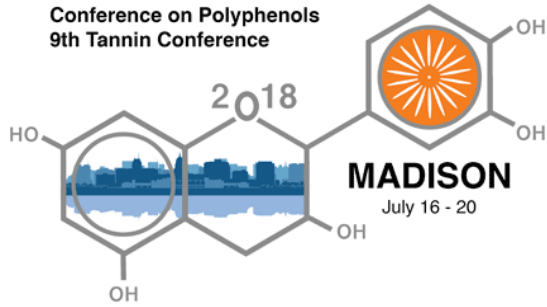


ICP+TC 2018
XXIXth International
Conference on Polyphenols
9th Tannin Conference



Depolymerized Condensed Tannins as Biobased Aromatic Building Blocks

Guillaume Billerach, Laurent Rouméas, Chahinez Aouf,
Eric Dubreucq and Hélène Fulcrand



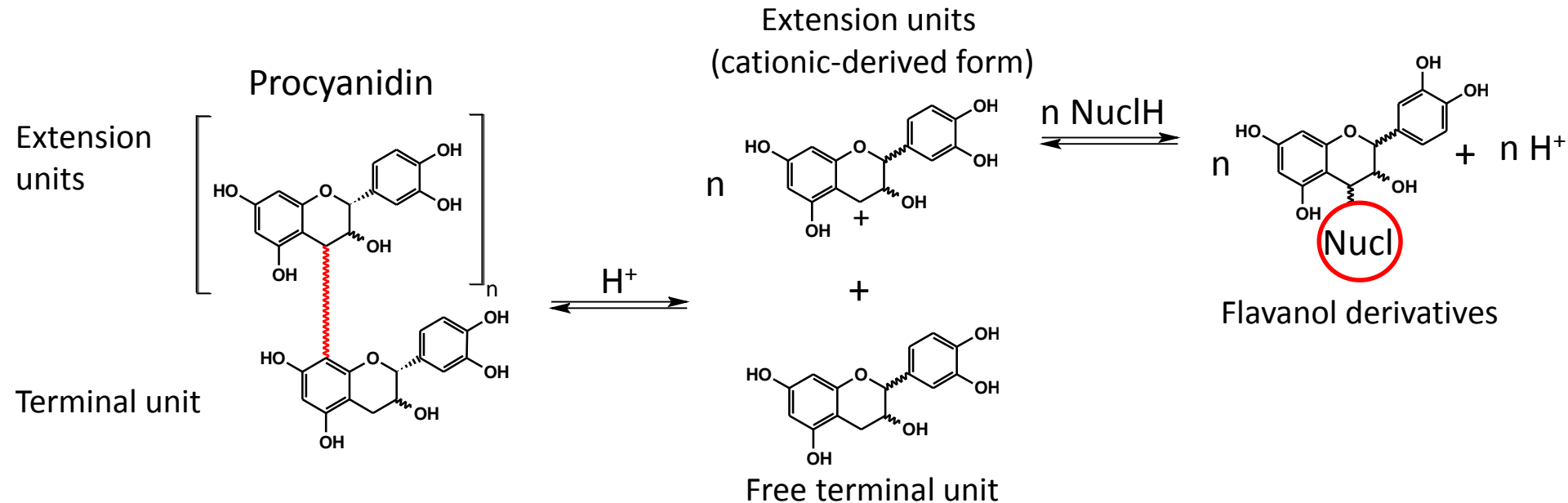
BILLERACH Guillaume
07/17/2018

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 688338



Background

- Condensed tannins are the 2nd most abundant source of aromatics
- Most current industrial uses imply more or less purified plant extracts
- **Depolymerization** enables their **standardization** for applications in speciality chemistry

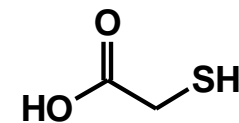


➔ Importance of the **nucleophile** (nature and concentration) to **displace the reaction equilibria**

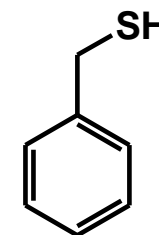
Background

- Many **analytical** depolymerization methods set up by the past, involving different nucleophilic trapping reagents in acidic conditions

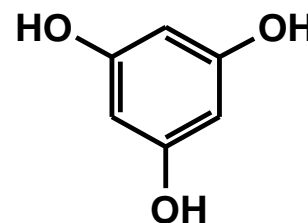
Scientists	Year	Nucleophiles
Bate-Smith	1954	∅
Betts et al.	1967	Thioglycolic acid and other thiols
Thompson et al.	1972	Benzylmercaptan
Brown and Shaw	1974	Benzenethiol, benzene sulfinic acid
Fletcher et al.	1976	Phloroglucinol, 2,4,6-trihydroxytoluene
Tanaka et al.	1994	2-Mercaptoethanol
Torres and Selga	2003	Cysteamine hydrochloride



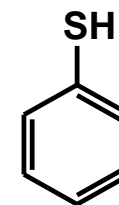
Thioglycolic acid



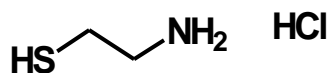
Benzylmercaptan



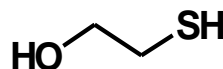
Phloroglucinol



Benzenethiol



Cysteamine hydrochloride

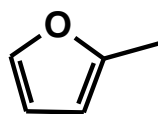
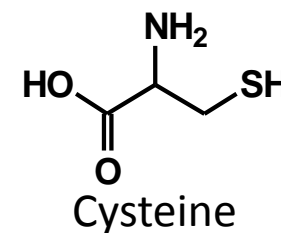
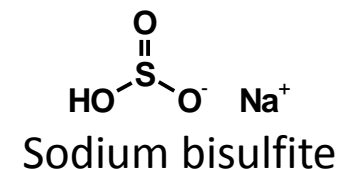


2-Mercaptoethanol

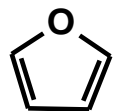
Background

- Other methods have been set up to develop **industrial applications** from depolymerization products of condensed tannins

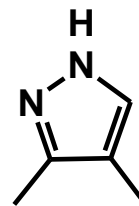
Scientists	Year	Nucleophiles
Foo et al.	1983	Sodium bisulfite
Nonaka et al.	2010	Cysteine, cystin, glutathion
Fu et al.	2010	Pyrrrole and pyrazole derivatives
Rouméas et al.	2014	Furan and derivatives



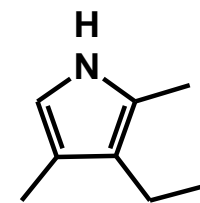
Sylvan



Furan



2,3-Dimethylpyrazole



Kryptopyrrole

- But flavanol derivatives obtained with mercaptans and sodium bisulfite exhibit **low stability in alkaline conditions**

➔ **Not consistent with a use as building blocks**

Objectives of the study

Problematic

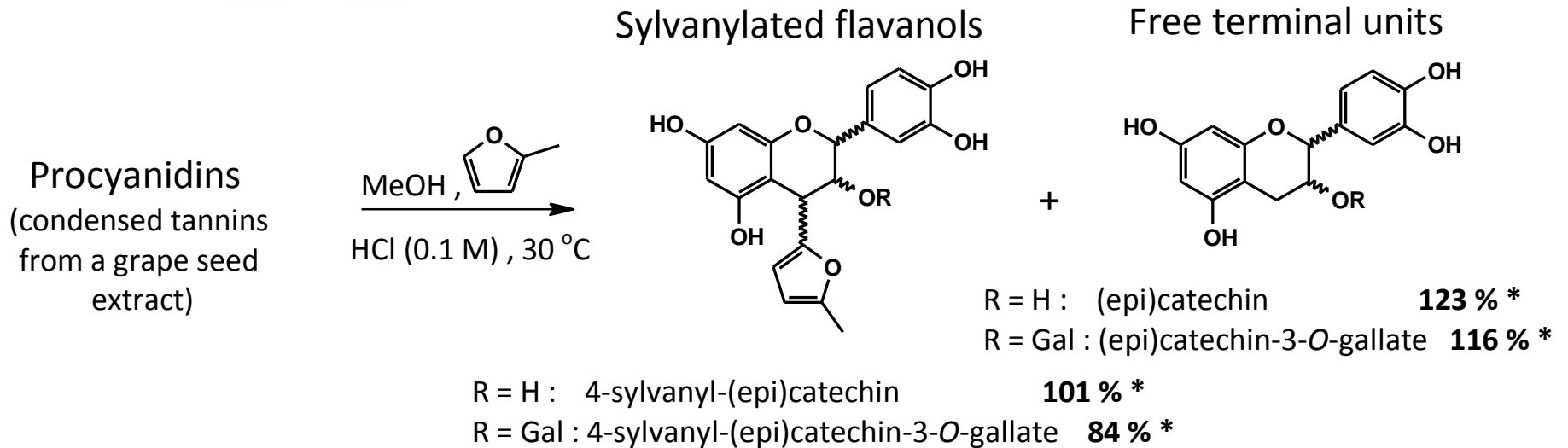
Can furylated flavanols be used to develop a relevant process for the valorization of condensed tannins in materials and speciality chemicals ?

Objectives

- I. Develop a depolymerization process with furan derivatives as nucleophilic trapping reagents
- II. Evaluate the stability of the furylated flavanols obtained and compare them to the thioetherified and phenol flavanols
- III. Identify new applications for the furylated flavanols

I. Production and characterization of furylated flavanols

Production of furylated flavanols



* Yields relative to analytical mercaptolysis

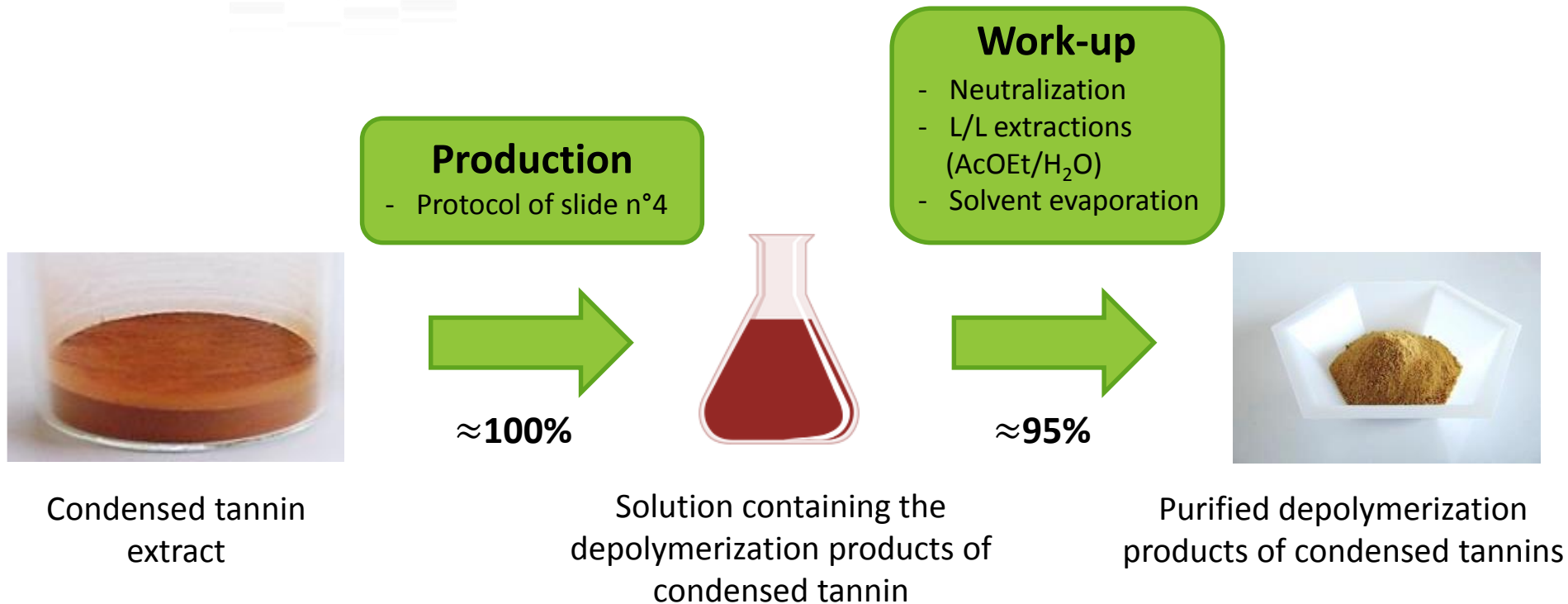
Highlights

- For the first time, procyanidins were **depolymerized with furan derivatives**
- The furylated flavanols obtained can be **entirely biobased**
- This process can be applied on tannin-rich **plant biomass** (tree barks, winery wastes)

Laurent Rouméas et al, *ACS Sustainable Chemistry & Engineering*, **2018**, 6, 1112-1120.
Laurent Rouméas et al, *World patent application*, **2014**, PCT/WO2016020615(A1).

I. Production and characterization of furylated flavanols

Recovery of the furylated flavanols



Identification of the depolymerization products

- Mono- and bi-dimensional NMR
- Mass spectrometry

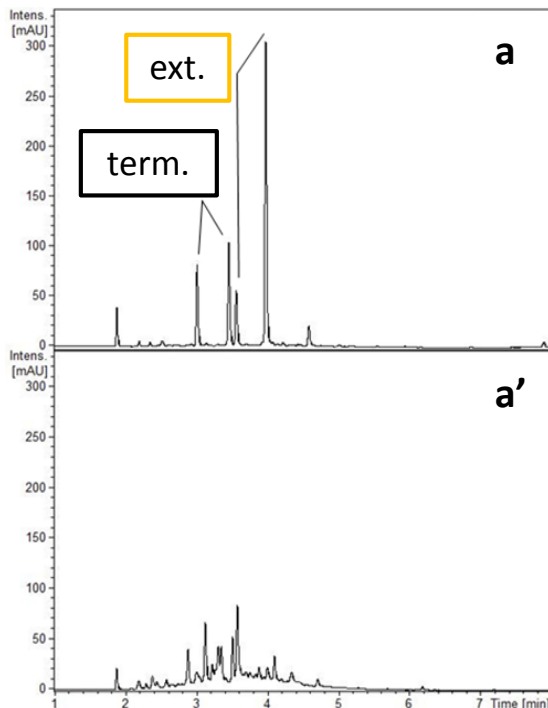
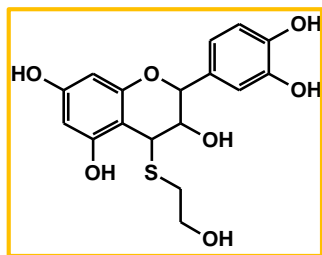
Laurent Rouméas et al, ACS Sustainable Chemistry & Engineering, 2018, 6, 1112-1120.
Laurent Rouméas et al, World patent application, 2014, PCT/WO2016020615(A1).

II. Stability of the furylated flavanols

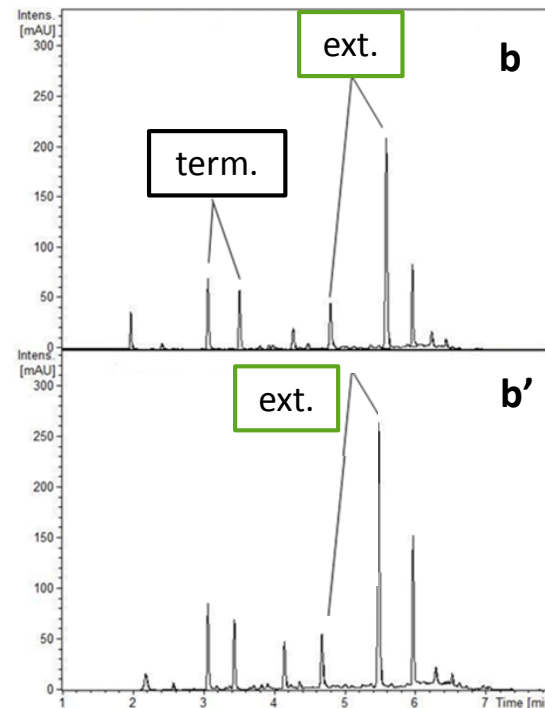
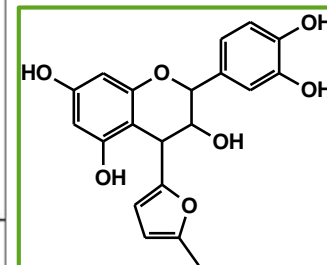
Stability in alkaline conditions

- Thioetherified and silylated flavanols were incubated in sodium borate aqueous buffer for 19 h at room temperature

Thioetherified flavanols



Silylated flavanols



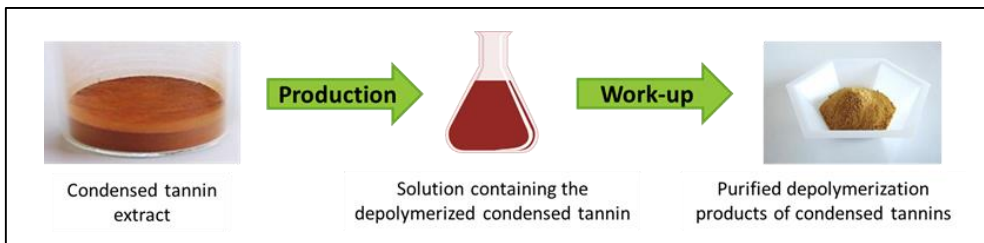
- ➔ The **thioetherified flavanols** were degraded in these conditions
- ➔ The **silylated flavanols** were not altered

Laurent Rouméas et al, ACS Sustainable Chemistry & Engineering, **2018**, 6, 1112-1120.

III. Applications: synthesis of tannin-based materials

Synthesis of epoxy resins

- Sylvanlated flavanols were produced, purified and glycidylated

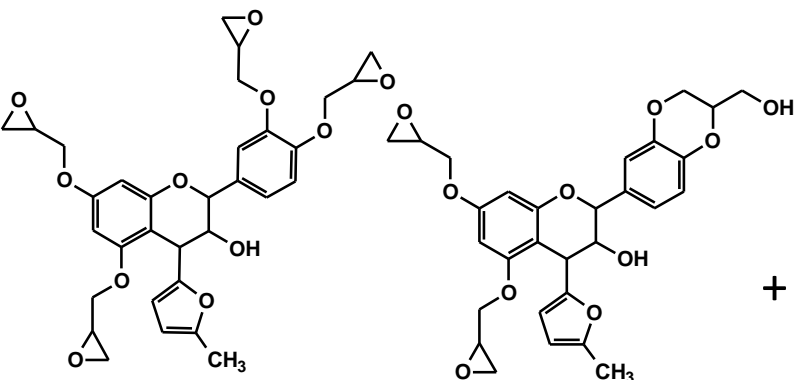


Glycidylation

- Epichlorohydrin
- Alkaline medium
- Work-up: AcOEt/H₂O ext.



Epoxy prepolymer



Main glycidyl-ethers composing the epoxy prepolymer

+

Furfurylamine
(as biobased hardener)

Formulation



Tannin-based epoxy resins

➔ Tannin-based epoxy resins were synthesized

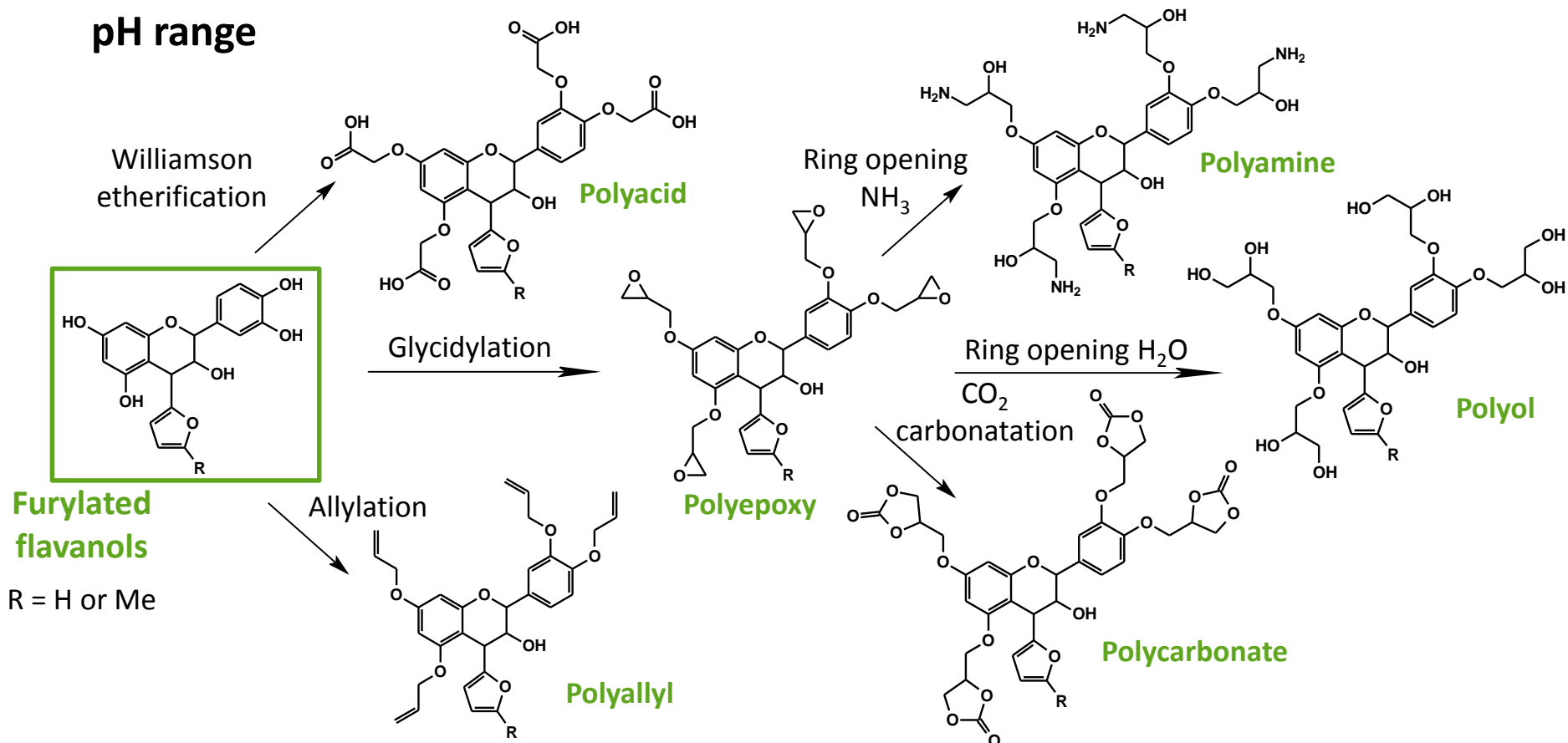
➔ They exhibited similar mechanical properties as commercial epoxy resins

Laurent Rouméas et al, World patent application, 2016, WO2016174334(A1).

III. Applications: synthesis of tannin-based materials

Prospects: Other possible functionalizations

- The stability of the furylated flavanols enable **functionalizations in a broad pH range**



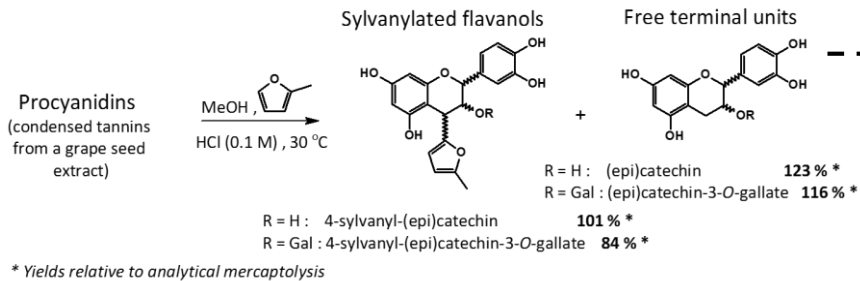
➔ Furylated flavanols appear as **promising biobased aromatic building blocks**

Laurent Rouméas et al, ACS Sustainable Chemistry & Engineering, **2018**, 6, 1112-1120.

Conclusion & Prospects

Production of furylated flavanols

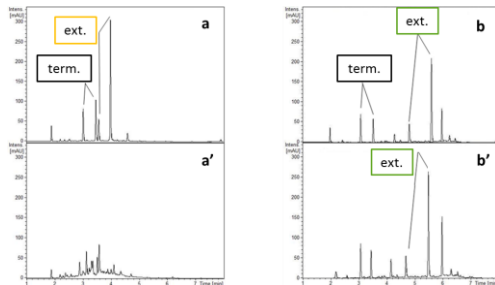
- Development of a depolymerization process of condensed tannins with furan derivatives



➔ Yields were equivalent to the ones of mercaptolysis

Characterization of the stability of the furylated flavanols

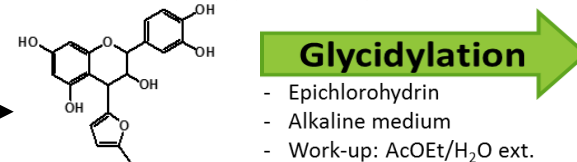
- Stability study in alkaline conditions



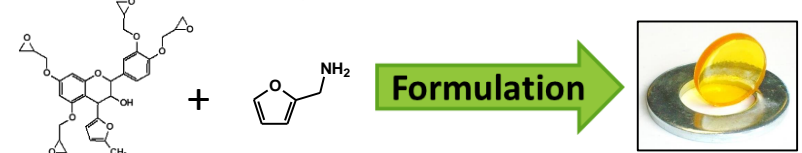
➔ Furylated flavanols are stable with respect to pH

Synthesis of tannin-based materials

- Synthesis of epoxy prepolymer



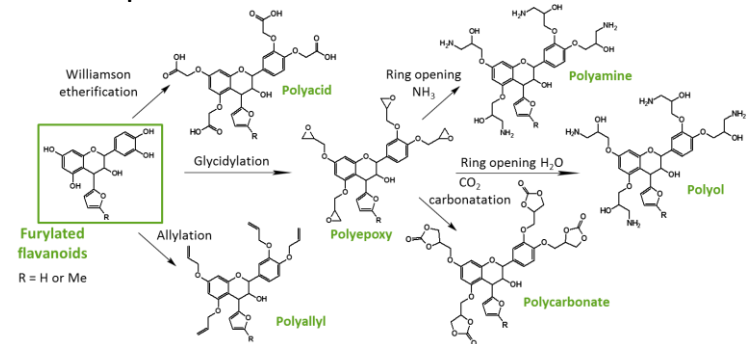
- Formulation of epoxy resins



➔ Tannin-based epoxy resins exhibited good properties

Prospects

- Other possible functionalizations



➔ New biobased phenolic building blocks

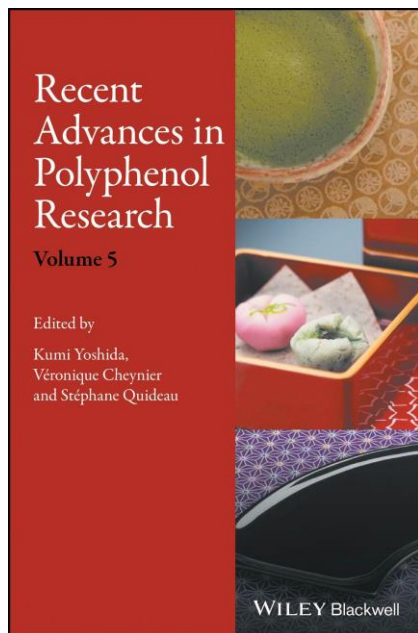


References

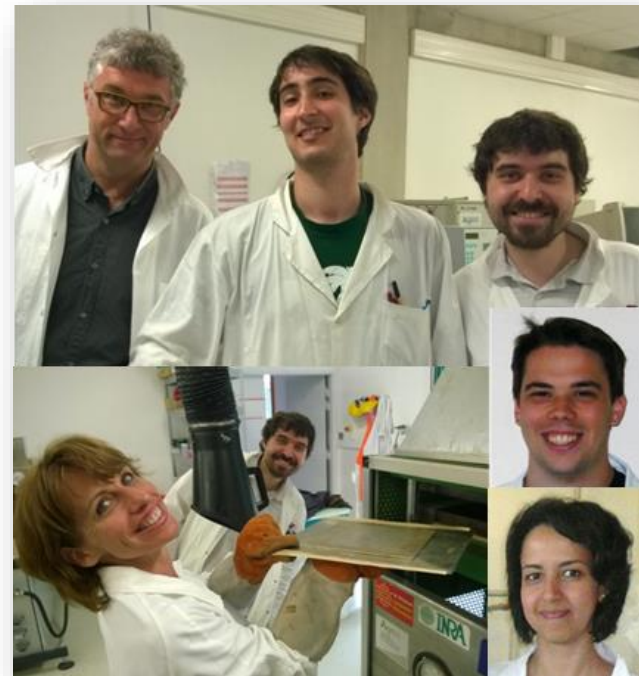
Rouméas, L., Fulcrand, H., Aouf, C. & Dubreucq, E.
Flavonoid derivative compounds and method for preparing same by
depolymerization of condensed tannins. Patent, **2014**, WO2016020615(A1).

Rouméas, L., Fulcrand, H., Aouf, C. & Dubreucq, E.
Biosourced compound having epoxide functions, method for the synthesis of such
a compound, and use thereof for producing epoxy resin. Patent, **2016**,
WO2016174334(A1).

Rouméas, L., Billerach, G., Aouf, C., Dubreucq, É. & Fulcrand, H.
Furylated Flavonoids: Fully Biobased Building Blocks Produced by Condensed
Tannins Depolymerization. *ACS Sustain. Chem. Eng.* **6**, **2018**, 1112–1120.



Recent Advances in Polyphenol Research Vol. 6
Chap. 12. Advances in thermosetting polymers



Thank you for your attention !

