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Review

Interactions between polyphenols and polysaccharides: Mechanisms and consequences in food processing and digestion

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ABSTRACT

Background: Interactions between intracellular polyphenols and **plant cell-walls** have received little attention, due to analytical limitations. It was difficult until recently to analyse the most implicated polyphenols, which are **proanthocyanidins** (aka condensed tannins), and because these weak interactions were too low for quantification. They are becoming recognized as a factor to understand extractability, functional and health effects of polyphenols.

Scope and approach: New approaches that have been used since the turn of the century are binding isotherms and isothermal titration calorimetry. They allow to investigate specifically these interactions, quantify the affinities between cell-walls and polyphenols as well as the impact of fruit maturation or processing, and the consequences on the finished beverages and food. This review will highlight results on this topic since 2001.

Key findings and conclusions: The most common polyphenols are phenolic acids and oligo or polymeric flavanols (proanthocyanidins), located inside the vacuole in intact plant cells. The proanthocyanidins bind spontaneously to the plant cell-wall polysaccharides through plant tissue disruption, for example during grinding, mastication or thermal treatments, etc. The highest affinity is observed with **pectins**, which may help explain some of the effects of maturation on polyphenol extractability, e.g. in wine making. Presence of proanthocyanidins together with the cell-walls in the lower gut further impacts on the production of colonic metabolites. This has profound consequences on the **extractability** and **bioavailability** of the polyphenols, on the functional characteristics of extracted polysaccharides, and on the fermentation kinetics of dietary fibers and polyphenols.

1. Introduction

In intact plant tissues, cell-walls, polyphenols and polyphenoloxidase (PPO) are present in distinct compartments. When cells are ruptured, e.g. by grinding and pressing, these three elements come in contact. Polyphenols react with cell-wall polysaccharides and can be oxidised by PPO. Winemakers, those who treat external timber with creosote, or laboratory workers using any form of chromatography all know this. The literature however when we started working on this topic in 1999 was sparse and disperse, in contrast to the abundance of data for protein/polyphenol interactions, concentrated on tannin and astringency perception. Three mechanisms can be jointly responsible for formation of polyphenol – cell-walls complexes. The first mechanism is non-covalent and consists in the adsorption of native and oxidised polyphenols to the cell-wall matrix, which will be detailed below. Two distinct mechanisms might lead to formation of covalent bonds, by reaction with cell wall polymers of polyphenols activated either (mechanism 2) by oxidation i.e. as quinones, (resulting primarily from action of polyphenoloxidase) or (mechanism 3) as carbocations, resulting from proanthocyanidin cleavage under acidic conditions, (Beart, Lilley, & Haslam, 1985). The developments in polyphenol analysis and purification allowed to set up simple systems that can be used to quantify these interactions, to modify the conditions and investigate structure/affinity relationships for polyphenols and for polysaccharides (Le Bourvellec, & Renard, 2005; Le Bourvellec, Bouchet & Renard, 2005; Le Bourvellec, Guyot & Renard, 2004a; Le Bourvellec et al., 2013; Renard, Baron, Guyot, & Drilleau, 2001). These methods and

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similar approaches have been used also to quantify interactions of proanthocyanidins from grape to grape cell-walls, especially from the grape skin (Fournand et al., 2006; Bautista-Ortin, Molero, Marin, Ruiz-Garcia, & Gomez-Plaza, 2015; Bindon, & Kennedy, 2011, Bindon, Basic & Kennedy, 2012, Bindon, Madami, Pendleton, Smith & Kennedy, 2014). More recently physical methods such as isothermal titration calorimetry were used to gain insight in the mechanisms (Le Bourvellec, Watrelot, Ginies, Imberty, & Renard, 2012; Watrelot, Le Bourvellec, Imberty, & Renard, 2013, 2014). In the last few years, new topics were (1) the impact of thermal treatments (Le Bourvellec et al., 2011; 2013), with formation of covalent adducts between polyphenols and cell-walls, and (2) consequences, both technological and for polyphenol bioavailability.

Polyphenols are for the most part present in cell vacuoles. The most studied models for polyphenol – polysaccharide interactions are apples and grapes, both of which are rich in condensed tannins, chemically identified as proanthocyanidins. Apple and pear fruits have both high concentrations of polyphenols (up to 7 g/kg fresh weight in the parenchyma of ripe fruit) and a relatively simple composition, notably in cider apples and perry pears. Procyanidins (flavan-3-ol oligomers and polymers) composed essentially of (−)-epicatechin are the main class in the fruit flesh of both apple and pear; their degree of polymerization vary between the cultivars and can be very high (>100). The other classes are phenolic acids, mostly chlorogenic acid, and (in apple only) dihydrochalcones (phloretine glycosides), and monomeric flavan-3-ols, again mainly (−)-epicatechin. All of this makes these two fruit eminently suitable for isolation of well-defined fractions. In grape skin, polyphenols are characterized by the presence of proanthocyanidins of high degree of polymerization (typically mean degree of polymerization of 20–40), including galloylated subunits i.e. presence of both procyanidins and prodelphinidins (Mané et al., 2007), followed by anthocyanins in red varieties, and phenolic acids.

Plant cell-walls are a complex, porous polysaccharidic material. In fruits and vegetables, they can be described by the type I model of Carpita & Gibeaut (1993) as composed of three interpenetrating but not interconnected networks: a cellulose/xyloglucan framework (>500 g/kg dry weight) is embedded in a pectin matrix (250–400 g/kg dw), locked into shape by cross-linked glycoproteins (extensin, about 10 g/kg dw). The cell-wall compositions of apple or grapes are well studied, and correspond well to this model (Renard, Voragen, Thibault, & Pilnik, 1991, 1990;; Vidal, Williams, O'Neil, & Pellerin, 2001; Doco, Williams, Pauly, O'Neill, & Pellerin, 2003; Vicens et al., 2009).

Consequences of polyphenol – polysaccharide interactions are far reaching in food processing. For example, they contribute to the selective extraction of polyphenols from apple to apple juice (Le Bourvellec, Le Quéré, & Renard, 2007; Renard et al., 2011), and even more important from grape to must, as has been clearly shown by Bindon, Kennedy or Gomez-Plaza's works (e.g. Bautista-Ortin et al., 2015; Bindon, Smith, & Kennedy, 2010b, 2010a; Revelette, Barak, & Kennedy, 2014; Ruiz-Garcia, Smith, & Bindon, 2014). They also result in the major part of the so-called "unextractable polyphenols" (Perez-Jimenez, Diaz-Rubio, & Sura-Calixto, 2013) or formation of pomaces, where cell-walls and (oxidised) polyphenols form a single material, with antioxidant capacity but also difficult re-extraction of the polyphenols and colours which may be detrimental for their valorisation as dietary fibers. They also modify the extractability of the cell-wall polymers (Le Bourvellec, Guyot, & Renard, 2009), decrease their enzyme susceptibility and affect their fermentescibility (Aura et al., 2013; Bazzocco et al., 2008). This has also nutritional impacts: polyphenol - cell-wall interactions limit bioavailability of polyphenols, but they may contribute to the formation of bioactive phenolic metabolites in the gut.

Main results on mechanisms, affinities, and consequences of polyphenol (primarily procyanidins) – cell-wall interactions will be presented.

2. Initial observations

2.1. In wine

Most of the major solutes present in the grape berry at harvest contribute to wine composition in proportion to their amount in the fruit. However Hazak, Harbertson, Adams, Ho, and Bin Han (2005) found that only a fraction of the tannin present in berries was extracted during winemaking. Studies on the extraction of skin proanthocyanidins in model hydroalcoholic solution have shown that the extraction is incomplete, while only 23% of available skin proanthocyanidins recovered. The structural features of extracted and non-extracted proanthocyanidins in terms of composition and mean degree of polymerization (mDP) were quite different. Extracted proanthocyanidins had a lower mDP, while non-extracted proanthocyanidins had both higher mDP and subunit galloylation percentage (Fournand et al., 2006). Some of the non-extracted tannins were tightly bound to the insoluble matrix of the grape berry. Winemaking process also influences proanthocyanidins extraction from skin and seed grapes. An increase of soluble solids and a decrease of the rate of proanthocyanidins extraction were observed with a reduction in grape berry crushing during fermentation (Cerpa-Calderon & Kennedy, 2008). It was suggested that the extraction of phenolic compounds was similar with a diffusion-controlled process influenced by temperature, cell permeability, ethanol concentration. During maceration, the application of pectin-degrading enzymes enhances the degradation of pectic fractions from grape cell-walls and leads to an increase of proanthocyanidins extraction (Ducasse et al., 2010). As maceration duration increases, concentration of (−)-epicatechin-3-*O*-gallate subunits (present in higher proportion in seed proanthocyanidins) increased and (−)-epigallocatechin subunit (from skin) decreased, as well as proanthocyanidins molecular size (Yacco, Watrelot, & Kennedy, 2016). This suggested that seed proanthocyanidin extraction increased with the time of maceration but might also be explained by binding of the proanthocyanidins to yeasts or grape biomass during fining on lees (Rodrigues, Ricardo-Da-Silva, Lucas, & Laureano, 2013). These findings have significant implications for wine production and have the potential to explain the discrepancies often observed between total proanthocyanidin concentration in grape tissues and the quantity of proanthocyanidins in wine (Fournand et al., 2006). In fact, the quantities found in wine are frequently lower than expected and show large differences depending on variety (Busse-Valverde, Bautista-Ortin, Gomez-Plaza, Fernandez-Fernandez, & Gil-Nunoz, 2012; 2010).

2.2. In apple juice

A similar phenomenon has also been observed to occur during apple juice processing and cider production. Studies, carried out at the Unité de Recherches Cidricoles, have highlighted a discrepancy, both quantitative and qualitative, between procyanidin concentrations in the apples and juices (Guyot, Marnet, Sanoner, & Drilleau, 2001, 2003) (Fig. 1). Although in apples the main polyphenol class is that of procyanidins, in apple juice phenolic acids become much more important. This was especially obvious for apples of Guillevic (GU) variety, containing primarily procyanidins of high degree of polymerization (DPn of 63) (Renard et al., 2011) (Fig. 1). Apple cells are disrupted during crushing and pressing steps to produce apple juice. Apple procyanidins can be selectively