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Current Opinion in Food Science

Polyphenol interaction with food carbohydrates and consequences on availability of dietary glucose

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Polyphenols are known to indirectly influence glucose metabolism, for example, via inhibition of digestive enzymes. Less clear is whether polyphenols can complex with, and directly reduce carbohydrate digestion. This is relevant because it can provide a practical mechanism to reduce caloric load of foods. Direct interaction of carbohydrates with monomeric polyphenols appears to have little practical consequence on glucose availability. Recent evidence supports strong and specific polymeric polyphenols (tannins, especially with MW > 1000) interaction with carbohydrate polymers via hydrogen bonding and hydrophobic interactions. For example, amylose component of starch forms non-digestible complexes with tannins. This is interesting because starch is the primary dietary source of glucose. Thus research efforts in this area should focus on optimizing and uncovering consequences of starch–tannin interactions.

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Current Opinion in Food Science 2016, **8**:14–18

This review comes from a themed issue on **Functional foods and nutrition**

Edited by **Rotimi Aluko**

For a complete overview see the Issue and the Editorial

Available online 25th January 2016

http://dx.doi.org/10.1016/j.cofs.2016.01.010

Introduction

Carbohydrates are the most abundant organic molecules on earth and play a central role in sustaining life. They contribute a majority of human metabolic energy, representing about 52% of US caloric intake [1,2], and up to 80% in poorer regions [2]. Carbohydrates are indispensable food ingredients due to their desirable impact on texture, color, flavor, and other crucial food quality attributes. Starch is the major dietary contributor (about two-thirds) of calories from carbohydrates [1]. The prominent role of carbohydrates in the diet implies that strategies that can reduce carbohydrate digestibility in foods would greatly benefit efforts to reduce caloric intake.

Polyphenols comprise a diverse group of secondary plant metabolites that perform various roles in plants, including structure, cell signaling, and natural defense, among others. Among the common natural polyphenols are phenolic acids, flavonoids, coumarins, lignans, and stilbenes [3]. Of particular interest among these polyphenols are the polymeric derivatives of flavonoids and phenolic acids (collectively known as 'tannins') which are capable of binding strongly to food macropolymers, especially proteins (including digestive enzymes), significantly altering their properties. Polyphenols have been extensively investigated for their potential contribution to health through antioxidant properties, cell signaling, and other mechanisms that are believed to help prevent various degenerative diseases such as cancer, diabetes, cardiovascular, and neurodegenerative diseases [4]. More recently, the increasing burden of obesity and associated problems globally has spurred a lot of research into possible direct role of the polyphenols in reducing available dietary calories.

Comprehensive recent review have discussed how polyphenols affect carbohydrate metabolism, largely focusing on their effect on digestive enzymes, membrane transporter proteins, and cell signaling mechanisms [5•,6,7], as well as polyphenol bioactivity [8]. Far fewer studies and reviews have specifically delved into the nature of direct polyphenol–carbohydrate interactions, and possible impact of such interactions on dietary carbohydrate digestion. We believe such direct interactions can be more impactful to nutritional fate of carbohydrates and deserve better attention. This review highlights the recent evidence available for direct polyphenol–carbohydrate interactions and possible effect on nutritional profile of carbohydrates.

What we know and can learn from protein–polyphenol interactions

Interaction of polyphenols with proteins and consequences of such interactions are well documented [9–12]. The vast majority of evidence indicates that the polyphenols interaction with proteins is highly dependent on, firstly, the molecular weight of the polyphenol, and secondly, the protein structure. High molecular weight (HMW) polyphenols (tannins), especially proanthocyanidins with degree of polymerization above three (MW > 1000)), bind efficiently with proline-rich proteins (e.g., human parotid salivary IB5 protein [13]), but poorly with small, tightly folded globular proteins [14]. The proline-rich proteins tend to have either an

open random-coil or collagen-like helical structural conformations [9,10], which provides the molecular flexibility and readily available binding sites for tannins. Tannin ligands can also form intermolecular cross-links between binding sites on adjacent protein molecules [12]. In general, conformational flexibility of both the tannin and protein contribute complementarily to protein–tannin binding efficiency [12,14]. Because polyphenols can act as polydentate ligands on protein surface through their hydroxyl groups and aromatic rings, higher degree of polymerization (DP) achieves higher binding efficiency [14,15].

Hydrophobic interactions and hydrogen bonding dominate protein–tannin interactions. The products of such interactions are generally non-digestible or only poorly digestible, and have been implicated in reduced feed efficiency of, for example, high tannin sorghums [16]. Whether carbohydrates can interact with polyphenols in a similar fashion is the subject of a growing body of research [5•,6,17–19,20••,21••]. We believe the mechanisms for protein–tannin interactions can be exploited to reduce carbohydrate digestion.

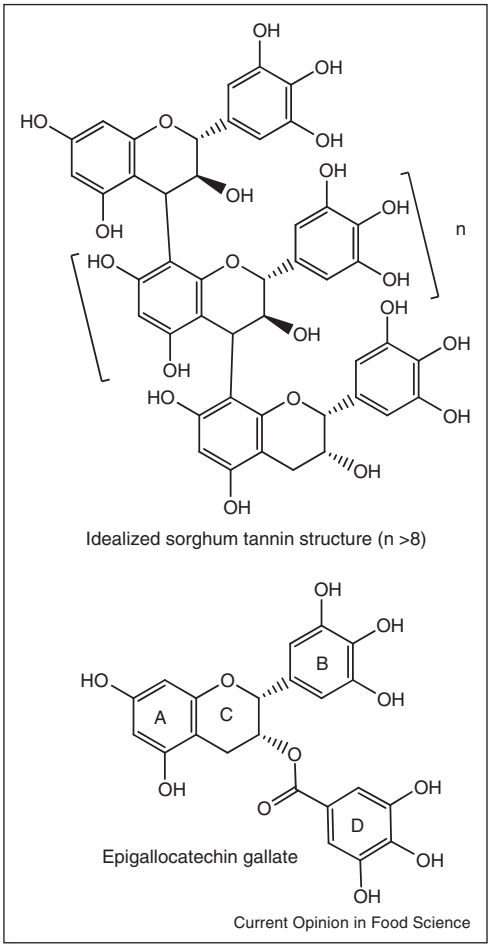
Evidence for carbohydrate–polyphenol interactions

Monomeric polyphenols

Even though monomeric polyphenols have been shown to interact with starch and other carbohydrates, including formation of inclusion complexes with amylose [22], such interactions appear to be rather modest, and have limited impact on nutritional release of glucose from starch [21••]. Studies with non-starch polysaccharides, support the limited binding ability of the monomeric polyphenols to carbohydrates [23]. The reports that have shown significant impact of monomeric polyphenols on starch digestibility are only for relatively high levels of the compounds, for example, 100 mg tea catechins/g starch [24]. At such high levels of polyphenols, direct enzyme inhibition becomes more likely.

Wu *et al.* [25], reported that tea catechins at ≥10% starch (w/w) substitution severely restricted amylose reassociation after cooking. Given that tea catechins are sterically bulky and highly hydrophilic (epigallocatechin-3-gallate (EGCG) dominates [24]), it is not likely that the hydrophobic core of amylose coil would include these molecules. A more likely interaction mechanism would be a weak partial inclusion of the B-ring of the EGCG (Figure 1) into the amylose core, anchored/stabilized by hydrogen bonding through the D-ring galloyl ester hydroxyl groups on the outside. The 3-gallate ester substitution was shown to increase bond energy between flavan-3-ols and β-cyclodextrin, and a similar interaction mechanism was proposed [26]. Interestingly, such high EGCG level increased digestibility of high amylose starch [24]. Based on the overwhelming evidence from

Figure 1



Structures of some of the polyphenols most commonly reacted with starch.

protein studies, there is no reason to believe carbohydrates can interact with monomeric polyphenols in ways that can be practically manipulated to reduce starch digestibility. Thus emerging studies show limited practical effect of monomeric polyphenols on starch digestibility *in vitro* and *in vivo* [21••,24,27].

Polymeric polyphenols (tannins)

Like with proteins, evidence shows that polyphenol interaction with carbohydrates is highly dependent on the MW of the polyphenols [19,23,26], the hydrophilicity of the polyphenol [26], and the structure of the carbohydrate [19,28••]. Tannins tend to be more hydrophobic, and have an abundance of hydroxyl groups in close proximity that are likely to strengthen their interaction with carbohydrates through H-bonding. Supporting the fact that interaction mechanisms of the tannins with carbohydrates are largely similar to proteins is the observation that pectin, a polysaccharide with an open 'egg-box' structure with hydrophobic pockets binds far more