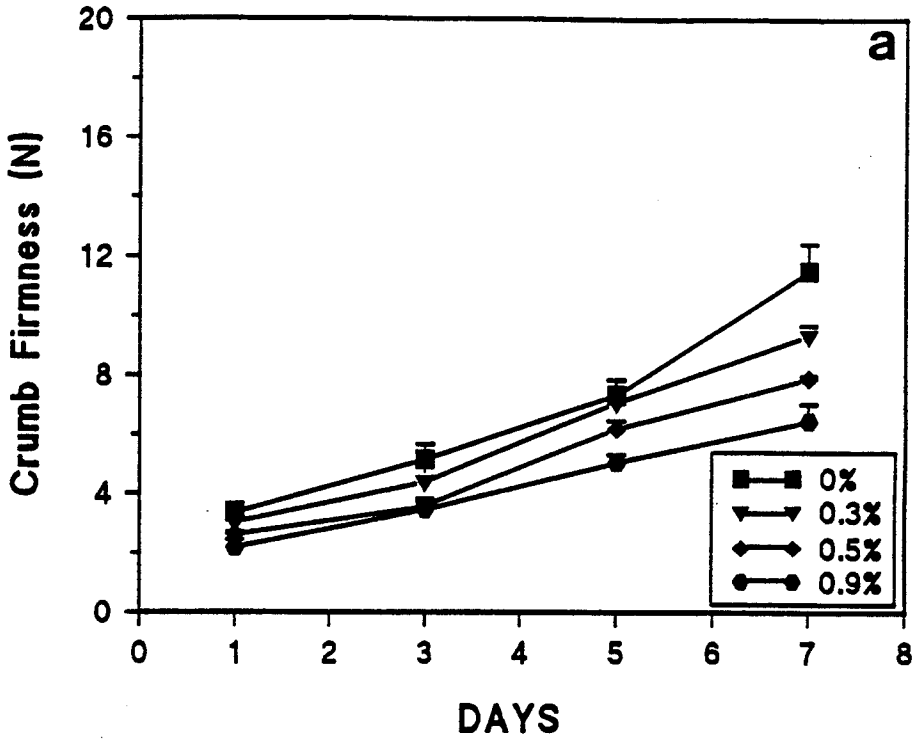
Table 22. A_w of control and fortified (with LMW arabinoxylan at different levels) bread crumbs made from the HY368 flour, stored at 7°C, over a period of seven days.

Level Added	A_w[x]			
	Day 1	Day 3	Day 5	Day 7
0%	0.961^{a1}	0.954^{b1}	0.948^{c1}	0.944^{d1}
0.3%	0.964^{a2}	0.959^{b2}	0.954^{c2}	0.951^{d2}
0.5%	0.968^{a3}	0.961^{b2}	0.960^{b3}	$0.955c^{c3}$
0.7%	0.970^{a4}	0.967^{b3}	0.959^{c3}	0.958^{c3}
0.9%	0.972^{a5}	0.966^{b3}	0.960^{c3}	0.957^{c3}

[x]Means of triplicate measurements; values followed by the same letter (row) or numeral (column) are not significantly different ($p \leq 0.05$).

staling of control and fortified bread crumbs was monitored by measuring the crumb firmness by the Ottawa Texture Measuring System. The firmness measurements are plotted as a function of storage time (at 7°C) in Figures 22 and 23. Although firmness increased (almost linearly) for both control and arabinoxylan-fortified bread crumbs over the seven days storage, the latter were found to be less firm than control bread crumbs in all cases. The crumb firmness also decreased with increasing amounts of arabinoxylans added. For example, after seven days of storage 2CW bread crumbs fortified with HMW arabinoxylans at 0.9% were found to be 22% less firm than those fortified at a 0.5% level (Fig. 22a). Similarly, bread crumbs with LMW arabinoxylans (Fig. 22b) at 0.9% supplementation were found 20% less firm than those at 0.5% after seven days of storage. In comparing the firmness between the two base flours (Figs. 22 and 23) similar trends in staling rates were observed. However, the firmness values of control and fortified bread crumbs of the HY368 flour were generally higher than those of the 2CW. It has been suggested that pentosans influence the texture of bread crumb by interacting with the gluten to form composite hydrated film networks (Michniewicz et al,1991) and also by increasing the water absorption of dough which in turn contributes to the texture of bread crumb. Water acting as a plasticizer of the gluten-starch matrix lowers the modulus of

Figure 22. Effect of added arabinoxylans (0-0.9%, w/w) on bread crumb firmness during storage at 7°C of breads baked from the 2CW flour.
(a) high molecular weight arabinoxylan, HMW,
(b) low molecular weight arabinoxylan, LMW.


a
Crumb Firmness (N)
20
16
12
8
4
0
0
1
2
3
4
5
6
7
8
DAYS
0%
0.3%
0.5%
0.9%

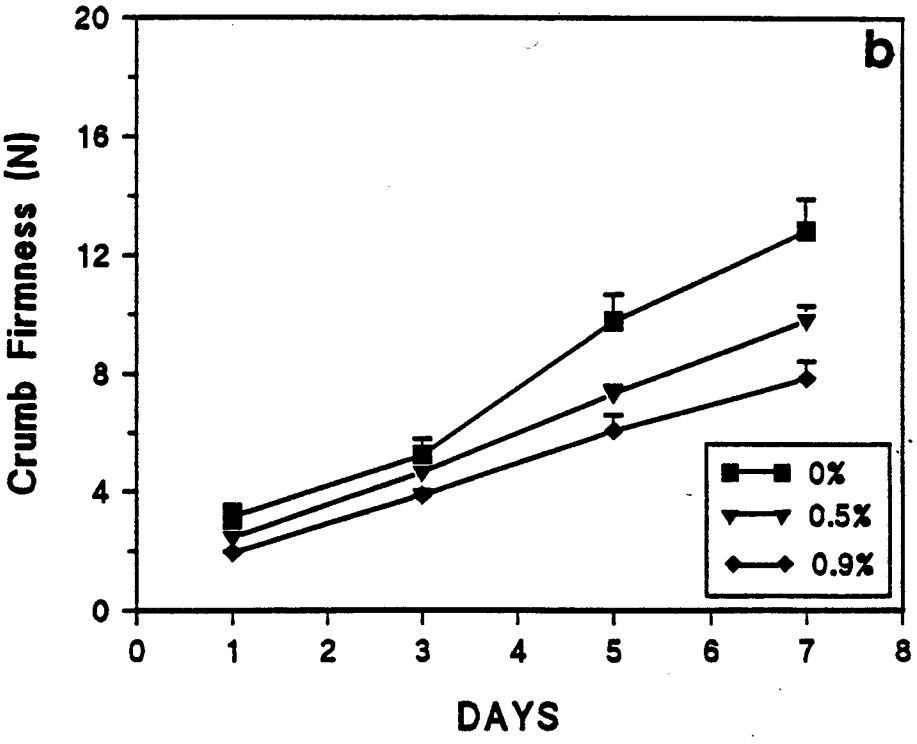
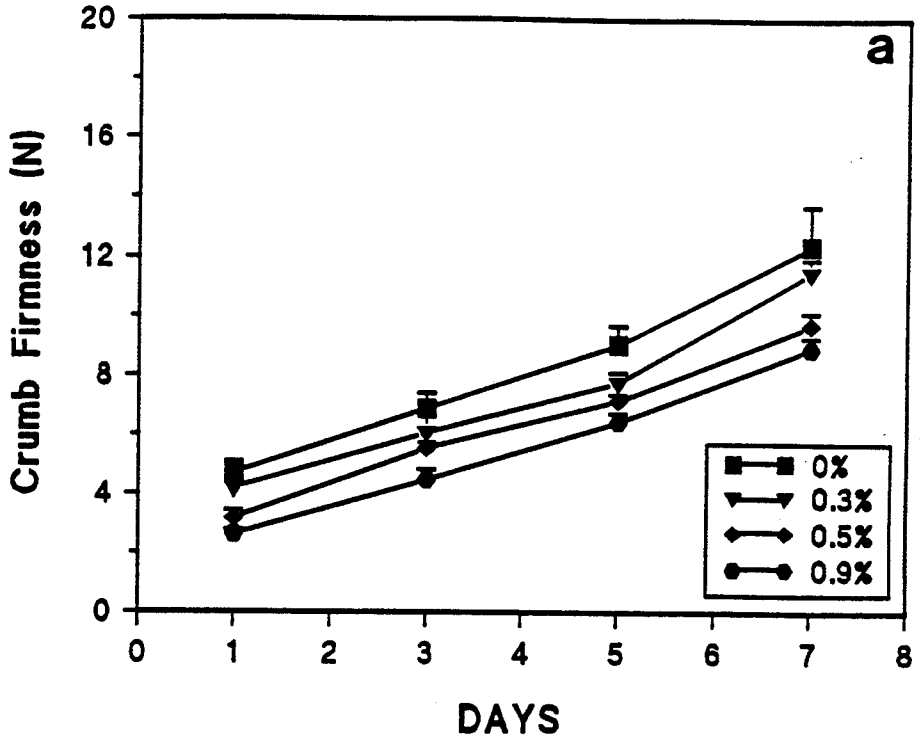
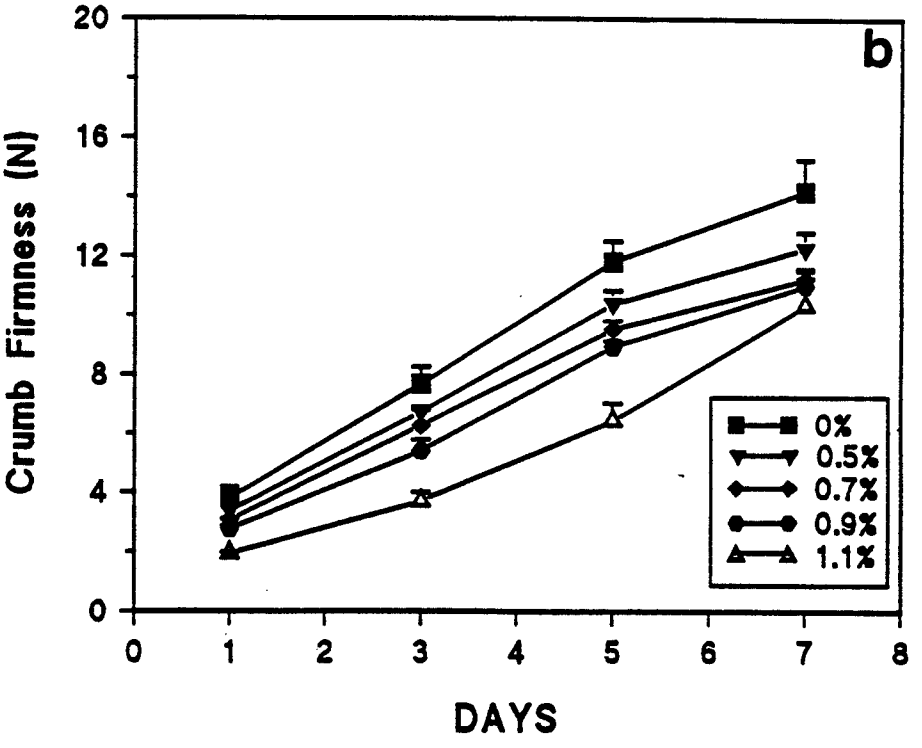

b
Crumb Firmness (N)
20
16
12
8
4
0
0
1
2
3
4
5
6
7
8
DAYS
0%
0.5%
0.9%

Figure 23. Effect of added arabinoxylans (0-1.1%, w/w) on the bread crumb firmness during storage at 7°C of breads baked from the HY368 flour.
(a) high molecular weight arabinoxylan, HMW,
(b) low molecular weight arabinoxylan, LMW.


a
Crumb Firmness (N)
DAYS
0%
0.3%
0.5%
0.9%


b
Crumb Firmness (N)
DAYS
0%
0.5%
0.7%
0.9%
1.1%

the composite network (Levine and Slade, 1990). The lower firmness values observed for bread crumbs fortified with arabinoxylans, compared to the control samples, are most likely due to their higher moisture content.

4.6.5 Bread staling studies by DSC

Starch recrystallization is considered as a major factor contributing to bread staling. Fearn and Russell (1982) and Russell (1983) applied differential scanning calorimetry to measure the structural changes of starch in bread during aging. They observed that when staled bread was heated in the DSC, a prominent endotherm peak was present around 50°C, which was absent in the fresh bread, and notably increased with storage time. This endotherm peak was due to the melting of retrograded amylopectin. In the present study, staling of control and fortified bread crumbs (with LMW arabinoxylan at two levels 0.5% and 0.9%) made from the flours (2CW and HY368) were studied by DSC by monitoring the changes in melting enthalpies of recrystallized amylopectin during storage (at temperature of 7°C). The results are summarized in Tables 23 and 24. The enthalpy values of arabinoxylan-supplemented bread crumbs were found to be higher than the controls for both flours. Also the ΔH values increased with increasing level of arabinoxylan added. These observations are consistent with the

Table 23. Enthalpy values (J/g)[x] of staling endotherm for arabinoxylan (LMW)-fortified and control bread crumbs of the 2CW flour, stored at 7°C.

DAY	CONTROL	+0.5%AX	+0.9%AX
1	3.5^{a1}	4.1^{b1}	4.4^{c1}
3	3.7^{a2}	4.3^{b1}	5.0^{c2}
5	4.5^{a3}	4.7^{b2}	5.3^{c2}
7	4.7^{a4}	5.1^{b3}	5.8^{c3}

Table 24. Enthalpy values (J/g)[x] of staling endotherm for arabinoxylan (LMW)-fortified and control bread crumbs of the HY368 flour, stored at 7°C.

DAY	CONTROL	+0.5%AX	+0.9%AX
1	3.7^{a1}	3.8^{a1}	4.9^{b1}
3	3.8^{a1}	4.6^{b2}	5.5^{c2}
5	3.9^{a1}	5.3^{b3}	5.7^{c3}
7	4.6^{a2}	5.5^{b3}	5.8^{c3}

[x]Means of triplicate measurements; values followed by the same letter (row) or numeral (column) are not significantly different ($p \leq 0.05$).

observations made by Zeleznak and Hoseney (1986) on the effect of moisture on staling kinetics. These researchers have found that for both wheat starch gels and bread systems, the moisture content of the sample is critical in determining the kinetics of amylopectin retrogradation (i.e. recrystallisation of outer short chain of amylopectin molecule). Using DSC, these authors have shown that between 20-40% water content there is an acceleration in the retrogradation rate with increasing moisture. In this moisture content range even a small change in water content greatly affected the kinetics of the process. In the present study, the obtained enthalpy values (for the amylopectin peak) were higher than those reported earlier (Czuchajowska and Pomeranz, 1989; Zeleznak and Hoseney, 1986). This can be attributed to the relatively lower storage temperature (7°C) adopted in these studies. It is known that with decreasing temperature there is an acceleration in the retrogradation events (Longdon and LeGrys, 1981). Moreover, the present data supports the findings of Michniewicz et al (1992) who observed an increase in the enthalpy of staling endotherm with added water-soluble and water-insoluble pentosans. There are many variables affecting the complex nature of the staling phenomenon and as such there is not a single technique that can provide a complete view of all events related to this process. The DSC technique measures

only the amount of recrystallized amylopectin which is affected by the moisture content. On the other hand, crumb firmness measurements provide information on the mechanical properties of the baked products which are also influenced by the amount of water present; water acts as a plasticizer of gluten and starch and thereby decreases the firmness of the crumb. Obviously, DSC and mechanical testing do not probe the same properties of the composite network structure in bread crumb. While starch retrogradation (determined from the DSC values) and firming occur concurrently during storage, they do not seem to exist in a cause-effect relationship as both processes are influenced in different ways by moisture content of the bread system.

5. CONCLUSIONS

The present study was undertaken to characterize chemically, physically and functionally the non-starch polysaccharides and in particular their arabinoxylan constituents from flours belonging to several wheat cultivars of the CWRS class. On the basis of this work the following conclusions can be drawn:

(1) Flours obtained from the grains of eight different varieties varying in their protein content and bread making quality showed differences in their pentosan content. Water-soluble pentosans were significantly correlated with starch damage ($r = 0.79$, $p \leq 0.05$) and ash contents of flours ($r = 0.68$ $p \leq 0.05$).

(2) There were also differences in the ferulic acid content among the arabinoxylans isolated from these flours, while very little variation was observed with respect to the degree of branching of these polysaccharides.

(3) Differences in the molecular size, as assessed by gel filtration and limiting viscosity measurements ($[\eta]$: 3.69-5.48dl/g), were also observed among the arabinoxylans.

(4) Oxidative gelation studies on arabinoxylans in aqueous solutions (H_2O_2/peroxidase) indicated that the gel network rigidity increases with the molecular size of the polymer. The amount of covalently bound ferulic acid was also an important determinant of gel strength.

(5) Wheat flours fortified with arabinoxylans exhibited higher water absorption (proportional to the amount of arabinoxylan added) and dough development time.

(6) The addition of arabinoxylan also had a beneficial effect on bread loaf volume which was dependent on the amount of arabinoxylan added, molecular size of the polymer as well as quality of the base flour.

(7) The arabinoxylan-fortified breads, although exhibited greater rates of amylopectin recrystallization, they had a softer crumb texture presumably due to their higher moisture content.

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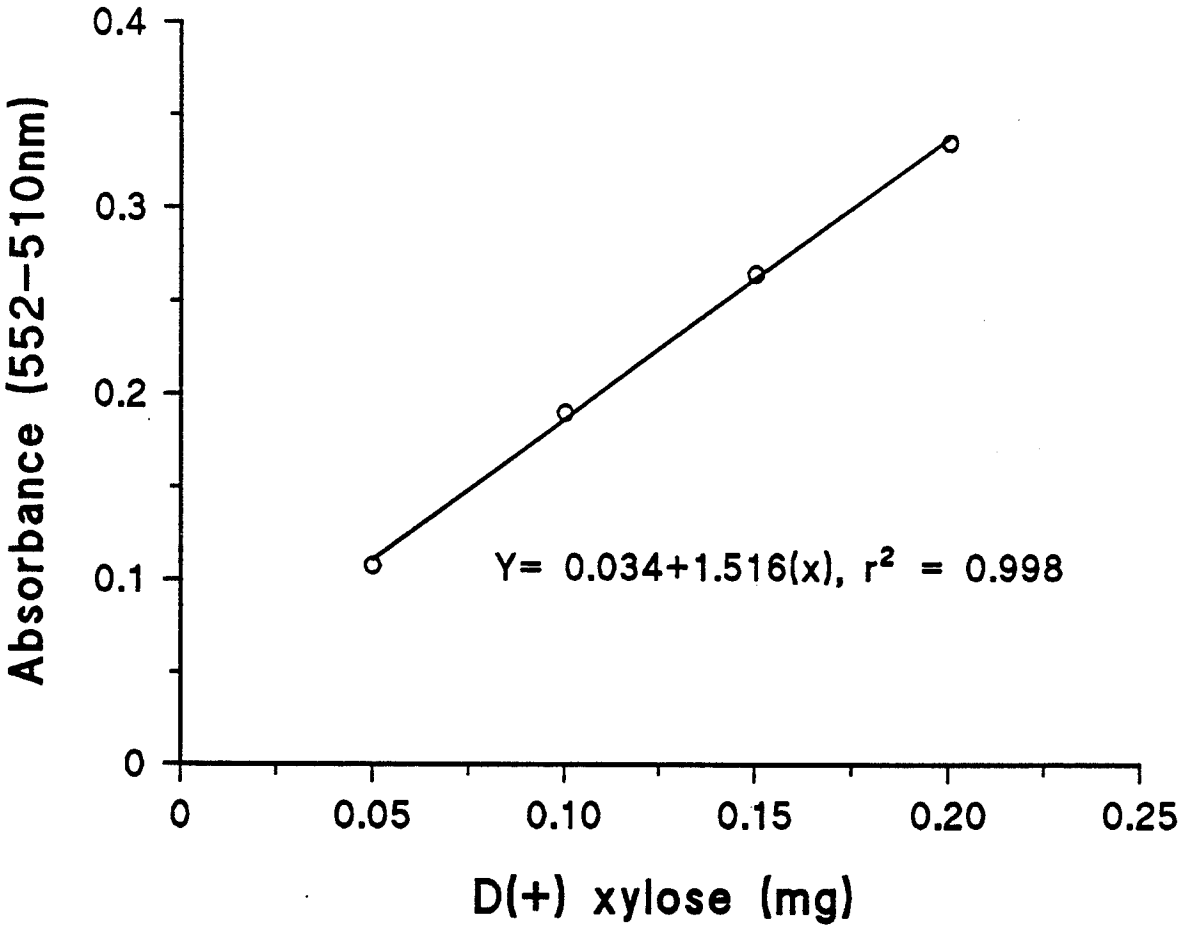
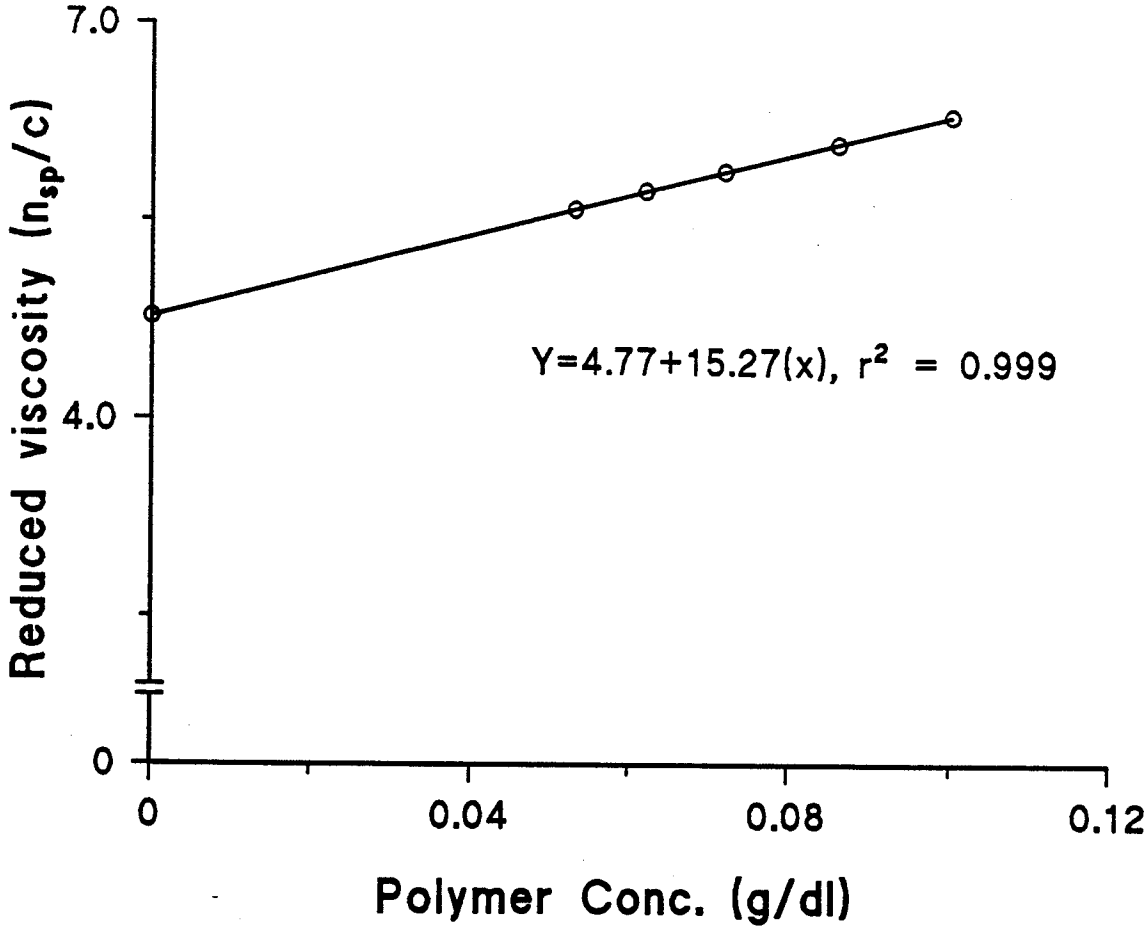
APPENDICES

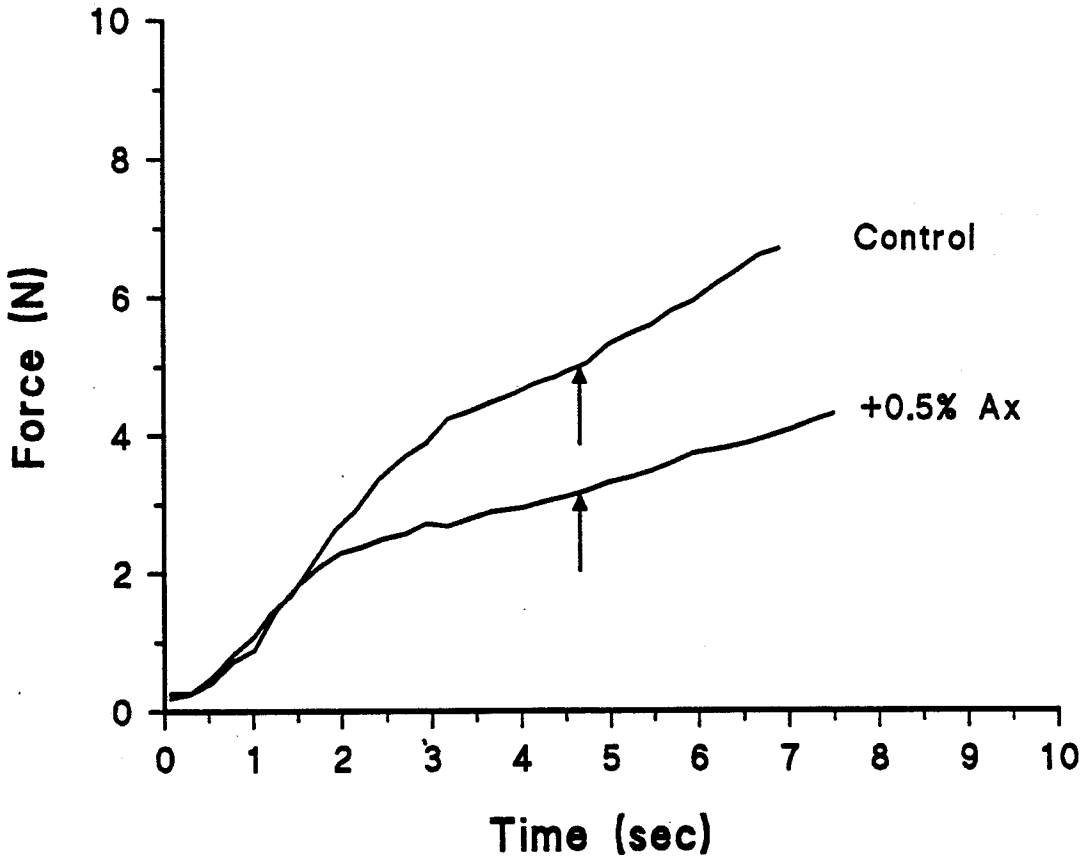
Appendix 1. Standard curve for the determination of total and water-soluble pentosans in wheat flour using the phloroglucinol method of Douglas (1981).


Absorbance (552–510nm)
0.4
0.3
0.2
0.1
0
0
0.05
0.10
0.15
0.20
0.25
D(+) xylose (mg)
Y= 0.034+1.516(x), r² = 0.998

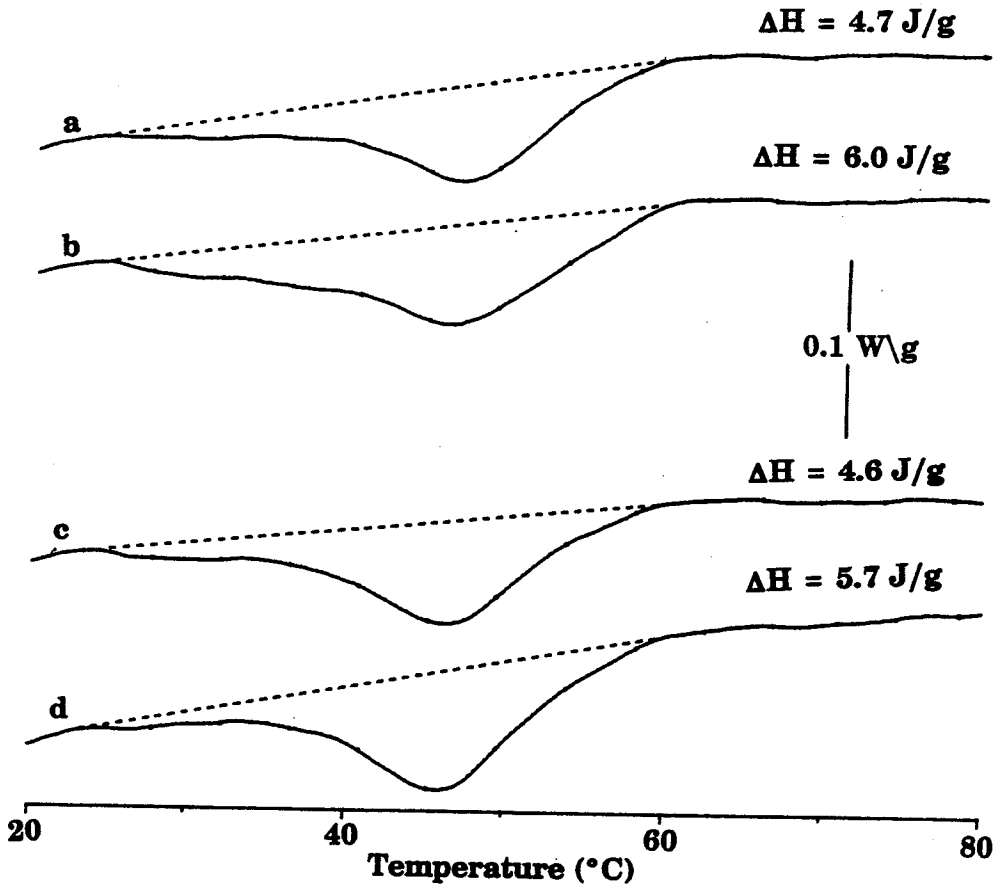
Appendix 2. Typical reduced viscosity, (η_{sp}/c), versus concentration curve of dilute arabinoxylan (cv. Neepawa) solutions at 25±0.1°C.


7.0
4.0
0
Reduced viscosity (n_{sp}/c)
Y=4.77+15.27(x), r^2 = 0.999
0
0.04
0.08
0.12
Polymer Conc. (g/dl)

Appendix 3. Compression force (N) versus time (sec) curves (following storage at 7°C for one day) of bread slices (12mm thick) of breads made from the HY368 wheat flour (control and HMW arabinoxylan-supplemented breads). The curves represent data up to 40% compression of bread slices using a 28 mm diameter plunger and a load cell of 11.36 kg with a cross head speed of 100 mm/min. Arrows indicate the force required for 25% compression.


10
8
6
4
2
0
Force (N)
0
1
2
3
4
5
6
7
8
9
10
Time (sec)
Control
+0.5% Ax

Appendix 4. DSC thermal curves of freeze dried bread crumbs (30% solids, w/w) after storage at 7°C for 7 days. Curves a and c represent control samples of 2CW and HY368 bread crumb, respectively. Curves b and d represent bread crumbs of fortified flours of 2CW and HY368 with LMW arabinoxylan (0.9%). The heating rate was 10°C/min.


ΔH = 4.7 J/g
a
ΔH = 6.0 J/g
b
0.1 W\g
ΔH = 4.6 J/g
c
ΔH = 5.7 J/g
d
20
40
60
80
Temperature (°C)