NATURAL POLYMERS

Polysaccharide II CELLULOSE 1

Cellulose is the most widespread BIOPOLYMER on Earth, up to 1,5×10^9 tons per annum is arising

Dr. Ladislav Pospíšil

Time schedule

LECTURE	SUBJECT
1	Introduction to the subject – Structure & Terminology of nature polymers, literature
2	Derivatives of acids – natural resins, drying oils, shellac
3	Waxes
4	Plant (vegetable) gums, Polyterpene – natural rubber (extracting, processing and modification), Taraxacum_kok-saghyz
5	Polyphenol – lignin, humic acids
6	Polysaccharides I – starch
7	Polysaccharides II – celullosis
8	Protein fibres I
9	Protein fibres II
10	Casein, whey, protein of eggs
11	Identification of natural polymers
	Laboratory methods of natural polymers' evaluation

LITERATURE 1

Lignocellulose Chemistry Kindle Edition

by Thomas Rosenau (Editor)

Technology and Applications of Polymers Derived from Biomass (Plastics Design Library) 1st Edition

Hemicelluloses and Lignin in Biorefineries (Green Chemistry and Chemical Engineering) 1st Edition

Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials (Advances in Polymer Science) 1st ed. 2016 Edition

LITERATURE 2

Cellulose & Cellulose Derivatives: Synthesis, Modification & Applications (Biochemistry Research Trends) UK ed. Edition

by Md. Ibrahim H. Mondal (Author, Editor)

Cellulose and Biomass

by Dwight Cowan (Editor)

Encyclopedia of Cellulose

by Dwight Cowan (Editor)

Lignocellulosic Biorefineries 1st Edition, Kindle Edition

by
Jean-Luc Wertz (Author)

LITERATURE 3

Cellulose and Cellulose Derivatives

by K. Kamide (Author)

Cellulose Solvents: For Analysis, Shaping and Chemical Modification (ACS Symposium Series) 1st Edition

by Tim Liebert (Editor), Thomas Heinze (Editor), Kevin Edgar (Editor)

ISBN-13: 978-0841200067
ISBN-10: 0841200068

Cellulose Science and Technology (Fundamental Sciences: Chemistry (Hardcover)) 1st Edition

Jean-Luc Wertz (Author), Jean P. Mercier (Author), Olivier Bédué (Author)

ISBN-13: 978-1420066883
ISBN-10: 1420073311

LITERATURE 4

An Introduction to the Chemistry of Cellulose Revised Edition

by J. T. Marsh (Author)
ISBN-13: 978-1406719673
ISBN-10: 1406719676

Wood and Cellulosic Chemistry, Second Edition, Revised, and Expanded 2nd Edition

by David N.-S. Hon (Author), Nobuo Shiraishi (Author)
ISBN-13: 978-0824700249
ISBN-10: 0824700244

Comprehensive Cellulose Chemistry, Functionalization of Cellulose (Volume 2) Volume 2 Edition

by Dieter Klemm (Author), Bertram Philipp (Author), Thomas Heinze (Author), Ute Heinze (Author), W. Wagenknecht (Author), D. Klemm (Author)
ISBN-13: 978-3527294893
ISBN-10: 3527294899

LITERATURE 5

Cellulose (Polymer Monographs) Volume 11 1st Edition

by Krassig (Author)
ISBN-13: 978-2881247989
ISBN-10: 2881247989

Cellulose Nitrate in Conservation (Research in Conservation) Paperback – April 1, 1988

Charles Selwitz (Author)

Cellulose

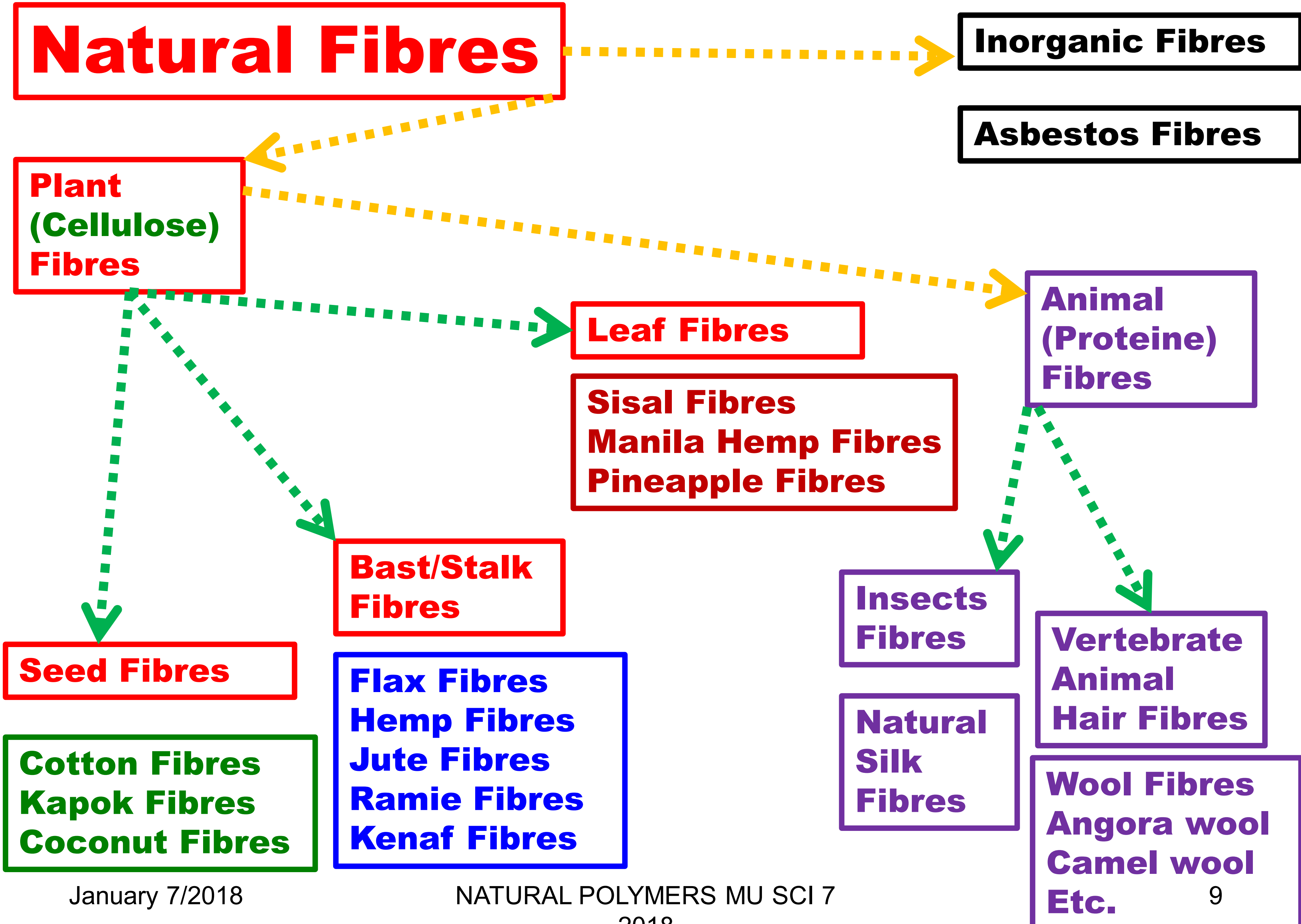
ISSN: 0969-0239 (Print) 1572-882X (Online)

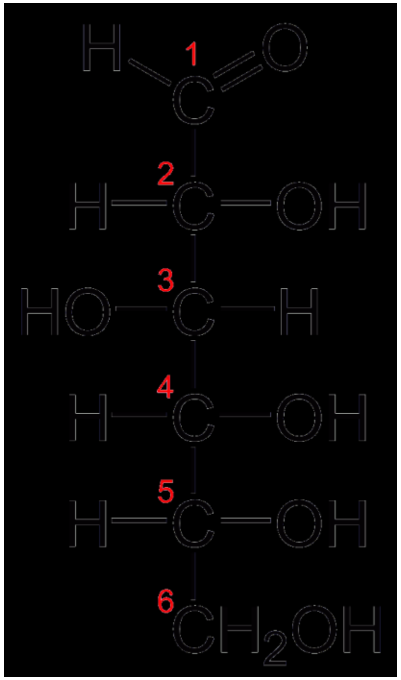
Description

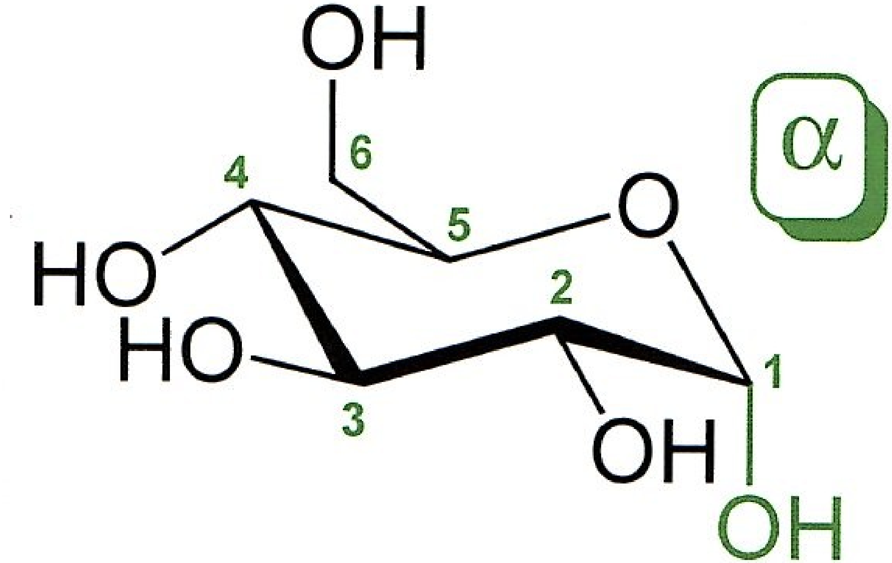
Cellulose is an international journal devoted to the dissemination of research and scientific and technological progress in the field of cellulose and related naturally occurring polymers. The journal is concerned with the pure and applied science of cellulose and related materials, and also with the development of relevant new technologies. This includes the chemistry, biochemistry, physics and materials science of cellulose and its sources, including wood and other biomass resources, and their derivatives. Coverage extends to the conversion of these polymers and resources into manufactured goods, such as pulp, paper, textiles, and manufactured as well natural fibers, and to the chemistry of materials used in their processing. Cellulose publishes review articles, research papers, and technical notes. hide

Cellulose is an international journal devoted to the dissemination of research and scientific and technological progress in the field of cellulose and related naturally occurring polymers. The journal is concerned with the pure and applied science of cellulose and related materials, and also with the development of relevant new technologies. This includes the chemistry, biochemistry, physics and materials science of cellulose …

1. **Cellulose Chemistry**
2. **Supramolecular stucture of Cellulose**
3. **Natural abundance of Cellulose**
4. **Solubility of Cellulose**
5. **Production of Cellulose**
6. **Use of Cellulose**
7. **Modification of Cellulose**
8. **Nanocellulose**


Natural Fibres
Inorganic Fibres
Asbestos Fibres
Plant (Cellulose) Fibres
Animal (Proteine) Fibres
Leaf Fibres
Sisal Fibres
Manila Hemp Fibres
Pineapple Fibres
Bast/Stalk Fibres
Seed Fibres
Flax Fibres
Hemp Fibres
Jute Fibres
Ramie Fibres
Kenaf Fibres
Cotton Fibres
Kapok Fibres
Coconut Fibres
Insects Fibres
Natural Silk Fibres
Vertebrate Animal Hair Fibres
Wool Fibres
Angora wool
Camel wool
Etc.




α
OH
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HO
HO
2
1
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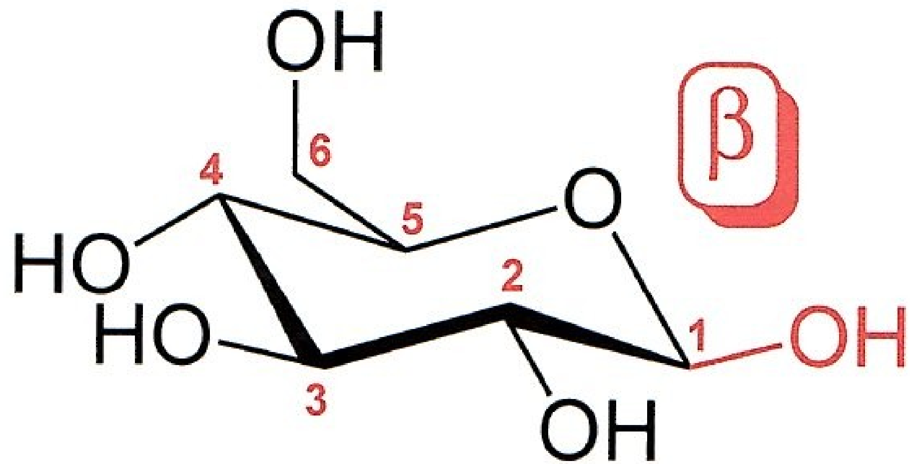
OH
OH


β
OH
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HO
2
1
OH
3
OH

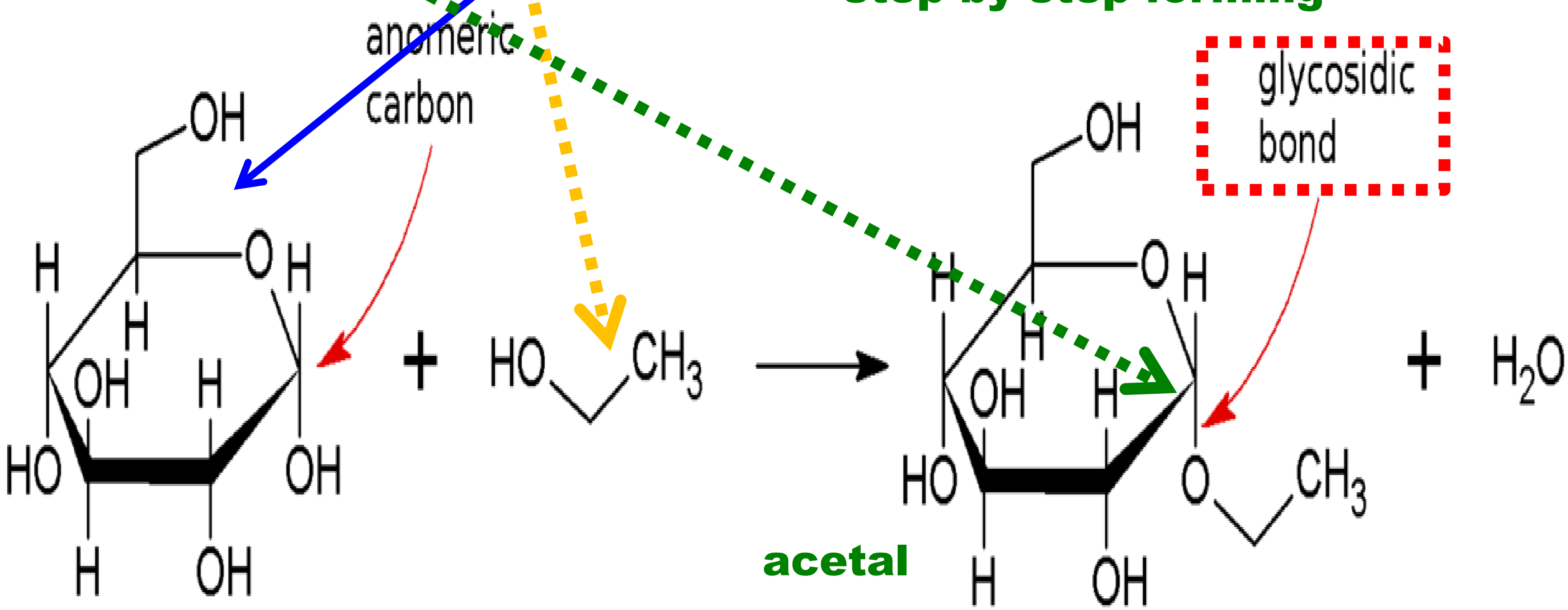
Formation of the Glykosidic Bond (Linkage)

HEMIACETAL Formation

A glycosidic bond is formed between the hemiacetal or hemiketal group of a saccharide (or a molecule derived from a saccharide) and the hydroxyl group of some compound such as an alcohol. A substance containing a glycosidic bond is a glycoside.

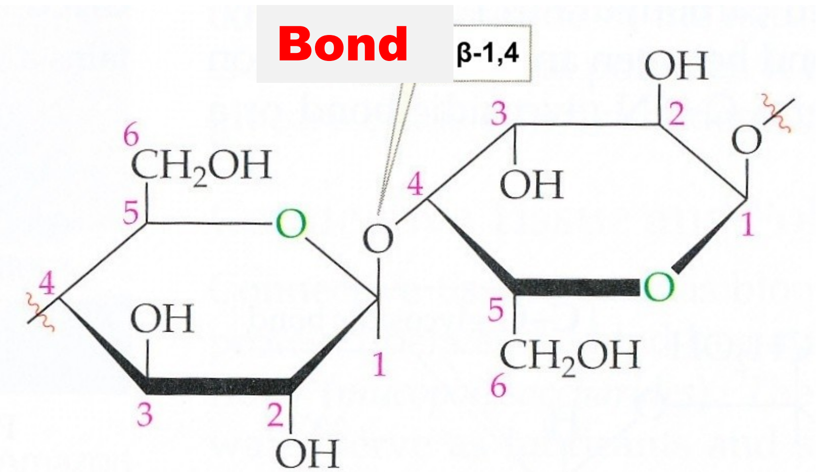
HEMIACETAL is able further react with another nucleophilic Group and so form **ACETAL** and to eliminate Water.

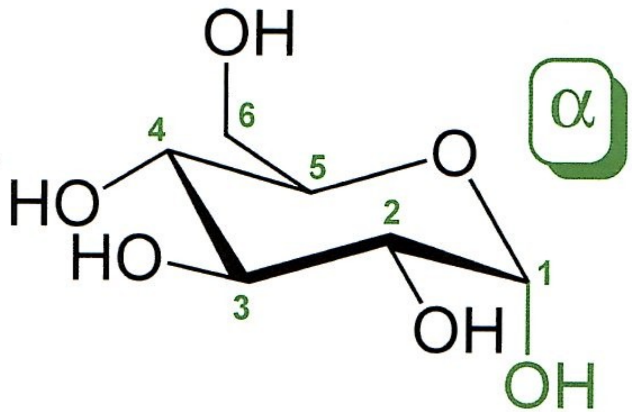
When is the further Reagent a Saccharide whit suitable –OH Group, the POLYSACHARIDE is step by step forming

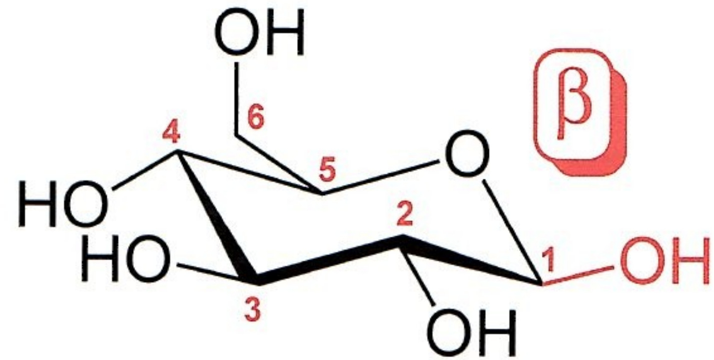


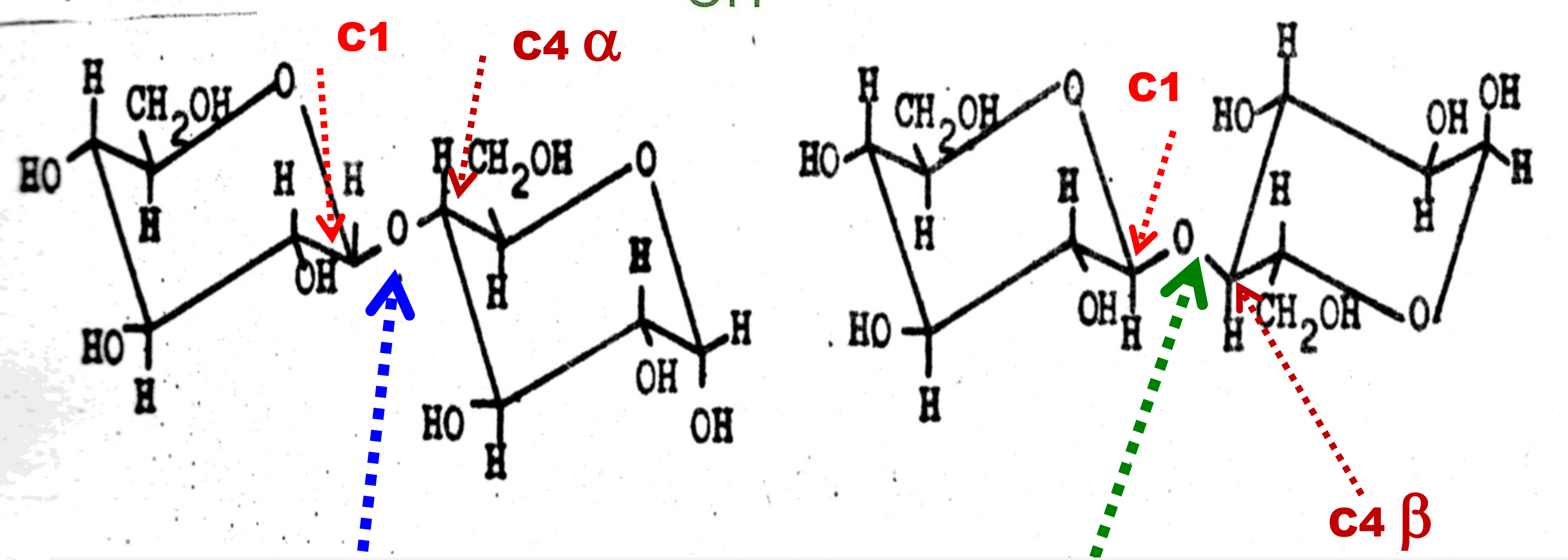
Cellulose

- ß-D-Glucose, ß-1,4 **glycosidic Bond**
- It forms the structure Skeleton of Plants
- It is not cleaved by Humans

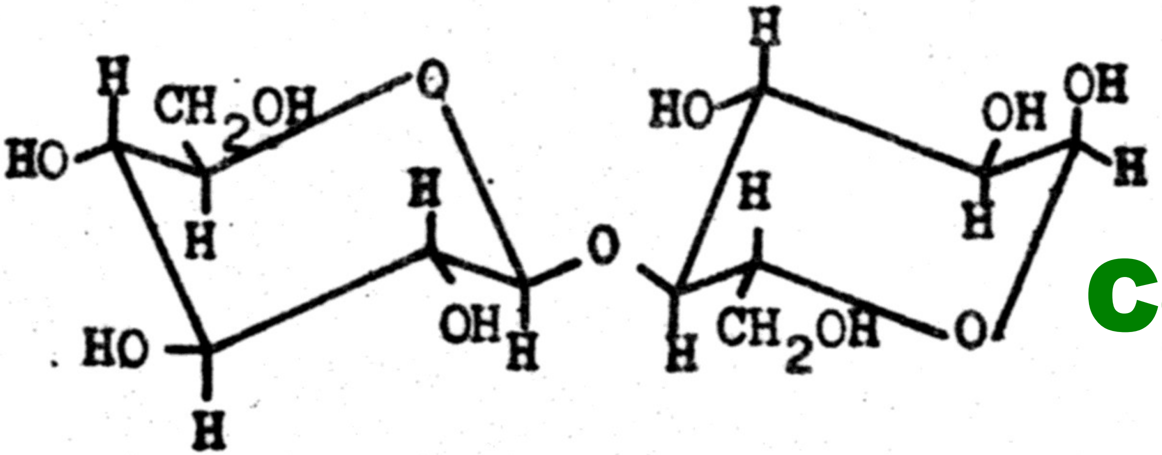




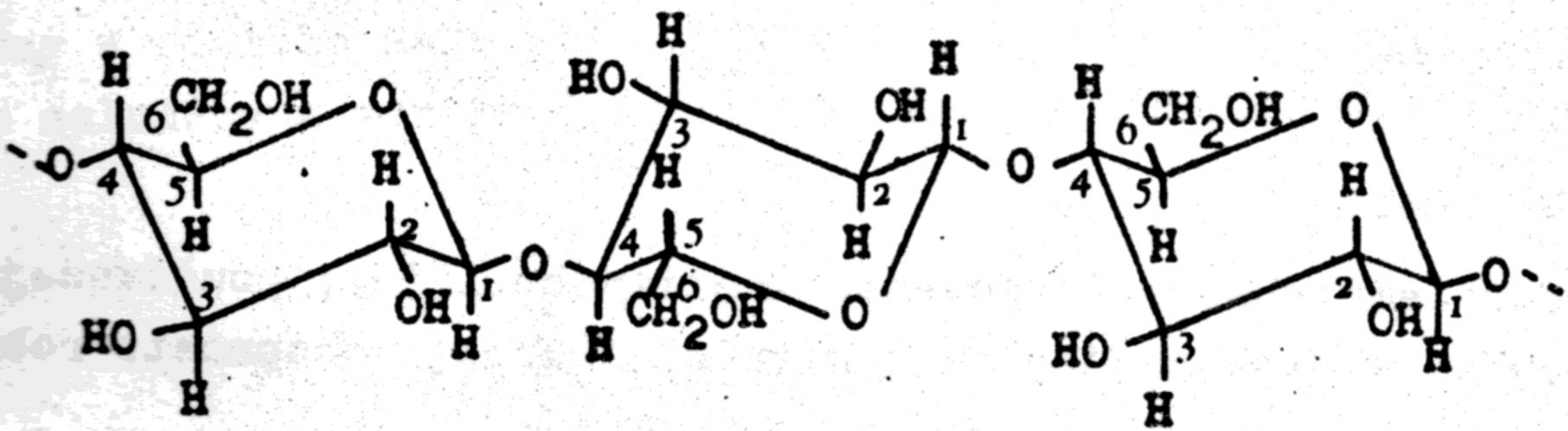




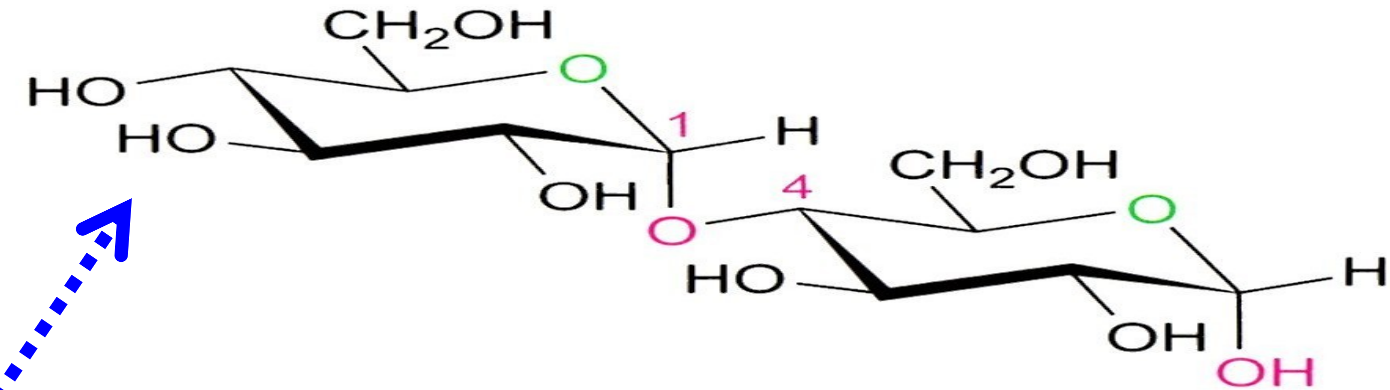
Maltose is the repeating unit of STARCH: α(1–4) dimer of GLUCOSE
Cellobiose is the repeating unit of CELLULOSE: β(1–4) dimer of GLUCOSE



Cellobiose

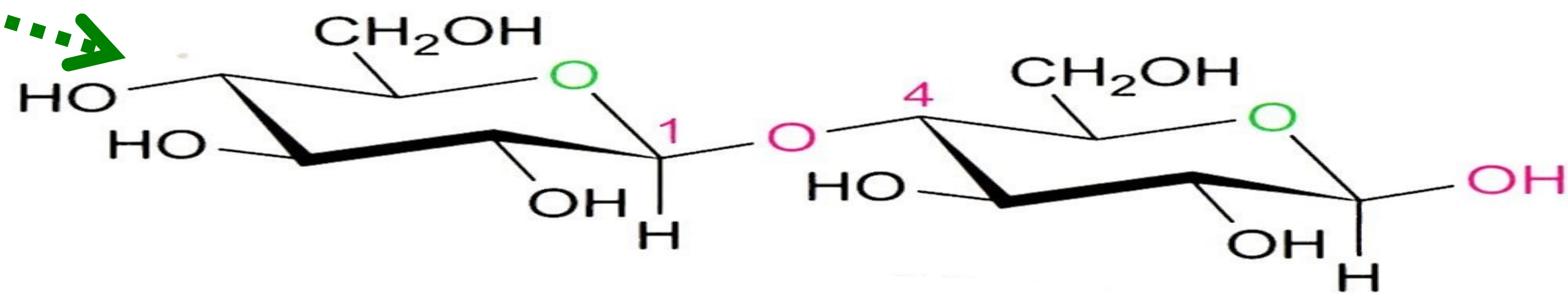


Linear Structure of CELLULOSE



maltosa je (1→4)-*α*-glykosid,
***α*-D-glukopyranosyl-(1→4)-*α*-D-glukopyranosa**
nebo
4-*O*-*α*-D-glukopyranosyl-*α*-D-glukopyranosa

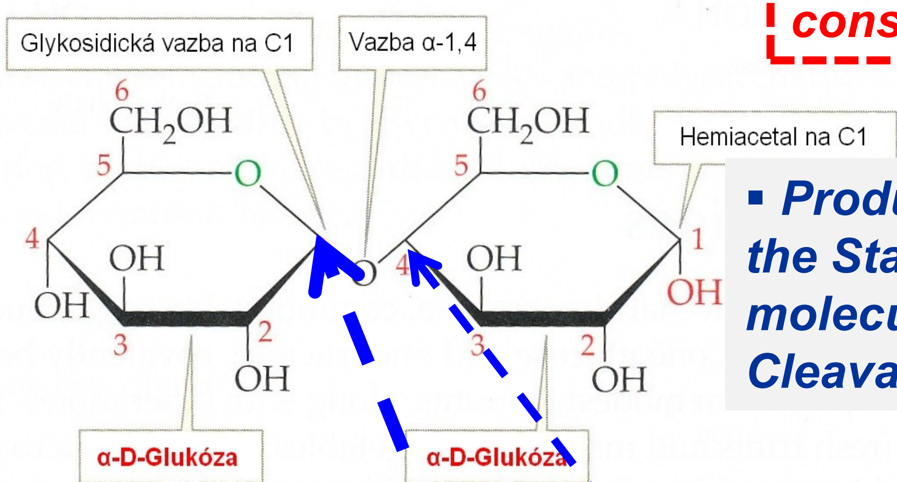
Maltose is the repeating unit of STARCH: α(1–4) dimer of GLUCOSE
Cellobiose is the repeating unit of CELLULOSE: β(1–4) dimer of GLUCOSE



cellobiosa je (1→4)-*β*-glykosid,
***β*-D-glukopyranosyl-(1→4)-*β*-D-glukopyranosa**
nebo
4-*O*-*β*-D-glukopyranosyl-*β*-D-glukopyranosa

Survey of the most important disaccharides

Maltose



- *Product of the Starch molecule Cleavage*

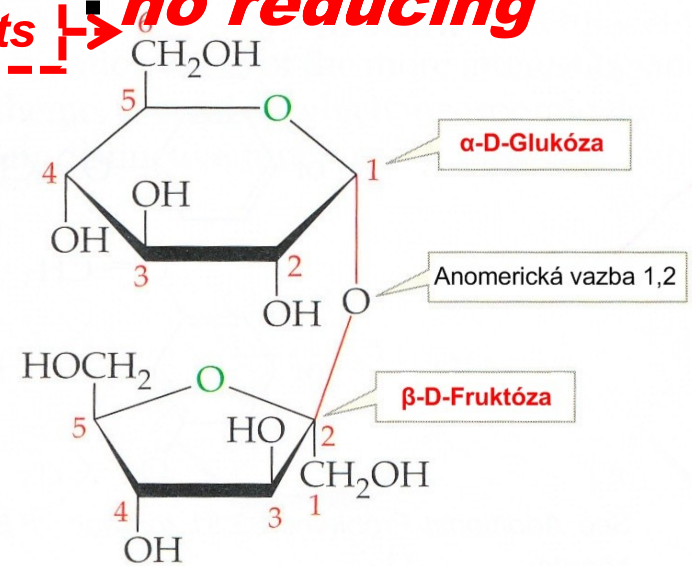
The Bond arose via Hemiacetal HYDROXYL from one constituent Molecule and NON Hemiacetal HYDROXYL from the other constituent Molecule

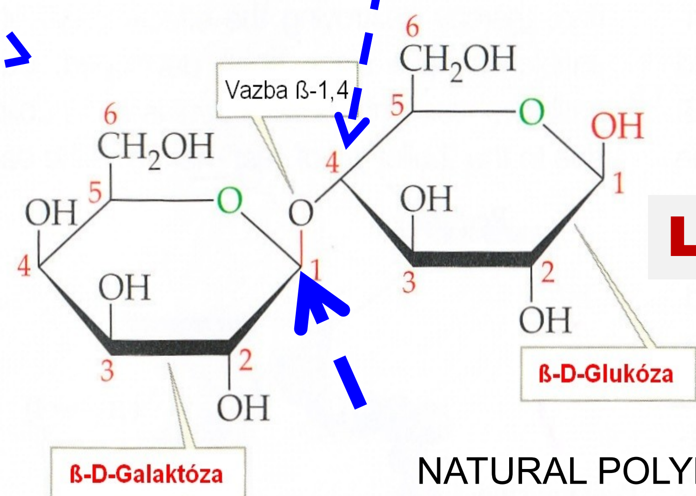
Reducing Sugars

The Bond arose via Hemiacetal HYDROXYLS from both constituent Parts

Saccharose

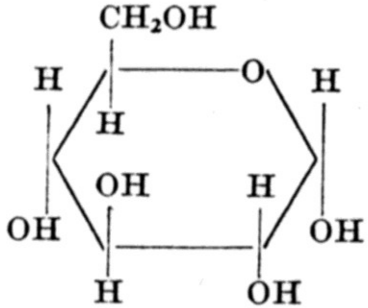
- beet-sugar, cane-sugar
- *no reducing*



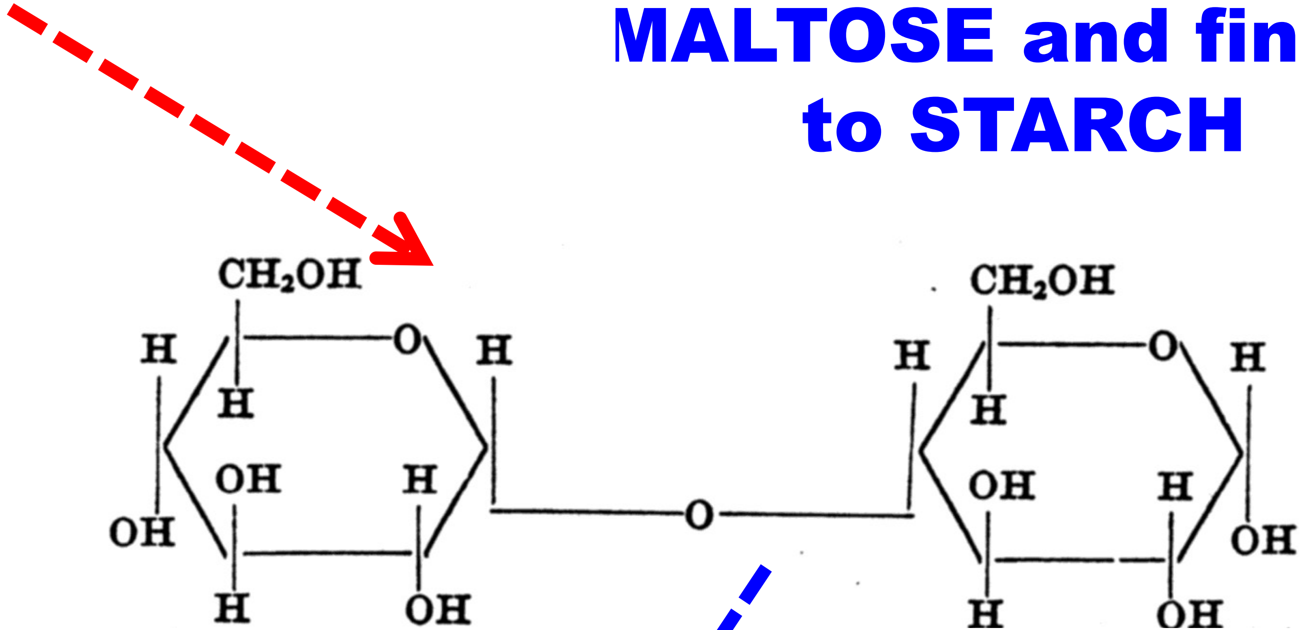


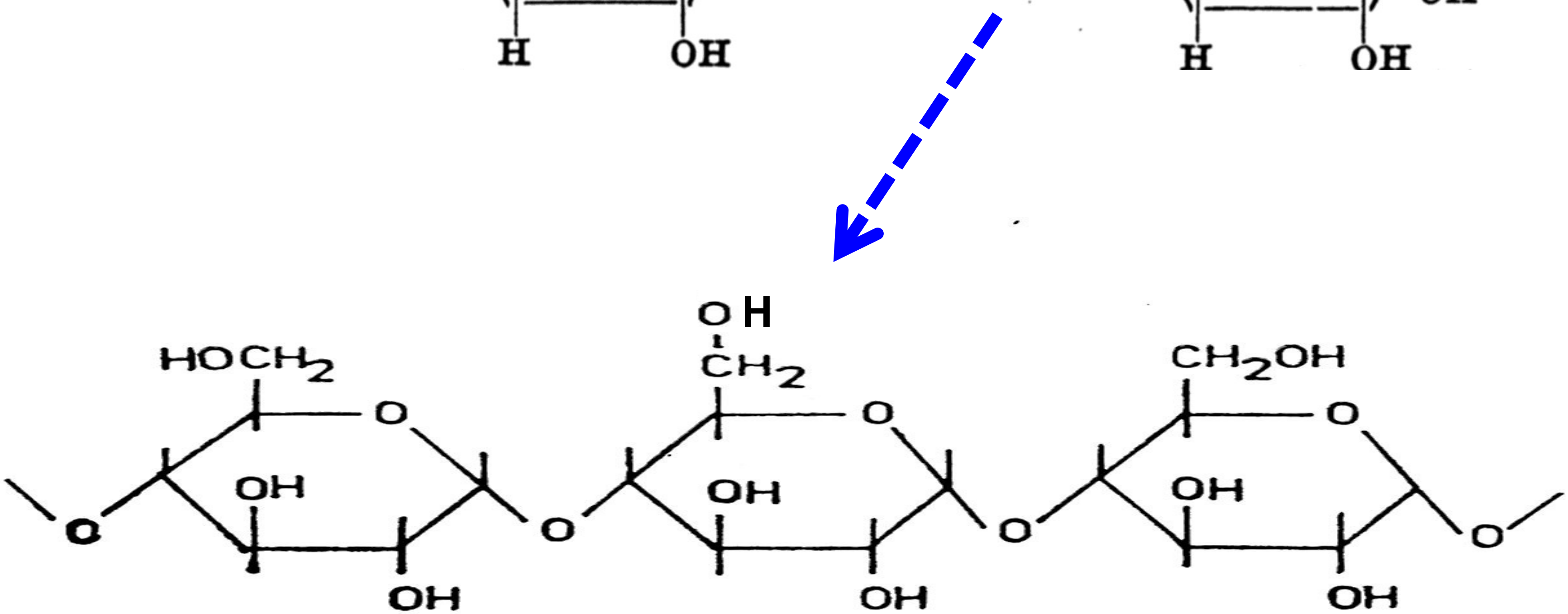
Lactose

The Path from GLUKOSE to MALTOSE and finally to STARCH

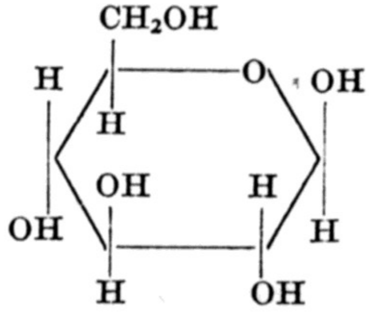


α - glukopyranóza

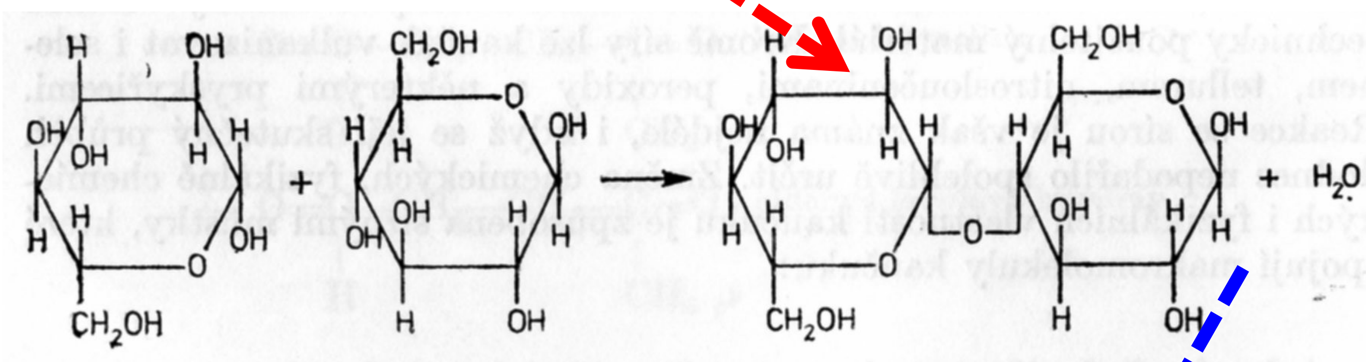




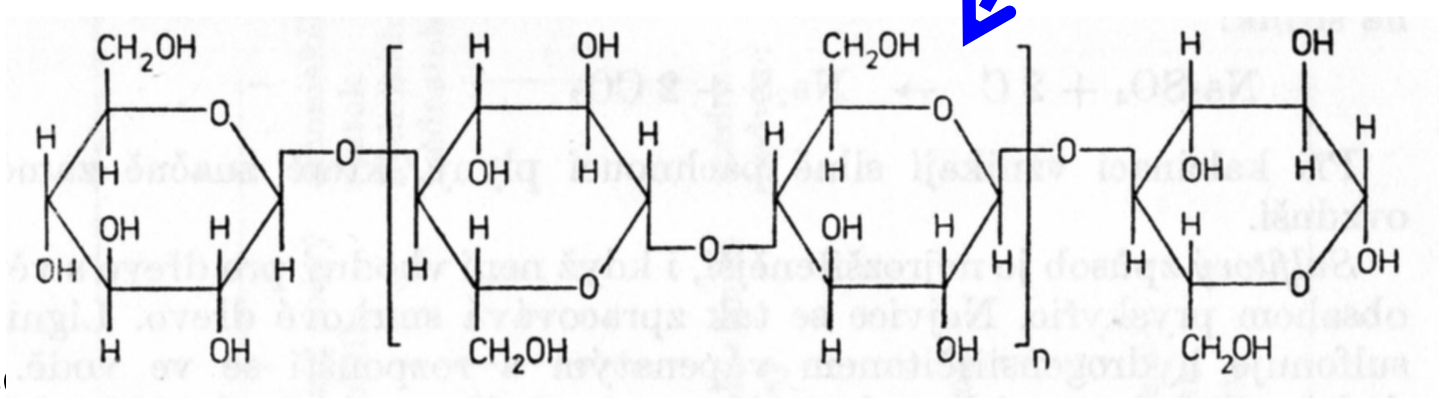
The Path from GLUKOSE to CELLOBIOSE and finally to CELLULOSE



β - glukopyranóza



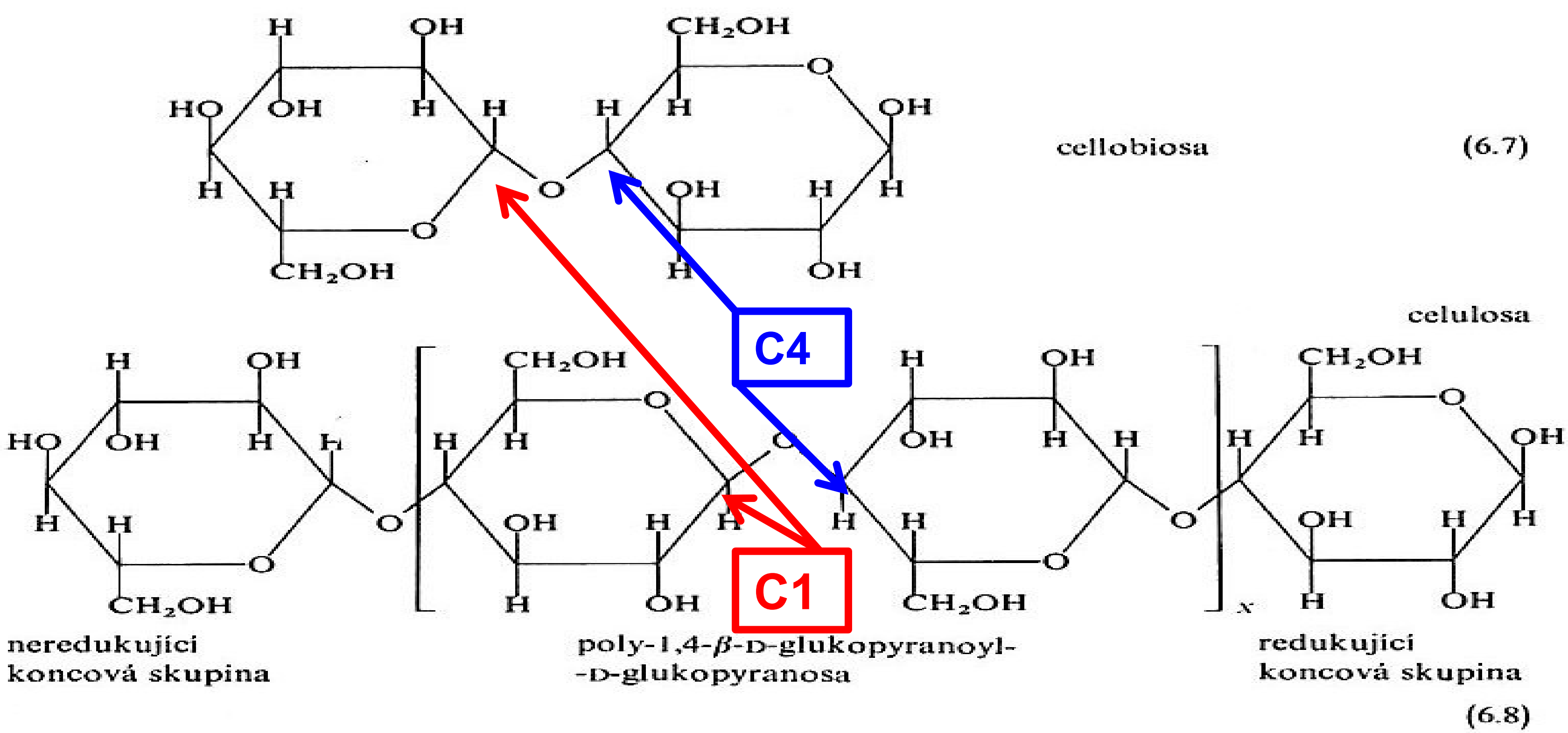
cellobiosa



celulosa

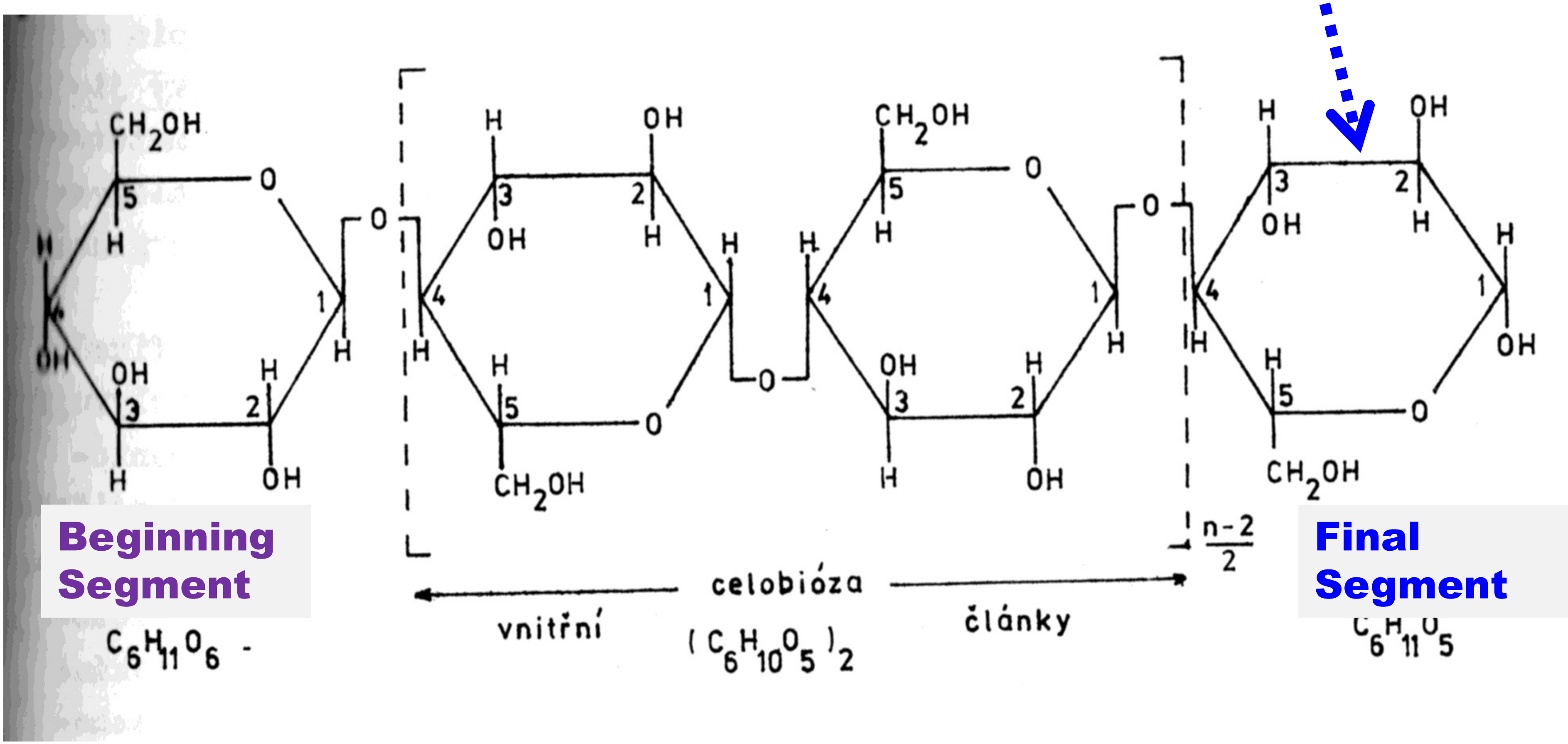
Cellulose Chemistry I/1

- **Cellulose** belong to the **Polysaccharides**
- **Cellulose form the main Part of the BIOMASS**
- Poly-(β–D-glucose) (**Simplified Name**)
- **Poly-1,4-β–D-glucopyranoyl-D-glucopyranose**



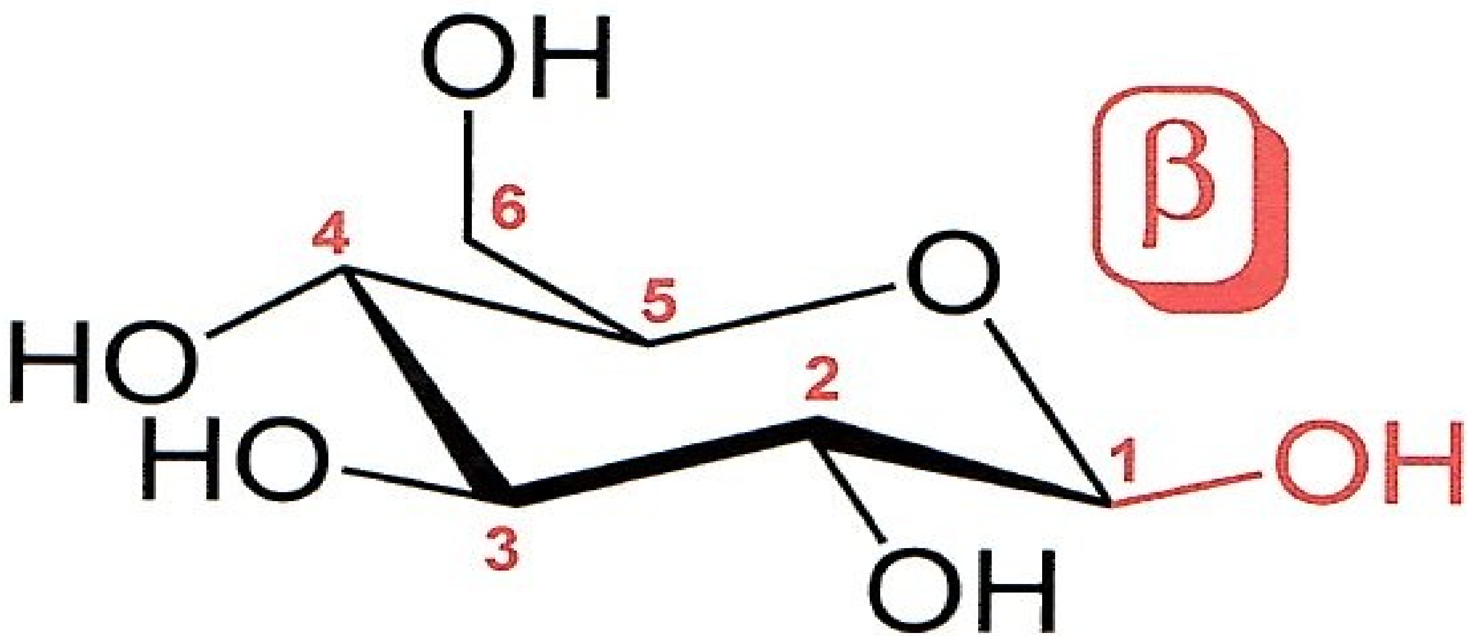
Cellulose Chemistry I/2

It is the REDUCING FORM, but due to very low Concentration *(the Macromolecule End Group only)* CELLULLOSE is only very low reducing Polysaccharide



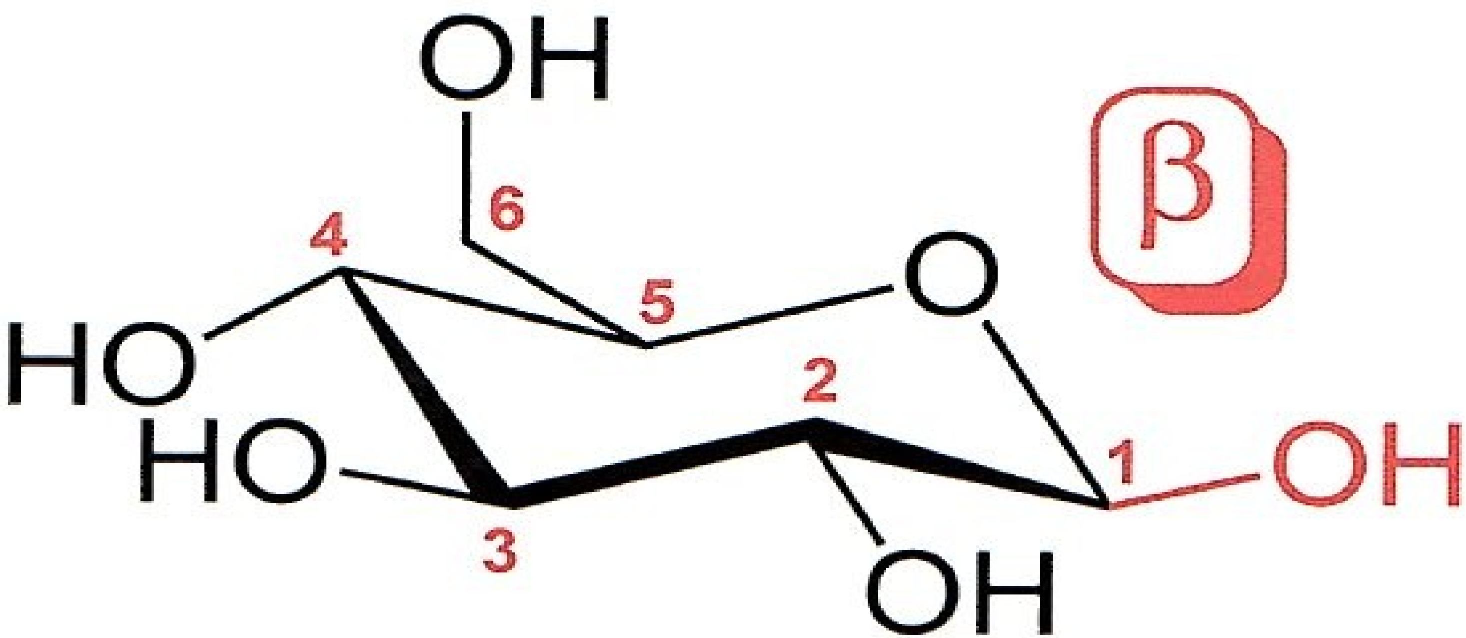
Cellulose Chemistry I/3

CELLULOSE is the High REDUCING POLYSACCHARIDE AFTER HYDROLYSE to GLUCOSE ONLY (ß-D-GLUCOSE)

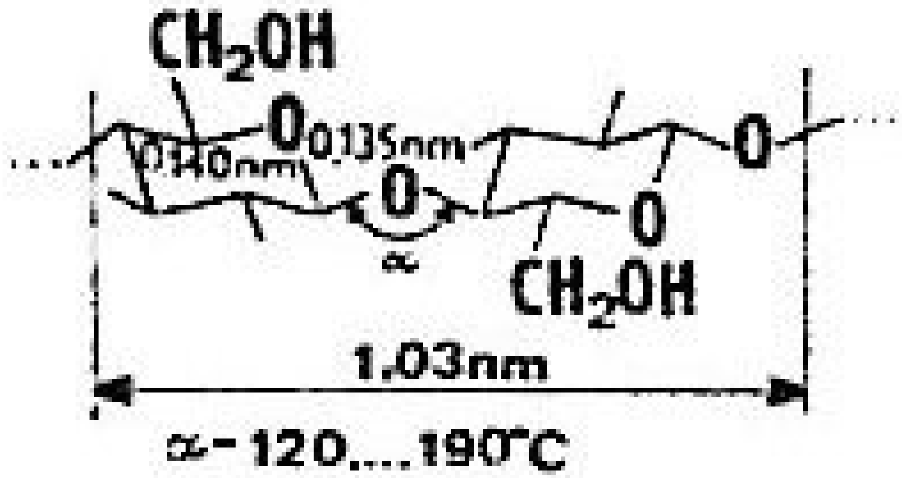


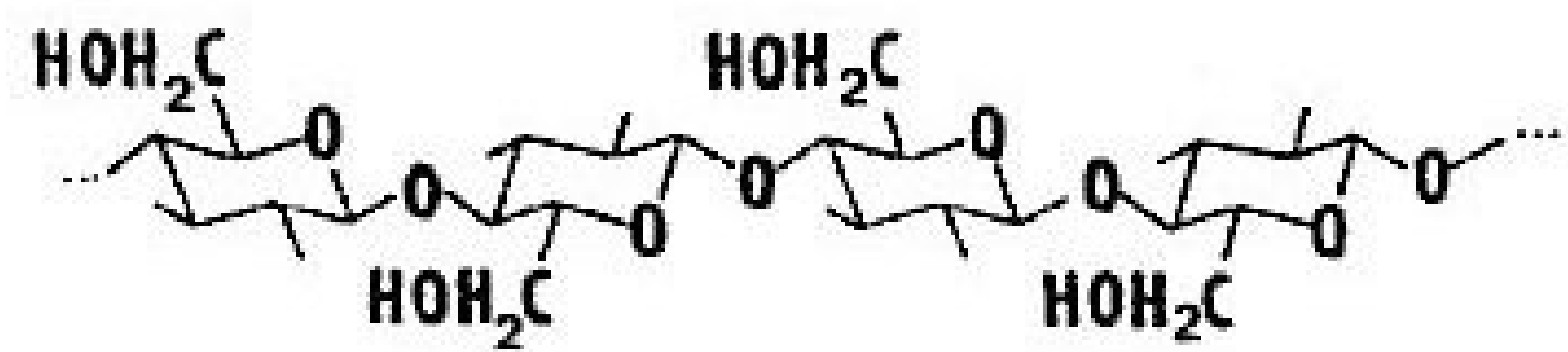
Cellulose Chemistry I/4

CELLULOSE as the reducing Polysaccharide is used for DEGREE OF POLYMERIZATION DETERMINATION BY END GROUPS METHOD, but which is assumed as LOW PRECISSE



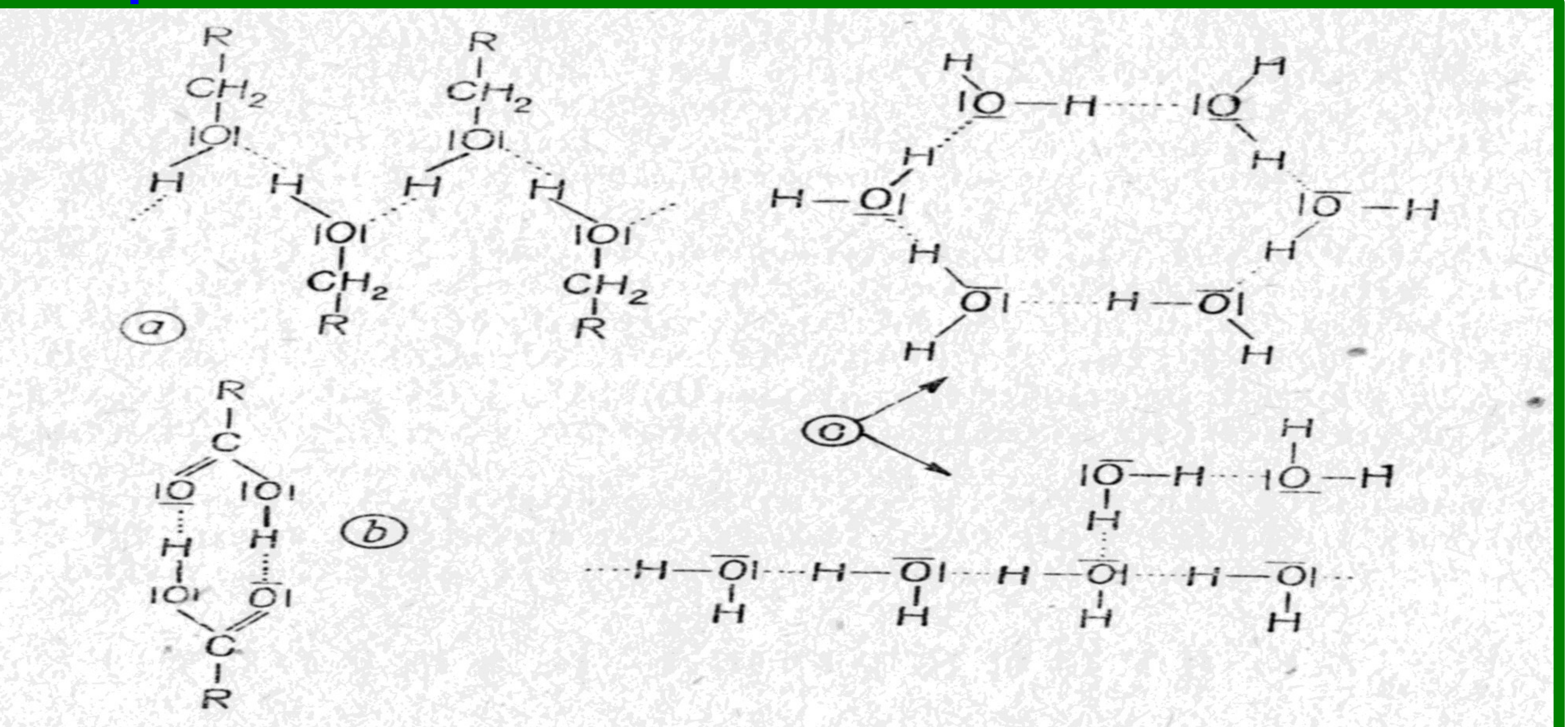
Cellulose Chemistry II





Revision is necessary!

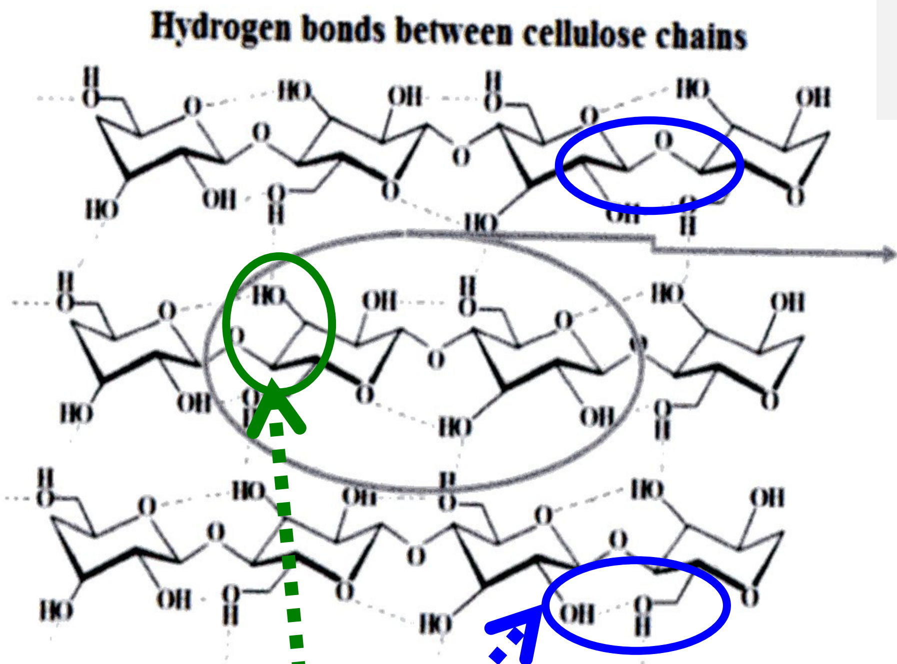
- **Hydrogen Bonds DO NOT HAVE Strength as high as classical Chemical Bond has.**
- **Hydrogen Bonds are easy broken.**
- **The new such Bond are restored immediately afterwards and there is Steady Association degree via Hydrogen Bonds at given Temperature**



Hydrogen Bonds in Liquids: a) Alcohol, b) Organic Acid, 3) Water

Cellulose Chemistry III/1

Hydrogen Bonds are as inside one Molecule, so between two neighbouring Molecules



Secondary Structure (Interaction in one Macromolecule Chain)

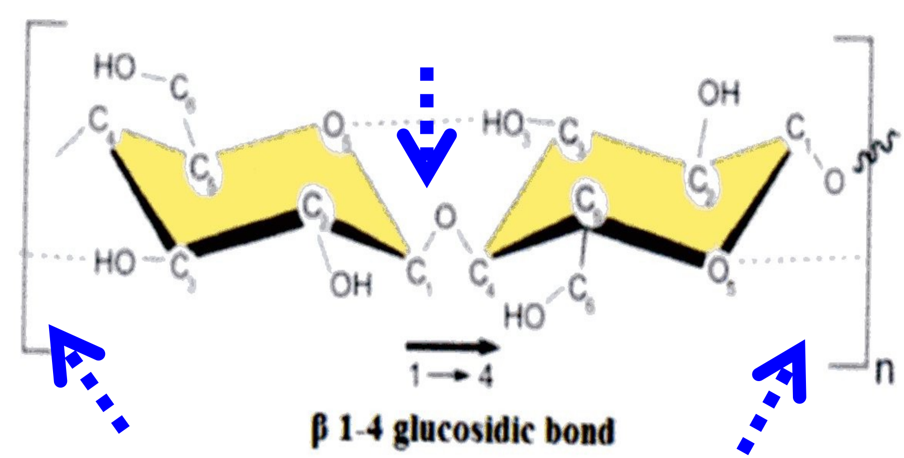
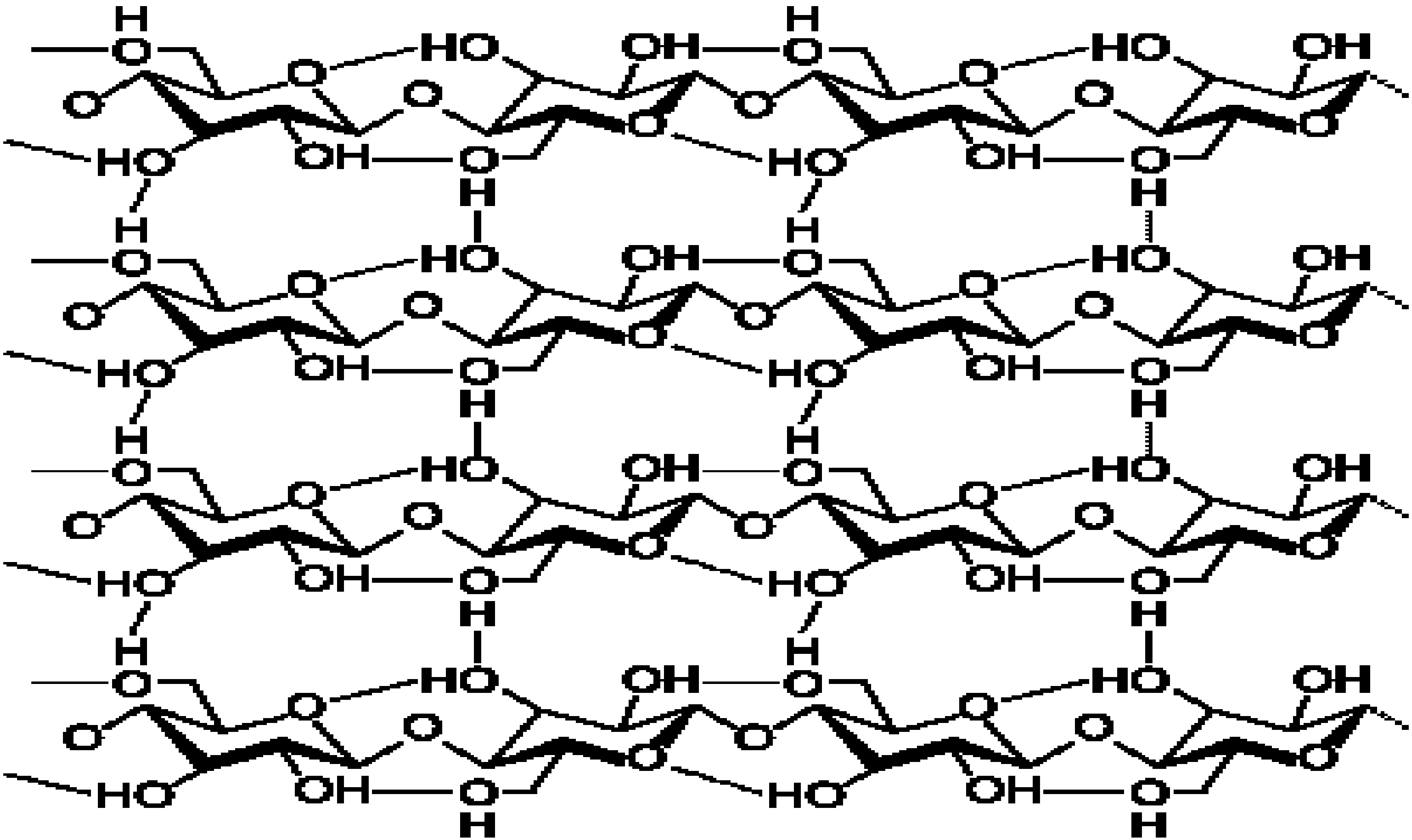


Figure 1. Molecular structure of a cellulose unit, showing the β 1-4 glucosidic bond and the intrachain hydrogen bonding (dotted line) (Adapted from [3]).

Tertiary Structure (Interaction between two or more Macromolecule Chain)

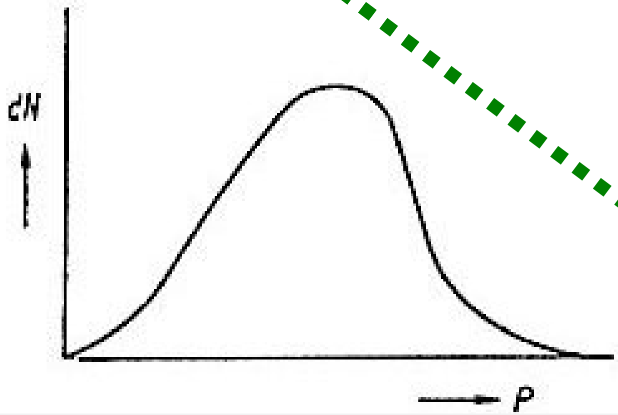
Cellulose Chemistry III/2

Once more Interactions both in one Macromolecule Chain and between two or more Macromolecule Chain)



Cellulose Chemistry IV

Short Fibers in the Cotton, which are not able to be spun to Thread (Waste Fibers, employed for the Chemical POLYMERANALOGIC MODIFICATION of Cellulose)



DEGREE OF POLYMERIZATION DISTRIBUTION – AN EXAMPLE ONLY!

Cellulose DEGREE OF POLYMERIZATION – NATIVE Cellulose

Raw Cotton	10 800
Linters	9 300
Flax	37 000
Ramie	12 400
Nettle	11 600
Sulfite Cellulose	3 100

$$P = M/162$$

Mean M_w (other Source accordingly)

Cotton	1,78 – 2,43 x 10^6
Sulfite Cellulose	0,60 x 10^6
Viscose Fibres	0,23 x 10^6

ANOTHER SOURCE (P):

- Cotton 15 000
- Sulfite Cellulose 5 – 9000
- Viscose Fibres 300

Alpha, beta and gamma celluloses have the same chemical structure, but celiluloses differ polymerisation degree (DP) and celluloses have diffrent solubility in 17,5% NaOH. Alpha cellulose doesn't dissolve in 17,5% NaOH and DP above 200. Beta cellulose dissolve in 17,5% NaOH and DP 30-200, but we can precipitated again from NaOH solution. Gamma cellulose dissolve in 17,5% NaOH and DP 10-30, but we can't precipitated again from NaOH slolution

The **alpha-cellulose is usually measure with the TAPPI's methods**, but not the beta and gamma celluloses. I suppose that the alpha is the most plentiful of these ones but I am interested to know what is the difference between these celluloses according to their chemical structure.

Cellulose Chemistry III b

Raw Cotton	10 800
Linters	9 300
Flax	37 000
Ramie	12 400
Nettle	11 600
Sulfite Cellulose	3 100

Linters =short Cotton Fibers, which are not able to be spun to Thread

In GENERAL:

- Bast Fibre and Cotton > HIGH P,
- Woody plant – LOWER P,
- REGENERATED Cellulose - LOW P

DEGREE OF POLYMERIZATION of various Celluloses

Cellulose	P	Cellulose	P
Ramie	3 500 – 4 600	Pine	1 000 – 1 200
Egyptian Cotton	3 000 – 4 000	Viscose Fibres	250 – 800
Linters	Approx. 1 400	α– Cellulose	>200
Linters boliled off	1 200 – 1 300	β– Cellulose	30 - 200
Linters bleached	Approx. 700	γ– Cellulose	10 - 30
Beech	1 200 – 1 400	Beech bleached	700 – 1 300
Poplar	1 200 – 1 400	Straw	Approx. 800

Cellulose Chemistry IV

- **The Figures of MW and P are different in different Source, except for COTTON**
- **<u>What could be the Reason:</u>**
  - **Various Natural Sources,**
  - **Various viscose Fibre Grades (<u>VERY PROBABLY</u>),**
  - **Various Measurement Methods**
- **<u>What is usually missing:</u>**
  - **MWD**
  - **Given of type MW (M_n or M_w)**

CELLULOSE PHYSICS I

- **DENSITY approx. 1,5 g/cm^3**
  - **This is an Effect of heteroatoms > higher Density then most of the SYNTHETIC POLYMERS (an Exception is e.g. PVC, PET and PA)**
  - **The Effect of Crystallinity > higher Density then Amorphous Parts of Macromolecules**

- **TENSILE STRENGHT approx. 300 Mpa**
  - **The Effect of an Fibre Orientation and Crystallinity**
  - **The TENSILE STRENGHT is LOWER at wet Conditions > the Effect of Water on Lowering an Interaction between a Fibrils, formed by Macromolecules**
- **WATER SORPTION is high approx. 7 % w/w at 20 °C a 65 % RH (relative Humidity)**

Cellulose Solubility

Solvent	Solubility	Associated Process
Water	Insoluble	Water Sorption, without Change of P_n
Solutions of some inorganic Salts ($ZnCl_2$, $AlCl_3$, $SnCl_4$ etc.)	Soluble	Part Hydrolysis >Change of P_n
Inorganic Acids (HCl, H_2SO_4, H_3PO_4 etc.)	Soluble	Part Hydrolysis >Change of P_n
Hydroxides of alkalic Metals	Soluble	Alcoholates Formation
Amine Complexes – Schweitzers Reagent	Soluble	Copper complexes formation
Alkylamines	Soluble	**I do not know**

Cellulose Solubility in 17,5 % w/w NaOH Water Solution after Wood delignification

Solvent 17,5 % w/w NaOH Water Solution	Solubility	Associated Process
α Cellulose	Insoluble	
β Cellulose	Soluble	By Acidification of Filtrate by Acetic Acid precipitate from the Solution Chains having P_n > 200, arisen during Delignification
γ Cellulose	Soluble	It remains in the Solution after Precipitation β **cellulose** and it is necessary to precipitate it using EtOH. It contains HEMICELLULOSES.

Cellulose Solubility in 17,5 % w/w NaOH Water Solution after Wood delignification – INTERNATIONAL NORM

INTERNATIONAL NORM	**ISO 692**
English Denomination	**Determination of alkali solubility**
Date of Issue	**1.10.1993**

Melting Points & Solubility of Saccharides and Cellulose

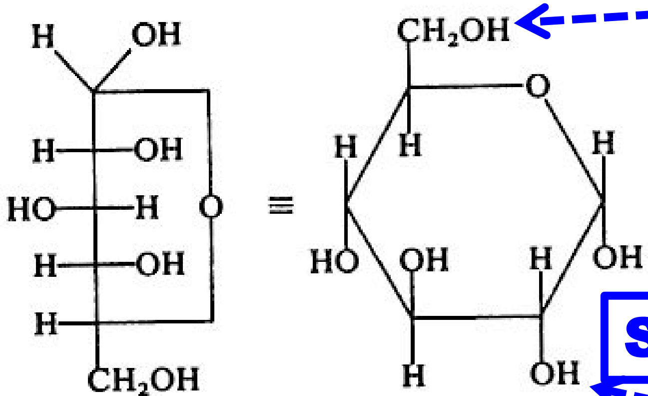
You can find also other Figures related to Temperature of Cellulose Decomposition!

It is given by:

- **Air or Inert Gas (Nitrogen, Helium etc.),**
- **Presence of the transition Valence Elements (mainly Fe^{+3}, Mn^{+2}, Co^{+2} etc.), which catalyse this Oxidation**

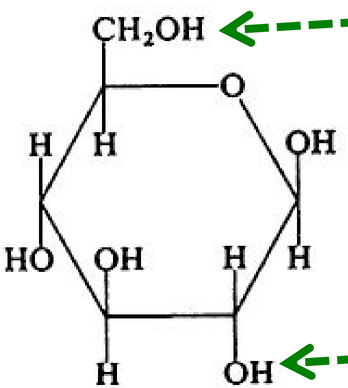
Substance	Melting point (°C)	Solubility in Water (% w/w)
Glucose	146	Approx. 909 - 1 200 g/L
Cellobiose	203 (Decomposition)	Approx. 12 g/L
Cellotriose	238 (Decomposition) ???	25 - 50
Cellotetrose	251 (Decomposition) ???	12,5 - 25
Cellopentose	> 226 (Decomposition)	5
Cellulose	270 (Decomposition)	Insoluble

STARCH versus CELLULOSE I



α-D-glukopyranosa
(α-glukosa)

STARCH is Polymer of α-D-glukopyranose

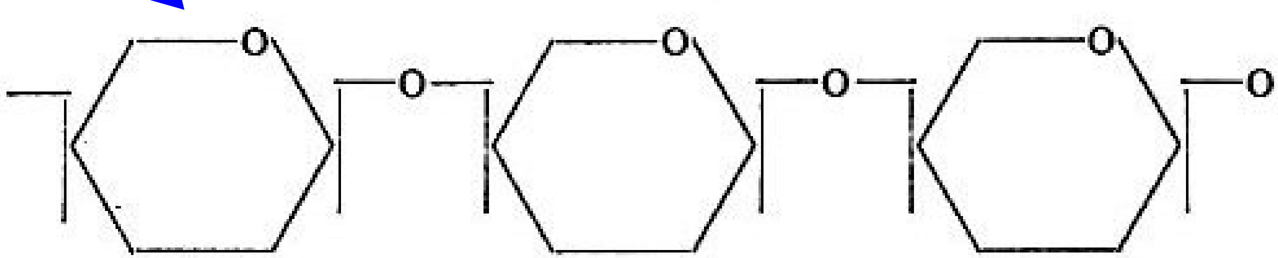


β-D-glukopyranosa
(β-glukosa)

CELULLOSE is Polymer of β-D-glukopyranose

STARCH (linear AMYLOSE) versus CELLULOSE II

STARCH is Polymer of α-D-glukopyranose



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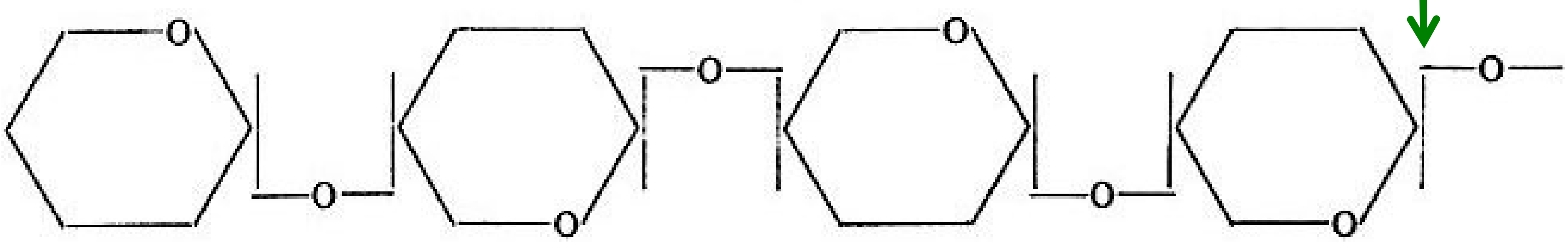
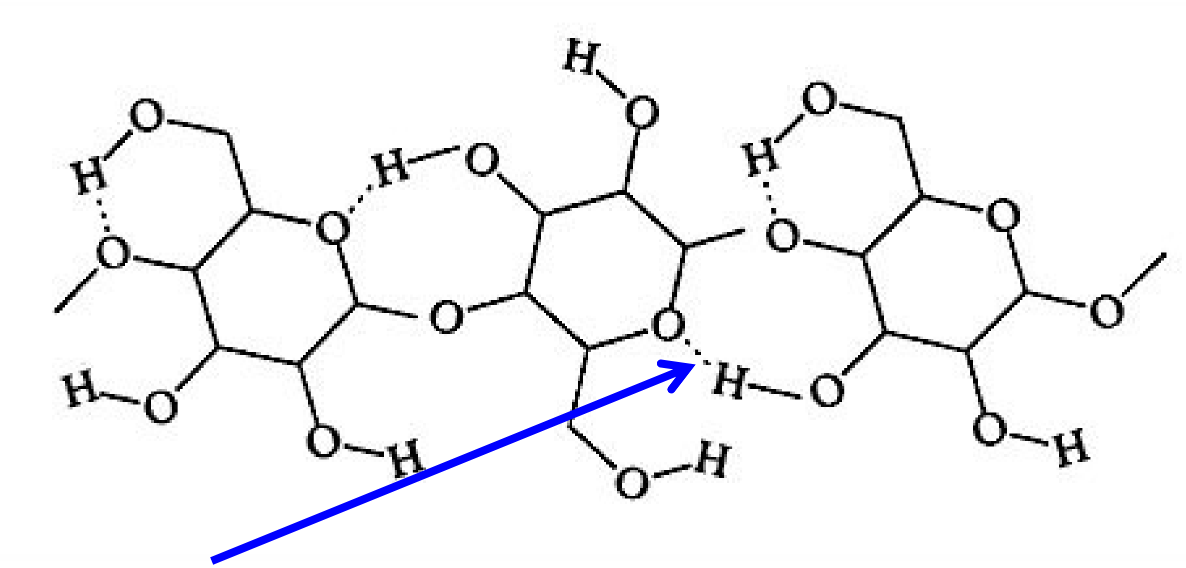


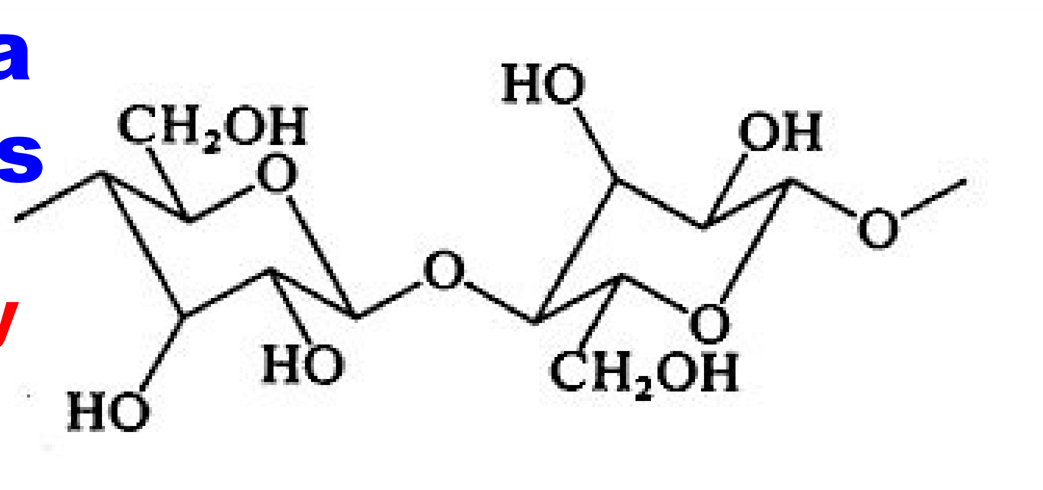
VI

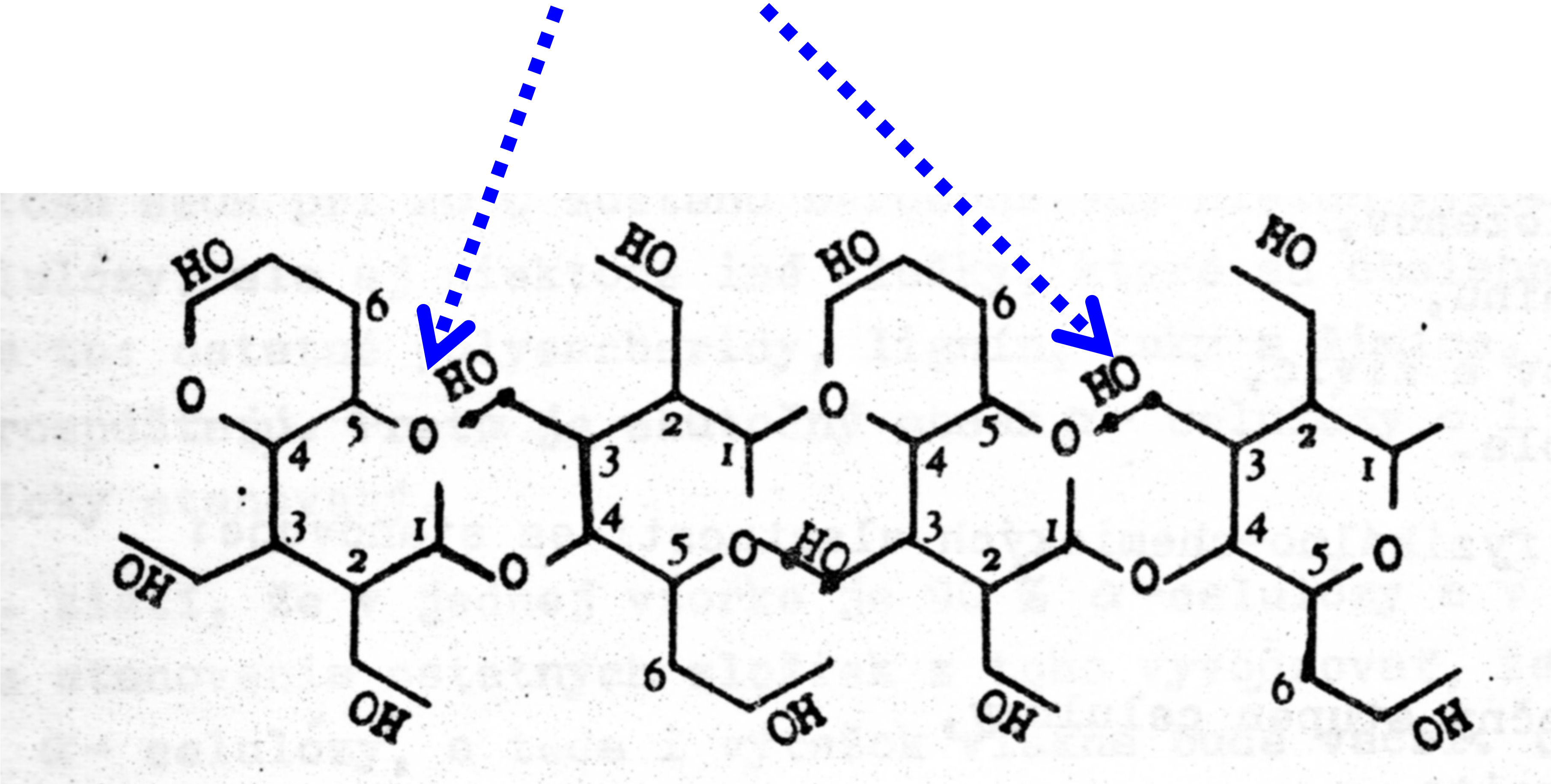
CELULLOSE is Polymer of β-D-glukopyranose



Strong Interactions via Hydrogen Bonds

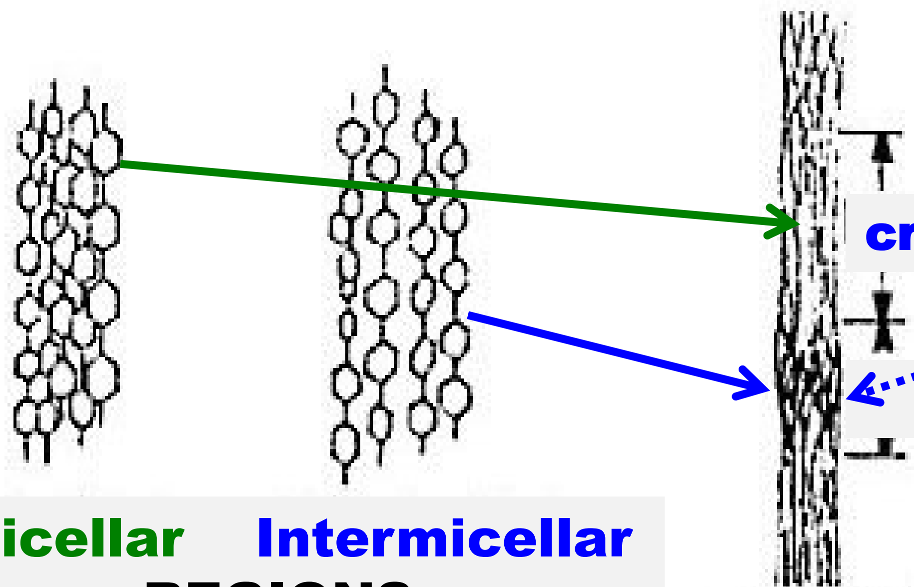
Other Possibility to represent Cellulose





Strong Interactions via Hydrogen Bonds

Supermolecular Structure of Cellulose I



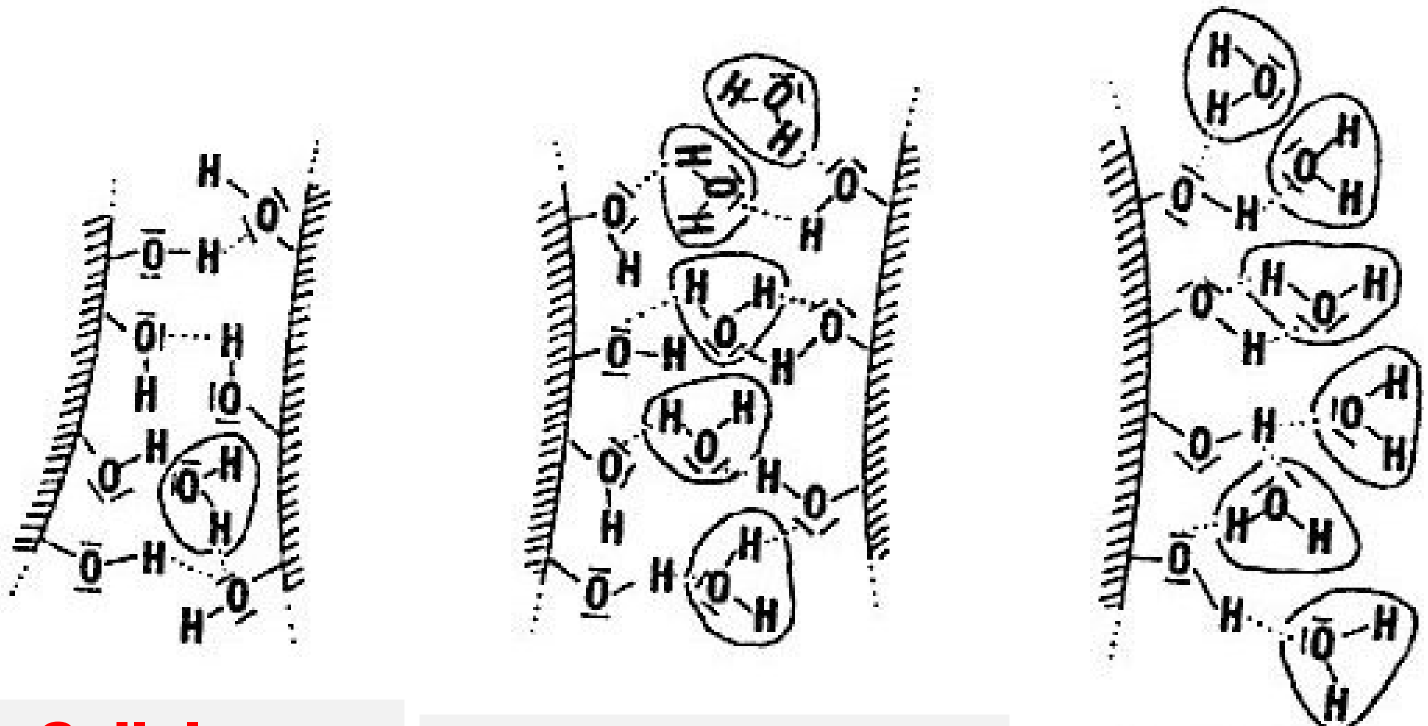
Space between the Microfibrils is filled by HEMICELLULOSE & LIGNIN

Colourless inert Substance Insoluble in Water, Density 1,55 g/cm^3

AMORPHOUS CELLULOSE:
- **easy to swell**
- **is more reactive than the crystalline one**

<u>Hierarchy of STRUCTURES in CELLULOSE:</u>
- **Macromolecule,**
- **Microfibril,**
- **Fibril,**
- **LAMELAE.**

Supermolecular Structure of Cellulose II



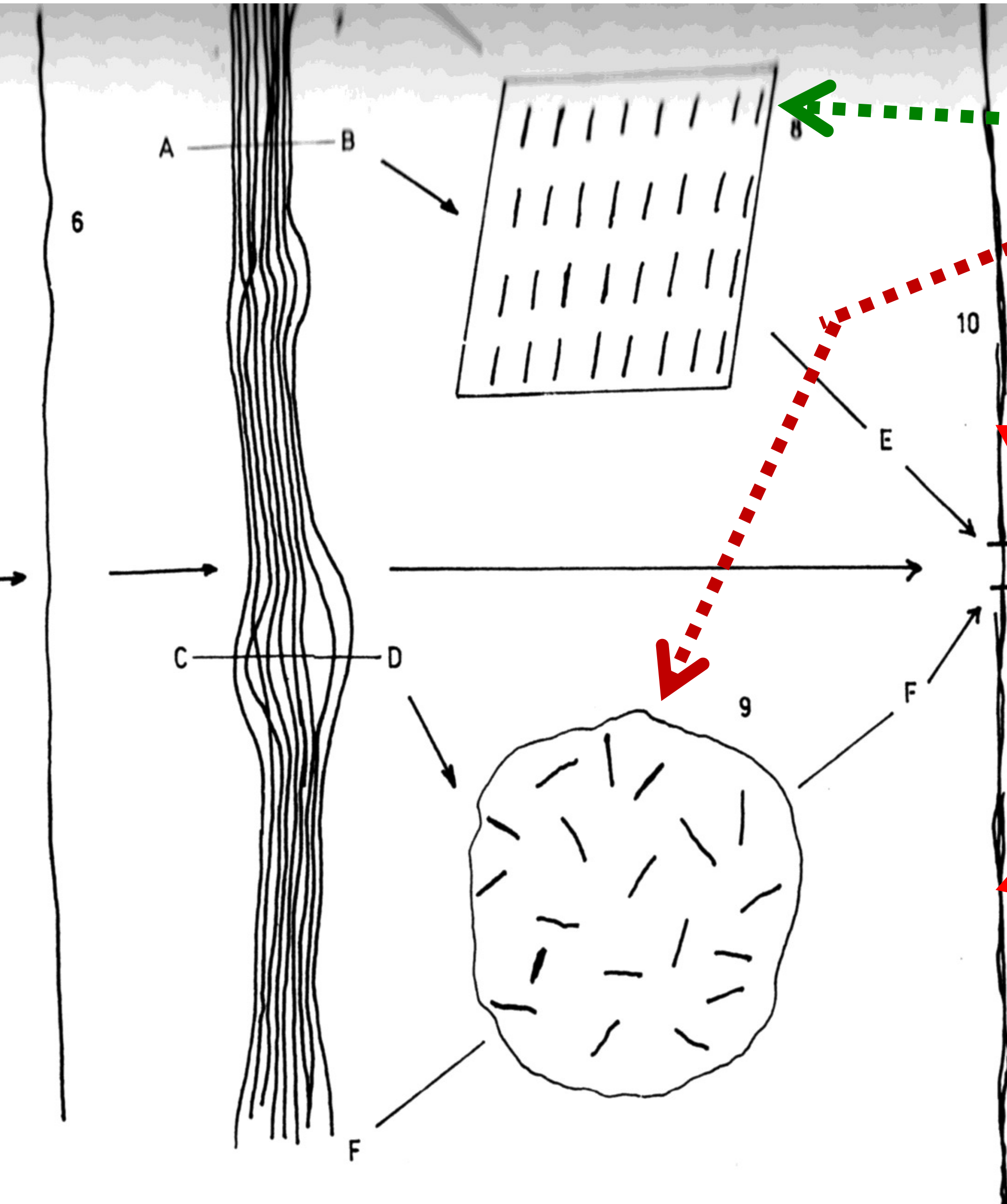
Native Cellulose

Swollen Cellulose

Colloidal Solution of Cellulose

Strong Interactions via Hydrogen Bonds

Supermolecular Structure of Cellulose III



A – B > Crystalline Part

C – D > Amorphous Part

8 Crosscut through the **CrystallinePart**

*9 Crosscut through the **Amorphous Part**, which is PARTLY (LENGTHWISE) ORIENTED*

> ***NEMATIC STRUCTURE***

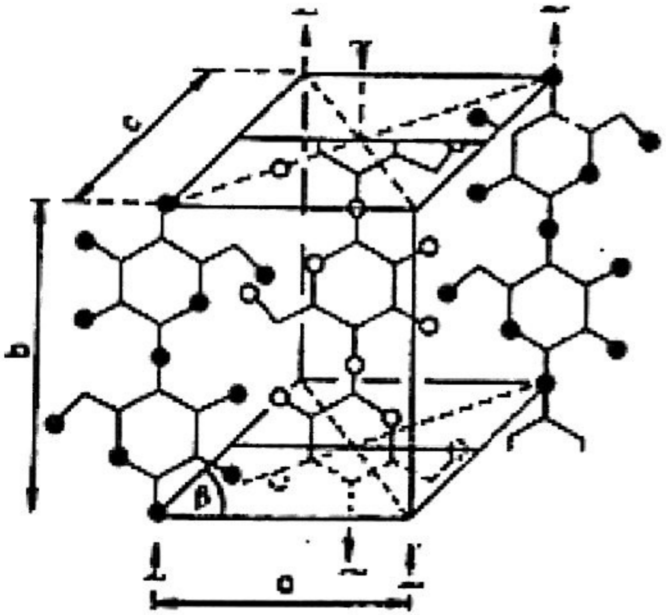
10 Bundle (ELEMENTARY FIBRIL, <u>MICROFIBRIL</u>)

<u>MADE OF SEVERAL MACROMOLECULES</u>

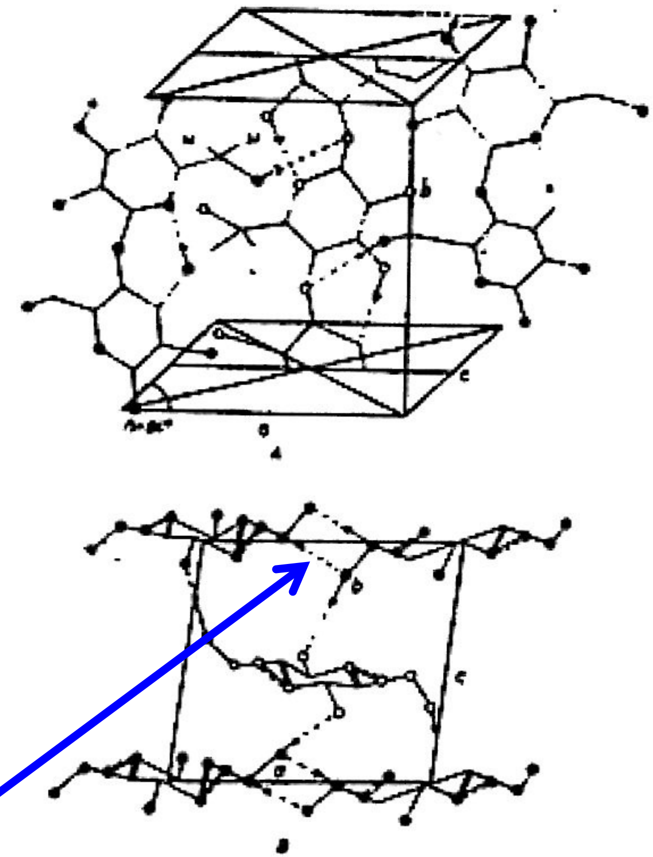
<u>MICROFIBRIL</u>:

- **THICKNESS is usually 3 – 30 nm**
- **LENGTH is usually Units of Microns**

Crystalline Structure of Cellulose I



Basic Cell of Cellulose



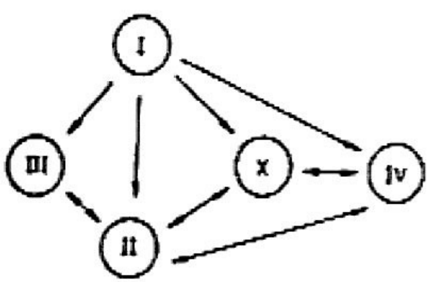
Strong Interactions via Hydrogen Bonds

Crystal lattice of Cellulose with marked Hydrogen Bonds

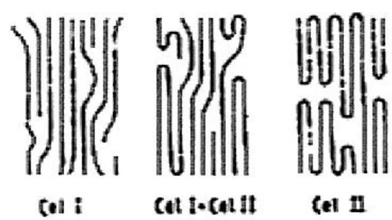
Crystalline Structure of Cellulose II

Parametre pre základné bunky celulózy — Tabuľka 2.5

	a (nm)	b (nm)	c (nm)	β (stupne)
I	0,82	1,03	0,79	83
II	0,80	1,03	0,91	63
III	0,77	1,03	0,99	58
IV	0,81	1,03	0,81	90
X	0,81	1,03	1,57	96



a



b

Scheme of Transition between Individual Polymorphid Forms of Cellulose

I – Native Cellulose

II – REGENERATED Cellulose

III – It is formed via Action of Ammoniac or Amine on I or II Cellulose

IV –by Heat Treatment + Glycerine on I or II Cellulose

X – via Action of HCl, H_2SO_4, H_3PO_4