Colloidal stability and reversible aggregation of oxidized tannins

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Colloidal stability and reversible aggregation of oxidized polyphenols

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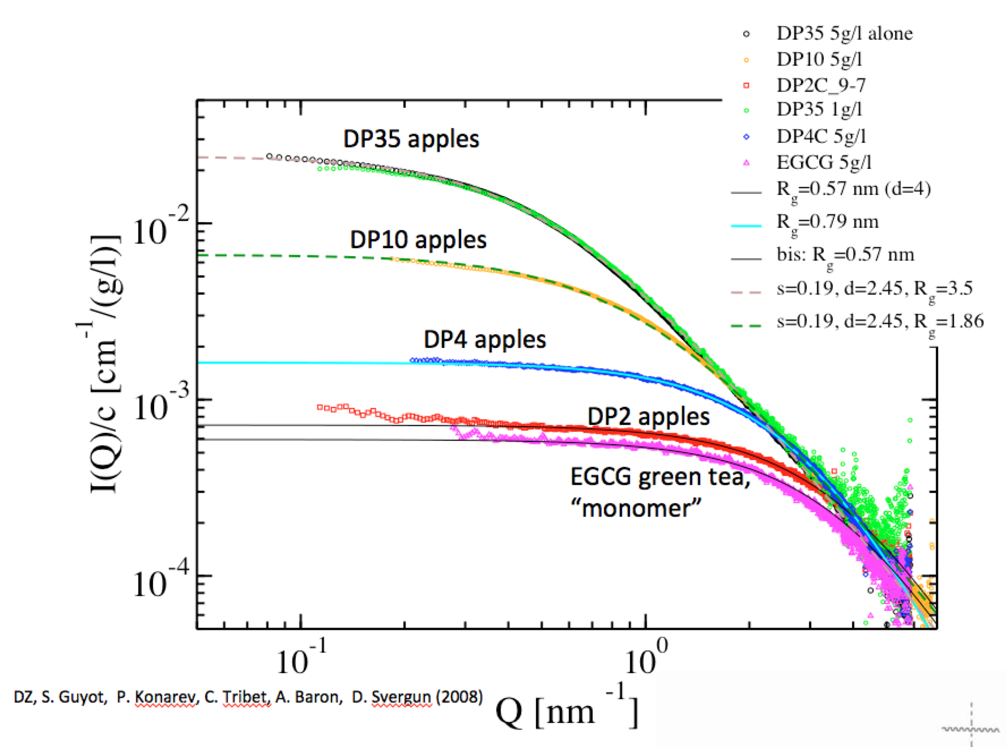
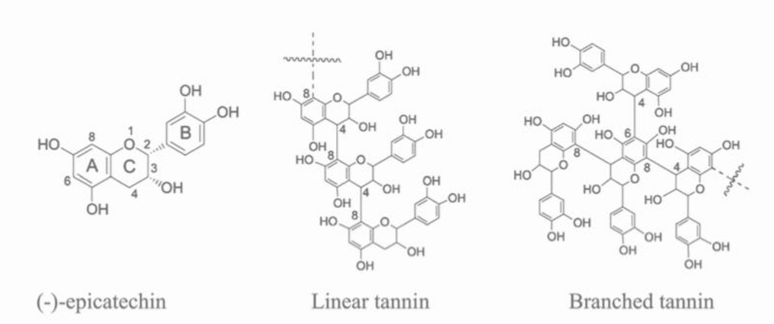
Introduction

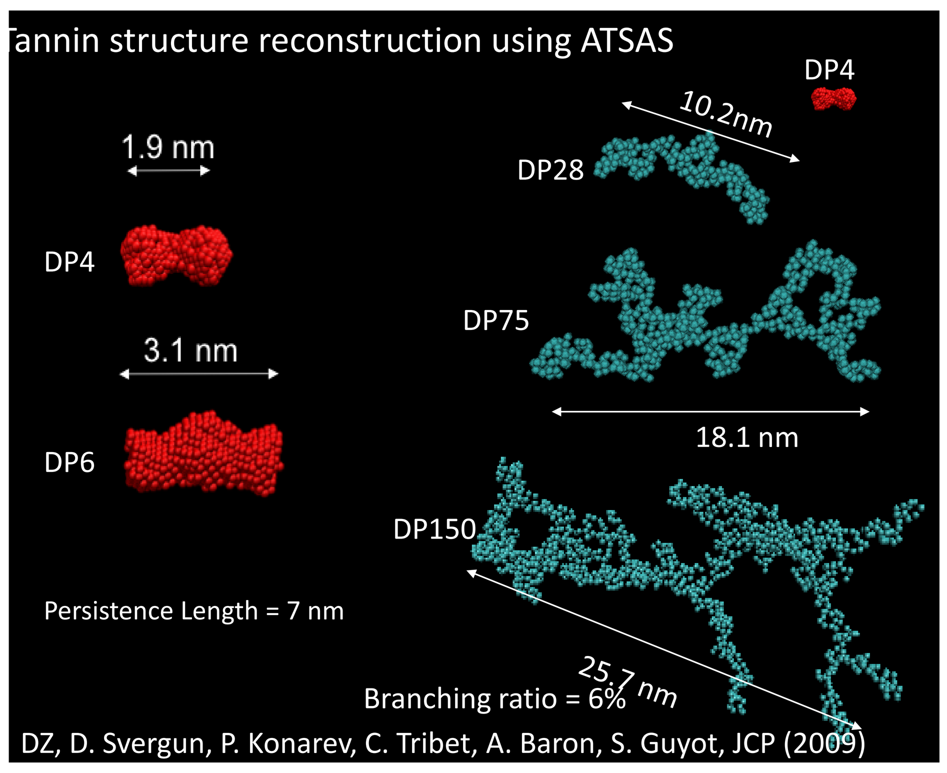
Propensity of tannins to self-aggregate and/or to denaturate proteins determines the colloidal stability of tannin-rich suspensions, which is relevant for their bioavailability and ageing ability, issues of interest in pharmaceutics and food technology. This work focuses on tannins ability to self-associate under oxidative and/or cooling stress in relation to the colloidal stability some alcoholic beverages from apples and of model systems.

SAXS study

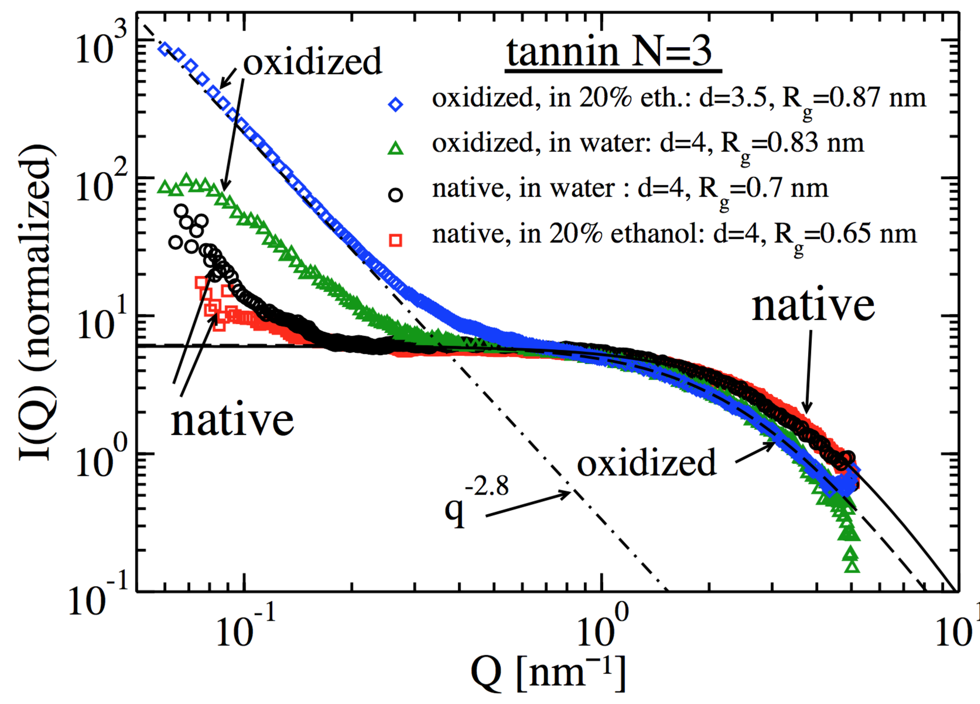
Apple Tannins polymers from Brittany (INRA Rennes) dissolved in water



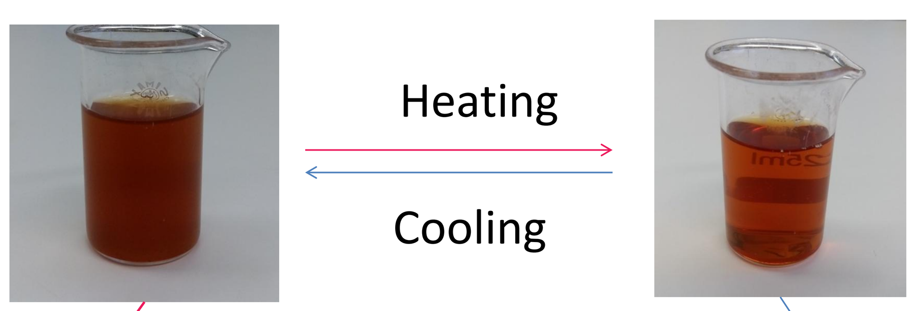




Effects of oxydation on tannin oligomer DP3

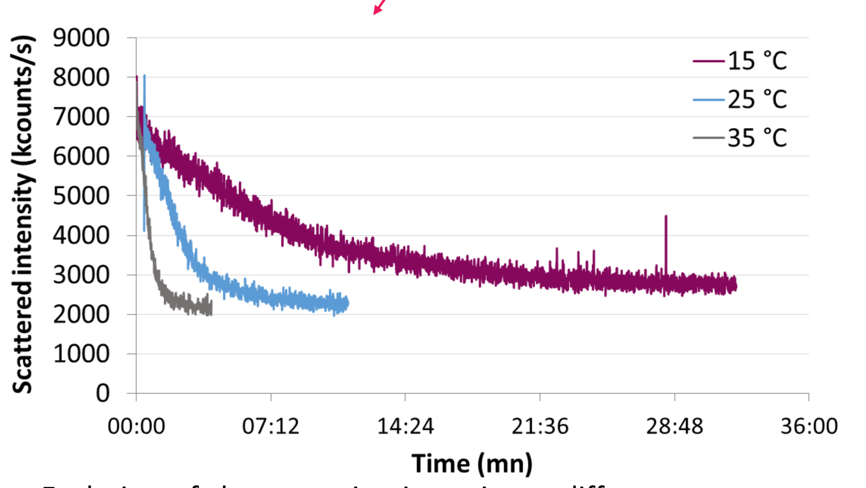


Reversibility of haze in pommeau

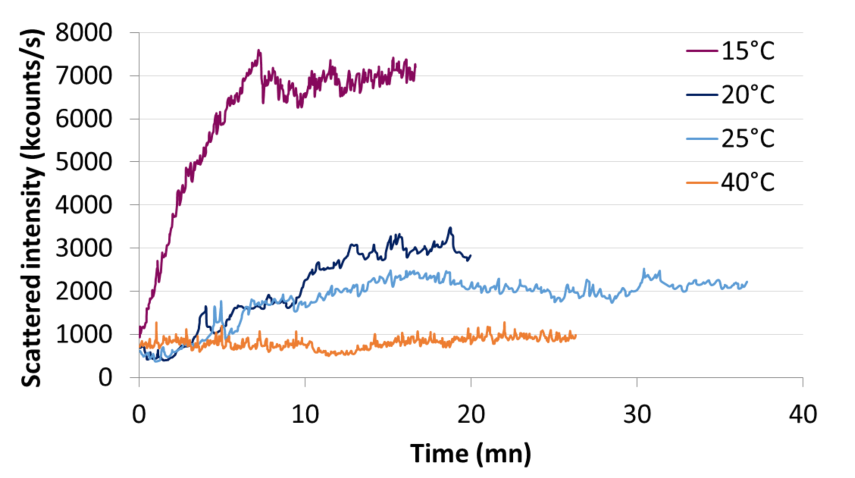


T-jump up: From 4°C up to different temperatures

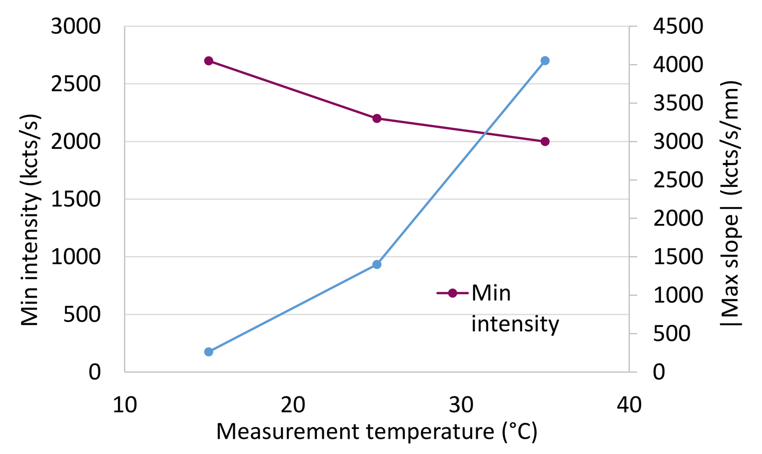
T-jump down: From 65°C down to different temperatures



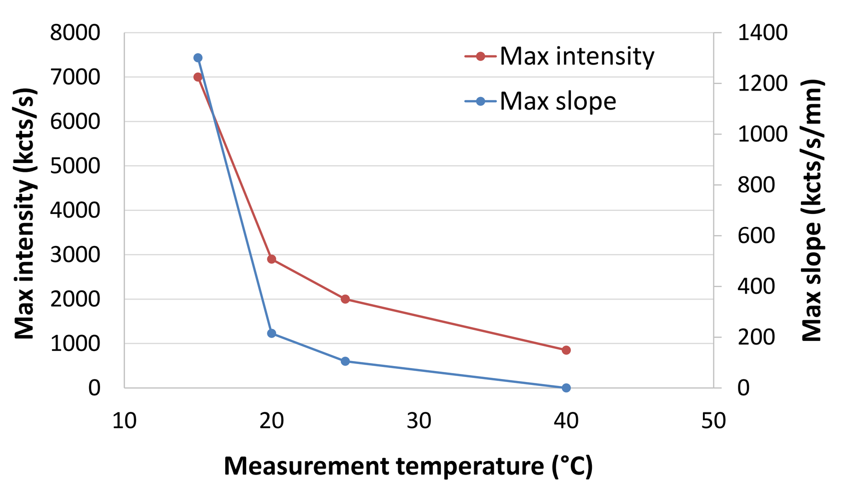
Evolution of the scattering intensity at different temperatures by a pommeau initially at 4 °C.



Evolution of the scattering intensity at different temperatures by a pommeau initially at 65 °C.



Minimum scattering intensity by pommeau after stabilization and absolute value of the maximum slope of the kinetic curve , as function of temperature..



Maximum scattering intensity by pommeau after stabilization and maximum slope of the kinetic curve, as function of temperature.

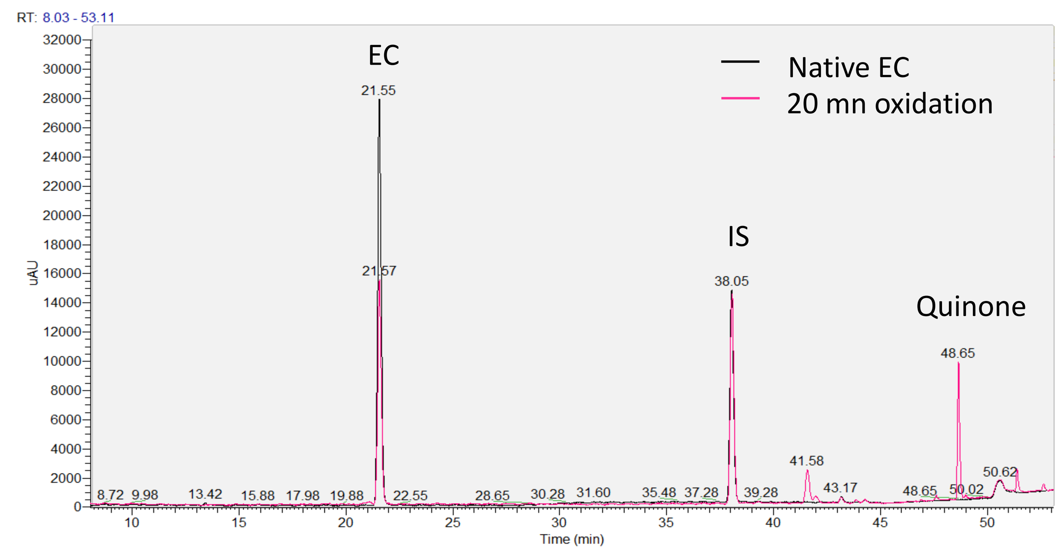
Warming: Mass fraction of remaining aggregates (min. intensity) and fragmentation rate (slope) are both affected by T-jump magnitude.

Cooling: Mass fraction of total aggregates (max. intensity) and aggregation rate (max. slope) are both affected by T-jump magnitude.

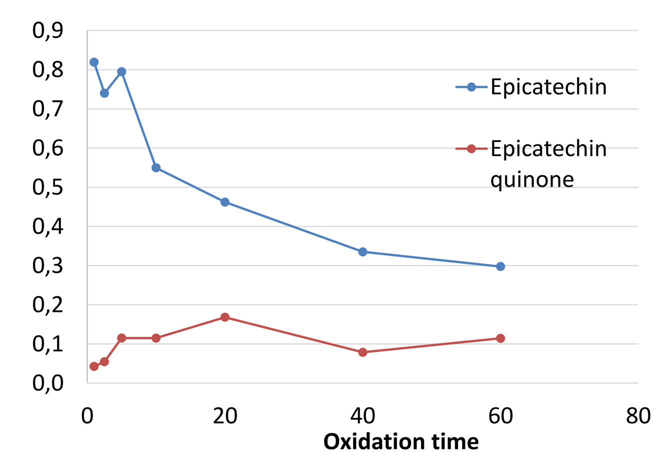
Fractions ? Chemical or physical ?

Aggregation of oxidized epicatechin

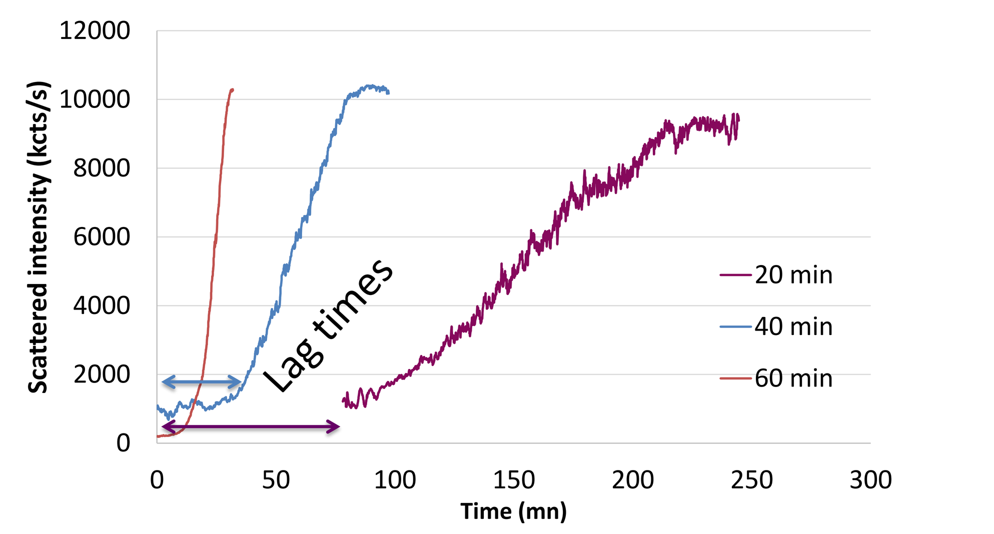
Oxidation of epicatechin was carried out by incubating a 3 g/L epicatechin solution with periodate fixed on anion exchange resin. Different incubation times were tested and the oxidation was assessed by liquid chromatography. Solutions were filtered at the end of oxidation time and observed on DLS, at 25 °C.



Compared chromatograms of (-)-epicatechin before and after a 20 minutes oxidation by periodate. The quinone is the first oxidation product of epicatechin. EC: (-)-epicatechin; IS: Internal Standard.



Evolution of the ratio between epicatechin or quinone and internal standard as a function of oxidation time.

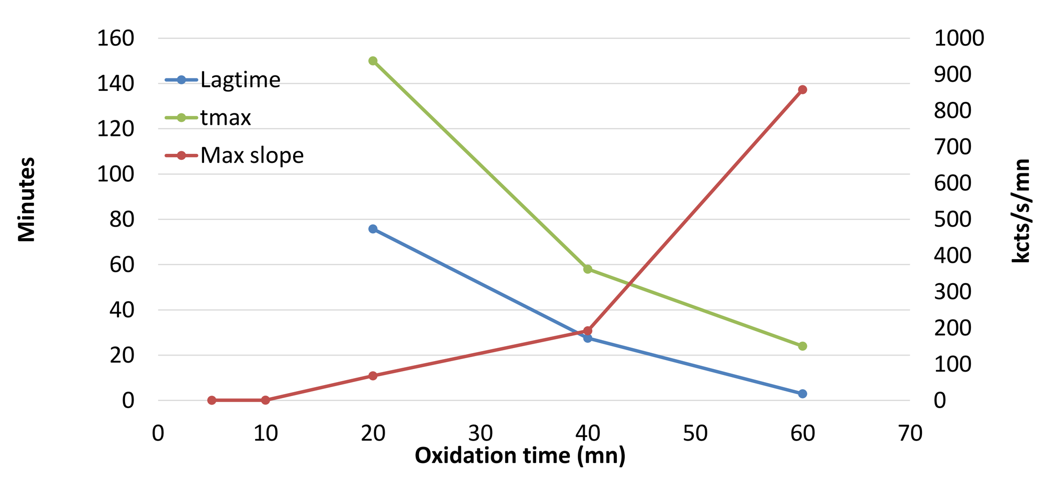


Evolution of the scattering intensity by a solution of epicatechin oxidized from 20 to 60 minutes.

Chemistry vs. Physics:

Lag time :
EC quinones + EC –> oxydized insoluble

Slope, intensity plateau:
Degree of oxydation and quantity of oxidized unsoluble species



Lag-time, maximum slope and time at the maximum slope of the kinetic curve shown above , as a function of the oxidation time.

Conclusion:

Self-aggregation of oxidized tannins was studied using SAXS, DLS and LC-MS. Aggregates formed at low temperature are reversibly re-dispersed by heating. The self-assocition kinetics is determined by the oxidation time and the T-jump. In particular, we find that post-oxidation aggregation starts after a lag time which decreases as oxidation time increases.

References
(1) Siebert, K. J. *Adv. Food Nutr. Res.* **2009**, *57*, 53–86.

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