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Chapter

Fibers: Healthy Component in Whole Wheat and Rye Flours

María Laura Gómez Castro, Claudia Cecilia Larregain, Ethel Noemi Coscarello and Roberto Jorge Aguerre

Abstract

The demand for foods made with whole grain ingredients that improve health continues to grow. The health benefits of whole grain cereal are well recognized and are attributed to the presence of dietary fiber and phytochemicals. Consumption of whole grain cereals has been associated with protection against cardiovascular disease and type 2 diabetes. The wheat and rye whole grain flours have a total fiber content that gives a healthy contribution for the daily feeding of the population. After applying a malting process, the composition of fibers is modified by increasing the fraction of soluble fibers. These fibers are prebiotic and improve flour functionality. In this chapter, we will study the properties of whole malted flour of wheat and rye and how it benefits health.

Keywords: functional flour, fibers in cereal, malting process, prebiotic, arabinoxylans

1. Introduction

Food and Agriculture Organization (FAO) of the United Nations and World Health Organization (WHO) expert's meeting in human nutrition agreed that carbohydrate intake should be at least 55 parts in 100 of total calories [1]. Caloric intake should be mainly complex carbohydrate available with low glycemic index. This recommendation emphasizes the consumption of foods that meet these properties. The term "fiber" means carbohydrate polymers, which are neither digested nor absorbed in the human small intestine. The properties of dietary fiber, as the retention capacity of water and oil, have beneficial results on food products by improving their organoleptic characteristics and their physiological effects on the human organism. The quality of the fibers varies according to the type of cereals and according to the processes that are carried out to obtain their flour. In previous works carried out in our laboratory and in other research centers, on rye malt, this procedure generates an increase of soluble fibers, maintaining total fiber content.

The flour made form rye has greater fiber content than the flour wheat. The properties of dietary fiber have beneficial physiological effects on the human organism. Some components of soluble fiber are called prebiotics, defined as food ingredients that positively affect the host.

Prebiotics are defined as nondigestible substances. The dietary fiber maintains biological activity within the human organism by selective stimulation of growth of beneficial microorganisms either naturally present or therapeutically

introduced to intestine. The intestinal microflora ferments prebiotics. Prebiotics saccharide belonging to the inulin group, GlcpFruf [α-D-fructopyranosyl-(β-D-fructofuranosyl) n-1-D-fructofuranose], Frup-Fruf [β-D-fructopyranosyl-(β-D-fructofuranosyl) n-1-D-fructofuranose] where n = 10–60; fructooligosaccharides, FOS (apart from oligofructose with n = 2–9 and, eventually, D-glucose, D-xylose, D-galactose and mannose residues) and non-digestible sugars, NDO. The oligofructose is present in wheat, onion, garlic, endive, leeks, asparagus, and others. In breast milk, the levels of oligosaccharides are relatively high, from 3 to 6 g/L; bifidobacterium selectively digests FOS and NDO and stimulates the development of colonies. Babies fed by the formula, that is, that refers to prebiotics, promote the development of probiotic bacteria, which inhibit the growth of pathogenic bacteria, the bacterial digestion of nutrients, especially proteins, and the decrease of their allergenicity. Probiotic bacteria synthesize cytoprotective short-chain acids, B and K vitamins, and polyamines and degrade the fiber by improving the action of the colon and by increasing the volume of feces [2].

Arabinoxylans (AX) (sometimes called pentosans) are the main non-cellulosic polysaccharides that are abundant in cereals. In the wheat and rye, they differ in their solubility in water, being some soluble and some others insoluble. Water-soluble and water-insoluble fractions are separated through stirring and from a centrifugation. These compounds have healthy benefits. The health benefits are prebiotic effect together with their ability antioxidant. This properties makes these are prevention agents of the colon cancer disease. At the metabolic level, the AX control glycemic and cholesterol levels are also immune regulator agents. During the later years, the research and interest of the AX have gathered considerable attention.

Arabinoxylans are composed of a chain, β(1–4) of xylose units, with variable branches of arabinose in (1–2) or (1–3) [3]. The solubility is modified according to the degree of substitution. The smaller the number of lateral branches, the greater the insolubility of the AX and the possibility of generating insoluble complexes [4]. The AX form viscous solutions with pseudoplastic behavior, and in the presence of certain oxidizing agents, the gels are much stronger and stable. This involves the action of ferulic acid in the formation of cross-links between the AX chains [5]. The texture of the bread increases during the cooking due to the cross-linking of the AX, whose natural levels in the wheat flour determine the quality of the bread, in the functional and nutritious properties [6].

2. Mechanism in the germination of cereals

Cereal beta-amylase is best known for the vital role it plays in the release of easily fermentable sugars from corn starch cereals to feed the production of alcohol by yeasts in beer brewing investigated because of its importance in this economically important brewing industry. Beta-amylases cereals are also used in other products of the food industry and in the analysis of starch. They are markers in the evaluation of cereals and in grain development studies. The enzymes β-amylases of cereals have been little studied at the physiological level.

In recent times, it was discovered that there are two categories of β-amylases, according to their pattern of tissue and taxonomic and physiological development. The classical β-amylases are present in the endosperm of the cereals of the family Triticeae of the subfamily Festucoideae of the grasses and the high levels of enzymatic activity, while the others are distributed in all tissues of the cereal but show less activity. The physiological phenomenology and the use of grain beta-amylases are discussed in relation to these two categories of enzymes [7]. The life

cycle of a grain of cereal is divided into stages of development and germination, divided by a latency period [8]. During germination, much of the amino acid supply necessary for the growth of emerging seedlings comes from the degradation of the storage proteins of the seeds. The latter are synthesized during the maturation of the seeds and are deposited in specialized vacuoles. Little is known about the proteolytic enzymes in germinated rye. In contrast, the proteases that appear during the germination of barley [9–11] and wheat [12] are well studied. Using a non-denaturing electrophoretic system with protein substrate incorporated in the gel, [13] detected seven proteolytic bands in green barley malt. Five of these bands were maximally active at pH 3.8. Up to 20 proteolytic bands could be detected in extracts of germinated wheat grains [14]. The information shows that the total proteolytic activity increases during germination [15] has been investigated the temporal pattern of appearance of proteinases during germination, the sensitivities to specific inhibitors, and the location of proteinases and separated 42 activities into the germinating grain of barley using two-dimensional (2-D) gel electrophoresis (IEF × PAGE). These substances were divided into five groups based on isoelectric point (pI) values, PAGE mobilities, and biochemical characteristic [16]. About two-thirds of these enzymes were cysteine proteinases. The barley cysteine proteinases apparently hydrolyze most of the hordes, which are the main storage proteins of the barley endosperm. The purification and characterization of some of these cysteine proteinases have been described in several reports [17–20]. In [21] initiated the characterization of proteases in malted rye using two different methods to analyze their activities. A qualitative 2D method was used to measure the heterogeneity of the proteases and a method with solutions of different substrates to measure the activities of the different proteinase groups. It was concluded that the selected Humbolt rye cultivar produces high levels of proteolytic activities [22]. It was germinated under optimal conditions of temperature, aeration, and humidity, and the proteolytic activities were monitored using capillary electrophoresis methods. The total proteolytic activity was significantly higher after soaking and increased during the first 3 days of germination, but not after that time. The hydrolyzing activity was maximal at pH 53.5 and 45–50°C. After grinding, there were marked increases in the levels of proteolytic activity. The use of specific inhibitors showed the presence of four kinds of proteinases. According to the precedents, it is evident that hydrolysis of storage proteins in rye during germination is probably due to cysteines and aspartic proteinases [23].

3. Arabinoxylans and viscosity in the process of malting

Rye contains considerably higher amounts of arabinoxylans (AX), especially water-extractable arabinoxylans (WEAX), than barley. The rye AX structure and its properties were described [24]. AX are cell wall non-starch polysaccharides and are constituted by a chain of β-1,4 units of xylopyranose. The α-arabinofuranose chain can bind to the C(O)-2 and/or C(O)-3 of the xylose residues. It contains some arabinose substituents that are esterified with ferulic acid in C(O)-5 [25]. The molecular masses, the degree and the configuration of the arabinose branching, and the degree of esterification with ferulic acid exert an important influence on the properties of the AX. Since WEAX can bind to many water molecules, it can change the viscosity of the solutions making them more consistent. Gels can be formed by oxidative cross-linking of AX macromolecules through ferulic acid residues. The AX of the rye grains, during the process of the germination, suffer an enzymatic degradation. The inner bonds of the main chain of the xylan are divided forming a greater quantity of shorter-chain AX molecules by the action of

the endoxylanase enzymes. Xylose residues are released from the nonreducing end since the β-xylosidases, while keeping the number of macromolecules constant, slightly decrease the length of the chain. The enzyme α-L-arabinofuranosidase releases arabinose from macromolecules, whereas feruloyl esterase hydrolyzes the bond between ferulic acid and arabinose residues [26]. AX represent a large part of the rye's dietary fiber, a soluble dietary fiber with their known health benefits for the consumer [27, 28] described in two studies, the positive effects of AX on postprandial insulin response in healthy individuals and improved metabolic control in diabetes patients. AX breakdown products have also been shown to display prebiotic properties [29–32, 40]. Certain proteins restrict access to water and enzymes to the endosperm starch. This situation is reversed during germination, when proteins and other components of the cellular apparatus are degraded and allow the passage of enzymes to the cellular interior. In this way, the extraction of starch and other compounds is increased. In the brewing industry, it is associated with a high nitrogen level at low starch content. The total nitrogen content of the malts obtained varied when the germination conditions changed. The difference between the highest and lowest values measured was 0.2%. But changes in germination conditions do not justify changes in the measurements obtained. The protein content in barley and rye from the beginning of germination did not vary significantly [33]. Nitrogen-containing compounds, being insoluble, will not form part of the mass during processing. In addition, some fractions of the soluble nitrogen (SN), like enzymes and free amino nitrogen (FAN), play important roles in the mashing process and during the fermentation, respectively. It was studied that the variations in SN measured produced from rye malts were large with values ranging between 694 and 862 mg/100 g. The highest SN contents were found in samples germinated for 96 h at 18°C, 130 h at 15°C, and 144 h at 10°C. In the germination of barley, storage proteins are mobilized, and some structural proteins are degraded. An increase in soluble nitrogen is generated in the malt, due to the large amount of peptides and extractable proteins in water. Protease enzymes influence the content of nitrogen compounds during maceration, although the greater amount of SN is formed in the malting. In rye, the content of SN does not appear to be influenced by the action of the proteolytic enzymes of the germinated malt. Previous studies show that free amino nitrogen (FAN), as an essential nutrient, is relevant in the growth of yeasts in the initial stage of fermentation. It was observed that at longer germination times, the FAN contents increase [34, 35]. In the maceration process, the starch is degraded by two enzymes, α-amylase and β-amylase, which act mainly generating maltose. Then, the maltose is fermented by yeasts that generate ethanol as a primary product. An increase in enzymatic activity has been observed, proportional to the time of germination. An increase in the total content of AX in the final malt has been observed, probably due to the loss of other compounds in respiration and formation of rootlets. The results of this study show which quality parameter of rye malt can be optimized by varying germination conditions. One of the most important factors, in the use of malt in the brewing industry, is the viscosity due to high amounts of WEAX. When the malt is used as a raw material for functional foods, its nutritional properties are used as a function of the AX and its decomposition products. According to the selected germination parameters, it is possible to direct the breakdown of the AX in the malt.

4. Prebiotic effects of cereal arabinoxylans

As reported before, in grains of wheat and related cereals, dietary fiber is predominantly composed of arabinoxylans (AXs). These cell wall components

typically consist of a linear backbone of β-(1–4)-D-xylopyranosyl units, which may be substituted by α-L-arabinofuranosyl units [36]. The structure and the physicochemical properties of AX from different layers in cereal kernels are very diverse. The cereal's arabinoxylans (AX) are the main dietary fibers in a balanced human diet. The physiological impact of AX consumption strongly depends on their structures and properties as different impacts on the microbial population and fermentation products in the intestinal tract of rats. The consumption of extractable arabinoxylan of wheat bran increases the mass of the cecal contents. It is known that the consumption of soluble fermentable fiber by rodents causes increase in the mass of the cecum content. Extensive fermentation of water-extractable arabinoxylan or arabinoxylan oligosaccharides reduce the pH, suppress relevant markers of the proteolytic breakdown, and induce a selective bifidogenic response [37].

5. Application of rye malt in the brewing industries

The malting technologies were optimized for barley. The new materials must then be compared with the malt to establish identity in the processes. Wheat malt is also very important in large quantities in the western world. The contents of extract in rye malts were also higher than in barley malts (usually >81% [38]. As rye does not have a shell, which represents approximately 10% of the barley's dry weight [32], the fermentation capacities in the rye parts (73 and 77%) are lower than in 80% barley [38] or wheat parts (>78%, [39]), because they contain lower soluble nitrogen compounds and WEAX. However, the content of SN in rye malt turns out to be higher than in barley malt [38]. A higher viscosity of rye malt is the main drawback when using the brewing industry. This impediment can be reversed by modifying the temperature and the germination period (10°C and h) [40].

6. Folate in germinated cereals

The effects of germination and subsequent oven-drying or freeze-drying on folate content in a number of wheat and rye cultivars were studied for producing folate-rich flour ingredients. As reported in previous studies [41–43], germination of wheat and rye resulted in a four- to sixfold higher folate content than untreated cereals, mainly due to an increase in 5-CH3-H4 folate (w4-fold). The increased folate content has been attributed to de novo synthesis of folate being accelerated because of increased demand for methyl groups (one carbon unit) during germination [43]. Oven-drying (50°C) did not significantly affect the folate content, which is in agreement with our previous findings that oven-drying of germinated grains is suitable for the production of folate-rich candidate ingredients [44]. It has recently reported that by addition of germinated wheat flour to native wheat flour, bread with a 65% higher folate content compared with conventional Egyptian baladi bread could be prepared [45]. Germinated cereal grains and flour could also serve as functional ingredients for the European bread-baking industry. Here, the folate content in the rye cultivars studied was approximately 25% higher than that in the wheat cultivars. This confirms findings by [46] that rye flour contains more folate than flour from other cereals such as wheat, triticale, barley, and oats. The folate content quantified in the four Swedish wheat cultivars tested (23–33 mg/100 g dry matter DM) is also similar to HPLC data (34–40 mg/100 g DM) reported for four Polish wheat cultivars [48]. In comparison to data from microbiological assays [47–49], the mean folate content in untreated wheat and rye cultivars was 30–40% lower in this study. HPLC methods generally tend to provide folate values which are around

30% lower than data from microbiological assays [46–48]. Furthermore, the sum of folate content was underestimated by lack of quantification of 5-HCO-H4 folate and 10-formyl-dihydrofolate. Other groups also reported difficulties in quantification of 5-HCO-H4 folate in cereal foods using HPLC [45–47]. Up to 40% 5-HCO-H4 folate was reported in untreated wheat and rye [45–48], and the content was not significantly affected by germination of rye [49]. Also 7–13% of 10-formyl-dihydrofolate was found in untreated and germinated rye cultivars by [49, 50], while [51] did not detect this form. This can partly explain the discrepancy between our results and data reported in the literature. The mean folate content in six rye and four wheat cultivars ranges from 23 to 39 mg/100 g DM, being approximately 25% higher in rye than in wheat. The folate content in both cereals by four- to sixfold increases in germination subsequent oven-drying, which is required for milling of germinated grains, does not affect the folate content. Germinated kernels and their flours are ingredients with increased folate content for use in bakery products [52].

7. Prevent the bitterness of whole grain flour

The whole grain rye is beneficial for health. However it may be bitter. The impact of nonvolatile chemical compounds on the bitter taste of rye was analyzed by the aid of enzymatic hydrolysis, releasing potentially flavor-active compounds from the rye matrix. Water suspension of whole grain rye flour was treated with hydrolytic enzymes, after portions of the rye suspensions were baked into crackers and assessed for their sensory profile as well as solubilized hydrolysis products. Heat treatment reduced the perceived bitterness. The treatment with enzyme preparation with high protease activity increased the bitterness of rye and also wheat flour both as suspension and as crackers. Other enzymes tested (with high polygalacturonase, endo-glucanase, xylanase, or amyloglucosidase activity) had no significant impact on the perceived bitterness. Thus, small molecular weight peptides were considered to be a significant contributor to the bitter note of rye [53].

8. Relationship between the consumption of wholegrain cereals and incidence of lifestyle-related diseases

The incidence of diseases originating from the current lifestyle, such as cardiovascular diseases (CVD), certain types of cancer, and type II diabetes [54–62], is diminished by the consumption of whole grains [63, 65, 66]. Although importance is given to fibers in food, all the mechanisms responsible for this behavior are still not fully understood. Metabolomics was used for this study, which is a research that determines, in this case in plasma, the set of metabolites that is produced in the ingestion of a certain substance by means of instrumental analysis, for example, proton nuclear magnetic resonance spectroscopy ^{1}H NMR, chromatography, and mass spectrometry; these results are processed by means of a statistical analysis through software with the aim of understanding the endogenous biochemistry that is produced. When high-fat diets are consumed, apolipoprotein profiles of pigs are similar to humans, and these animals suffer atherosclerotic lesions similar to those that arise in humans [64]. Therefore, the pig is a suitable model to study the hypocholesterolemic effects of cereals. Barley and oats have been studied because of their high β-glucan content [60, 61, 67, 68]. However, there were no studies on whole meal rye breads; for this reason, using metabolomics as a tool, the positive effects of these breads were studied and compared with wheat breads in hypercholesterolemic pigs. The pigs were fed with rye-based (n = 9) or wheat (n = 8) bread with high-fat

content and similar levels of dietary fiber for 9–10 weeks. Fasting plasma samples were collected 2 days before and after 8 and 12 days of consuming the experimental diets, while the postprandial samples were taken after 58–67 days, and the spectra of the ^{1}H NMR samples were made. The main component of the analysis (PCA) in the ^{1}H-NMR spectra of the plasma samples revealed a clear separation in the metabolite profiles of the plasma samples of the integral rye diet with respect to the samples of the diets of non-integral wheat both on day 8 and day 12 and at slaughter. In order to determine the differences in the metabolites of the two diets, a discriminant regression analysis by partial least squares (PLS-DA) was performed. On both day 8 and slaughter, an increase in the spectral intensities of the signals was observed at 3.29 ppm of the plasma samples of the animals that consumed rye compared with the samples of the animals that consumed the non-integral wheat, which is consistent with a chemical change for the different N(CH3)3 groups [64]. It has been demonstrated using liquid chromatography with LC-MS mass spectrometry detector that this response should be attributed to betaine [65]. We can affirm that the intake of a diet with high-fiber rye breads in hypercholesterolemic pigs increases betaine, which can be considered a biomarker because it is present in all the samples of the animals that consumed this diet with rye, which is not verified whether this biomarker can be used in a mixed diet [69, 70] since it has been shown that betaine is absorbed and increases in serum concentrations [72, 74]. Betaine acts as a methyl donor in the reaction of betaine-homocysteine methyltransferase that converts homocysteine into methionine [71, 73–76]. This is beneficial since plasma homocysteine is a risk factor for CVD [77, 78]; this property can be expected that betaine is involved in the prevention of CVD through this route. In addition, the concentration of plasma betaine is inverse to the amount of the following parameters, non-HDL serum cholesterol, triglycerides, and percentage of body fat, waist circumference, and systolic and diastolic blood pressure [79]. This study demonstrates a relationship between the intake of rye bread and the concentration of plasma betaine. Furthermore, in the analysis of the regressions, contributions of this diet to the chain of fatty acids linked to lipoproteins were observed; this behavior is not clear; however it could lead to an alteration in the composition [80].

Another study compared whether the postprandial glucose and insulin responses to whole-grain rye bread are less than wheat bread, and these responses were observed in two different types of rye bread. Rye breads are based on wholemeal flour and are thus rich in dietary fiber (DF). The dietary fiber content of our rye is 15 ± 17%, arabinoxylans (8 ± 10%), beta-glucan (2 ± 3%), and cellulose (1 ± 3%) being the main chemical constituents [81, 82]. Mainly due to its high DF content, wholemeal rye bread may reduce the health risks associated with coronary heart disease [79] and colon, breast, and prostate cancer [83, 84]. Slowly digestible carbohydrates have been suggested to be nutritionally most desirable, improving metabolic variables not only in diabetes and hyperlipidemia but also in healthy subjects [82, 83]. Although the glycemic index (GI) is a criticized concept [84], it is a widely used method for classification of different foods according to their effect on postprandial glucose levels. It has been analyzed that the glucose and insulin responses of different rye breads and other rye products have been reported to be variably lower than those of wheat bread [85]. The lowest GI values (66–80) have been reported for pumpernickel-type breads containing intact kernels [86–89]. There is a consensus that intact botanical structure protects the encapsulated starch of the kernel against the hydrolysis [90, 91]. The amount of whole kernels in the bread has been concluded to be more effective in reducing the glucose and insulin responses than the high-fiber content as such [86–88, 92]. The GI of food is generally to increase by the heat processing. However, there is exception to this rule, that is, pasta manufacture and most pasta products having a GI value of 50 ± 70 [93]. Low temperature and

long-time baking may slow the digestion of bread by increasing the retrogradation of amylose and hence the amount of resistant starch (RS) in the product [94]. RS passes the small intestine without digestion and is available as energy only after colon fermentation. Rye bread contains organic acids and their salts; the latter are supposed to lower postprandial glucose and insulin responses [95–98] either by interfering the action of hydrolytic enzymes in the small intestine or by delaying gastric emptying [94]. The majority of the studies concerning glycemic responses of rye bread has been conducted in diabetic patients. In this study it was determined in healthy subjects whether the postprandial glucose and insulin responses to rye bread (whole kernel bread) are lower than those to wheat bread. Furthermore it was evaluated out if various types of rye breads give different glucose and insulin responses (wholemeal crispbread vs. wholemeal bread).

Standardized breads through an in vitro analysis of the hydrolysis rate of starch with a content of 43 ± 61 g of available carbohydrates, were consumed at a breakfast by 20 subjects (10 women and 10 men) with normal glucose tolerance. Eight samples of blood were taken from the subjects, postprandial for a period of 3 h. Eight samples of blood were taken from the subjects, postprandial for a period of 3 h. The results of the plasma insulin of the samples of the subjects who consumed whole wheat rye bread were lower than the samples of the subjects who consumed the wheat bread (45 min $P = 0.025$, 60 min $P = 0.002$, 90 min $P = 0.0004$, 120 min $P = 0.050$, 150 min $P = 0.033$); however there was no difference in glucose responses. We can conclude that wheat bread produces a greater postprandial insulin response than whole grain rye bread, but there is no difference in glucose response [99].

9. Conclusions

It is necessary to understand the impact of enzymes in AX and the behavior of rye proteins during the malting process. Although in the case of wheat this is studied with more depth, there is still no mass commercialization of wheat bread products. The malted and unmalted whole grain of rye and wheat contains fibers that are beneficial to prevent noncommunicable diseases. In malted flour compared to unmalted flour, the amount of soluble fibers increases. However, it is necessary to conduct research with cereals from different countries and compare the composition of these functional flours to apply them to different food products.

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