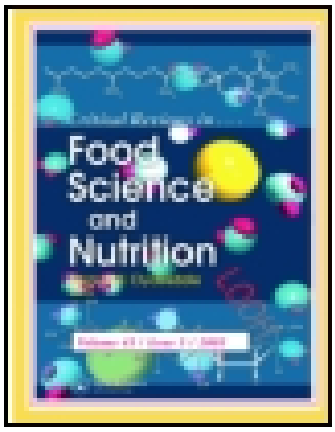

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Enhancement of attributes of Cereals by Germination and Fermentation: A Review

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The nutritional quality of cereals and the sensorial properties of their products are sometimes inferior as compared to other sources of food which is due to the lower protein content and starch availability, the presence of determined antinutrients (phytic acid, tannins and polyphenols) and the coarse nature of the grains. To ameliorate the nutritional qualities of cereals, they are processed in a number of ways.This review summarises the enhancement in the nutritional value as well as the functional characteristics of cereals due to germination and fermentation treatment.The protein concentration increases and the amino acid profile is balanced by germination and fermentation.The antinutritional factors are reduced increasing the mineral availability from the cereals. Germination enhances the quality of nutrients and bioactive compounds of cereals thereby increasing the content in proteins, amino acids, sugars and vitamins.The functional properties of cereals is enhanced due to generation of biofunctional substances, increase in protein solubility, invitro protein digestibility and lowering of glycemic index.

Keywords germination, fermentation, cereals, nutritive value, functional properties

INTRODUCTION

Cereals and pseudo cereals are an important source of macronutrients. FAO latest forecast for world cereal production in 2012 stands at 2419 million tonnes whereas the world coarse grain production is 1248.2 million tonnes (www.fao.org).Cereal grains provide significant quantities of energy, protein and selected micronutrients in the animal and human diet and are considered to be one of the most important sources of dietary proteins, carbohydrates, vitamins, minerals and fibre for people all over the world (Dordevic et al., 2010). The cereal group provides important amounts of most nutrients (Truswell, 2002) and forms an important part of a balanced diet i.e. one that provides all the food groups in the nutrition education pyramid or plate and all recommended dietary intakes(Tiwari and Cummins, 2009). Recent studies have shown that cereal grains contain constituents that have demonstrated health benefits for humans, such as antioxidants and anti-disease factors (Juntunen et al., 2000; Karppinen et al., 2003; Rieckhoff et al., 1999). For instance, phytic acid was found to play a major role in the treatment of cancer, hypercholesterolemia, hypercalcuria and kidney stones (Plaami, 1997). Other studies have also demonstrated that diets high in carbohydrate, rich in dietary fiber, and largely of cereal origin, allowed withdrawal of oral hypoglycaemic agents or a reduction of insulin dose in diabetic subjects (Pathak et al., 2000).Additionally, several health claims on grain dietary components have been approved by the FDA in the USA(Ragaee et al.,2006).

However, the nutritional quality of cereals and the sensorial properties of their products are sometimes inferior or poor in comparison with milk and milk products. The reasons behind this are the lower protein content, the deficiency of certain essential amino acids (lysine), the low

starch availability, the presence of determined antinutrients (phytic acid, tannins and polyphenols) and the coarse nature of the grains (Chavan and Kadam, 1989a). Three important factors that restrict the nutritional value of cereals are the swelling of the macronutrient starch upon cooking; limited protein content and quality; and low content and bioavailability of the micronutrients iron and zinc (Mouquet et al., 2008; Nout, 1993). A number of methods have been employed with the aim of ameliorate the nutritional qualities of cereals (Blandino et al., 2003). Additionally, several processing technologies which include cooking, germination, milling and fermentation, have been put into practice to improve the nutritional properties of cereals, although probably the best one is fermentation (Mattila-Sandholm, 1998; Pugalenthi and Vadivel, 2005). This is the main reason why a large proportion of cereals are processed into foods and beverages by fermentation prior to consumption (Nout, 2009). As a unit operation in food processing, fermentation offers a large number of advantages, including: food preservation, improved food safety, enhanced flavor and acceptability, increased variety in the diet, improved nutritional value, reduction in anti-nutritional compounds and in some cases, improved functional properties(Westby et al.,1997).When considering the multitude of foods made from cereals one has to recognize that their greater part has been subjected to fermentation processes taking place at least at one step of their generation where endogenous enzymes, bacteria, yeast and moulds play roles either singularly or in combination, and contribute to the creation of a great variety of products (Hammes et al.,2005).

Many biochemical changes occur during fermentation, leading to altered ratio of nutritive and anti-nutritive components of plants, which affect product properties such as bioactivity and digestibility (Heiniö et al., 2003; Katina, Laitila et al., 2007). Moreover,

several volatile compounds are formed which contribute to a complex blend of flavours (Chavan and Kadam, 1989a). The presence of aromas such as diacetyl acetic acid and butyric acid make fermented cereal based products more appealing (Blandino et al.,2003; Gupta et al.,2010). The changing conditions during fermentation contribute to the activation of enzymes present, and adjustment of pH selectively enhances performance of certain enzymes, such as amylases, proteases, hemicellulases and phytases. The enzyme-induced changes, together with microbial metabolites, bring about the technological and nutritional effects of fermented cereal foods (Poutanen et al., 2009). Cereals are one of the most suitable substrates for the development of foods containing probiotic microorganisms (in most cases lactic acid bacteria or bifidobacteria) and may also have prebiotic properties due to the presence of non-digestible components of cereal matrix(Charalampopoulos et al., 2009; Kedia et al., 2007). Probiotic organisms have been known to have a role in improving metabolism, lowering of cholesterol levels in blood, stimulation of the immune system, detoxification of potential carcinogens etc. (Nomoto, 2005; Smoragiewicz et al., 1993). Literature indicates that probiotic foods not only have several potential health benefits but also have nutritional benefits (Sharma and Ghosh, 2006).

Additionally, germination has been claimed to improve the nutritive quality of cereals and has been used for centuries for the purpose of softening the kernel structure, improving its nutritional value, and reducing anti-nutritional effects (Tian et al., 2010). The prime objective of germination is to promote the development of hydrolytic enzymes that are inactive in raw seeds (Ayernor and Ocloo, 2007). During germination (i.e. hydrothermal treatment in ambient conditions) the biosynthetic potential of grains is exploited and a number of hydrolytic enzymes

are synthesized. The reactions in germinating grain lead to structural modification and the synthesis of new compounds, some of which have high bioactivity and can increase the nutritional value and stability of the grains (Kaukovirta-Norja et al., 2004).

The aim of this paper is to review the existing literature on the effect of germination and/or fermentation of cereal grains on their nutritive quality and functional properties as affected by processing techniques and conditions. In addition some of cereal based fermented products and the major micro organisms involved are tabulated under Table 1.

Nutritional changes

Many biochemical changes occur during germinating or malting, which affect product properties such as structure, bioactivity, flavour, stability and digestibility (Heinio¨ et al., 2003; Katina et al., 2004, Katina, Liukkonen et al., 2007; Salmenkallio- Marttila et al., 2001). Germination triggers the enzymatic activity of sprouting seeds, leading to the breakdown of proteins, carbohydrates and lipids into simpler forms (Nout and Ngoddy, 1997) and also activates proteases which are active in degrading proteins, thereby increasing nutrient bioavailability (Taylor et al., 1985). Hydrolytic enzymes are activated and they decompose starch, non- starch polysaccharides and proteins, which leads to the increase of oligosaccharides, and aminoacids in barley (Rimsten et al., 2003), wheat (Yang et al., 2001), oat (Mikola et al., 2001) and rice (Manna et al., 1995).

Protiens

Wu (1983) observed that, during germination oat seed proteins were degraded to increase the soluble protein content, so that oat protein properties were improved without any chemical modifications being required. After germination and subsequent drying, oat malts

contain free sugars and amino acids (Correia et al., 2008) and can be used as good replacements for barley malt in the brewing industry, as well as ingredients in some convenience foods (Taylor et al., 1998). The chemical composition of malted oat seeds depends on the conditions and the level of germination (Wilhelmson et al., 2001) and its sensory profile depends on the processing parameters of subsequent drying such as drying speed and temperature profile (Heiniö et al., 2001), as well as drying methods. Therefore, the level of germination and drying will affect oat product quality and commercial utilization. The protein concentration of oat seeds slowly increased from 18.98% to 22.02% due to the germination process as reported by Tian et al. (2010). The increase of these proteins might be attributed to the dry weight losses through respiration during malting. Thus, the germinated oat seeds on a unit weight basis would contain more seeds and therefore more nitrogen than the ungerminated material (Dalby and Tsai, 1976). Free amino acid contents increased continuously after steeped and reached 0.37% by the end of germination, which was almost 10-fold as compared with the raw oats as the proteins in the raw oat seeds were degraded and converted into a soluble state after germination (Tian et al., 2010). They further studied the effect of germination on the amino acid profile of germinated oat seeds and reported that the threonine content increased after 72 h and subsequently increased 30% until 144 h of germination. The change of valine was similar with threonine except the amplitude was smaller whereas the contents of isoleucine presented continuously increasing since germinated for 24 h, and reached 2-fold of raw oats at the end. The lysine content of germinated oats was always higher than that of raw oats, and the highest one was 1.22 g/100 g dry weight when germinated for 144 h. Hamad and Fields (1979) reported an increase in available lysine in germinated oat seeds based on

Terahymena pyriformis W. assay. Dalby and Tsai (1976) found an increase in lysine content expressed as percent of dry weight of oat seeds during germination whereas Wu (1983) observed increases in lysine content of more than 10%. The in vitro protein digestibility (IVPD) increased from 33.9% in the ungerminated finger millet seeds to 55.4% at 96 h, an increase of 64%, which could have been caused due to partial solubilization and some proteolysis, which usually occurs during sprouting (Mbithi-Mwikya et al., 2000). This is evidenced by an increase in water-soluble proteins and free amino acids in sprouted seed meal (Buera et al., 1984). This increase in IVPD in finger millet was accompanied by a similar increase in trypsin activity, from 0.10 to 0.26 trypsin units (TU) in the raw and 96 h germinated finger millet, respectively, indicating a decrease in the level of trypsin inhibitor activity (TIA). Tannin content in the raw sample of finger millet was 0.27 mg per 100 g dry matter which decreased steadily and by 60 h it was undetectably low. The decreased tannin activity in this experiment also contributed to the observed increase in IVPD. Tannins have been found to inhibit digestive enzymes and thereby lower digestibility of most nutrients, especially protein (Maxson et al., 1973). The observed reduction in tannin content in germinated seeds has been attributed to the formation of hydrophobic associations of tannins with seed proteins and enzymes and not due to actual loss or degradation of tannins per se (Butler et al., 1984). A decrease in tannin content in sorghum has also been attributed to leaching in the sprouting medium (Veerabhadrappa et al., 1978) and increased activity of poly-phenol oxidase and other catabolic enzymes as observed by Kruger (1976) in wheat. Similarly, Gilay and Field (1981) also reported 1.8 folds increase in thiamine, riboflavin and niacin contents of corn sprouts on germination.

Carbohydrates

The reducing sugar content and the amylase activity of rice were found to increase as germination progressed by Veluppillai et al. (2009). Endogenous amylase activity also increased significantly ($P<0.05$) during germination. The increase in reducing sugar content and amylase activity were linear up to three days. Ayrenor and Ocloo (2007) observed that the reducing sugar content and amylase activity increased significantly ($P<0.05$) during rice germination up to nine days. Mbithi-Mwikya et al. (2000) found a large increase from 3.8 to 35.0 mg maltose per g of dry matter in diastatic activity during the germination period in finger millet. The increase was gradual up to 48 h germination, but became rapid thereafter and is caused by an increase in activity of amylase enzymes developed during germination. Malleshi and Desichakar (1983) found that the maximum development of amylase activity usually occurs after 4 d in millet.

The oat starch content decreased significantly from nearly 60% to nearly 20% as the total amylase in this period reached to six times as much as that in raw oats, moreover, the free sugar content increased about 3-4 folds during malting as reported by Tian et al.(2010).In a study conducted by Arora et al.(2010) on germinated barley flour food mixtures the concentration of total, reducing and non-reducing sugars increased and starch content decreased significantly as compared to non-germinated barlet food mixtures which might be due to enzymatic hydrolysis of starch to simpler sugars during germination.

Minerals

In plants, phytic acid is one of the main inhibitors of the availability of divalent cations such as Fe^{2+}, Ca^{2+} , Mg^{2+} and Zn^{+}. The phosphate groups of phytic acid (inositol

hexakisphosphate) form stable complexes with such cations, thus preventing their bioavailability. The bioavailability of minerals from foods is defined as the proportion of the minerals that can be absorbed and utilized within the body (Larsson et al., 1997; Lestienne, Besancon et al., 2005; Lestienne, Icard-Vernie`re et al., 2005; Lestienne, Mouquet-Rivier et al., 2005). Solubility of minerals, pH of intestinal lumen, dietary factors and residence time at the absorption site influences the bioavailability of minerals (Larsson et al., 1997). Soaking of millet, soya bean, maize, sorghum, and mung bean at 30 °C for 24 h decreased the contents of phytic acid by 4–51% (Lestienne, Besanc¸on et al., 2005; Lestienne Icard-Vernie`re et al., 2005; Lestienne, Mouquet-Rivier et al., 2005), and soaking of sorghum flour (80% extraction) at room temperature for 24 h reduced phytic acid levels by 16–21% (Mahgoub and Elhag, 1998). Soaking of pounded maize for 1 h at room temperature already led to a reduction of phytic acid by 51% (Hotz et al., 2001). Germination of sorghum for 4 d reduced phytic acid by 68–87% (Mahgoub and Elhag, 1998). With longer germination times, HCl-extractability of calcium, iron and zinc in pearl millet was increased by 2–16%, 15–45% and and 12–25%, respectively (Badau et al., 2005).

Mbithi-Mwikya et al. (2000) further observed that sprouting was effective in increasing the HCl extractability of the minerals where calcium and iron extractability increased from 76.9 and 18.1% in the raw finger millet to 90.2 and 37.3%, respectively and extractability of Zn, a trace element, increased from 65.3 to 85.8% at 96 h germination which was due to decrease in phytate content from 0.36 to 0.02 g per 100 g dry matter. Similar findings have been observed in faba beans, where phytate levels decreased by up to 77% during a 10 d germination period (Eskin and Wiebe, 1983). Mbithi-Mwikya et al.(2000) concluded that most of the nutritionally

important changes, namely lowering of bulk density, antinutrient reduction and increase in IVPD, occurred to a significantly large extent at 48 h of germination and germinating the seeds for longer than 48 h would result in further dry matter loss without much improvement in nutritional quality.

Grains contain living cells, and have variable levels of different biocatalytic activities. During malting and fermentation, when grains are hydrated in ambient conditions, both endogenous and added enzymes and micro-organisms start to modify the grain constituents (Katina, Laitila et al., 2007). Germinated rice grains showed an increased content in reducing sugars, total protein contents and vitamins, mainly B vitamin, a very important element required for the growth of *Lb. plantarum* (Ruiz-Barba and Jimenez-Diaz, 1995). From the research done it is evident that germination enhances the quality of nutrients and bioactive compounds of cereals thereby increasing the content in proteins, amino acids, sugars and vitamins, so it has been proposed for the growth of probiotic bacteria (Trachoo et al., 2006). This further provides a natural way to reduce the volume of the material to be transported, to destroy undesirable components, to enhance the nutritive value and appearance of the food, to reduce the energy required for cooking and to make a safer product (Simango, 1997; Ali et al., 2003). Billings (1998), Chavan and Kadam (1989b) also observed that fermentation is one of the oldest and most economical methods of producing and preserving food and leads to a general improvement in the shelf life, texture, taste and aroma of the final product. The common fermented products obtained by cereal fermentation and the major microorganism involved for their productions are listed under table 1.

Lactic acid bacteria have also been shown to increase the content of the B-complex vitamins in fermented foods (Friend and Shahani, 1984). During the process of fermentation, acids and alcohols are produced which inhibit the growth of common pathogenic microbes. As a result of fermentation, pH is lowered, which helps to improve the shelf life of fermented foods (Sindhu and Khetarpaul, 2005). During the fermentation of corn meal the concentrations of available lysine, methionine, and tryptophan increase (Nanson and Field, 1984). In the same way, fermentation significantly improves the protein quality as well as the level of lysine in maize, millet, sorghum, and other cereals (Hamad and Fields, 1979). The levels of folates, free phenolic acids, total phenolic compounds, lignans and alkylresorcinols were increased especially by fermentation of germinated rye, which also resulted in lower pH when compared with native rye flour, the level of folate was increased up to seven-fold and that of free phenolic acids by up to ten-fold after germination and fermentation. Tailored fermentation thus offers a tool to further increase the bioactive potential of wholemeal rye (Katina, Laitila et al., 2007).

Bacterial enzymatic hydrolysis has been shown to enhance the bioavailability of proteins by increasing the production of free amino acids, which can benefit the nutritional status of host particularly if the host has a deficiency in endogenous protease production (Arora et al.,2010). Sourdough fermentation (30 °C for 4 h) led to a reduction of 60% of phytic acid in whole wheat flour with a >30% increase of iron and zinc during in vivo absorption in rats (Lopez et al., 2003; Leenhardt et al., 2005). After 12 h of accelerated fermentation, 60% of phytic acid in sorghum was degraded (Mahgoub and Elhag, 1998) although a complete removal of phytic acid was not reported. Wet processing technologies can help to reduce phytic acid so that solubility of minerals in foods could be increased (Liang et al.,2008). Sourdough

fermentation can influence the nutritional quality by decreasing or increasing levels of compounds, and enhancing or retarding the bioavailability of nutrients. Fermentation of both wheat (Hassan et al., 2008; Salmenkallio-Marttila et al., 2001) and rye (Katina, Laitila et al., 2007) brans has been shown to be an effcient pre-treatment method of bran both in order to improve sensory quality of bran-containing bread, and to degrade antinutritive factors, such as phytic acid, in order to improve mineral bioavailability (Hassan et al., 2008; Lioger et al., 2007). Pre-fermentation of bran with yeast and lactic acid bacteria improved loaf volume and crumb softness during storage (Salmenkallio-Marttila et al., 2001; Katina et al., 2006). Phytic acid is concentrated in the aleurone layers of grains and has a strong chelating capacity. By forming insoluble complexes with dietary cations, it impairs mineral absorption in humans. Phytases are able to dephosphorylate phytate, forming free inorganic phosphate and inositol phosphate esters, which have less capacity to influence mineral solubility and bioavailability (Poutanen et al., 2009).

Fermentation also provides optimum pH conditions for enzymatic degradation of phytate and release minerals such as manganese (which is an important growth factor of LAB), iron, zinc and calcium (Blandino et al., 2003).Arora et al. (2010) found an enhancement of 14% and 11% in thiamine and niacin contents when the food mixture of germinated barley was fermented with probiotic curd. Similarly, Khetarpaul and Chauhan (1989) reported marginal increase in thiamine content of pearl millet by pure culture fermentation of *L. acidophilus*, whereas the concentration of thiamine improved almost 2–3 folds when fermentation was carried out by *Saccharomyces diastaticus* and *Saccharomyces cervisiae*, respectively.According to Sripriya et al. (1997) the total free amino acids increased rapidly by about 4–5 folds during

germination and doubled at 18 h fermentation. Similarly, Elkhalifa et al. (2007) also reported a significant increase in the content of lysine and methionine as a result of fermentation.

The decrease in starch content was from 67 to 59% for Standard variety and from 69 to 63% for Ugandi variety of pearl millet as observed by Hag et al.(2002) which could be attributed to yeast growth, breaking down sugars to ethanol and carbon dioxide (Pederson, 1971). A significant ($P \leq 0.05$) decrease in polyphenols was first observed after 2 h fermentation and further significant ($P \leq 0.05$) reductions at 4, 6, 8, 10, 12 and 14 h for the Standard cultivar. This decrease in total polyphenol content could be due to microbial activity during the fermentation process. The reduction in phytic acid content from 943 to 380 mg /100 g (59.5% reduction) for Standard cultivar and from 1076 to 580 mg/100 g (46.1% reduction) for Ugandi cultivar of pearl millet was reported by Hag et al. (2002). Generally, fermentation is known to cause a greater reduction in phytic acid than other anti-nutrients and this could be due to the low pH of fermented dough, which is considered to be optimum for phytase activity. A significant increase ($P \leq 0.05$) in the IVPD of these two millet cultivars from 72.7 to 83.6% for Standard cultivar and from 70.4 to 81.6% for Ugandi cultivar were caused by fermentation and could be attributed to the partial degradation of complex storage proteins to more simple and soluble products (Chavan et al., 1988); it could also be attributed to the degradation of tannins, polyphenols and phytic acid by microbial enzymes (Hag et al., 2002). Ali et al. (2003) observed an increase in IVPD from 69.0 to 77.5%, after 14 h, for Madelkawya fermented dough and from 76.9 to 86.8%, after 14 h, for Population 1/Shambat fermented dough of pearl millet genotypes. The results indicate that fermentation causes a highly significant ($P \leq 0.05$) improvement in IVPD and an increase in protein availability for both pearl millet cultivars. Khetarpaul and

Chauhan (1990) observed an improved IVPD of pearl millet when subjected to germination and even better when further fermented.

Functional changes

Germination is a well-known biotechnical process for fine-tuning the perceived flavour and for improving the bioactivity of cereal grains and at the same time is also an effective method for adjusting the flavour of cereals, and in particular the subsequent heat treatment process is an important factor for flavour formation (Przybylski and Kaminski, 1983; Heinio, et al., 2001). In germination, alkaline pH promotes the formation of compounds yielding a caramel-like odour. Germinated grains, such as rye, wheat and barley malt, are a good source of free amino acids and sugars, which act as flavour precursors for the odour-active compounds (Heinio et al., 2003). More than 30 volatile compounds occurring in thermally treated rye malt extracts have been identified, including pyrazines, pyrazoles, pyranones, pyridines, pyrimidines, furans, furanones, phenols, esters, aldehydes, ketones and alcohols (Przybylski and Kaminski, 1983). Amongst the functional properties of proteins, solubility is probably the most critical because it affects other properties such as emulsification, foaming and gelation (Kinsella, 1976).

The high proteolytic activity during germination leads to an increase in the protein solubility resulting from hydrolysis of the storage proteins in germinated sorghum flours (Elkhalifa and Bernhardt, 2010). The applicability of germinated flour in food preparations where maximum solubility of proteins is desired looks very promising. The germination process is also one of methods used to improve the functionality of oat seed protein (Kaukovirta-Norja et al., 2004). The decomposition of the high molecular weight polymers during germination leads to the generation of bio-functional substances and the improvement of the organoleptic

qualities due to softening of texture and increase of flavor in barley (Beal and Mottram, 1993), finger millet (Subba Rao and Muralikrishna, 2002), oat (Heinio et al., 2001) and rye (Karppinen et al., 2000).

Problems usually associated with the cooking of brown rice have been resolved and more bio-functional substances have been generated by germination. GABA is a promising compound from the view point of bio-functionality (Kayahara, 2002) and many researchers are using it to develop GABA-rich foods (Kayahara, 2002). Total dietary fiber, total ferulic acid and gamma-aminobutyric acid (GABA) contents of the pre-germinated brown rice were higher than those of ordinary brown rice or polished rice. The wheat bread prepared with 30% of the puffed pre-germinated brown rice contained more GABA, free sugars, such as maltose, compared with the ordinary wheat bread (Ohtsubo et al., 2005). From the viewpoint of supplying GABA-rich foodstuff, germination of brown rice grains is thought to be a valid processing method. Ohtsubo et al. (2005) found that the extrudate of germinated brown rice seems to have bio-functional activities because it contains much more oryzanol (323%), inositol (331%), total ferulic acid (382%) and total dietary fiber (550%) than ordinary polished rice.

Hence, rice can be modified by germination to improve its functionality (Saman et al., 2008). During saccharification process, other enzymes contained in malted rice are also activated to break down starch and release more sugars and oligosaccharides, especially isomalto-oligosaccharides which are potentially prebiotic (Mizubuchi et al., 2005). Prebiotic oligosaccharides can be used as functional food ingredients to provide useful modifications to the physiochemical properties of foods. It has been reported that these oligosaccharides have various physiological functions and improve the intestinal microflora by selective

proliferation of bifidobacteria (Parracho, 2007). They also stimulate mineral absorption, have anticancerogenic potential, and reduce both plasma cholesterol and blood glucose levels (Crittenden and Playne, 1996). Among these sugars, isomalto-oligosaccharides (IMO) have received considerable interest as prebiotic in recent years. IMO have demonstrated their useful in normalizing bowel movement, increasing stool bulk, colon microbial activity, as stimulate growth of Bifidobacterium and Lactobacillus and systemic immunity (Chung and Day,2004;Chen,2001;Hirayama,2002).

Phenolic compounds present in oats contribute to functional and nutritional properties of the grain. Tian et al. (2010) found more than a 4-fold increase in phenolic compound contents was found in the oat seeds after germination for 120 h, and up to 0.90% in dry weight. This could also be attributed to the better extractability of phenolic compounds from the kernel structures after germination. A similar result was observed by Kaukovirta-Norja et al. (2004). Avenanthramides are a group of phenolic compounds with high bioactivities such as anti-inflammatory, antiatherogenic and antioxidants, which exist exclusively in oat seeds (Dimberg et al., 1993). The processes of steeping and germination resulted in increased levels of avenanthramides (Skoglund, 2008).

According to Poutanen et al. (2009) sourdough fermentation may influence gut heath by several mechanisms: 1) modulating dietary fibre complex and its subsequent fermentation pattern, 2) producing exopolysaccharides with prebiotic properties and 3) possibly providing metabolites from LAB fermentation which influence gut microbiota. The use of sourdough in baking of gluten-free bread has been efficient in improving product texture and to delay staling of gluten-free breads (Moore et al., 2006, 2008). Improved textural properties have

been reported for sourdough-made sorghum breads. Sourdough has also been studied for gluten degradation to render it suitable for celiac persons. Germinated cereals or other proteases enable an extensive degradation of proteins in sourdoughs in fermentation protocols that may be used to develop new products for individuals with gluten intolerance (Ga¨nzle et al., 2008).Thus, proteolysis by lactic acid bacteria has been suggested as new tool for food processing for celiac persons (De Angelis et al., 2006; Di Gagno et al., 2008; Rizzello et al., 2007). The use of selected sourdough cultures to eliminate risks of contamination by gluten and to enhance the nutritional properties of gluten-free bread was highlighted by Di Gagno et al. (2008). Formation of oligo- and polysaccharides with prebiotic potential has been also shown by Lactobacillus reuteri LTH5448 and *Weissella cibaria* 10M in sorghum sourdoughs (Schwab et al., 2008).

Elkhalifa and Bernhardt (2010) found a significant increase in the Nitrogen Solubility Index of sorghum grains which might be due to gradual degradation of reserve proteins into amino acids and short peptides caused by increasing the levels of protease enzymes. This leads to an increase in the nutritive value of germinated sorghum by increasing its in vitro protein digestibility; as such partially hydrolysed storage proteins may be more easily available for pepsin attack (Bhise et al., 1988). These results suggest that flour derived from the three days germinated sorghum would be a good gel-forming or firming agent, and would be useful in food systems such as pudding and snacks which require thickening and gelling as proteins are denatured due to the germination and, thus, caused more aggregation. Elkhalifa and Bernhardt(2010) further reported an increase of Water Absorbtion Capacity (WAC) of the sorghum flour on germination which could be attributed to an increase in protein content and

change in the quality of protein upon germination and also breakdown of polysaccharide molecules; hence the sites for interaction with water and holding water would be increased. Germination also significantly ($P < 0.05$) increased the oil absorption capacity (OAC), emulsion activity (EA) and stability (ES) of sorghum flour by 19%, 33% and 21% for the three properties after three days of germination. Akubor and Obiegbuna (1999) also reported an increase in OAC and an improvement of EA and ES of millet flour by germination. The higher oil-binding capacity of sorghum flour suggests that this flour would be useful in formulation of foods where an oil holding property is an important consideration (Elkhalifa et al., 2005). Germination may have caused dissociation and partial unfolding of polypeptides that expose the hydrophobic sites of amino acids, which aids hydrophobic association of the peptide chains with the lipid droplets, so that the net result was that a much greater volume/ surface area of protein was made available, and emulsification capacity was enhanced (Kinsella, 1976; Nir et al., 1994). Similarly, the hypothesis of conversion of oligomeric proteins to simple proteins and/or the synthesis of new proteins during germination may have increased the soluble proteins. Soluble proteins are more surface active and are known to promote oil in- water emulsion (Subba Rao and Srinivasan, 1988). On the other hand, germination may cause partial denaturation and may increase the EA due to increased hydrophobicity giving a positive correlation between emulsifying activity and surface hydrophobicity (Wang and Kinsella, 1976). Several workers have also reported a positive correlation between protein solubility and the EA and ES of the protein (Yasumatsu et al., 1972). The capacity of proteins to enhance the formation and stabilization of emulsion is important for many applications in cakes, coffee whiteners, and frozen desserts. In these products

varying emulsifying and stabilizing capacities are required because of different compositions and stresses to which these products are subjected (Elkhalifa et al., 2005).

Owing to a large increase in the surface area in the liquid/air interphase, proteins denature and aggregate during whipping. This property is important for flour used in many leavening food products such as baked goods, cakes and biscuits (Belitz and Grosch, 1999). The ungerminated sorghum grain flour did not show any foaming capacity (FC), which was also reported by Elkhalifa et al. (2005) whereas germinating sorghum for more than one day shows some foaming capacity and the value increased with increasing germination time until it reached its maximum value (11.5%) at the end of germination period. This may be due to the fact that during germination, the amount of solubilised proteins increased, resulting in improved FC. Germination also improves the foaming stability (FS) of sorghum flour at 60 min. The FS tended to increase with increasing germination time. Germination may have caused surface denaturation of the proteins and reduced the surface tension of the molecules, which gave good foamability. The FC and FS are generally determined by the loss of liquid resulting from destabilization 'leakage' that is measured as a volume decrease. However, conformational changes taking place during germination of proteins may have an effect on foam stability of the cereal flours (Elkhalifa et al., 2005). The capacity of proteins to form stable foams with gas by forming impervious protein films is an important property. FS is important because the usefulness of whipping agents depends on their ability to maintain the whip as long as possible (Lin et al., 1974).

Dordevic et al. (2010) concluded that fermentation affected the bioactive constituent in buckwheat extracts where Total Phenolic Content (TPC) increased from 50.7 mg gallic acid

equivalent (GAE)/g dry extract in native unfermented sample to 53.2 mg GAE/g dry extract in extract fermented with S. *cerevisiae* and 59.4 mg GAE/g dry extract in extract fermented with L. *rhamnosus*. In wheat, TPC varied from 16.2 mg GAE/g dry extract to 18.4 and 20.7 mg GAE/g dry extract, respectively in those three samples, and in barley the respective values were 16.4, 18.5 and 20.1 mg GAE/g dry extract. Rye showed the lowest TPC of 13.3 mg GAE/g dry extract in the unfermented sample, 16.2 mg GAE/g d.e. in extract fermented with S. *cerevisiae* and 18.4 mg GAE/g d.e. in extract fermented with L. *rhamnosus*. These results can be explained by the fact that levels of bioactive compounds can be modified during fermentation by the metabolic activity of microbes. Also fermentation-induced structural break down of cereal cell walls may occur, leading to the liberation and/or synthesis of various bioactive compounds (Katina, Liukkonen et al., 2007). During fermentation, enzymes such as amylases, xylanases and proteases derived from the grain and microbes contribute to the modification of grain composition (Katina, Laitila et al., 2007; Loponen, et al., 2004), and, as mentioned, bound phenolics may be released by enzymatic treatment of samples prior to extraction (Bartolome and Gomez-Cordoves, 1999; Krygier et al., 1982a,b). The type of fermentation clearly determined the degree of modification of the levels of most bioactive compounds in the examined cereals. This might be due to differences in the pH of different fermentations, knowing that optimum pH influences the liberation of cell wall degrading enzymes originating from the cereal kernel (Boskov- Hansen et al., 2002). Other authors have also demonstrated that fermentation has a positive influence on TPC and antioxidative activity of cereals, but the degree of influence depended on microorganism species (Kariluoto et al., 2006).

It has been stated that a moderate decrease of pH to 5.5 during sourdough fermentation is sufficient to reduce phytate content of whole-wheat flour by about 70% by the endogenous phytase present in the flour (Leenhardt et al., 2005). Enzymatic phytate degradation depends on many fermentation parameters: phytase activity present, particle size of the flour, acidity, temperature, time and water content (Harinder et al., 1998; De Angelis et al., 2003). Sourdough fermentation was shown to be effective in solubilising minerals in whole-wheat flours, but to be less effective with bran. Calcium and iron solubilisation during fermentation was effective in finely milled bran particle size, whereas no solubilisation was detected in coarse bran (Lioger et al., 2007) Lopez et al. (2001) showed that pre-fermentation of bran with lactic acid bacteria increased phytate breakdown (up to 90%) and increased magnesium and phosphorus solubility. Absorption of zinc, magnesium, and iron was also higher in rats fed sourdough baked bread (Lopez et al., 2003).Yeast fermentation has repeatedly been shown to increase the folate content in the baking process of both wheat (Kariluoto et al., 2004) and rye (Liukkonen et al., 2003; Kariluoto et al., 2004, 2006; Katina, Laitila et al., 2007). In rye fermentation the levels of folates more than doubled (Liukkonen et al., 2003). Kariluoto et al. (2006) compared the ability of different yeasts and lactic acid bacteria to effect the folate content in a rye sourdough, and concluded that the effects of sourdough bacteria are minimal, but the synthesis of folate by yeast can increase the content over three-fold in the best case.

In the recent work of Lopez et al. (2001), the influence of yeast fermentation, and sourdough fermentation without and with yeast, were compared on degradation of phytic acid. Their results show that both types of sourdough fermentation reduce phytic acid content up to 62%, whereas conventional yeast fermentation reduced it only by 38%. Furthermore,

acidification formed during sourdough fermentation also increased magnesium and phosphorus solubility with 20–30%. This effect was even more pronounced if the bran fraction of wheat (rich in phytic acid) was fermented with lactic acid bacteria; the percentage of phytic acid breakdown was near 90%, whereas 40% of phytate was remained in traditional French bread (Lopez et al., 2001).

The major carbohydrate sources in a western diet contain rapidly digestible starch. Consequently, many common starchy foods like bakery goods, breakfast cereals, potato products and snacks produce high glycemic responses (Poutanen et al., 2009). There are strong indications that the large amounts of rapidly available glucose derived from starch and free sugars in the modern diet (foods with high glycemic index, GI, and high insulin index, II) lead to periodic elevated plasma glucose and insulin concentrations that are detrimental to health (Barclay et al., 2008). The fermentation of wheat and rye flour matrix with lactic acid bacteria (sourdough process) has been shown to lower GI of wholemeal barley bread (Liljeberg et al., 1995; O¨ stman, 2003) and wheat bread (De Angelis et al., 2006; Maioli et al., 2008), and insulin index (II) of rye breads with varying fibre content (Juntunen et al., 2003). Several mechanisms have been proposed for the ability of sourdough processing to reduce starch digestibility. The effect is assumed to be mainly due to formation of organic acids, especially lactic acid, during fermentation. The physiological mechanisms for the acute effects of acids appear to vary; whereas lactic acid lowers the rate of starch digestion in bread (Liljeberg et al., 1995), acetic and propionic acids appear instead to prolong the gastric emptying rate (Liljeberg and Bjo¨rck, 1998). Chemical changes taking place during sourdough fermentation have been postulated to diminish the degree of starch gelatinisation (O¨stman,

2003) which would partly explain lower digestibility of sourdough fermented cereal foods. Furthermore, recent results demonstrate that sourdough fermentation increases the amount of free phenolic compounds (Katina, Laitila et al., 2007), which may also have an impact on lowering the GI/II (Solomon and Blannin, 2007).

Sourdough fermentation has been reported to increase folate content (Kariluoto et al., 2004; Liukkonen et al., 2003), decrease tocopherol and tocotrienol content (Liukkonen et al., 2003; Wennemark and Jaegerstad, 1992), and decrease or increase thiamin content depending on the process (Ternes and Freund, 1988). The presence of yeast seems to favour formation of folates (Kariluoto et al., 2004) and thiamin (Ternes and Freund, 1988). Formation of acidity can both increase levels of bioactive compounds (such as total amount of phenolic compounds) or decrease levels of some compounds (such as thiamin, ferulic acid dehydrodimers, tocopherols and tocotrienols) (Boskov-Hansen et al., 2002; Liukkonen et al., 2003; Ternes and Freund, 1988).

Significant levels of antioxidants have been detected in cereals and cereal-based products (Baublis et al., 2000; Emmons et al., 1999). Cereals also contain a wide range of chemical classes with antioxidant activity (Adom and Liu, 2002). They are rich in phenolic acids and saponins, while phytoestrogens and flavonoids are present in small quantities (Senter et al., 1983). Wheat extracts have shown potential antioxidant properties as wheat phenolics appear to serve as powerful antioxidants through radical scavenging and/or metal chelation (Liyana-Pathirana et al., 2006; Liyana-Pathirana and Shahidi, 2006), while barley contains substantial amounts of phenolic anti-oxidants that effectively s cavenge peroxyl, DPPH, and hydroxyl radicals, and effectively control oxidation of LDL cholesterol, thereby

having a great potential in the development of nutraceuticals rich in antioxidants (Madhujith and Shahidi, 2006, 2007). It has been suggested that antioxidants may contribute to the health benefits of cereal-based foods by reducing the incidence of aging-related chronic diseases including heart diseases and some types of cancer (Miller et al., 2000). Cereals are known to contain certain amount of antinutritive components, such as salts of phytic acid (myoinositol hexakisphosphates, phytates), which are not very soluble and of very limited digestibility (Guenter, 1997) as well as hemicelluloses that are associated with cellulose and pectic substances and comprise several nonstarch, noncellulosic polysaccharides, including xylans (arabinoxylans and 4-0-methylglucuronoxylans), galactomannans, glucomannans, ß-D-glucans (3- and 4-linked), ß-D-glucan-callose (3-linked), and xyloglucans (4-linked ß-D -glucans with attached side chains) (Chesson, 1987). The ß-glucans and arabinoxylans have been recognized as antinutritive factors in cereals (Bedford, 1995). Throughout history, fermentation has been used to improve product properties. Previous studies have shown that microorganisms start to modify plant constituents during fermentation (Katina, Liukkonen et al., 2007). Dordevic et al. (2010) found that fermentation with L. *rhamnosus* had a positive influence on DPPH inhibitory effect in cereals. For buckwheat, scavenging effect of the DPPH radical increased from 82.5% in the unfermented sample to 86.0% in the sample fermented with L. *rhamnosus,* leading to IC_{50} values of 76.7 and 63.4 µg/ml, respectively. Similar increase in scavenging of the DPPH radical after fermentations with L. *rhamnosus* was also noticed in rye (45.0% and 50.4%, respectively), barley (36.6% and 42.9%, respectively) and wheat (31.0% and 35.9%, respectively).

Sourdough baking is also consistently shown to deliver breads with slow starch digestibility and hence low glycemic responses, and has shown promise in improving texture of gluten-free bread for celiac patients (Poutanen et al., 2009).

Fermentation has been shown to increase the antioxidativity (DPPH radical scavenging activity) in the methanol extracted fraction of rye sourdough, concurrently with increased levels of easily extractable phenolic compounds (Liukkonen et al., 2003).Fermentation of rye bran with yeast was also shown to increase the level of free ferulic acid (Katina, Laitila et al., 2007). The antioxidant capacity of traditional rye breads baked with sourdough has been shown to be clearly higher than of commonwhite wheat bread, the highest values reported for breads made with wholemeal our (Michalska et al., 2007; Martinez-Villaluenga et al., 2009). Very recently, it was shown that wheat bran bioprocessed with yeast fermentation in combination with cell wall hydrolytic enzymes increased the in vitro bioaccessibility of phenolic compounds as well as the colonic end metabolite 3-phenylpropionic in breads (Mateo et al., 2009a).

In wheat bran, ferulic acid is the most abundant phenolic compound. Ferulic acid is a structural component in cell walls, cross-linking cell wall polysaccharides. Since most of ferulic acid is covalently bound to the cell wall structures, its bioavailability in physiological conditions is suggested to be low. Recent results (Mateo et al., 2009b; Napolitano et al., 2009) show that bioavailability of ferulic acid can be increased by processing of cereal bran and fibre with fermentation and enzyme treatments. We have also shown that the release of dietary fibre associated lignans and phenolic acids together with other phytochemicals of the

aleurone layer of the rye grain may be modulated by fermentation (Katina, Laitila et al., 2007; Katina, Liukkonen et al., 2007).

Conclusions

The nutritional and sensorial properties of cereals and psuedocereals can be enhanced by their germination and fermentation which leads to improved product properties by changing increased nutritional value and better digestibility of the grains making them better food material than the raw grains. Germination and fermentation of cereal grains can enhance the level of many bioactive compounds, aid in suppression of hazardous microorganisms, improve food safety, texture improvement etc. and so have a huge growth potential for the food industry and may be explored by the development of new ingredients, reengineer processes and products. With the increased urbanization consumers demand convenience foods of a consistent quality so traditional processing systems will have to adapt accordingly where the major challenge in fermenting cereal grains lie in combining good sensory qualities with increased nutritional and therapeutic values. Moreover, up gradation of the production of cereal fermented foods to the industrial level demands for the identification and isolations of the microorganism involved, improvement in the process controls, genetic improvement in the microorganisms involved for maximizing he desirable quality attribute in the food.

The future viability and the success of these fermented cereal products depends on their consumer acceptance who must be convinced f their benefits so attention should be paid that the traditional positive attitude associated with the germinated and fermented foods is not compromised by these biotechnological developments.

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Table 1:Major cereals based fermented foods and the micro-organisms involved

S. No.	Product	Main Cereal	Microorganisms involved	Outcome of fermentation	References
1.	Mawe	Maize(*Zea mays*)	*Lactobacillus fermentum, Lb. cellobiosus, Lb. brevis, Lb. curvatus, Lb. buchneri, Weissella confusa, Candida krusei, Candida kefyr, Candida glabrata, Saccharomyces cerevisiae*	formation of acidity, flavour, and enhancement of digestibility	Hounhouigan et al., 1994 Hounhouigan et al., 1999
2.	Kenkey	Maize(*Zea mays*)	*Lactobacillus fermentum, C. krusei (Issatchenkia orientalis)* and *S. cerevisiae* Lb. casei, Lb. lactis, Lb. plantarum, Lb. brevis, Lb. acidophilus, Lb. fermentum, Lb. casei,	level of available lysine increased from 1.3 in maize kernels to 3.3 g per 16 g nitrogen in ready-to-eat kenkey; flavour compounds (2,3-butanediol, butanoic acid, lactic acid, 3-methylbutanoic acid, octanoic acid, 2-phenylethanol, and propanoic acid) are formed	Jespersen et al., 1994 Nche et al., 1995 Blandino et al 2003 Olsen et al. (1995), Olasupo et al. (1997)
3.	Tchoukoutou	Sorghum(*Sorghum bicolor,Sorghum vulgare*)	*S. cerevisiae* and lactic acid bacteria.	solubility of iron in raw sorghum (3% of total Fe) was increased to approx 20% of total Fe in tchoukoutou protein with a high digestibility	Kayode et al., 2007 Nout, 1987.
4.	Uji	Maize(*Zea mays*) Sorghum(*Sorghum bicolor,Sorghum vulgare*), finger	Lactobacillus plantarum, Lb. fermentum, Lb. cellobiosus and Lb. buchneri, Pediococcus acidilactici and Pc. Pentosaceus,L. mesenteroids	formation of taste and flavour principles, liquefying the starch gel,	(Mbugua, 1985), (Mbugua, 1991). Lee,1997;Onyango et al. (2003, 2004)

		millet			
5.	Jiu	Sorghum and a mixture of wheat, barley and peas (‘‘daqu’’)	(Rhizopus, Mucor, Aspergillus spp.) bacteria (acetic acid bacteria, lactic acid bacteria, bacilli and yeasts (Saccharomyces, Candida, Hansenula spp.)	Source of energy, stimulates the digestive system	(Zhang et al., 2007),) (Wang et al., 2008)
6.	Ben-Saalga	Pearl millet (Pennisetum glaucum	The lactic acid bacteria in the natural fermentation include Lb. fermentum, Lb. plantarum and Pediococcus pentosaceus as majority organisms	Antinutritional components of pearl millet, e.g., phytate was found to be degraded on average from 0.46 to 0.22 g per 100 g dry matter, i.e. by more than 50% in commercial Ben- Saalga. Increase in dietary uptake of proteins and minerals	(Sifer et al., 2005). (Mouquet et al., 2008) (Lestienne et al., 2005). Tou et al. (2006)
7.	Jnard	Finger millet (Eleusine coracana).	Amylomyces rouxii, Rhizopus oryzae, Endomycopsis fibuligera, S. cerevisiae, Enterococcus faecalis, P. pentosaceus and others		(Tamang et al., 1988) (Hesseltine and Ray, 1988)
8.	Idli	Rice (Oryza sativa), Black gram (Phaseolus mungo)	Leuconostoc mesenteroides, Lb. fermentum, Ent. faecalis,Pc. dextrinicus and yeasts especially Sacch. cerevisiae, Debaryomyces hansenii, Pichia anomala and Trichosporon pullulans.Geotrichum candidum, Torulopsis holmii, Torulopsis candida and Trichosporon pullulans	leavening of the batter and flavour formation, starch degradation and gas formation, as well as to the accumulation of vitamin B and free amino acids increase of all essential amino acids and in the reduction of antinutrients (such as phytic acid), enzyme inhibitors and flatus sugars	(Nout et al., 2007;Nout 2009 Blandino et al 2003 (Chavan & Kadam, 1989a; Shortt, 1998). (Steinkraus et al., 1983). Soni and Sandhu (1999); Aidoo et al. (2006); Nout et al. (in press) Balasubramanian and Viswanathan (2007)

					Farnworth (2005)
9.	Mifen	Rice (Oryza sativa)	Lactobacillus, Leuconostoc, Pediococcus, Streptococcus, Enterococcus and Aerococcus spp. and the yeasts S. cerevisiae, Candida rugosa, and Candida tropicalis	protection against microbial spoilage, as well as the modification of the amorphous region of the starch granules which facilitates their gelatinization during cooking. better eating (chewing) qualities	(Lu et al., 2005).
10.	Kishk (Fugush)	Wheat(bulgur)	Lactobacillus plantarum, Lactobacillus casei and Lactobacillus brevis, Bacillus subtilis and yeasts, *S. cerevisiae*	excellent preservation quality, richer in B vitamins	(Beuchat, 1983; Chavan & Kadam, 1989);Tamime and McNulty (1999)
11.	Ogi	Maize(*Zea mays*)	Lb. plantarum, Lb. fermentum, Leuc. mesenteroides, and Sacch.cerevisiae		Odunfa and Adeyele (1985), Adeyemi (1993), Ijabadeniyi (2007), Omemu et al. (2007
12.	Boza	Wheat,millet,rye	Boza Lb. plantarum, Lb. brevis, Lb. rhamnosus, Lb. fermentum, Leuc. mesenteroides subsp. dextranium		Hancioglu and Karapinar (1997), Moncheva et al. (2003), Botes et al. (2007), Todorov et al. (2008)