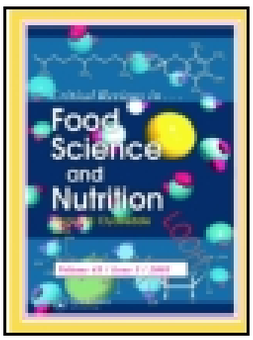

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Occurrence, types, properties and interactions of phenolic compounds with other food constituents in oil-bearing plants

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Abstract

Phenolic phytochemicals have become of interest due to their therapeutic potential, particularly with regards to their anti-cancer, anti-inflammatory, hypolipidemic, and hypoglycemic properties. An evolving area of research involving phenolics in foods and their products pertains

to the functional, biological, and nutritional consequences resulting from the binding between certain phenolic compounds and the macronutrient and micronutrient constituents of foods. The goal of this review is to provide a summary of studies investigating endogenous phenolic interactions with major components in food systems, including carbohydrates, proteins, lipids, minerals and vitamins, with a focus on the phenolic compounds and nutrients in oil-bearing plants. Another major objective is to provide a comprehensive overview of the chemical nature of phenolic interactions with food constituents that could affect the quality, nutritional and functional properties of foods. Such information can assist in the discovery and optimization of specific phenolic complexes in plant-based foods that could be utilized towards various applications in the food, nutraceutical and pharmaceutical industries.

Keywords: Phenolics; nutrients; interactions; functional properties; proteins; carbohydrates; lipids; minerals; antioxidant; health; anti-microbial.

Introduction

Little information has been reported about the interactions of phenolic compounds with other important food components such as proteins, carbohydrates, lipids and minerals (Le Bourvellec and Renard, 2012; Alu'datt et al., 2013b; Gallo et al., 2013; Ozdal et al., 2013; Alu'datt et al., 2014a; Alu'datt et al., 2014b). The frequent occurrence of interactions of phenolic compounds with other food components in food systems may affect the digestibility and palatability of foods (Beauchamp and Maller, 1977; Alu'datt et al., 2013b; Alu'datt et al., 2014a), as well as their nutritional value (Mennen et al., 2005). Indeed, the chemical nature of phenolic compounds allow them to interact with other food components, both macronutrients and micronutrients, through hydrogen bonding (Loomis and Battaile, 1966), covalent bonding (Mason, 1955), hydrophobic interactions (Hagerman and Butler, 1978) and ionic bonding (Rubino et al., 1996). The precise mechanisms of interactions between phenolic compounds and other food components are not well established. The presence of such interactions between phenolic compounds and proteins may affect the physical, chemical and physicochemical properties of food systems, including gelation, emulsification, foaming and water holding capacity (Alu'datt et al., 2013b; Alu'datt et al., 2014a). The interactions of phenolic compounds with proteins, carbohydrates and lipids may also impart antioxidant properties to these food components or help protect them against oxidation (Ratty and Das, 1988). Protein-phenolic interactions and lipid-phenolic interactions have been studied both *in vitro* and *in vivo* (Le Bourvellec and Renard, 2012; Ali, 2002; Alu'datt et al., 2013b; Alu'datt et al., 2016a; Alu'datt et al., 2016b). This review focuses on the interactions between phenolics and nutrients occurring in

oil-bearing plants such as soybeans, canola, flaxseeds and olives. These plants are rich sources of phenolics, oils and proteins with a broad range of biological and functional properties which can be influenced by the occurrence of specific interactions between phenolics and the plant/food matrices.

Phenolic compounds

Phenolic compounds are major plant secondary metabolites, structurally extremely diverse. In plant-derived foods and food products, phenolic compounds are responsible for major organoleptic and nutritional properties, and are useful for numerous practical applications (Cheynier et al., 2015). The nomenclature of phenolics depend on their chemical composition and structure. Shahidi and Naczk (2004) reported that phenylpropanoid and cinnamic acid derivatives are called phenolic acids. More specifically, phenolic compounds can be divided according to chemical structure into simple phenols (e.g., phenol, cresol, thymol and orcinol), phenolic acids (e.g., gallic, protocatechuic, vanillic and syringic acids), aldehyde forms of phenolic acids (e.g., vanillin, syringaldehyde and *p*-hydroxybenzaldehyde), phenylacetic acids, acetophenones, phenylpropanoid and their derivatives, chromones and coumarins (e.g., umbelliferone and aesculetin), and cinnamyl alcohols (e.g., coniferyl, sinapyl, syringyl and *p*-coumaryl alcohols). Phenolic compounds exist in plants and plant-based foods in both the free form and bound to other food components depending on their chemical structures and properties (Bravo, 1998). For example, four forms of phenolic compounds have been reported in oil seeds, namely free, esterified, etherified, and insoluble bound phenolic acids (Alu'datt et al., 2013a; Kozlowska et al., 1975; Kozlowska et al., 1983; Krygier et al., 1982). Complex phenolic

compounds such as hydrolysable tannins (tannic acid), condensed tannins (proanthocyanidins, e.g., procyanidins), lignans (e.g., secoisolariciresinol), flavones and isoflavones (e.g., daidzein) are formed by condensation of several units found in simpler phenolic compounds (Shahidi and Naczk, 2004).

Phenolic compound interactions with food components

Protein-phenolic interactions

The interactions of simple phenolic compounds with proteins in model systems have been investigated, including the interaction between sinapine and bovine serum albumin (BSA); the phenolic-protein complex formation was favored under neutral and basic pH conditions (Smyk and Drabent, 1989). Zadernowski (1987) reported that BSA binds with the ester bond of sinapine. Galloyl-D-glucose, a phenolic glycoside, also has the ability to bind to BSA; this ability is enhanced in the presence of galloyl ester groups (Beart et al., 1985). Soybean proteins have been shown to interact with chlorogenic, caffeic, cinnamic and gallic acids and the flavonoids flavone, apigenin, kaempferol, quercetin and myricetin (Wang and Murphy, 1994; Alu'datt et al., 2013b); these interactions lead to the reduced availability and, consequently, reduced nutritional value of lysine, cysteine and tryptophan residues in soybean proteins (Wang and Murphy, 1994).

Procyanidin compounds, a class of phenolic oligomers (condensed tannins), have a great structural diversity and a specific affinity for proteins (Ricardo-da-Silva et al., 1991; Alu'datt et al., 2013b; Alu'datt et al., 2016a; Alu'datt et al., 2016b). The interactions between proteins and procyanidins are affected by solvent composition, ionic strength, pH and temperature (Asano et

al., 1982; Asquith and Butler, 1986; Ricardo-da-Silva et al., 1991; Alu'datt et al., 2013b).

Tannins in general have the capability not only to bind to but also precipitate proteins from aqueous solution (Mehansho et al., 1987). The formation of tannin-protein complexes depends on the size, conformation and charge of the protein molecule and the size, length, and flexibility of the tannin (Shahidi and Naczk, 1995). Proteins with globular structures, such as ribonuclease, lysozyme and cytochrome C, generally have low affinity to bind with tannins, while proteins with open structures (e.g., gelatin) have a higher affinity to bind with tannins (Hagerman and Butler, 1981). Artz et al. (1987) showed that tannins need at least three flavanol subunits to be effective in precipitating proteins. In contrast, simple flavanols do not precipitate proteins (Artz et al., 1987). Tannins and their oxidized forms can interact with essential amino acids and other nutrients (Ohlson and Anjou, 1979). The precipitation of tannin-protein complexes is pH sensitive (Hagerman and Butler, 1978). In that regard, Naczk et al. (1996) reported that the solubility of tannin-protein complexes was the lowest at pH 0.3-3.1, while uncomplexed BSA, fetuin, collagen and pepsin precipitated at pH 3.0-5.0.Condensed tannins extracted from canola hull precipitated 3.0-59.0 mg BSA/g hull (Leung et al., 1979). In mammals, the interaction between proline-rich salivary proteins and dietary tannins results in an astringent taste (Mehansho et al., 1987).

Tannins interact with proteins due to the inherent chemical and structural properties of the proteins and tannins, in the form of hydrophobic interactions between the aromatic ring of the tannin and the hydrophobic region of the protein as well as the formation of hydrogen bonds (Hagerman and Butler, 1980; Oh et al., 1980; McManus et al., 1985; Hagerman, 1989; Hagerman et al., 1998; Le Bourvellec and Renard, 2012).

Many vegetable protein products can bind to phenolic compounds through different mechanisms, such as covalent bonding, hydrogen bonding, ionic bonding, hydrophobic interactions and electrostatic interactions (Mason, 1955; Loomis and Battaile, 1966; Rubino et al., 1996; Loomis, 1974; Hagerman and Butler, 1978). For example, Rubino et al. (1996) suggested that thomasidioic acid can bind with canola proteins at pH 7.0 and 8.5 through hydrophobic interactions.

Proteins also interact with phenolic compounds by hydrogen bonding via the hydroxyl groups in phenolic compounds and the carbonyl groups of the peptide bonds or due to oxidation to quinines, which bind with the reactive groups of proteins (Loomis and Battaile, 1966). Shahidi and Naczk (1995) reported that phenolic-protein complexes formed at both low and high concentrations of proteins due to the formation of hydrophobic interactions. Butler et al. (1984) suggested that, at physiological pH, phenolic compounds (tannins) and proteins from sorghum do not interact through ionic binding.

The interaction between polyphenols and polypeptides is responsible for the occurrence of haze or chill phenomena through haze active (HA) sites. The haze phenomenon has been noted in beer, wine and juice (e.g., grape and apple juices), and it is generally desirable to remove haze-active materials (Heatherbell, 1976; Hough et al., 1982; Siebert et al., 1996). The main components of chill and permanent hazes consist of polypeptides, polyphenols, as well as minor amount of metals (Djurtoft, 1965). The major phenolic compounds identified in haze are anthocyanins, such as procyanidin, prodelphinidin, and propelargonidin (Bengough and Harris, 1955; McFarlane et al., 1955); lignin; and phenolic acids, including ferulic, sinapinic, vanillic, syringic, gallic, protocatechuic, and caffeic acid (Harris and Ricketts, 1959; Harris, 1965). The

major components of chill haze are polyphenolic compounds, while permanent haze results from condensed tannins.

Ali (2002) reported that the thermal stability of BSA proteins was affected by the presence of gallic acid at pH 7.0, and that the thermal stability of proteins increased as a result of interactions with phenolic compounds. These interactions were affected by temperature and pH (Ali, 2002). Alu'datt et al. (2013b) determined the presence of protein-phenolic interactions in soybean protein isolates and of protein-phenolic-lipid interactions in flaxseed protein isolates. Alu'datt et al. (2016a) and Alu'datt et al. (2016b) reported that the phenolic–protein interactions in isolated protein fractions from nigella species and from byproducts of flaxseed and soybean protein residues have antioxidant properties.

From a nutritional standpoint, certain protein-phenolic interactions have been found to interfere with the digestion of macronutrients (proteins, lipids and polysaccharides). This occurs when the interactions inactivate specific digestive enzymes (Griffiths, 1986; Kuhnert et al., 2011), or when non-digestible protein complexes are formed as a consequence of interactions with phenolic compounds. The latter has been evidenced in bean paste fortified with onion skin (Sęczyk et al., 2015). In this study, the formation of non-digestible protein-phenolic complexes in the fortified bean paste reduced the *in vitro* digestibility of white bean albumins and globulins compared to the non-fortified paste.

Carbohydrate-phenolic interactions

Phenolic-carbohydrate complexes are common in most plant foods such as fruits, legumes, cereals, oil-bearing plants and beverages. The chemical nature of phenolic compounds allows them to conjugate covalently with monosaccharides, disaccharides as well as

oligosaccharides (Bravo, 1998). Glucose is the most common sugar associated with phenolic compounds. Galactose, rhamnose, xylose, arabinose, glucuronic acid and galacturonic acid are also common phenolic compounds (Bravo, 1998). Generally, phenylpropanoids and simple phenolic compounds, such as hydroxybenzoic acid and benzaldehyde derivatives, are covalently linked with polysaccharides in the cell wall (Wallace et al., 1991). Naringenin and hesperidin can occur either as O-glycosides or C-glycosides and are commonly found in citrus foods and prunes (Herrmann, 1988).

Anthocyanins include compounds with glycosidic linkages with anthocyanidins, such as pelargonidin, malvidin and cyanidin. In addition to glycosylation, common linkages occur with aromatic and aliphatic acids as well as methyl ester derivatives (Mazza, 1995). Simple phenolic acids and flavonoids represent the majority of plant phenolic compounds. Some of these phenolic compounds can be linked to plant cell wall components through an ester linkage, such as polysaccharides, which can be extracted from the fiber matrix by alkaline hydrolysis (Bravo, 1998). Non-extractable polyphenolic compounds of high molecular weight and some simple phenolic compounds bound to dietary fiber remain insoluble in organic solvents (Bravo et al., 1994). In model plant cell wall systems made of bacterial cellulose and cellulose-pectin composites, Padayachee et al. (2012) showed that individual phenolic acids bound to different extents to the cell wall, with caffeic acid > chlorogenic acid > ferulic acid. Their findings suggest that nutritionally significant amounts of phenolic acids may bind to plant cell walls, potentially restricting the bioavailability of phenolic acids in the small intestine. Phenolic compounds may thus be delivered to the large intestine where fermentation and metabolism by gut bacteria can occur (Padayachee et al., 2012). It is noteworthy that physiological conditions in the human

gastrointestinal tract, including acid hydrolysis in the stomach, may act positively on the extraction of phenolic compounds *in vivo* as they are progressively released from polysaccharide and protein bonds, thus becoming more available for absorption and to exert their biological effects in humans (Oliveira and Pintado, 2015; Sęczyk et al., 2015). Saura-Calixto et al. (2017) estimated that about 48% of the total dietary polyphenols are bioaccessible in the small intestine, while 42% become bioaccessible in the large intestine.

Interactions of carbohydrates with phenolic compounds can decrease the digestibility of dietary carbohydrates, as evidenced Sęczyk et al. (2015) with white bean paste fortified with onion skin. This group found that the formation of non-digestible polysaccharide-phenolic complexes in the fortified paste decreased the *in vitro* digestibility of starch compared to the non-fortified paste.

Lipid-phenolic interactions

Suberins and cutins are a class of polyphenolic compounds composed of polymerized phenylpropanoids with long-chain fatty acids, fatty alcohols (18-30 carbon atoms) or hydroxyl fatty acid and dicarboxylic acids with 14 to 30 carbon atoms, which are the main constituents of cell walls (Davin and Lewis, 1992; Graça, 2015). In these biopolyesters, phenolic compounds are covalently bond to lipid components. Balde et al. (1991) reported that phenolic acids and their long-chain fatty esters are found in the bark of stems. Similarly, propolis is composed of esters of phenolic acids and their derivatives with fatty alcohols (Banskota et al., 2001; Castaldo and Capasso, 2002). Chemical synthesis using benzoic and phenolic acids to produce phenolic-lipid esters has been investigated using acidic catalysts, basic catalysts and lipase catalysts (Gutman et al., 1992; Humeau et al., 1995). The esterification of cinnamic and *p*-hydroxybenzoic acids with

short- or medium-chain fatty acids using lipase has been described by Stamatis et al. (1999). Other authors have reported on the esterification of phenolic acids using long-chain fatty alcohols to produce phenolic-lipid compounds (Lue et al., 2005). The synthesis of ascorbyl palmitate using Novozym 435 and produced from ascorbic acid with palmitic acid methyl ester or palmitic acid was also reported (Humeau et al., 1995). Transesterification of ethyl ferulate with triolein in toluene using Novozym 435 to produce feruyl monoolein and feruyl diolein has been reported (Compton et al., 2000), as well as the transesterification of cinnamic acid with triolein in organic solvent, which produced a combination of monoleyl-1(3)-cinnamate and dioleyl-2-cinnamate (Karboune et al., 2005).

Alu'datt et al. (2014b) reported the presence of naturally occurring lipid-phenolic interactions in virgin olive oil resulting from the conjugation of *p*-hydroxybenzoic acid and tyrosol with glycerides. In their work, both the free and bound phenolic extracts from virgin olive oil displayed antioxidant action, α-amylase and angiotensine 1-converting enzyme (ACE) inhibitory activities, as well as antiproliferative effects in two colorectal cancer cell lines. Thus, some of the beneficial biological effects attributed to the phenolic compounds in olive oil (e.g., hydroxytyrosol and tyrosol) (Rafehi et al., 2012) could be mediated by the formation of complexes with glycerides.

Mineral-phenolic interactions

The formation of tannin-metal complexes can lead to important anti-microbial properties (Scalbert, 1991; Mila and Scalbert, 1994). Numerous authors have also suggested the use tannins as modifiers to fine-tune the rheological properties of minerals and clays (e.g., mineral chelators from wastewater and components of anticorrosive primers and inks) (Randall et al., 1974;

Grimshaw, 1976; Seavell, 1978). Simple phenolic compounds have been used to precipitate copper and zinc in model systems and it has been reported that the formation of phenolic-metal complexes is influenced by the concentrations of their individual constituents (McDonald et al., 1996). Other factors like pH influence the formation of these complexes. The capacity of four phenolic compounds naturally occurring in olives and in virgin olive oil (namely, oleuropein, hydroxytyrosol, 3,4-dihydroxyphenylethanol-elenolic acid (3,4-DHPEA-EA), and 3,4-DHPEA-EA dialdehyde) to complex ferric ions at different pH was reported by Paiva-Martins and Gordon (2005). At pH 5.5, the complexes between ferric ions and 3,4-DHPEA-EA or 3,4-DHPEA-EA dialdehyde were found to be relatively stable, suggesting that the antioxidant activity of both phenolic compounds at pH 5.5 is partly due to their metal-chelating activity (Paiva-Martins and Gordon, 2005). While the ability of phenolic compounds to chelate metal ions can be beneficial (e.g., to limit oxidation), it can also be undesirable when it leads to anti-nutritional effects by reducing the bioavailability of essential minerals (e.g., calcium, iron and magnesium) present in foods.

Vitamin-phenolic interactions

Interactions between antioxidants and synergistic modes of action are increasingly being recognized as important mechanisms by which antioxidants exert their protective effects in foods and in living organisms. Vitamin antioxidants include vitamin C and vitamin E (tocopherols), while non-vitamin antioxidants include carotenoids and polyphenols. Antioxidant interactions between polyphenols, tocopherols and carotenoids have been reported (Pedrielli and Skibsted, 2002; Skibsted, 2012). Pedrielli and Skibsted (2002) suggested that polyphenols show synergism with tocopherol through regeneration of tocopherol from its oxidized form. This synergism

seems to be controlled thermodynamically as the regeneration follows the order of the reduction potentials (Pedrielli and Skibsted, 2002). Likewise, polyphenol-carotenoid synergism is thought to result from the regeneration of carotenoids active as antioxidants in the lipid phase by the water-soluble polyphenols at lipid/water interfaces (Skibsted, 2012). Antioxidant interaction between polyphenols and carotenoids may explain the special role of these non-vitamin antioxidants. Carotenoids act as electron donors reducing lipid radicals in cell membranes and may be subsequently regenerated at interfaces by the hydrophilic polyphenols; this synergism seems to be controlled thermodynamically (Skibsted, 2012).

Properties of food phenolic complexes

Health benefits

The consumption of olive oil and oil seeds has been reported to have protective effects on the development of breast, prostate and colon cancers (Keli et al., 1996; Lipworth et al., 1997). Several studies showed that oleuropein, verbascoside and tyrosol, which are some of the predominant phenolic compounds found in the olive plant, have anti-tumor properties as well as benefits for myocardial vascular disease prevention (Lee et al., 1993; Saracoglu et al., 1995; Maimeskulova and Maslov, 1998; Saenz Garcia et al., 1998; Omar, 2010). Oil seeds containing polyphenolic compounds can reduce the oxidation of low density lipoprotein (LDL) (Wiseman, 1996). Polyphenolics also have hypoglycemic effects (Trovato et al., 1993). Several studies have demonstrated the capacity of phenolic compounds to scavenge peroxyl radicals, hydroxyl radicals, and superoxide anions and to chelate transition metal ions (Assmann et al., 1997). Naturally occurring protein-phenolic interactions and lipid-phenolic interactions in food system, such as olive oil, soybean proteins, flaxseed proteins, nigella species and byproducts of flaxseed

and soybean protein residue, can affect the rheological and biological properties including antioxidant, antihypertensive and antiproliferative activities (Alu'datt et al., 2013b; Alu'datt et al., 2014a; Alu'datt et al., 2014b; Alu'datt et al., 2016a; Alu'datt et al., 2016b).

Flaxseed is one of many plant species that is widely studied for its potential health benefits and its use as or in nutraceuticals (Haumann, 1993). It is a natural source of phytochemicals such as flavonoids, coumarins, lignans and phenolic acids (Caragay, 1992). Lignans and other phenolic compounds in flaxseed have been implicated in potential human health benefits that include phytoestrogenic, antioxidant, anti-carcinogenic (e.g., against breast cancer and prostate cancer) and cardio-protective properties (Oomah and Mazza, 1998; Clifford, 2000; Anonymous, 2001). Lignans have also been shown to stimulate the synthesis of sex hormone binding globulin, which improves the clearance of circulating estrogen (Pszczola, 2001). Enterolactone and enterodiol have been detected in the urine during the reproductive cycle of pregnancy, and showed a negative relationship with estrogen (Setchell et al., 1983). Many authors have suggested that lignans play an important role in hormone metabolism (Setchell et al., 1983) and in reducing breast cancer (den Tonkelaar et al., 2001; Dai et al., 2002). Dietary lignans may also play an important role in preventing prostate and colon cancer (Jenab and Thompson, 1996; Lin et al., 2001).

Simple and complex phenolic compounds in soybean have been studied extensively in relation to their estrogenic, anti-cancer, anti-mutagenic and antioxidant properties (Makela et al., 1995; Wiseman, 1996; Miyazawa et al., 2001). Soybean isoflavones and other phenolic compounds have been reported to provide anti-carcinogenic effects towards different types of cancers (Schweigerer et al., 1992; Makela et al., 1995). Some studies found that the consumption

of soybean products has beneficial effects on human health against myocardial vascular disease via the phenolic compounds inducing lower LDL and higher high density lipoprotein (HDL) concentrations (Potter et al., 1996; Nilausen and Meinertz, 1998).

Antimicrobial effects

Different classes of phenolic compounds inhibit the growth of a wide range of gram-positive and gram-negative bacteria (Beuchat and Golden, 1989). There are several reports about the antimicrobial effects of polyphenol compounds against *Staphylococcus aureus*, *Salmonella enteritidis*, as well as *Bacillus cereus T* spores (Tranter et al., 1993; Tassou and Nychas, 1994; Tassou and Nychas, 1995). Likewise, phenolic compounds inhibit growth and delay the formation of sporulation produced by *Aspergillus parasiticus* (Gourama and Bullerman, 1987). Several studies also found that phenolic compounds, such as *p*-hydroxybenzoic acid, vanillic acid, and *p*-coumaric acid, inhibit the growth of *Escherichia coli*, *Klebsiella pneumoniae* and *B. cereus* (Calis et al., 1988; Pardo et al., 1993; Aziz et al., 1998). Capasso et al. (1995) reported that the presence of polyphenolic compounds and phenolic acid inhibit the growth of phytopathogenic *Pseudomonas syringae*, *P. savastanoi* and *Corynebacterium michiganense*. Phenolic compounds have further been studied for their antiviral activity against the human respiratory syncytial virus (Kernan et al., 1998) and HIV-1 (Narayan and Rai, 2016). Some of these compounds also seem to exert prebiotic effects (Cardona et al., 2013).

Nutritional and physiological properties

Phenolic compounds can reduce the digestibility and absorption of proteins, lipids and carbohydrates (Griffiths, 1986; Bravo, 1998; Landete, 2011). For instance, many studies reported the inhibition of galactosidase and amylolytic enzymes by phenolic compounds, the reduction in

the digestibility of dietary carbohydrates (Sęczyk et al., 2015), and the decrease in glycemic response (Thompson et al., 1984). Such effects may be beneficial in applications aimed at reducing hyperglycemia and hyperlipidemia. However, caution is warranted to avoid undesirable malabsorption of important nutrients whose bioaccessibility may be reduced as a consequence of interactions with phenolic compounds, as reported by Sęczyk et al. (2015) in fortified bean paste.

Possible undesirable effects of phenolic compounds, including anti-nutritional effects related to their ability to combine with some dietary proteins and fibers, chelate certain metals and inhibit certain digestive enzymes, have been documented in animals fed excessive amounts of anti-nutritional factors (e.g., certain phenolic compounds) (Mangan, 1988; Lipinski et al., 2017). Anti-nutritional effects are unlikely at the doses that characterize typical daily intakes of phenolic compounds by humans.

Some phenolic compounds with galloyl and catechol groups have been shown to have a negative effect on cation absorption in animal models (Bravo, 1998). Flavonoids, such as catechins; phenolic acids, such as chlorogenic acid; and polymerized products tend to lead to reduced iron bioavailability (South et al., 1997; Hurrell et al., 1998). However, Garcia-Lopez et al. (1990) reported no effect of tannins from soybean, chickpeas or red kidney beans on iron absorption in rats. In animal models, Kies and Umoren (1989) reported a reduction in copper absorption after the consumption of tea (rich in polyphenols), whereas Vaquero et al. (1994) reported an increase in the absorption of copper after the consumption of breakfasts containing tea. These discrepancies may be due to the fact that the binding (chelation) parameters are affected by many factors, such as temperature, pH, mineral concentrations and ionic strength, concentration of other nutrients, as well as types and structures of phenolic compounds.

The negative effects of polyphenolics on the bioavailability of metals, such as copper and iron, are thought to be related to hydroxyl radical production (Thompson et al., 1976), as chelation of these metals is one mechanism by which polyphenolic compounds can exert their antioxidant activity. Coudray et al. (1999) reported that the presence of chlorogenic and caffeic acids lowers zinc absorption rates in rats. Some reports suggested negative effects of polyphenolic compounds on the bioavailability of sodium (Freeland et al., 1985) and aluminum (Fairweather-Tait Piper et al., 1991), but no adverse effect has been detected regarding the bioavailability of manganese, calcium and magnesium in animal models (Fraile and Flynn, 1992; Jansman et al., 1993).

Antioxidant properties

The roles of phenolic compounds as antioxidants have been described in terms of protecting living cells against oxidative damage as well as maintaining the quality of food and food products by delaying deterioration and preserving nutritional value (Shahidi and Naczk, 2004). Phenolic compounds have a variety of mechanisms for their action as antioxidants. These mechanisms include terminating free radicals by the donation of hydrogen atoms, decomposing the primary products of oxidation to non-radical species, and inhibiting the formation of peroxidation-derived compounds by preventing continued hydrogen removal from substrates (Shahidi and Naczk, 2004). Phenolic constituents also seem to support the action of other important antioxidants (Skibsted, 2012). Such concerted actions by antioxidants are highly relevant for food stability, human nutrition and the prevention and management of chronic diseases. Additional modes of action of phenolic compounds, also involving cellular protection but extending beyond antioxidant activity, are being increasingly recognized. These include

modulatory actions in cells through modulation of cell-signaling pathways, enzymatic activity, and epigenetic modifications that regulate gene expression (Giampieri et al., 2014; Tsao, 2010).

The chemical structure of polyphenol compounds with higher molecular weights allows them to have greater antioxidant abilities compared to simple phenolic compounds, due to the presence of hydrogen atoms in ethyl or *n*-butyl substituent groups (Shahidi et al., 1992). Ratty and Das (1988) reported the high antioxidant ability of foods that contain flavonoids due to an increase in the degree of hydroxylation. Polyphenols have been shown to inhibit the chain reactions of reactive oxygen species that cause oxidation (Fuhrman et al., 1995). Afanas'ev et al. (1989) further reported that polyphenols prevent the formation of primary chain reactions by acting as terminators for the initial radicals (e.g., hydroxyl radicals).

The dietary lignans secoisolariciresinol diglucoside and secoisolariciresinol, present in flax, sunflower, sesame and pumpkin seeds, also display antioxidant properties (Niemeyer and Metzler, 2002), as do the soy isoflavones daidzein, genistein and glycitein (Murakami et al., 1984). Aglycones seem to have superior antioxidant activity compared to the parent isoflavone glycosides (Hayes et al., 1977). Syringic, vanillic, caffeic, ferulic, *p*-coumaric and *p*-hydroxybenzoic acids in soybean were also found to have antioxidant activity (Arai et al., 1966; Hammerschmidt and Pratt, 1978; Pratt and Birac, 1979). The order of antioxidant activity of soy isoflavones is glycitein > daidzein > genistein > quercetin > 6,7,4'-trihydroxyisoflavones, while, for phenolic acids, the order is *p*-coumaric acid > ferulic acid > chlorogenic acid > caffeic acid (Arai et al., 1966; Hammerschmidt and Pratt, 1978; Pratt and Birac, 1979).

Oleuropein, a hydroxytyrosol derivative present in large amounts in olive leaves and fruits, was found to have a weak antioxidant activity (Tsimidou et al., 1992; Alu'datt et al.,

2013a), but hydroxytyrosol and some of its derivatives are potent antioxidants (Montedoro et al., 1993; Refehi et al., 2012). The observation that virgin olive oils with a high polyphenol content are more resistant to auto-oxidation is consistent with the high antioxidant activity of olive oil polyphenols which contribute to the auto-oxidative stability of olive oil (Montedoro, 1992; Tsimidou et al., 1992; Alu'datt et al., 2013a; Alu'datt et al., 2014b). Olive oil was showed to have a superior oxidative stability compared to sunflower, rapeseed, soybean and sunflower oils (Vidrih et al., 2010). Less stable oils may benefit from enrichment (fortification) with phenolic antioxidants. Interactions with other food components may influence the antioxidant properties of phenolic compounds. For instance, the antioxidant activity of cocoa polyphenols was decreased upon interaction with milk proteins, possibly because of the existence of weak protein-polyphenol interactions (Gallo et al., 2013).

Conclusions and directions for future research

The presence of hydroxyl and other functional groups on the aromatic ring in phenolic compounds allow them to interact endogenously with other food constituents, including proteins, carbohydrates, fats, minerals and vitamins. This can give rise to a great variety of interactions and complexes involving phenolic compounds, nutrient and non-nutrient food components, as well as food matrices. Only a few studies have investigated the significance of these phenolic-food component interactions in terms of the physicochemical, nutritional, biological and nutraceutical properties of food systems and plant-based ingredients. The investigation of such interactions using various novel approaches should be undertaken to identify the phenolic complexes that have high potential for functional, nutraceutical and pharmaceutical applications

in the health and agri-food sectors. This review article indicates a lack of studies on the identification of phenolic complexes on the functional properties of foods (e.g., ingredient solubility, emulsion stability, foaming stability, water holding capacity, gelling, organoleptic attributes and preserving) and on their physiological and health effects. Thus, the following aspects warrant consideration in future studies:

1. Understanding of the mechanisms of phenolic-nutrient and phenolic-food matrix interactions in food systems, with a view to enhance the organoleptic (e.g., color, flavor and taste), functional and nutritional properties of foods.
2. Characterization of plant-based food systems for the presence of phenolic-food constituent complexes that can be isolated, characterized and optimized for specific applications.
3. Identification of phenolic complexes that show high potential for specific functionalities, and testing their activities and roles in biological systems *in vivo*.
4. Assessing the health benefits of phenolic complexes in relation to chronic diseases prevention and weight management, and investigating the use of these compounds as natural ingredients for fortifying food or developing new nutraceutical andpharmaceutical applications.

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