MECHANISMS PROPOSED FOR THE OXIDATIVE GELATION OF SOLUBLE WHEAT FLOUR ARABINOXYLANS

Alexandru Stoica*, Ana-Maria Hossu*, Maria Iordan*
*Valahia University of Targoviste, Faculty of Environmental Engineering and Biotechnologies, Food Engineering Department, B-dul Unirii, nr. 18-20, code 130082, Romania.
E-mail: stoicaandi@yahoo.com, anahossu@yahoo.co.uk, marianaiordan@yahoo.com .

Abstract

Oxidative gelation of soluble arabinoxylans in doughs from wheat or rye flours is an important process for their rheological properties that affect quality of bread. Therefore, understanding the mechanisms governing the arabinoxylans oxidate gells formation sparks further interest of researchers in the field, being developed a series of theories that are presented in this article.

Keywords: oxidative gelation, arabinoxylans, ferulic acid, flour.

INTRODUCTION

Concentrated water-soluble pentosan solutions form a gel at room temperature in the presence of oxidants. This unique property of oxidative gelation of flour water-solubles was first described by Durham (1925) and later shown to be caused by the pentosans (Miller and Hoseney, 1999; Moore et al., 1990). Gelation was affected by the pentosan concentration, oxidant concentration, pH, ash, and presence of organic compounds (Baker et al 1943, Neukom et al 1967, Painter and Neukom 1968).

Cell-wall polysaccharides in foods are a complex group of components differing widely in physical properties and nutritional effects. Information about the composition and organization of plant cell walls is fundamental for our understanding of the molecular mechanisms of cell-wall polysaccharides that are of technological and nutritional importance (Anderson et al, 2006).

Polysaccharides serve the growing plant as a structural component that maintains the tissue integrity, as a conduit structure for the movement of water and low-molecular-weight solutes that help maintain osmotic pressure, and as a barrier against microbe and insect penetration. In foods, they control rheological properties, water binding, and the sensory perception of texture, and they are important sources of nutrients and dietary fiber.

Wheat pentosans consist of soluble and insoluble linear arabinoxylans and branched arabinogalactans.

The soluble arabinoxylans are responsible for the high viscosity of their solutions in water (Autio, 2006).

THE ACTORS: ARABINOXYLANS

Arabinoxylan (AX), a neutral non-starch polysaccharide from cereal grains, is constituted of a linear backbone of β-(1/4)-linked D-xylopyranosyl units to which α-L-arabinofuranosyl substituents are attached through O-2 and/or O-3 (Fincher & Stone, 1974) (fig. 1). Some of the arabinose residues are ester linked on (O)-5 to ferulic acid (FA) (3-methoxy, 4 hydroxy cinnamic acid) (Smith & Hartley, 1983; Carvajal-Millan et al., 2006). FA is concentrated in the cell wall of the outer coverings of wheat kernel (Wang, 2003).

Ferulic acid has three potential reactive sites: two on the aromatic ring and one at the activated double bond. These reactive sites could serve to cross-link polymers and increase their molecular size (Moore et al., 1990).

It is necessary to make a distinction between AX and arabinogalactan-peptides (AGP), another class of non-starch polysaccharides found in the endosperm of wheat. In spite of large differences between AX and AGP in both structure and properties, they have often been and sometimes still are regarded or studied as

one group called pentosans (Courtin and Delcour, 2002).
Arabinoxylans can be divided into soluble water-extractable (WE-AX) and insoluble water-unextractable arabinoxylans (WU-AX) (Vardakou et al., 2004). The chemical structures of wheat WE-AX and WU-AX are basically the same, the WU-AX having a slightly higher molecular weight. The differences in extractability are probably due to differences in chemical and physical interactions. Substituents such as phenolic acids, acetyl groups and proteins may be found in cereal arabinoxylans. A highly substituted arabinoxylan fraction linked to wheat gluten has recently been found (Autio, 2006).
While the degree of substitution of WE-AX would not influence the conformation or the rigidity of the WE-AX, the presence of diferulic acid bridges between WE-AX would lead to molecules with an increased molecular weight and changed conformational properties (Courtin and Delcour, 2002).
The total and water-soluble pentosans comprise about 1.4 to 2.1% and 0.54 to 0.68% of the wheat grain on a dry matter basis. The WS pentosans are extractable with cold water, whereas alkali is needed to extract the WIS pentosans. The solubility of the pentosans varies widely with climatic conditions. The percentage of soluble pentosans is higher in the endosperm than in the bran and shorts fractions (Autio, 2006).

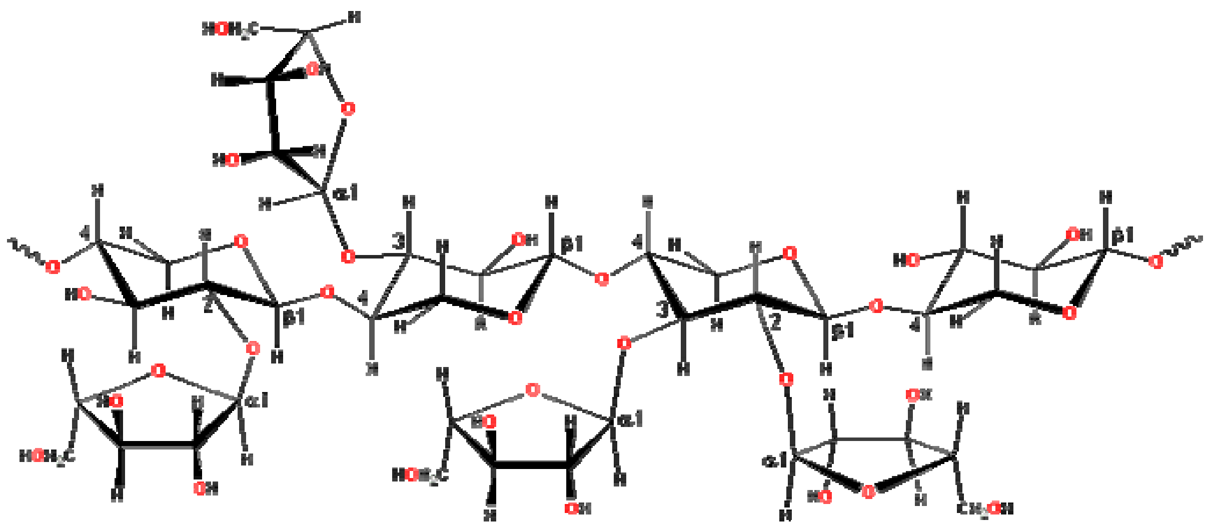

***Figure1* –** The structure of wheat flour arabinoxylans (after Chaplin, 2004).

POSSIBLE REACTION IN OXIDATIVE GELATION

Pentosans form gels with an oxidizing agent. The water-holding capacity of oxidized arabinoxylans is clearly greater (75 to 90%) than that of oxidized pentosans that also contain arabinogalactans (40 to 60%) (Autio, 2006).
Upon oxidation by some chemical or enzymatic free radicals generating agents (laccase, peroxidase, H2O2 system), WE-AX can gel through diferulic acid covalent crosslinking (Figueroa-Espinoza & Rouau, 1998; Geissman & Neukom, 1973; Hoseney & Faubion, 1981; Izydorczyk, Biliaderis & Bushuk, 1990). Five main diferulic acids (di-FA) (5-5', 8-5' benzo, 8-O-4', 8-5' and 8-8' di-FA) are identified in gelled WE-AX, the 8-5' and 8-O-4' forms being always preponderant (Figueroa-Espinoza, Morel & Rouau, 1998; Schooneveld-Bergmans, Dignum, Grabber, Beldman & Voragen, 1999; Vansteenkiste, Babot, Rouau & Micard, 2004) (fig. 2).

The involvement of a trimer of ferulic acid (4-O-8', 5'-5"-dehydrotriferulic acid) in laccase crosslinked wheat WEAX has been recently reported (Carvajal-Millan, Guigliarelli, Belle, Rouau, & Micard, accepted for publication). In addition to covalent cross-links (di-FA, tri-FA), the involvement of physical interactions between AX chains was suggested to contribute to the arabinoxylan gelation and gel properties (Carvajal-Millan, 2006; Vansteenkiste et al., 2004). The main result of oxidative cross-linking is a strong increase in the viscosity of AX in solution. When the AX concentration is sufficiently high, a gel is formed (Courtin and Delcour, 2002).

WE-AX gels present interesting properties like neutral taste and odour, high water absorption capacity (up to 100 g of water/g of dry polymer) and absence of pH or electrolyte susceptibility (Izydorczyck & Biliaderis, 1995).

Neukom and Markwalder (1978), Hoseney and Faubion (1981) suggested several hypotheses for the oxidative gelation mechanism, but no consensus could be found:

(1) Arabinoxylan ferulic acid is linked to tyrosine residues or to ferulic acid complexed with protein;

(2) arabinoxylan ferulic acid is linked to N-terminal protein groups;

(3) part of ferulic acid is bound to the glycoprotein and serves as a bridge between the protein and pentosan; or

(4) a covalent binding of protein with the arabinoxylan chain via a ferulic acid group is involved.

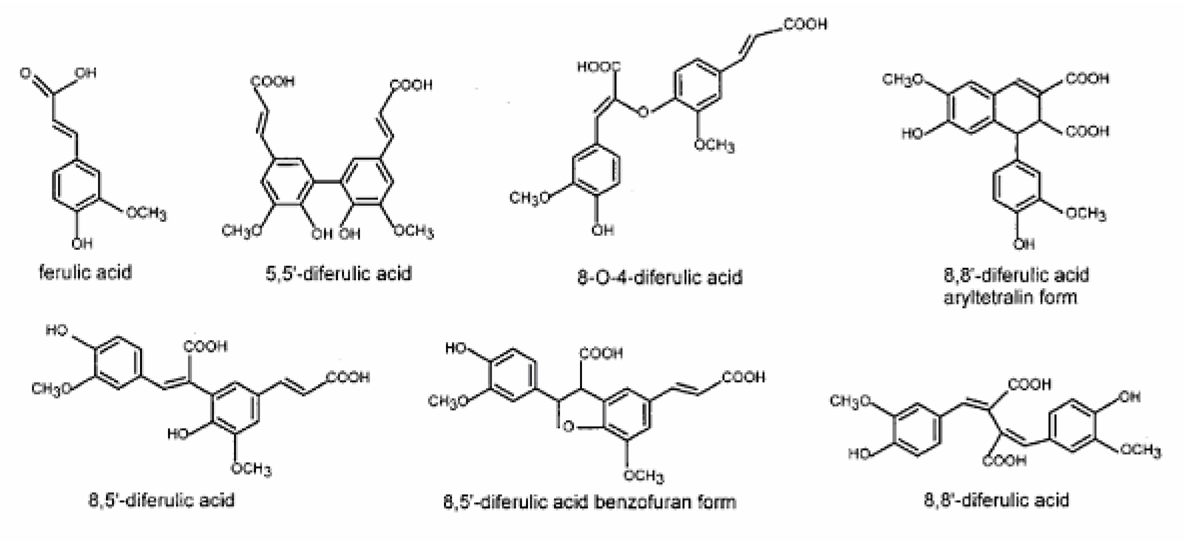

Figure2. Schematical presentation of ferulic acid and diferulic acid structures.

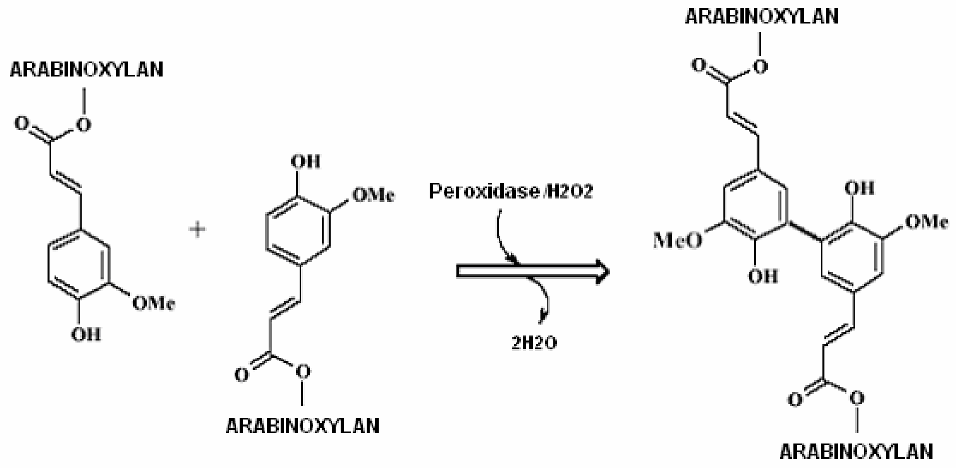

Figure 3. Formation of diferulic acid in oxidative gelation (after Neukom and Markwalder, 1978).

Numerous hypotheses concerning the mechanism of oxidative gelation have been developed, but none have been substantiated. Ferulic acid associated with the polysaccharides may be involved in cross-linking pentosans (Fausch et al 1963, Geissmann and Neukom 1973, Neukom 1976, Hoseney and Faubion 1981).
Neukom and Markwalder (1978) suggested involvement of the aromatic nucleus to form diferulic acid bridges. Sidhu et al (1980) and Hoseney and Faubion (1981) pointed to the activated double bond as the cross-linking site. Hoseney and Faubion (1981) suggested that a protein thiyl radical added to the activated double bond (Moore et al., 1990).
Hoseney and Faubion found that bromate, iodate and ascorbic acid did not lead to gelation, while Neukom and Markwalder state that periodate does produce it; so if this reaction has any relevance to the oxidative improvement of doughs by bromate or iodate, Neukom's suggestion would seem to bear slightly more weight. On the other hand, the gelation reaction may be related only to the improving effects of oxygen, in which case the question of mechanism is still open.

REFERENCES

1. ANDERSSON, R., WESTERLUND, E., ÅMAN, P., 2006 - Cell-Wall Polysaccharides: Structural, Chemical and Analytical Aspects. In *Carbohydrates in Food*, Taylor & Francis, LLC.
2. AUTIO, K., 2006 - Functional Aspects of Cereal Cell-Wall Polysaccharides. In *Carbohydrates in Food*, Taylor & Francis, LLC.
3. BORDEI, D., TEODORESCU, F., TOMA, M., 2000 – *Ştiinţa şi tehnologia panificaţiei*. Editura AGIR, Bucureşti.
4. CARVAJAL-MILLAN, E., GUILBERT, S., DOUBLIER, J.L., MICARD, V., 2006 - Arabinoxylan/protein gels : Structural, rheological and comtrolled release properties. *Food Hydrocolloids, 20,* p. 53-61.
5. CHAPLIN, M., 2004 - Water Structure and Behavior. London South Bank University. London. http://www.lsbu.ac.uk/water/.
6. COURTIN, C., DELCOUR, J.A., 2002 - Arabinoxylans and endoxylanases in wheat flour bread-making. *Journal of Cereal Science, 35,* p.225-243.
7. FIGUEROA-ESPINOZA, M.C., ROUAU, X., 1998 - Oxidative Cross-Linking of Pentosans by a Fungal Laccase and Horseradish Peroxidase: Mechanism

of Linkage Between Feruloylated Arabinoxylans. *Cereal Chem., 75 (2)*.
8. IZYDORCZYK, M., BILIADERIS, C.G. AND BUSHUK, W., 1991 - Physical properties of water soluble pentosans from different wheat varieties, *Cereal Chem*., 68, p.145.
9. IZYDORCZYK, M. S., BILIADERIS, C. G., 1995 - Cereal arabinoxylans: Advances in structure and physicochemical properties. *Carbohydrate Polymers, 28,* 33–48.
10. MILLER, K.A., HOSENEY, R.C., 1999 - Effect of oxidation on the dynamic rheological properties of wheat flour-water doughs. *Cereal Chemistry, 76, ian.-febr.,* 100-104.
11. MOORE, A.M., MARTINEZ-MUNOZ, I., HOSENEY, R.C., 1990 - Factors Affecting the Oxidative Gelation of Wheat Water-Solubles. *Cereal Chem., 67 (1),* p.81-84.
12. STAUFFER, C.E., 1990 - *Functional additives for bakery foods.* Van Nostrand Reinhold, New York.
13. VARDAKOU, M., et al., 2004 - Synergy between enzymes involved in the degradation of insoluble wheat flour arabinoxylan. *Innovative Food Science and Emerging Technologies, 5,* p.107-112.
14. WANG, M., 2003 - Effect of pentosans on gluten formation and properties. *Thesis Wageningen University.*