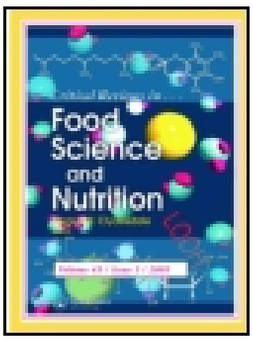


Taylor & Francis
Taylor & Francis Group

Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: http://www.tandfonline.com/loi/bfsn20

Phenolic acids in cereal grain: occurrence, biosynthesis, metabolism and role in living organisms

Kinga Stuper-Szablewska & Juliusz Perkowski

To cite this article: Kinga Stuper-Szablewska & Juliusz Perkowski (2017): Phenolic acids in cereal grain: occurrence, biosynthesis, metabolism and role in living organisms, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2017.1387096

To link to this article: http://dx.doi.org/10.1080/10408398.2017.1387096

PHENOLIC ACIDS IN CEREAL GRAIN: OCCURRENCE, BIOSYNTHESIS, METABOLISM AND ROLE IN LIVING ORGANISMS

Kinga Stuper-Szablewska, Juliusz Perkowski

Department of Chemistry, Poznan University of Life Sciences, Wojska Polskiego 75, 60-625 Poznan, Poland

Corresponding author: kstuper@up.poznan.pl

ABSTRACT

Studies on plant metabolism, including those on cereals, increasingly focus on plant phenolic compounds, e.g. phenolic acids and flavonoids. The aim of this study was to present a comprehensive picture of major phenolic acids in grain, starting from their biosynthesis, their occurrence and finally their role in the vegetation of cereals. It is clearly connected with the polygenic plant resistance to pathogens, particularly toxin-forming fungi. Other crucial aspects include the transformations that take place during the technological processing of grain, their metabolic pathway in the human organism as well as the presentation of the health-promoting effect of grain processing products containing phenolic acids. These compounds are used as precursors of bioactive compounds commonly applied both for therapeutic purposes and in the cosmetics, engineering and food industries. An advantage of phenolic acids is the fact that they may be metabolized by microorganisms found in nature and thus they provide an alternative to the increasing load of man-made chemicals in the environment.

Keywords: phenolic acids, cereals, microscopic fungi, metabolic pathway, human organism

INTRODUCTION

Epidemiological studies, clinical trials and experimental research conducted in recent years have shown that consumption of wholegrain products has a beneficial effect on the human organism (Gibson et al., 2010). In order to obtain products of high health-promoting value it is essential to modify the contents of bioactive compounds at every stage of plant production, starting from growing crops, through all the technological processes to which grain is subjected, to the final product (Fig. 1). Cereal grain contains a wide spectrum of compounds termed bioactive components, characterised by high availability to humans. They are defined as plant origin chemicals, actively improving our overall health and reducing the risk of several civilisation-related diseases (Saxena et al., 2012). Studies have shown a significant correlation between the intake of phytochemicals and a reduced frequency of cardiovascular disease and cancer. As it results from literature data, to date research has focused mainly on phytochemicals and antioxidants from fruit and vegetables. However, the latest literature reports suggest that phytochemicals contained in cereal grain, thanks to its common consumption, has an identical or even greater effect on reducing the risk of many diseases (Liu, 2007; Madhujith and Shahidi, 2007, 2009). This is confirmed by studies indicating that the presence of bioactive components in considerable amounts is not always correlated with their intensive effect. It was shown that the synergistic action of a complex of bioactive compounds is based on a different mechanism than that of its individual components (Gangopadhyay et al., 2015). In the case of cereal grain and its processed products it is crucial that they constitute the foundation of the food pyramid, which is reflected e.g. in their per capita consumption of approx. 100 kg/year. Thus the daily intake of bioactive compounds coming from cereal grain is high and accounts for over 50% of their total

intake. Among phytochemicals identified in cereal grain the most important role is played by polyphenols, of which a special group is composed of phenolic acids. These compounds exhibit first of all a multifaceted antioxidant action. The greatest amounts of phenolic acids are found in the outer part of the aleurone layer, the seed coat and in the germ (Zhou and Yu, 2004). They are most frequently connected with polymers of the cell wall through covalent bonds, which is crucial for the appropriate course of immune mechanisms in plants. Phenolic acids as secondary metabolites are synthesized in plant cells. This synthesis is influenced by stress factors, with aliphatic compounds being primary metabolites, serving as substrates in these processes. This is the first stage in the biosynthesis of phenolic acids during plant vegetation in the field, as presented in Fig. 1. These compounds collected from plants are used by other living organisms in a given environment. Firstly, phenolic acids may be metabolised by cereal pathogens such as fungi from the genus *Fusarium*. In this case the mechanisms have not been fully clarified and information on the subject given in literature is superficial. It pertains mainly to yeast *Candida albicans* (Teodoro et al., 2015). Researchers have suggested that phenolic acids formed in grain exhibit antifungal and antibacterial action (Cowan, 1999). There are also some remarks on their inhibitory effect on fungi from the genus *Fusarium* during biosynthesis of mycotoxins produced by fungi from that genus (Ismaiel et al., 2015). Figure 1 presents the importance of phenolic acids and their activity, whose characteristics are altered during the successive stages of technological processing of cereal materials.

It has been shown that technological processes applied in the case of grain have a significant effect, both on the contents and activity of phenolic acids in the final product. The last stage of the process for phenolic acids is their metabolism and activity in the consumer's body. Acids

transformed during digestion processes into readily accessible forms are transported in the bloodstream to target sites in human cells. In this respect the importance of phenolic acids contained in plants results from their multifaceted effect on the human organism (Middleton et al., 2000). To a considerable extent these effects are connected with the regulatory influence of these compounds on redox processes taking place in living cells, primarily the maintenance or restitution of the redox equilibrium disturbed by the developing oxidative stress (Rizvi at al., 2010). Phenolic acids have a broad spectrum of action, which in view of the availability of cereal grain makes it a global issue, particularly since they are bioactive compounds exhibiting antioxidant properties.

The aim of this study was to present a comprehensive picture of major phenolic acids in grain, starting from their biosynthesis, their occurrence and finally their role in the vegetation of cereals. Other crucial aspects include the transformations that take place during the technological processing of grain, their metabolic pathway in the human organism as well as the presentation of the health-promoting effect of grain processing products containing phenolic acids. In this paper the literature review has been supplemented with the results of investigations conducted by the authors. Since not all processes in the pathway have been comprehensively presented in literature, unpublished data originating from the studies conducted by the authors have also been given.

1. VEGETATION OF CEREALS

1.1. GRAIN

Cereal grain is a rich source of bioactive compounds. These include such antioxidants as phenolic acids, their esters and glycosides, aventramides, flavonoids, phytoestrogens (lignans), phytosterols, tocopherols and tocotrienols, carotenoids, melatonin, inositol phosphates, glutathione, micro- and macroelements, as well as nutrients, antinutrients and non-nutrients contained in kernels (Gui-Fang Deng et al., 2013; Liu 2007). Among these compounds those which exhibit antioxidant properties play a significant role, in the case of cereals these are phenolic acids (hydroxycinnamic: caffeic, ferulic, *p*-coumaric and sinapic acids; hydroxybenzoic: gallic, *p*-hydroxybenzoic, protocatechuic, vanillic and syringic acids). The greatest amounts of these acids are found in the seed coat, the aleurone layer and in embryos, while only trace amounts are found in the starchy endosperm of kernels (Gui-Fang Deng et al., 2012; McKeehen et al., 1999). Among them the dominant compounds include derivatives of cinnamic acids, particularly ferulic, p-coumaric and syringic acids. Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is the main phenolic acid found in cereals, with approx. 75% found in the kernel husk, approx. 15% in the grain endosperm and the rest in the aleurone layer (Balashubashini et al., 2003). Esterified residues of ferulic acid are capable of binding and forming ferulic dimers. It is believed that diferulic bridges provide a natural protective barrier against pathogen attack. Moreover, a relationship was found between wheat kernel hardness and ferulic acid content (Irving et al., 1989). Among commonly grown cereals oat is characterised by

the strongest antioxidant properties. Oat flour contains large amounts of ferulic acid, as well as caffeic, protocatechuic, p-hydroxybenzoic or vanillic acids. In turn, in oat embryos esters of caffeic and ferulic acids are dominant (Rice-Evans, 1999; Slavin et al. 2000; Kähkönen et al. 1999). Rye, wheat and barley grain are other rich sources of phenolic acids. Ferulic acid also predominates in these materials, but they additionally contain p-coumaric and vanillic acids. These acids are found in the form of aglycones or bound with other acids, sugars or polysaccharides (Kahkonen et al. 1999; Baublis et al. 2004, Zieliński 2002). Buckwheat, also called a pseudocereal, contains more phenolic compounds than kernels of the main cereals, while additionally it is a rich source of nutrients, particularly flavonoids such as rutin, quercetin, orientin, isoorientin, vitexin and isovitexin. Among phenolic acids buckwheat contains primarily p-coumaric and gallic acids (Zieliński et al. 2014a, b, Dziedzic et al. 2009). Available data show that the largest numbers of health-promoting acids are found in the seed coat of grain (Stuper-Szablewska et al., 2016). According to various authors, total contents of these compounds expressed in terms of dry matter range from 74 to 93 mg/100g raw material, as presented in Table 1.

Tyrosine and phenylalanine are precursors of most the above-mentioned phenolic acids, as from these 2 compounds cinnamic acid and its hydroxy derivatives are formed as a result of deamination (Fig. 2). In plant tissues phenolic acids are found in the low molecular weight forms (water-soluble in the cytosol or fat-soluble bound with waxes), as well as the esterified or etherified forms bound with cell wall polymers. They are components of lignins and tannins hydrolysed in the form of esters and glycosides. Moreover, forms of phenolic acids bound with other compounds were also identified, e.g. with flavonoids, fatty acids and sterols, or bound with

cell wall polymers. Hydroxycinnamic acids are found in tissues of cereals in ester combinations with hydroxycitric (Kumar et al., 2014), gluconic (Lambert, 2013) acids as well as 4-methoxyaldaric acid as 2-*o*–ferul–4–methoxyaldaric acid. Kernel embryos are rich in fat-soluble esters of caffeic and ferulic acids, whose natural function is connected with antioxidant protection of lipids contained in grain (Slavin et al., 2000). Ferulic, p-coumaric and vanillic acids contained in cereal grain (Zieliński, 2002) are found both in the free form and forms esterified with acids, sugars or polysaccharides (Baublis et al., 2000). Ferulic acid and its dimers are components of the primary cell wall. The monomer binds covalently with mono-, polysaccharides of the cell wall, as well as glycoproteins and cutin (Bourne et al., 1998). Ferulic acid is contained in hemicelluloses (Sen et al., 1994). The role of phenolic acids in plant metabolism has not yet been fully clarified. The capacity to synthesise them is connected with the resistance to infection acquired by plants (Agrios, 1997). Their antioxidant action is known, as it results from the presence of hydroxyl groups in acid molecules, connected with the benzene rings, as a result of which phenolic acids are readily oxidised (Natalia et al., 2013).

One of the main sites of free radical formation in cells is the mitochondrion (the mitochondrial respiratory system). In the course of electron transport the chain protein complexes constantly generate the superoxide anion radical. Reactive oxygen species (ROS) are also formed in the mitochondria during cell oxygen starvation. Hypoxia conditions may cause a feedback mechanism reducing the flow temperature through the respiratory chain and thus leading to increased O_2^{*-} production. Another source of free radicals in the cell involves the microsomal electron transport chain. Mitochondria are also sources of reactive nitrogen species and nitrogen radicals. The formed NO_2 oxidises and reduces many significant biomolecules, including

polyunsaturated fatty acids, mono amino acids or even whole proteins (Bochkov et al., 2010). The function of this enzyme complex is both to synthesise spheroid hormones and to participate in biotransformation reactions, e.g. of pesticides. The phenolic acids investigated in this paper exhibit varied antioxidant activity, dependent mainly on their structure. The antioxidant activity of a compound increases with an increase in the number of hydroxyl groups in the molecule, while additionally the presence of one or two methoxy groups in the ring improves the capacity of the acids to scavenge free radicals. The *ortho* substitution of the electron donor group enhances stability and the antioxidative properties of phenolic acids (Shahidi et al., 1992).

Based on a literature review and investigations conducted by the authors of this study concerning the antioxidant activity of phenolic acids the capacity of these acids to bind free radicals was found to be as follows:

t-cinnamic> gallic>caffeic>benzoic>sinapic>syringic>ferulic> p-coumaric>vanillic> >vanillin>chlorogenic>4-hydroxybenzoic

The high antioxidant activity of cinnamic acid derivatives, such as ferulic acid, results from the presence of a double bond in the propionic chain, which via resonance contributes to stabilisation of the phenoxyl radical. Moreover, the carboxyl group of the acid acts on the phenolic ring due to its negative effect on the capacity of the hydrogen atom of the phenolic ring to electron transfer. Ferulic acid, having one hydroxyl group in the *para* position and one methoxy group in the *meta* position, exhibits a lower antioxidant activity than caffeic acid (two hydroxyl groups in the *meta* and *para* positions) or sinapic acid (two methoxy groups in the *meta* and *para*

positions). p-Coumaric acid has a lower antioxidant activity than ferulic acid due to the presence of only one hydroxyl group.

1.2. THE EFFECT OF MYCOBIOTA ON CONTENTS OF PHENOLIC ACIDS IN CEREAL GRAIN

Factors having a significant effect on the contents of phenolic acids in cereal grain may be divided into biotic and abiotic. Biotic factors include infection caused by pathogenic microorganisms, infestation by saprophytic microorganisms, contact with microbial metabolites, presence of insects as well as other plants. Abiotic factors include mainly temperature (high, cool, freezing), solar radiation (high, low), drought, oxygen deficit, mechanical factors (wind, snow cover, ice cover) and chemical compounds (salinity, toxins, mineral deficiencies). The effect of the above-mentioned biotic and abiotic factors on plants is referred to as stress. It is first manifested in the reduction of photosynthetic activity of plants. Leaf surface area decreases, the degradation of photosynthetic pigments is accelerated, the function of stomata is disturbed and adverse changes take place in the intensity of gas exchange. These changes may lead directly to the deterioration of grain quality. The occurring stresses also induce natural resistance mechanisms in plants (Fernandez-Orozco et al., 2011). As a result, bioactive compounds are produced in plant cells. Among them a significant role is played by antioxidant compounds, while their presence in cereal grain depends significantly on the cereal species, cultivar preferences and plant adaptation to environmental conditions during growth and development. The presence of both saprophytic and pathogenic microorganisms may disturb the natural equilibrium in crops. Oxidative free radical reactions then start to dominate (Lemańska et al.,

2001). Such a condition in plant cells is referred to as oxidative stress, during which plants develop an antioxidant defence mechanism: enzymatic and non-enzymatic. The former is based on antioxidant enzymes (Borkowski et al., 2005). The latter mechanism is based on low molecular weight antioxidants, mainly phenolic compounds, which may delay the initiation phase or disrupt the chain of free radical reactions (Lemańska et al., 2004). The presence of phenolic acids in the raw material, and thus also in the final product, is advantageous thanks to their health-promoting properties. An example of increased plant resistance to adverse environmental conditions may be provided by the induction of systemic acquired resistance (SAR) (Góral et al., 2015). Under natural conditions it is manifested in plants as a result of pathogen activity (Kurasiak-Popowska et al., 2016). One of the mechanisms, which play a considerable role in plant response to stressors, is the antioxidant mechanism. A significant effect of massive infection by *Fusarium* fungi on the induction of a non-enzymatic antioxidant mechanism was observed, which was also confirmed by the recorded total phenolic acid contents and antioxidant activity (Kulik et al., 2017). The presence of phenolic acids is of considerable importance in defence mechanisms during pathogenesis, through inhibition or activation of such enzymes as pectinases, plant amylase, phenoloxidase, succinate dehydrogenase, pancreatic RNase, while in the case of barley - amino acid activating enzymes (Xu et al., 2014). The morphogenetic effect of phenolic acids has also been reported (Li et al., 2010). These compounds have a significant effect on chloroplast activity and as a result – also on the entire process of photosynthesis, e.g. benzoic acid may inhibit the latter process in chloroplasts. Stress invoked by chemical protection is difficult to explain due to the dual action of chemical pesticides, causing changes both in plants and in fungi. Natural origin phenolic acids are

potential alternatives to chemical pesticides used in agriculture. Natural origin substances that are effective fungicides used against *Fusarium oxysporum* include chlorogenic, ferulic and benzoic acids (Barkai-Golan, 2001). In the case of *Sclerotinia sclerotiorum* (causing sclerotinia rot) the action of preparations containing chlorogenic and ferulic acids effectively inhibits infection by this fungus (Martinez et al., 2011). Phenolic acids in terms of their toxicity towards *Fusarium graminearum* are ordered as follows: chlorogenic<p-hydroxybenzoic<caffeic<syringic<p-coumaric<ferulic acid (Atanasova-Penichon et al., 2016). Phenolic acids exhibit significantly higher antifungal activity against *F. culmorum*. Literature studies have shown that phenolic acids prevent the production of toxic secondary metabolites (mycotoxins) by certain fungal strains. Boutiny (2007) observed the inhibitory effect of cinnamic, sinapic, caffeic, p-coumaric, chlorogenic and ferulic acids on the production of type B trichothecenes in the case of *F. graminearum* and *F. culmorum*, whereas derivatives of benzoic acid, except for syringic acid, activated mycotoxin biosynthesis. Massive infection with *Fusarium* fungi stimulated the production of phenolic acids in grain. The concentration of ferulic acid and other derivatives of cinnamic acid is several times greater in grain samples artificially inoculated with *Fusarium* fungi in comparison to naturally infested samples growing under identical cultivation conditions (Kurasiak-Popowska et al., 2016).

2. METABOLIC PATHWAYS OF PHENOLIC ACIDS IN MYCOBIOTA CELLS

The commonly available natural sources of phenolic acids in the course of evolution resulted in the development of several mechanisms for their degradation by microorganisms. This is of particular importance, since these compounds are precursors for many biologically active compounds.

Factors having a significant effect on metabolism of phenolic compounds include a reduction of microbial growth by phenolic compounds, exhibiting a strong biological activity. The white rot fungus *Schizophyllum commune* partly degrades cinnamic, p-coumaric and ferulic acids in two reactions of side chain reduction and cleavage. As a result of a reduction of the carboxyl group in the γ position of the side chain and the hydrogeneration of the double bond between C_α-C_β carbon atoms cinnamic acid is transformed to 3-phenyl–1– propanol (Fig. 3A).

As a result of β–oxidation p-coumaric acid is transformed to the final product, i.e. p-hydroxybenzoic acid, or is reduced to 3(p-hydroxyferulic)–1-propanol (Fig. 3B). Transformation of ferulic acid leads to the formation of vanillin (Fig. 3C). Vanillic acid is formed as a result of its oxidation. In turn, through the action of demethylase this acid is transformed to protocatechuic acid. A similar biotransformation of p-coumaric acid is produced by another fungus *Paecilomyces varioti*.

In the case of gallic acid the first stage consists of the oxidative cleavage with a simultaneous decarboxylation, producing cis-aconitic acid participating in the Krebs cycle (Fig. 4). This process was observed in *Aspergillus Niger*, which also metabolises gallic acid through decarboxylation to pirogallol (Bhat et al., 1998, Zeida et al., 1998). This compound undergoes oxidative cleavage to cis-acontane. In turn, the gallic acid pathway producing pyruvate and oxalacetate has been described in *Aspergillus flavus* (Bhat et al., 1998).

3. TECHNOLOGICAL PROCESSES AND PHENOLIC ACID CONTENTS IN CEREAL MILLING PRODUCTS

The effect of processing on phenolic acid contents and their antioxidant activity is not absolutely clear. A decrease in the contents of natural antioxidants in the product may be associated with an increase in their antioxidant activity, since the formed antioxidants are more readily available. An example may be provided by the decomposition of cell walls under the influence of heating or enzymatic hydrolysis, enhancing the bioavailability of β-carotene. In turn, factors reducing the antioxidant potential in the processing of plant materials include oxidation of the antioxidant, complexing with other food components, enzymatic modifications, increased oxidative potential of the medium and the transition of the antioxidant form into prooxidative (Grajek, 2003). Milling of cereal grain causes a reduction of antioxidant activity in the final product (Slavin, 1999; Wołoch et al., 2003). The effect of the hydrothermal process on the amounts of polyphenols and on the activity of the plant material depends on the plant raw material. For example, Zieliński et al., 2001 observed a 5-fold increase in the contents of the dominant ferulic acid in the cereal material following the extrusion process. Thermal processing of barley and oat markedly reduced the activity of extracts obtained using the buffer solution to eliminate superoxide dismutase (SOD). In turn, the analysis using the $ABTS^{\cdot+}$ free radical showed a slightly greater antioxidant activity of extracts from cereal extrudates in comparison to the input material. Not only processing but also long-term storage of plant raw materials enhances the processes of enzymatic or chemical oxidation of polyphenolic compounds, while the degree of these changes depends on the type of the raw material or environmental factors, e.g. temperature, pH, water activity, time and oxygen level.

For example, it was found that enzymatic oxidation causes a much greater reduction of antioxidant activity than chemical oxidation, while during chemical oxidation of polyphenols temperature has a considerable effect on their activity (Van der Sluis et al., 2001). In turn, partial oxidation of polyphenols may result in their increased capacity to bind free radicals in comparison to unoxidised polyphenols. Such a phenomenon has been observed e.g. in the case of catechin subjected to enzymatic oxidation; however, a greater oxidation state led to the loss of antioxidant activity. Increased capacity to bind free radicals by partially oxidised polyphenols may be explained by their greater capacity to release hydrogen atoms from hydroxyl groups at aromatic rings and/or an increased capacity to maintain unpaired electrons by aromatic rings through delocalization in the shell (Van der Sluis et al., 2001). Antioxidant food components may also react with one another, which leads to changes in antioxidant activity that are difficult to predict, and the applied technological processes may additionally influence the type of these changes. This is connected mainly with redox reactions between antioxidants or antioxidants and lipid oxidation products (Van der Sluis et al., 2001). Technological processes performed on plant origin materials influence contained antioxidants. Some of these processes cause degradation of antioxidant compounds and reduce their contents, while others may increase their levels and availability. In the case of hydrothermal processes a significant role is also played by the resistance of a given compound.

Preliminary processing and milling of cereal grain causes significant losses of polyphenols contained in the outer layers of kernels. As a result, milling products are poorer in these compounds.

Thermal processes affecting grain, including extrusion and drying, increase the amount of phenolic acids in the material by several fold, particularly in the case of ferulic acid. Changes occurring during fermentation and germination also increase the levels of polyphenols in grain.

Storage also has a significant effect on the contents of antioxidant compounds in plant materials. During long-term storage enzymatic and chemical oxidation of these compounds take place, with the rate and intensity of these changes depending on environmental conditions (Gumul et al., 2007; Zieliński et al. 2012). However, as a result of technological processes the content of antioxidants decreases, amounting in light (unroasted) buckwheat groats to 18.8 mg/100g, while in dark (roasted) groats it is approx. 4 mg/100g.

Phenolic acids as bioactive food components are not always desirable in the final product. Technological processes currently used in beer production have been developed among other things to remove phenolic acids causing product clouding; however, this has resulted in reducing its shelf life. This is connected with decreased concentrations of natural antioxidants in beer. Presently conducted studies on the application of ferulic acid in beer production have shown that one active site found in the molecule of this acid is blocked by active proteins causing clouding. In this way the use of ferulic acid improves the quality and health-promoting properties of the final product (Szwajgier and Targoński, 2005).

4. THE ROLE OF PHENOLIC ACIDS IN THE HUMAN ORGANISM

Oxidative stress, manifested in the excessive activity and/or increased concentrations of reactive oxygen species (ROS), i.e. free radicals, hydrogen peroxide, singlet oxygen, etc., as a result of disturbed natural equilibrium between their generation and neutralisation by endogenous antioxidant systems, is considered to be a major pathogenic factor in the etiology of most

civilisation-related diseases (Melo et al., 2011; Hollman et al., 2012). In therapy and prevention of oxidative stress plant origin polyphenols serve the role of exogenous antioxidants, which thanks to diverse redox mechanisms are capable of efficiently supporting the endogenous defence system of the organism (Mladěnka et al., 2010). The discovery of the phenomenon of oxidative stress and its effect on human health produced considerable interest in antioxidants, including plant origin antioxidants, their role in therapy and health protection, potential toxicity, guidelines for possible supplementation, sources, etc.

Polyphenols neutralise free radical attack on vascular walls, protect cholesterol and lipids in the blood against oxidation, as well as reduce intravascular inflammations and limit platelet aggregation. Phenolic acids, particularly ferulic acid, are highly active compounds exhibiting antimutagenic activity (Wargovich et al., 1985). They show strong activity in inhibiting DNA damage, resulting in their anticancer effect. Caffeic acid exhibits a neuroprotective action (Pereira et al., 2012). In the case of diabetics desirable dietary components include phenolic acids such as ferulic and coumaric acids, causing effective reduction of blood glucose level thanks to the enhanced activity of glucokinase, production of glycogen in the liver and increased blood insulin level (Virgili et al., 2000). However, in order to fully utilise the protective effect of polyphenolic compounds it is necessary to maintain a constantly high level of these compounds in the blood with a balanced diet, particularly rich in plant origin products. Phenolic acids exhibit varied biological activity in the human organism. Among other things, they contribute to the scavenging of free radicals, chelation of metal ions, changes in enzyme activity and protein availability. They also protect against photooxidative skin damage, with caffeic acid being more active in this respect than ferulic acid. Epidemiological studies have shown that intake of high

amounts of phenolic acids (40 mg/kg body mass) is connected with a decreased level of γ-glutamyl transpeptidase, which is a biomarker of the early phase of oxidative stress. Phenolic acids show an advantageous synergistic effect with other biologically active compounds contained in the diet. In turn, their metabolites may exhibit lower biological activity, including antioxidant. The availability of phenolic acids depends on the form (free vs. bound), in which they penetrate the alimentary tract and on the location in the plant. Water soluble forms are more readily available and absorbable in the upper section of the digestive tract. Bound forms are available as a result of enzymatic activity of intestinal microflora, taking place in the final section of the gut (Hinneburg 2006). Phenolic acids, not being completely absorbable in the small intestine, may reach the large intestine causing several physiological effects. Due to the high content of chlorogenic acid in plant materials and products its metabolism has been investigated in numerous studies and thus it has been relatively well-described. Following intravenous administration of chlorogenic acid it was found in an unaltered form in the urine. Such a form was not detected after its oral administration. Thus its absorption from the alimentary tract requires hydrolysis to caffeic and quinic acids in the small intestine, or microbial metabolism in the large intestine. In the initial sections of the alimentary tract chlorogenic acid epimerises to a mixture of 3-, 4- and 5-caffeoylquinic acids (Fig. 5). The gastric environment, in which pH is approx. 2, does not lead to its hydrolysis, since it is stable under these conditions. Partial hydrolysis of chlorogenic acid takes place in the small intestine. Esterase was detected both in the intestinal walls and in the lumen. Approximately one third of chlorogenic acid intake is absorbed in the small intestine. The rest reaches the large intestine, where it is metabolised by

the intestinal microflora (three strains of *Echerichia coli*, two strains of *Lactobacillus gasseri* and one strain of *Bifidobacterium lactis*) (Gallardo et al., 2006).

Administration of chlorogenic acid promotes the growth of the above-mentioned bacteria, of which some exhibit probiotic properties. As a result, this acid may be a substance with a potential prebiotic action (Hwang et al., 2006). Caffeic acid, after being released from chlorogenic acid by the small intestine enzymes or esterase of the gut microflora, becomes available and may exhibit biological activity in intestinal walls as well as other tissues and organs, also in the form modified by enzymes, primarily hepatic. Caffeic acid may enter combinations with glucuronic acid, with this reaction being catalysed by UDP-glucuronyl transferase (Lukyanova et al., 2007). Glucuronylation most probably takes place in the liver, but it is also possible in the small and large intestines. Ferulic and isoferulic acids are found in methylated form in blood plasma. A combination of phenolic acids with glucuronic and sulfuric acids reduces their antioxidant properties. Free caffeic acid, which has not been absorbed by intestinal walls, is further modified through the activity of the gut microflora, as a result of which after biohydrogenation dihydrocaffeic (3-(3,4-dihydroxyphenyl)-propionic) acid is formed, while further as a result of dehydroxylation 3-(3-hydroxyphenyl)-propionic and 3-phenylpropionic acids are formed. The two latter acids are absorbed by the large intestine walls and in the liver undergo β-oxidation to benzoic and hydroxybenzoic acids, followed by their glycination. Finally 3-hydroxyhippuric and hippuric acids are formed, which are excreted with the urine. Some amount of chlorogenic acid, absorbed in the upper small intestine, influences the biological effect first of all in the cardiovascular system, while the portion metabolised in the large intestine has an effect primarily on that organ (Madlener et al., 2007). Glucuronides of p-coumaric,

ferulic and icoferulic acids have also been identified in the plasma, while glucuronides of ferulic, isoferulic and vanillic acids were detected in the urine. Ferulic acid in the organism may originate directly from food or may be a metabolic intermediate of caffeic acid. In turn, isoferulic acid is not found in food and originates from the biotransformation of caffeic acid. Approximately 10% of caffeic acid from the hydrolysis of chlorogenic acid is excreted with the urine in unaltered form. Apart from caffeic acid, quinic acid is also formed as a result of chlorogenic acid hydrolysis and it is dehydroxylated and aromatised by the gut microflora. The greatest concentration of chlorogenic acid metabolites in the urine is found within the first four hours after intake. Ferulic acid is introduced with food mainly in the form bound by covalent bonds with insoluble dietary fibre. Considerable amounts (95%) are released through fermentation only in the large intestine, while as little as 5% is released in the stomach and the small intestine. Initially dietary fibre is hydrolysed by enzymes, including xylanases, its molecular mass is reduced, thus promoting the availability of bacterial ferulic acid esterase, which releases ferulic acid. A study by Kroona et al. showed that after deesterification ferulic acid remains in its free form, dissolved in the chyme, where it is further intensively metabolised by the intestinal microflora in processes also involved in the caffeic acid metabolic pathway. Ferulic acid is absorbed after being released, first of all in the stomach and the small intestine, while it is to a limited extent in the large intestine. For this reason the bioavailability of ferulic acid bound with cereal dietary fibre is limited and much lower than that of caffeic acid depsides (Wink 2010). In the plasma it is found mainly in the form of glucuronates or sulfonates at approx. 75%, while it is only 25% in the free form. After methylation in the liver gallic acid penetrates to blood and is excreted with the urine as 3-,4-methoxygallic and 3,4-dimethoxygallic

acids. It has not been clarified whether it is formed in the stomach from acid hydrolysis of the higher polymerised ellagitannins or due to the action of intestinal microflora (Larrosa et al., 2006). According to Konishi et al., 2005, absorption of both gallic acid and epigallocatechine is very limited in relation to that of caffeic acid. Literature data indicate that phenolic acids in the alimentary tract retain their antioxidant activity, although in its lower sections it is smaller. Biological activity is observed for phenolic acid metabolites also in the plasma. They may have a beneficial effect on certain bacterial strains, which participate actively in their metabolism on the intestinal level (Konishi et al., 2006).

Concluding remarks

The need for phenolic acids is high, both on the part of industry and living organisms. These compounds are used as precursors of bioactive compounds commonly applied both for therapeutic purposes and in the cosmetics, engineering and food industries. This demand is likely to accelerate significantly, in view of the attempts to provide products with the highest possible health-promoting properties, as required by consumers. An advantage of phenolic acids is connected with the fact that they do not contribute markedly to the degradation of the natural environment, as they may be metabolized by microorganisms found in nature and thus they provide an alternative to the increasing load of man-made chemicals in the environment.

REFERENCE

1. Adom, K.K., and Liu R.H. (2002). Antioxidant activity of grains. J. Agric. Food Chem. **50**: 6182-6187.
2. Agrios, G.N. (1997). Plant diseases caused by Mollicutes: phytoplasmas and spiroplasmas. In: Plant Pathology, 4th; ed.: G.N. Agrios. New York: Academic Press. 457-470.
3. Atanasova-Penichon, V., Barreau, Ch., and Richard-Forget, F. (2016). Antioxidant Secondary Metabolites in Cereals: Potential Involvement in Resistance to Fusarium and Mycotoxin Accumulation. Front. Microbiol. **7**: 566-572.
4. Balashubashini, S., Rukkumani, R., and Menon V.P. (2003). Protective effect of ferulic acid on hyperlipidemic diabetic rats. Acta Diabet. **40**: 118-122.
5. Barkai-Golan, R. (2001). Postharvest Diseases of Fruits and Vegetables. Development and Control. Elsevier. **6**: 418-423.
6. Baublis, A.J., Clydesdale, F.M., and Decker, E.A. (2000). Antioxidants in wheat-based breakfast cereals. Cer. Foods World. **45**: 71-74.
7. Bhat, T.K., Singh, B., and Sharma, O.P. (1998). Microbial degradation of tannins – A current perspective. Biodegrad. **9**: 343-357.
8. Biesalski, H.K. (2009). Bioactive compounds: Definition and assessment of activity. Nutriti. **25**: 1202-1205.
9. Bochkov, V.N., Oskolkova, O.V., Birukov, K.G., Levonen, A-L., Binder, Ch. and Stockl Ch. (2010). Generation and Biological Activities of Oxidized Phospholipids. Antiox. and Red. Sig.**12**: 1009 – 1059.

10. Borkowski, T, Szumusiak, H, Gliszczyńska-Świgło, A, Rietjens, I.M.C.M., and Tyrakowska B. (2005). Radical scavenging capacity of wine anthocyanins is strongly pH-dependent. J Agric Food Chem. **53**: 5526–5534.
11. Bourne, L.C. and Rice-Evans, C. (1998). Bioavailability of ferulic acid. Biochem. Biophys. Res. Commun. **253**: 222–227.
12. Cao, G., Sofic, E. and Prior R.L. (1996). Antioxidant capacity of tea and common vegetables. J. Agric. Food Chem. **44**: 3426-3431.
13. Cowan, M.M. (1999). Plant Products as Antimicrobial Agents. Clin. Microbiol. Rev. **12**: 564–582.
14. Fernandez-Orozco, R., Roca, M., Gandul-Rojas, B., and GallardoGuerrero, L. (2011). DPPH-scavenging capacity of chloroplastic pigments and phenolic compounds of olive fruits (cv. Arbequina) during ripening. J Food Compos Anal. **24**: 858-864.
15. Gallardo, C., Jimenez, L., and Garcia-Conesa, M.-T. (2006). Hydroxycinnamic acid composition and in vitro antioxidant activity of selected grain fractions. Food Chem. **99**: 455-463.
16. Gangopadhyay, N., Hossain, H., Rai, D.K., and Brunton, N.P. (2015). A review of extraction and analysis of bioactives in oat and barley and scope for use of novel food processing technologies. Molec. **20**: 10884-10909.
17. Gibson, T.M., Ferrucci, L.M, Tangrea, J.A., and Schatzkin, A. (2010). Epidemiological and Clinical Studies of Nutrition, Semin Oncol. **37**: 282–296.

18. Góral, T., Stuper-Szablewska, K., Buśko, M., Boczkowska, M., Walentyn-Góral, D., Wiśniewska, H., and Perkowski J. (2015). Relationship between genetic diversity and Fusarium toxin profile of winter wheat cultivars. Plant Pathol J. **31**: 1-19.

19. Górecka, D., Hęś, M., Szymandera-Buszka, K., and Dziedzic K. (2009). Contents of selected bioactive components in buckwheat groats. Acta Sci Pol Technol Aliment. **8**: 75-83.

20. Grajek, W. (2003). Changes in the antioxidant potential of plant materials in processing and digestion processes. Food. Science. Technology. Quality. **4**: 26-35. (In polish)

21. Gui-Fang, D., Xiang-Rong, X., Ya-Jun, G., En-Qin, X., Sha, L., Shan, W., Feng, Ch., Wen-Hua, L., and Hua-Bin, L. (2012). Determination of antioxidant property and their lipophilic and hydrophilic phenolic contents in cereal grains. J. Funct. Foods. **4**: 906-914.

22. Gui-Fang, D., Xiang-Rong, X., Zhang, Y., Li, D., Ren-You, G., Hua-Bin, L. (2013). Phenolic Compounds and Bioactivities of Pigmented Rice. Crit. Rev. Food Sci. Nutrit. 2013, **53**: 296-306.

23. Gumul, D., Korus, J., and Achremowicz, B. (2007). The influence of extrusion on the content of polyphenols and antioxidant/antiradical activity of rye grains (Secale cereal L.). Acta Sci Pol. **6**: 103–111.

24. Hinneburg, I., Dorman, H.J.D., and Hiltuen R. (2006). Antioxidants activities of extracts from selected culinary herbs and spices. Food Chem. 97: 122-129.

25. Hollman, P.C.H., and Katan M.B. (1997). Absorption, metabolism and health effects of dietary flavonoid in man. Biomed Pharmacol. **51**: 305-310.

26. Hwang, H.J., Park, H.J., Chung, H.J., Min, H.Y., Park, E.J., Hong, J.Y., and Lee, S.K. (2006). Inhibitory effects of caffeic acid phenethyl ester on cancer cell metastasis mediated by the down-regulation of matrix metalloproteinase expression in human HT1080 fibrosarcoma cells. J. Nutrl. Biochem. **5**: 356-362.

27. Irving, D.W., Fulcher, R.G., Bean, M.M. and Saunders, R. M. (1989). Differentiation of wheat based on fluorescence, hardness and protein. Cer. Chem., **66**: 471-477.

28. Ismaiel, A.A., and Papenbrock, J. (2015). Mycotoxins: Producing Fungi and Mechanisms of Phytotoxicity. Agriculture. **5**: 492-537.

29. Kähkönen, M.P., Hopia, A.I., Vuorela, H.J., Rauha, J-P., Pihlaja K., Kujala T.S., and Heinonen M. (1999). Antioxidant activity of plant extracts containing phenolic compounds. J. Agric. Food Chem. **47**: 3954-3962.

30. Kesarwani, A., Chiang, P-Y., and Chen, S-S. (2014). Distribution of phenolic compounds and antioxidative activities of rice kernel and their relationships with agronomic practice. Scien.World J. **2**: 46-52.

31. Konishi, Y., Hitomi ,Y., Yoshida, M., and Yoshioka, E. (2005). Pharmacokinetic study of caffeic and rosmarinic acids in rats after oral administration. J Agric Food Chem. **53**: 4740–4746.

32. Konishi, Y., Zha,o Z., and Shimizu, M. (2006). Phenolic acids are absorbed from the rat stomach with different absorption rates. J Agric Food Chem. **54**: 7539–7543.

33. Kulik, T., Stuper-Szablewska, K., Bilska, K., Buśko, M., Ostrowska-Kołodziejczak, A., Załuski, D., and Perkowski J. (2017). trans-cinnamic and chlorogenic acids affect the secondary metabolic profiles and ergosterol biosynthesis by Fusarium culmorum and F. graminearum sensu stricto. Toxins. **9**: 198-208.

34. Kumar, N., and Pruthi, V. (2014.) Potential applications of ferulic acid from natural sources. Biotech. Reports. **4**: 86-93.

35. Kurasiak-Popowska, D., Stuper-Szablewska, K., Nawracała, J., and Perkowski, J. (2016). Phenolic acid content in wheat grain of different genotypes. UNCUYO. **8**: 1853-8665.

36. Lambert, F., Zucca, J., Ness, F., and Aigle, M. (2013). Production of ferulic acid and coniferyl alcohol byconversion ofeugenolusing a recombinantstrainof Saccharomyces cerevisiae. Flavour Fragr. J. **29**: 14–21.

37. Larrosa, M., Tomás-Barberán F.A., and Espín J.C. (2006). The dietary hydrolysable tannin punicalagin releases ellagic acid that induces apoptosis in human colon adenocarcinoma Caco-2 cells by using the mitochondrial pathway. J. Nutr. Biochem. **17**: 611-625.

38. Lemańska, K., Szymusiak, H., Tyrakowska, B., Zieliński, R., Soffers, A.E.M.F., and Rietjens, I.M.C.M. (2001). The influence of pH on the antioxidant properties and the mechanism of antioxidant action of hydroxyflavones. Free Radic Biol Med. **31**: 869–881.

39. Li, Z.-H., Wang Q., Xiao R., Pan C.-D., and Jiang, D.-A. (2010). Phenolics and Plant Allelopathy. Molec. **15**: 8933-8952.

40. Liu, Q., and Yao, H. (2007). Antioxidant activities of barley seeds extracts. Food Chem. **102**: 732-737.

41. Liu, R.H. (2007). Whole-grain phytochemicals and health. J Cereal Sci. 46: 207-219.
42. Lukyanova, L.D., Storozheva, Z.I., Proshin, A.T. (2007). Corrective effect of flavonoid containing preparation extralife on the development of Parkinson's syndrome. Bull. Exp. Biol. Med. **144**: 42-45.
43. Madhujith, T., and Shahidi, F. (2008). Antioxidant and antiproliferative potential of pearled barley (Hordeun vulgare L). Pharm. Biol. **46**: 88-95.
44. Madhujith, T., and Shahidi ,F. (2009). Antioxidant potential of barley as affected by alkaline hydrolysis and release of insoluble-bound phenolics. Food Chem. **117**: 615-620.
45. Madlener, S., Illmer, C., Horvath, Z., Saiko P., Losert A., Herbacek I., Grusch M., Elford H.L., Krupitza G., and Bernhaus, A. (2007). Gallic acid inhibits ribonucleotide reductase and cyclooxygenases in human HL-60 promyelocytic leukemia cells. Cancer Lett. **245**: 156-162.
46. Martínez, J.A., Valdés, R., Gómez-Bellot, M.J., and Bañón, S. (2011). Effects of índole-3-acetic acid on Botrytis cinerea isolates obtained from potted plants. 63rd International Symposium on Crop Protection (ISCP 2011), Ghent, Belgium.
47. McKeehen, J.D., Busch, R.H., Fulcher, R.G. (1999). Evaluation of wheat (Triticum aestivum L.) phenolic acids during grain development and their contribution to Fusarium resistance. J. Agric. Food Chem. **47**: 1476–1482.
48. Melo, E.A., de Lima, V.L.A.G., Maciel, M.I.S. (2006). Polyphenol, ascorbic acid and total carotenoid contents in common fruits and vegetables. Braz J Food Technol. **9**: 89-94.

49. Middleton, E.Jr., Kandaswami, C., and Theoharides, T.C. (2000). The effects of plant flavonoids on mammalian cells: Implications for inflammation, heart disease, and cancer. Pharmacol. Rev. **52**: 673-751.

50. Mladěnka, P., Zatloukalová, L., Filipský, T., and Hrdina, R. (2010). Cardiovascular effects of flavonoids are not caused only by direct antioxidant activity. Free Rad. Biol. Med. **49**: 963–975.

51. Müller, N., Hempel, M., Philipp, B., and Gross, E.M. (2007). Degradation of gallic acid and hydrolysable polyphenols is constitutively activated in the freshwater plant-associated bacterium Matsuebacter sp. FB25, Aquat. Microb. Ecol. **47**: 83-90.

52. Natalia, N.R., Claire, D., Lullien, P.V., and Valerie, M. (2013). Exposureorreleaseofferulicacid from wheat aleurone: impact on its antioxidant capacity, Food Chem. **141**: 2355–2362.

53. Pereira, E., Barros, L., Martins, A., and Ferreira, I.C.F.R. (2012). Towards chemical and nutritional inventory of Portuguese wild edible mushrooms in different habitats. Food Chem. **130**: 394-403.

54. Rice-Evans, C. (1999). Screening of phenolic and flavonoids for antioxidant activity, antioxidant food supplements in human health. Academic Press. London. **16**: 49-63.

55. Rizvi, S.I., Jha, R., and Pandey, K.B. (2010). Activation of erythrocyte plasma membrane redox system provides a useful method to evaluate antioxidant potential of plant polyphenols. Methods Mol Biol. **594**: 341-348.

56. Saxena, M., Saxena, J., and Pradhan, A. (2012). Flavonoids and phenolic acids as antioxidants in plants and human health. Int. J. Pharm. Sci. Rev. Res.,**16**: 130-134.

57. Sen, A., Bevgvirsou, D., Miller, S.S., Atkinson, J., Fulcher, F.G. and Avvason, J.T. (1994). Distribution and microchemical detection of phenolic acids, flavonoids and phenolic acids amides in maize kernels. J. Agril .Food. Chem. **42**: 1879-1883.

58. Shahidi, F., and Wanasundara, P.K.J.P.D. (1992). Phenolic antioxidants. Crit Rev Food Sci Nutr. **32**: 67– 103.

59. Slavin, J., Marquart, L., and Jakobs, D.Jr. (2000). Consumption of whole-grain food and decreased risk of cancer: proposed mechanisms. Cer. Foods World. **45**: 54-58.

60. Slavin, J.L., Martini, M.C., Jacobs, D.R., and Marquart, L. (1999). Plausible mechanism of protectiveness of whole grains. Am. J. Clin. Nutr. **70**: 459-463.

61. Slavin, J. L., Jacobs, D., and Marquart, L. (2000). Grain processing and nutrition. Crit. Rev. Food Scien. Nutrit. **40**: 309-326.

62. Stuper-Szablewska, K., Kurasiak-Popowska, D., Nawracała, J., and Perkowski J. (2016). Study of metabolite profiles in winter wheat cultivars inducted by Fusarium infection. Cereal Res Com. **44**: 572-584.

63. Szwajgier, D., and Targoński, Z. (2005). Arabinoxylans from malt source of natural antioxidant-ferulic acid and dietary fiber in beer. Food. Science. Technology. Quality. **4**: 27-41. (In polish)

64. Teodoro, G.R., Ellepola, K., Seneviratne, Ch.J., Koga-Ito, C.Y. (2015). Potential Use of Phenolic Acids as Anti-Candida Agents: A Review. Front Microbiol. **6**: 1420-1435.

65. Van der Sluis, A.A., Dekker, M., De Jager, A., Jongen, M.F. (2001). Activity and Concentration of Polyphenolic Antioxidants in Apple: Effect of Cultivar, Harvest Year, and Storage Conditions. J. Agric. Food Chem. **49**: 3606–3613.

66. Virgili, F., Pagana, G., Bourne, L., Rimbach, G., Natella, F., Rice-Evans, C., Packer, L. (2000). Ferulic acid excretion as a marker of consumption of a French maritime pine (*Pinus maritima*) bark extract. Free Rad. Biol. Med. **28**: 1249-1256.

67. Wargovich, M.J., Eng, V.W.S., and Newmark, H.L. (1985). Inhibition by plant phenols on ben- zo(a)pyrene induced nuclear aberrations in mammalian intestinal cells: A rapid in vivo assessment method. Food Chem Toxic. **23**: 47-49.

68. Wink, M. (2010). Biochemistry, physiology and ecological functions of secondary metabolites. In Biochemistry of Plant Secondary Metabolism (second edition), ed. M. Wink, New York: Wiley–Blackwell Publ. 1-17.

69. Wołoch, R., Pisulewski, P. (2003). Influence of technological processes on the antioxidant properties of roasted and burnt populations of barley and oats. Food. Science. Technology. Quality. 2: 42-49. (In polish)

70. Xu, T.-F., Zhao, X.-C., Jiao, Y.-T., Wei, J.-Y., Wang, L., and Xu, Y. (2014). A Pathogenesis Related Protein, VpPR-10.1, from Vitis pseudoreticulata: An Insight of Its Mode of Antifungal Activity. PLoS ONE. **9**: 95102.

71. Zeida, M., Wieser, M., Yoshida, T., Sugio, T. and Nagasawa, T. (1998). Purification and characterization of gallic acid decarboxylase from Pantoea agglomerans T71. Appl Environ Microbiol. **64**: 4743–4747.

72. Zhou, K., and Yu, L. (2004). Effects of extraction solvent on wheat bran antioxidant activity estimation. LWT. **37**: 717-721.

73. Zieli, A., Ki, H., and Kozłowska, A.H. (2000). Antioxidant activity and total phenolics in selected cereal grains and their different morphological fractions. J Agric Food Chem. **48**: 2008-2016.

74. Zielinski, A.A.F., Haminiuk, C.W.I., Alberti, A., Nogueira, A., Demiate, I.M., and Granato, D. (2014a). A comparative study of the phenolic compounds and the in vitro antioxidant activity of different Brazilian teas using multivariate statistical techniques. Food Res. Internat. **60**: 246-254.

75. Zielinski, A.A.F., Haminiuk, C.W.I., Nunes, C.A., Schnitzler, E., Van Ruth, S. M., and Granato, D. (2014b). Chemical composition, sensory properties, provenance, and bioactivity of fruit juices as assessed by chemometrics: a critical review and guideline. Comp. Rev. Food Sci. Food Saf. **13**: 300-316.

76. Zieliski H., Kozłowska H., and Lewczuk B. (2001). Bioactive compounds in the cereal grains before and after hydrothermal processing. Innovative Food Sci. Emerg. Technol. **2**: 159-169.

77. Zieliski, H. (2002). Low molecular weight antioxidants in the cereal grains – a review. Pol. J Food Nutr. Sci.**11**: 3-9.

Fig 1. Factors influencing the content and activity of phenolic acids

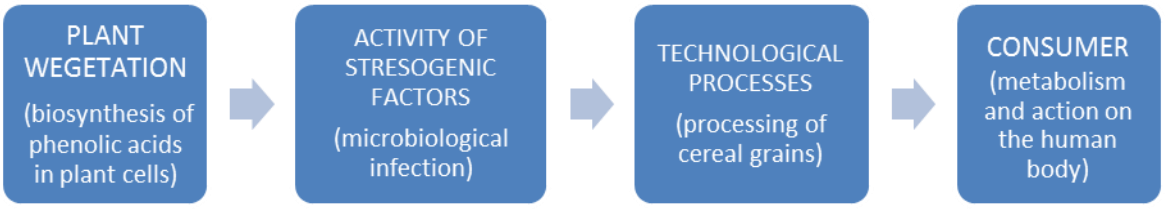


Fig. 2. Hypothetical simplified scheme of the phenylpropanoid pathway for the synthesis of phenolic acids

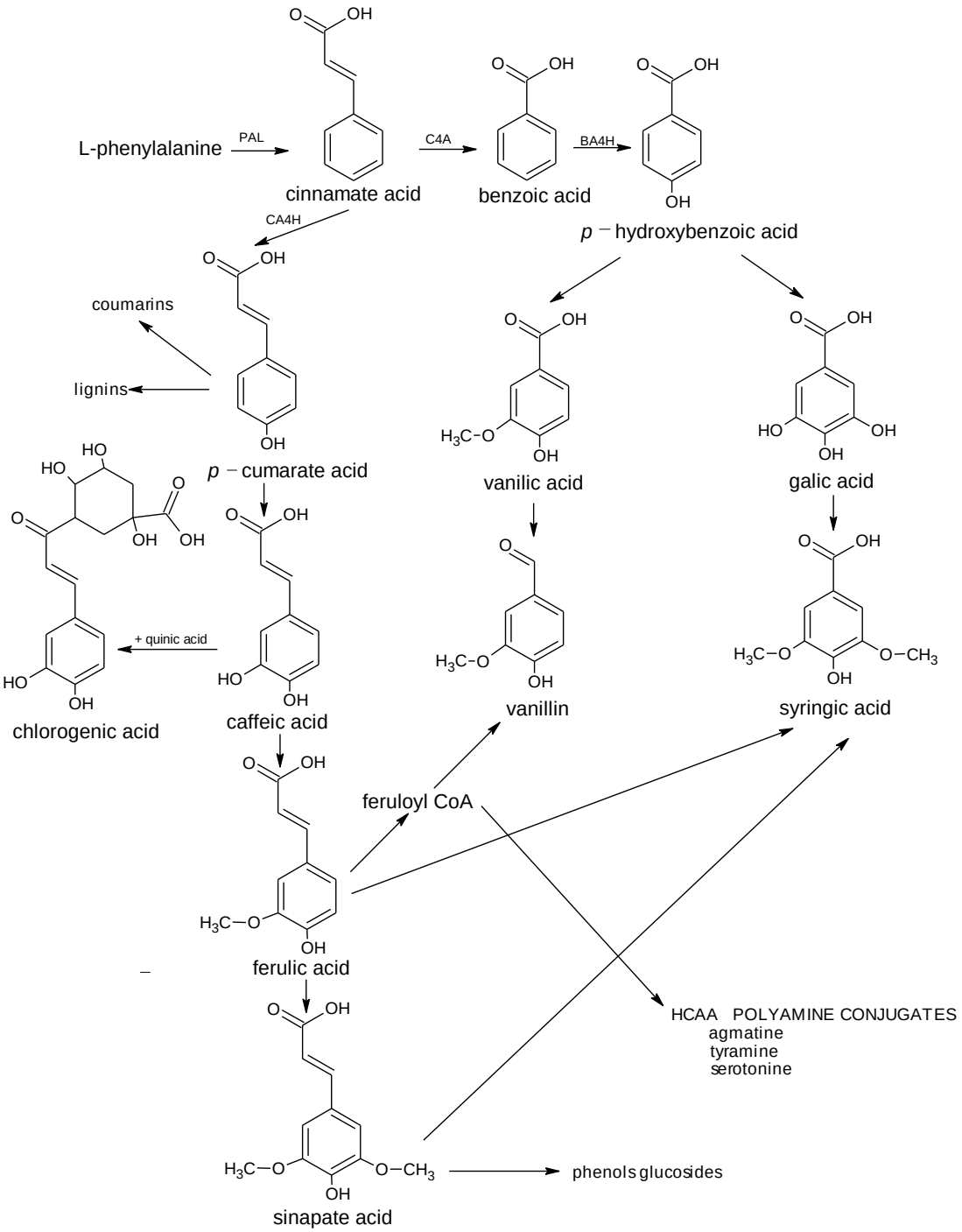
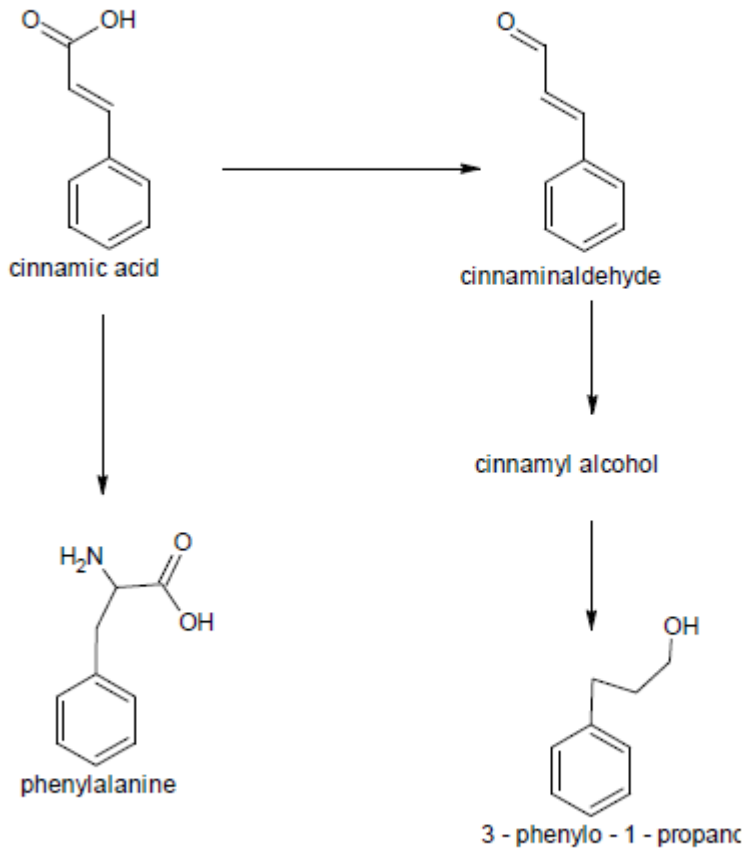
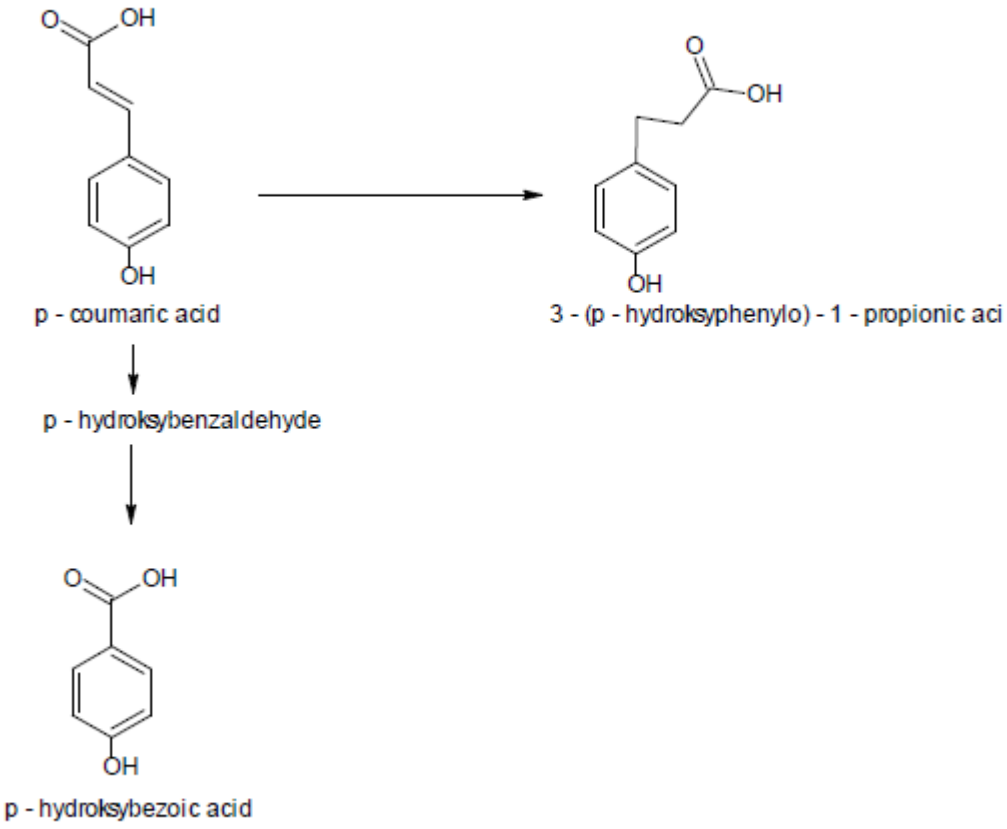


Fig. 3 Biotransformation of cinnamic acid and its hydroxyl derivatives.

A



B



C

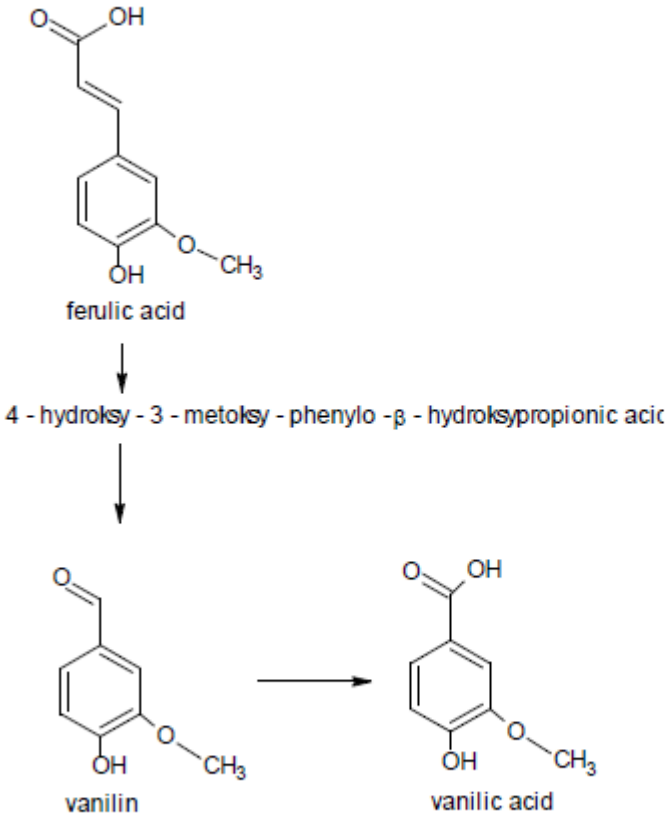


Fig. 4. Microbiological degradation of gallic acid.

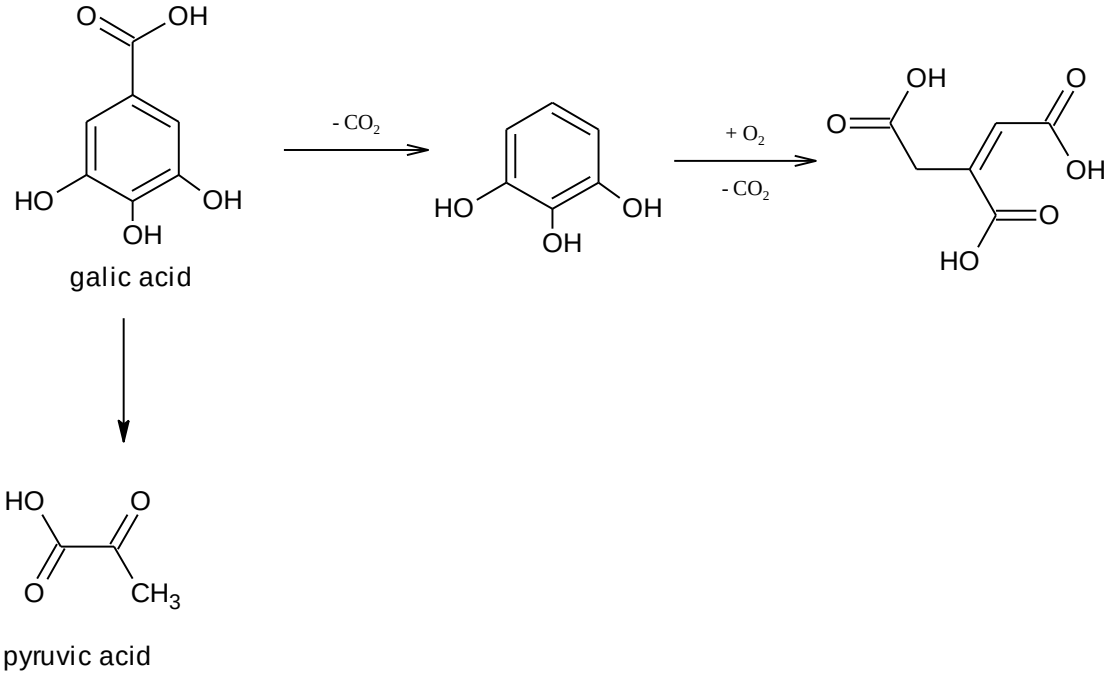


Fig. 5. A scheme of the metabolic pathway of chlorogenic, caffeic and ferulic acids in the human organism

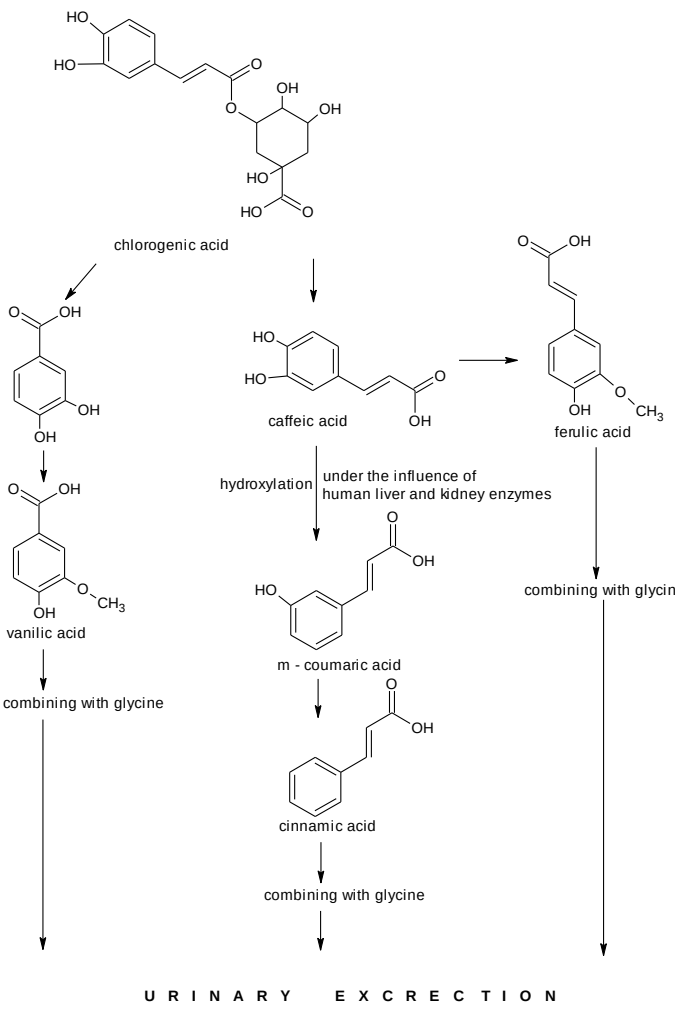


Table 1 Total contents of phenols, contents of selected phenolic acids and determined antioxidant potential of cereals (Adom and Liu, 2002; Kurasiak-Popowska et al., 2016; Liu 2007; Zieliski 2002; Zieli 2000; Stuper-Szablewska et al., 2016)

	Compound	Common wheat	Durum wheat	Oat	Rye	Rice	Buckwheat
Phenylcarboxylic acids (mg/kg)	Gallic	1-37 21	-	2-47 27	-	-	120-175 152
	4-Hydroxybenzoic	1-82 42	-	-	-	7-14 9	10-29 20
	Vanillic	30-70 37	-	1-10 2	20-30 25	1-3 1	-
	Syringic	1-62 40	9-37 13	-	20-39 23	-	-
	Vanillin	6-250 59	-	14-38 29	17-28 20	-	10-24 17
	Benzoic	1-71 40	-	-	-	-	-
Phenylacrylic acids (mg/kg d.w.)	Chlorogenic*	10-69 37	-	-	-	-	-
	Caffeic	2-90 44	-	10-27 16	-	1-5 2	1-5 3
	p-Coumaric	1-63 40	10-60 31	20-28 22	28-51 40	-	170-280 224
	Ferulic	270-1446 776	149-970 408	10-28 19	720-1040 914	1-26 18	10-49 37
	Sinapic	2-707 69.7	-	-	-	-	29-59 40
	t-Cinnamic	3-83 44	1-24 10.	-	-	-	58-86 69
TPC (mg/kg d.w.)		836-1694 905	1107-2080 1859	1490-3270 2122	640-869 719	195-298 240	1690-3570 2940

Table 2. Antioxidant activity of phenolic acids (author analysis).

Acid	VCEAC	ABTS
Benzoic	177.8	103.2
Caffeic	204.3	495.7
Chlorogenic	12.3	57.1
t-Cinnamic	812.3	314.9
p-Coumaric	58.6	94.2
Ferulic	88.3	117.6
Gallic	425.6	706.5
4-Hydroxybenzoic	9.3	36.9
Sinapic	121.0	194.5
Syringic	115.7	207.5
Vanillic	32.5	83.4
Vanillin	20.7	67.8

Table. 3 Contents of total polyphenols and major phenolic acids in selected cereal products.

Source**:** The authors' study based on own research and literature (Biesalski et al., 2009; Cao et al., 1998; Dziedzic et al., 2009; Kesarwani et al., 2014; Mattila et al. 2005; Stuper-Szablewska et al., 2016).

Cereal product	Total phenols (mg/kg d.m.)	Phenolic acids	
		type	content (mg/kg d.m.)
Rye flour	1366	Ferulic Sinapic p-coumaric Vanillic	860 120 41 22
Rye bran	4190	Ferulic Sinapic p-coumaric Caffeic	2800 480 140 77
Wholemeal wheat flour	1342	Ferulic Sinapic p-coumaric Caffeic	890 63 37 37
White wheat flour	167	Ferulic Sinapic Vanillic p-coumaric	120 8 4 3,8
Wheat bran	4527	Ferulic Sinapic p-coumaric Caffeic	3000 200 90 38
Barley flour	450	Ferulic p-coumaric Sinapic Vanillic	250 40 11 7,1
Corn flour	601	Ferulic Sinapic p-coumaric Caffeic	380 57 31 26
Oat bran	651	Ferulic Sinapic	330 90

		Syringic Vanillic	28 24
Wholemeal oat flakes	472	Ferulic Sinapic Syringic Vanillic	250 55 20 18
Buckwheat flour	248	p-hydroxybenzoic Caffeic Sinapic p-coumaric	110 85 21 15
Millet groats	373	Ferulic p-coumaric Vanillic p-hydroxybenzoic	260 18 11 3
Pasta	156	Ferulic Sinapic p-coumaric p-hydroxybenzoic	120 17 3,6 2,4
White rice	197	Ferulic p-coumaric Sinapic p-hydroxybenzoic	120 38 17 13
Brown rice	376	Ferulic p-coumaric Sinapic p-hydroxybenzoic	240 76 20 17