Constitution biochimique des fibres végétales

B Chabbert, UMR FARE , Reims

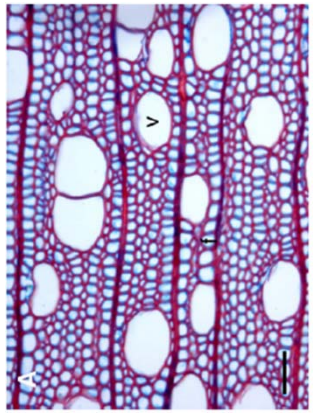
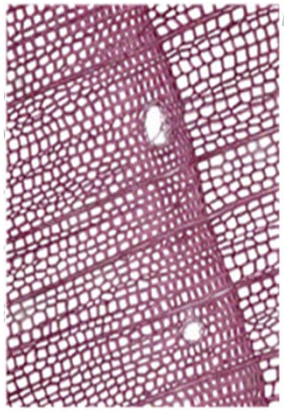
MECAMAT 2014

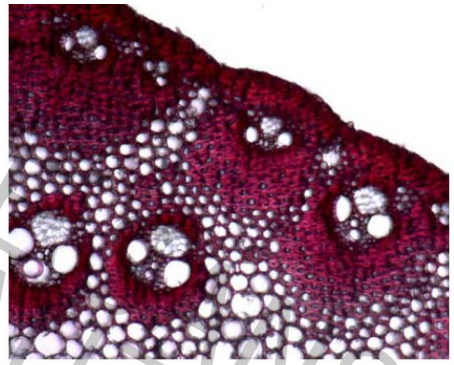
Polymorphisme des fibres végétales









Polymorphisme des Fibres végétales : origine botanique

Source de fibres			Caractéristiques anatomiques	
Bois	Pin Peuplier	Conifères Feuillus	Cambium	Trachéides Fibres, vaisseaux
Tige: partie externe (partie interne)	Lin, chanvre kénaf, jute	Dicot	Procambium Fibres périphoémiennes Cambium Cambium	Sclérenchyme faisceau Fibres, vaisseaux
Paille Tiges entière	Bagasse Miscanthus	Monocot	Procambium	
Feuille (nervure)	Sisal, abaca	Monocot	Procambium Faisceau vasculaire	Fibres vaisseaux
Graine (trichomes)	Coton	Dicot	Epiderme	Fibres isolées

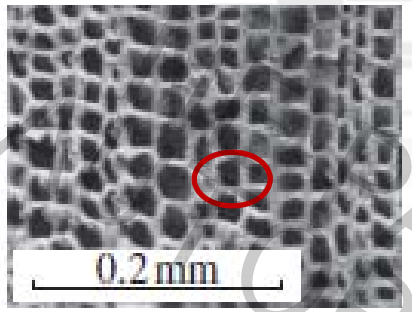
Constituants des parois végétales:
polymères majoritaires

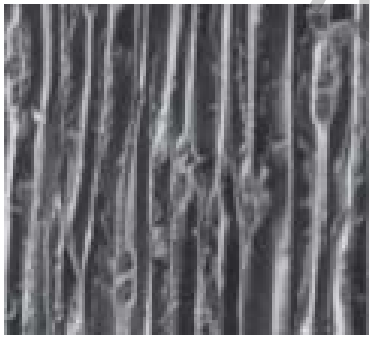
- **Polysaccharides**
  - Pectines
  - Hémicellulose
  - Cellulose
- **Phénols**
  - Lignine
- **Protéines**
  - Glycoprotéines
- **Minéraux**
- **Extractibles**
- **Eau**

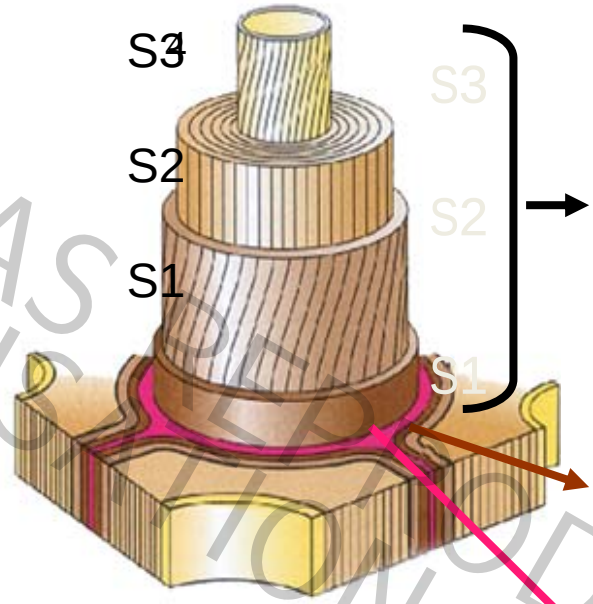
Caractéristiques communes

Teneur et composition très variable

Fibres végétales = parois végétales







Paroi secondaire
Cellulose /hemicellulose/ lignin

Paroi primaire
Cellulose-hemicellulose/pectines-**lignine**

Lamelle moyenne
Hemicellulose/pectines-**lignine**

Fibre trachéide

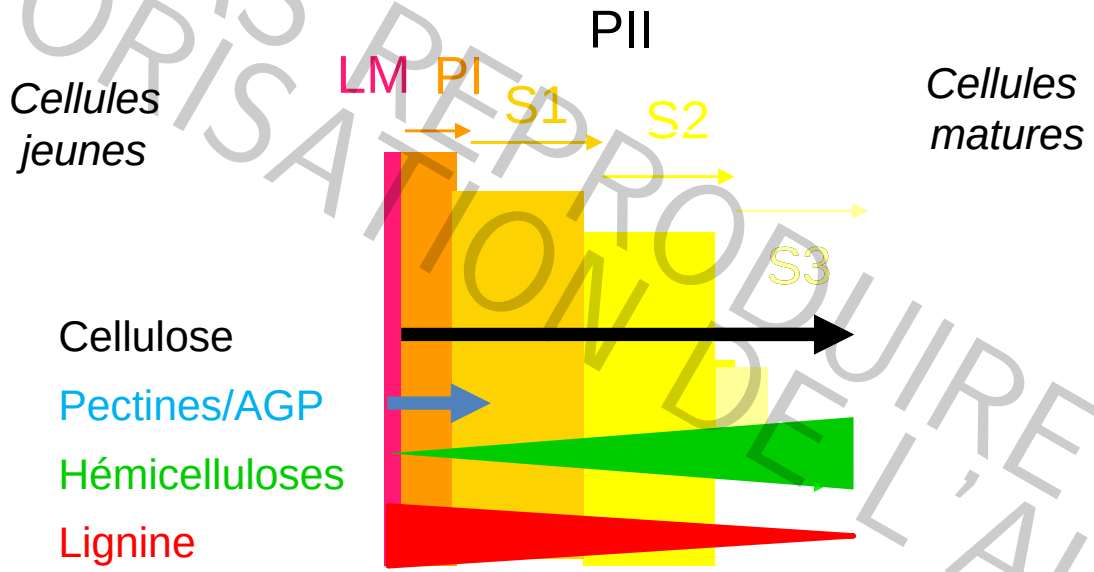
% masse	cellulose	hémicellulose	lignine
Paroi primaire	15	15	70
S1	28	27	45
S2	45	35	20
S3	47	38	15

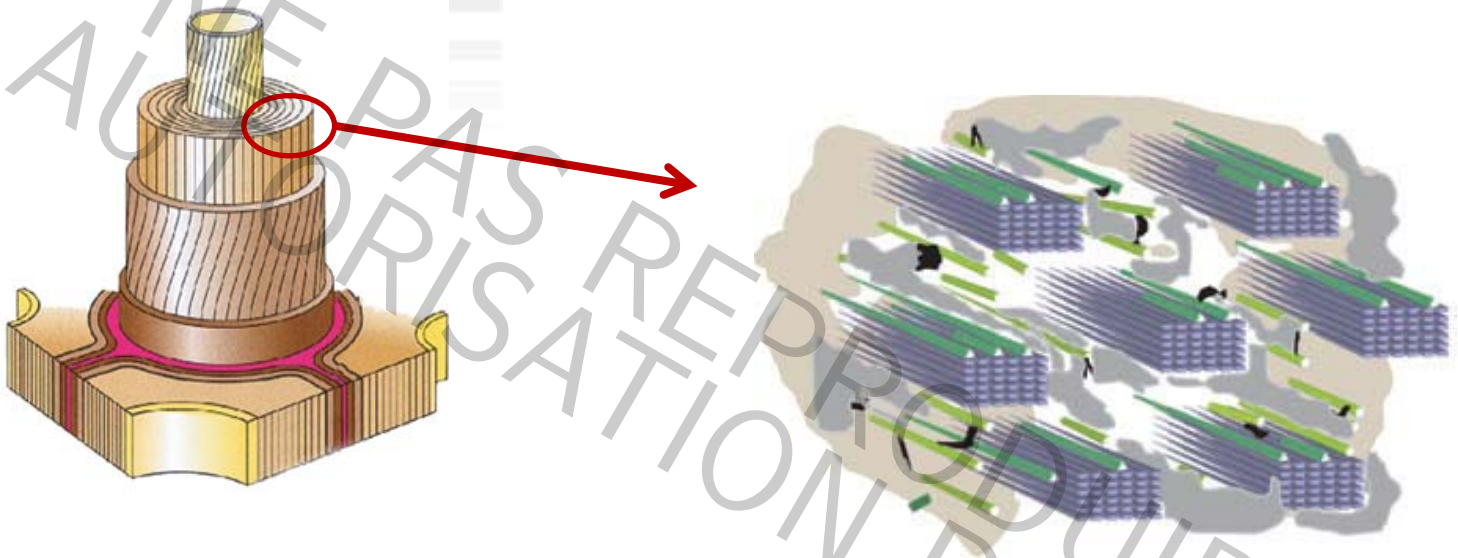
Gradient de composition chimique

Gibson , 2012

Gradient chimique des fibres liée à la construction des parois

Ensemble d'évènements biologiques coordonnés et contrôlés (épaississement des parois fonction de la cellule, environnement….)



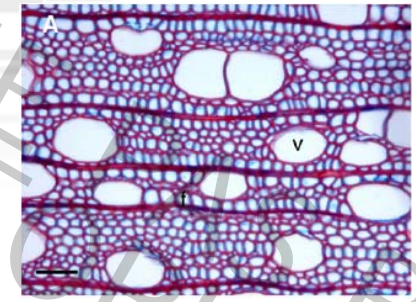


Armature cellulosique

Matrice amorphe

Interaction matrice /cellulose

Morphologie et Composition chimique



Fibres xylémiennes

Fibres courtes

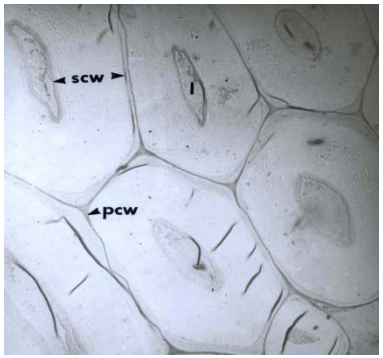
Sclérenchyme

Fibres longues

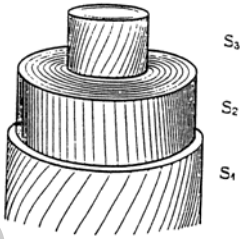
	Longueur (mm)	Cellulose %	Lignines %	Polysaccharides non cellulosiques %
Lin (sclérenchyme)	10-60	80	2-3	10
Feuillus	3	40-50	20-25	25-35
Résineux	1-2	40-50	30	20-30

	chanvre	lin
Longueur, µm	5-55	10-60
Diamètre, µm	13-40	8-30
Cellulose, % cristallinité	60 55	70-80 70
Polysaccharides % non cellulosiques	15	10
Lignine, %	2-3	2-3

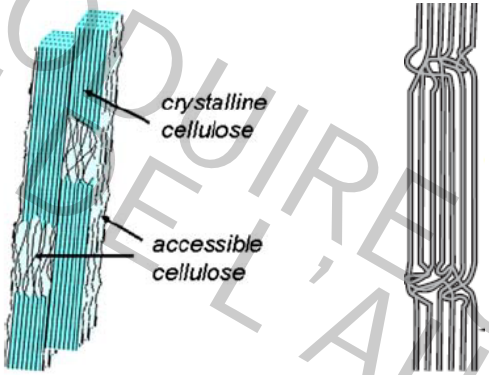
Cellulose /paroi secondaire



Structure multicouche de la paroi
Orientation des strates S1, S2, S3
de la paroi secondaire

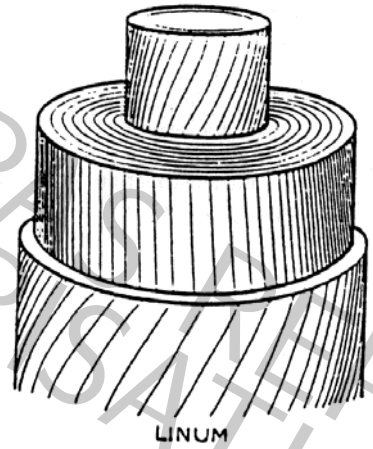


Degré de polymérisation
Degré de cristallinité de la cellulose



Salmen, Bergstrom, 2009, Morvan, 2005

La cellulose cristalline, constituant majoritaire



Cellulose fortement orientée
Angle des microfibrilles 6 -10°

Diffraction rayons X
Fibres primaires

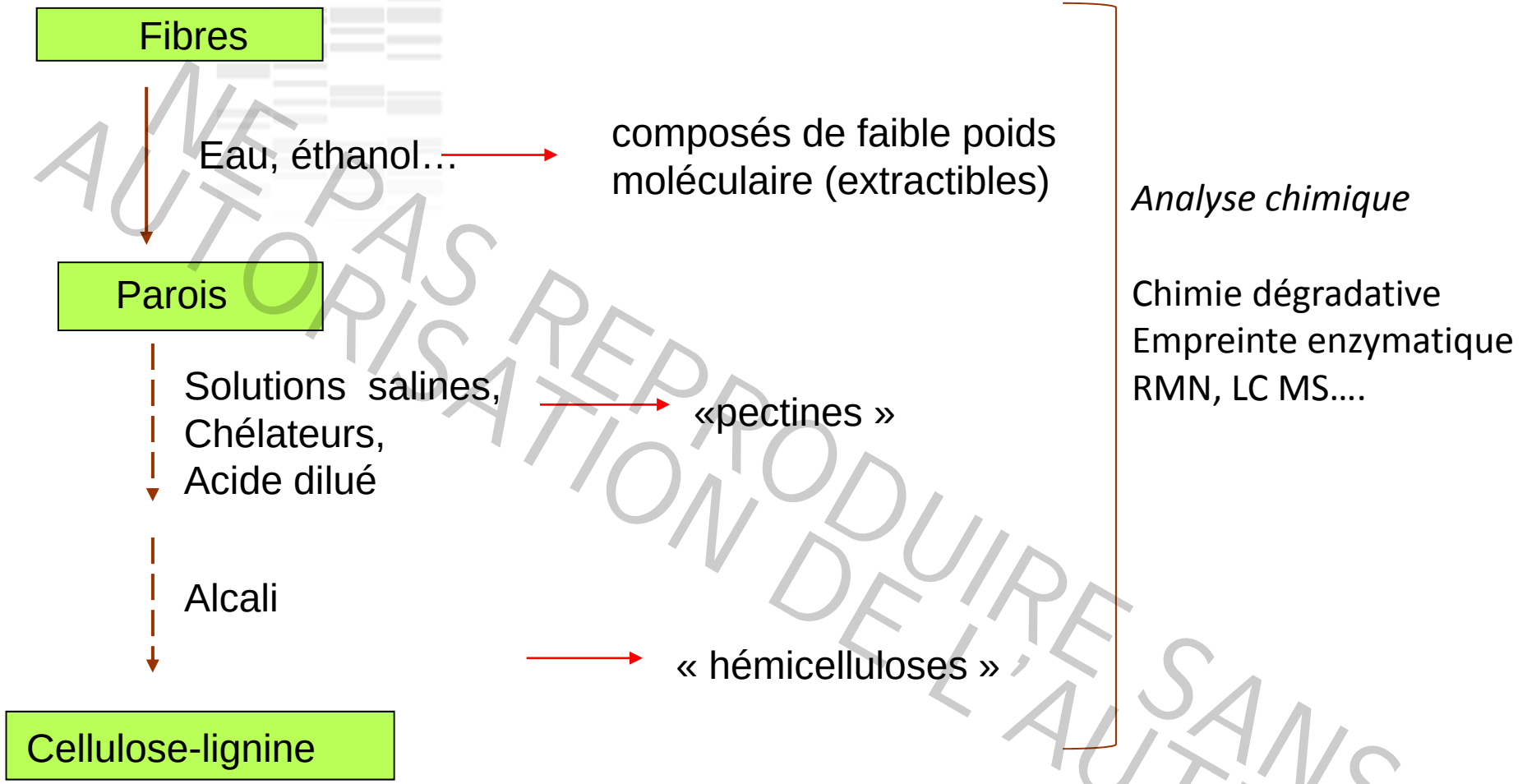
		Taille des cristaux (A)		
	Cr.I.	D (101)	D (10-1)	D (002)
Lin	64	58	67	57
Chanvre	53	30	54	40

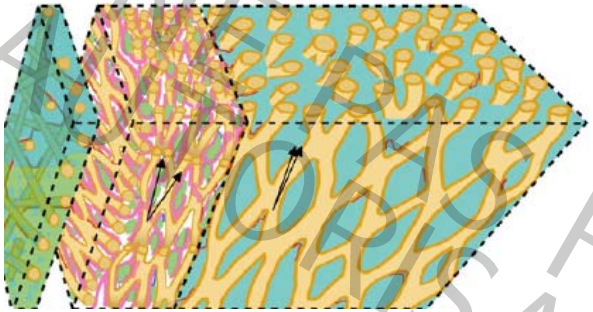
Bonatti et zal, 2004, Mellerowic, 2012

Chimie des Fibres : approches expérimentales

- Chimie dégradative (fibres et polymères extraits)
- Spectroscopies : infrarouge, RMN,..
- Topochimie /microscopies
  (immuno)cytochimie, microspectroscopies IR, fluorescence, Raman…)
- Nanomicroscopies (TEM, FE-SEM, AFM /nanoIR, Surface force ….)

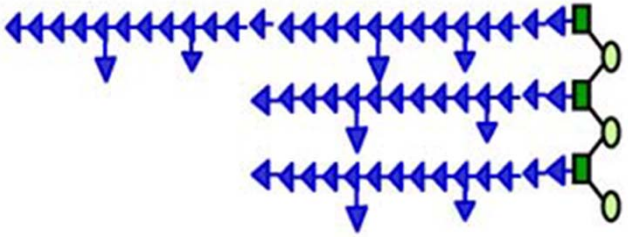
- Modifications physico chimiques, enzymatiques
- Comportement physicochimique des fibres

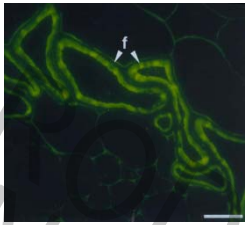




les parois secondaires de lin: pectines

Rhamnogalacturonanes ramifiés par des longues chaïnes de galactanes
Arabinogalactanes (arabinogalactanes protéines)

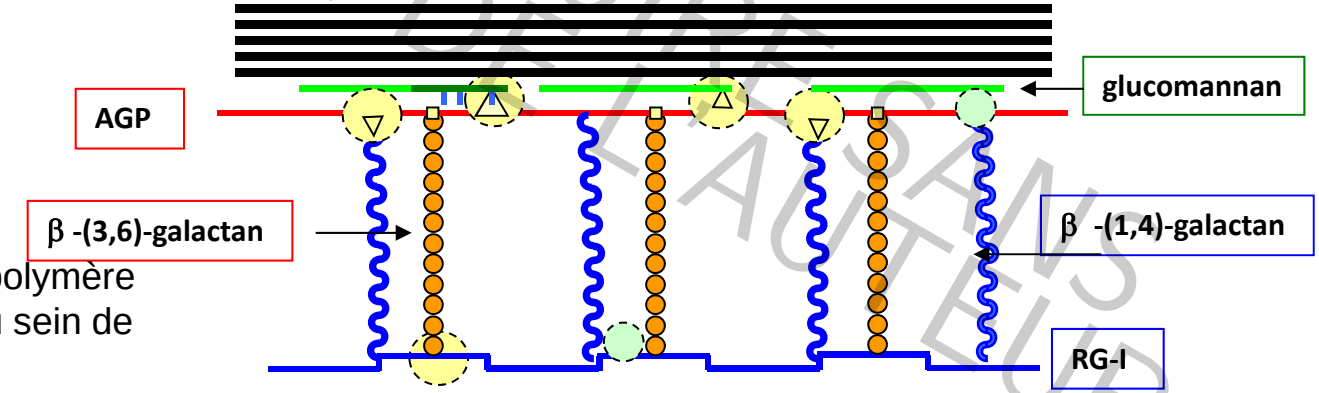




Immunarquage galactanes

- Interactions non covalentes entre matrice et cellulose (galactanes, mannane)

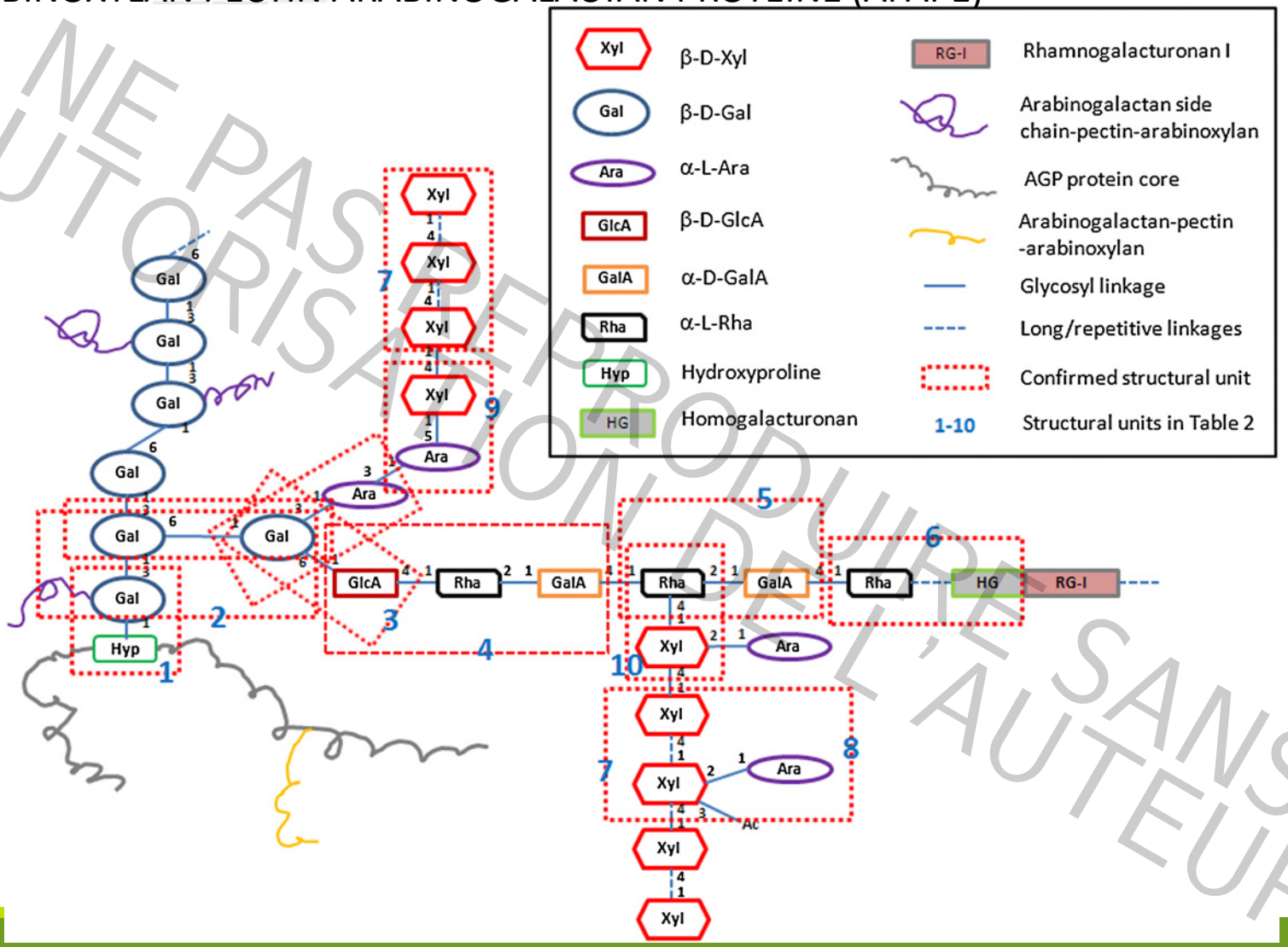
- Multiples associations inter-polymère covalentes /non covalentes au sein de la matrice



Morvan et al, 2004

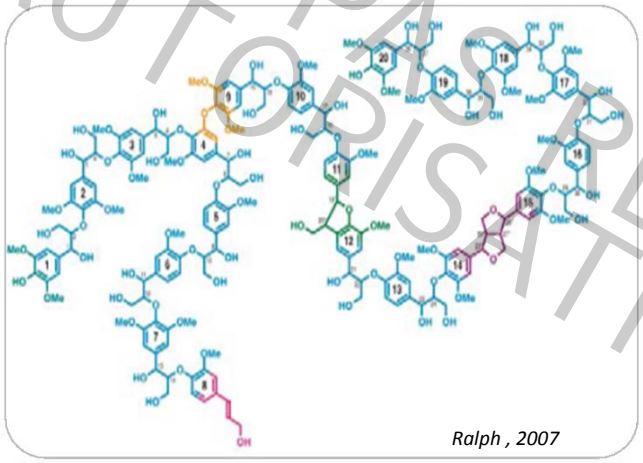
Réseau pectine- protéine- hemicellulose

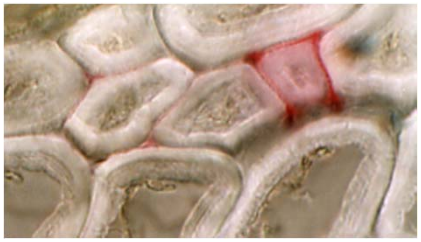
ARABINOXYLAN PECTIN ARABINOGALACTAN PROTEIN1 (APAP1)



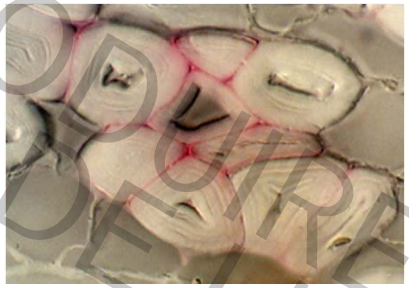
Tan et al, 2013

Distribution des lignines





Lin



Chanvre

Lignines

- Lamelle moyenne /paroi primaire

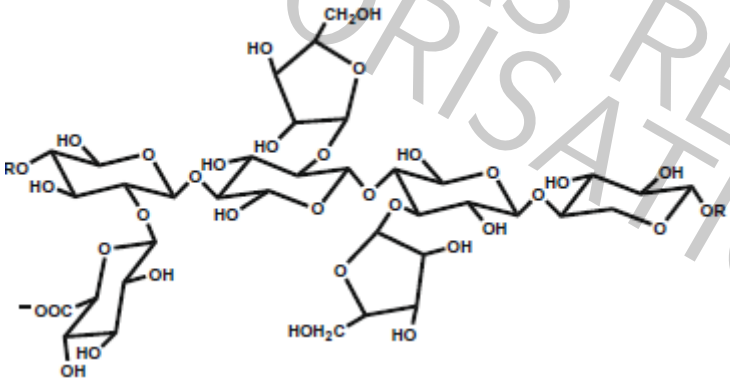
Composition des polysaccharides des fibres de chanvre

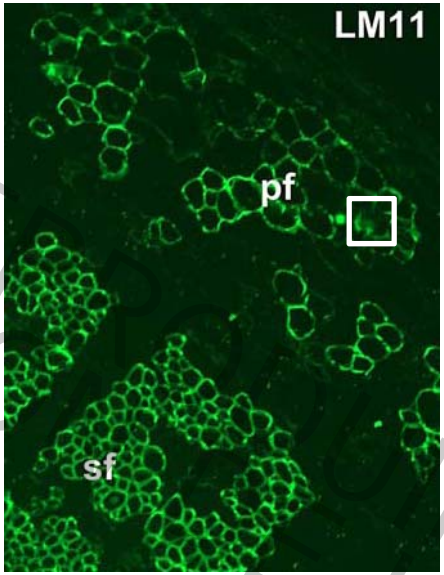
Maturation	1 Végétatif	2	3	4 Maturité graine
acide galacturonique	2.4	1.8	2.0	1.8
rhamnose	1.5	1.3	1.3	1.3
arabinose (pectines)	2.8	2.2	2.3	2.1
galactose (pectines)	4.3	3.6	3.1	2.7
xylose	2.8	2.9	3.1	2.7
mannose	3.2	3.9	4.3	4.4
glucose (hémicelluloses)	7.3	13.5	15.1	11.8
protéines glycoprotéines	4.8	3.4	2.7	1.6

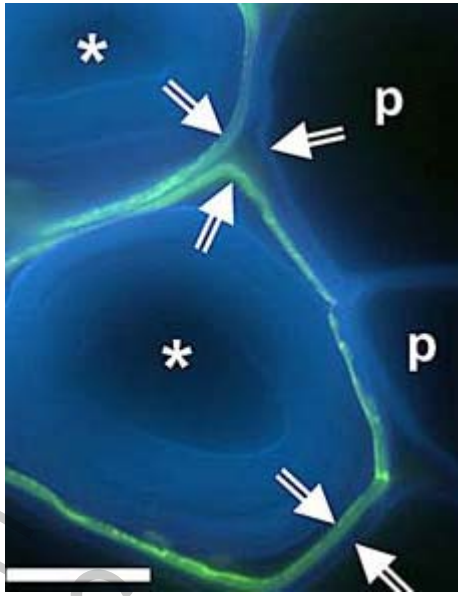
Crônier et al, 20O5

Distribution des polysaccharides non cellulosiques (fibre de chanvre)

Immunomarquage xylanes







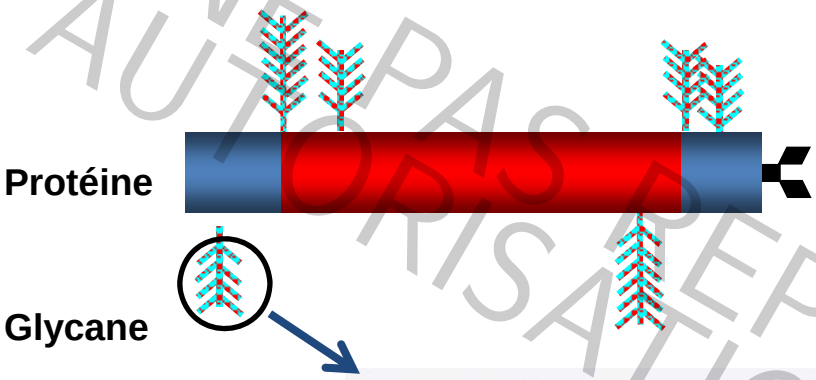
xylanes

- parois primaires
- absents des parois secondaires (différent des fibres de bois)

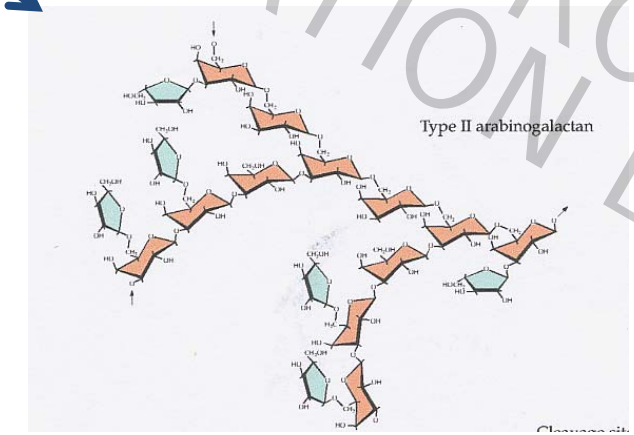
Blake et al, 2008

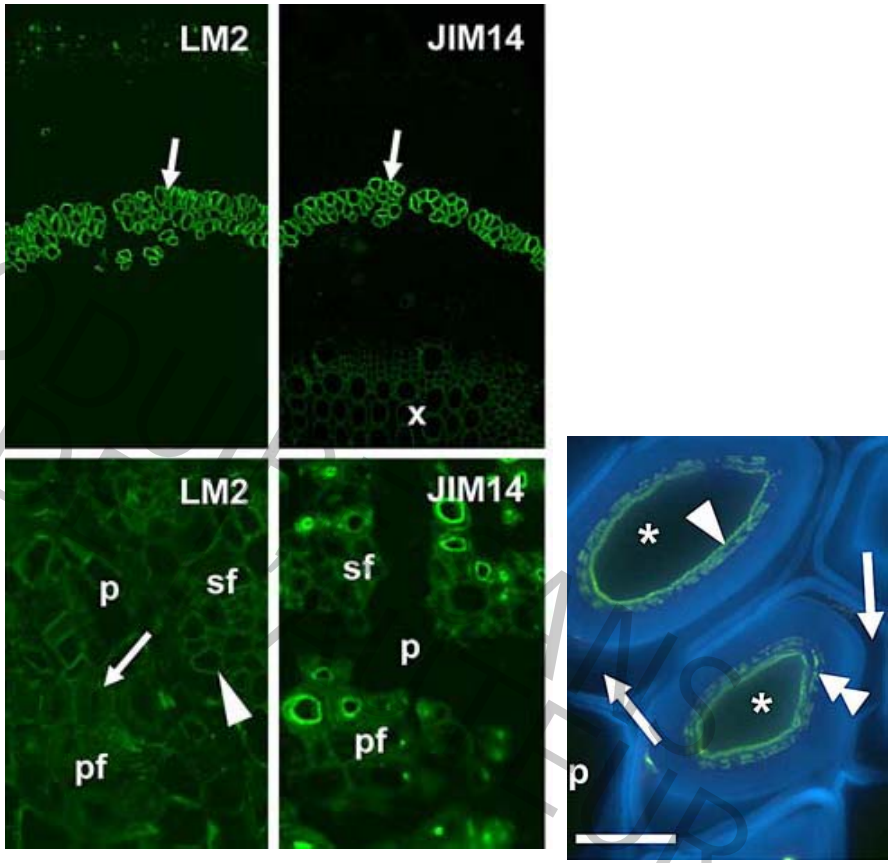
Distribution des polysaccharides non cellulosiques (fibre de chanvre)

Immunomarquage glycoprotéines



Arabinose
Galactose



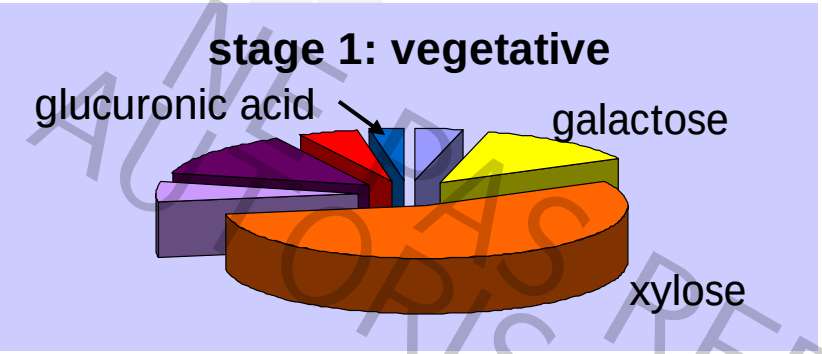


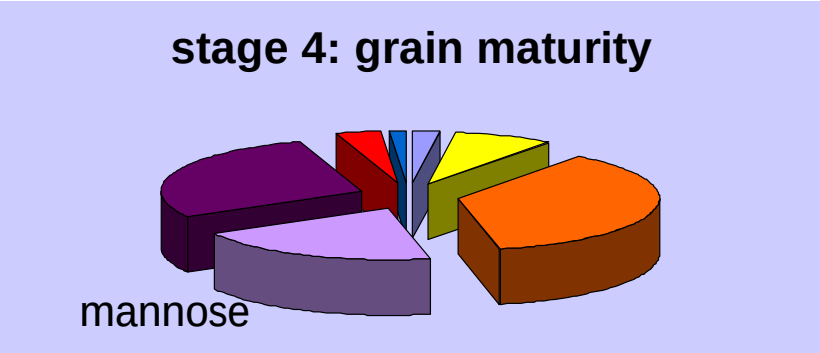
Arabinogalactanes protéines

- parois secondaires (zone interne)

Blake et al, 2008

Extraits 1M NaOH

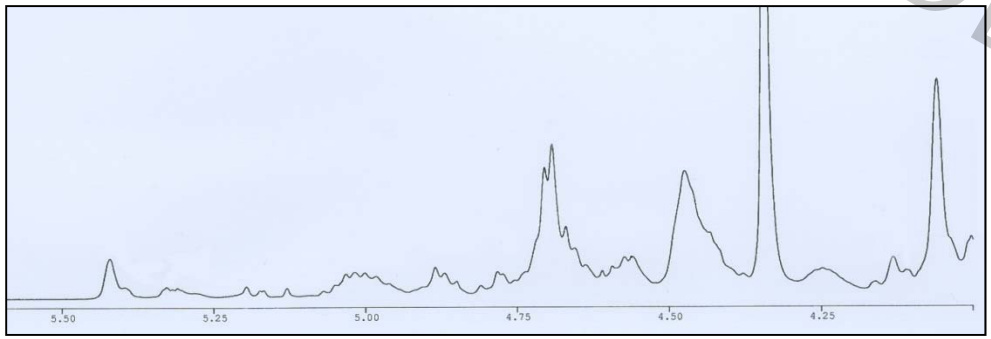




Glucomannanes de fibres de chanvre (RMN ^{1}H)

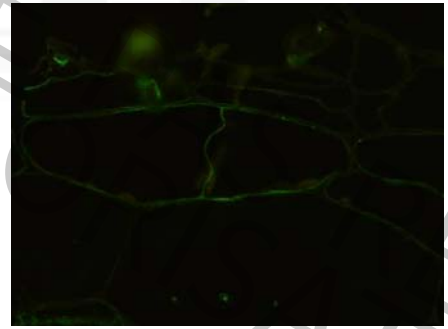
β-(1 $\rightarrow$ 4)- glucomannanes

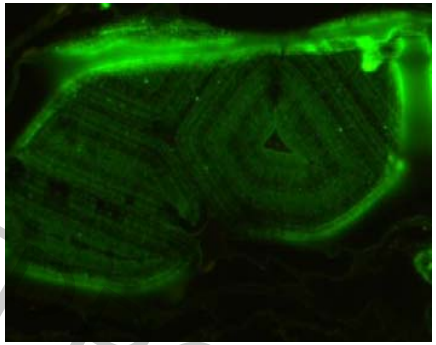
Acétylation en C2/C3 du mannose



galactanes glucomannanes

Chanvre





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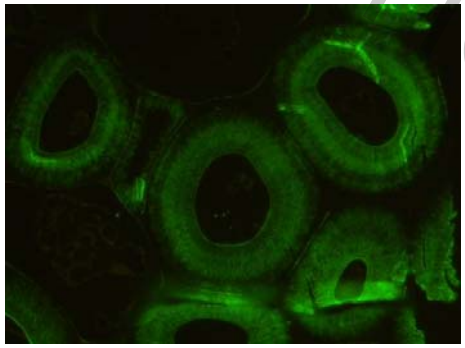
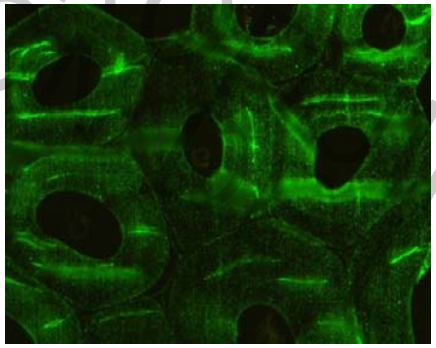
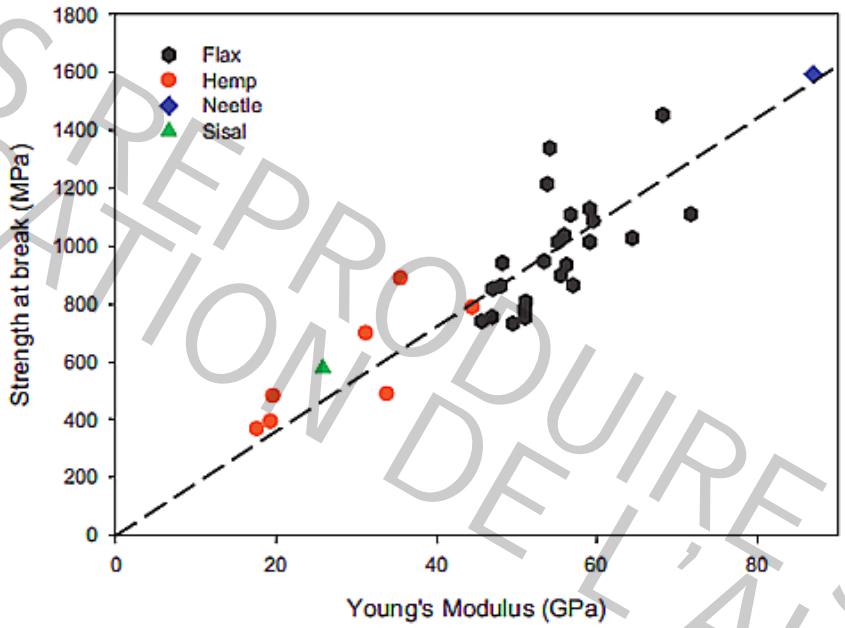




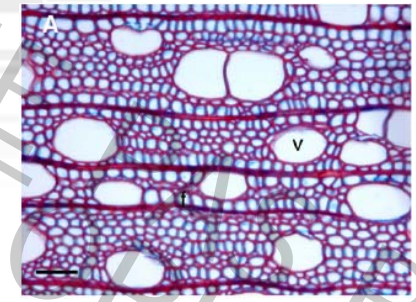
Chabbert et al, 2014, unpublished

Fibre longues lin et chanvre :
Variations de propriétés mécaniques liées à l'architecture de la matrice polysaccharidique



Marrot et al, 2013

Morphologie et Composition chimique



Fibres xylémiennes

Fibres courtes

Sclérenchyme

Fibres longues

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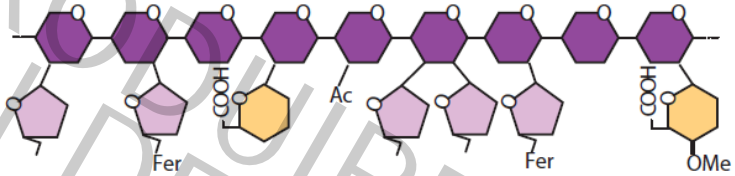
Feuillus	3	40-50	20-25	25-35
Résineux	1-2	40-50	30	20-30

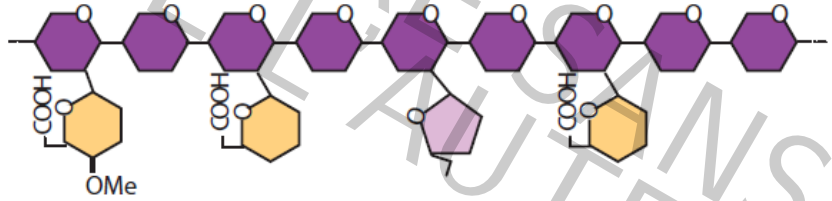
Hemicelluloses des fibres courtes

(% dry matter)	*Graminées*	*Feuillus*	*Conifère*
Glucuronoxylane	-	20-30	-
Glucuronorabinoxylane	40-50	Traces	5-15
Glucomannan	0-5	2-5	-
Galactoglucomanne	-	-	10-30

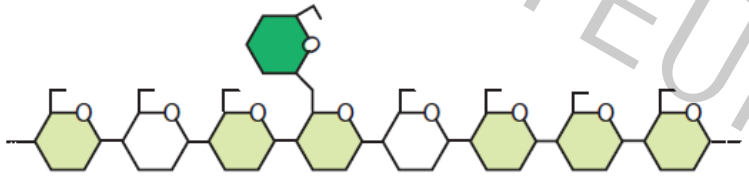
Glucuronoxylane



Glucuronoarabinoxylane

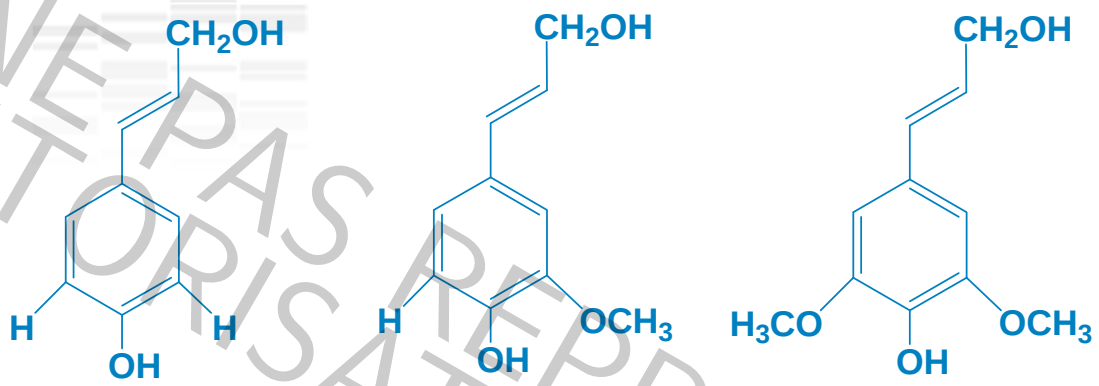


Galactoglucomanne



Scheller and Ulvskov , 2010

Les fibres courtes ont des parois lignifiées



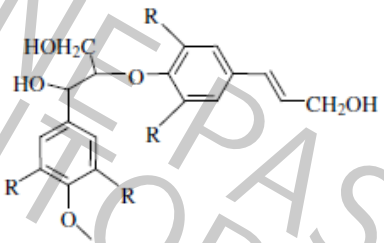
= H lignine = G lignine = S lignine

conifères = 90 % G lignine

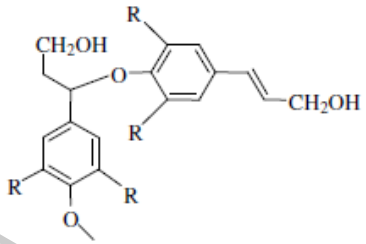
angiospermes * = G/S lignine (proportions variables)

Plusieurs types de liaisons intermonomères

Liaisons « non condensées »: cibles des dégradations chimiques



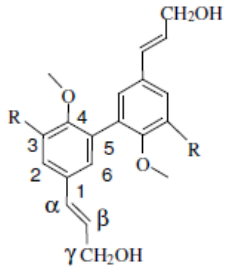
β–O–4



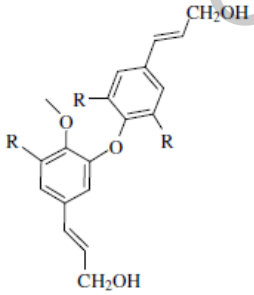
α–O–4

méthodes de caractérisation des lignines

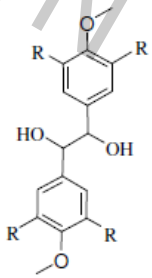
Liaisons « condensées »



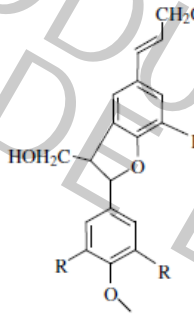
5–5



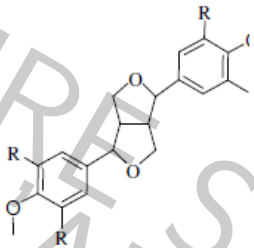
4–O–5



β–1



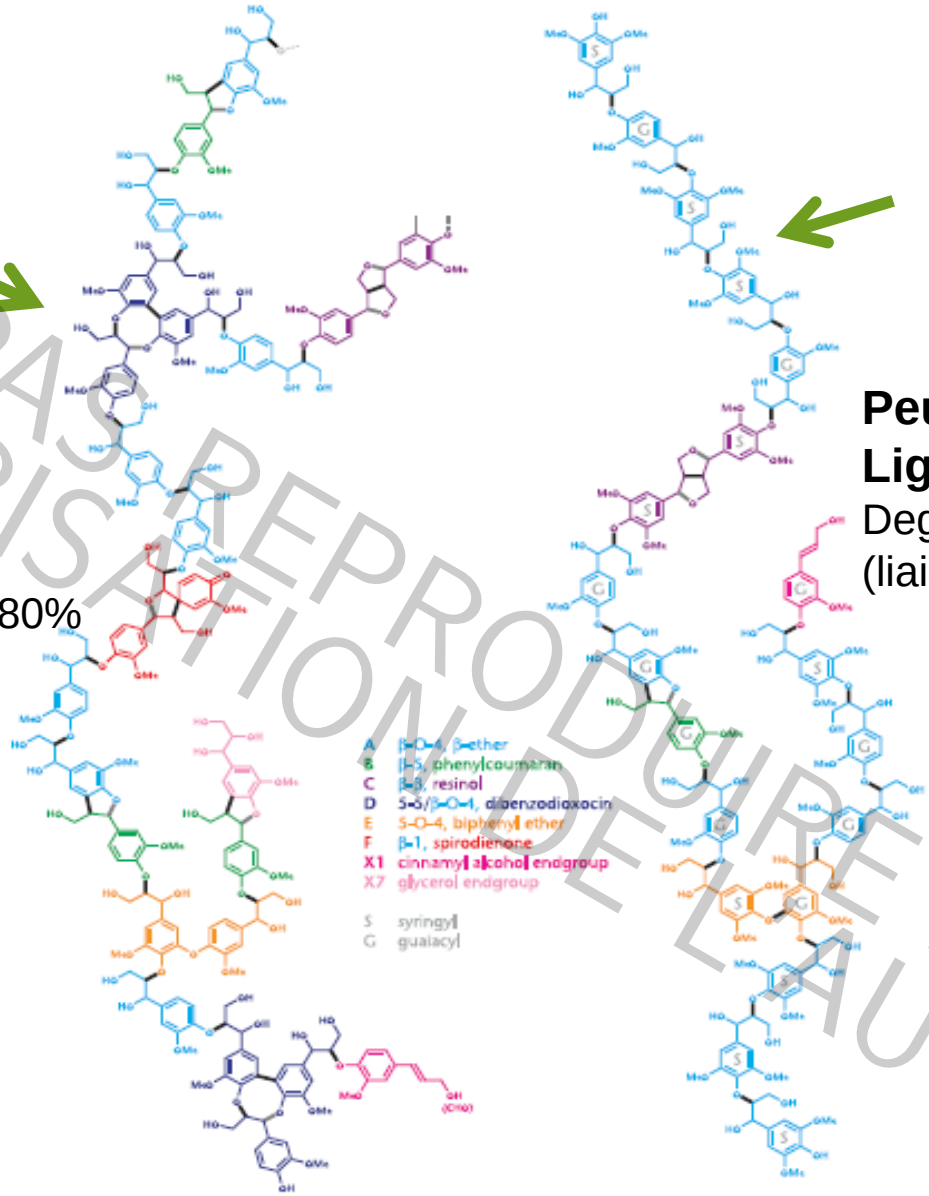
β–5



β–β

Points de ramifications

Domaines linéaires



Epicéa
Lignine G
Degré de condensation 80%
(liaisons condensées)

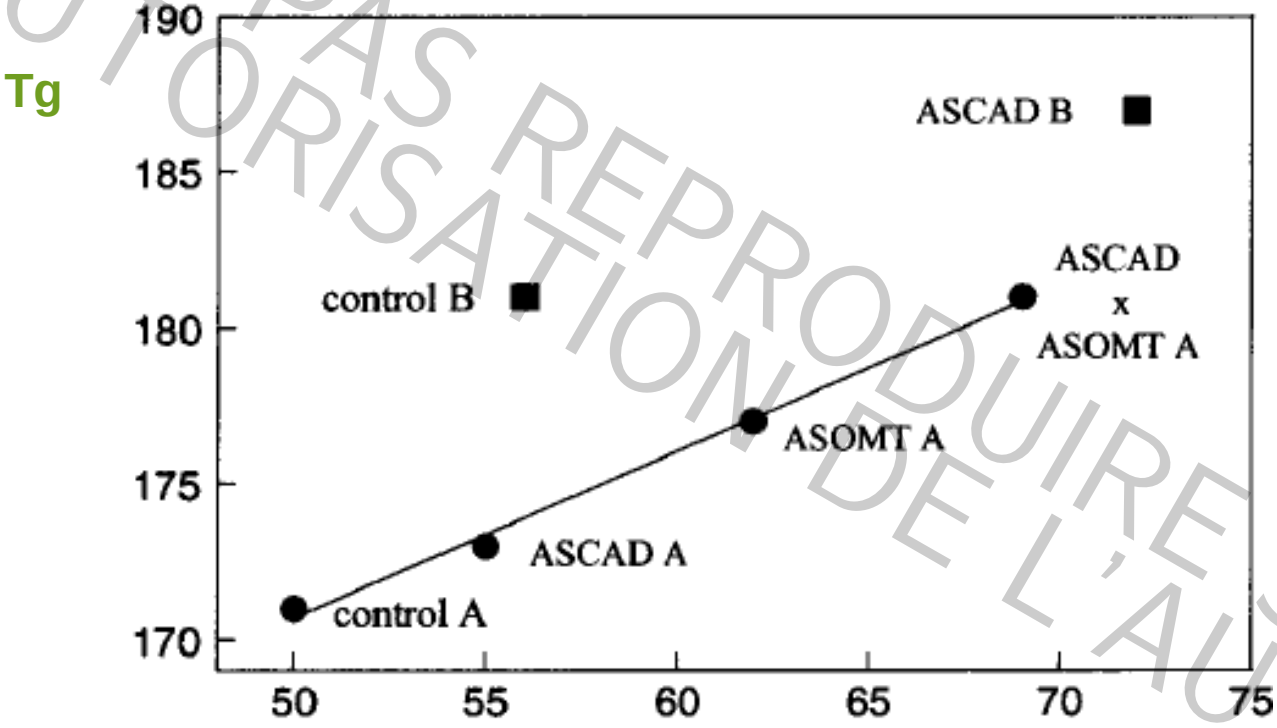
Peuplier
Lignine S/G
Degré de condensation 50%
(liaisons condensées)

Ralph et al, 2007

INRA SCIENCE & IMPACT

Structure de la lignine et propriétés thermiques

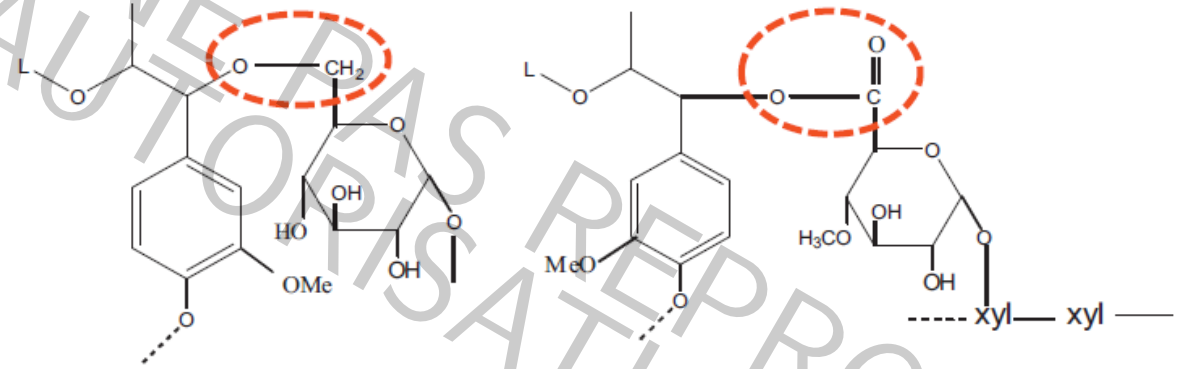
Lignine extraites de plantes transgéniques :
qualité variable (composition et degré de condensation) selon modulation/sous-expression des gènes de biosynthèse des monolignols

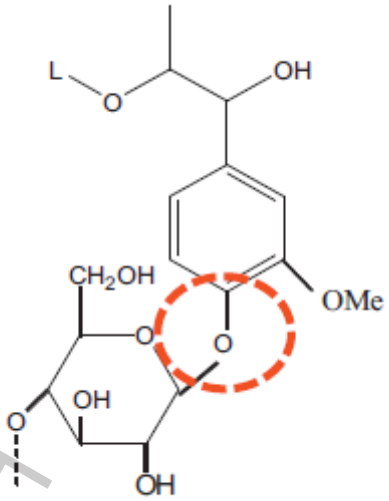


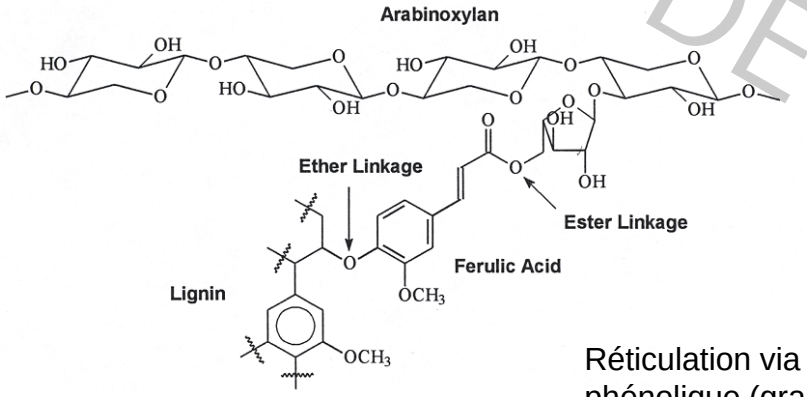
% unités engagées dans les lignines « condensées »

Baumberger et al, 2002

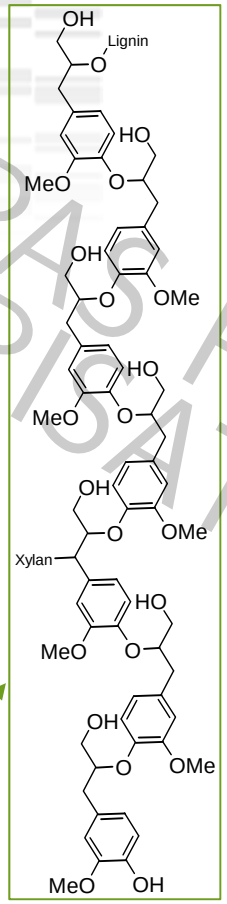
Interactions covalentes lignines –hémicelluloses :





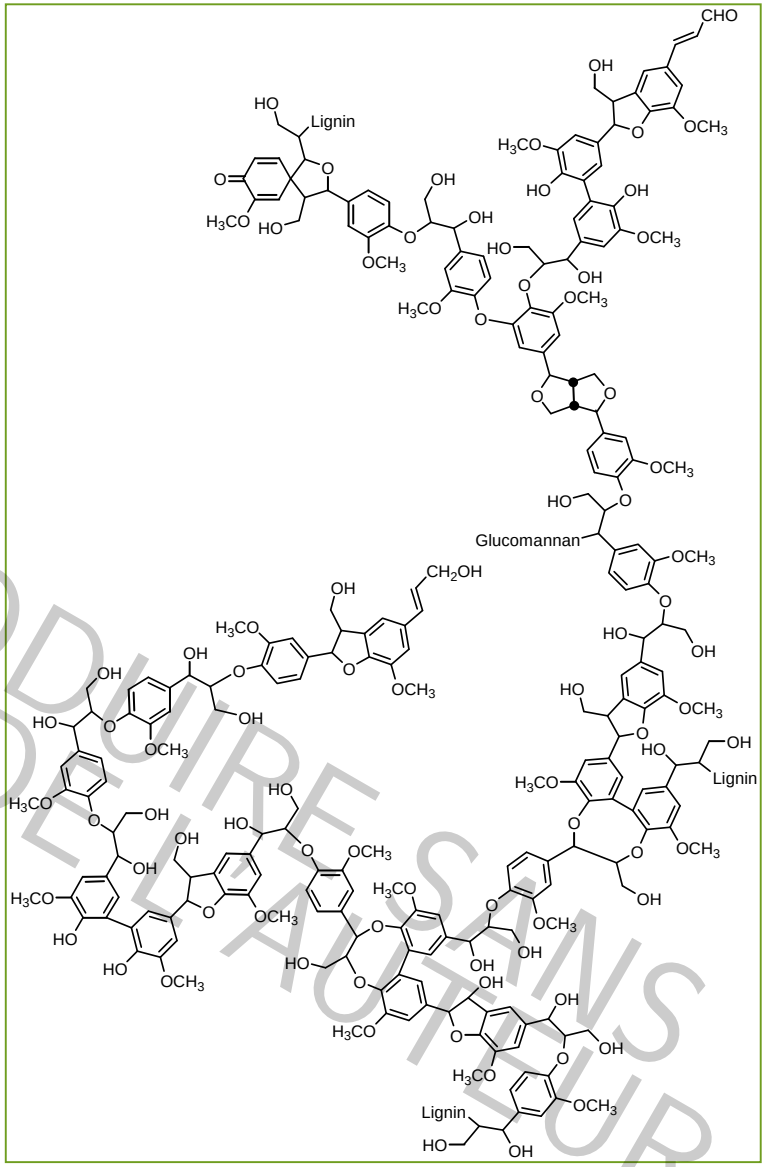


Réticulation via acide phénolique (graminées)



Lignine-xylane

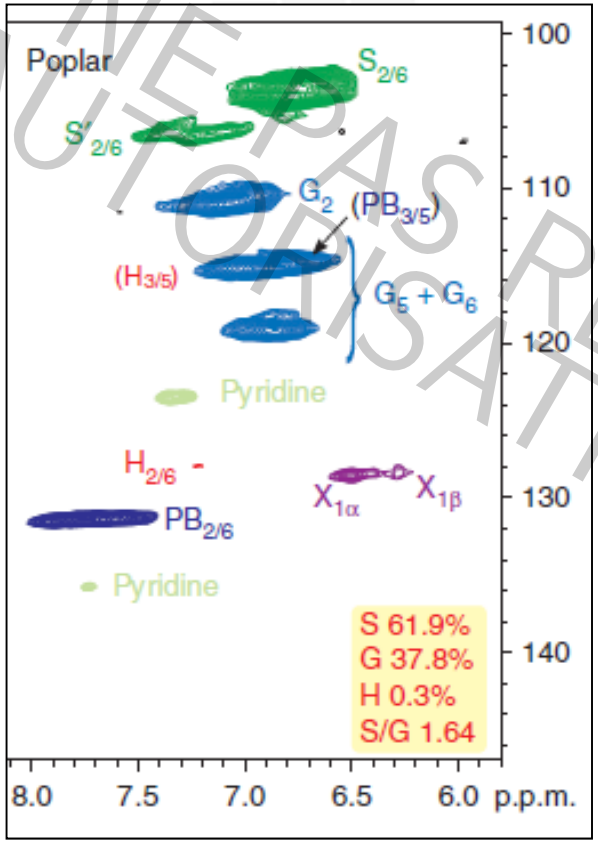
Lignin-glucomannane

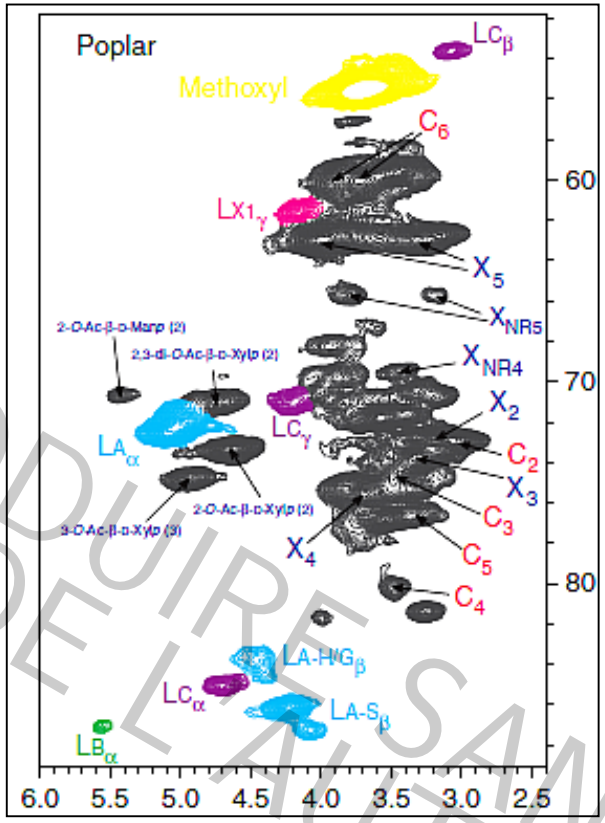


Gellerstetdt, G ,2009, séminaire lignines

Analyse parois lignifiées RMN 2D

Ultrabroyage des parois, solubilisation



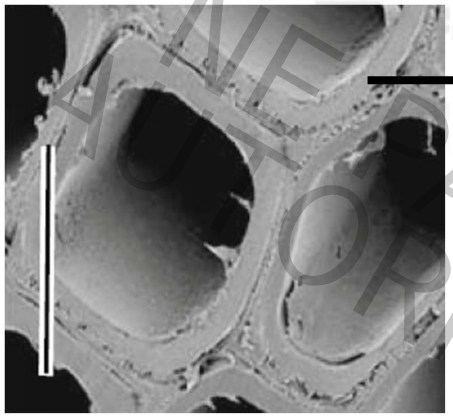


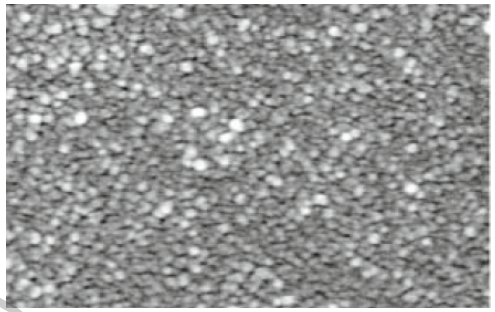
Information structurale des constituants pariétaux

Mansfield et al, 2012

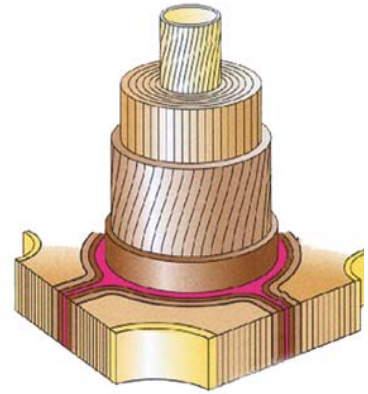
Microscopie électronique à balayage (FESEM)

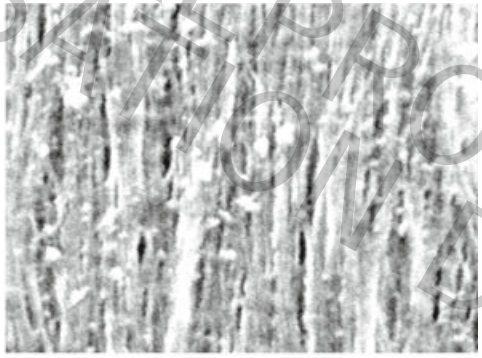
Architecture

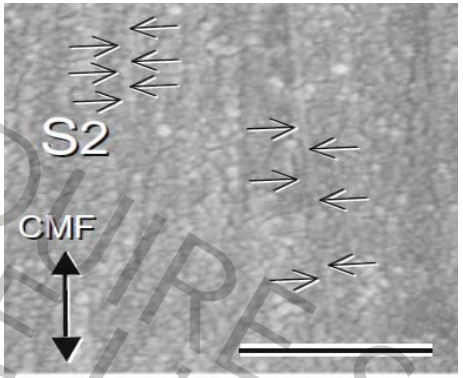




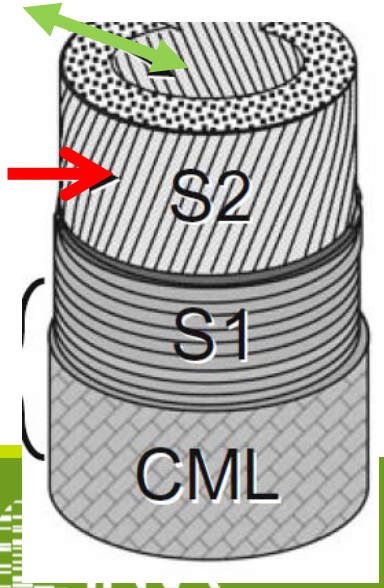
S2

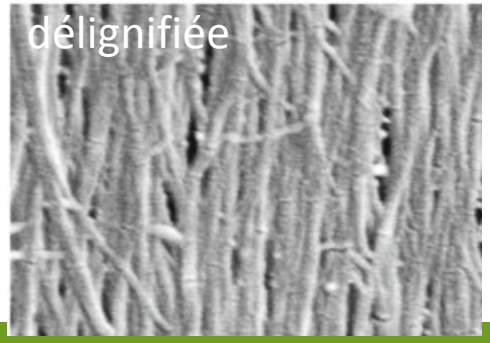


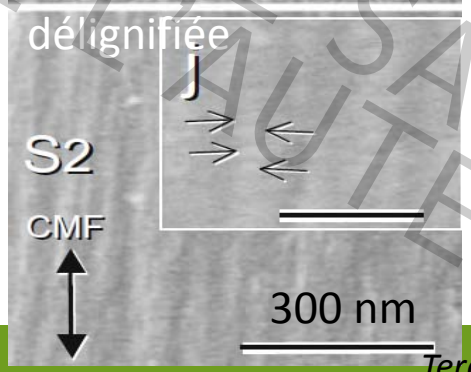




délignification





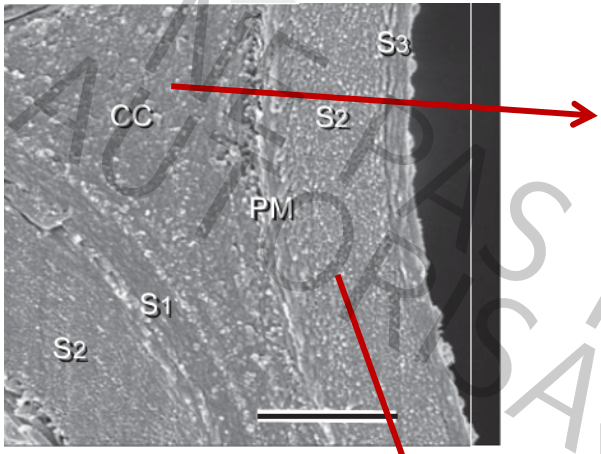


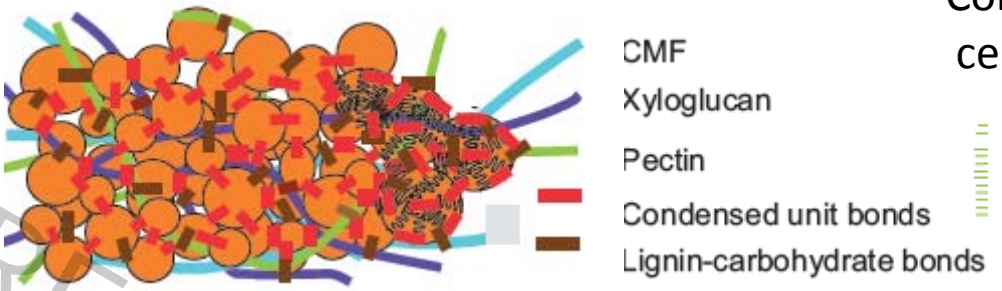
Terashima et al, 2004

Surface de la strate S2 en formation

S2 différenciée

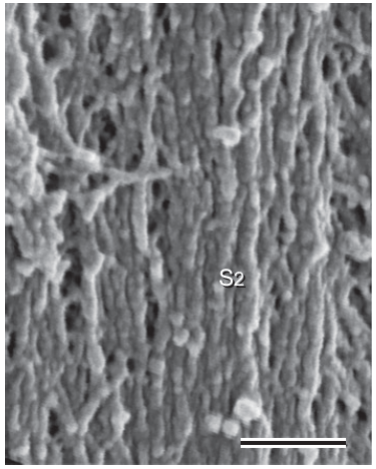
Différents réseaux lignine/polysaccharide dans les parois

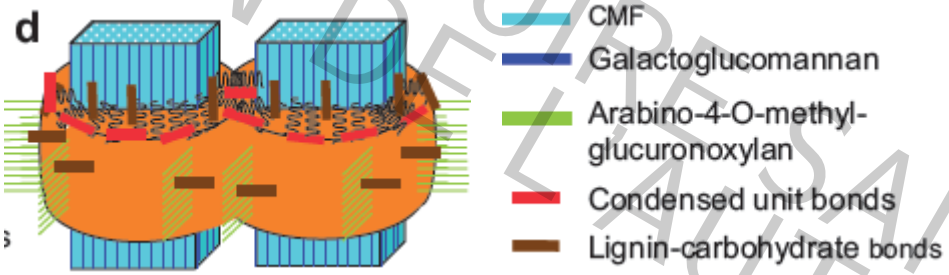




Coin des cellules

Organisation globulaire des complexes lignine – hémicelluloses parallèles aux microfibrilles dans la paroi secondaire

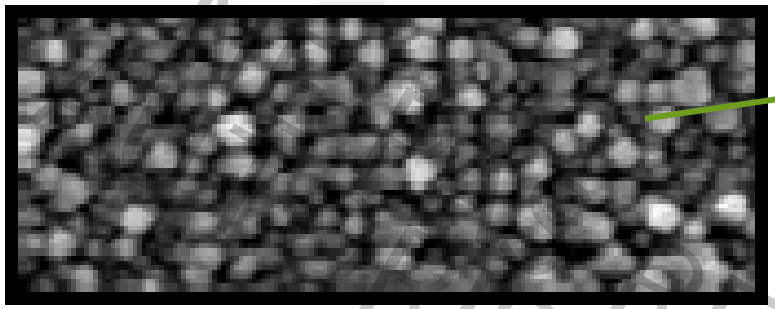


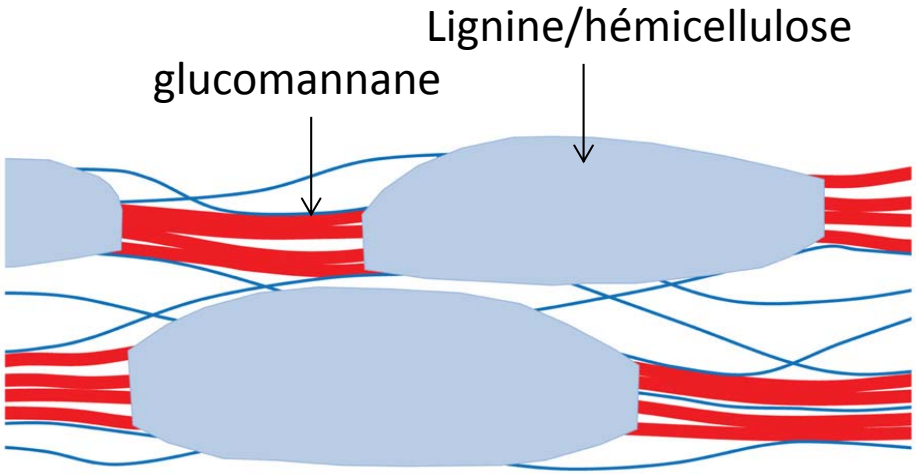


Paroi secondaire (S2)

Orientation des complexes lignine-hémicellulose parallèle aux microfibrilles dans la paroi secondaire

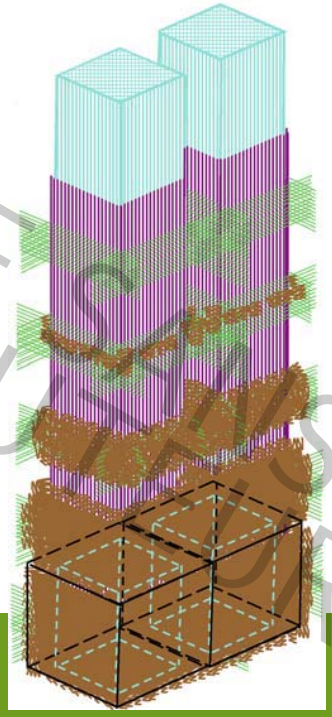
Terashima 2011





Les microfibrilles (3-4 nm) forment un réseau de macrofibrilles (12-20 nm) (hémicellulose/ lignine)

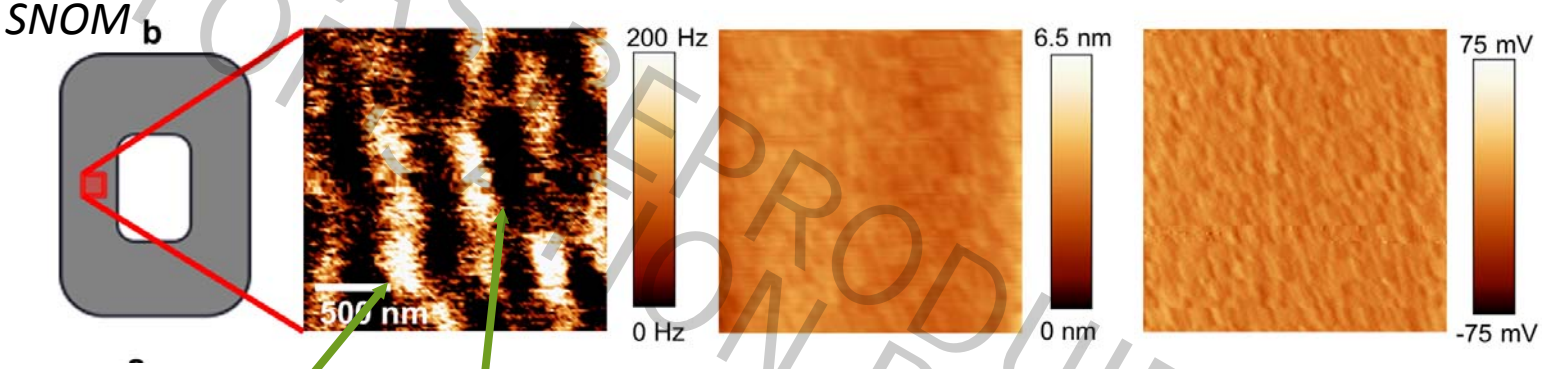
Glucomannanes : hémicelluloses préférentiellement associées aux microfibrilles (conifères)



Salmen et Burgert 2009, Terashima 2011, Cosgrove et Jarvis, 2012

Topochimie des arrangements de polymères ?

Couplage Microscopie de force atomique (AFM fluorescence, Raman…)



Keplinger et al, accepté

Fibres végétales: structure organisée

Plante

Transformations

Contraintes mécaniques et physico-chimiques

Défibrage, process,…

T°, eau…

Organe

Macro

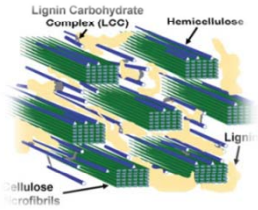
Tissu

Micro

Cellule

Paroi

Supramoleculaire



Réseau de polymères

Moleculaire