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Review

Interactions of polyphenols with carbohydrates, lipids and proteins

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ABSTRACT

Polyphenols are secondary metabolites in plants, investigated intensively because of their potential positive effects on human health. Their bioavailability and mechanism of positive effects have been studied, *in vitro* and *in vivo*. Lately, a high number of studies takes into account the interactions of polyphenols with compounds present in foods, like carbohydrates, proteins or lipids, because these food constituents can have significant effects on the activity of phenolic compounds. This paper reviews the interactions between phenolic compounds and lipids, carbohydrates and proteins and their impact on polyphenol activity.

Contents

1. Introduction

Plant foods contain components important for human development and health, like vitamins, proteins, and minerals. Phenolic compounds are plant secondary metabolites but they are also an important part of plant foods. They are being widely studied due to potential positive effects of polyphenol-rich foods. Polyphenols have shown various positive bioactivities, like anticarcinogenic properties (Bellion et al., 2010). The polyphenol influence on cardiovascular health and cancer was reviewed by Hollman et al. (2011). On the other hand, some activities of polyphenols are being reassessed, such as their direct antioxidant activities inside the organism and the biological relevance of antioxidant activities in cardiovascular disease protection (Hollman et al., 2011). It is increasingly emphasized that there are multiple bioactivities of polyphenols in the human organism that are important to understand, such as the role of their metabolites, the effects on the modulations of enzymes (Hollman et al., 2011) and interactions with other macromolecules (Le Bourvellec & Renard, 2012).

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In order to have effects within the human organism, phenolic compounds should be released during digestion and then absorbed in the gut in a certain amount (Parada & Aguilera, 2007). That is why their bioaccessibility and bioavailability are subjects of various studies and reviews (Adam et al., 2002; Duarte & Farah, 2011; Manach, Williamson, Morand, Scalbert, & Rémésy, 2005; Serra et al., 2010). Bioaccessibility is defined as the amount of an ingested compound that is available for absorption in the gut (Palafox-Carlos, Ayala-Zavala, & Gonzalez-Aguilar, 2011). The FDA has defined *bioavailability* as the rate and extent to which the active substances or therapeutic moieties contained in a drug are absorbed and become available at the site of action (Parada & Aguilera, 2007).

Various studies deal with the determination of how much of the polyphenols can be absorbed into the circulation system after they get into the body (Adam et al., 2002; Serra et al., 2010). Evidences suggest that polyphenols are absorbed in a relatively low amount. The absorption of isoflavones and gallic acid is the best, followed by catechins, flavanones, and quercetin glucosides. Proanthocyanidins, galloylated tea catechins and anthocyanins are the least well absorbed (Manach et al., 2005). New evidence offers some new views on the bioavailability. Czank et al. (2013) studied the bioavailability of $^{13}C_5$ labeled cyanidin-3-glucoside, by collecting blood, urine, breath and fecal samples from human volunteers. The results showed that anthocyanins are more bioavailable than previously perceived ($12.3 \pm 1.3\%$) and that their metabolites are present in the circulation for $\leqslant$48 h after ingestion. Procyanidins are abundant in many foods like apples, berries, and nuts, and are therefore consumed regularly by many people. Recent findings offers some additional understanding of the bioavailability since it was shown that not only B type dimers but also A type dimers are bioavailable (Appeldoorn, Vincken, Gruppen, & Hollman, 2009). Study has shown that the dose of polyphenol ingested has important impact in the bioavailability. Namely, higher doses can show different effects than lower doses of ingested polyphenols. Specifically, it was shown that chlorogenic acid from coffee had reduced bioavailability in humans when ingested in higher doses (Stalmach, Williamson, & Crozier, 2014). Moreover, it has become clear that nutrients like proteins, carbohydrates and lipids that surround polyphenols inside the gastrointestinal tract, have a great impact on the bioaccessibility and bioavailability of polyphenols. Indeed, many such nutrients have a very complex, porous structure which trap polyphenols and, as a consequence, change their availability for absorption. Studies conducted in recent years have shown the importance of these interactions (Chanteranne et al., 2008; Schramm et al., 2003). Moreover, these interactions with nutrients could give polyphenols a very different role. They could protect polyphenols from oxidation during their passage through the gastrointestinal tract and deliver them to the colon more intact. Here they can be metabolized under the influence of microflora. Recent studies describe the role of dietary bioactive compounds, intestinal microbiota and polyphenol metabolites (MacDonald & Wagner, 2012; Tuohy, Conterno, Gesperotti, & Viola, 2012). Furthermore, it is suggested that a positive, antioxidant environment could be created in the gastrointestinal tract, by the delivery and release of polyphenols. There polyphenols, as antioxidant compounds, can protect nutrients as proteins, lipids and vitamins, from oxidation. In addition to these mentioned activities, they also can interact with proteins producing protein precipitation and loss of nutritional value, enzymatic activity, and other biological effects (Tomás-Barberán & Andrés-Lacueva, 2012). It has become increasingly clear that polyphenols have many potential bioactivities in the human body which are affected by interactions of polyphenols with other macromolecules (Le Bourvellec & Renard, 2012).

Interactions between polyphenols and molecules from food were mostly based on different non-covalent hydrophobic interactions (Yuksel, Avci, & Erdem, 2010). Hydrogen bonds are also important as in the case of interactions between polyphenols and proteins (Frazier et al., 2010; Shpigelman, Israeli, & Livney, 2010), and polyphenols and carbohydrates (Saura-Calixto, 2011). The interaction between proteins and plant phenols can lead to covalent bonds as well (Kroll, Rawel, & Rohn, 2003). The conditions for forming covalent bonds are the capability of phenols to form quinone or semi-quinone radicals (in a two-step reaction). The reaction proceeds with polymerization (Kroll et al., 2003).

This paper reviews the recent literature about the interactions between phenolic compounds and other molecules present in food (proteins, carbohydrates, and lipids), the nature of these interactions and their significance.

2. Phenolic compounds

A high number of compounds belong to the group of phenolics (phenolic acids, acetophenones, phenylacetic acid, hydroxycinnamic acids, coumarins, naphthoquinones, xanthones, stilbenes, flavonoids) (Crozier, Jaganath, & Clifford, 2009). The most important ones occurring in plants are flavonoids, phenolic acids, stilbenes and lignans (Crozier et al., 2009). Their chemical structure is more or less complex and can vary from very simple molecules to very complex ones.

Flavonoids, as one of the largest group of phenolic compounds, can be further classified into several subcategories like anthocyanidins, flavonols, flavanols (catechins and proanthocyanidins), flavanones, flavones and isoflavones (Crozier et al., 2009). They have a similar basic structure consisting of two phenyl groups linked together with three-carbon bridge commonly cyclized with oxygen. They are differentiated according to the degree of unsaturation and degree of oxidation of the three-carbon segment. Moreover, various sugar molecules can be bound to the flavonoid structure over their hydroxyl groups, which make the structure of these molecules more complex. In fact they are commonly found in glycosidic forms. Glycosylation makes them more soluble in water. Acylation of the glycosides is also common. One or more of the sugar hydroxyls can be derivatized with an acid such as acetic or ferulic acid. The structure of some flavonoids can be even more complex. Gallotannins (hydrolysable tannins) and proanthoyanidins (condensed tannins) are compounds from flavanol group which have several basic units of polyphenols interconnected into a larger, more complex structure (Crozier et al., 2009; Landete, 2011). Gallotannins are esters of gallic acid and a polyol, usually glucose (Landete, 2011). Proanthocyanidins or condensed tannins are high-molecular weight polymers with flavan-3-ols as basic structural units ((epi)catechins and (epi)gallocatechins). Interflavanoid linkages are acid labile and anthocyanidin molecules are created after the acid hydrolysis in alcoholic solutions (Crozier et al., 2009).

Ellagitannins which belong to the hydrolysable tannin class are esters of hexahydroxydiphenic acid and a polyol, usually glucose or quinic acid (Landete, 2011). They can also form complex molecules.

On the other hand, phenolic acids are a group of plant phenols that have relatively simple structures but can also be linked to sugar units. They are a large group of hydrophilic phenols.

As it can be seen, phenolic compounds are a diverse group of compounds composed of simple molecules of low molecular weight up to very complex molecules of high-molecular weight. Because of the great diversity in their structure, they have different properties, such as solubility and polarity which enable them to have different interactions with other molecules. They can interact with each other and with other molecules that surround them. Bigger molecules have a much greater number of hydroxyl groups as this makes them susceptible to a very large number of interactions