



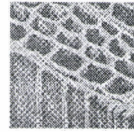
### Potentialities of wood extractives as wood preservatives

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### Wood constituents



Cellulose  
Hemicelluloses  
Lignin  
Extractives  
Mineral matters  
(K, Ca, Mg, Si)

+

Sap  
Stock (starch)

sapwood



### Wood extractives

- ☼ Few % only
- ☼ Very various chemical structures  
Tannins, quinones, stilbenes, tropolones,...
- ☼ Give particularities to the wood  
Colour, odour, natural durability



### Natural durability

Understanding of the natural durability  
mechanisms

- ☼ Duraminisation phenomenon
- ☼ Knowledge of the extractives
  - Quantity
  - Identification
    - Families of compounds
    - Molecules
  - Interactions



### Natural durability

- ☼ Informations on tropical woods  
in the Cirad database
- ☼ Selection of wood naturally durable



### Transfer natural durability ???

- ☼ Use timber at its best
- ☼ Obtain wood extractives  
(from wastes)
- ☼ Use these extractives  
as active ingredients  
for wood preservation

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\*000084593\*

## Pyrethrum & Pyrethroids



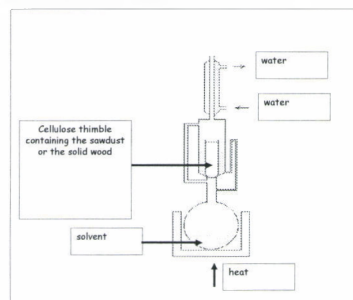
## Some studies on going in our lab

## IMPORTANCE OF THE WOOD SECONDARY METABOLITES ON THE PHYSICAL PROPERTIES AND THE DURABILITY OF FOUR TROPICAL WOOD SPECIES FROM CAMEROON

Four timbers from Cameroon :  
 Mansonia (bete) (*Mansonia altissima*),  
 Bubinga (*Guibourtia tessmannii*),  
 Moabi (african pearwood) (*Baillonella congolensis*),  
 Padauk (*Pterocarpus soyauxii*).

Study of the influence of wood extractives on some physical properties and on the durability against termites

## Extraction



Soxhlet apparatus + evaporation (under vacuum)

## Extraction

Two successive extractions using soxhlet apparatus, and the following solvents :  
 (1) a mix of ethanol-toluene (1:2 v:v),  
 (2) water.

Extraction have been carried out on both ground sawdust (5 replicates) and on wood samples of dimensions 10x20x10 mm (L,R,T) (10 replicates)

## Extraction - Results

Timber	Extraction yield (% m/m on dry basis) (average)					
	Solid wood			Sawdust		
	Ethanol-Toluene	Water	Total	Ethanol-Toluene	Water	Total
Mansonia	6.84	4.36	11.20	12.5	2.70	15.20
Bubinga	2.28	3.69	5.97	3.90	3.80	7.70
Moabi	2.08	9.82	11.90	7.24	2.11	9.35
Padauk	13.86	3.44	17.30	11.44	3.59	15.03

## Colour

The colour of the solid wood samples has been measured before and after the two extractions, on several places, using a spectro-colorimeter (Datacolor - Microflash 100 V4.0).

The illuminant is A10, and the results are given in the CieLab system.

L : scale going from black (0) to white (100)  
a\* : scale going from green (-) to red (+)  
b\* : scale going from bleu (-) to yellow (+)

## Colour

Timber	Wood colour (average)					
	Before extraction			After extraction		
	L	a*	b*	L	a*	b*
Mansonia	39.72	3.95	4.98	44.81	9.42	16.86
Bubinga	43.77	15.12	14.59	39.97	12.81	13.51
Moabi	54.78	11.92	20.26	43.36	11.30	14.73
Padauk	43.36	29.28	21.20	37.73	28.08	22.84

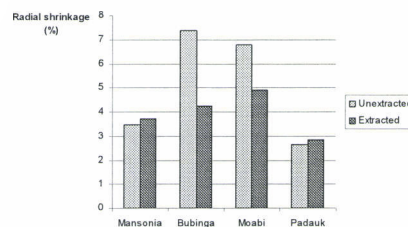
## Shrinkage

The unextracted and extracted specimens were successively :

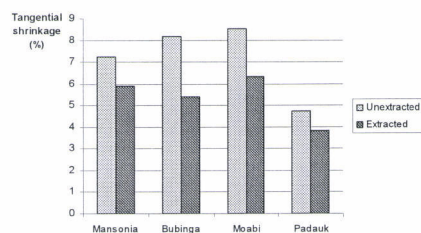
- water saturated
- and progressively dry to an anhydrous state in order to determine the radial and tangential shrinkage

The shrinkage is determined according to the directives of the standard NF B 51-006 (measures in the radial and tangential directions)

## Radial shrinkage

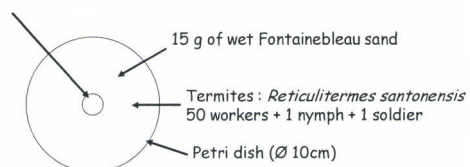


## Tangential shrinkage



## Termite tests

400 mg of unextracted and extracted sawdust compacted into small disc (Ø 5mm)  
(3 replicates)





## Termite tests

The test devices were kept 5 weeks at 27°C, 75% RH.

At the end of the test :

- the number of termites still alive is counted
- the survival rate of the workers is calculated.

Controls were done with pine sapwood sawdust and with sand only.



## Termite tests

Timber	Survival rate of termite workers (%) (average)		
	Unextracted sawdust	Sawdust extracted with ethanol-toluene	Sawdust extracted with ethanol-toluene and water
Mansonia	0	0	42
Bubinga	46	36	54
Moabi	0	42	46
Padouk	4	14	18
Control with pine sapwood sawdust	68	-	-
Control with sand only	0	-	-



## Conclusion

In this preliminary study, wood extractives have been shown to have an influence on colour, as well as on the radial and tangential shrinkage. Moreover, and as expected, they also have a great impact on the durability towards termites. It also appeared that the extracts obtained with an ethanol-toluene extraction or with a water extraction have a different activity against termite attacks.

This work should carry on with the chemical analysis of these extracts.



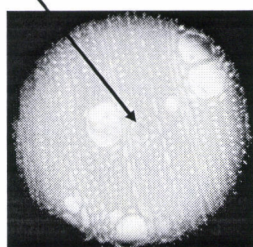
## Study on Rosewood and Ocotea

- Both from the Lauraceae family and both very durable against termites
- Rosewood (*Aniba parviflora*)  
Very well known  
Perfume industry (Chanel n°5)  
Chemistry of essential oil well studied (linalool)  
« a studycase »
- Ocotea (*Ocotea rubra*)
- Timbers from French Guyana



## Rosewood and Ocotea

Cell with essential oil



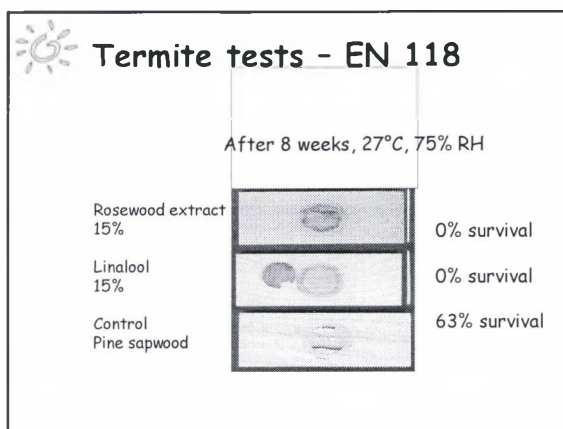
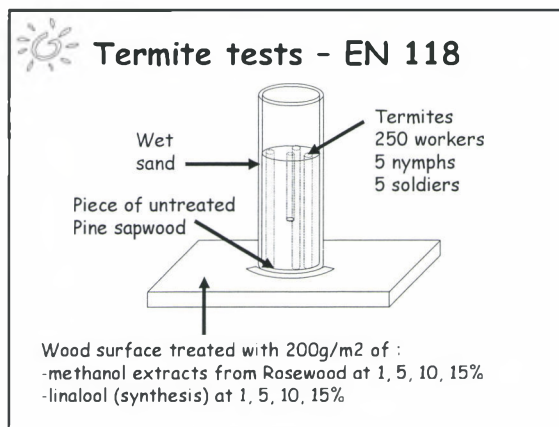
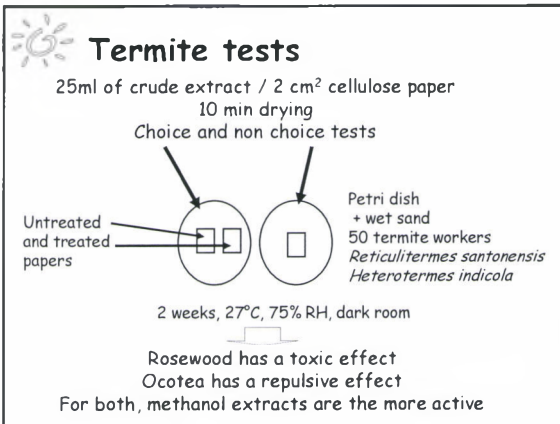
Rosewood (x 200)




## Extraction


- Sawdust in solvent under stirring  
For 12h at room temperature (20°C)  
1 vol sawdust/5 vol solvent
- Methanol, Pentane, Dichloromethane
- Evaporation under vacuum






 **Rosewood**

- Natural durability can be imparted to the presence of linalool  
This compound appears to be an effective active ingredient
- But the eco-toxicity of the extractives is extremely high

 **Ocotea**

- Study carried on with Ocotea
- Sawdust extracted in a soxhlet different solvents
- Methanol, Acetone, Ethylacetate, Dichloromethane
- Evaporation under vacuum

 **Ocotea**

- Termite screening tests with Petri dishes  
Non choice and choice tests
- Acetone extracts were the most effective  
Threshold between 6.2% and 3.5% m/m
- No effect of acetone alone
- Standard tests EN117 & EN118 with acetone extracts

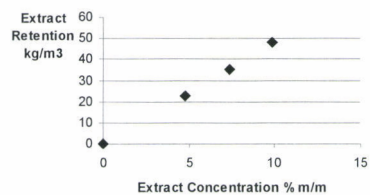


## EN117

- ✗ Wood = Pine sapwood (*Pinus sylvestris*)  
Wood blocks 50 x 25 x 15 mm (L,R,T)
- ✗ Treatment solutions  
Acetone alone  
Ocotea extracts in acetone  
[C] = 5%      7.5%      10% m/m  
→ [C] = 4.80%      7.39%      9.88% m/m
- ✗ Impregnation  
Vacuum / Atmospheric pressure
- ✗ + Wood left for 2 hours in the treatment solution



## Treatment



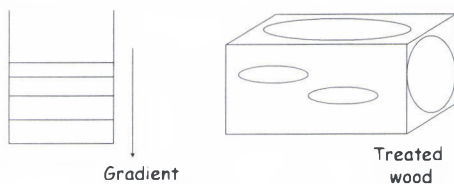
[C] = 4.80%      7.39%      9.88% m/m  
[R] = 23.84      34.96      48.39 kg/m³

5 replicates for acetone (solvent only)  
3 replicates for extract solutions



## Treatment

- ✗ Ocotea extracts = Really thick paste
- ✗ Pasty treatment solution in acetone



Need to stir every 10 min  
the treatment solution

Need for formulation

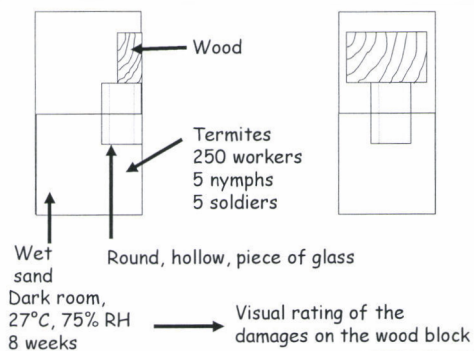


## Drying

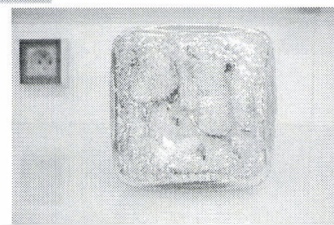
- ✗ EN 117 standard = 4 weeks
- ✗ Treatment with acetone  
Acetone = very volatile solvent
- ✗ Treated wood left to dry at 20°C, 65% RH  
until constant mass is obtained
- ✗ Drying period for the tests = 15 days



## Termite test

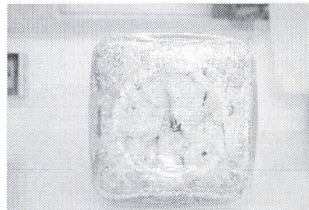


Acetone  
control





Ocotea 7.5%



## Termite test

✗ Visual rating of the damage

0	No attack	Durable
1	Tentative of attack	
2	Slight attack	Moderately durable
3	Mean attack	Sensible
4	Strong attack	

1 sample  
with a  
rating of 2  
is tolerated

Samples		Biological results				
		Concentration	Maturation		Worker survival	Degree of termite attack
		% (m/m)	Sample	Average	%	
Solvent control	1		0.0		0%	3
	2	0	0.0	0.0	54	4
	3		0		50	4
Treated samples	6	4.80	23.809		0	1
	8		23.468	23.84	0	1
	9		24.243		0	1
	13		35.503		0	2
	14	7.39	35.732	34.96	0	2
	19		33.643		0	1
	10		45.886		0	1
	11	9.88	51.078	48.39	0	2
Virulence control	15				80.8	4
	17					
	18				50	4

Samples		Biological results				
		Concentration	Retention		Worker survival	Degree of termite attack
		% (m/m)	Sample	Average	%	
Solvent control	1		0.0		0%	3
	2		0.0		54	4
	3		0		50	4
Treated samples	6		23.809		0	1
	8	4.80	23.468	23.84	0	1
	9		24.243		0	1
	13		35.503		0	2
	14	7.39	35.732	34.96	0	2
	15		33.643		0	1
	10		45.886		0	1
	11	9.88	51.078	48.39	0	2
Virulence control	12		48.196		0	1
	16				80.8	4
	18				50	4



## Termite test

- ✗ Ocotea extracts give a protection to the treated wood against termite activity
- ✗ The best protection is given by the treatment ocotea 4.80%
- ✗ Remark  
The termite attack occur where the wood is less « covered » by the treatment (the treatment solution is very pasty)

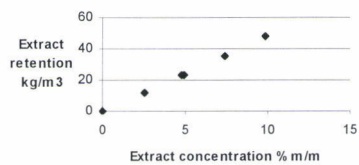


## Termite test

- ✗ The EN117 test has been realized again with Ocotea acetone extract  
at 5% (exact concentration 4.89% m/m)  
and 2.5% (exact concentration 2.51 % m/m)



## Treatment



[C] = 2.51 %      4.89 % m/m  
[R] = 12.29      23.37 kg/m³

The results of retention fits well with the results obtained before

Toxic threshold ???

Samples		Biological results				
		Concentration	Retention		Worker survival	Degree of termite attack
			Sample	Average		
		% (m/m)	kg/m <sup>3</sup>		%	
Treated samples	30	2.51	12.388	23.37	0	1
	33		12.213		0	2
	34		12.280		0	1
	20	4.89	22.983	12.29	0	1
	21		23.714		0	1
	24		23.410		0	1
Virulence control	18 T				60.8	4
	19 T				69.6	4

Validation of the test



## Results

- ✗ The best protection is given by ocotea extract around 5%

BUT

There is a real need for a formulation in order to

- have a very homogenous treatment on the wood
- optimize the crude extract concentration
- have the best protection



## EN118

- ✗ Wood = Pine sapwood (*Pinus sylvestris*)  
Wood blocks 200 x 40 x 10 mm (L,R,T)

- ✗ Treatment solutions

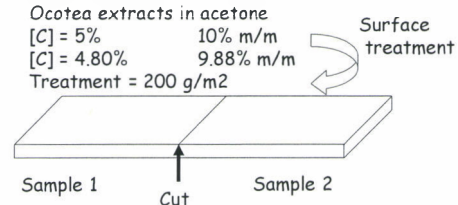
Acetone alone

Ocotea extracts in acetone

[C] = 5%

[C] = 4.80%

Treatment = 200 g/m²

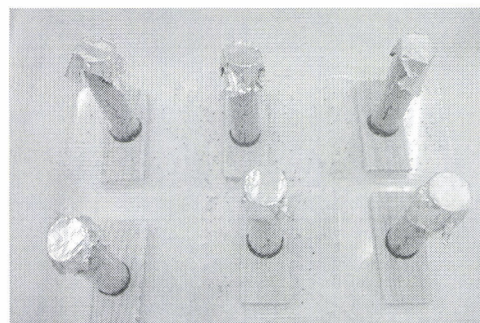
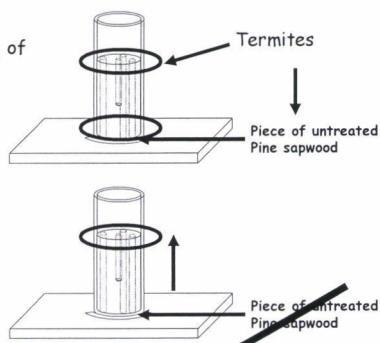


Beginning of the test

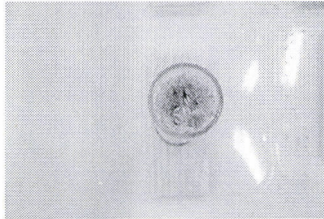
Week 1

Week 2  
Week 3

Week 4 No activity



Ocotea 10%



Ocotea 10%

The termites are above the sand in the test devices (repulsive effect)

Samples		Ocotea acetone extract		Biological results	
		Theoretical dose g/m <sup>2</sup>	Applied dose g/m <sup>2</sup>	Worker survival %	Degree of termite attack
Treated samples C = 4.80%	1			0	4
	2	200	201.34	0	4
	3			0	4
	4	200	202.23	0	4
	5			0	4
	6	200	193.64	0	4
Treated samples C = 9.88%	1			0	2
	2	200	200.05	0	2
	3			0	2
	4	200	198.22	0	2
	5			0	2
	6	200	203.68	0	2
Treated samples Acetone	1	200	199.95	58.4	4
	2	200	233.43	53.6	4
	3	200	200.12	49.2	4
Virulence control	2			51.20	4
	2			71.6	4
	3			77.20	4

Protection not sufficient for a preventive treatment



## EN118

- ✗ Test carried on again with treatment solutions of Ocotea extracts  
at 15% (exact concentration 15.21 %) and 20% (exact concentration 20.39 %)
- ✗ Treatment = 200 g/m<sup>2</sup>

Samples		Ocotea acetone extract		Biological results	
		Theoretical dose g/m <sup>2</sup>	Applied dose g/m <sup>2</sup>	Worker survival %	Degree of termite attack
Treated samples C = 15.21%	1			0	1
	2	200	215.76	0	2
	3			0	2
	4	200	202.60	0	2
	5			0	2
	6	200	213.38	0	1
Treated samples C = 20.39%	1			0	2
	2	200	212.40	0	3
	3			0	2
	4	200	221.70	0	2
	5			0	3
	6	200	202.88	0	3
Virulence control	T4			50.00	4
	T5			61.6	4
	T6			72.4	4

Validation of the test



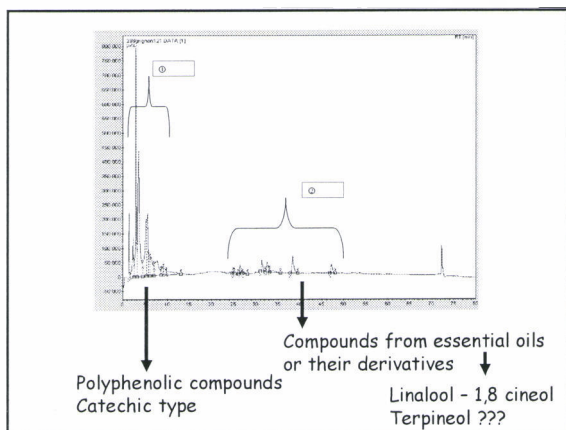
## Results

- ✗ There is a protection given by the application of ocotea extracts as a preventive treatment  
  
BUT  
The termite attack occurs where the wood is « less covered » by the surface protection  
  
There is a real need for a formulation in order to
  - have a very homogenous treatment on the wood
  - optimize the crude extract concentration
  - have the best protection



## Chemical analysis of ocotea acetone extracts





### Conclusion

Promising results  
But...

Need to optimize the threshold for the termite tests  
Need for a formulation

Ecotoxicity test to be carried out

Think about the environmental impacts

### Studies on *Eperua*

Chemical understanding of the natural durability of 2 species of *Eperua*:  
*Eperua falcata* - *Eperua grandiflora*

### *Eperua*

Family : *Cesalpiniaceae*

Species : *Eperua falcata*  
*Eperua grandiflora*

### Similarities

Timber: red brown timber streaked with resin veins

Mechanical wood with interesting properties: mid-heavy mechanical properties

### Similarities

<i>EPERUA FALCATA</i>	<i>EPERUA GRANDIFLORA</i>
• Density : 0,86 g/cm <sup>3</sup>	• Density : 0,92 g/cm <sup>3</sup>
• MOE : 14400 kg/cm <sup>2</sup>	• MOE : 16800 kg/cm <sup>2</sup>
• Shrinkage:	• Retrait :
2,1% radial - 6,1 % tangential	2,7 % radial- 7,2% tangential
• Use : joinery, carpentry, wood floor, stakes	• Use : joinery, carpentry, wood floor, stakes





## But...



### Durability :

*Eperua falcata* very durable  
(Class 1)

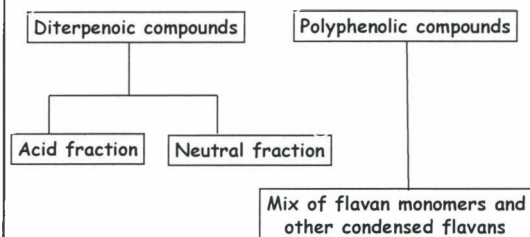
*Eperua grandiflora* slightly durable  
(Class 3)



### Chemistry:



## Chemical composition



## In vitro tests



No fungal growth



anti fungal activity



Growth retarded



Activity important



Normal growth



No anti fungal activity



## Anti fungal activity

	<i>Eperua falcata</i>	<i>Eperua grandiflora</i>
Diterpenoic fraction	Activity  (1.74 % m/v)	Perturbation
Acid fraction	Activity  (1.14 % m/v)	No activity
Neutral fraction	No activity	No activity
Polyphenolic fraction	Perturbation	Perturbation

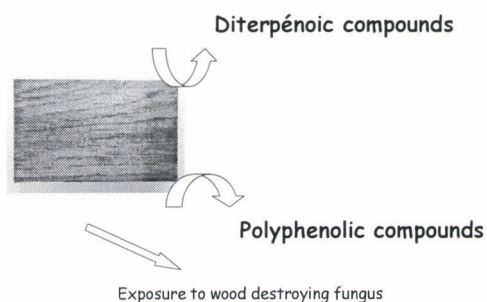
These tests bring us some answers



But we have to take into account the interaction between wood & extractives

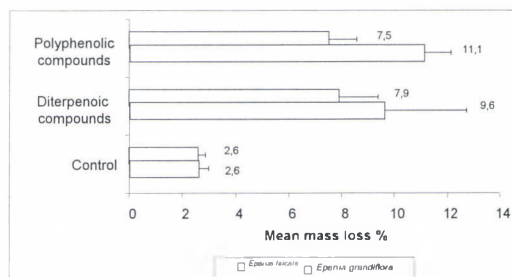


## In-vivo tests



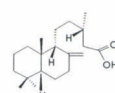


### Role of extractives in natural durability mechanisms

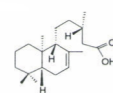


### Chemical composition of the acid fraction

<i>Eperua falcata</i>	<i>Eperua grandiflora</i>
2 compounds ⇒ Eperuic acid ⇒ Cavitic acid	



Eperuic acid

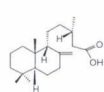


Cavitic acid

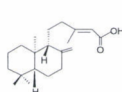


### Composition chimique de la fraction acide

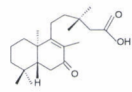
<i>Eperua falcata</i>	<i>Eperua grandiflora</i>
2 compounds ⇒ Eperuic acid ⇒ Cavitic acid	4 compounds ⇒ Eperuic acid ⇒ Copalic acid ⇒ 7-oxalabd-8-en-15-oic acid ⇒ un-identified dimer



Eperuic acid



Copalic acid



7-oxalabd-8-en-15-oic acid



### Conclusion



The high natural durability of *Eperua falcata* lies on the presence of eperuic acid and cavitic acid



The polyphenolic compounds also take part in the mechanisms of natural durability for both *Eperua* species.



### To carry on...

- ☼ Characterize the anti-fungal and insecticide activity of wood extractives from the large diversity found in tropical forests
- ☼ Identify, classify the molecules responsible for the natural durability of very durable wood species
- ☼ Try to apprehend the relation between structure and activity



### In terms of development



Up-grade the wood wastes from the wood industry (1st & 2nd transformation)



Promote « unknown » wood species



Use these compounds as active ingredients for the formulation of wood preservatives with more respects towards human health and environment.

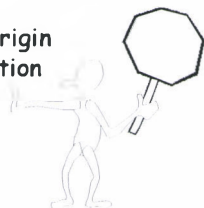
A product from natural origin  
is not always the ideal solution



Synthesis ?



How to use it ? Formulation ?  
Efficacy and environmental impacts ?



End life -Wastes -Re cycling ?

行政院農業委員會林業試驗所主管科技計畫  
九十四年度細部計畫說明書

加強與法國之木材科學交換合作研究(5/5)  
The project for strengthening the cooperation in wood  
science technology between R.O.C. and France(5/5)



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農委會林業試驗所  
中華民國九十四年一月

