

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

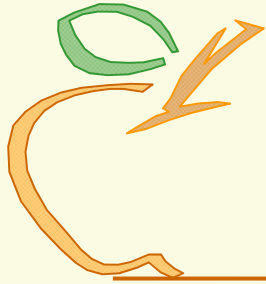
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INRA, Université d'Avignon et des Pays du Vaucluse

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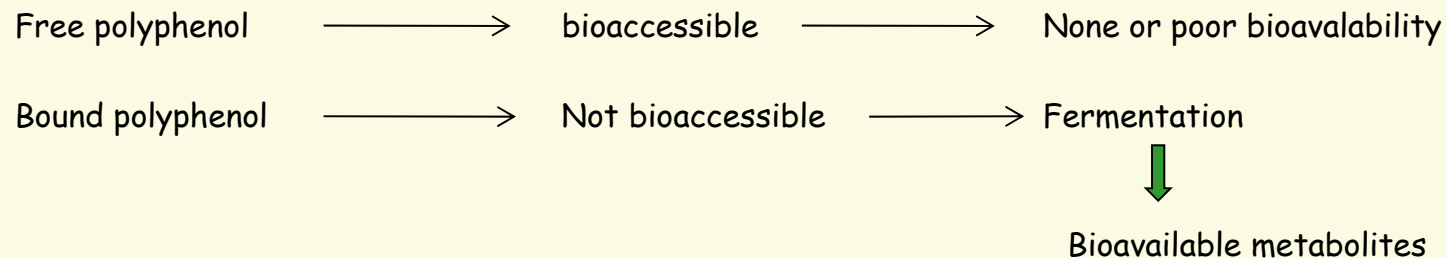
Why attempt to understand these interactions?

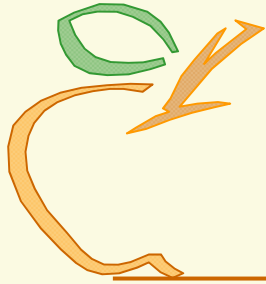
↳ Extraction of polyphenols

- Transfer from fruit to juice (wine, cider) or extraction to tea, coffee, chocolate...
- Major impact on colour and bitterness, astringency, « body »
- Need to understand the mechanisms for extraction vs. retention

↳ Health effects:

- Antioxidants: prevention of oxidation in the stomach
- Specific actions - interaction with receptors
 - **Must be bioavailable - phenols or metabolites**
 - **Relevance of colonic fermentation metabolites**





↖ Introduction

- Polyphenols & cell walls

↖ Quantifying the interactions

- Binding isotherms

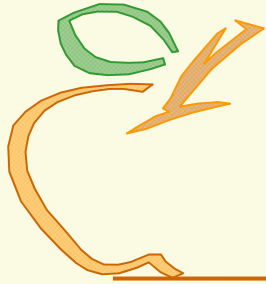
↖ An example of consequences

- Modification of cider composition

↖ Conclusion & perspectives

- Colonic fermentation

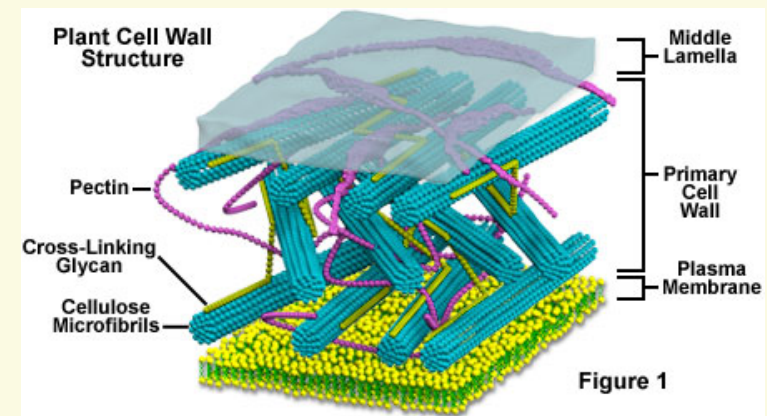
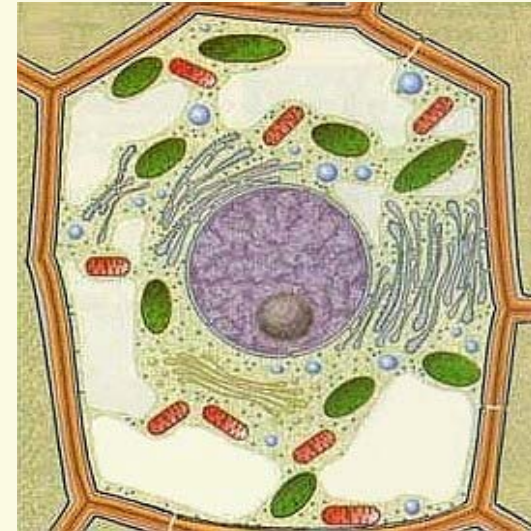


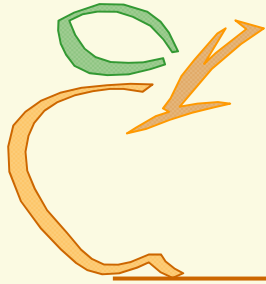


Cell walls

- ↳ Surround the plant cells
- ↳ Structural in the cell walls
 - Protection and structure

- ↳ A complex assembly of macromolecules
 - Mainly polysaccharides
 - Cellulose microfibrils
 - Pectins
 - Hemicellulose
 - Minor amounts of glycoproteins
 - Polyphenols (FeA, lignin...)

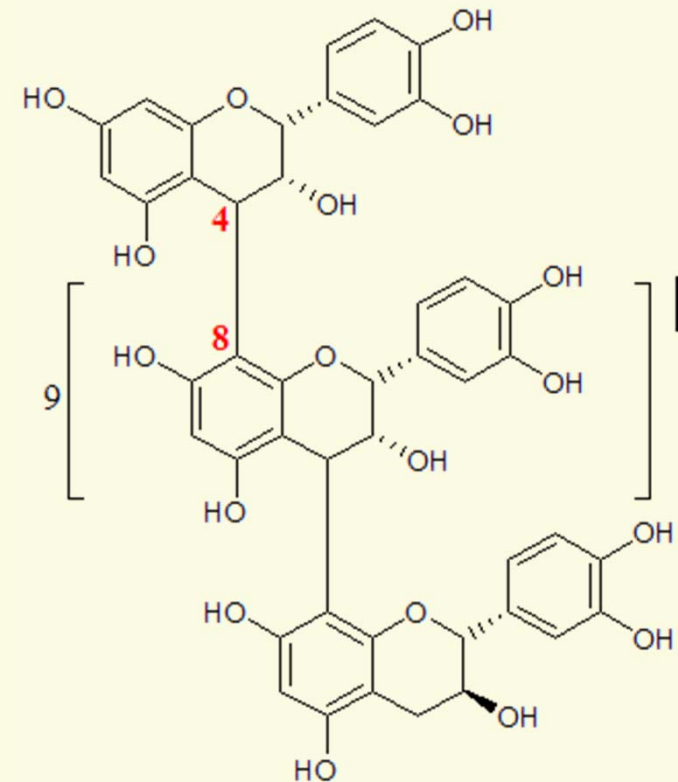


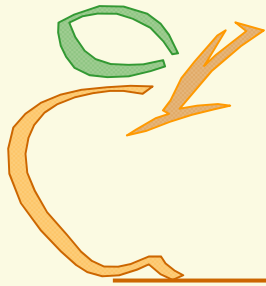


Proanthocyanidins

↳ Proanthocyanidins = « condensed tannins »

- Flavanol oligo and polymers
- Intracellular
- Characterized by:
 - Constitutive unit
 - Interflavanol binding
 - Degree of polymerization
- Abundant in apple and pear:
procyanidins
 - Epicatechin (catechin)
 - B-type, primarily 4-8 binding
 - DP usually 3-8, up to a 100
 - Concentrations up to 5 g/ kg





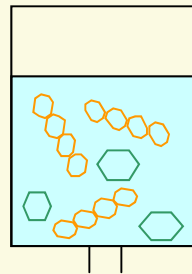
Quantifying interactions by binding isotherms

Model suspensions

Purified procyanidins



Cell walls
Devoid of phenolics



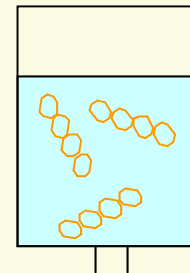
1-Incubation

2-Filtration



Bound procyanidins

- Freeze-dry and thiolysis

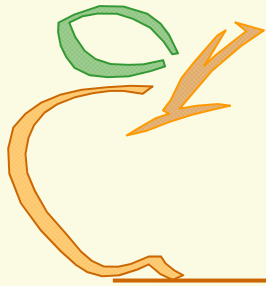


Free procyanidins

- OD 280 nm
- Freeze-dry and thiolysis

What can be compared:

- Physico-chemical conditions (pH, T°, ionic strength, solvent...)
- Proanthocyanidins structure and size
- Cell walls: origin and pretreatment, drying...



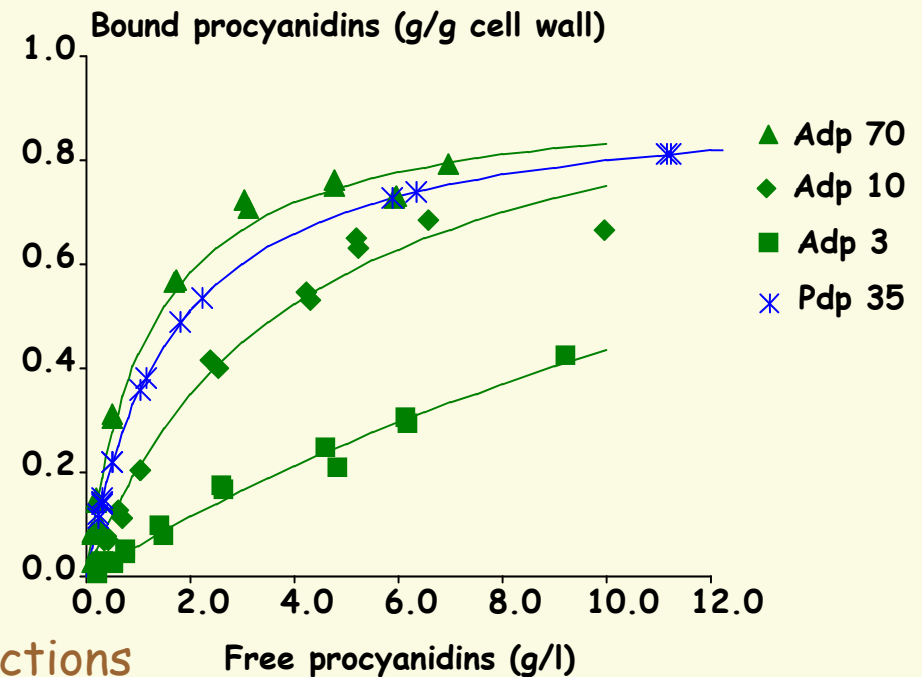
Procyanidins adsorb spontaneously to cell walls

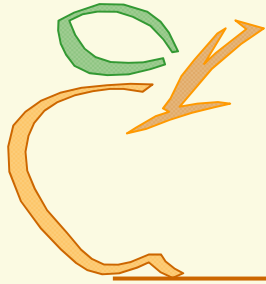
Binding isotherms

$$PPf = \frac{N_{\max} \cdot K_L \cdot [PP_L]}{1 + K_L \cdot [PP_L]}$$

Binding

- H-bonds and hydrophobic interactions
- Totally reversible using appropriate solvent (not water!)
- Binding increases with DP of procyanidins
- Amounts adsorbed vary with initial concentrations, cell wall mode of production and physico-chemical conditions
- High affinity for pectins, no impact of protein





Modifying cell wall affinity for procyanidins

↳ Extraction of pectins

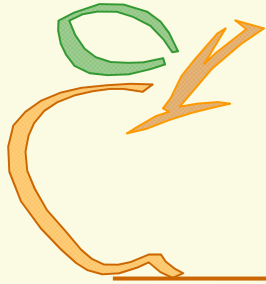
- Chemical extraction or heat-treatment
- Decreased affinity

↳ Modifying surface properties by drying

- Mild drying (solvent-exchange) vs harsh drying

- Increase specific area and decrease porosity
- Decrease affinity and increase max absorption

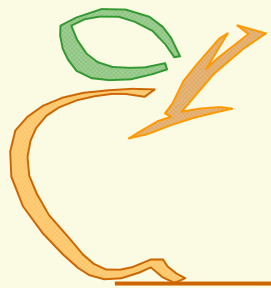




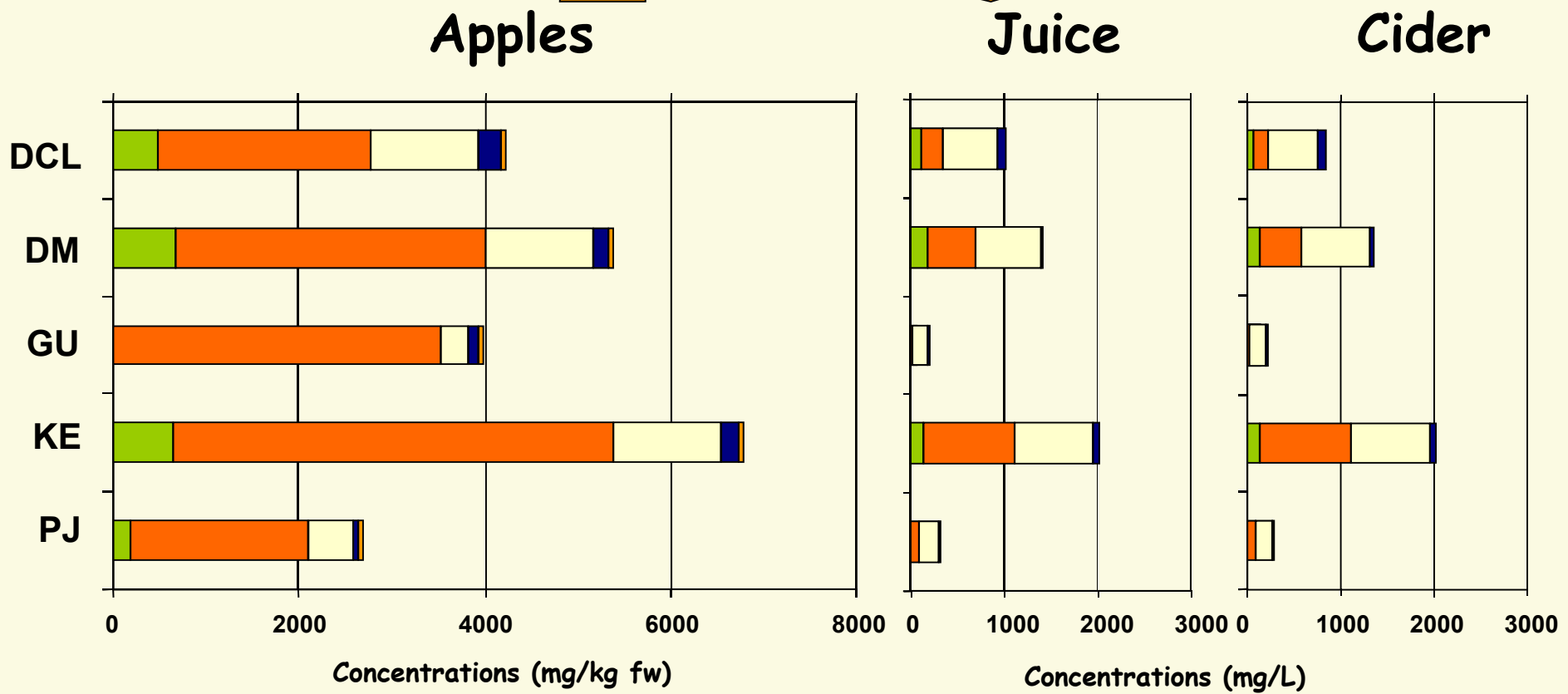
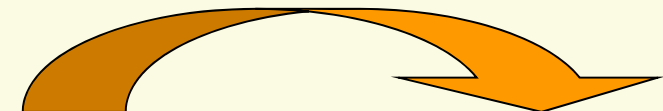
Polyphenols and cider

- ↳ **Organoleptic characters**
 - Colour, bitterness and astringency
- ↳ **Evolution of phenolic composition during processing**
 - Polyphenol extraction from the fruit:
 - *Modification of structures (oxidation)*
- ↳ **Experiments with isolated procyanidins indicate an effect of temperature**
 - Extraction at different temperatures
 - Apples with different average degrees of polymerisation
 - Different levels of oxidation :
 - No oxidation for impact of non-covalent interaction



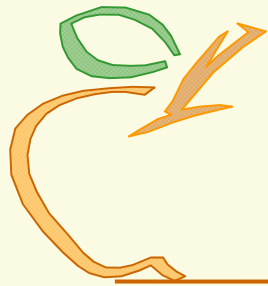


Phenolic composition changes from apple to juice



- Monomeric catechins
- Procyanidins
- Hydroxycinnamic acids
- Dihydrochalcones
- Flavonols





Extraction of procyanidins does vary with pressing temperature

Experiment:

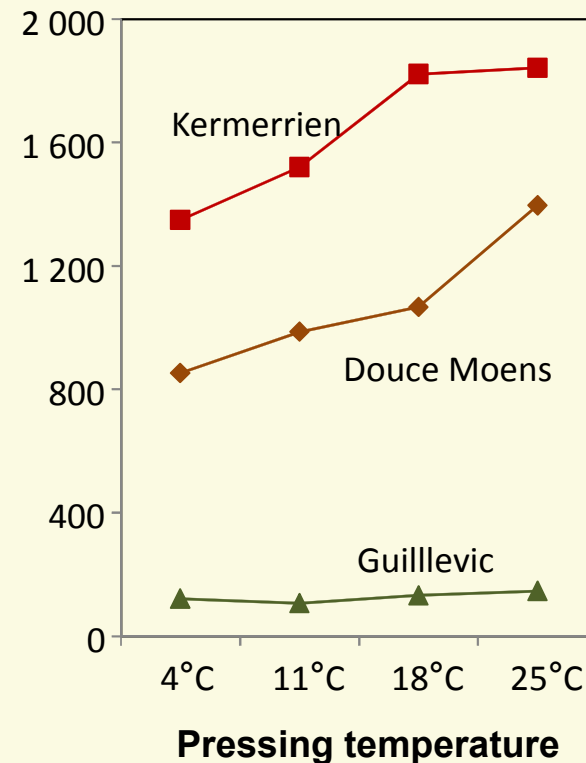


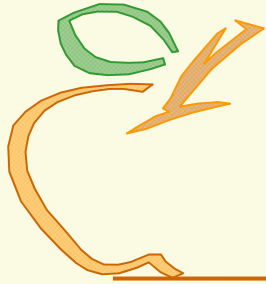
- Three varieties
 - DM: DP = 3, GU: DP = 63, KE: DP = 3.5
- Four temperatures
 - 4°C, 11°C, 18°C, 25°C
- Inerted press and juice with NaF

Extraction variation with temperature is validated

The model designed from experiments with isolated cell walls and procyanidins gives satisfactory previsions

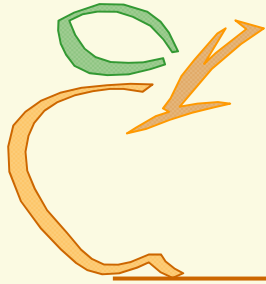
Concentration (mg/L)





Conclusions and perspectives

- ↖ **Procyanidins bind spontaneously to cell walls**
 - This is very common artefact:
 - Procyanidins in all Rosaceae...
 - And can be an artefact in cell wall preparation
- ↖ **Consequences**
 - In food processing and for procyanidins health impact
- ↖ **What about heating ?**
 - Evolution of non-covalent adducts ?
 - Formation of covalent adducts ?
- ↖ **Fate of non-covalent adducts in the gut ?**
 - Impact of non-covalent adducts vs procyanidins alone on :
 - Short fatty acid production
 - Procyanidin colonic metabolites production
 - Microbiota



The main contributors

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↳ Pôle Agronomique Ouest

« Cidre et Polyphénols » 2000-2004

↳ FP6 FLAVO and ISAFRUIT



↳ ANR TEMPANTIOX



↳ FP7 DREAM



Thank you for your attention
Looking forward to welcoming you soon at:



2nd Euro-Mediterranean Symposium on Fruit and Vegetable Processing

An integrated view on sustainability and how it can interact with quality, safety and the consumers

Avignon, 4-6 April 2016

For more info:

<https://colloque.inra.fr/fruitvegprocessing2016>

