

Ferulic Acid in Cereals – a Review

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Abstract

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Phenolic acids represent the most common form of phenolic compounds in the cereal grain and many other plants. The phytochemical ferulic acid is found in the leaves and seeds of many plants, but especially in cereals. It is the most abundant phenolic acid in common cereals, representing up to 90% of total phenolic compounds. Ferulic acid has been reported to have many physiological functions, including antioxidant, antimicrobial, anti-inflammatory, and anti-cancer activities. It is an antioxidant which neutralises free radicals (superoxide, nitric oxide, and hydroxyl radical) which could cause oxidative damage to cell membranes and DNA. Like many other antioxidants, ferulic acid reduces the level of cholesterol and triglyceride, thereby reducing the risk of heart disease.

Keywords: bioactive compounds; phenolic acid; antioxidant; antimicrobial; whole grain

Grains consist of many phenolic compounds, not having homogeneous dispersion in pieces such as phenolic acids, flavonoids, tannins, and lignans (KANDIL *et al.* 2012). Phenolic compounds are secondary metabolites of plants widely distributed in foods of plant origin. They are involved in defence against ultraviolet radiation or aggression by pathogens (MANACH *et al.* 2004; ROCHA *et al.* 2012). Phenolic acids are the most widespread phenolic compounds in grains, and settle in crusts of piece such as mostly pericarp, testa, and aleurone (KANDIL *et al.* 2012). These substances can accumulate in different plant tissues and cells during ontogenesis and under the influence of environmental factors. Therefore various phenolics can be localised to different parts of the plant (WEIDNER *et al.* 2000).

Phenolic acids are evaluated in two groups: hydroxybenzoic acid derivatives and hydroxycinnamic acid derivatives (KARAMAĆ *et al.* 2005; MATTILA *et al.* 2005). Caffeic acid, chlorogenic acid, sinapic acid, ferulic acid, and *p*-coumaric acid are derivatives of hydroxycinnamic acid. These acids widely occur in bound forms because they are bound to structural compounds of the cell wall (ADOM & LIU 2002; WANG *et al.* 2013). It is informed that approximately 85% of phenolic acids are in the bound form in maize, approximately 75% in wheat and oat, and 62% in rice (ADOM & LIU 2002). Cinnamic acids have been categorised as bioactive ingredients of the diet (KROON & WILLIAMSON 1999; SHAHIDI & CHANDRASEKARA 2010; TEIXERIA *et al.* 2013).

Ferulic acid (Figure 1) is 4-hydroxy-3-methoxycinnamic acid (BOURNE & RICE-EVANS 1998; MATTHEW & ABRAHAM 2004) while ferulic acid accounts for the highest level of hydroxycinnamic acids in grains (SMITH & HARTLEY 1983; WEIDNER *et al.* 1999; COGHE *et al.* 2004; GANI *et al.* 2012; KANDIL *et al.* 2012). Generally, they occur together in the crust of fruits, roots and in crusts of vegetables, and especially in bran fractions of grains (ZHAO & MOGHADASIAN 2008). It is stated that ferulic acid found in dietary strand fractions, especially its free form, has important functions for protecting the human health (GUO & BETA 2013). It is stated that ferulic acid, because of its high antioxidant effect, will lessen many risks of diseases such as cancer and diabetes (SRINIVASAN *et al.* 2007; ANSON *et al.* 2009; ACOSTA-ESTRADA *et al.* 2014).

Ferulic acid can be found free, dimerised or esterified with polysaccharides and proteins in the cell wall (FAZARY & JU 2007). Cereal brans contain significant quantities of ferulic acid and of its oxidatively coupled products (called diferulic acids or ferulic acid dehydrodimers). In addition, the authors also showed

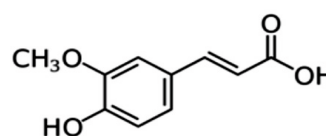


Figure 1. Chemical structure of ferulic acid (PRASAD *et al.* 2007)

Table 1. Ferulic acid in cereal grain botanical fractions ($\mu\text{g/g}$) (NDOLO & BETA 2014)

	B	W	O	M
Whole grain	731	689	367	1 788
Pericarp	2 807	3 517	2 758	18 400
Aleurone	1 329	3 365	748	4 836
Germ	565	823	571	863
Endosperm	119	111	98	169

B – barley; W – wheat; O – oat; M – maize

that diferulic acids formed by microbial esterase digestion of ferulic acid or their reduced dimers can be formed by colonic microbiota hydrogenation reactions of diferulic acids (BELOBRAJDIC & BIRD 2013). Diferulic acids are potent antioxidants and ester-linked to the cell wall polymers and they are found in various forms such as 5-5-, 8-O-4-, 8-5-, and 8-8-diferulic acid (RALPH *et al.* 1994; ANDREASAN *et al.* 2001). These compounds are present in high contents in the rye and wheat bran (BONDIA-PONS *et al.* 2009). The highest diferulic acid contents in cereals were found in popcorn, followed by maize, rye, barley, oats, and wheat (ranging between around 250 and 475 $\mu\text{g/g}$ of flour) (JILEK & BUNZEL 2013). Diferulic acids may play an important role in dietary fibre by influencing the chemical structure of dietary fibre components (BUNZEL *et al.* 2001). Studies have shown that esterified diferulates can be released from cereals by intestinal enzymes, and that free diferulic acids can be absorbed and enter the circulatory system (ANDREASEN *et al.* 2001). In addition, bound antioxidative phenolic acids in cereals may provide a protective effect in the colon upon release by mi-

crobial fermentation (SHAHIDI & CHANDRASEKARA 2013). Also, some studies demonstrated that diferulic acids are more effective antioxidants than ferulic acid (ANDREASEN *et al.* 2001).

Especially, researches on physiological functions of ferulic acid have increases in recent years. Many applications of ferulic acid in the food industry have also been discovered. The aim of this study is to attract attention to effects of processes such as grinding, fermentation, and cooking during the processing of grains.

Contents of ferulic acid in grains

Phenolic acids are in free and bound forms in grains (ADOM & LIU 2002; ARRANZ *et al.* 2010; GANI *et al.* 2012). HOLTEKJOLEN *et al.* (2008) observed that in some cereals such as barley and wheat, phenolic acids are mainly found in the insoluble fraction (bound). Free phenolic acids are found in the outer layer of the pericarp. Bound phenolic acids are esterified to cell walls; acid or base hydrolysis is required to release these bound compounds from the cell walls matrix (HAHN *et al.* 1983; KIM *et al.* 2006; GANI *et al.* 2012). In general, ferulic acid is concentrated in the outer layer of cereal grains and the lowest ferulic acid was determined in the endosperm layer (NDOLO *et al.* 2013). It is seen in Table 2 that in four kinds of grains, the pericarp fraction has the highest level of ferulic acid. Moreover, it is understood that maize, among the used grains in the study, has the highest content of ferulic acid in all fractions. Ferulic acid at the highest level in wheat bran is a structural element of cell wall polysaccharides and most of them are covalently

Table 2. Ferulic acid contents of some cereals and fractions

Grains	FA contents (mg/100 g)	References
Refined maize bran	2610–3300	ZHAO & MOGHADASIAN (2008); ZHAO <i>et al.</i> (2005)
Soft and hard wheat bran	1351–1456	ZHAO & MOGHADASIAN (2008)
Rye bran	280	ZHAO & MOGHADASIAN (2008); MATTILA <i>et al.</i> (2005)
Maize, dehulled kernels	174	ADOM & LIU (2002)
Whole-wheat kernels	64–127	ZHAO & MOGHADASIAN (2008); ADOM & LIU (2002)
Whole-wheat flour	89	MATTILA <i>et al.</i> (2005)
Whole grain rye flour	86	ZHAO & MOGHADASIAN (2008); MATTILA <i>et al.</i> (2005)
Whole brown rice	42	ZHAO & MOGHADASIAN (2008); ADOM & LIU (2002)
Maize flour	38	MATTILA <i>et al.</i> (2005)
Whole oats	25–35	ADOM & LIU (2002)
Whole grain barley flour	25–34	MATTILA <i>et al.</i> (2005)
Oat bran	33	ZHAO & MOGHADASIAN (2008); MATTILA <i>et al.</i> (2005)

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bound with the structures of the cell wall (SINGH *et al.* 2013). It is stated that the quantity of free ferulic acid in grains is 0.1–0.5%, most of it bound with polysaccharides and sterols (ZHAO & MOGHADASIAN 2008).

Wheat bran is a good source of ferulic acid and ferulic acid in brans is esterified to hemicelluloses of the cell walls. Wheat grain contains approximately 0.8–2 g/kg ferulic acid in dry matter and this corresponds to 90% of total polyphenols in wheat. For this reason, it is informed that ferulic acid will be used as a marker of wheat antioxidants. As for ferulic acid contents, grains can be ranked as maize, wheat, oat, and rice (GANI *et al.* 2012). Among the grain brans, maize bran contains ferulic acid at the highest level. Wheat bran has more ferulic acid than rye and oat bran (Table 2).

Effect of fermentation, germination, and grinding

The free ferulic acid quantity in grains is low but during the processes of fermentation, germination, and cooking, it turns from the bound form into the free form, being healthier (SINGH *et al.* 2013). While it is stated that germination in grains will affect ferulic acids differently, the germination process will also change the contents of ferulic acid (HÜBNER & ARENDT 2013). YANG *et al.* (2001) observed that after the first stage, i.e. wheat has germinated, there are no changes in ferulic acid contents or there is no limited reduction but in the processing stage of germination, there is an important increase in the ferulic acid quantity.

It is known that fermentation and germination cause an increase in some components. Recent results (NAPOLITANO *et al.* 2009) have shown that bioavailability of ferulic acid can be increased by the processing of cereal bran and fibre with fermentation and enzyme treatments during food production. MOORE *et al.* (2009) has determined a 75–130% increase in the free ferulic acid content in pizza dough during the 48-h fermentation period. The changes in ferulic acid composition during dough fermentation observed in this study could potentially be a result of enzymatic hydrolysis of insoluble bound or soluble conjugated ferulic acid by enzymes produced from yeast or other microorganisms and enzymes present in the dough. Moreover, they obtained the same results in yeast fermentation of rye bran (KATINA *et al.* 2007).

It is implied that grinding affects the antioxidant capacity of bioactive components in grains (KTENIOU-DAKI *et al.* 2014). FINOCCHIOARO *et al.* (2007) stated

that grinding caused the total antioxidant reduction in red and white rice and this reduction can amount to 51–87% depending on the degree of grinding. In addition, they observed that grinding also caused a reduction in ferulic and sinapic acid.

Effect of cooking

Complex physico-chemical changes can occur during the food process. Antioxidant features of food components can be affected during the process depending on practiced process (KALT 2005; MOORE *et al.* 2009). It is known that thermal processes such as cooking will cause changes in the chemical composition of cereal products. Cooking results in an increase in free ferulic acid quantity and in a reduction in bound ferulic acid quantity. It is thought that the reason for an increase in free ferulic acid quantity is that some parts of bound ferulic acid in dough will be in the free form due to the effect of cooking conditions (MOORE *et al.* 2009; ABDEL-AAL & RABALSKI 2013).

Temperature is one of the most important factors affecting the antioxidant activity, and generally it causes a reduction in antioxidant activity. MARINOVA & YANISHLIEVA (1992) observed that ferulic acid antioxidant activity at 25–100 centigrade did not change in purified lard triacylglycerols. Consequently, food processing, such as thermal processing, fermentation, and freezing, contributes to the release of bound phenolic acids (LIU 2007).

Effects of ferulic acid on health

Human body is sensitive to free radicals and reactive oxygen species causing serious diseases such as atherosclerosis and cancer (YOUNG & WOODSIDE 2001; OU & KWOK 2004). Free radicals in human body are affected by internal and external factors of production. It is stated that superoxide and hydroxyl, causing many diseases, will be produced in body. It is mentioned that superoxide sugars, thiol groups, and adrenaline molecules will be produced by oxygen (OU & KWOK 2004).

It is expressed that phenolic acids in commonly consumed grains are antioxidant components. Phenolic acids have an effect in methyl linoleate oxidation for stopping, free radicals for scavenging, and human LDL cholesterol oxidation for stopping (ABDEL-AAL & RABALSKI 2013).

The protective effects of whole grain cereals against heart disease and certain cancers may be due to the antioxidant effects of phenolics (PRICE *et al.* 2008). Phenolic compounds, especially phenolic acids, are the main antioxidant contributors in wholegrain products (KIM *et al.* 2007; VERMA *et al.* 2009; ABDEL-AAL & RABALSKI 2013). Ferulic acid has quite a high antioxidant effect (GRAF 1992; RICE-EVANS *et al.* 1996; KERN *et al.* 2003; LIN *et al.* 2005; PRICE *et al.* 2008; ITAGAKI *et al.* 2009; RÉBLOVÁ 2012) and it is stated that because of this effect, it has been used as a food additive for preventing oxidation in Japan (ITAGAKI *et al.* 2009).

Ferulic acid with high antioxidant effect has a high radical scavenger effect for free radicals such as hydrogen peroxide, superoxide, hydroxyl radical, and nitrogen dioxide. It scavenges 92.5% of hydroxyl radicals in 250 mg/l concentration (OU & KWOK 2004). It is stated that hydroxycinnamic acid in the colon is an ester with cell wall polysaccharides but it can be in the free form by the effect of esterase originating from bacteria. These acids can be both absorbed and changed into other components by bacteria in the colon. 95% of total feruloyl groups in the body pass in the free form in the colon, they have an important role for protecting against the cancer by means of antimutagenic effect (KROON *et al.* 1997; FERGUSAN *et al.* 2003). MORI *et al.* (1999) studied the effects of ferulic acid on oral cancer in rats by feeding ferulic acid in the diet at a dose of 0.5 g/kg after exposure to 4-nitroquinoline-1-oxide for 5 weeks in drinking water at a dose of 0.02 g/kg. The results from this study suggest that ferulic acid has chemopreventive activity on oral cancer. In addition, it is stated they will have an important role in the body for the defence system for stopping the form of *N*-nitroso components of caffeic and ferulic acid (KUENZIG *et al.* 1984). The nitrogen dioxide radical is known to be a toxic agent produced in the metabolism of nitrates and nitrites. ZHANG *et al.* (1998) showed that hydroxycinnamic acid derivatives, including ferulic acid, sinapic acid, and caffeic acid, scavenged nitrogen dioxide radicals.

Antimicrobial effect

Ferulic acid has quite a common antimicrobial effect, it has an effect against Gram-negative, Gram-positive bacteria, and yeasts (JEONG *et al.* 2000; TSOU *et al.* 2000). It shows a strong inhibitory effect against the

Escherichia coli, *Klebsiella pneumoniae*, *Enterobacter aerogenes*, *Citrobacter koseri*, *Pseudomonas aeruginosa*, *Helicobacter pylori*, and *Shigella sonnei*, having an effect on the human gastrointestinal microflora (LO & CHUNG 1999; OU & KWOK 2004). It is already present in the composition of anti-inflammatory drugs (JEONG *et al.* 2000). In addition, it is emphasised that ferulic acid has shown antibacterial activity against *Bacillus subtilis* and *Streptococcus pneumonia* (MATHEW & ABRAHAM 2004). It is accentuated that ferulic acid has the strongest antifungal effect among 12 phenolic acids against *Sclerotinia sclerotiorum*, *Fusarium oxysporum*, *Alternaria sp.*, *Botrytis cinerea*, and *Penicillium digitatum* (OU & KWOK 2004).

In studies involving the analysis of plant phenolic acids, these acids are released by alkali treatment and the hydrolysates are acidified. Then these acids are extracted with a suitable organic solvent at low pH. The most commonly used solvents are methanol, ethanol, acetone, ethyl acetate, and their combinations (DAI & MUMPER 2010).

Ferulic acid is generally determined by various chromatographic methods. To determine the amount of ferulic acid it is possible to use high-performance liquid chromatography (HPLC) (KOVÁČOVÁ & MALINOVÁ 2007; LAOKULDILOK *et al.* 2011), thin-layer chromatography (TLC) (SHARMA *et al.* 1998), high-performance thin layer chromatography (HPTLC) (SHARMA *et al.* 2007), capillary tube electrophoresis (SHARMA *et al.* 2007; ATURKI *et al.* 2008), and colorimetry (GARCIA *et al.* 2002; TEE-NGAM *et al.* 2013). HPLC currently represents the most popular technique for analysis of phenolic compounds. HPTLC is also proposed for analysis of ferulic acid. It is stated that this method is useful in both qualitative and quantitative analysis for routine assays in pharmaceutical and food industries within acceptable limits (HINGSE *et al.* 2014).

Conclusion

Ferulic acid, reducing the risk of serious diseases such as diabetes, cholesterol, heart diseases, and cancer, is a useful phenolic acid for the human health. It is both a good antioxidant and a good antimicrobial, therefore nowadays it is a natural alternative instead of synthetic additives. Like many bioactive components, ferulic acid has a higher level in the outer layers of the in grains, therefore the consumption of whole grain and its production, with whole flour or bran, increases their importance in terms of healthy diet.

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