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Polyphenols and polysaccharides are located in two distinct compartments in vivo: vacuoles and cell walls respectively. When cells are ruptured during chewing for example, these compounds bind together, which limits bioaccessibility of polyphenols and extractability of polysaccharides. It has already been shown that procyanidins (condensed tannins) interact with polysaccharides and that the affinity of procyanidins for pectins is higher than for hemicelluloses [1]. The pectins - procyanidins adsorption mechanism involves hydrogen bonds and hydrophobic interactions [2]. We present here a characterization by microcalorimetry and phase diagram of interactions between procyanidins and pectins, and the impact of the structure of both pectins and procyanidins.

Procyanidins with intermediate and high degrees of polymerization (DP9 and 30) were extracted from freeze-dried pulps of cider apple cultivars (cv. "Marie Ménard" and "Avrolles" respectively) as described in [1]. Rhamnogalacturonans (RG) and homogalacturonans (HG) of low (30) and high (70) degrees of methylation were prepared from commercial apple pectin as described in [3]. Different hairy regions with a variation of neutral sugars composition were extracted from apple pomace (AHR), or from sugar beet pulp (SBHR) or from apple, pear and onion (MHRa, MHRp and MHRo). Those MHRs (Modified Hairy Regions) fractions were a kind gift from Dr Henk Schols. Pectic fractions (3.75 mmol/L galacturonic acid equivalent), dissolved in citrate/phosphate buffer pH 3.8 were titrated by procyanidins (7.5 mmol/L epicatechin equivalent) in VP-ITC instrument (Microcal®, GE Healtcare). After precipitation, supernatants of procyanidins in buffer and pectins in procyanidins solution were analyzed by HPLC-DAD after thioacidolysis and HPSEC.

Microcalorimetry demonstrated that association between procyanidins and commercial pectins, HG, RG, AHR and HR-H were driven by entropy indicating that hydrophobic interactions are implicated. However an unfavorable entropy contribution was obtained between procyanidins and MHRp and MHRo suggesting association via hydrogen bonds. Procyanidins DP9 associated with commercial pectins and hairy regions with comparable affinity constant (in the order of $10^3$ $M^{-1}$) but not with HG. Procyanidins of DP30 interacted with all pectic regions. The higher the degree of methylation of HG, the higher the affinity. Hairy regions (AHR and MHRp rich in arabinose, SBHR and MHRo rich in galactose) showed different affinity constants (574 $M^{-1}$ for AHR and 875 $M^{-1}$ for MHRp against 5390 $M^{-1}$ for SBHR). The supernatant contained procyanidins with a much decreased DP ($\Delta DP = -20.5$) after interaction with AHR, while DP increased ($\Delta DP$ of 5.8) with SBHR. The largest procyanidins preferentially aggregated with AHR, while the smallest aggregated with SBHR.

The structure and conformation of both pectins and procyanidins influenced the interactions. Others methods such as surface plasmon resonance will be used to determine kinetic of association and dissociation of procyanidins/pectins complexes.

Keywords : Polysaccharides, condensed tannins, association, ITC.

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