

CARBOHYDRATES POLYMERS

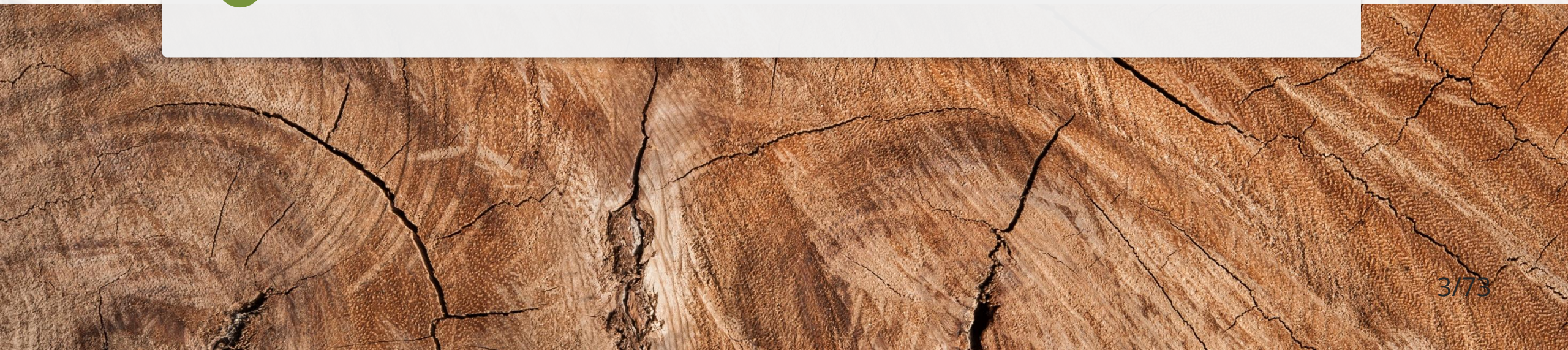
Prof. dr hab. Magdalena Zborowska

Wood Chemistry

Start Course

Carbohydrates – main information

1. Cellulose – occurrence, structure
2. Hemicelluloses – occurrence, structure
3. Starch and pectines – occurrence, structure
4. Carbohydrate reactivity





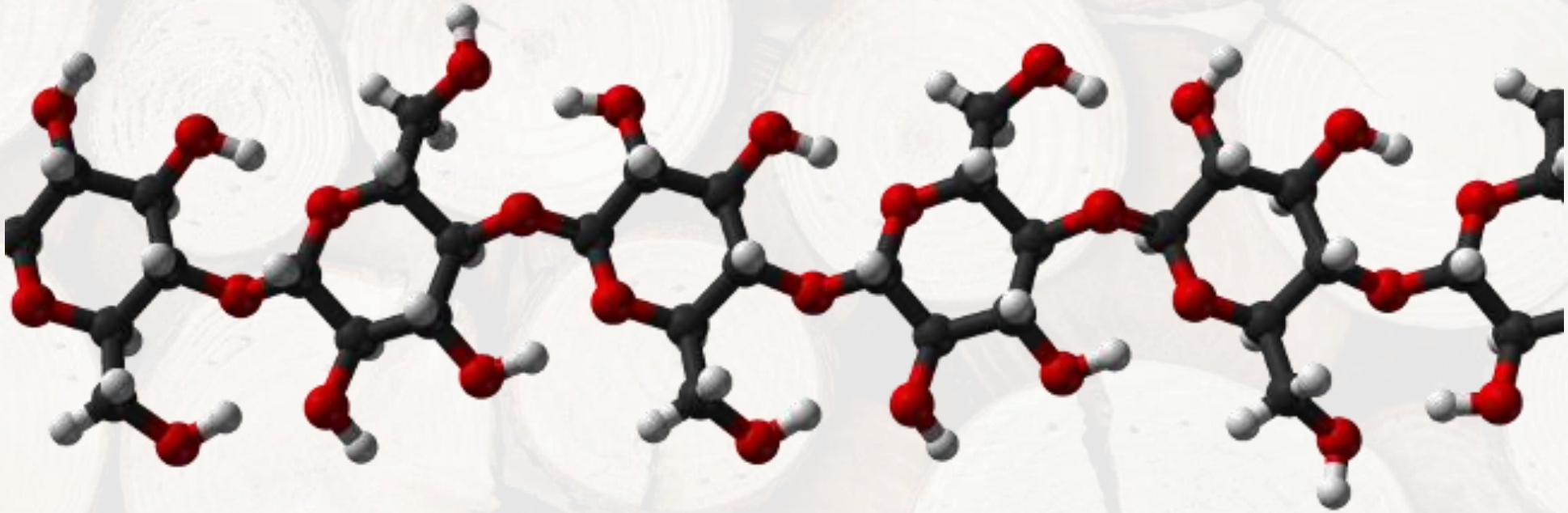
Carbohydrates polymers

Cellulose and hemicelluloses – occurrence, structure

Carbohydrates

The major carbohydrate portion of wood is composed of cellulose and hemicelluloses (polioses) polymers with minor amounts of other sugar polymers such as starch and pectines.

The combination of cellulose (40–45%) and the hemicelluloses (15–25%) is called holocellulose and usually accounts for 65–70 percent of the wood dry weight.



Check your knowledge

List the main carbohydrate components of wood

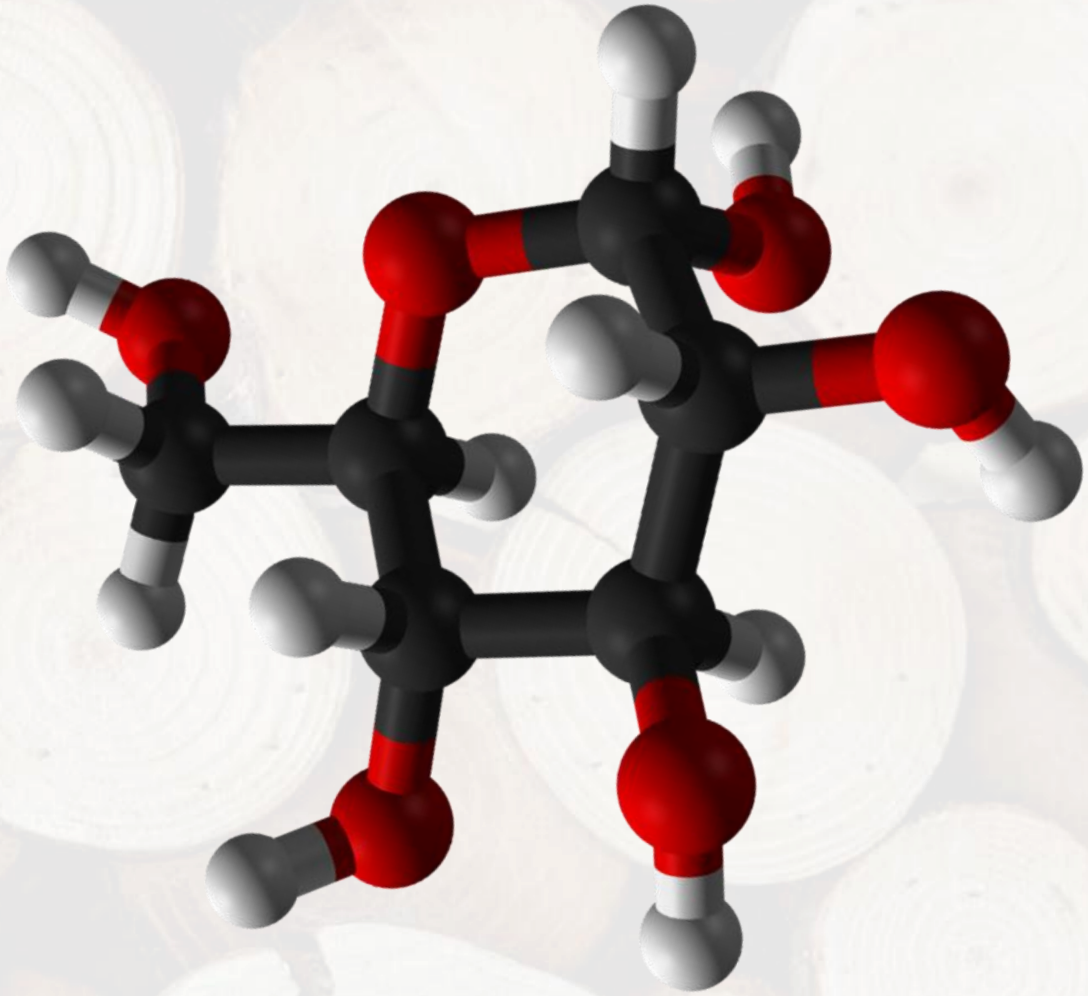


You should already know the answer.

However if you don’t, please repeat the course.

Carbohydrates - structures

Carbohydrates are made up of simple sugars, mainly D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid and lesser amounts of other sugars such as L-rhamnose and D-fucose.



Cellulose - occurrence

Cellulose is the most abundant organic chemical on the Earth. Earth's plants produce at least 100 billion (10^{11}) tons of cellulose each year – hundreds of times greater than the amount of plastics produced in the same time.

The content of cellulose differs in plants.

cotton 95-99%



wood 40-50%



straw 35-40%



Cellulose - occurrence

- Some fungi have a cell wall made of cellulose (however, for most fungi this wall is made from chitin, another abundant macromolecule).
- Algae, some amoeba and even some invertebrate animals (mostly marine invertebrates known as tunicates) also produce cellulose. In sea squirts, for example, cellulose helps larvae metamorphose into adults and is also part of the 'tunic', a kind of exoskeleton.
- Surprisingly, perhaps, some bacteria can also produce cellulose.

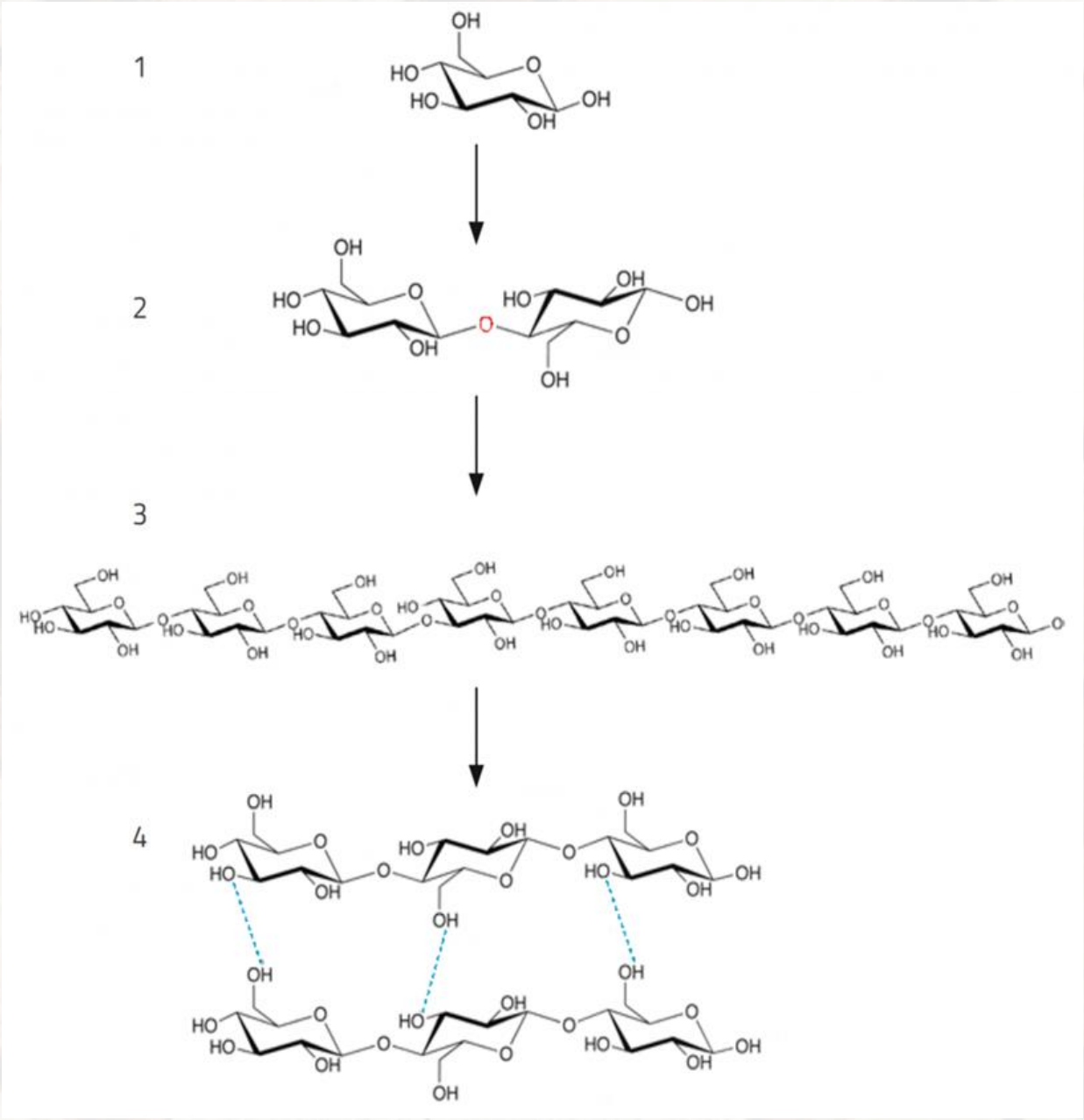


The sea squirt Ciona intestinalis which has an exoskeleton containing cellulose
Stefan Siebert Photography

Cellulose - structure

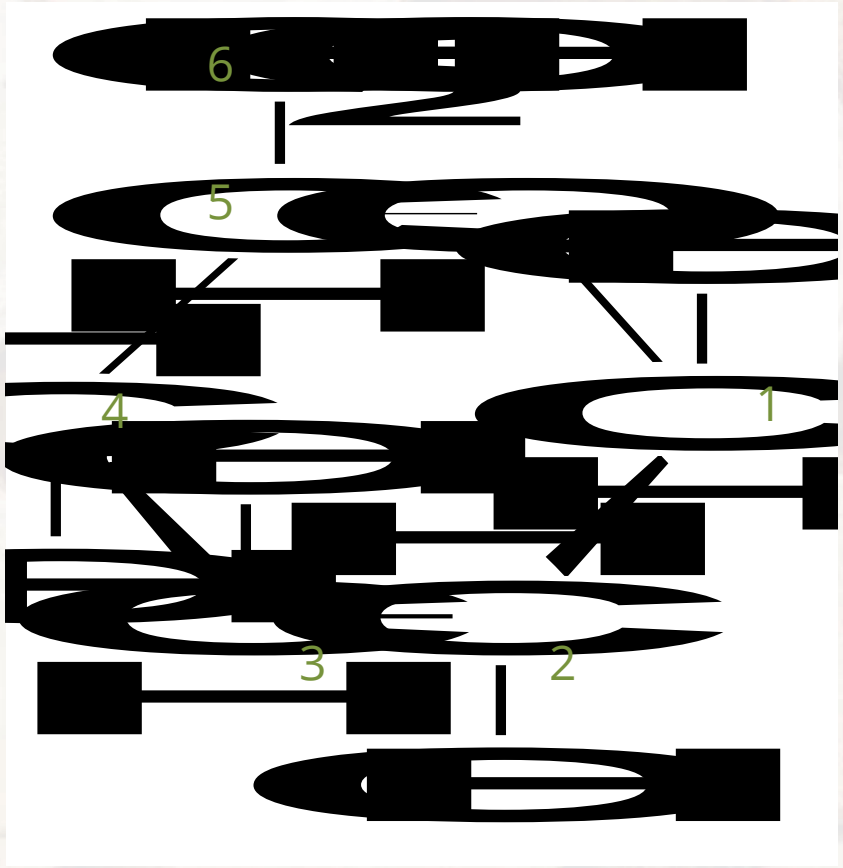
Cellulose is a β-(1→ 4)-glucan (1). The building block for cellulose is actually cellobiose, since the repeating unit in cellulose is a two sugar (2). Cellobiose assembles into unbranched, linear molecules consisting of 200 – 15 000 ß-D-glucopyranosyl residues via ß 1-O-4 glycosidic bonds (3). Linear cellulose chains in which adjacent glucose residues are rotated against each other by 180°, additional ones are stabilised by hydrogen bonds (4) and van der Waals forces.

Click on green numbers to learn more



Cellulose – glucose units

The basic chemical unit (mer) of cellulose is β-D-glucopyranose.



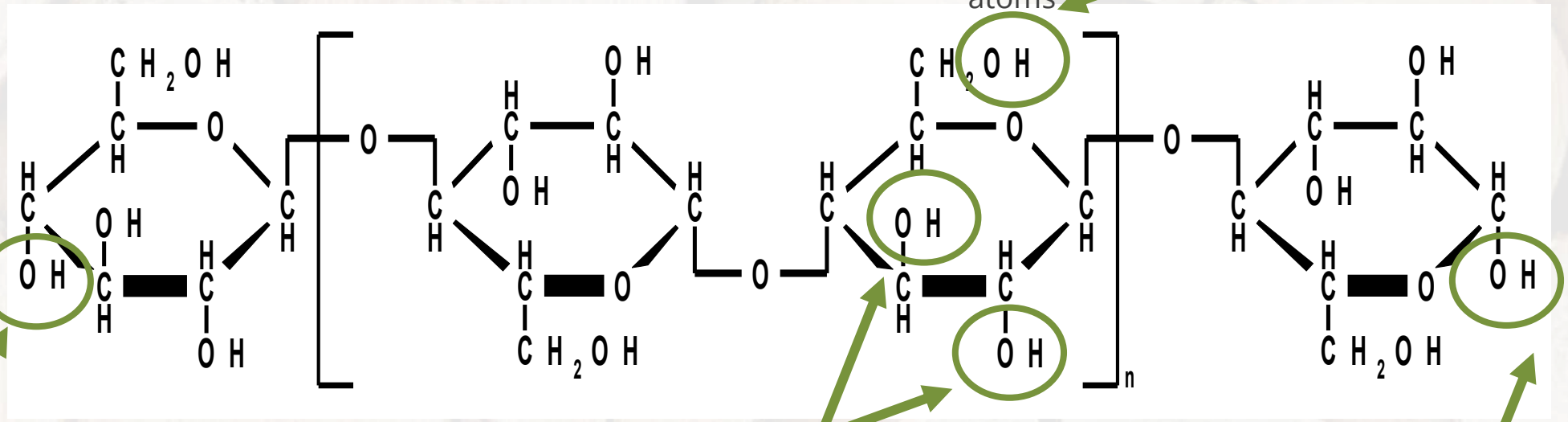
Pay attention to the numbering of the carbo
atoms and position of hydroxyl groups!

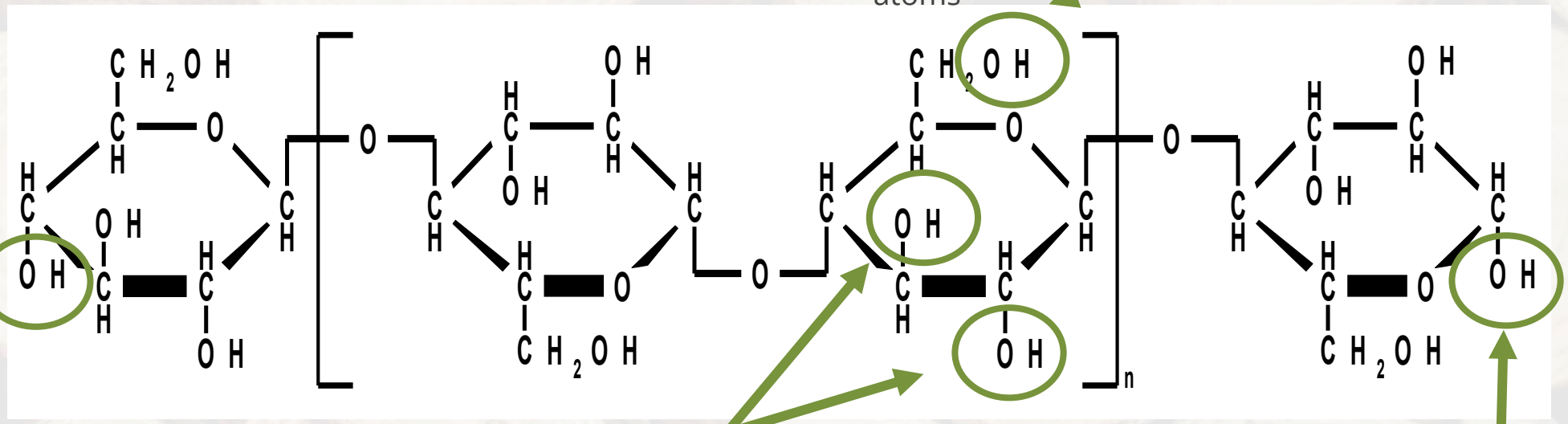
Cellulose – function groups

The ends of the cellulose chain contain different types of β-anhydroglucose units, i.e. the reducing end with a free hemiacetal (or aldehyde) group at C-1, and the non-reducing end with a free hydroxyl at C-4.

The primary and secondary carbon atoms differ in their reactivity. Primary atoms are 10x more reactive than secondary atoms.

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The primary and secondary carbon atoms differ in their reactivity. Primary atoms are 10x more reactive than secondary atoms.

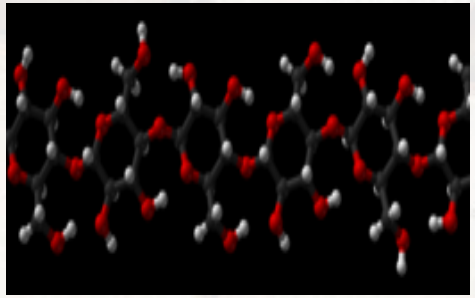
The ends of the cellulose chain contain different types of β-anhydroglucose units, i.e. the reducing end with a free hemiacetal (or aldehyde) group at C-1, and the non-reducing end with a free hydroxyl at C-4.

Cellulose – bonds 1/2

β(1→4)-glycosidic linkage

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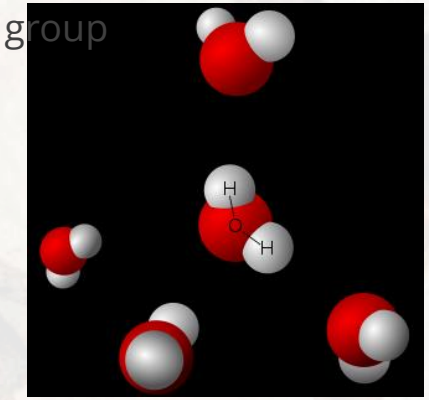
a type of covalent bond that joins a carbohydrate (sugar) molecule to another group, which may or may not be another carbohydrate



hydrogen bonds

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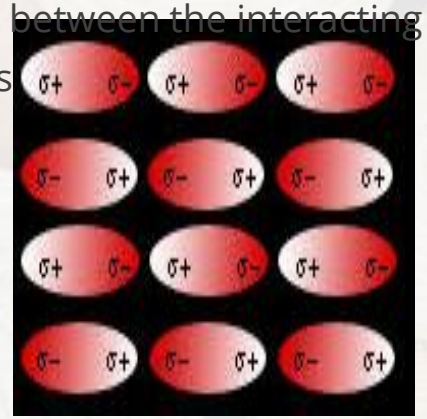
a partial intermolecular bonding interaction between a lone pair on an electron rich donor atom, particularly the second-row elements nitrogen (N), oxygen (O),
or fluorine (F) and the antibonding molecular orbital of a bond between hydrogen (H) and a more electronegative atom or group



van der Waals forces

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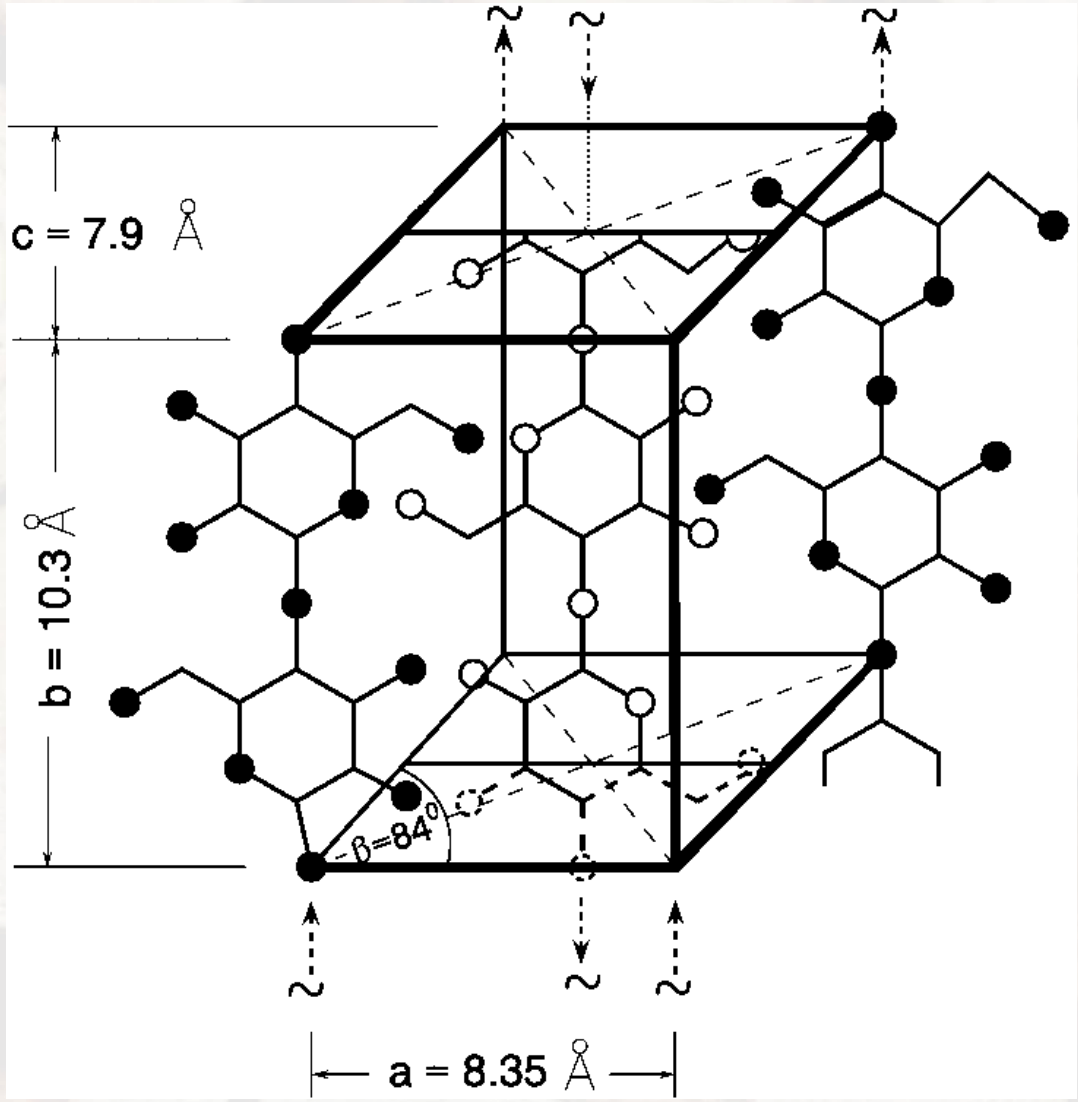
is a distance-dependent interaction between atoms or molecules, these interactions
are not due to chemical electron bonding; they are relatively weak and therefore more prone to interference. The van der Waals force declines quickly at greater distances between the interacting molecules



Cellulose – bonds 2/2

In the cellulose crystal, the location of the bonds is as follows:

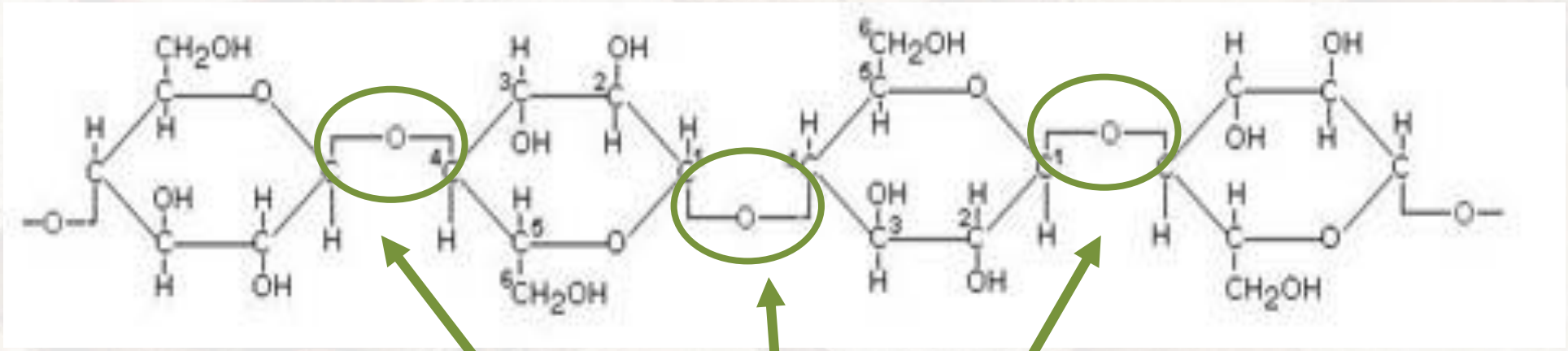
- along the b axis there are major valence forces, i.e. β(1→4)-glycosidic linkage with a binding energy above 209 kJ/mol;
- along the a axis there are weaker forces - hydrogen bonds - with an energy of 62.8 kJ/mol;
- along the c axis, there are the weakest forces - van der Waals with an energy of about 33.5 kJ/mol.



Cellulose crystal according to the Meyer-Misch model

Cellulose – β-(1→4)-glycosidic bonds

A cellulose chain is unbranched with glucose residues put together via strong beta -1, 4 linkages, which allow the molecule
to form long and straight chains. This straight chain conformation is ideal for the formation of strong fibers. For wood cellulose, the degree of polymerization (DP) is around 10,000, for cotton cellulose around 20,000.



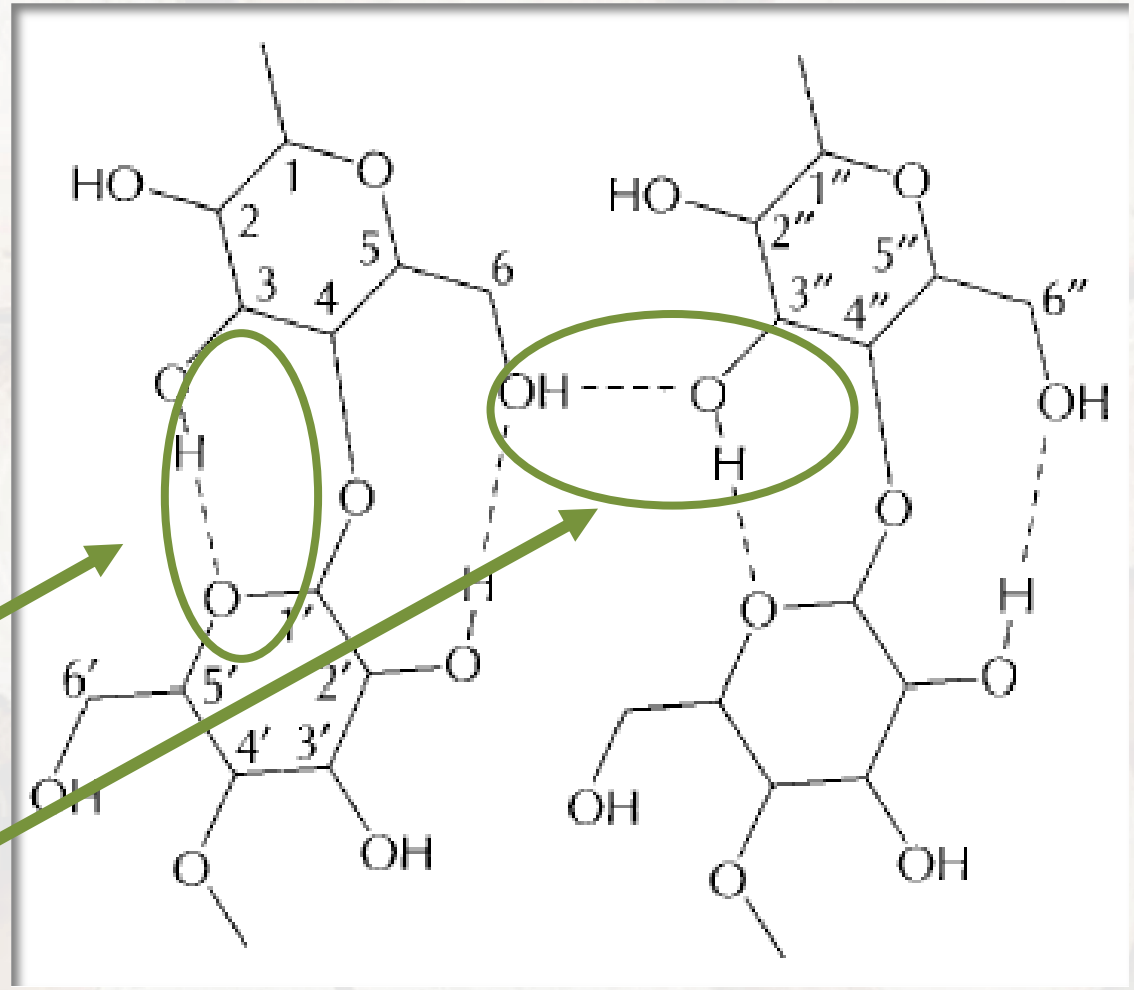
β-(1→4)-glycosidic bonds

Cellulose – hydrogen bonds 1/2

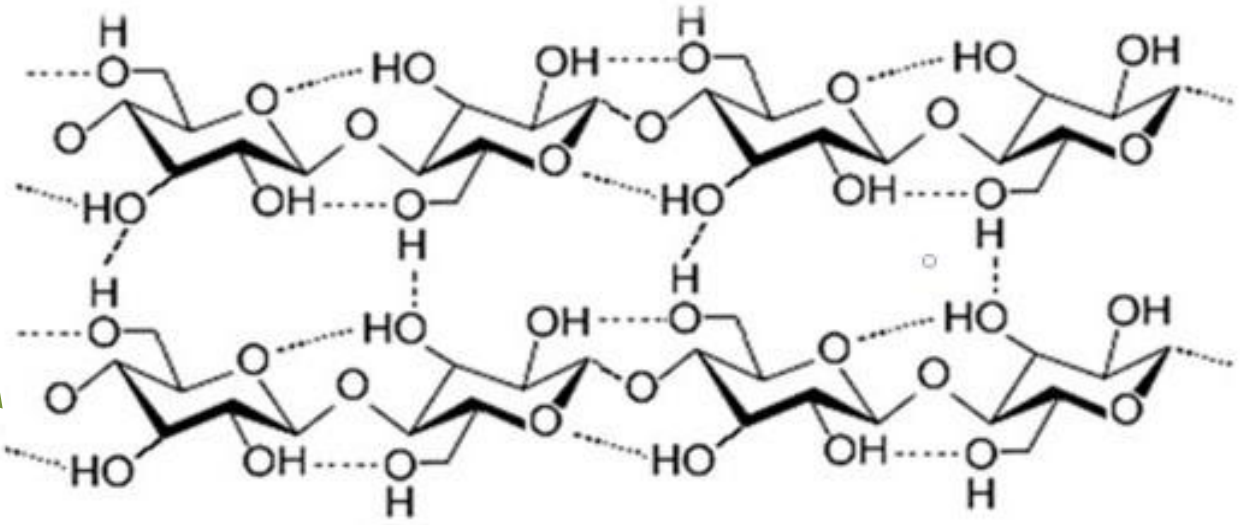
Hydrogen bonds in cellulose are formed due to numerous hydroxyl groups and oxygen atoms.

The hydrogen bonds in cellulose are internal (e.g. the OH C3 group and the O atom of the adjacent glycosidic ring) and extra-molecular (e.g. the OH C6 and the OH C3 group of the glucose ring of the adjacent chain)

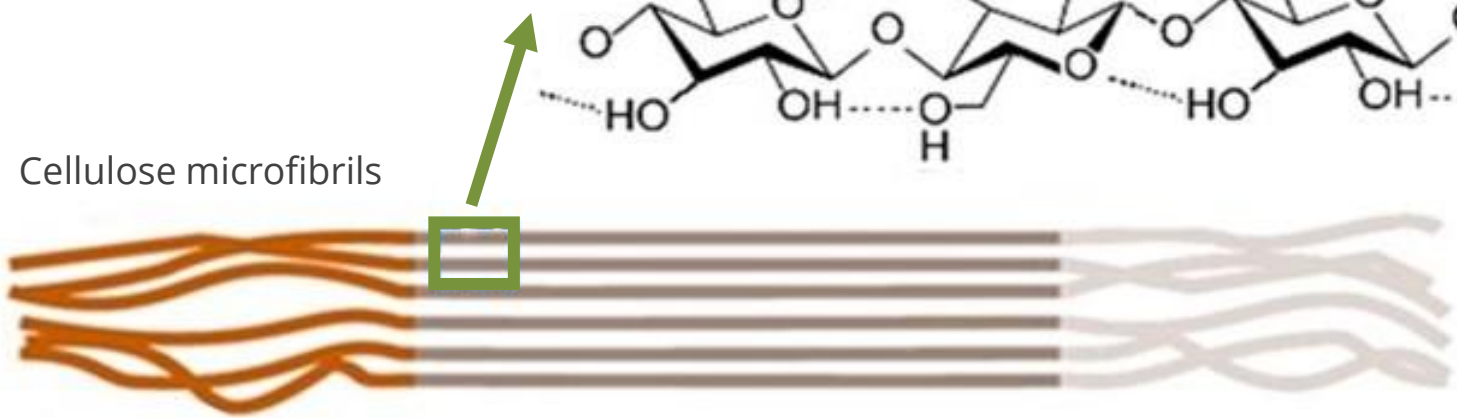
Hydrogen bonds are of a great importance for cellulose, they affect its properties, such as swelling, solubility, hygroscopicity, and the ability to react chemically.



Hydrogen bonding within and between cellulose molecules



Cellulose microfibrils



Amorphous region

Cristalline region

Amorphous region

The presence of hydrogen bonds causes the formation of oriented areas between the chains, the so-called crystalline region in which there is a perfect order
in three spatial directions.

The amorphous regions are characterized by a less perfect order in the arrangement of molecules, they run at greater distances from each other, hydrogen bonds are not present here with such an intensity.

Check your knowledge

List the types of bonds in the cellulose structure and explain their function in the formation of cellulose structure



You should already know the answer.

However if you don’t, please repeat the course.

Cellulose – supramolecular structures 1/3

A parameter termed the crystallinity index (CI) has been used to describe the relative amount of crystalline region in cellulose.

This parameter is different for celluloses and depends on the raw material.

cellulose		crystallinity index[%]
Natural cellulose	cotton	95
	hemp	96
	ramie	72
	wood	70
Cellulose after chemical treatment	pine kraft pulp	68
	rayon	45
	fortisan	74

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Fortisan - a fibre produced by deacetylation of cellulose acetate.

Cellulose – supramolecular structures 2/3

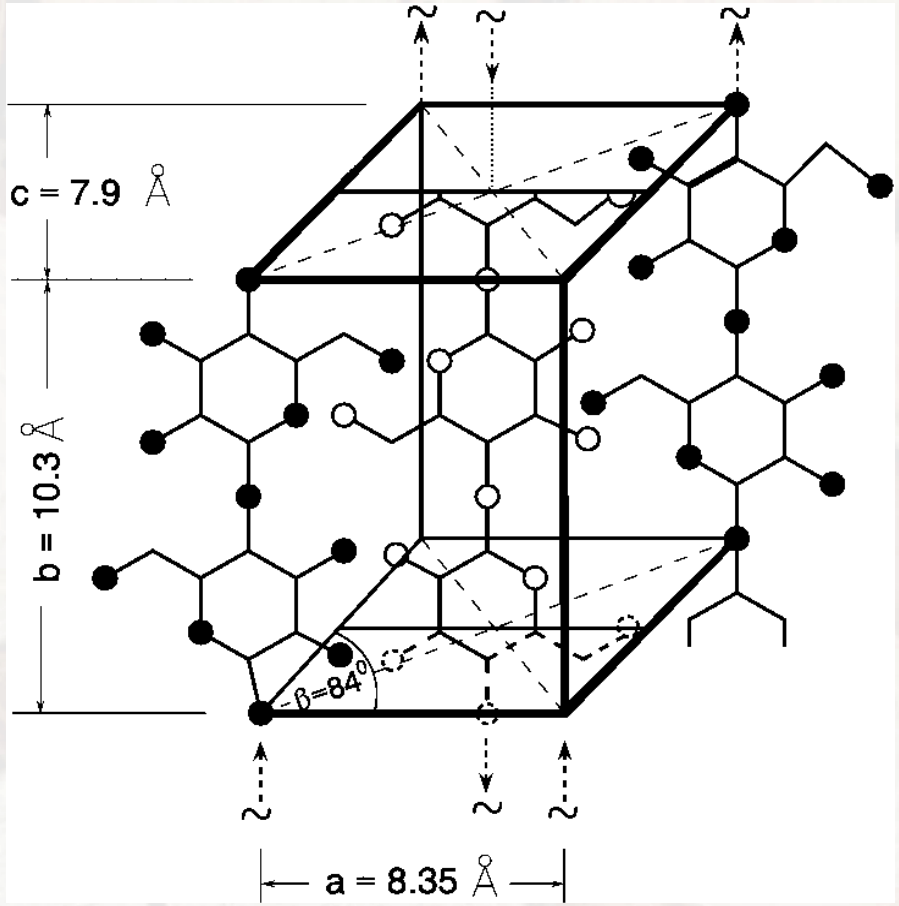
There are 4 types of crystal structures (polymorphous forms) in cellulose which differ in dimensions and the angle of the crystallite

The basic crystal structure is found in native cellulose, so-called cellulose I.

Click on green words to learn more

Crystal structure is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material.

Cellulose occurring in natural raw materials, not subjected to physico-chemical treatment.



Cellulose – supramolecular structures 3/3

Unit cell dimensions of various cellulose polymorphous forms.

polymorph	a-axis (Å)	b-axis (Å)	c-axis (Å)	angle	source
cellulose I	8,3	10,3	7,9	84°	cotton, wood, ramie, linen, etc.
cellulose II	7,9	10,3	9,1	62°	Natural: seaweed marine *Halicystis osterhoutii* Product of chemical transformation: merc rayon, merc cotton
cellulose III	7,7	10,3	9,9	58°	
cellulose IV	8,1	10,3	7,9	90°	

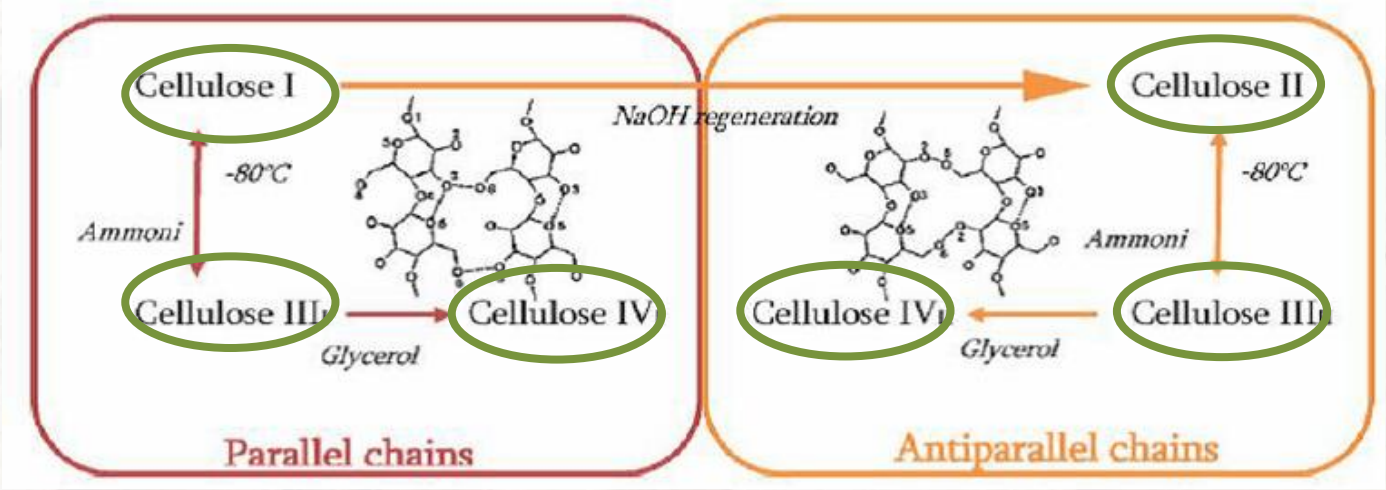
Polymorphism is the ability of a solid material to exist in more than one form or crystal structure.



Click on green words to learn more

Cellulose – polymorphus lattices 1/2

Cellulose when treated with aqueous sodium hydroxide (NaOH) solutions has a considerable impact on morphology, molecular and supramolecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure of fibrils in cellulosic fibres.



Cellulose I, the so-called native cellulose, is the form found in nature, and it occurs in two allomorphs, I_α (triclinic) and I_β (monoclinic). The relative amounts of celluloses Iα and Iβ vary with the source of the cellulose, with the Iβ form being dominant in higher plants.

Cellulose II, or regenerated cellulose, emerges after re-crystallization or mercerization with aqueous sodium hydroxide. It is the most stable crystalline form. The major distinction between these two forms of cellulose lies in the layout of their atoms: cellulose II has antiparallel packing, whereas the chains in cellulose I are in a parallel direction.

Cellulose III is obtained by ammonia treatment of cellulose I or II, and cellulose IV is finally produced from cellulose III by treatment with glycerol.

Check your knowledge

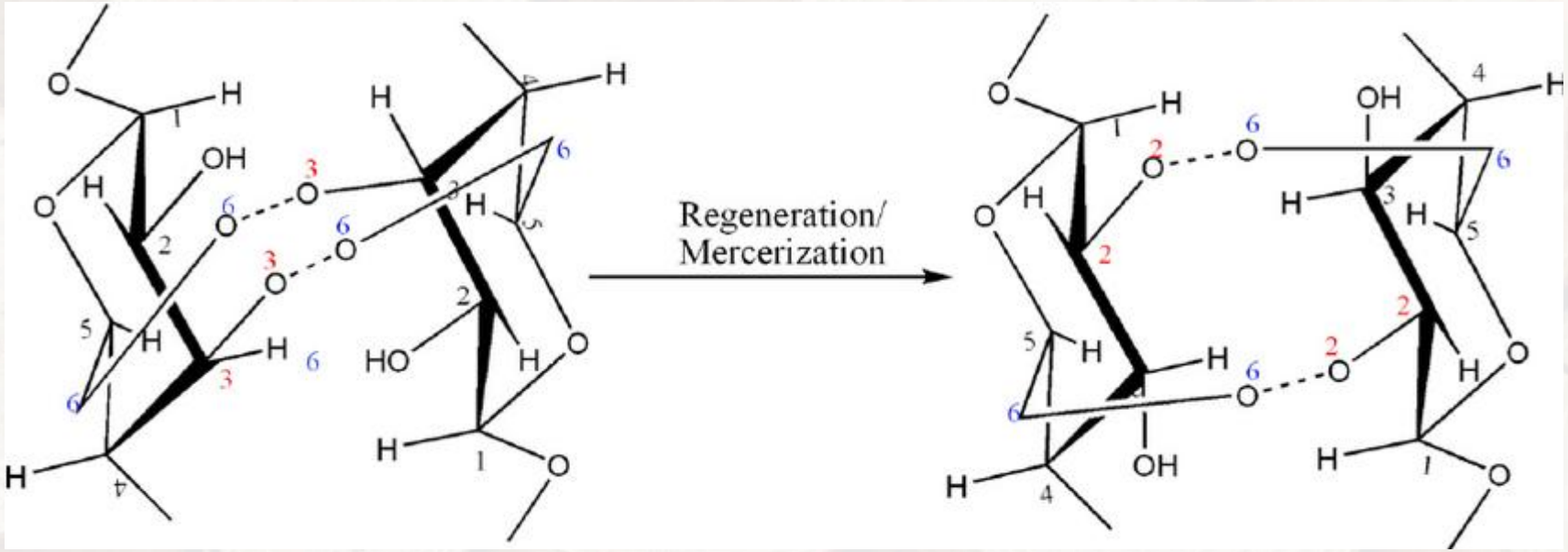
Indicate differences between cellulose I, cellulose II, cellulose III and cellulose IV



You should already know the answer.

However if you don’t, please repeat the course.

Cellulose – polymorphus lattices 2/2



cellulose I

cellulose II

Click to learn more

Hemicelluloses – occurrence 1/2

Hemicelluloses are the components whose percentage and the structure is different in the softwood and hardwood.

The percentage ranges from 13 to 37% and for softwood is lower than for hardwood.

The softwood has a high proportion of hexoses units (mannose and galactose).

The hardwood has a high proportion of pentoses (xyloses) and acetyl groups.



Hemicelluloses – occurrence 2/2

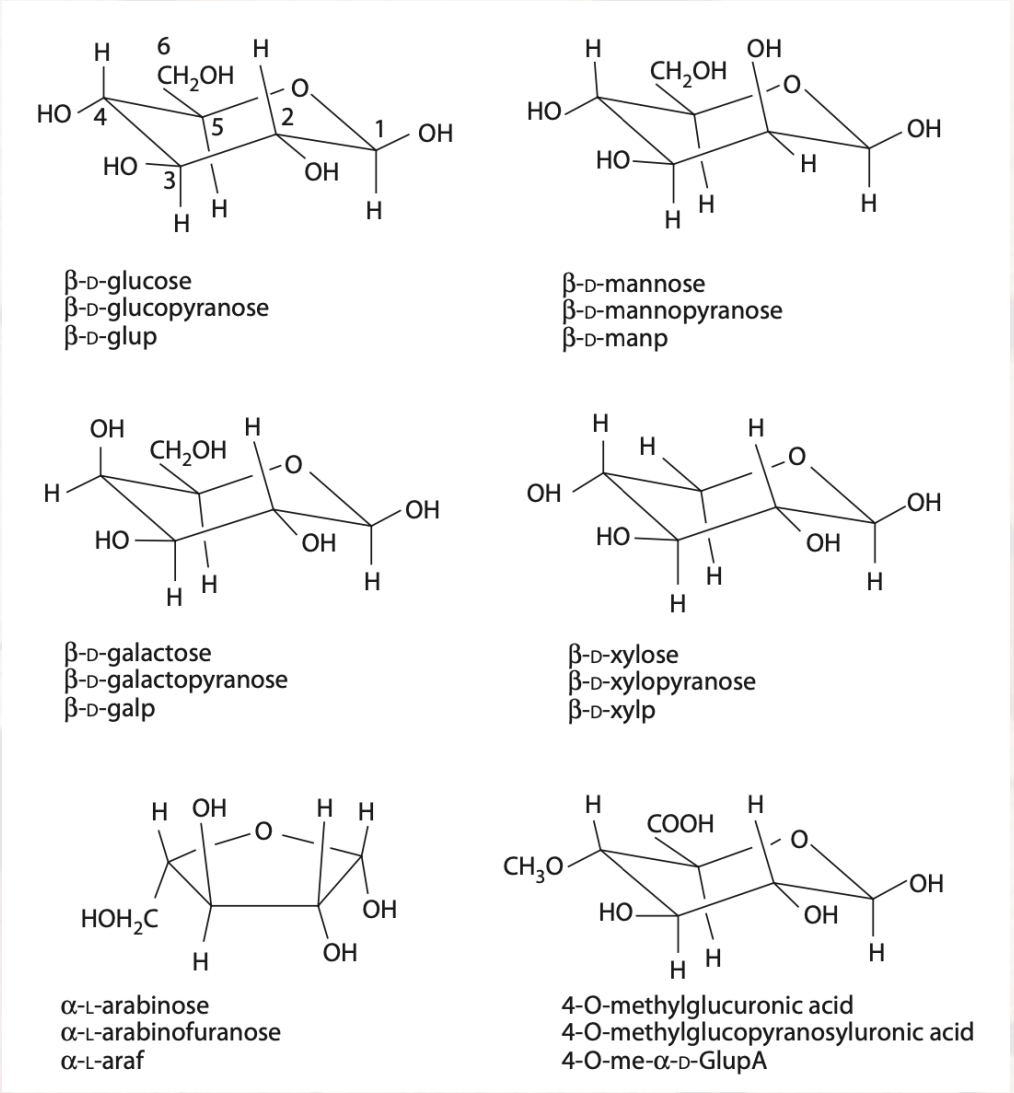
sources		hemicelluloses [%]	pectins [%]
flax	*Linum usitatissimum*	14-18.6	1.8-2.3
jute	*Corchorus capsularis, C. olitorius*	12-20.4	0.2
manila banana	*Musa textilis*	21	0.8
agave sisal	*Agava sisalana Perrine*	10-13	0.8-2
hibiscus hibiscus	*Hibiscus Cannabinus*	21	2
hemp arm	*Boehmeria nivea Gaud, variety tenacissima*	13.1-15	1.9-2
hemp	*Cannabis sativa L.*	17.9-22	0.9
cotton	*Gossypium spp. (commonest G. hirsutum)*	2-5.7	5.7
coconut fiber	*Cocos nucifera L.*	0.3	4
banana	*Musa acuminata L.*	6-19	3-5
agave henekwen	*Agava fourcroydes Lemaire*	4-28	3-4
sugarcane	*Sacharum officinarum*	30	10
pineapple leaves	*Acanas Comosus*	16-19	2-25
wood	-	17-37	-

Hemicelluloses – structure 1/3

The sugar units (anhydro-sugars) making up the polyoses can be subdivided into groups such as:

- pentoses (xylose, arabinose);
- hexoses (glucose, mannose, galactose);
- hexuronic acids (glucuronic acid, 4-O-methylglucuronic acid, galacturonic acid);
- deoxy-hexoses (ramnose, fucose).

Click to learn more



Formulas of the main sugar
units of hemicelluloses.

Check your knowledge

List main units of polyoses



You should already know the answer.

However if you don’t, please repeat the course.

Hemicelluloses – structure 2/3

Hemicelluloses found in wood tissue are heterogeneous structures of mixed sugar units

The most abundant hemicellulose components of wood are:

group of hemicelluloses	component	wood species
xylanes	O – acetyl- 4 – O – methylglucuronoxylan	hardwood
	arabino - 4 – O – methylglucuronoxylan	softwood
mannans	glucomannan	hardwood
	O - acetylo-galactoglucomannan	softwood
galactans	galactan	hardwood
	arabinogalactan	softwood

Click on green words to learn more

Xylans are polyoses generally with a homopolymer backbone of xylose which are linked by beta-(1-4) glycosidic bonds.

Mannans from wood are characterised by a heteropolymer backbone consiting of mannose and glucose units.

Galactans are highly branched.

Check your knowledge

List main hemicellulose groups of hardwood and softwood

You should already know the answer.

However if you don’t, please repeat the course.



Hemicelluloses – structure 3/3

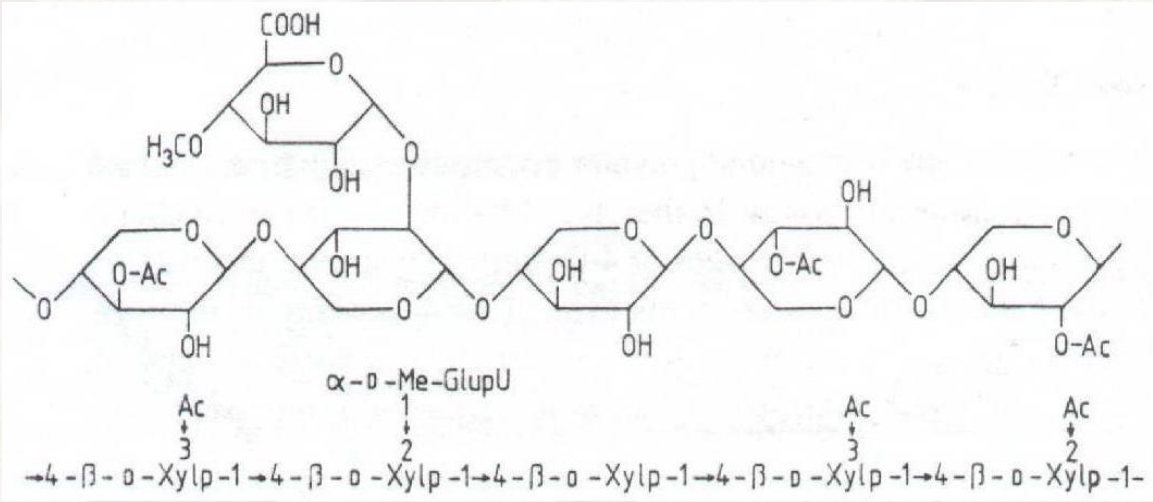
- hardwood xylanes;
- softwood xylanes;
- hardwood mannans;
- softwood mannans;
- hardwood galactans;
- softwood galactans.

Click on each name to learn more



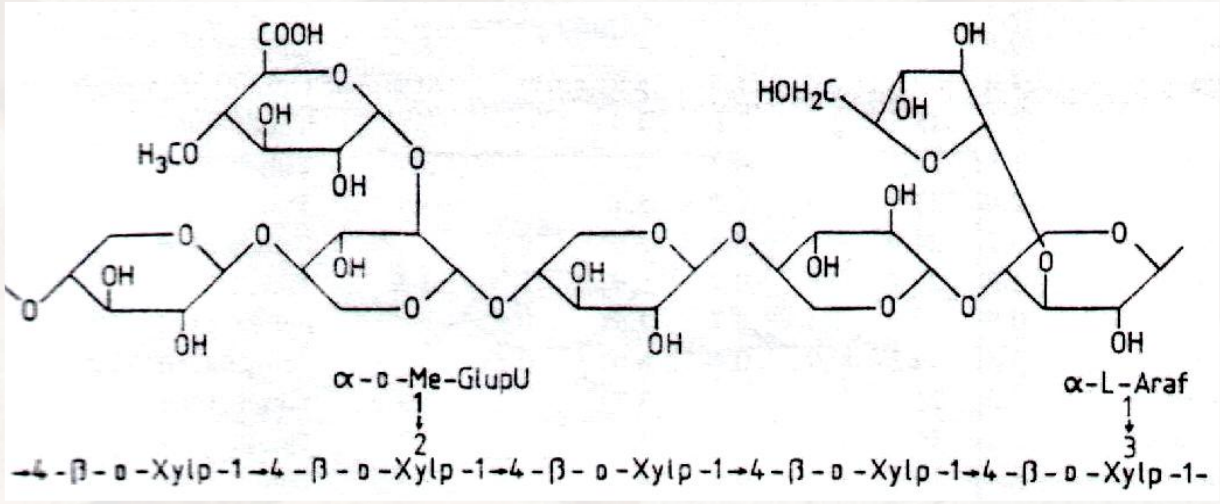
Hardwood xylanes

name	main chain	side branches
O-acetyl-4-O-methylglucuronoxylan	DP 100-200 ▪ ß-d-xylopyranose radicals linked by a ß(1-4) glycosidic bond ▪ hydroxyl groups on C2 and C3 of ß-D-xylopyranose radicals replaced with acetyl groups ($COCH_3$)	• short ß-D-xylopyranose chains linked to the main chain by ß(1-2) and ß(1-3) glycosidic bonds • 4-O-methyl-α-D-glycuronic acid molecules connected to the main chain (ß-D-xylopyranose) through ß(1-2) and ß(1-3) glycosidic bonds



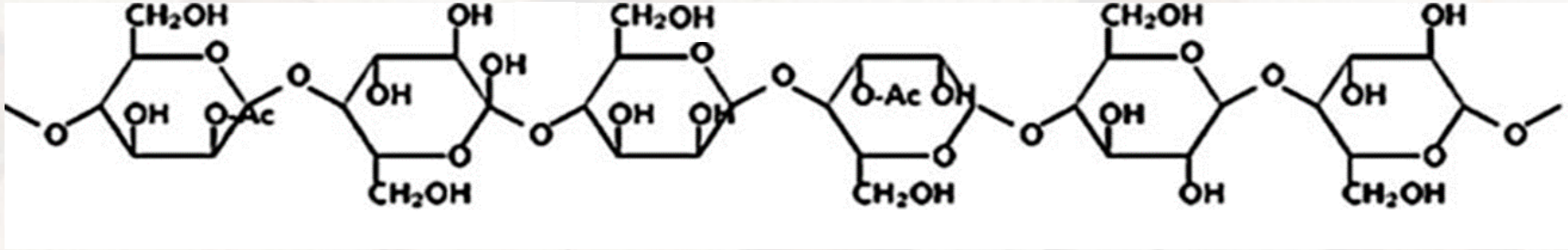
Softwood xylanes

name	main chain	side branches
arabino-4-O-methylglucuronoxylan	DP 70-130 ▪ ß-D-xylopyranose radicals linked by a ß(1-4) glycosidic bond	• α-L-arabofuranose molecules linked to the main chain by α(1-3) glycosidic bonds • 4-O-methyl-α-D-glycuronic acid molecules linked to the main chain by ß(1-2) glycosidic bonds; the frequency of this molecule is greater than in the hardwood species



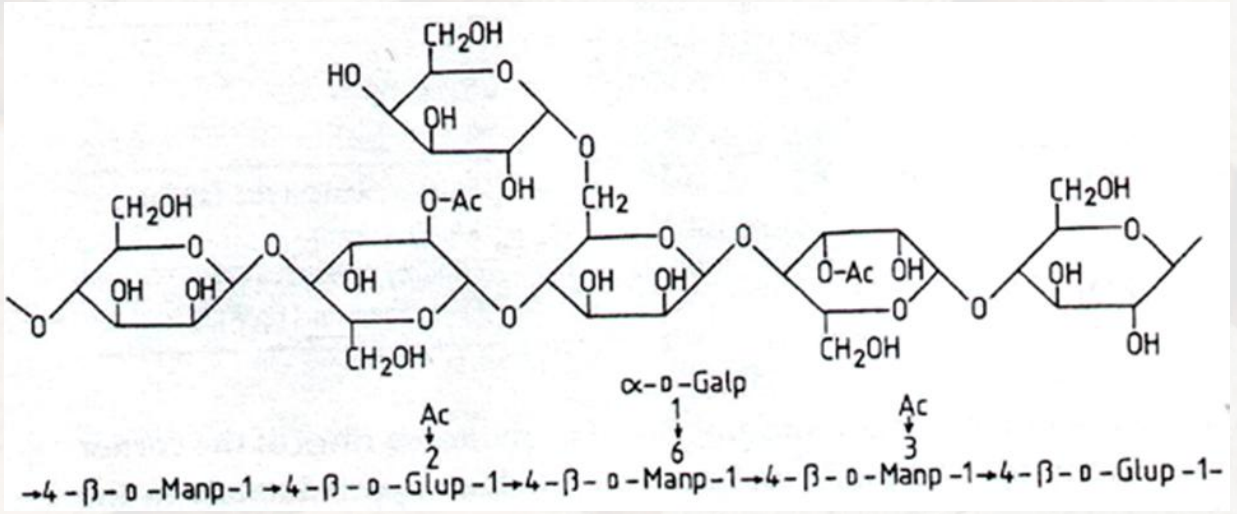
Hardwood mannans

name	main chain	side branches
glucomannan	DP 60-70 ▪ ß-D -mannopyranose and ß-D-glycopyranose radicals connected by a ß(1-4) glycosidic bond; glucose to mannose ratio 1.5-2.0: 1.0 ▪ hydroxyl groups on C2 and C3 are rarely replaced with acetyl groups ($COCH_3$)	• lack



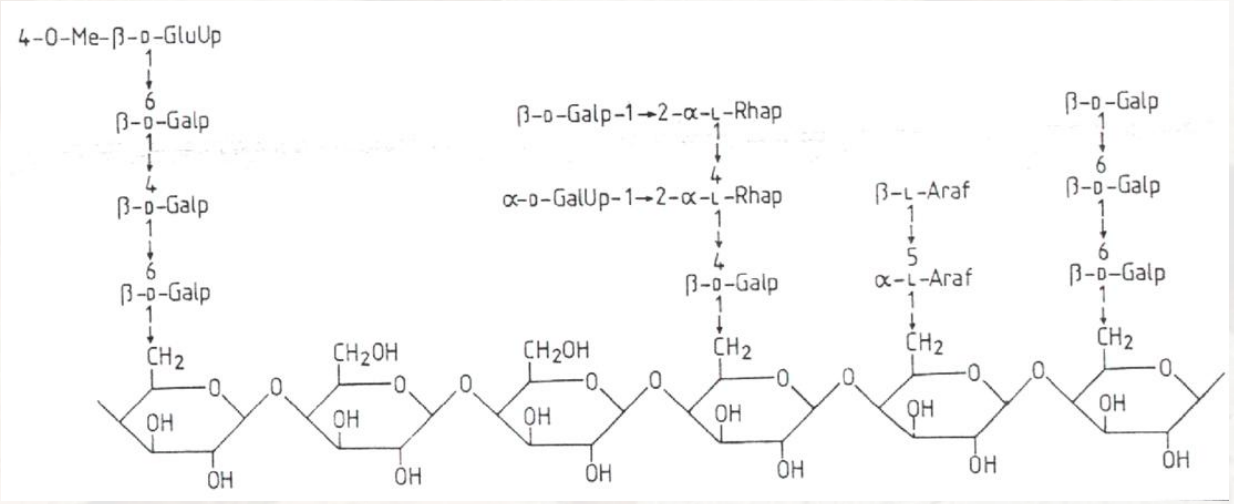
Softwood mannans

name	main chain	side branches
O - acetylo-galactoglucomannan	▪ ß-D-mannopyranose and ß-D-glycopyranose radicals connected by a ß(1-4) glycosidic bond; ▪ numerous hydroxyl groups at C2 and C3 are replaced with acetyl groups ($COCH_3$).	• α-D-galactopyranose molecules linked to the main chain by α(1-6) glycosidic bonds; the galactose: glucose: mannose ratio is from 1: 1: 3 to 0.1: 1: 3



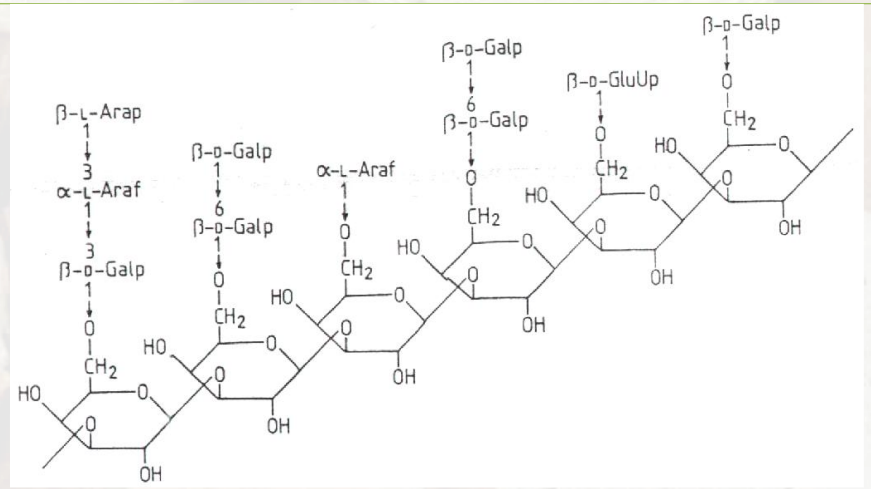
Hardwood galactans

name	main chain	side branches
galactan (but occurs also in the reaction of coniferous and deciduous wood species)	▪ ß-D-galactopyranose radicals linked by a ß(1-4) glycosidic bond.	• 4-O-methyl-α–D-glucuronic or ß-D-galacturonic acid linked by a ß(1-2) or (1-6) glycosidic bond; • sporadic molecules of α–L-rhamnopyranose, α–L arabinofuranose,



Softwood galactans

name	main chain	side branches
arabinogalactan	▪ ß-D-galactopyranose radicals linked by a ß(1-3) glycosidic bond.	• ß-D-galactopyranose molecules linked by ß(1-6) glycosidic bonds; • L-arabinofuranose molecules linked by ß(1-6) glycosidic bonds; • sporadically α-L-arabopyranose, α-D-xylopyranose molecules connected by a ß(1-3) glycosidic bond and ß –D- glycuronic acid connected by (1-6) or (1-4) glycosidic bonds.



Cellulose vs. hemicelluloses – structure

	cellulose	hemicelluloses
Mononers	glucose	mix of sugars
Polymer chain length	long (5μm)	short
M.W.	high (10 000 units)	low (hundred units)
Polymer typology	linear	branched
Side groups substitution	no substitution	on C2, C3 and C6
Polymer morphology	crystallinie+amorphous	amorphous
Solubility	low	high
Reactivity	less reactive	more reactive
Hydrolysis	partial	readily (susceptible)

Click to learn more

Check your knowledge

List the most important differences between cellulose and hemicelluloses structure

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However if you don’t, please repeat the course.

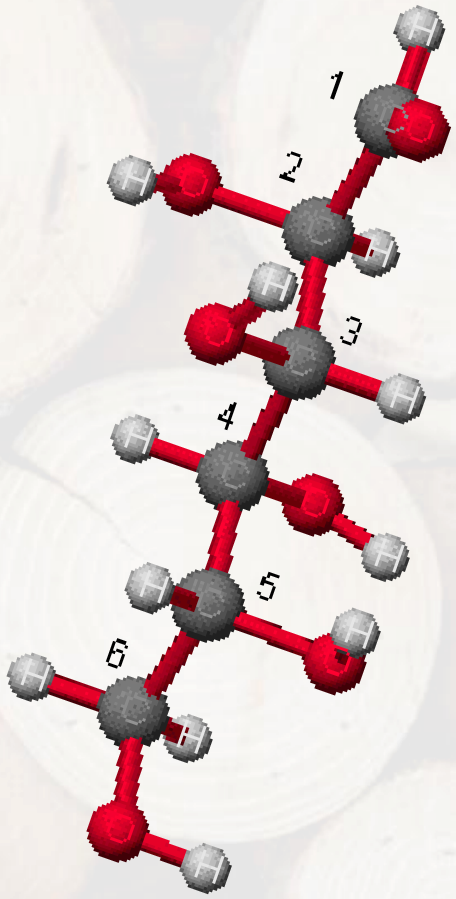


Hemicelluloses structure – property dependence

Hemicelluloses limit the stretchiness of the cell wall by linking adjacent microfibrils and preventing them from sliding against each other for unlimited distances. Because of this, hemicelluloses are involved in controlling cell enlargement.

Hemicelluloses are classified on the basis of their component sugars. Xylose, mannose, and galactose form the hemicellulose backbone, whereas arabinose, glucuronic acid, and galactose form the side chains. The latter confer different chemical characteristics on the hemicellulose, for example, hemicelluloses that contain acids in their side chains are water-soluble. Other hemicelluloses are insoluble in water.

Digestibility/fermentability of the hemicelluloses (by intestinal microflora) is also influenced
by the particular sugars and their positions. For example, hexose and uronic acid are more readily recognized by bacterial enzymes than the other hemicellulose sugars, so hemicelluloses containing them are more easily broken down by bacteria.





Carbohydrates polymers

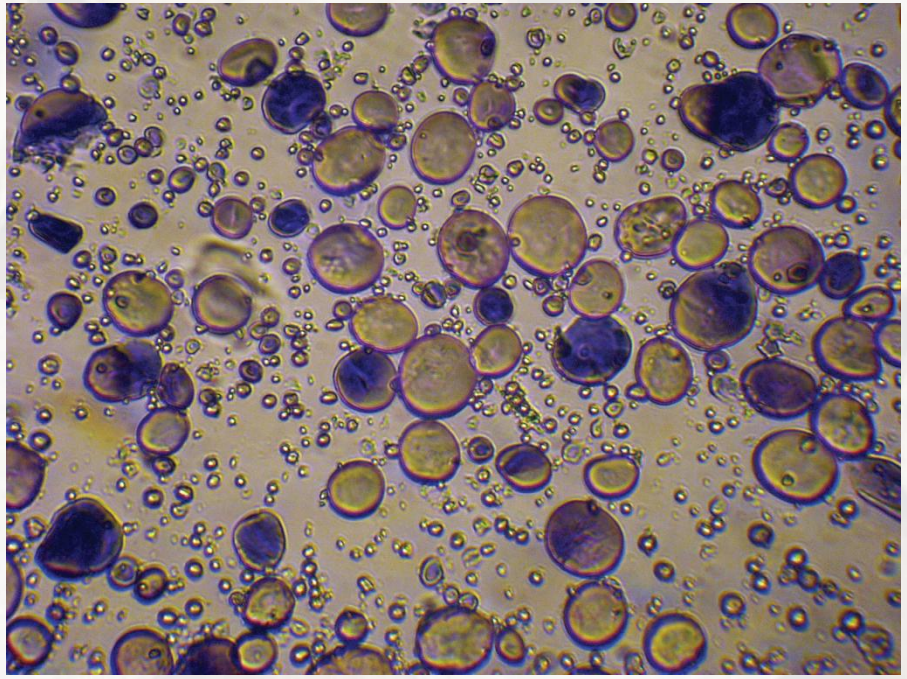
Starch and pectins – occurrence, structure

Starch - occurrence

The starch is present in storing tissues, e.g. in parenchyma cells of softwood and hardwood.

It is the principal reserve polysaccharide and is produced by most green plants as energy storage.

Click to learn more



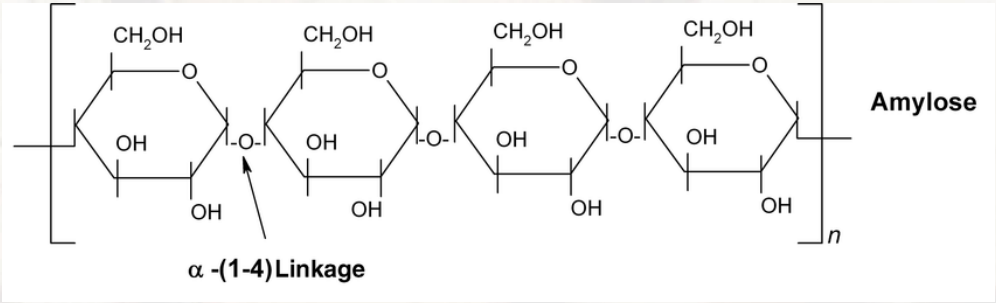
Starch – structure

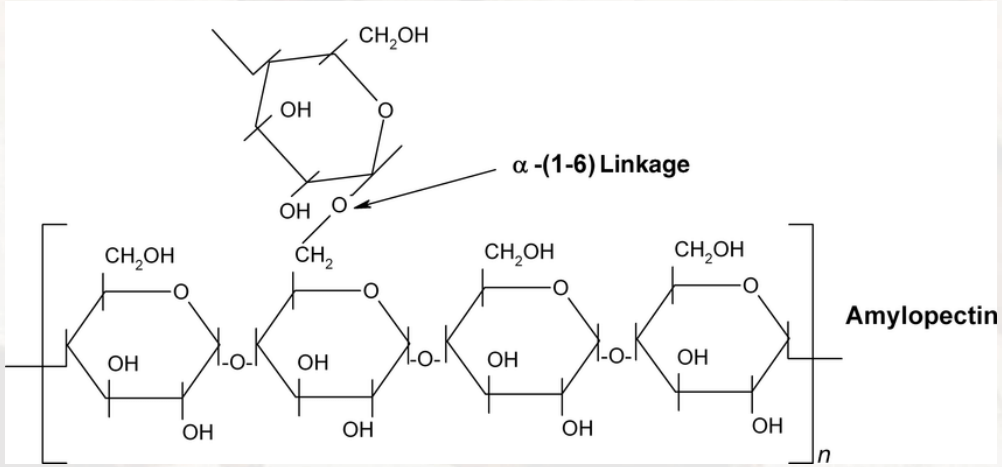
Starch consists of both amylose and amylopectin.

Linear amylose has a backbone of α(1-4)-linked glucose units.

Amylopectin has the same backbone, but is partly branched via α(1-6) linkages.

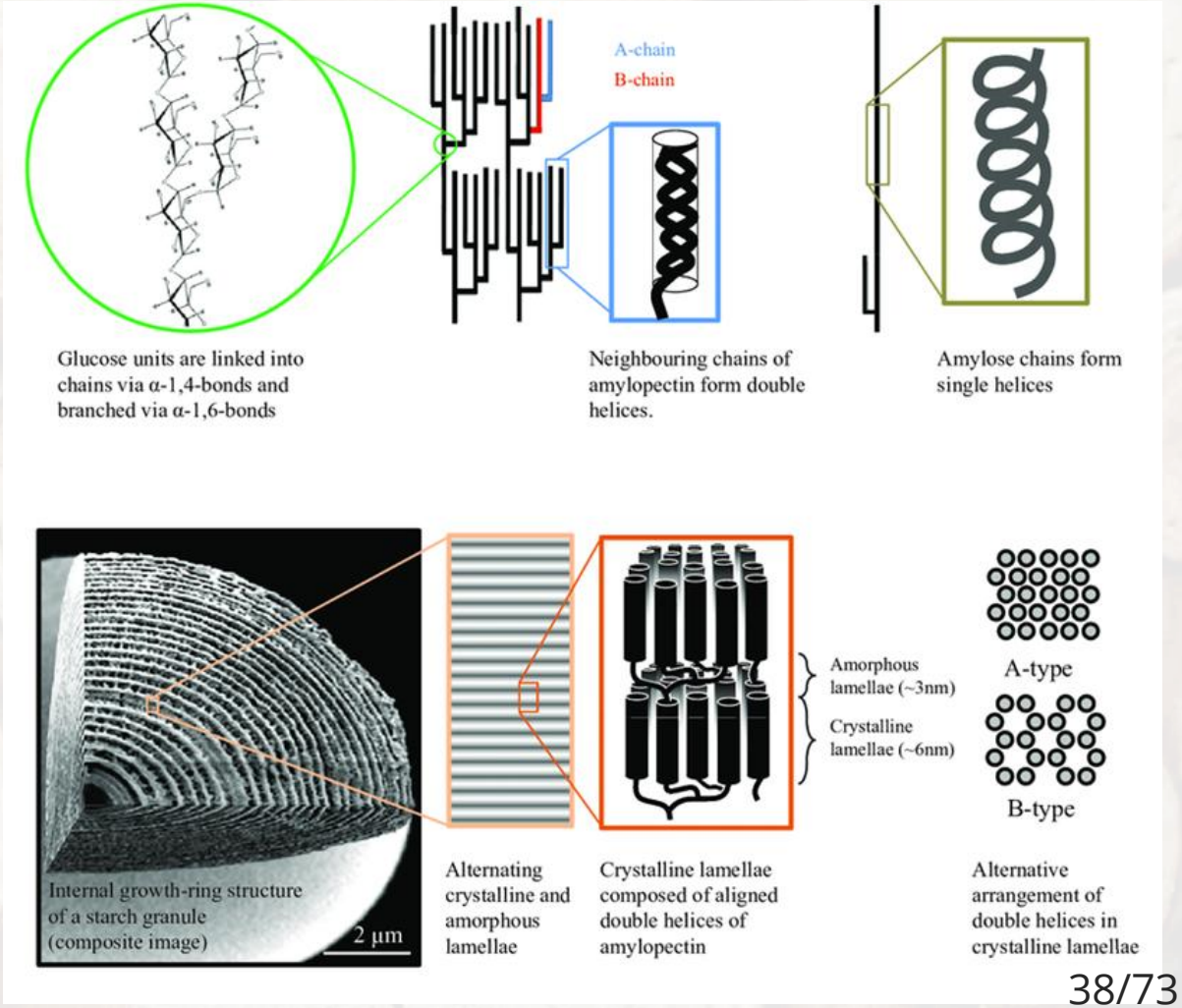
Click on green words to learn more





Starch – why not cellulose?

In the case of the α-glycosidic bond, the pyranose rings are oriented at an angle of approximately 120 °, which gives a helical structure of starch molecules with 6 glucose units per rotation. Thus, starch only exists in the form of granules and not in the form of fibers like cellulose.



Check your knowledge

What determines the difference in the structure of cellulose and starch?

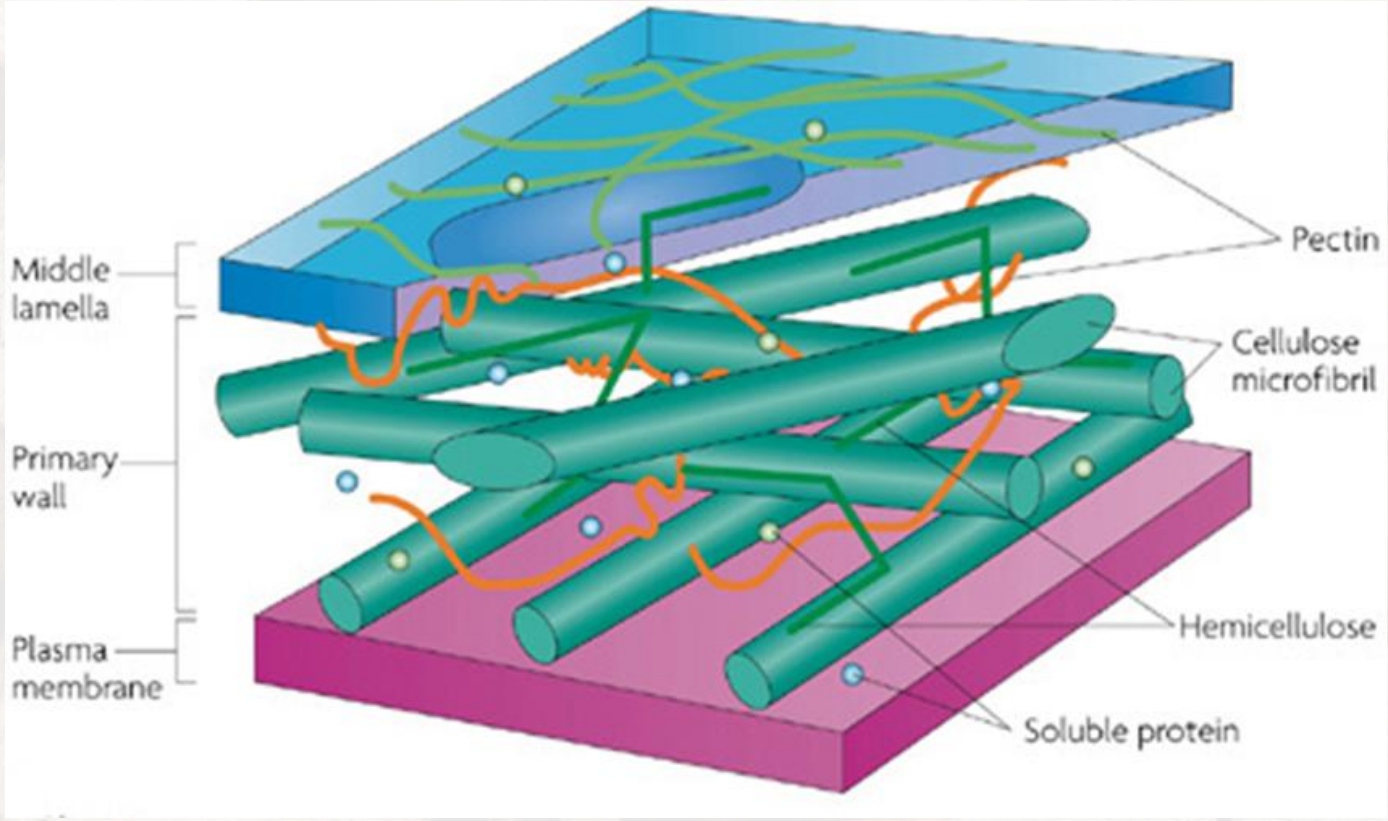


You should already know the answer.

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Pectins - occurrence

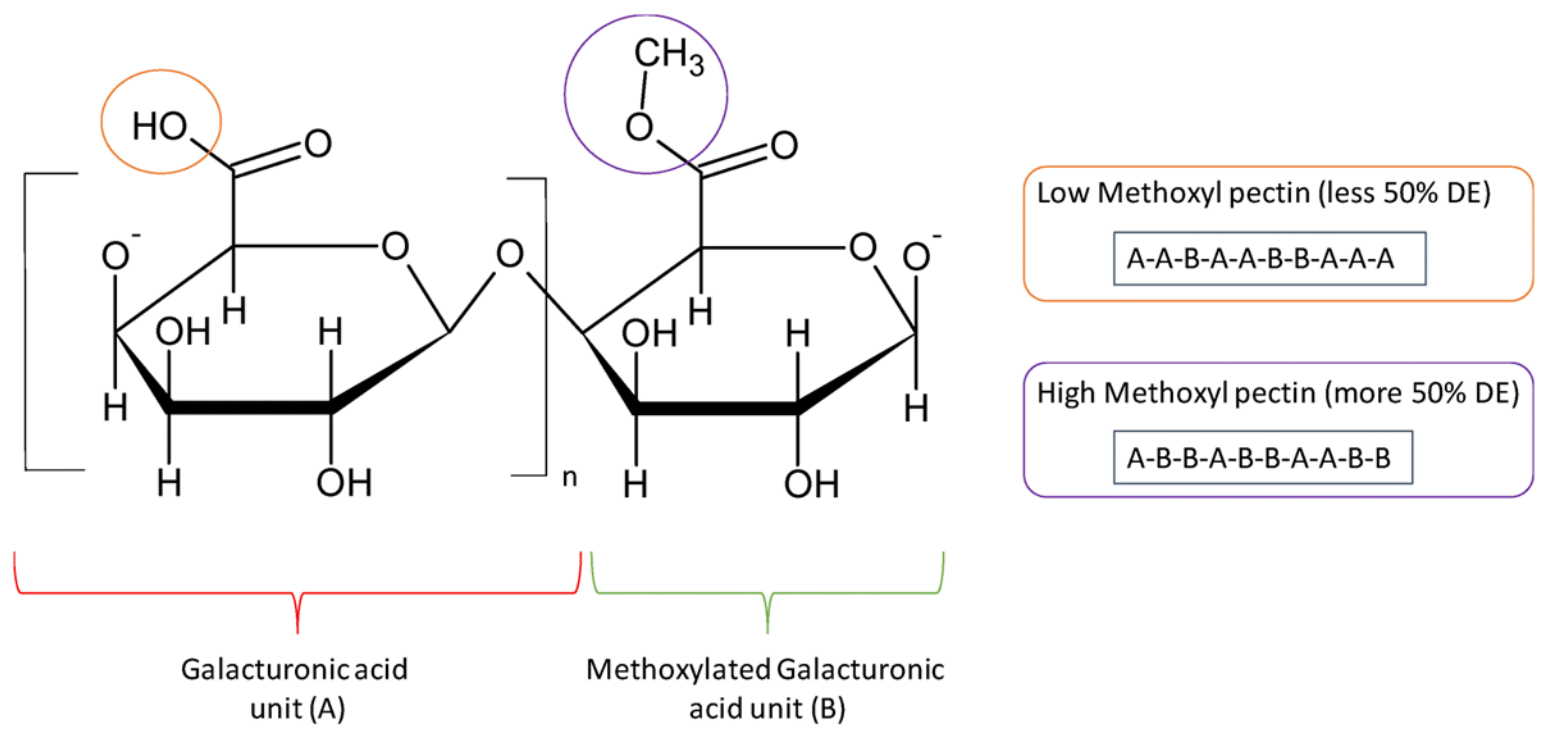
Pectins form part of the primary cell wall of plants and most of the middle lamella between adjacent cells. They're like intercellular glue.



Pectins - structure

The structure of a pectin macromolecule includes a linear backbone of α(1-4)-linked D-galacturonic acid residues, in which the carboxyl groups can be free (unit A LM) or esterified with methyl (unit B HM). The side chains of rhamnogalacturonate are sporadically attached to the main chain of D-galacturonic acid.

Some regions of pectin are involved in the formation of calcium ions-pectin cross-links.



Pectins – properties 1/2

These are water-soluble, highly hydrophilic polysaccharides that form gels in solution.

Because pectins attract so much water, they are responsible for the spongy, flexible nature of growing plant cells (the walls of which may be more than 65% water!).

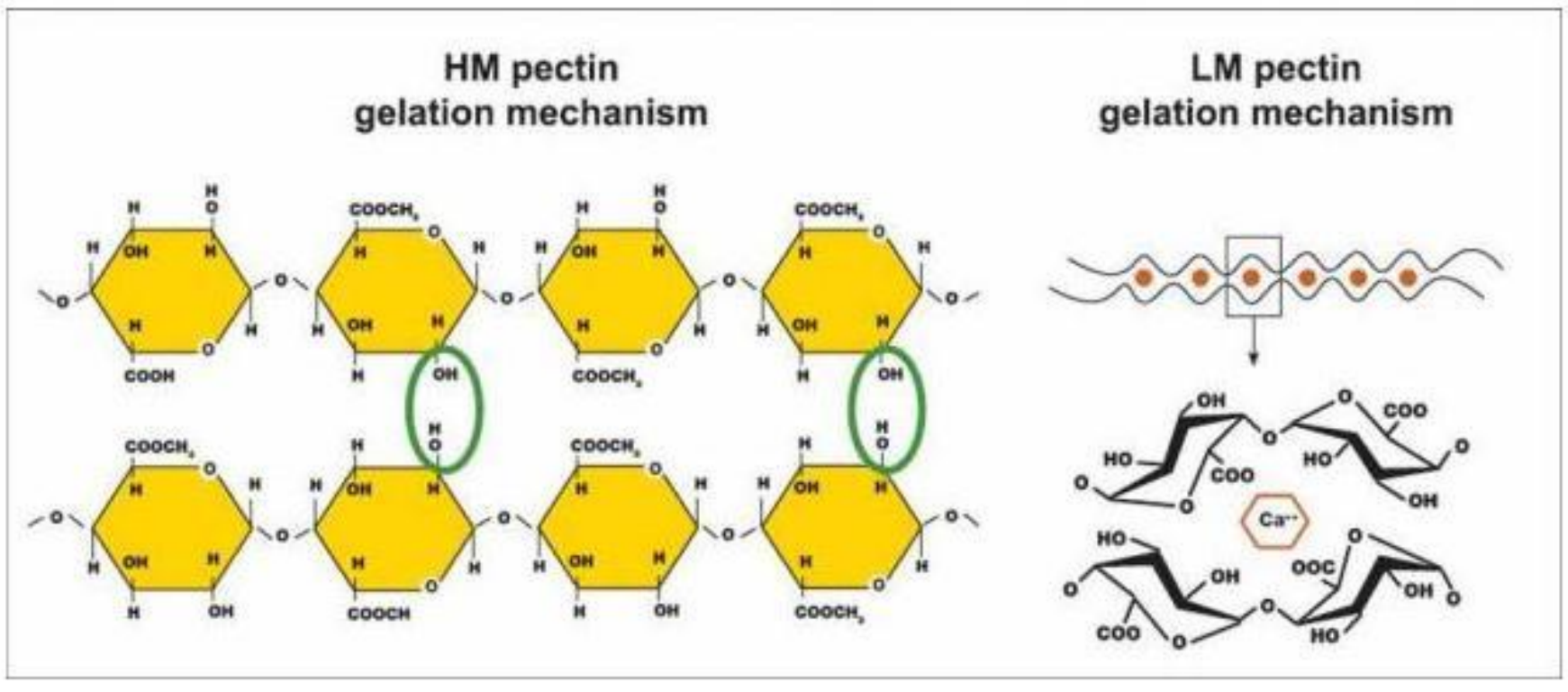
The solubility rate in water is related to the degree of polymerisation and the number and distribution of methyl ester groups. The higher the degree of esterification, the better the solubility of pectins.

Pectins which are involved in the formation of calcium ions-pectin cross-links are very important for the growth and development of plants due to their impact on both the rigidity and integrity of plant tissues. These pectins are insoluble in water.



Pectins – properties 2/2

The degree of methylation expressed as the ratio of methyl-esterified carboxyl groups to the total amount of galacturonic acid units, is one of the key parameters related to gelling capability.



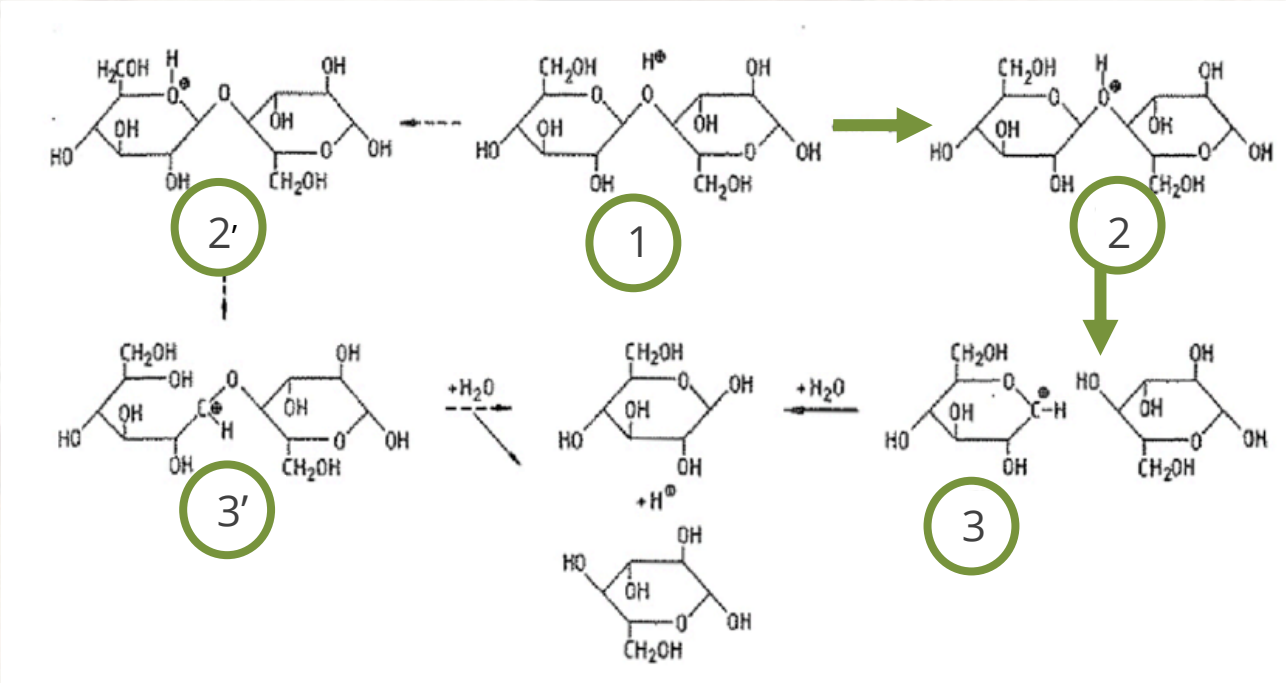


Carbohydrates polymers

Carbohydrate reactivity
Reations in acidic medium

Acidic hydrolysis

Mechanism of acid hydrolysis of glycosidic bonds in starch, cellulose, and hemicellulose into monosaccharide.



→ Dominant pathway

1 step – the proton of the catalizing acid interacts rapidly with the glucosidic oxygen linking two sugar units, forming a so-called conjugated acid (2). This step
is followed by a slow cleavage of the C-O bond yielding an intermediate cyclic carbonium cation (3).

The protonation may also occur at the ring oxygen (2′), resulting in ring opening and a non–cyclic carbonium cation (3′).

Probably both modifications of protonation take place with a greater likelihood of the cyclic cation in the most cases.

The carboinium cation finally initiates rapid addition of water molecule, resulting in the stable end product and release of the proton.

Factors influencing hydrolysis

- Hydrolysing medium (acid):
  - kind and concentration;
  - pH value;
  - strength;
  - temperature and pressure;
- Hydrolysed sample (carbohydrates):
  - physical structure and accessibility in the case of heterogeneous hydrolysis;
  - conformation effects;
  - ring structure and substituents.

Click on green phrases to learn more

Check your knowledge

List factors influencing hydrolysis



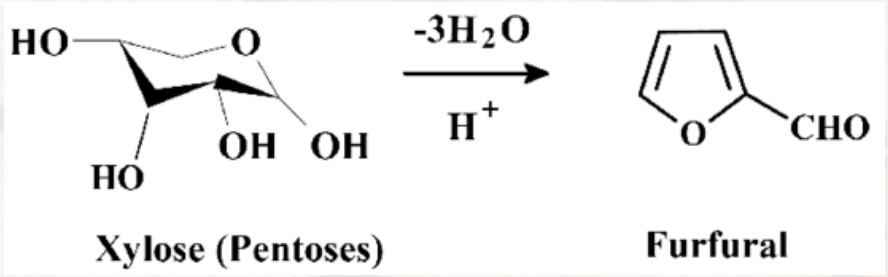
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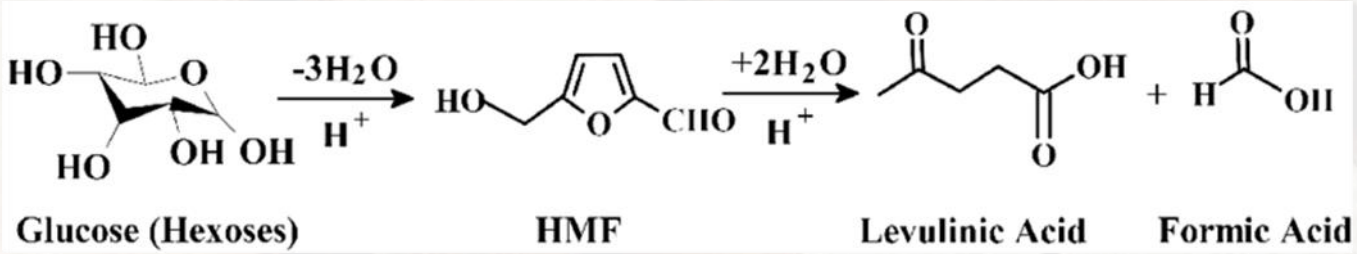
Dehydratation

Dehydratation reaction occurring typically during thermal treatments of polysaccharides. In addition, they are also rather unavoidable side reactions under acidic hydrolysis conditions, causing a decomposition of hydrolysed sugars.

Acid – catalysed dehydratation of xylose (pentose) to furfural.



Acid – catalysed dehydratation of glucose (hexose) to levulinic acid and formic acid with HMF as intermediate.



Oxidation

The oxidation reaction is usually encountered during acidic pulping and bleaching processes.

The oxidation of polysaccharides, besides a glycol cleavage,
may be discussed in terms of reactions at:

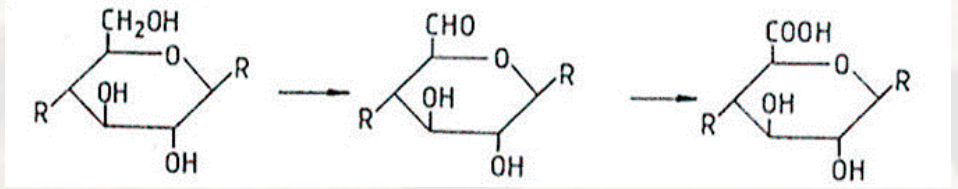
- the reducing end groups;
- the hydroxyl groups (C6, C2, C3);
- oxygen in the glucose ring.

Important final products are:

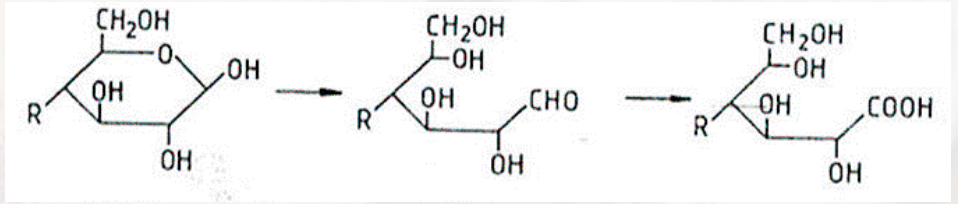
- uronic acids (glucuronic acid (1));
- aldonic acids (gluconic acid (2));
- aldaric acids (glucaric acid (3));
- pentonic acids (xylonic acid (4));
- [illegible]boxylic acids (5)).

Click on green numbers to learn more

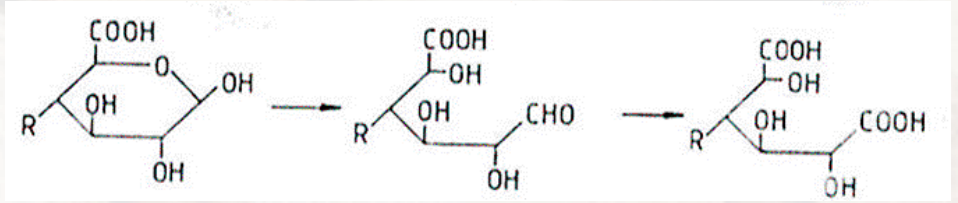
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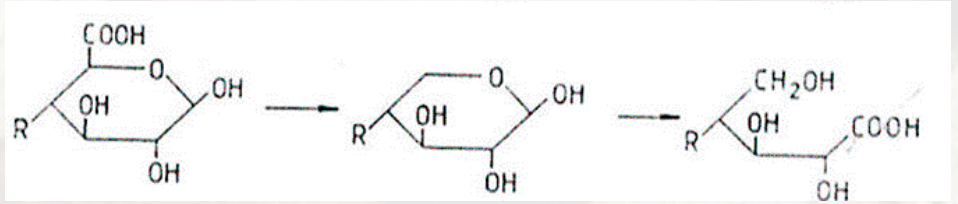
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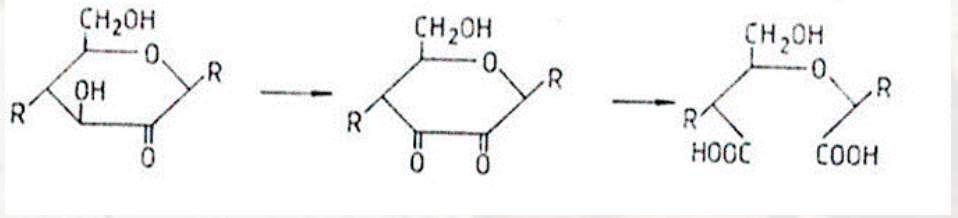
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4



5





Carbohydrates polymers

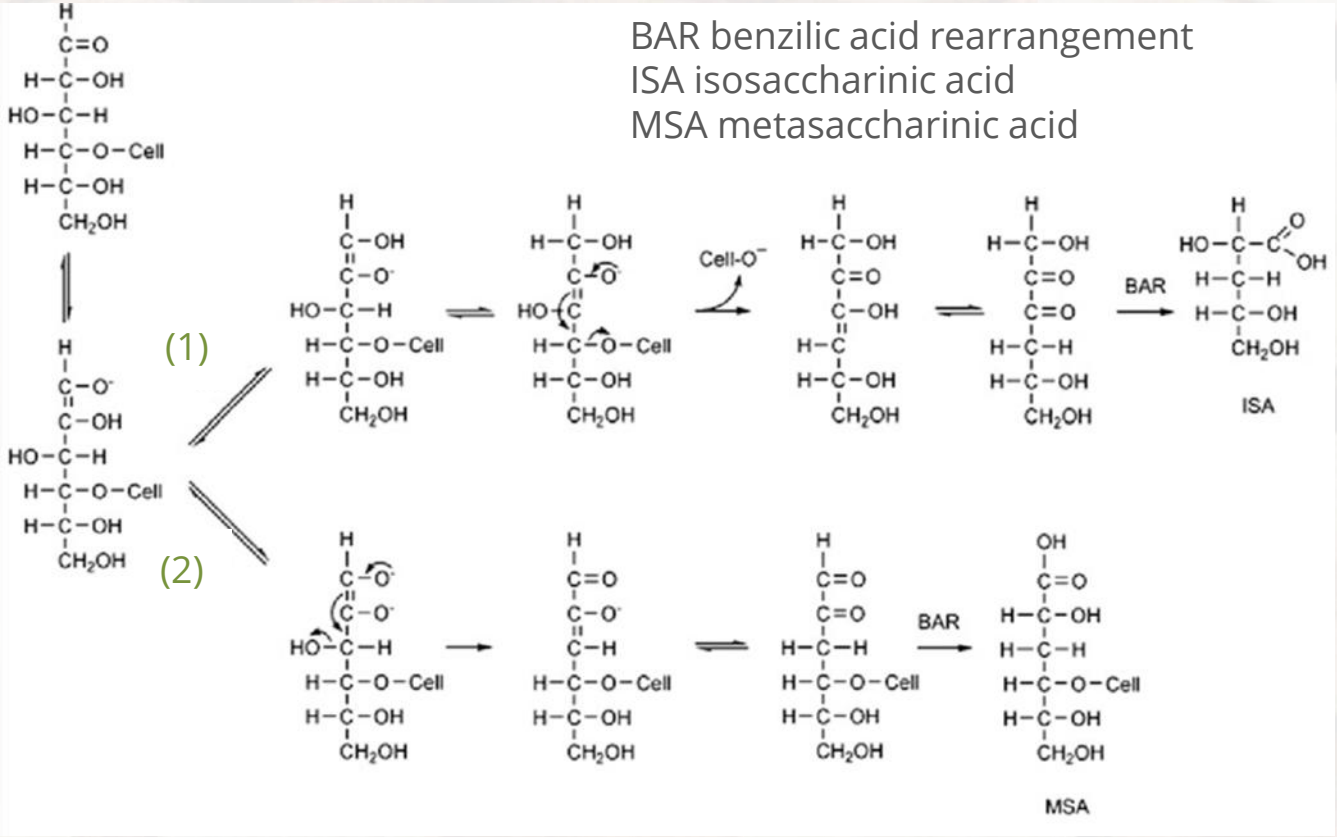
Carbohydrate reactivity
Reations in alkaline medium

Alkaline hydrolysis

Cellulose reactions and the main reaction products in alkaline media:

- peeling reaction path (1);
- stopping reaction path (2).

Click on green numbers to learn more



(1) The peeling off reaction (beta-elimination) of the reducing end group and their conversion to isosaccharinic acids is the most important contribution to yield loss during the steeping reaction

The accessible reducing end group of the cellulose is transformed to an enediol via keto-enol tautomerism.
Under alkaline conditions, the 2,3-enediol is deprotonated to an enolate, which promotes b-alkoxycarbonyl elimination at the C4 carbon atom, followed by benzilic acid rearrangement to form a-or b-isosaccharinic (3-deoxy-2-C-(hydroxymethyl)-pentonic acid) acid. Retroaldol reactions of the enediol may lead to additional short chain degradation products.

(2) The stopping reaction. The deprotonation of the 1,2-enediol causes b-hydroxycarbonyl elimination. After benzilic acid rearrangement, the formation of an alkali-stable glucometasaccharinic acid end group is observed. The stopping or termination reaction was shown to occur only with alkali concentrations sufficiently high to produce the dianionic intermediate, whereas
the peeling-off reaction is effective through both the mono- and the dianions. Thus, the stopping reaction rate is more increased with rising alkali concentrations than the peeling reaction.

Check your knowledge

List stages of alkali hydrolysis



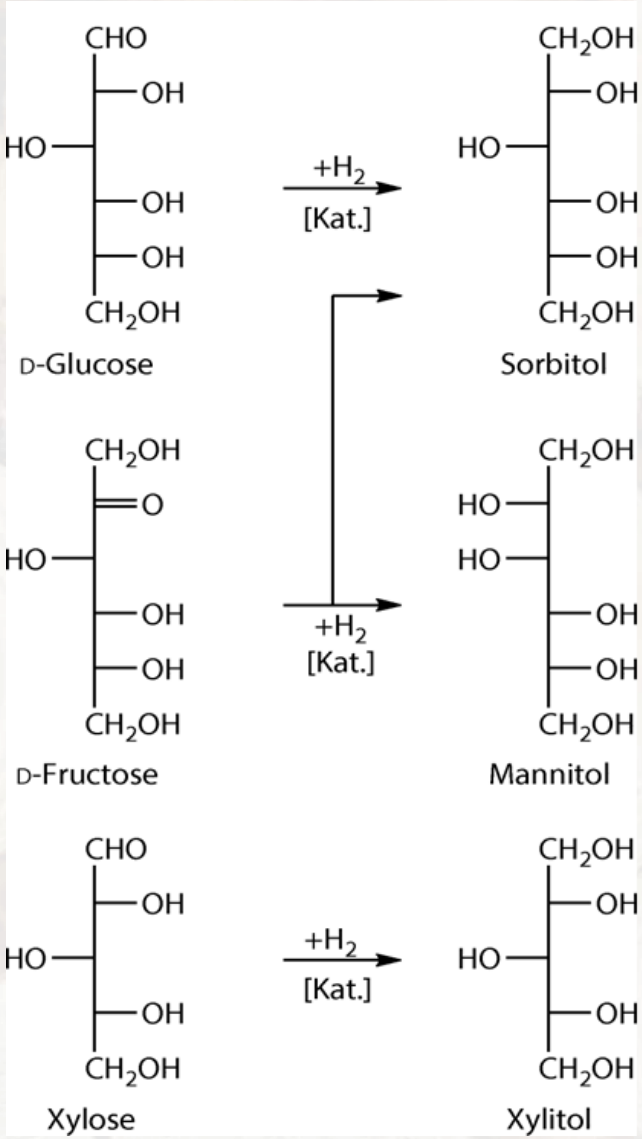
You should already know the answer.

However if you don’t, please repeat the course.

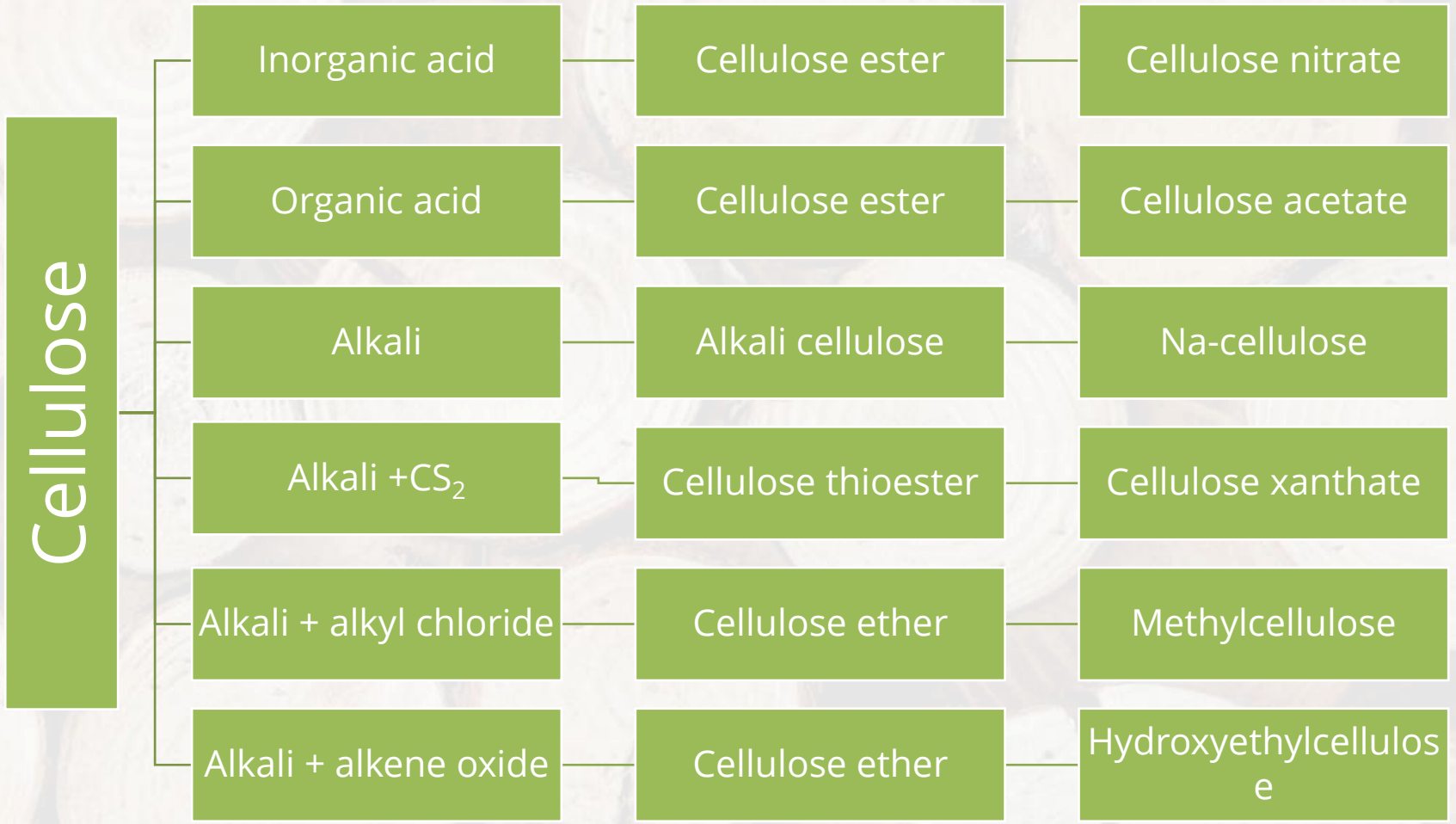
Hydrogenation of sugars

Catalytic hydrogenation of sugars into hexitols, including sorbitol and mannitol is of a great industrial importance due to hexitols application in the food, medical, chemical, and petroleum industries

Due to the isomeric function of the keto-group in fructose, both sorbitol and mannitol are formed from fructose



Derivates of cellulose

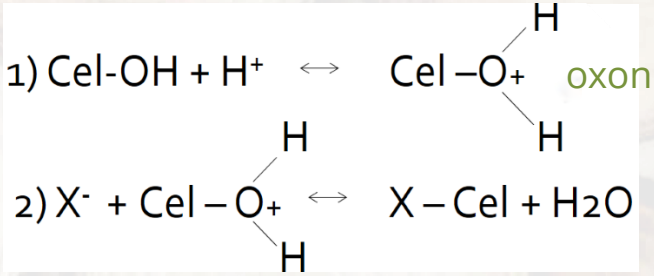


Cellulose esters

Esters are products of the reaction of an alcohol with inorganic or organic acids. The reaction mechanism depends on the type of acid.

Nucleophilic substitution with inorganic acids:

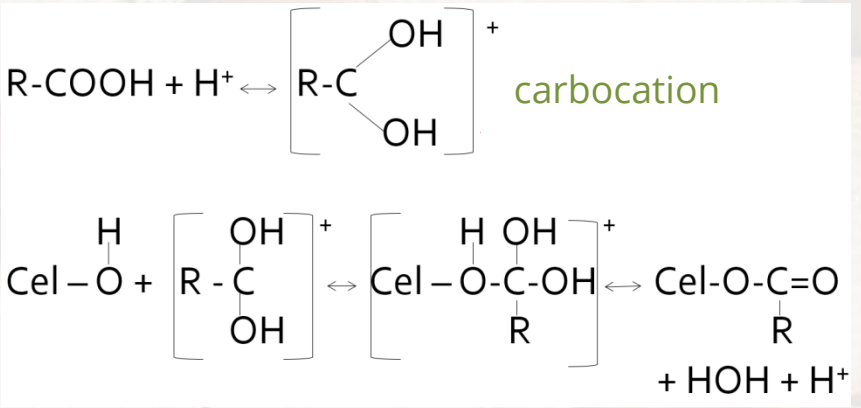
- formation of an oxonium ion;
- estrification.



$ROH + HO\text{-}NO_2 \rightarrow RO\text{-}NO_2 + H_2O$

Nucleophilic addition with organic acids:

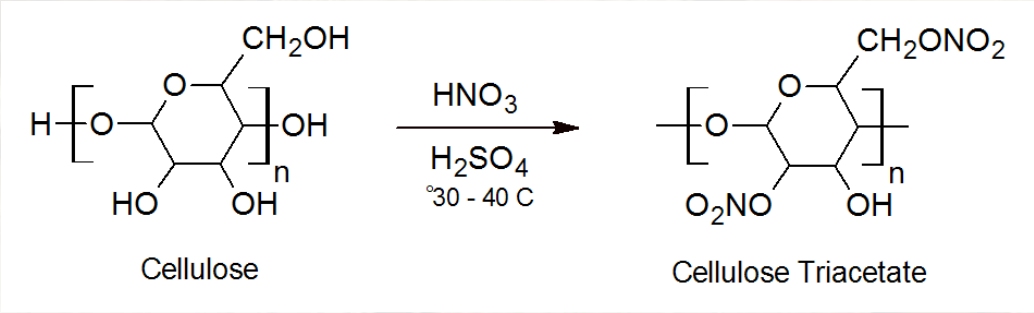
- protonation of an oxygen atom and formation of a carbocation;
- estrification.



$ROH + HO\text{-}COCH_3 \rightarrow RO\text{-}COCH_3 + H_2O$

Cellulose nitrate

For the higher level of nitration, the application of acid mixtures consisting of aqueous nitric and sulphuric acids is necessary.



Disadvantages

formation of cellulose sulphate by-product.

Advantages

- facilitating the diffusion of nitric acid into the cellulose fibre;
- dehydrating the reaction medium, so that limits the gelation of the fibre;
- catalysing the reaction.

Check your knowledge

List advantages and disadvantages of sulphuric acid presence during cellulose nitration

You should already know the answer.

However if you don’t, please repeat the course.



Application

- collodion – composition: nitrocellulose, ethyl alcohol and ether; the flexible type is often used as a surgical dressing or to hold dressings in place; non-flexible collodion is often used in theatrical make-up;
- guncotton - nitrocellulose with a high nitrogen content (12.0-13.5%) and a high degree of polymerization (DS=2.4-2.8; SP=2000); used for the production of explosives;
- celluloid - composition: nitrocellulose (70-74%) (SE=2.0-2.3; SP=500), camphor (20-30%), dyes and fillers (1.5-3%), currently withdrawn from production due to its flammability;
- nitrocellulose lacquer - nitrocellulose containing 11.5 to 12.0% nitrogen with a low degree of polymerization (DE=1.9-2.3; SP=200).

Click on green phrases to learn more

Cellulose acetate

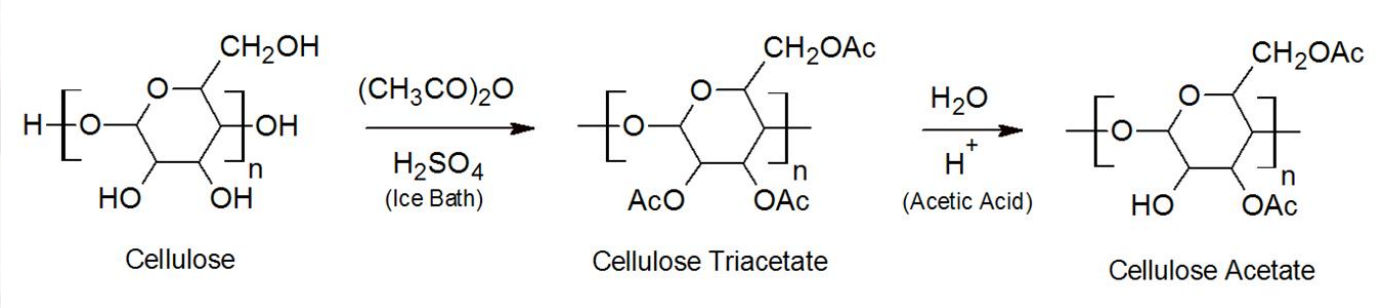
There are several reactions that produce cellulose acetate:

- mixture of acid anhydrides and sulphuric acid
  - $HO\text{-}SO_2\text{-}OH + CH_3COOCOCH_3 \rightarrow HO\text{-}SO_2\text{-}O\text{-}COCH_3 + CH_3COOH$
  - $3nHO\text{-}SO_2\text{-}O\text{-}COCH_3 + [C_6H_7O_2(OH)_3]n \rightarrow [C_6H_7O_2(OCOCH_3)_3]n + 3nH_2SO_4$
- acid chloride
  - $[C_6H_7O_2(OH)_3]n + 3nCH_3\text{-}CO\text{-}Cl \rightarrow [C_6H_7O_2(O\text{-}CO\text{-}CH_3)_3]n + 3nHCl$
- ketene
  - $[C_6H_7O_2(OH)_3]n + 3nCH_2{=}CO \rightarrow [C_6H_7O_2(O\text{-}CO\text{-}CH_3)_3]n$



Cellulose acetate

Action of sulphuric acid:



Disadvantages

- cellulose acetolysis;
- the formation of cellulose sulphate.

Advantages

- catalysis of the reaction
- cellulose swelling.

Check your knowledge

List advantages and disadvantages of sulphuric acid presence in cellulose acetate



You should already know the answer.

However if you don’t, please repeat the course.

Application

- cellulose acetate fibre – cellulose acetate with a high acetyl content (36-45%) and DE 2.2-3.0; one of the earliest synthetic fibres; its lustrous sheen and smooth, satiny texture makes it a good synthetic alternative to silk;
- cellulose acetate film or safety film - cellulose acetate with a high acetyl content (36-45%) and DE 2.2-3.0; is used as a base material for photographic emulsions; it is replacement for unstable and highly flammable nitrate film;
- cellulose acetate plastic - cellulose acetate with a low acetyl content (22-32%) and DE 1.2-1.8; is used for the production of glass frames; has high transparency, oil resistance and smooth skin feel;
- cellulose acetate lacquers - cellulose acetate with a low acetyl content (22-32%) and DE 1.2-1.8; form coatings that are resistant to the action of light and of heat up to 200°C; they do not adhere well to the base and have a low resistance
to alkalinity; are not widely used in industry because of their low solubility
ompatibility with many natural resins.

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Cellulose xanthate

Cellulose xanthate is produced in several stages:

- treatment with sodium hydroxide to obtain alkali cellulose (1);
- grinding and maturing in air, where it oxidizes and reduces the molecular weight;
- treatment with carbon disulfide, which leads to the formation
  of cellulose xanthate (2) ;
- dissolution in sodium hydroxide to form viscose;
- hydrolysis and reduction of DS (3a);
- introduced into spinning nozzles to produce a fibre ;
- a bath with sulphuric acid and sodium sulphate, in which
  lated (3b).

Click on green numbers to learn more

Application

- viscose rayon - many types and grades of viscose fibres and films exist; some imitate the feel and texture of natural fibres such as silk, wool, cotton and linen. The fibre is used to make textiles for clothing and other purposes;
- cellophane paper - transparent sheet with low permeability to air, oils, greases, bacteria and water; it makes it useful for food packaging; cellophane is highly permeable to water vapour; cellophane is used in transparent pressure-sensitive tape and many other similar applications;
- polynosic fibres - during the preparation the freshly formed fibre is in a gelatinous state and is composed of a xanthate of highly esterified cellulose. This makes
  it possible to put the fibre through a substantially higher degree of plastic elongation. Products made from the fibres retain their shape well
  and are relatively wrinkle-free. Polynosic fibres are strong and exhibit reduced stretch. Their one defect is brittleness.

Click on green phrases to learn more

Cellulose ethers

Etherification represents the second large group of modification reactions to which cellulose may be subjected. These reactions have involved benzylation, allylation, cyanoethylation, acetalation and reactions with epoxides.

Click to learn more

Cellulose ethers

As in cellulose, the OH-groups are not very easily accessible for an etherification, the starting material has to be converted to alkali cellulose (alkali-consuming process), or at least the cellulose has to be pre-swollen in alkali (processes without alkali consumption).

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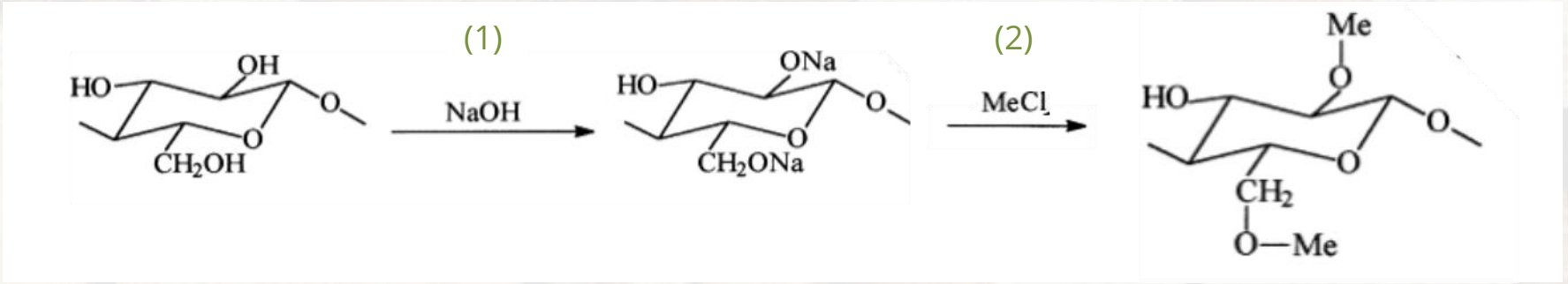
Cellulose ethers obtained by alkali-consuming process	Cellulose ethers obtained by proces without alkali consumption
Methylcellulose (MC)	Hydroxyethylcellulose (HEC)
Ethylcellulose (EC)	Hydroxypropylcellulose (HPC)
Propylcellulose (PC)	Hydroxybutylcellulose (HBP)
Benzylcellulose	Cyanoethylcellulose
Carboxymethylcellulose (CMC)	Carboxyehtylcellulose

Methylcellulose

Methylcellulose is produced in the following stages:

- treatment with sodium hydroxide (NaOH) to obtain alkali cellulose (1);
- alkali cellulose reaction with an etherifying agent such as iodomethane, chloromethane or dimethyl sulphate (2);
- purification and removal of by-products is applied by washing in hot water, followed by drying and pulverization of the prepared MC.





cellulose

alkali cellulose

methylcellulose

Application

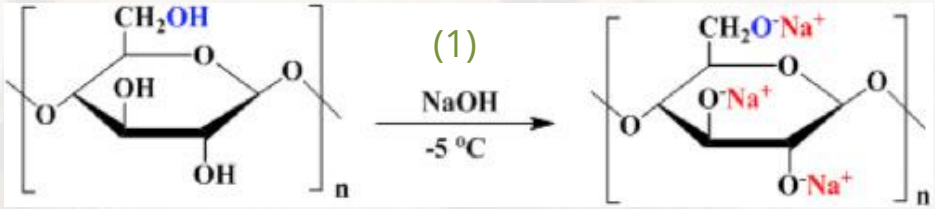
- glue - commonly used as a bookbinding adhesive for paper, as well as sizing paper and fabrics, thickening water baths for marbling paper, used to loosen and clean off old glue from spines and book boards, or added to PVA
  to slow down its drying time;
- thickener and emulsifier - in the food (E461), cosmetics, construction, paper and textile and construction industries;
- impregnating agent - excellent rheology modifier (thickener), binder, film-forming, water-retaining agent, suspending agent, surfactant, lubricant, protective colloid used in paper maintenance.

Click on green phrases to learn more

Hydroxyethylcellulose

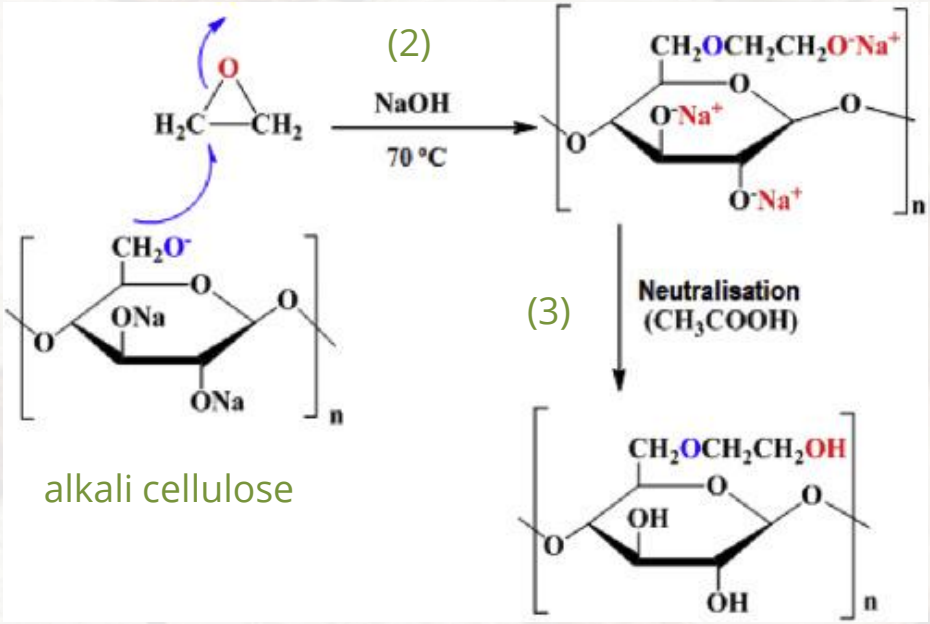
Hydroxyethylcellulose is produced in the following stages:

- the cellulose was mixed with NaOH to obtain alkali cellulose (1);
- the mercerised cellulose, which reacts with ethylene oxides in aqueous medium, is carried out in the presence of an alkali catalyst (i.e. sodium hydroxide) at 70 °C (2);
- the synthesised material was neutralised by acetic acid (3).



cellulose

alkali cellulose



alkali cellulose

hydroxyethylcellulose

Application

- the textile industry for the impregnation of textiles, used for sizing and finishing;
- the pharmaceutical industry in the production of emulsions;
- the cosmetics industry as a stabilizer;
- building materials (joints, joint fillers, gypsum mixtures);
- gelling agent in the production of hydrogels (drugs, cosmetics implants, contact lenses, soap);
- thickening printing inks.

Click on green phrases to learn more

Check your knowledge

List the most important applications of cellulose ethers



You should already know the answer.

However if you don’t, please repeat the course.

Summary

In this course you've learnt about:

- Cellulose – occurrence, structure
- Hemicelluloses – occurrence, structure
- Starch and pectines – occurrence, structure
- Carbohydrate reactivity



Congratulations!

You’ve finished Carbohydrates polymers course.

