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

A Thesis

Submitted to the Faculty

of

Graduate Studies

The University of Manitoba

by

Onkar S. Rattan

In Partial Fulfillment of the
Requirment for the Degree

of

Master of Science

Food Science Department

August 1992

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ISBN 0-315-77897-0

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by

ONKAR S. RATTAN

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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TO MY PARENTS

ACKNOWLEDGEMENTS

I wish to express my deep gratitude to my advisor, Dr. C.G. Biliaderis for his encouragement, boundless patience and invaluable scientific advice throughout the course of studies. His continuous interest in my progress was fundamental to the successful completion of this project and contributed immensely to my education.

The technical assistance of R. Zillman in the milling and baking laboratory and J. Roger with HPLC analyses is deeply appreciated.

Special thanks are also due to W. Johnson for his assistance with the electrophoresis and Paul Stephen for his computer expertise.

The help and encouragement of my fellow students and staff members at the Food Science Dept., University of Manitoba, is sincerely appreciated.

The financial support from the National Research Council of Canada is also gratefully acknowledged.

Finally, I would like to express my special thanks to Kulwinder for her patience and faith in me.

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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.

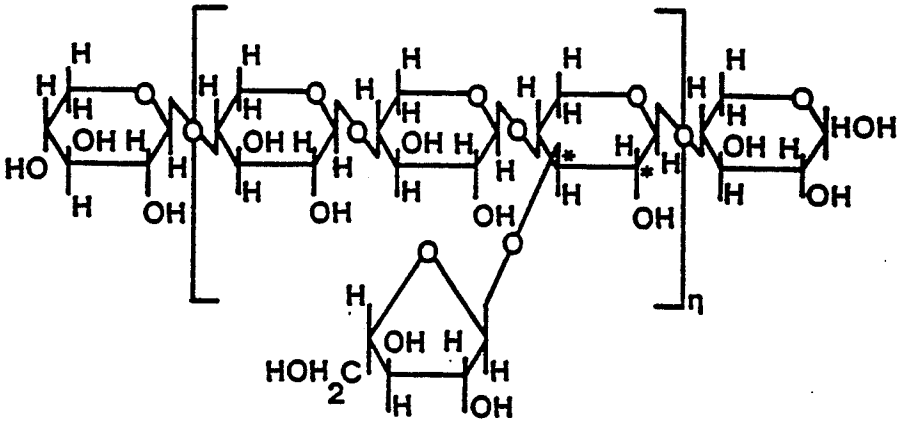
2.2 Chemistry of water-soluble pentosan constituents

2.2.1 Arabinoxylan

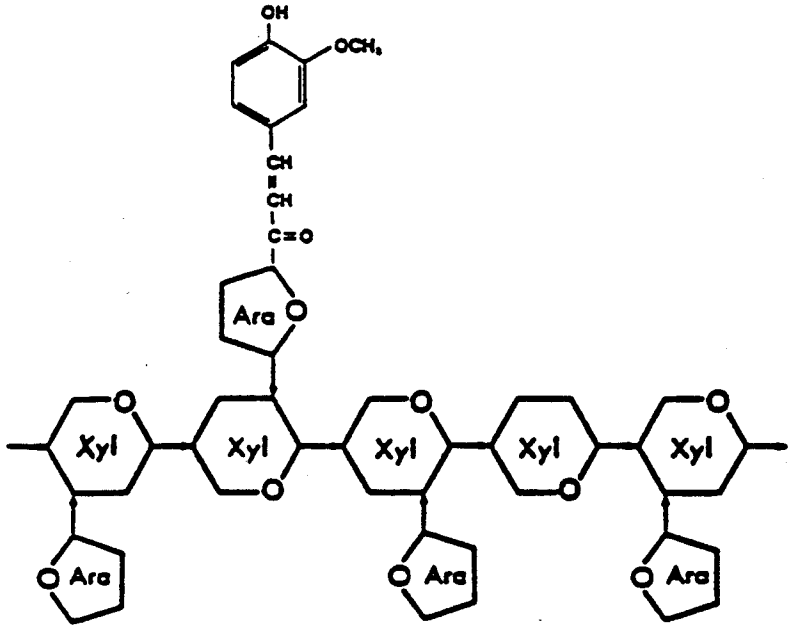
Arabinoxylan constitutes the bulk of water-soluble pentosans (Montgomery & Smith, 1955; Perlin, 1951). It is made up of a linear chain backbone of β(1-4) glycosidically linked D-xylose residues. To this xylan backbone, α,L-arabinose residues are attached randomly at the C_2 or C_3 carbons of xylose residues (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

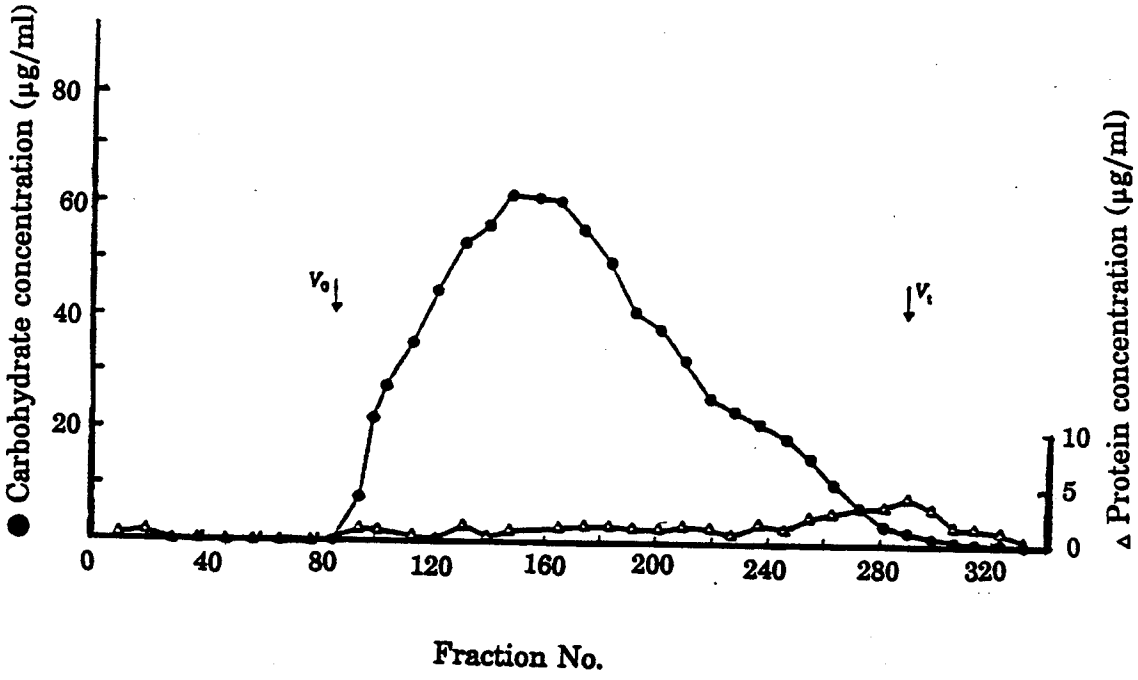


b



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.

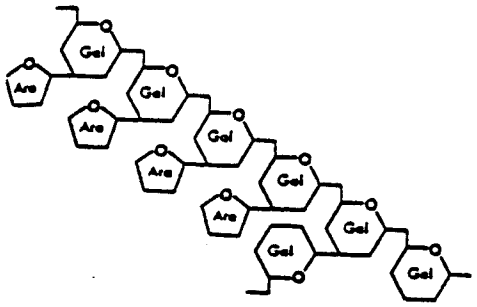
arabinoxylans is the presence of ferulic acid. This phenolic acid is covalently linked to the O_5 atom of arabinose residues via ester linkages (Fausch et al, 1963; Smith & Hartley, 1983), as shown in Figure 1. Ferulic acid plays an important role in the functional properties of arabinoxylans especially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

2.2.2 Arabinogalactan

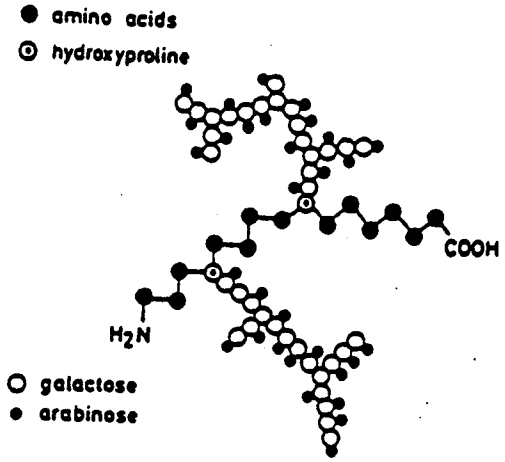
The structure of the arabinogalactan-peptide constituent of water soluble pentosans was independently studied by two groups (Fincher and Stone, 1974; Neukom et al, 1975). In both studies it was found that arabinogalactan has a highly branched structure in which galactopyranosyl units are glycosidically linked to each other through $\beta(1-3)$ and $\beta(1-6)$ 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