Characterisation of industrial barks for their tannin contents for further green-wood based adhesives applications

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INTRODUCTION
Context and motivations

WOOD PANELS & FIBREBOARDS INDUSTRY

- ✓ France : 6.7 Millions m^3 of wood panels produced in 2005 (2^d largest production in EU)
- ✓ 70-100 kg/m^3 of adhesives in panels

  ⇔ 5-12%, w/w (~500 000 T/y)
- ✓ Usually based on **urea-formaldehyde** mixture (amino resin UF & MUF)
- ✓ Recently, formol has been classified as a probable human carcinogen and its use could be limited in the near future

➔Need to develop **new and environmentally friendly adhesives**

INTRODUCTION
Context and Motivations

WOOD PANELS & FIBREBOARDS INDUSTRY

- ✓ Alternatives of formol-based adhesives
  - Used of scavenger and lower the qty of formol in the formulation (molar ratio F/U ⇲)
  - Phenolic resin (phenol+ formol) => less formol released
  - Isocyanate-based adhesives (pMDI) but costly and could also be restricted
  - Partial substitution by green chemicals :

    Binder (protein) + Plasticizer (from bio-products)

➔ **Natural phenols : tannins already used in few panel & board productions**

INTRODUCTION
Context and motivations

TANNINS

- ✓ Wood adhesives from condensed flavonoid tannins (*catechine*)
  - Acacia (Mimosa), Quebracho, Pine (*pinus radiata*) tannins in South Africa, South America and Australia, Japan …
  - Tannin-based adhesives : partial or total substitution of phenol in phenol/formol formulation,
    - » tannin/hexamine or tannin/iso-cyanate
  - World production: 200 000 T/year ➔ still too low for large industrial use
- ✓ **Limitation :**

  - not really industrial tannin extraction in Europe,

  - reactivity of tannin / nature (polymerisation duration, adhesive properties)

INTRODUCTION
Context and motivations

TANNINS

- ✓ Tannin from wood-bark residues from pulp mill
  - Bark ~7-12 % w/w of the tree: std pulp mill (100 000 T/y pulp) → ~10 000 T/y barks
  - In pulp mill : bark is used for energy recovering
  - Softwood barks are especially rich in condensed flavonoid tannins

- ✓ Objectives
  - Study the potential of several industrial **wood barks wastes from pulp mills** for tannin extraction, and further for their adhesive properties,
  - Develop **aqueous extraction of tannin**,

    easy industrial scale-up

INTRODUCTION
Objectives

Tannin Extraction from pulp mill bark wastes

- ✓ Optimisation of aqueous extractions of condensed tannins
  - alkaline conditions or sulfite are the chemicals preferred for tannin extraction
  - urea as a nucleophile improves tannin extract quality
  - A too high temperature increases extraction yield but leads to worse adhesives properties

  ➔ **Therefore, extraction conditions, such as temperature, time, L/V ratio and bark pre-treatment need also to be set**

- ✓ Analytical characterisation of tannin extracts using different spectrophotometric analyses and Pyr-GC/MS

MATERIALS AND METHODS

Tannin Extraction and characterisation

✓ Bark samples

- 5 different barks were sampled in pulp mills :
  - spruce, maritime pine, aleppo pine, douglas fir and eucalyptus
- Dryness of fresh wood barks was between 40% to 70%.
- stored at –18℃, freeze dried and milled (particles Ø <1mm) before organic extraction.
- In case of large aqueous extraction: air-dried and ground (particles <3 mm

Tannin extraction and characterisation

✓ Extraction

- **Analytical organic extraction**
  - 250 mg of o.d. bark were extracted with 2x5 ml of **acetone/water (70/30, v/v) in a ultra-sonic** bath for 20 minutes at 20℃. After centrifugation, the supernat ant was collected.
- **Aqueous extraction**
  - 100 g of o;d. bark were extracted by 500 ml of aqueous solution at 75℃ during 1h, under reflux. The extra ct was filtrated on sintered glass N°1 before analysis.
  - Four different aqueous solution were tested :
    - » aqueous solution: tap water,
    - » urea solution containing 2% of urea
    - » urea/sulphite solution containing 2% urea and 2% sulphite
    - » sulphite/carbonate solution containing 2% sulphite and 0.5% carbonate

MATERIALS AND METHODS

Tannin extraction and characterisation

✓ Spectroscopic analyses

- Phenolic compounds: Folin-Ciocalteu method

  Tannic acid was used as standard. 0.5 ml of 1N Folin-Ciocalteu reagent and 2.5 ml of 2% sodium carbonate solution are added to 0.05 – 1 ml of extract. Absorbance is measured at 725nm after 40 min of reaction
- Total phenols content: UV measurement at 280nm as described by Antoine *et al. (2004)* using mimosa tannin as standard.
- Condensed tannins were determined according to butanol/HCl method, using catechine and mimosa tannin as standards.

✓ Pyr-GC/MS analysis

- 0.1 – 0.3 mg of dried extract
- Pyrolab 2000, 500℃/4s,
- GC/MS: HP1 (30 m x 0.25 mm, film thickness 0.25 µm),

  Temperature prog: 50℃ (1min) – 5℃/min – 300℃

RESULTS: Tannin Extraction

ANALYTICAL EXTRACTION & CHARACTERISATION

Characteristic of acetone/water (70/30, v/v) extracts of wood barks

(g/100g of o.d. bark)	Extraction yield	Total phenols (UV 280nm)[1]	Phenolics (FC)[2]	Condensed tannins[3]
Spruce	**26.6**	26 ± 1	4,7 ± 0,1	11,0
Aleppo pine	**30.1**	*5 ± 1**	7,5 ± 0,1	16,6
Douglas fir	**22.8**	11 ± 1	3,6 ± 0,1	6,7
Maritime pine	**10.2**	3 ± 1	0,8 ± 0,1	1,2
Eucalyptus	**6.5**	2 ± 1	0,2 ± 0,1	0,2

[1]eq. mimosa tannin , [2]eq. tannic acid, [3]eq. catechine
* after 0.45µm glass membrane filtration

RESULTS: Tannin Extraction

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Highest extraction yields for **aleppo pine**, **spruce** and **douglas fir** barks

RESULTS: Tannin Extraction

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Highest phenol/phenolic contents in **allepo pine, spruce** and **douglas fir**

RESULTS: Tannin Extraction

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* after 0.45µm glass membrane filtration

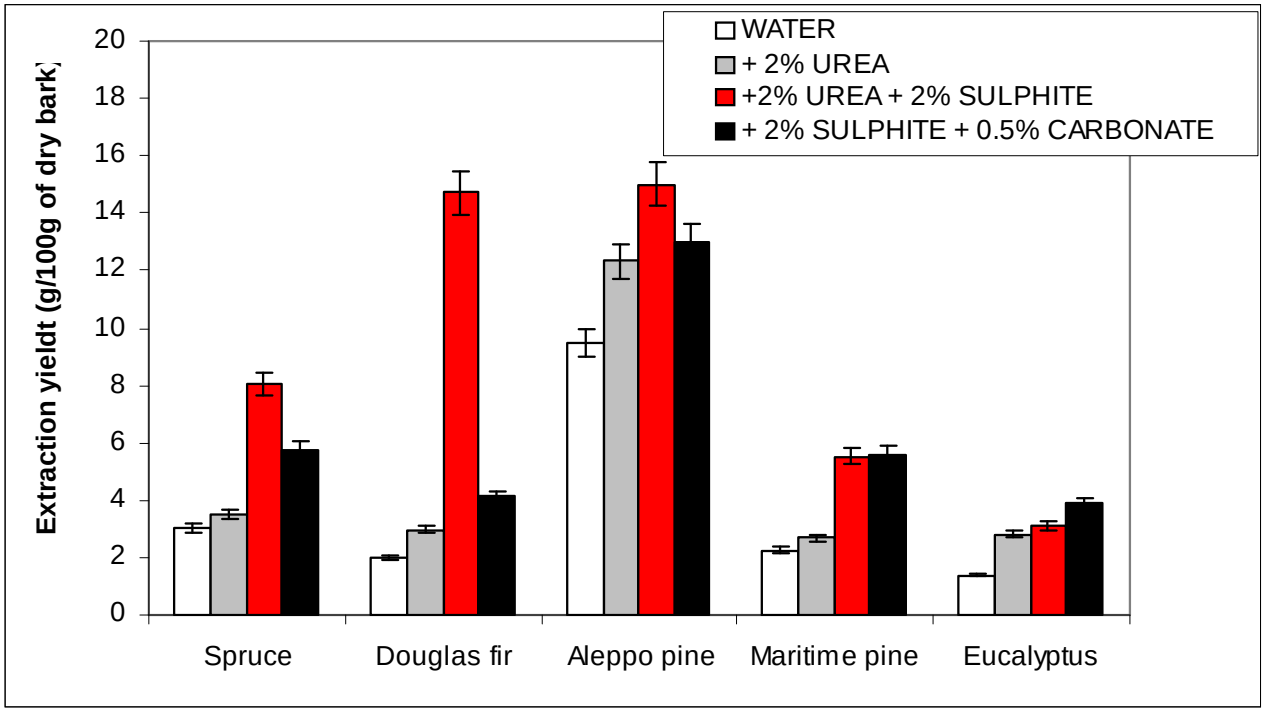
Highest extraction yields for **pine**, **spruce** and **douglas fir** barks

Highest phenol contents in **spruce**, **douglas fir** and **allepo pine**

1/3 to 1/2 of bark extracts were constituted of condensed tannins (maritime pine and eucalyptus contain much less condensed tannins)

RESULTS: Tannin extraction

OPTIMISATION OF AQUEOUS EXTRACTION

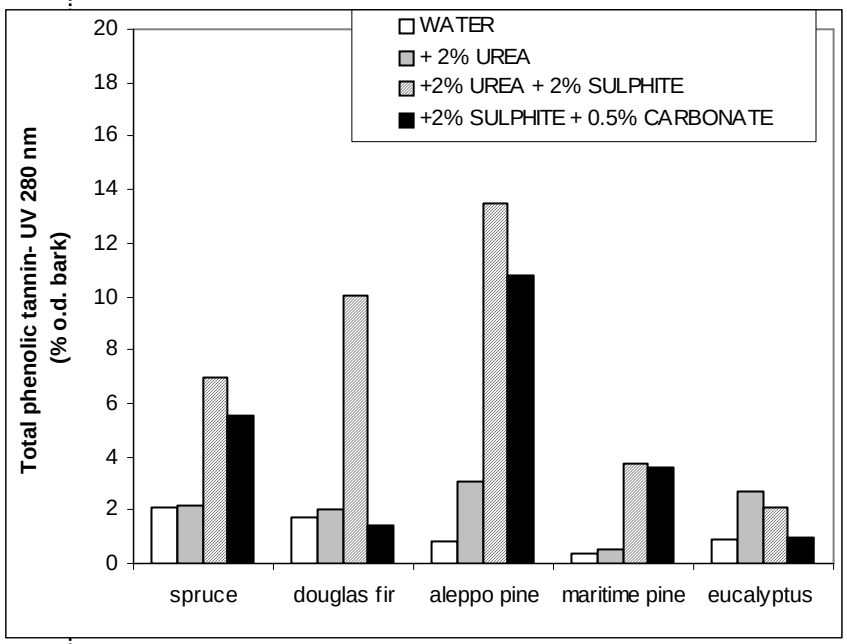


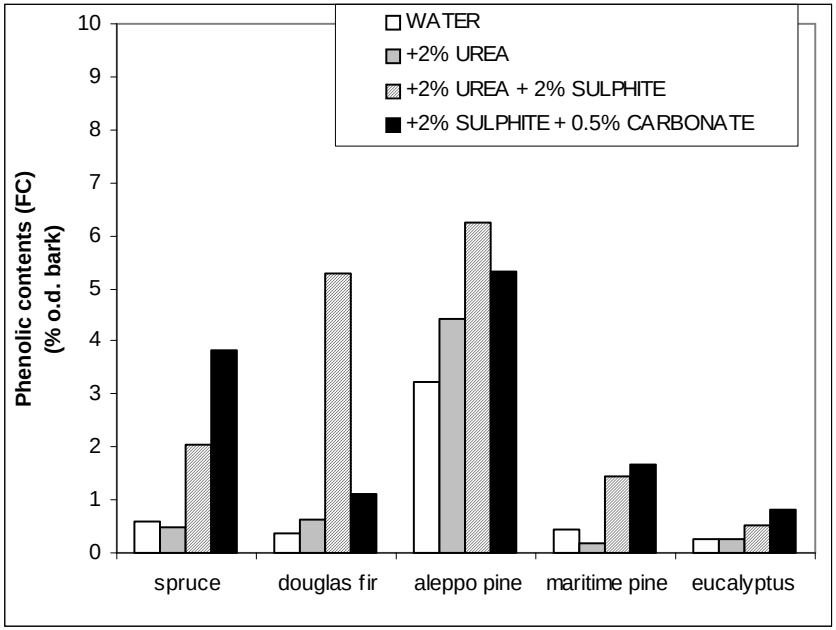
Highest extraction yield (10-15%): Aleppo pine & Douglas fir

Urea/sulphite

RESULTS : Tannin extraction

OPTIMISATION OF AQUEOUS EXTRACTION

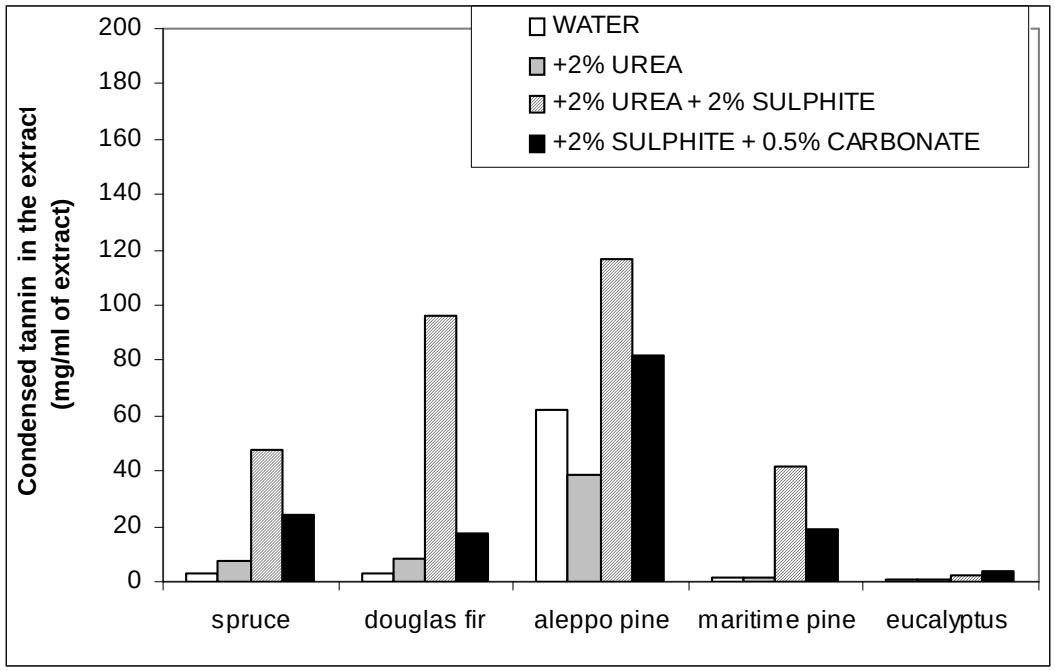




Urea/sulphite extracts : high total phenol contents
Highest phenolic contents : **aleppo pine** and **douglas fir**

RESULTS: Tannin extraction

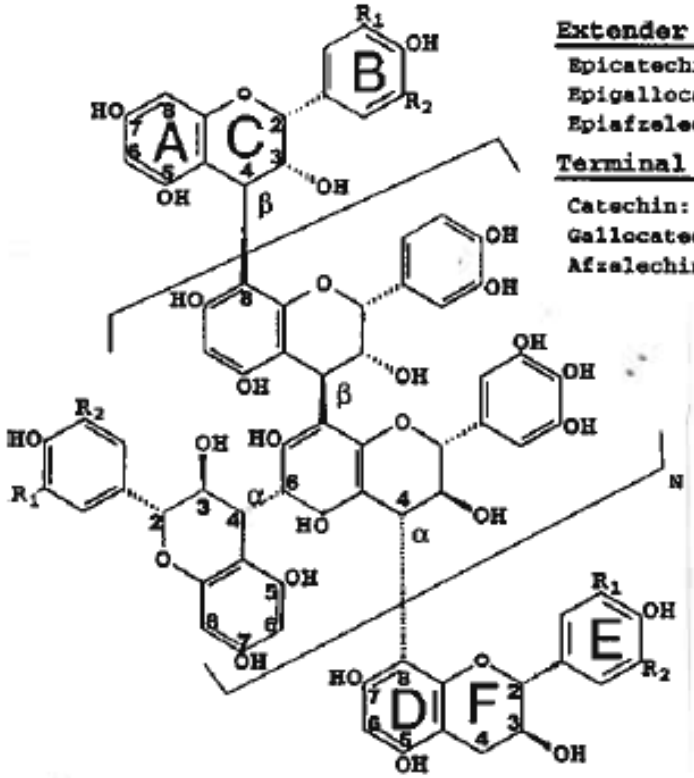
OPTIMISATION OF AQUEOUS EXTRACTION OF INDUSTRIAL BARKS



Urea/sulphite in favor of condensed tannins extraction

RESULTS: Pyr-GC/MS

Pyr-GC/MS : structural elucidation of tannins



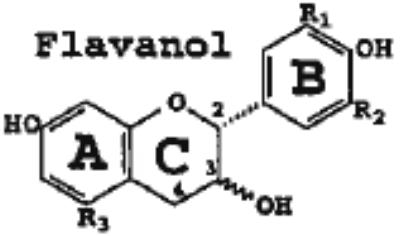
Extender Unit "ACB":

Epicatechin: R_1=OH, R_2=H
Epigallocatechin: R_1=R_2=OH
Epiafzelechin: R_1=R_2=H

Terminal Unit "DFE":

Catechin: R_1=OH, R_2=H
Gallocatechin: R_1=R_2=OH
Afzelechin: R_1=R_2=H

Condensed Tannin



R_1=OH, R_2=H, R_3=OH:
- = Catechin (PC)
- = Epicatechin (PC)

R_1=OH, R_2=OH, R_3=OH:
- = Gallocatechin (PD)
- = Epigallocatechin (PD)

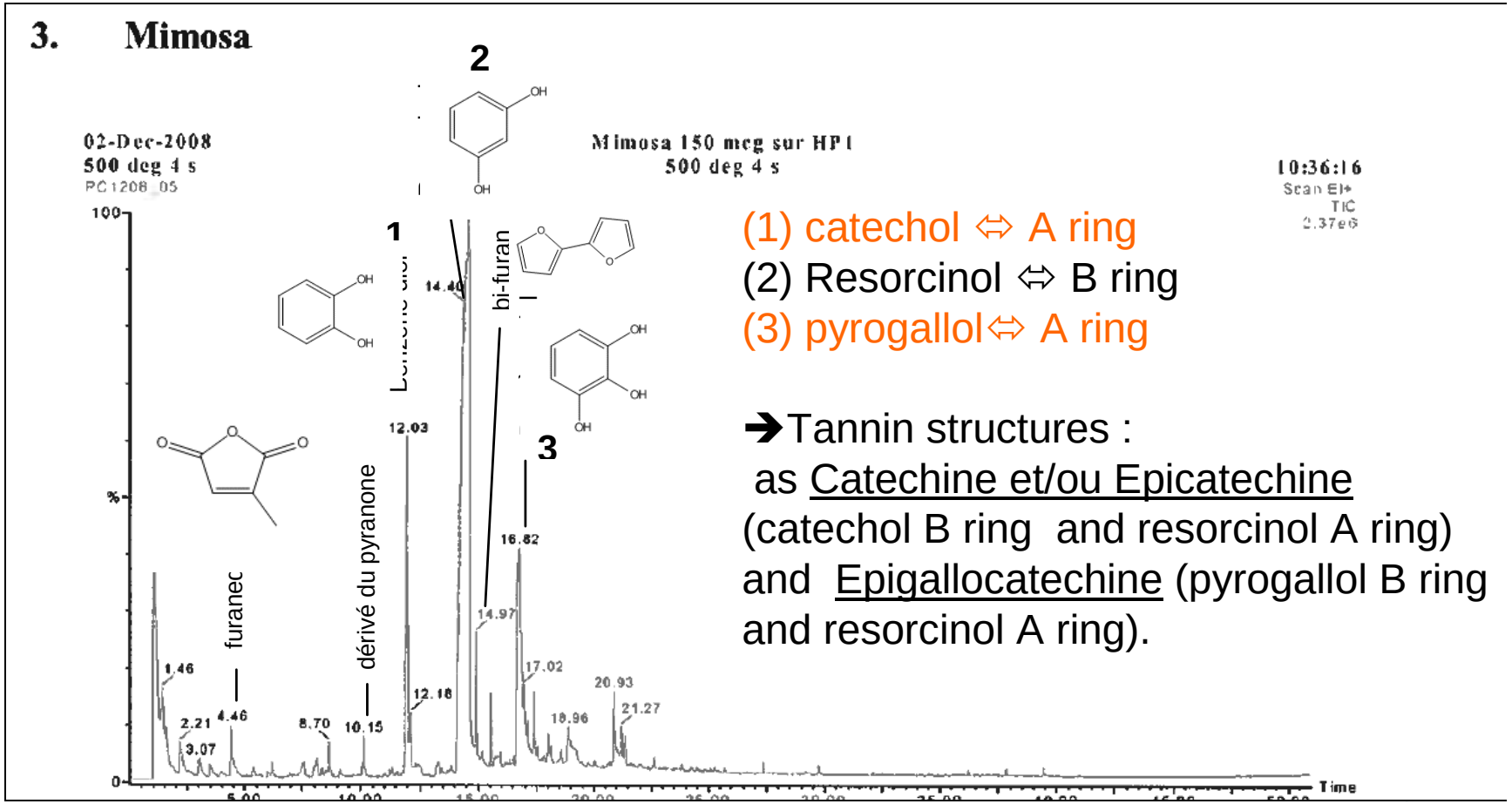
R_1=H, R_2=H, R_3=OH:
- = Afzelechin (PP)
- = Epiafzelechin (PP)

R_1=H, R_2=H, R_3=H:
- = Guibourtinidol
- = Epiguibourtinidol

R_1=OH, R_2=OH, R_3=H:
- = Fisetinidol
- = Epifisetinidol

RESULTS: Pyr-GC/MS

Pyr-GC/MS of a reference sample



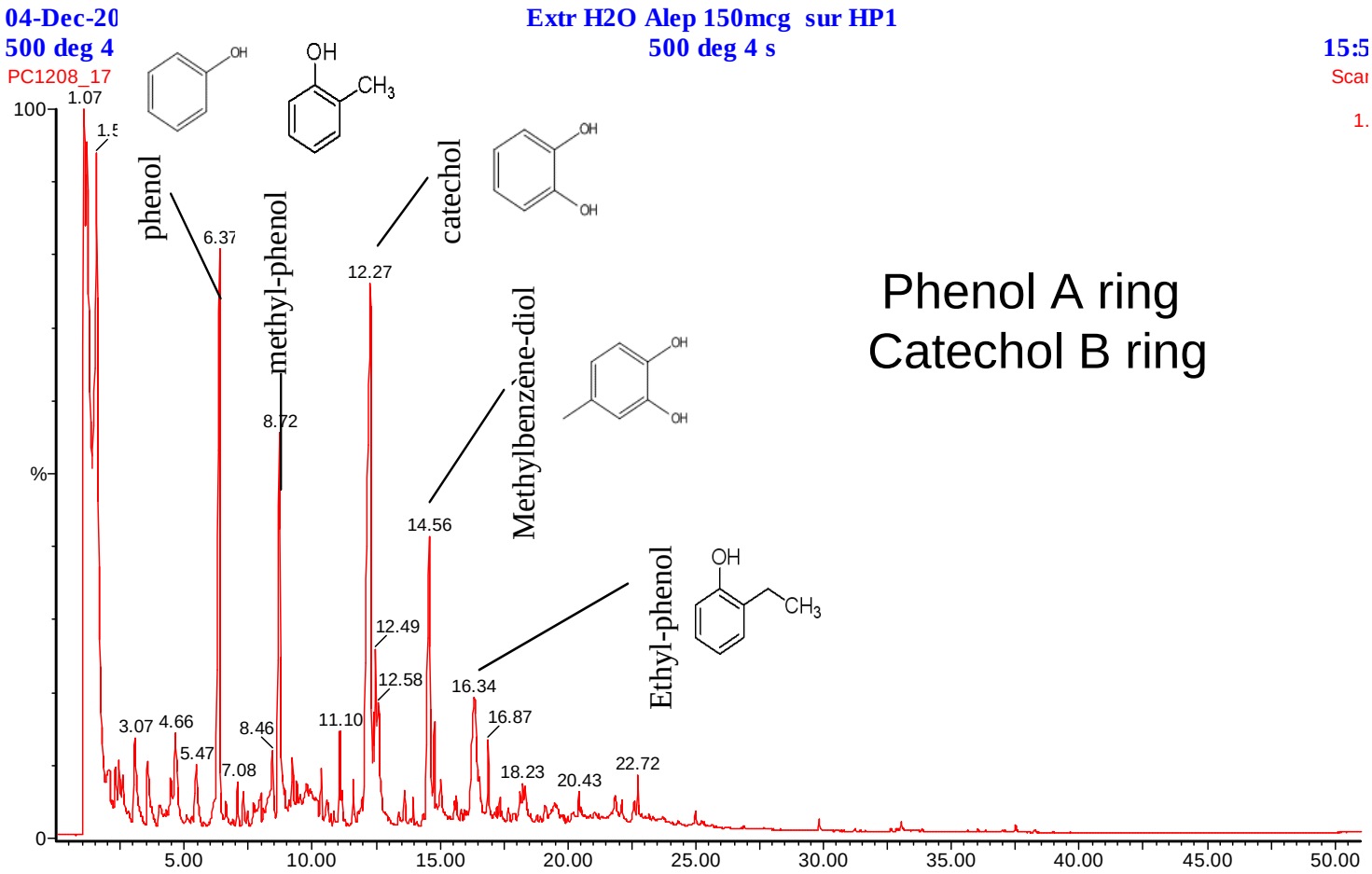
(1) catechol ⇔ A ring
(2) Resorcinol ⇔ B ring
(3) pyrogallol⇔ A ring

➔Tannin structures :
as Catechine et/ou Epicatechine (catechol B ring and resorcinol A ring) and Epigallocatechine (pyrogallol B ring and resorcinol A ring).

RESULTS: Pyr-GC/MS

Aleppo pine extracts

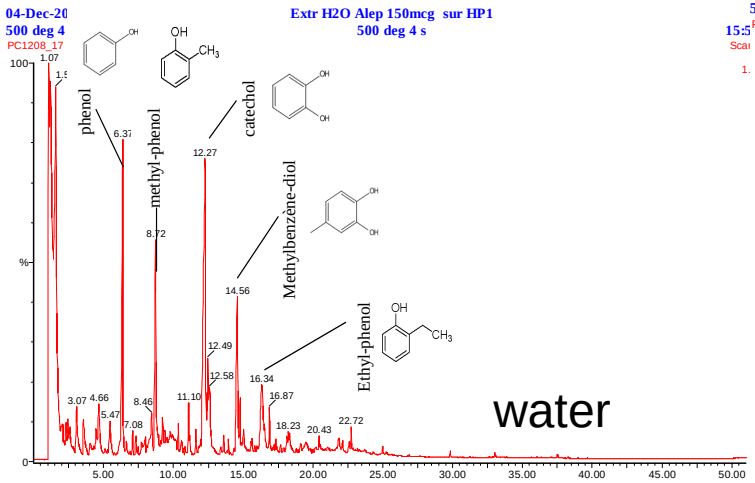
Water extract



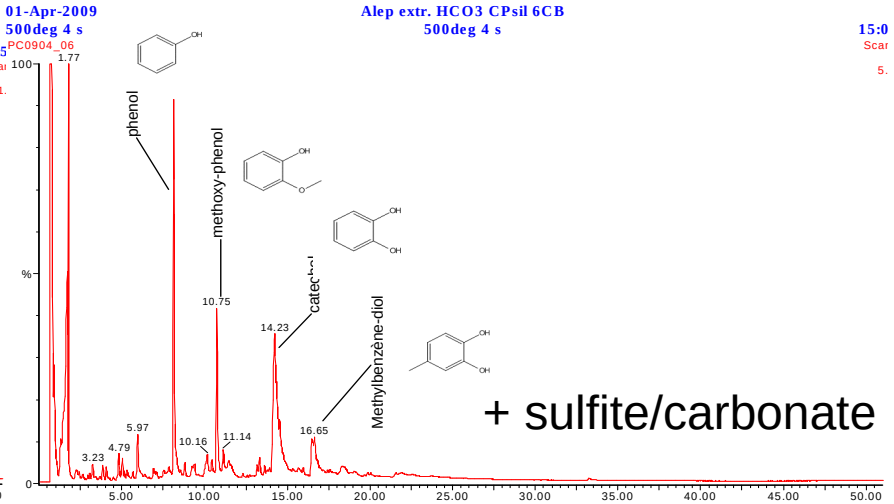
Phenol A ring
Catechol B ring

RESULTS: Pyr-GC/MS

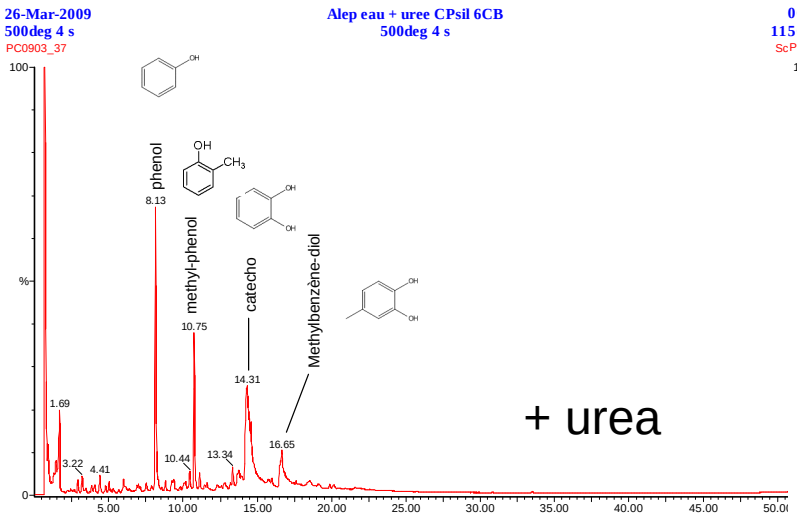
Aleppo pine extracts



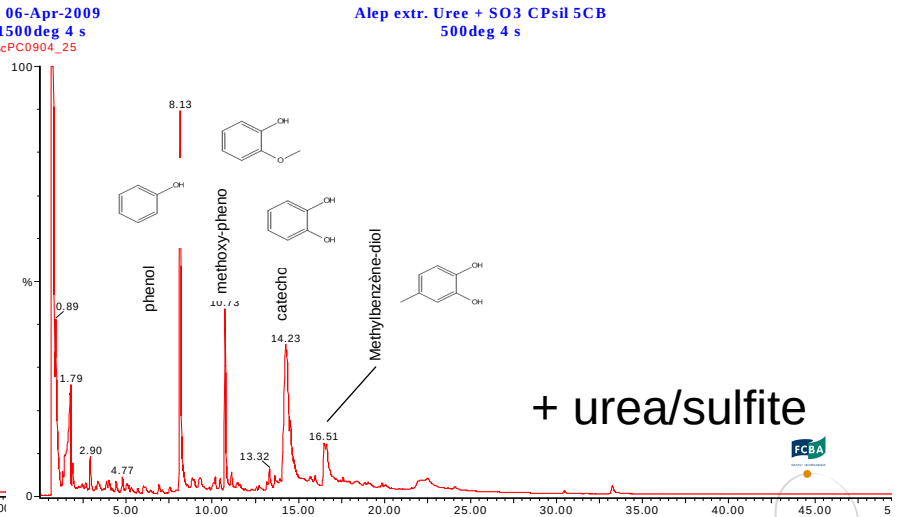
water



+ sulfite/carbonate



+ urea



+ urea/sulfite

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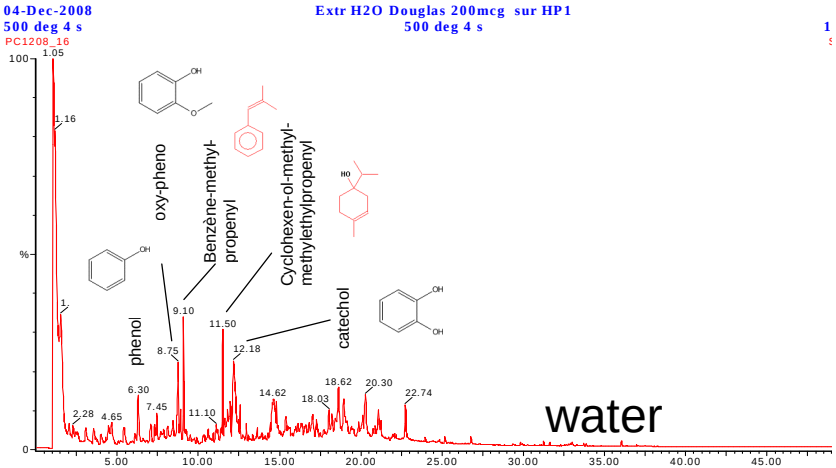
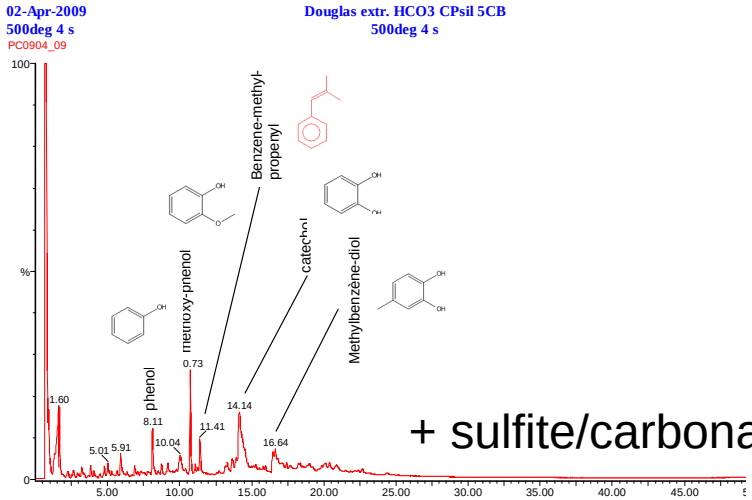
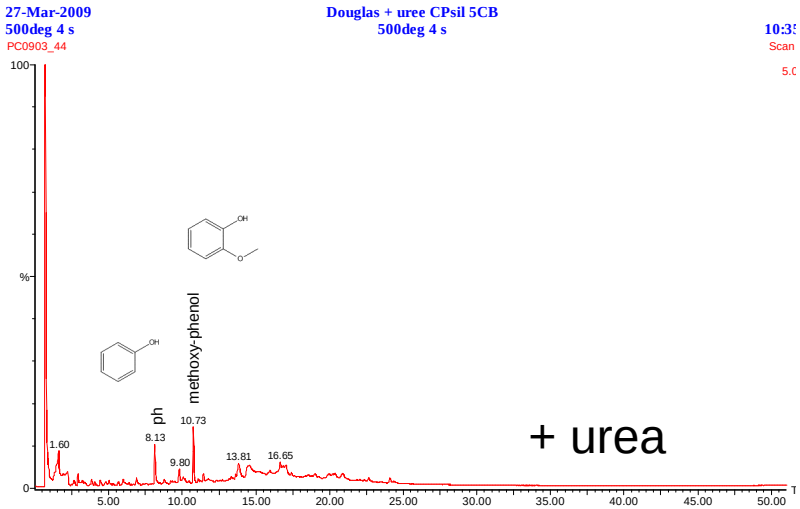
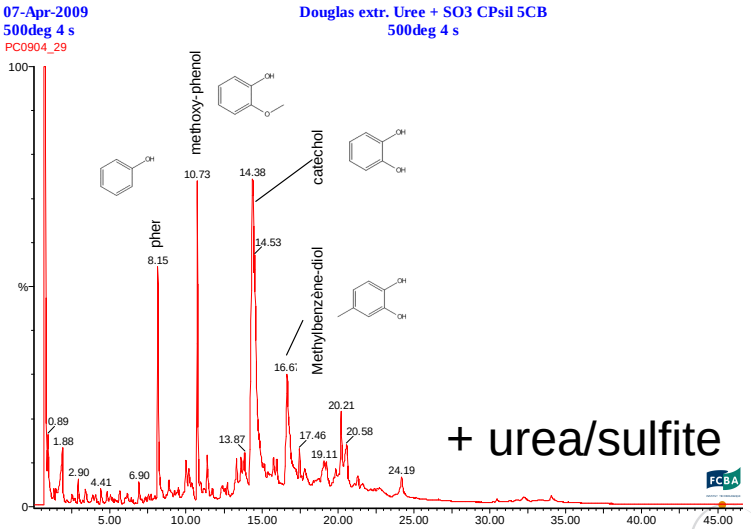
RESULTS: Pyr-GC/MS

Douglas fir extracts



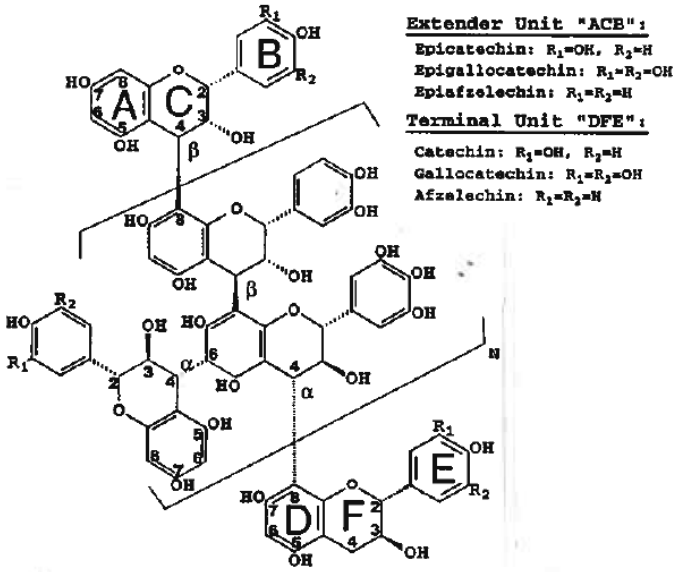






RESULTS: Pyr-GC/MS

Summary



condensed tannin structure

In all aqueous extracts,
but especially urea+sulfite

Douglas bark tannin ()
phenol type A ring (R1 = H)
catechol type B ring (R1 = OH) rich

Aleppo pine bark (all aqueous extracts)
phenol type A ring (R1 = H)
catechol type B ring (R1 = OH) *rich*

RESULTS: Adhesives properties

ADHESIVE PROPERTIES (LERMAB)

Water : Euca, spruce, douglas fir
Urea : Aleppo pine
Urea/sulphite : spruce, douglas, aleppo pine
Sulphite/carbonate : aleppo pine, maritime pine

RESULTS: Adhesives properties

ADHESIVE PROPERTIES (LERMAB)

Water : Euca, spruce, douglas fir

Urea : Aleppo pines

Urea/sulphite : spruce, douglas, aleppo pine

Sulphite/carbonate : aleppo pine, maritime pine

LARGE-SCALE EXTRACTION

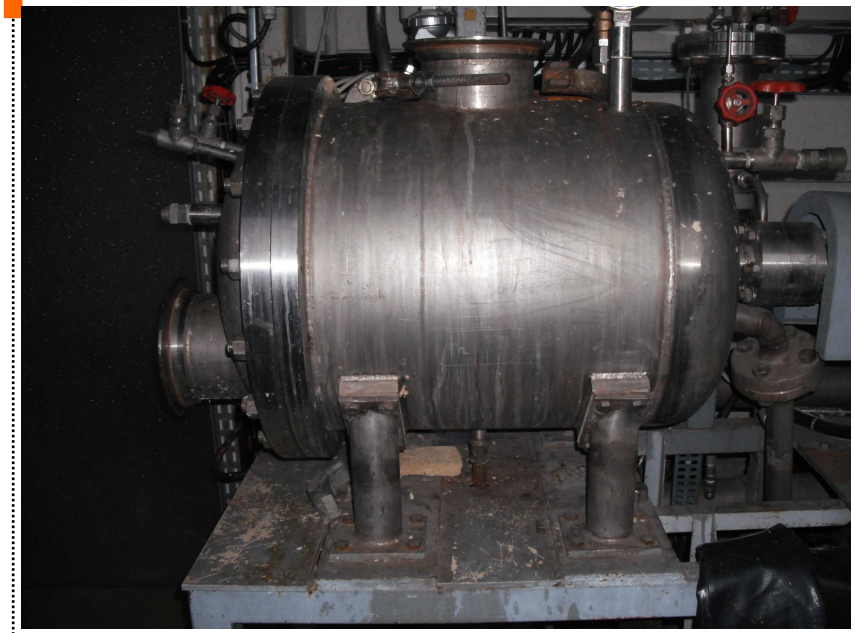
✓ Large Aqueous Extraction

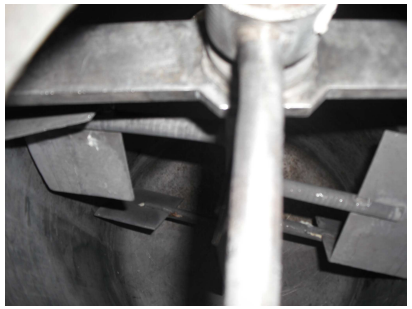
- 10 kg eq.sec, L/V = 5 L / 1 kg
- coarse milled bark + extraction 2% urea + 2% sulphite
- agitated thermo-regulated reactor 75℃/1h
- centrifugation : tannin extract + extracted barks

✓ **Aleppo pine**, **spruce** and '**mill blend**' (20% black pine + 20% maritime pine + 30% norway pine + 10% aleppo pine + 15% spuce + 5% douglas fir)

➔ **tannin extracts for the preparation of adhesive formulations and production of wood panels at pilot-scale**

LARGE SCALE STUDY





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LARGE SCALE STUDY: Preliminary results

	Dryness (%)	Extract Yield (%)	Prepared extract(kg)
Spruce	**95.6%**	**27%**	**2.8**
Aleppo pine	**83.5%**	**46%**	**2.5**
Mill Blend	**84.7%**	**33%**	**2.8**

➔Higher amount of extract at large scale

>> Lab-scale

≥ Acetone/water extraction

?? Quality and Reactivity

CONCLUSIONS

BARK EXTRACTION : TANNIN UTILISATION in ADHESIVES

- ✓ Aqueous extraction are well suitable and easily to up-scale
  Water + 2% urea + 2% sulphite

- ✓ Softwood species : Spruce, Allepo pine, Douglas fir
  Extraction yield of 10-15%

  ➔ An aqueous extraction of softwood barks in pulp mill before heat recovering can be realistically foreseen

- ✓ Economical Evaluation
  - Adhesives 300 $/ T,Tannin extract 600 $/ T
  - Bark / Heating recovery : 20 €/T

  ➔ Tannin recovery =10 % of initial bark ➔ ➔ 1 000 T/y tannin

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- ✓ ENCE-Pontevedra