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Plant fibres: cell wall and structure of cellulose

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CHEM-E2140

Learning outcome

After this lecture, you will be able to :

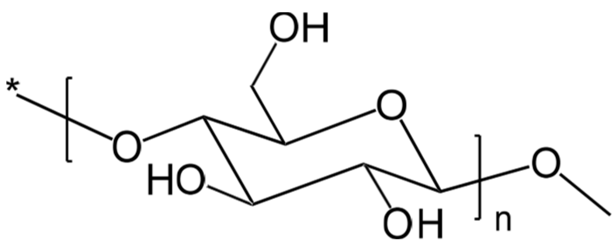
- Answer the questions: where does cellulose come from?
- Distinguish herbaceous and woody plants (main source of cellulose)
- Describe the main points of cell wall ultrastructure: chemistry, morphology, and hierarchy
- Distinguish molecular vs. supramolecular structure with cellulose
- Recognize the crystalline polymorphs of cellulose

Contents

(1) What is cellulose
(2) Sources of cellulose
(3) Plants: basics definitions
(4) Woody plants and herbaceous plants
(5) Wood structure and plant cell types
(6) Plant cell walls: hierarchical structure of fibres
(7) Chemical structure of fibres
(8) Isolation of fibres from plant matrix
(9) Cellulose structure: molecular vs. supramolecular
(10) Cellulose structure: crystalline forms of cellulose

What is cellulose

- Cellulose is a polysaccharide biosynthesized in nature
- Main structural (load bearing) component of all plants
- The most abundant biopolymer on earth (10^{12} tons produced per year)

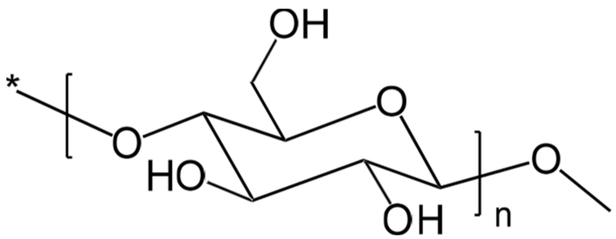


- Poly (1,4-β-D-glucopyranose)
- Linear homopolymer
- Forms semi-crystalline microfibrils
- Recalcitrant
- Insoluble

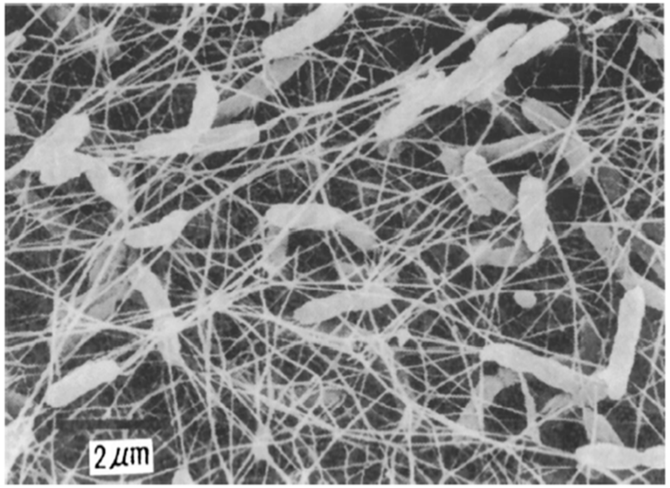
Sources of cellulose

Cellulose is produced via biosynthesis in nature

There are three known sources of cellulose:
(1) Certain species of bacteria (bacterial cellulose)
(2) Tunicates (animal cellulose)
(3) Plants (plant cellulose)



Bacterial cellulose



- Some species of bacteria are able to biosynthesize cellulose (notably *acetobacteria xylinum*)
- The cellulose is extracellular, it is not in the bacteria but extruded by the bacteria
- Bacterial cellulose is the only pure form of cellulose in nature, no other components are synthesized with cellulose
- Microfibrils in bacterial cellulose are generally larger than in other cellulose grades

Tunicate cellulose

- Tunicates are small marine animals
- They are the *only species of animals* that biosynthesize cellulose
- The body of a tunicate is surrounded by a test or a tunic where the cellulose is produced
- Tunicate cellulose is in the form of microfibrils that are highly crystalline compared with most plant celluloses

Plants

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What is a plant?

By plants, people usually refer to *green plants*:

- Flowering plants (angiosperms)
- Gymnosperms
- Mosses
- Clubmosses
- Hornworts
- Liverworts
- Ferns
- Green algae

Two main features of all plants:

- Possess cell walls with cellulose as the main structural material
- Get most of their energy from photosynthesis

Categorisation of plants

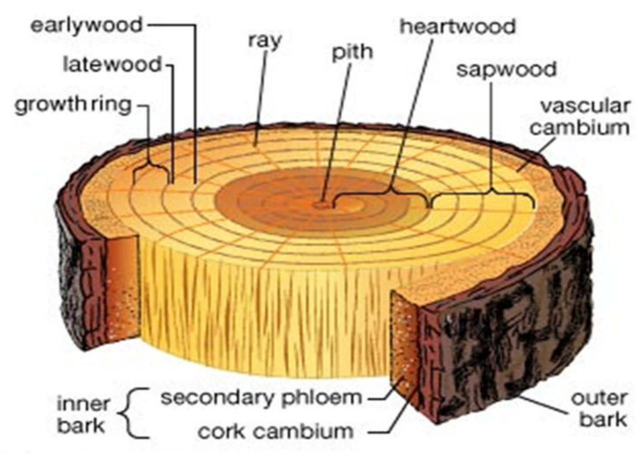
Plants can be categorised in many ways; however, from the point of view of fibre materials, the most sensible division is to:

- **Herbaceous plants**
  - Agro fibres
  - At least the part above ground dies after the growing season
- **Woody plants**
  - Wood fibres
  - Remain alive during dormant season; reinforced by secondary xylem

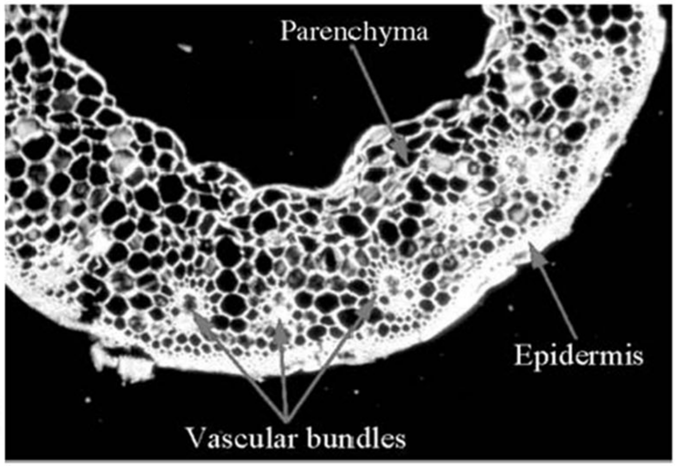
Herbaceous *vs.* woody plants

Localization of growth

(a) Woody plant



(b) Herbaceous plant



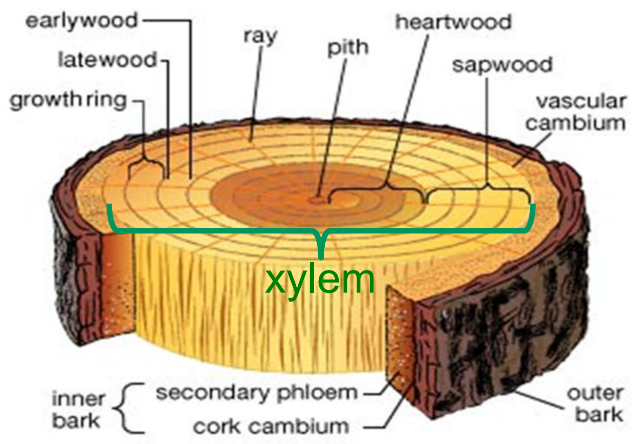
Growth occurs by cell division in vascular cambium

Growth occurs by cell division in vascular bundles

Herbaceous *vs.* woody plants

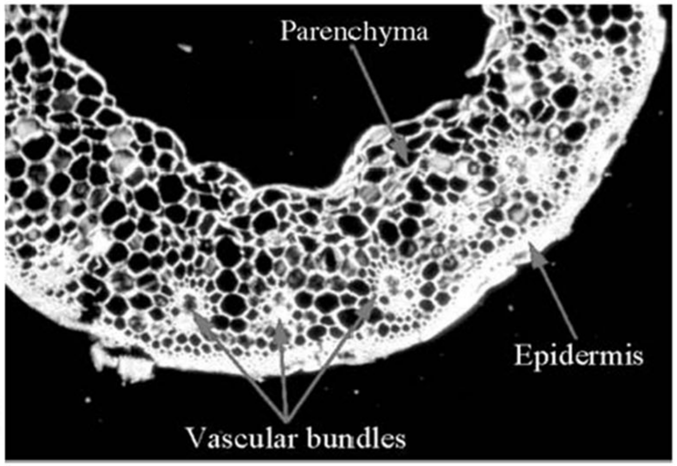
Strength distribution

(a) Woody plant



Strength provided by fibres all over the xylem

(b) Herbaceous plant

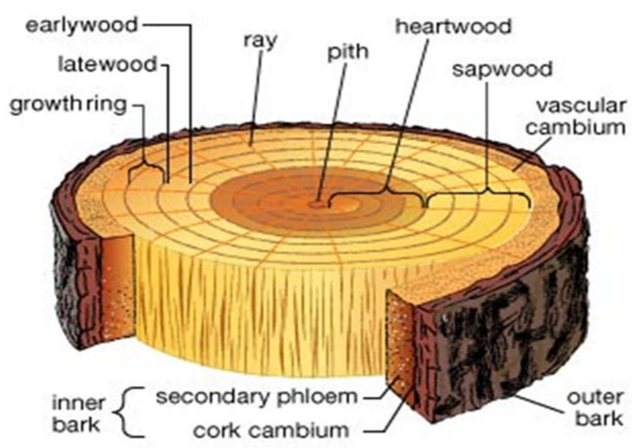


Much of the strength provided by epidermis (cellulose+silica) and fibres

Herbaceous *vs.* woody plants

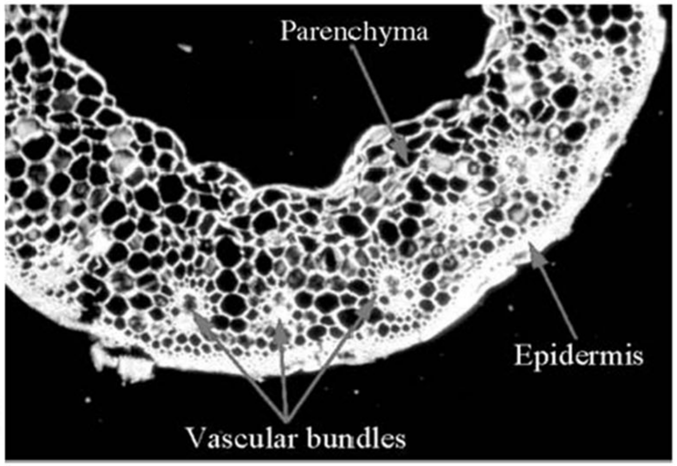
Water transport

(a) Woody plant



Water transport occurs through xylem fibres

(b) Herbaceous plant



Water transport occurs mainly through vascular bundles

Common plants in fibre technology

Woody plants:

- Trees
- Shrubs

Herbaceous plants:

- Flax
- Cotton
- Jute
- Kenaf
- Bamboo
- Ramie
- Sisal

Wood structure and plant cell types

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Heartwood and sapwood

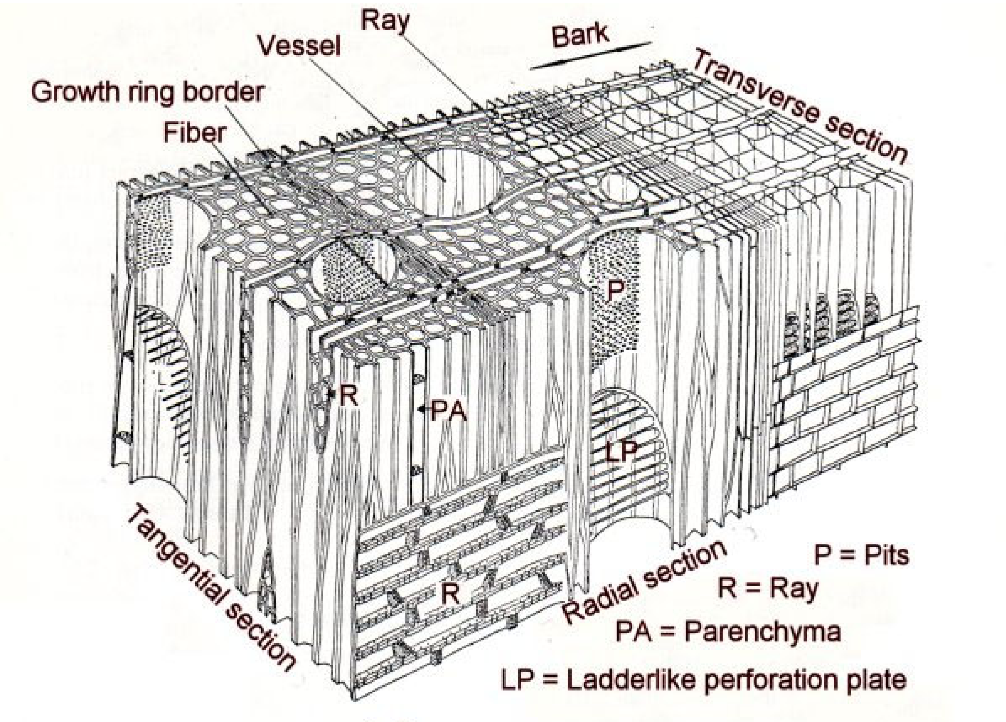
SAPWOOD
- conducts water and minerals nutrients
- has (also) living tissue

→ active tissue

HEARTWOOD
- does not take part in water conduction
- high extractives content

→ inactive tissue
- protects wood against rot or insect decay

Fibres, vessels, parenchyma cells



Fibres: strength, water transport
Vessels: water and nutrition transport
Parenchyma: storage of water and nutrition

Softwood *vs.* hardwood

Softwood: from coniferous trees (evergreens, ones that have needles)
Hardwood: from deciduous trees (ones that have leaves)

Softwood *vs.* hardwood

SOFTWOOD	HARDWOOD
EARLYWOOD AND LATEWOOD DISTINCTION	NO CLEAR DISTINCTION
~90% OF WOOD CELLS ARE TRACHEIDS (FIBRES)	WIDER VARIETY OF WOOD CELLS - ONLY 30-70% FIBRES
	WIDER CHEMICAL DIVERSITY

Ultrastructure of plant fibres

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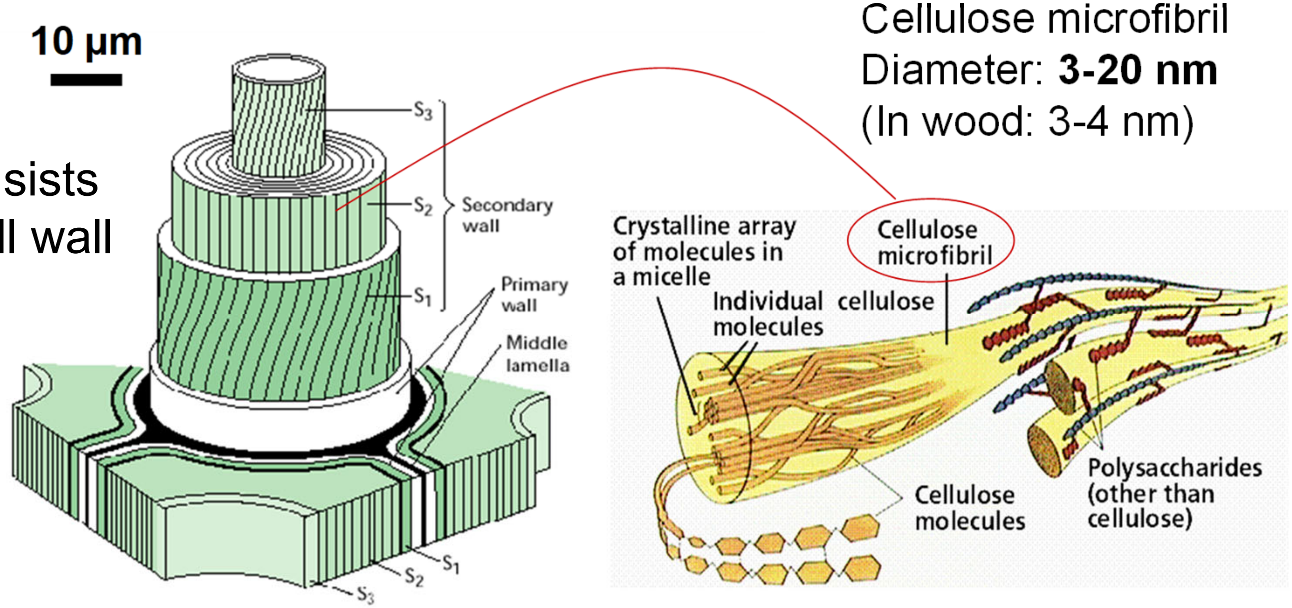
Wood fibre

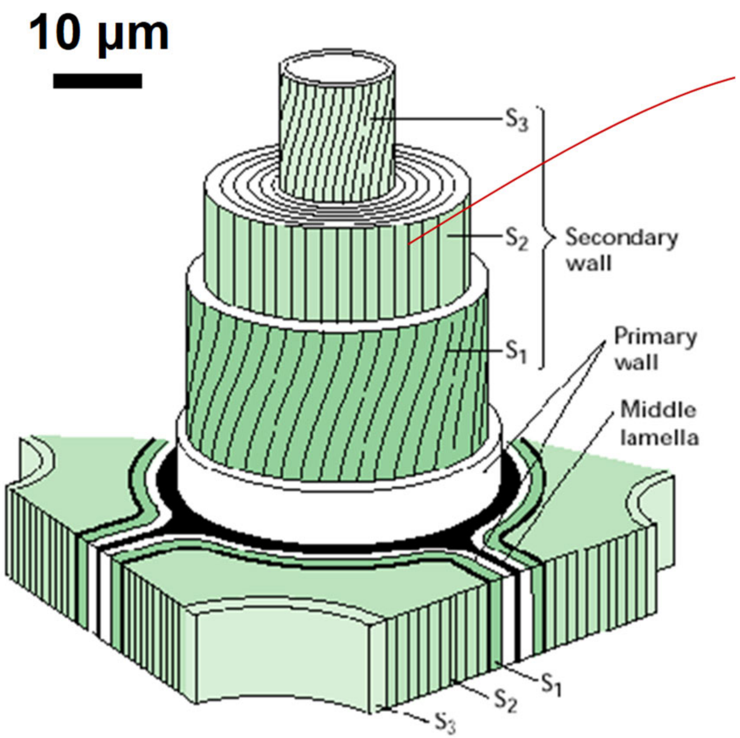
Wood fibres, like many other plants fibres, contain a secondary wall that yields exceptional strength to the fibre

Cellulose microfibril
Diameter: **3-20 nm**
(In wood: 3-4 nm)

Wood fibre consists of a layered cell wall matrix

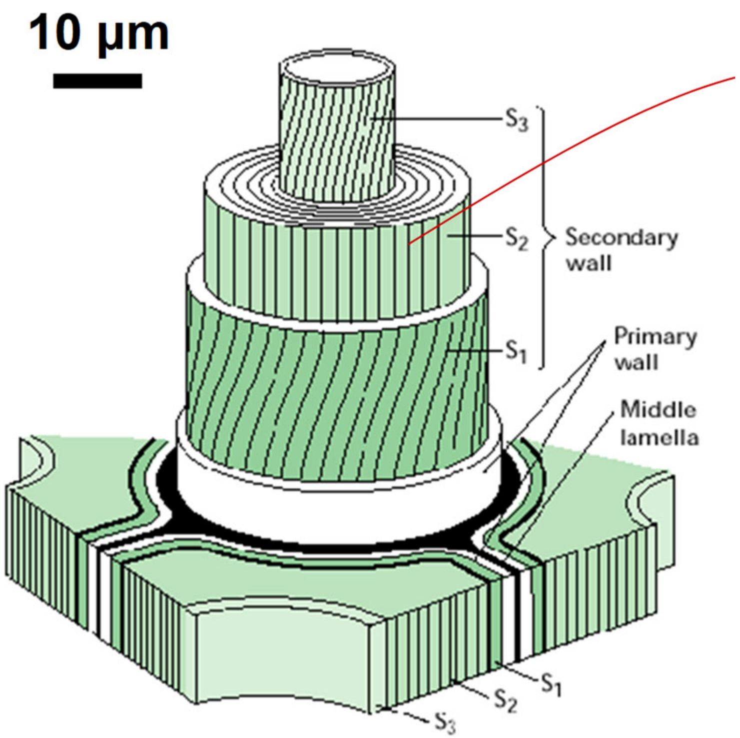


Wood fibre



Wood fibre cell wall consists of semi-crystalline cellulose microfibrils with amorphous lignin and hemicellulose in between.

Wood fibre



- Cellulose microfibrils are oriented in the secondary wall and arbitrarily aligned in the middle lamella
- The “fibril angle” affects the tensile strength of fibres a great deal

Chemical composition of fibres: the lowest hierarchical level

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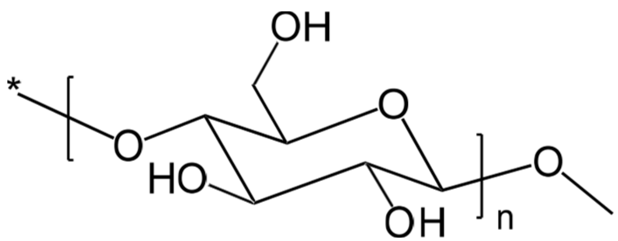
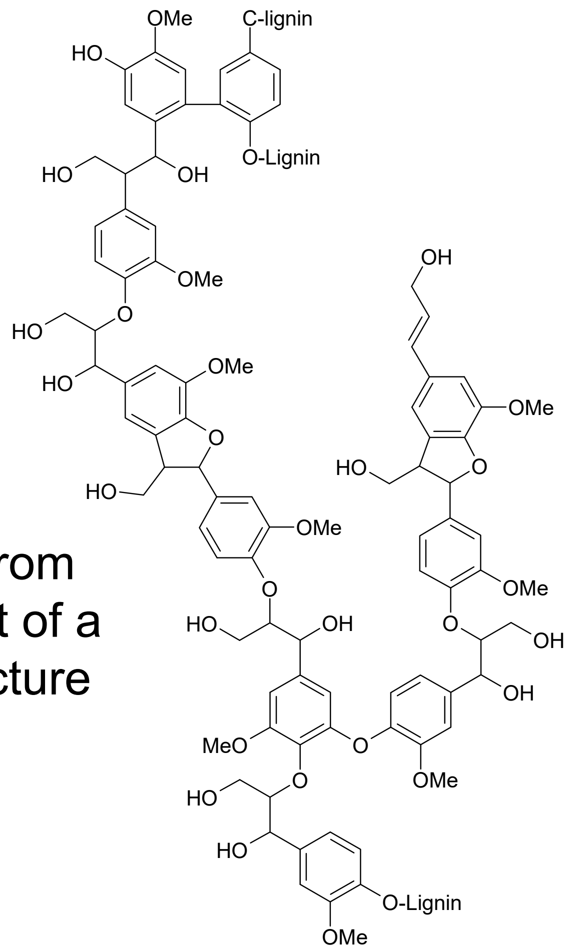
Cellulose: main structural element



- Poly (1,4-β-D-glucopyranose)
- Linear homopolymer
- Forms semi-crystalline microfibrils
- Recalcitrant
- Insoluble

Lignin

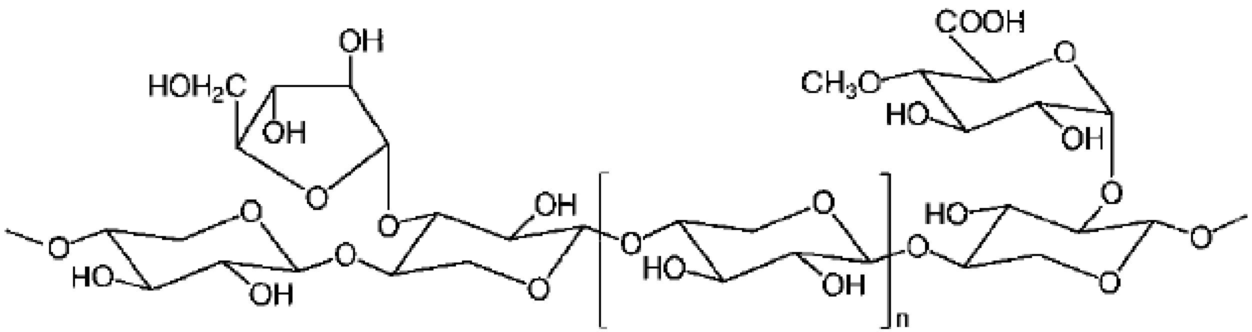


Example from a fragment of a lignin structure

- Non-linear polyphenol
- Structurally extremely diverse
- Glues fibres together as the main component in middle lamella
- Hydrophobic: controls the amount of water inside the cell wall
- Responsible for the brown colour of wood (pulping and papermaking aim at removing lignin as completely as possible)

Hemicellulose

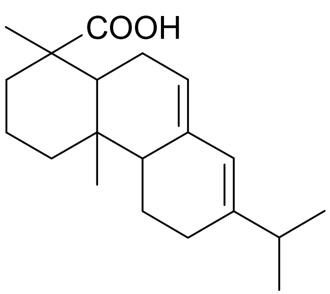
Example from a structure of arabinoglucuronoxylan, a common hemicellulose in conifers



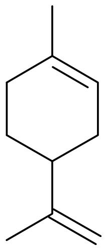
Hemicelluloses are heteropolysaccharides with low DP (<200) and they form amorphous structures in the cell wall

Extractives

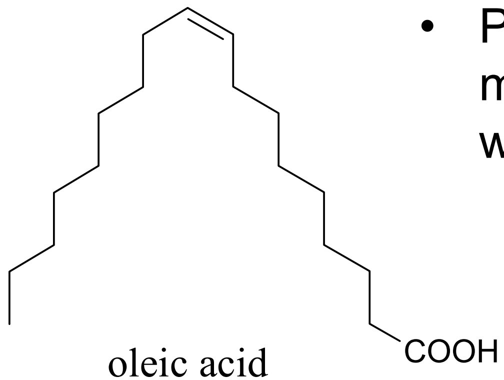
Some examples of common extractives



abietic acid
(diterpenoid)



limonene
(monoterpene)



oleic acid
(fatty acid)

- Part of the wood matrix, not part of the wood cell wall *per se*

- Small molecular (not polymers) organic compounds that can be extracted with an organic solvent
- Thousands of different extractives abound

Chemical composition of wood

	Softwood	Hardwood
CELLULOSE	40 %	40-50 %
LIGNIN	27-33 %	19-25 %
HEMICELLULOSE	23-30 %	23-40 %
EXTRACTIVES	5-10 %	5-10 %

Isolation of fibres

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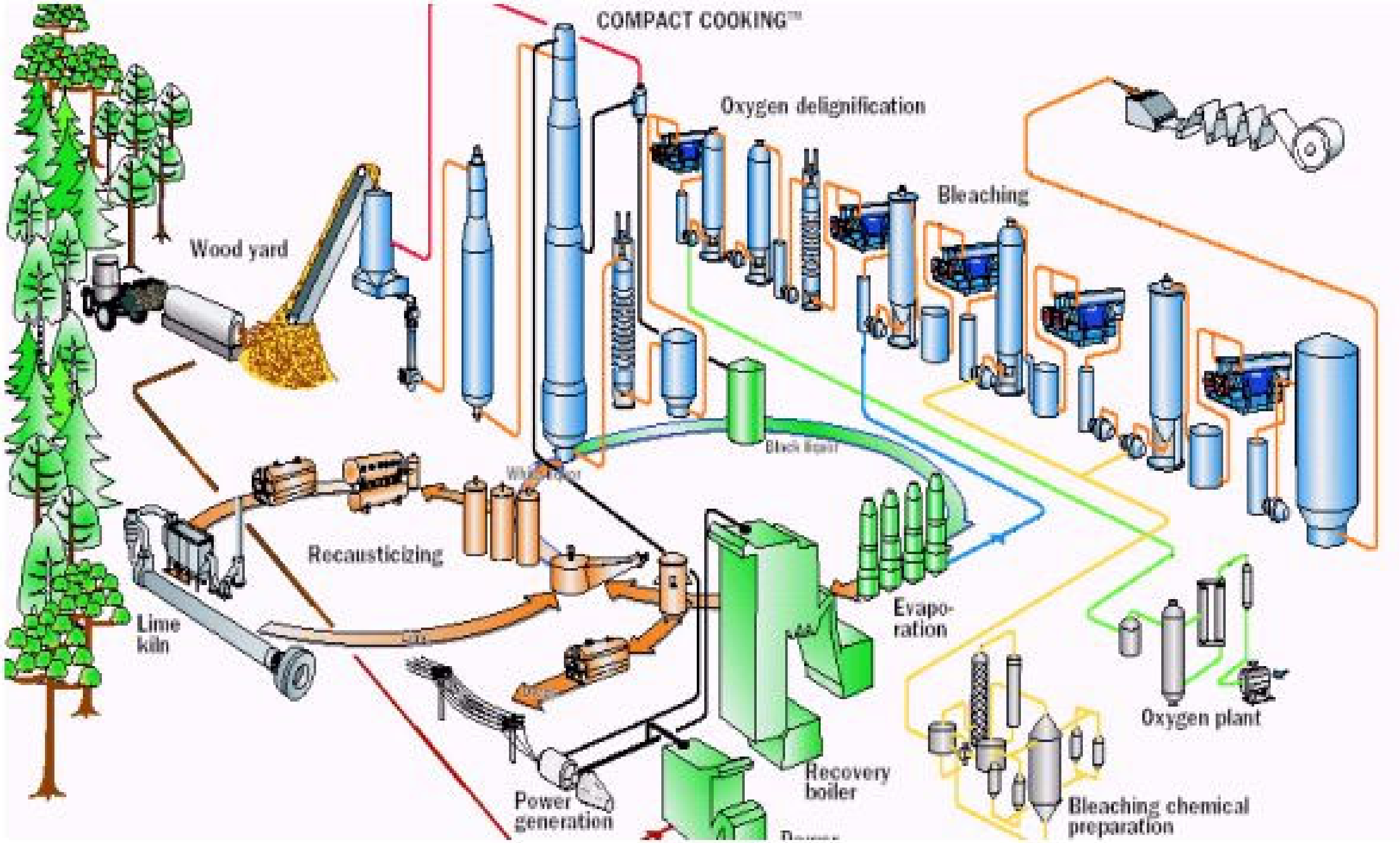
Basic isolation methods

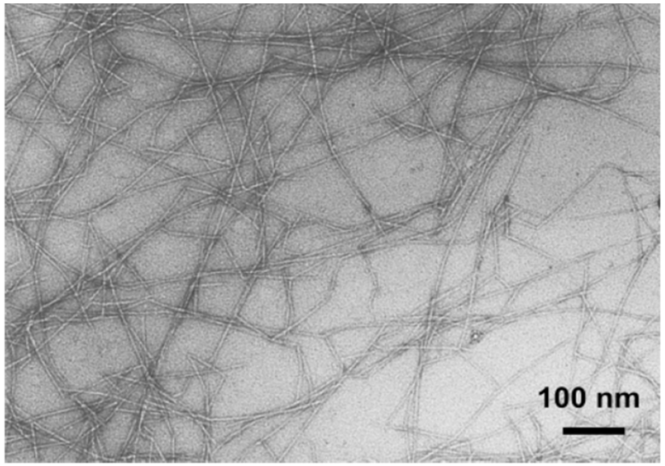
- In order to utilize fibres, they must be isolated from a plant matrix that confines them to a rigid template
- Wood fibres are generally isolated by:
  - Mechanical force (mechanical pulping)
  - Chemical means (chemical pulping)

Kraft process plant

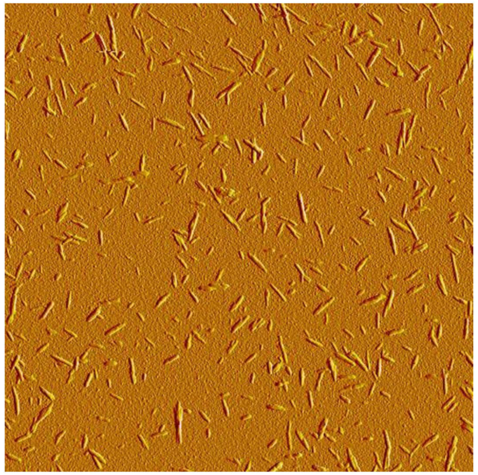


Note: isolation of nanocellulose

Cellulose nanofibrils



Cellulose nanocrystals



- At present, isolated plant fibres are further disintegrated to nanocellulose
- Nanocelluloses are also made mechanically and/or chemically
- Promising new materials in future applications

Summary on plant cells and cellulose

- Plant fibres stem from woody or herbaceous plants
- Tracheids (fibres), vessels, and parenchyma are the main types of plant cells
- Plant cell is a hierarchical construction made of cellulose, hemicellulose, and lignin
- Wood fibres are separated by either mechanical or chemical pulping
- Disintegration of wood fibres results in nanocellulose

Supramolecular structure of cellulose

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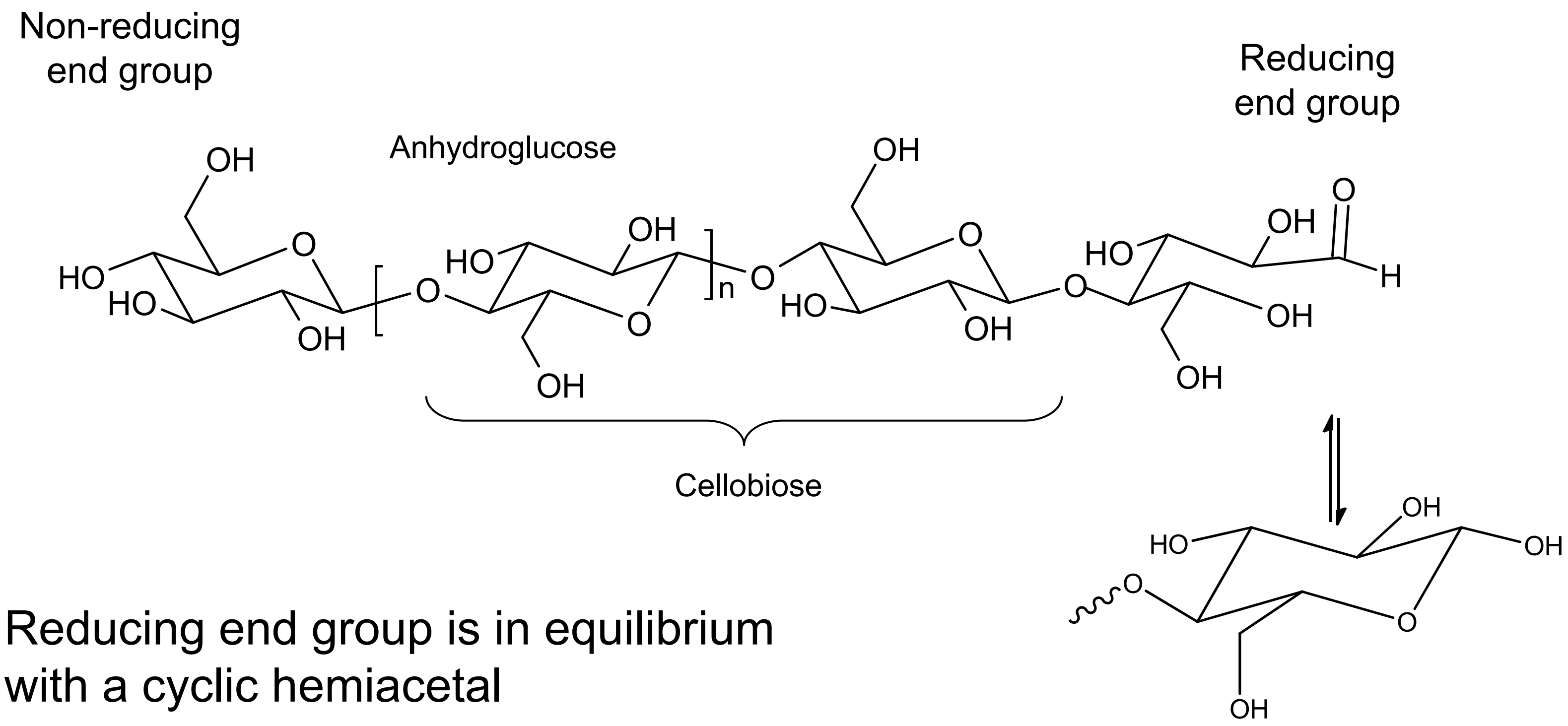
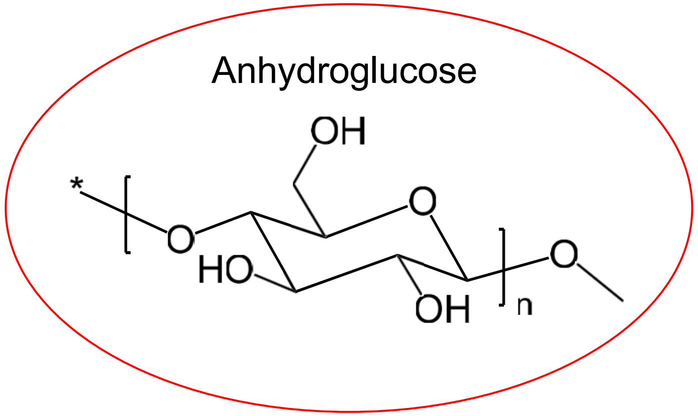
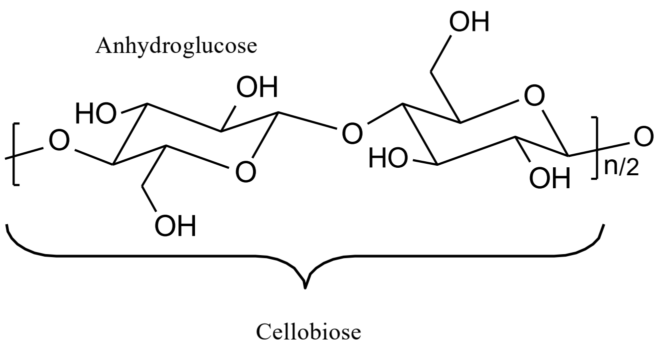
Molecular structure of cellulose



- Reducing end group is in equilibrium with a cyclic hemiacetal

Note on the molecular structure





- Often cellobiose is presented as the repeating unit (n/2) of cellulose
- In a cellulose crystal, the adjacent anhydroglucose units are twisted 180º with respect to each other

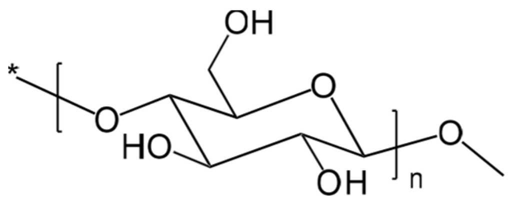
→ Therefore, cellobiose drawn this way is often presented as the repeating unit

- However, cellulose does not need to be inside a crystal (it can be, e.g., in solution)

→ **Anhydroglucose is the actual repeating unit (monomer) of cellulose**

Molecular *vs.* supramolecular structure

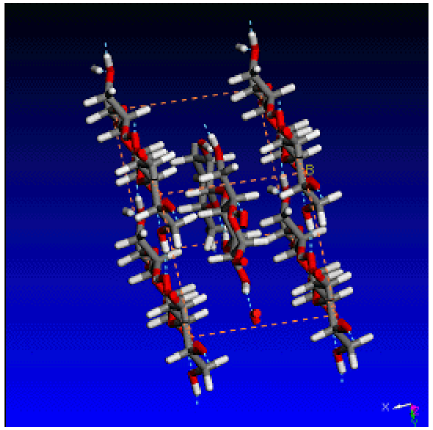
Molecular structure



- (1→4)-β-D-glucopyranose
- high native DP (~5000-15000)

Structure revealed:
Freudenberg
Liebigs Ann. Chem. **1928**, *461*, 130.
Haworth *Nature* **1930**, *126*, 438.

Supramolecular structure



- individual cellulose chains linked together by intermolecular bonding

Structure revealed (cellulose I_α ja I_β):
Nishiyama et al.
J. Am. Chem. Soc. **2002**, *124*, 9074.
J. Am. Chem. Soc. **2003**, *125*, 14300.

Crystalline forms (polymorphs) of cellulose

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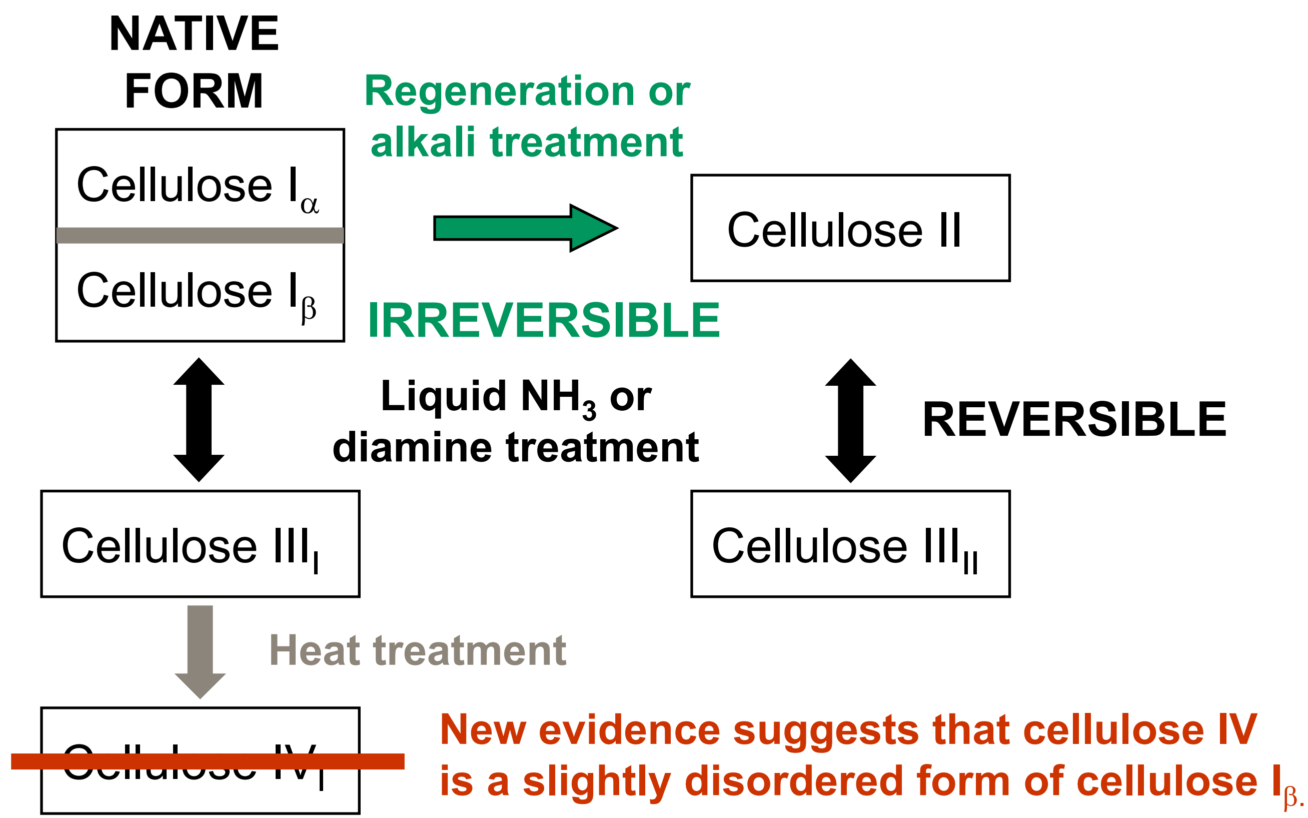
Cellulose polymorphs



Methods for measuring crystalline form and crystallinity of cellulose

- X-ray diffraction
- Solid state Nuclear Magnetic Resonance (NMR) spectroscopy
  specifically: cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR

Most applied methods, generally regarded as the most reliable

- Electron diffraction
- Neutron scattering
- IR spectroscopy
- Raman spectroscopy

Native cellulose: cellulose I_α cellulose I_β

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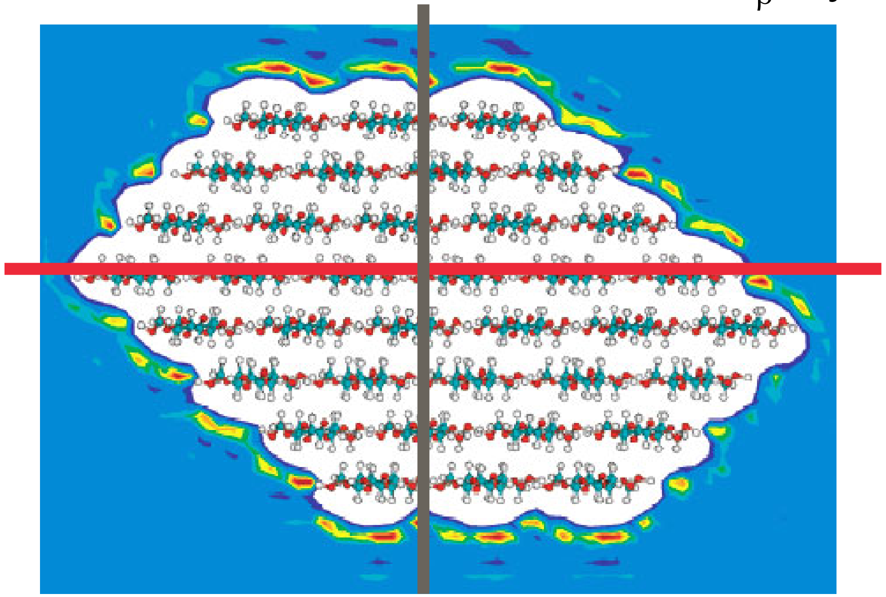
Cellulose I crystal

Cellulose chains form sheets which are connected with each other

Radial cross section of a cellulose I_β crystallite:



6 × 6 model (not confirmed!)
→ 36 cellulose chains

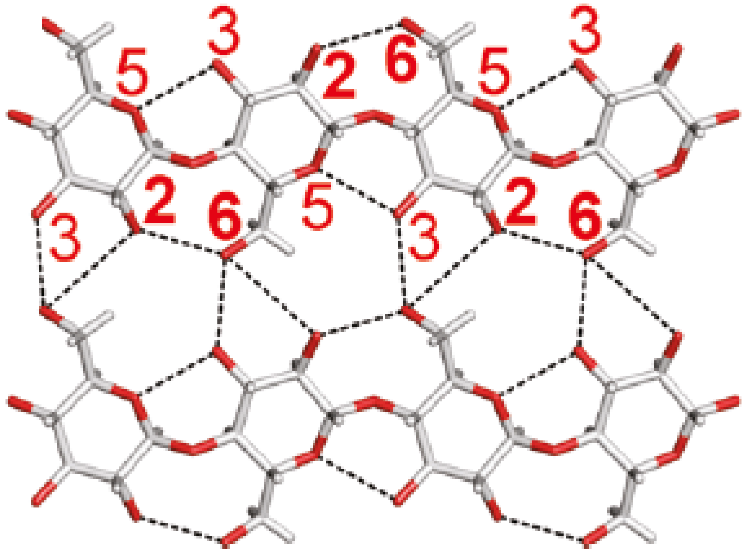
Within the sheets:
hydrogen bonds

Between the sheets:
van der Waals bonds

Cross sectional image taken from: Gross and Chu *J. Phys. Chem. B* **2010**, *114*, 13333.

Cellulose I: hydrogen bonding

Sheet in cellulose I



Main hydrogen bonds:

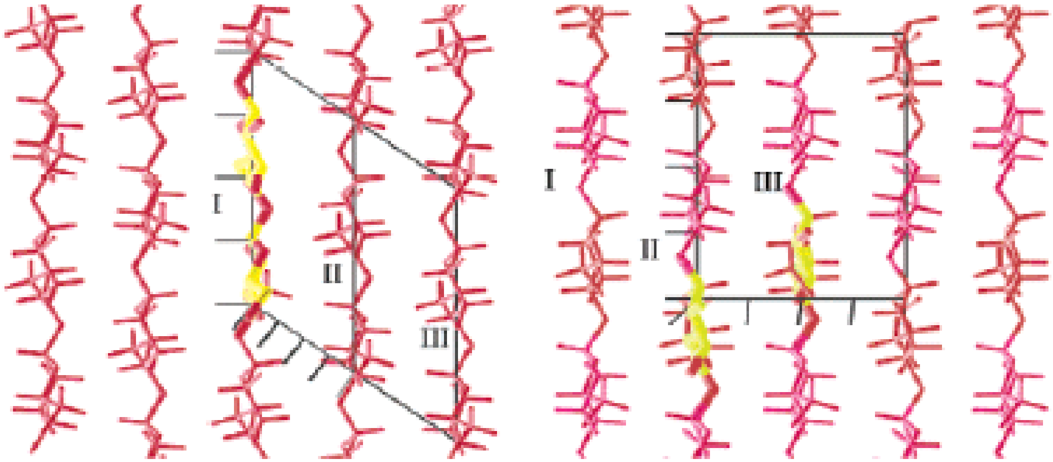
- 3→5 intramolecular bond lends rigidity to the cellulose chain
- 2→6 intramolecular bond
- 3→6 intermolecular bond keeps the sheets together

NOTE: Cellulose chains in cellulose I crystals run parallel

Distinction between I_α and I_β

Two forms of native crystalline cellulose exist: I_α and I_β.

Atalla and Vanderhart *Science* **1984**, *223*, 283.



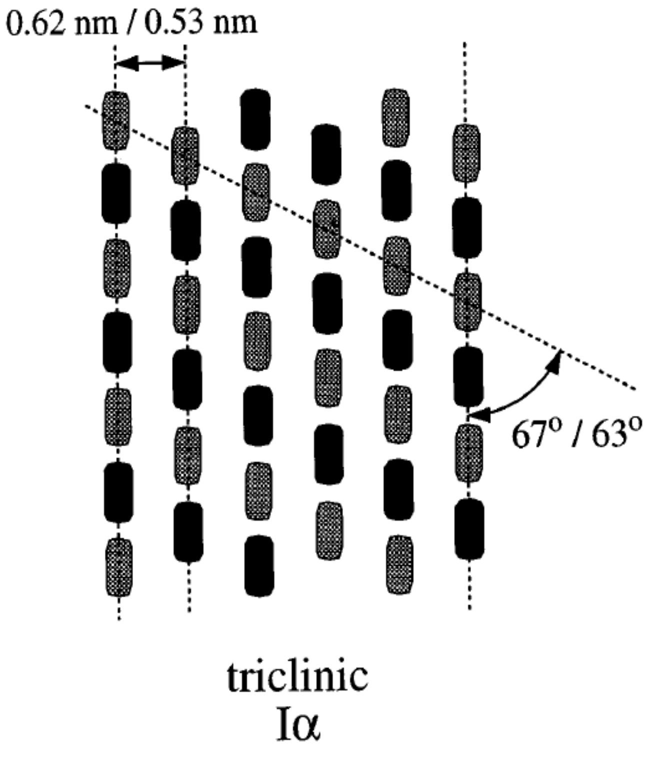
I_α: one chain triclinic
- dominant in, e.g., bacterial cellulose and algae

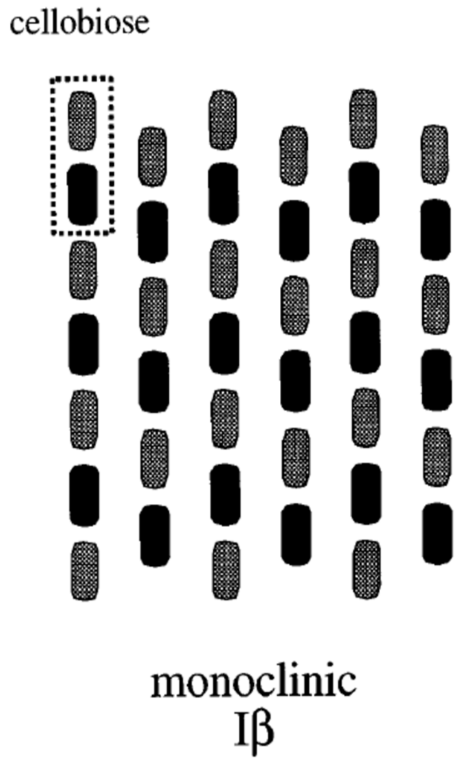
I_β: two chain monoclinic
- dominant in higher plants (e.g. wood, cotton)

Crystallographic details in 1Å resolution (cellulose I_α ja I_β):

Nishiyama et al.
J. Am. Chem. Soc. **2002**, *124*, 9074.
J. Am. Chem. Soc. **2003**, *125*, 14300.

Distinction between I_{α} and I_{β}





Baker et al. *J. Struct. Biol.* **1997**, *119*, 129.

Distinction between I_α and I_β

- Cellulose I_β is the predominant form in higher plants (wood, cotton etc.) and tunicate (cellulose in tunicate animals)

- Cellulose I_α is the predominant form in algae and in cellulose emitted by microbes (bacterial cellulose)

NOTE: Cellulose I_α and cellulose I_β ALWAYS coexists with each other in nature, usually within the same microfibril.

Regenerated cellulose: cellulose II

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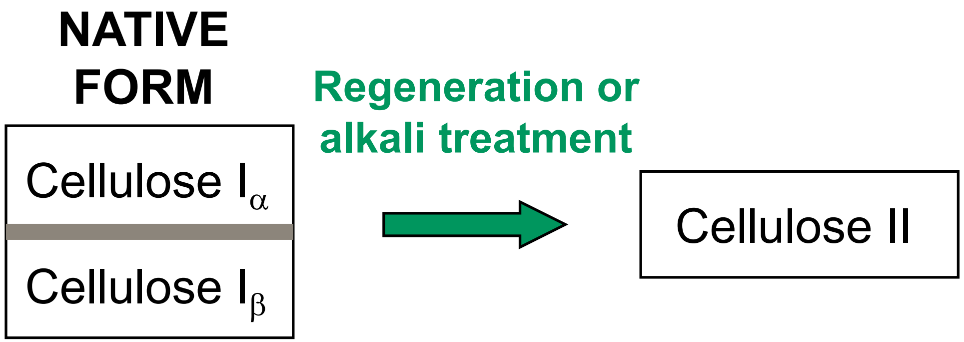
Emergence of cellulose II

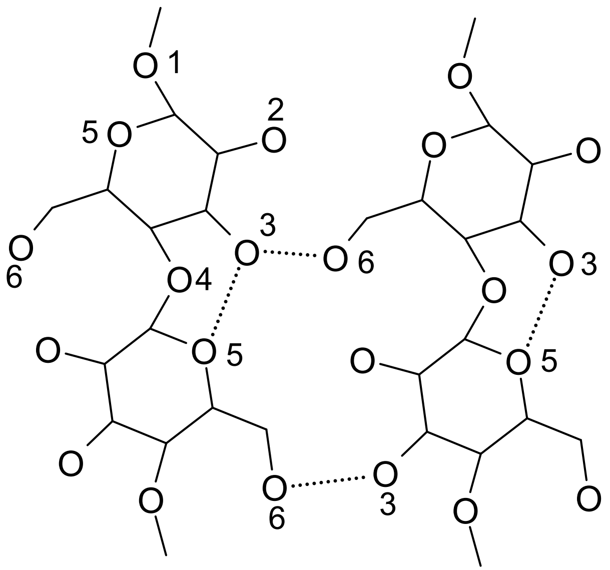


"Man-made" form of cellulose
Preparation by: - dissolving the cellulose / regeneration
- swelling in concentrated alkali (e.g. > 10% NaOH)

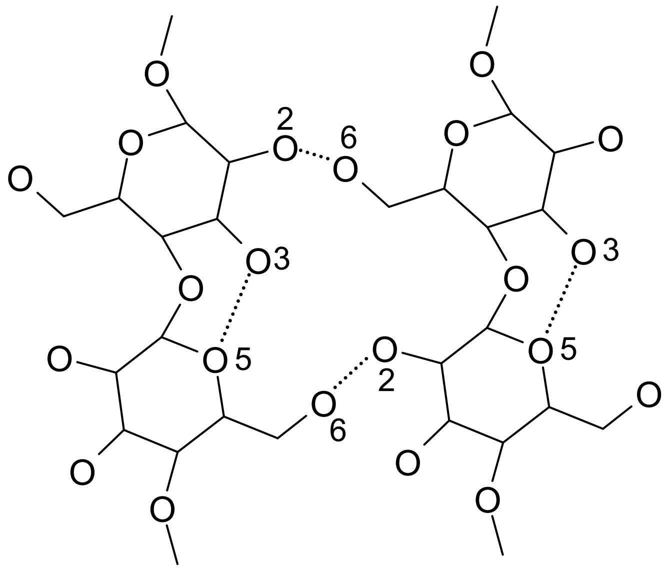
Silk-like texture of cellulose II materials means that they are widely applied in textile industry.

Distinction between cellulose I and II

Cellulose I



Cellulose II



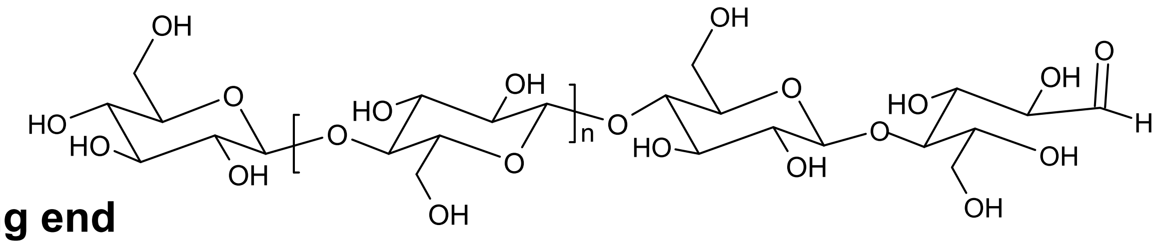
Note: hydrogens have been omitted to enhance clarity

Hydrogen bonding patterns within the sheets are different.

Distinction between cellulose I and II

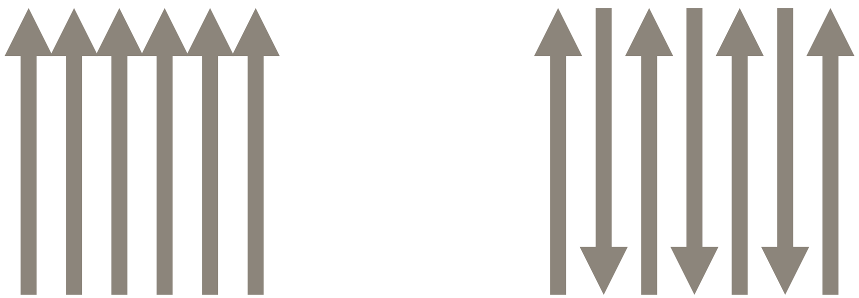
Cellulose chain has a direction:

Non-reducing end



Reducing end

Cellulose I | Cellulose II

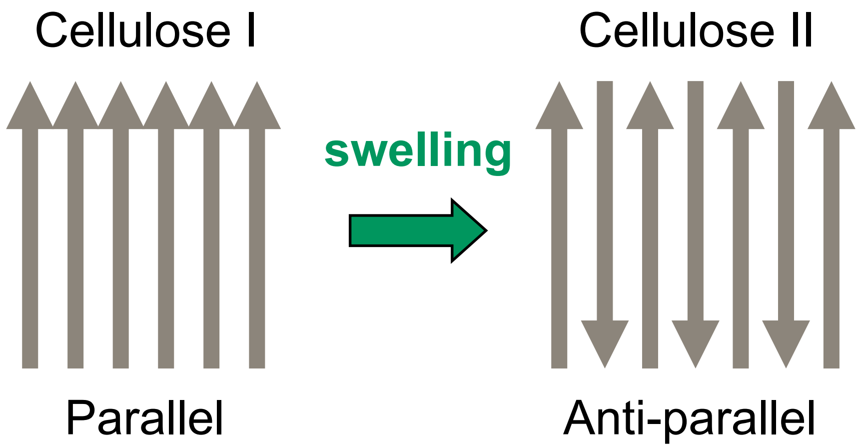


Parallel | Anti-parallel

Dilemma of anti-parallel cellulose II

Cellulose II preparation by: (a) dissolving the cellulose / regeneration
(b) **swelling in concentrated alkali**

How is it possible for the cellulose chains to transform from parallel to anti-parallel without dissolution?

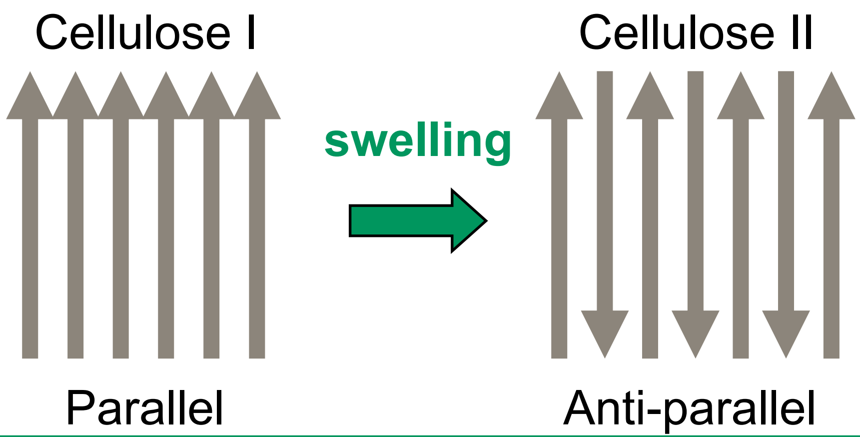


Dilemma of anti-parallel cellulose II

- Cellulose crystals in parallel microfibrils run in opposite direction
- NaOH swells the crystals
- Anti-parallel arrangement is thermodynamically more favourable than parallel arrangement

→ **HYPOTHESIS:**

Cellulose chains in parallel microfibrils intermingle and form new antiparallel crystals



Cellulose III

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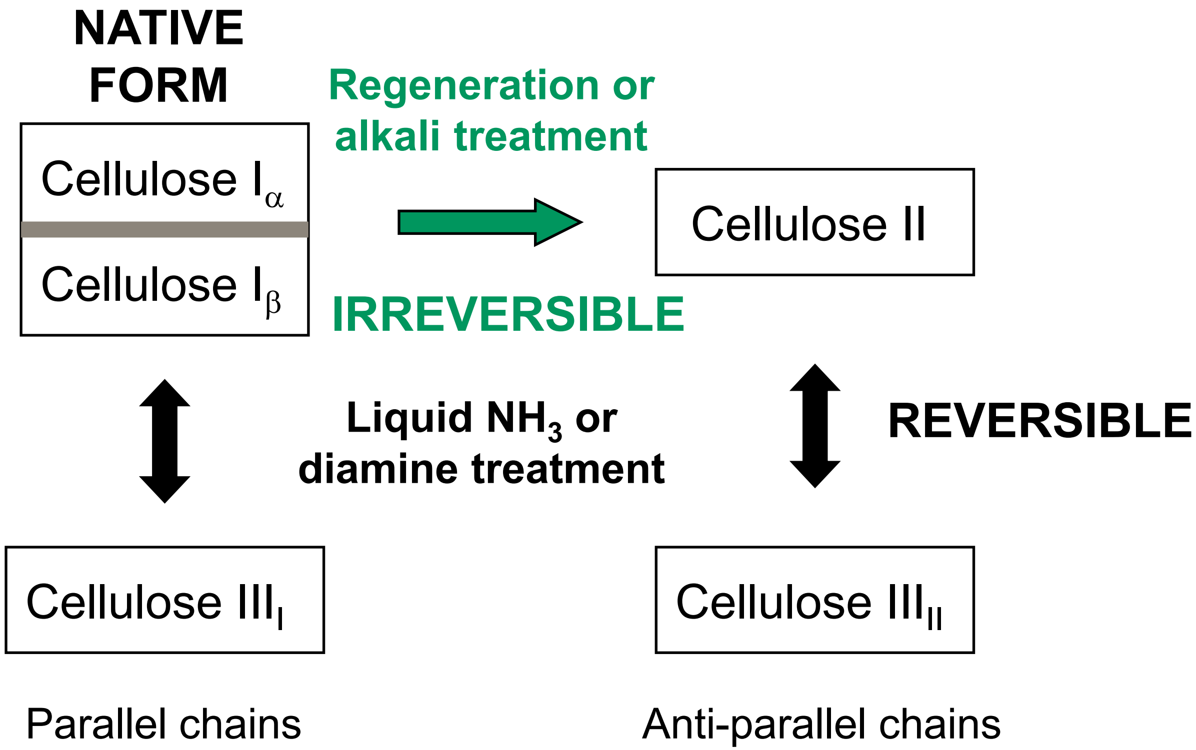
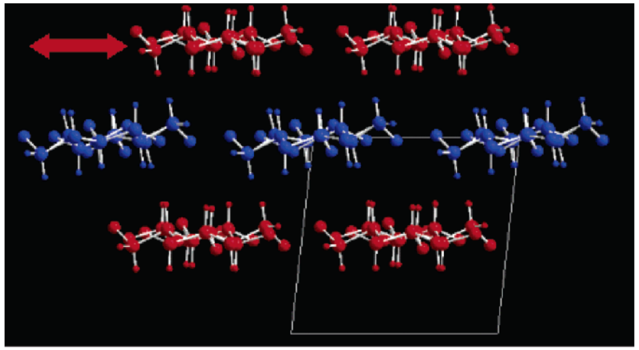
Conversion to cellulose III



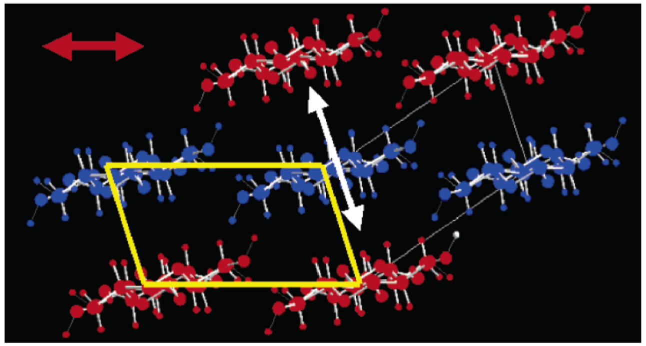
Hess and Trogus *Ber.* **1935**, *B68*, 1986–1988.

Conversion: cellulose $I_\beta \rightarrow$ cellulose III

Cellulose I_β

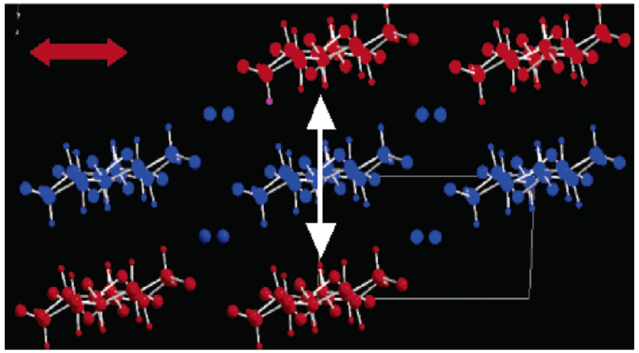


Cellulose III_I



NH_3 (l)

Ammonia-cellulose I complex

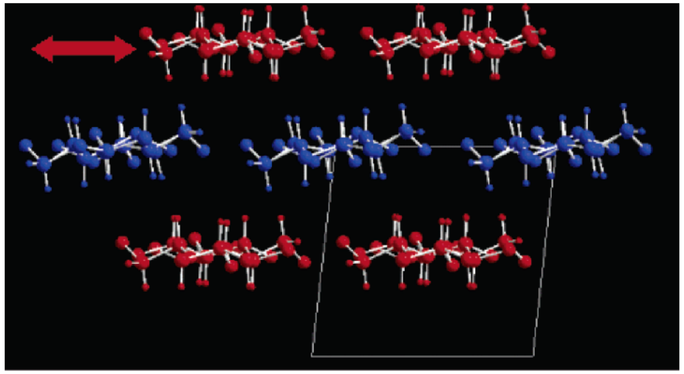


NH_3 removal
(e.g. evaporation)

Wada et al. *Macromolecules* **2006**, *39*, 2947.

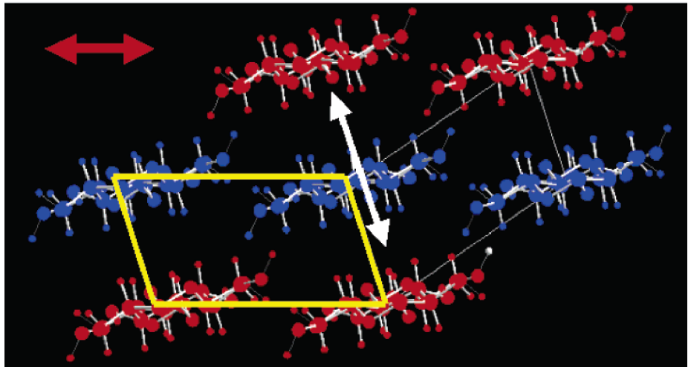
Distinction: cellulose I and cellulose III

Cellulose I_{β}



- Hydrogen bonds only between cellulose molecules within the sheets
- van der Waals bonds between the sheets

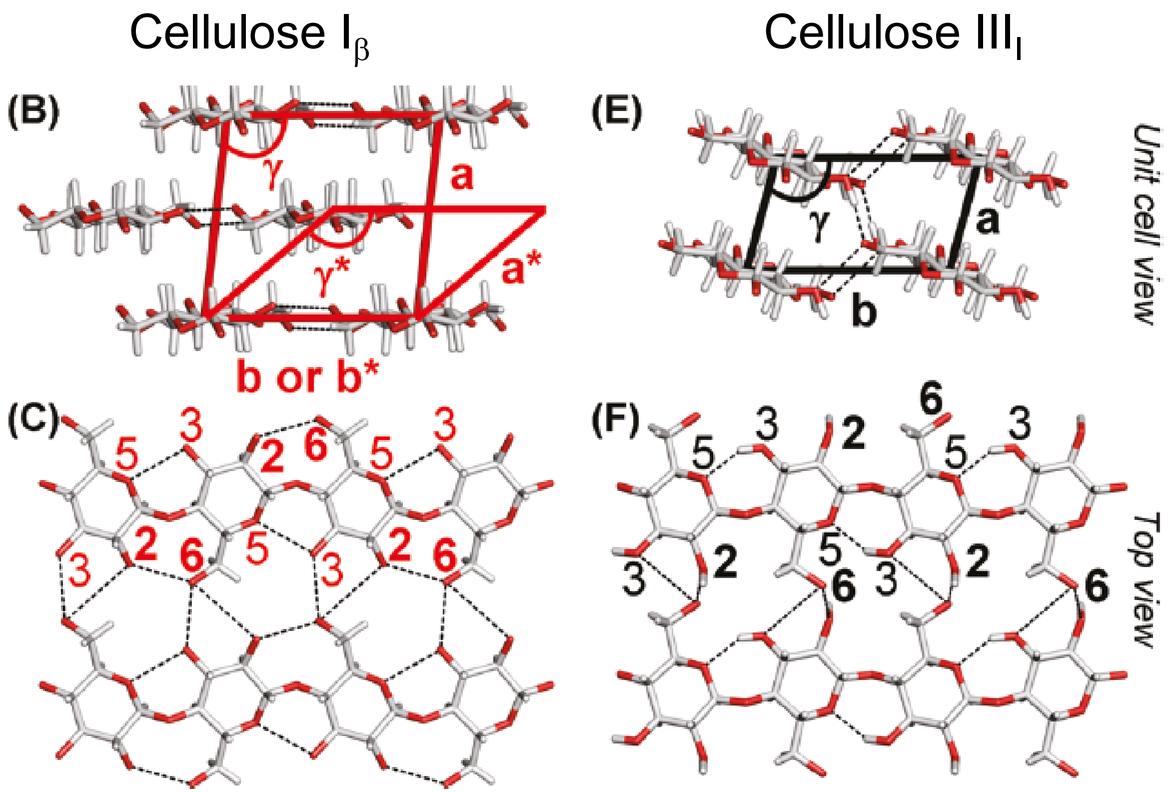
Cellulose III_{I}



- Hydrogen bonding also between the sheets

Wada et al. *Macromolecules* **2006**, *39*, 2947.

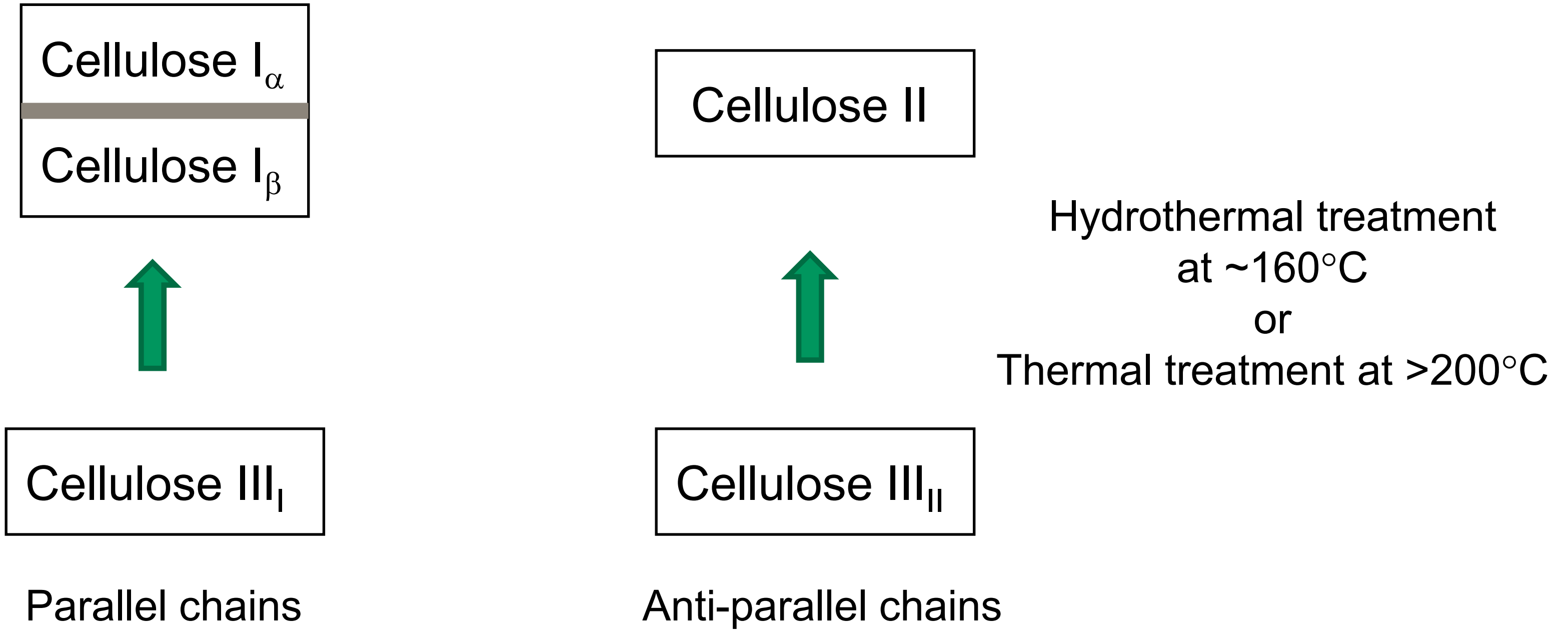
Distinction: cellulose I and cellulose III



Chundawat et al. *J. Am. Chem. Soc.* **2011**, *133*, 11163.

Reversibility of cellulose III conversion

- Cellulose III can be converted back to its starting material



Chanzy et al. *Carbohydr. Res.* **1987**, *160*, 1.
Wada et al. *Macromolecules* **2001**, *34*, 3271.

Cellulose IV

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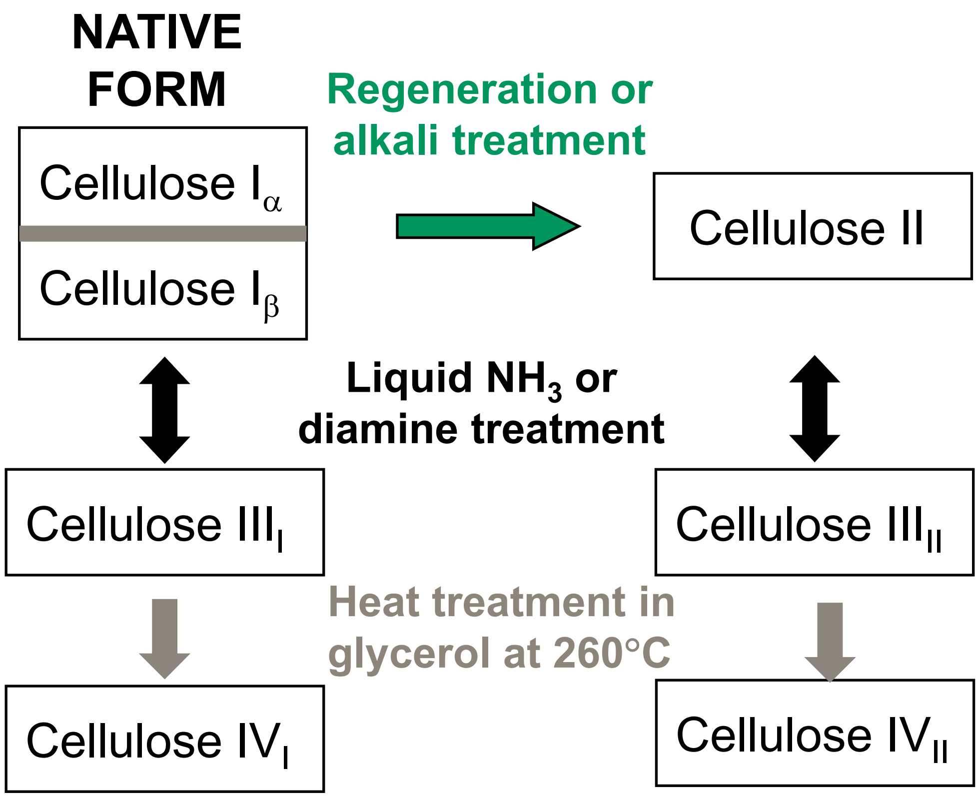
Conversion: cellulose III → cellulose IV



Hutino and Sakurada *Naturwissenschaften* **1940**, *28*, 577.

Conversion: cellulose III $\rightarrow$ cellulose IV – recent evidence

Recent evidence from FT-IR spectroscopy, solid state NMR spectroscopy, X-ray diffraction and diffraction simulations:

Wada et al. *Biomacromolecules* **2004**, *5*, 1385.
Newman *Cellulose* **2008**, *15*, 769.

- Credible proof that cellulose IV_I is not a genuine allomorph
- Cellulose IV_I is seen as a distorted form of cellulose I_β

Some implications of the crystalline forms of cellulose

Aalto University
School of Chemical
Technology

Elastic modulus

Form	Elastic modulus
Cellulose I	138 GPa
Cellulose II	88 GPa
Cellulose III_I	87 GPa
Cellulose III_{II}	58 GPa

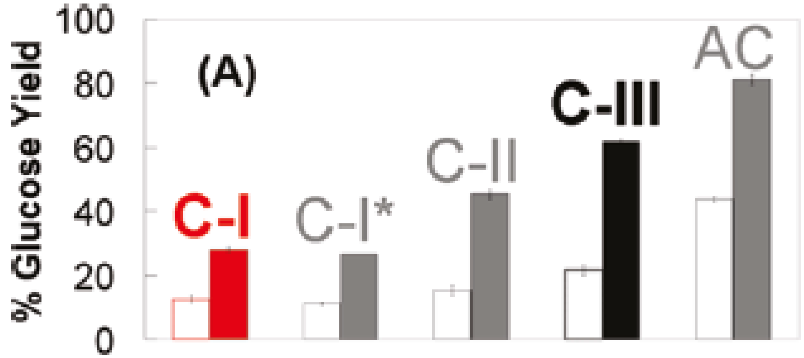
The values are estimates for pure crystalline forms (based on XRD data)

→ Native cellulose I is decidedly stiffer and stronger than the “man-made” forms

Nishino et al. *J. Polym. Sci. B* **1995**, *33*, 1647.

Hydrolytic degradation: cellulose I *vs.* III

Glucose yield from enzymatic hydrolysis of different cellulose allomorphs



C-I: cellulose I

C-I*: ammonia-cellulose complex

C-II: cellulose II

C-III: cellulose III

AC: amorphous cellulose

Chundawat et al. *J. Am. Chem. Soc.* **2011**, *133*, 11163.

Summary on cellulose polymorphs

- Cellulose exists in several crystalline polymorphs:
  - cellulose I_α and I_β (native forms)
  - cellulose II (prepared regeneration or alkaline treatment)
  - cellulose III_I and III_{II} (prepared by liquid ammonia treatment)

- Cellulose polymorphs are physically different and they differ in reactivity

NOTE: Cellulose is virtually never 100% crystalline; it is semi-crystalline. Semi-crystallinity will be a key issue in the next lecture.