



School of Industrial and Information Engineering
Course 096125 (095857)
Introduction to Green and Sustainable Chemistry

 POLITECNICO DI MILANO



Polysaccharides

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

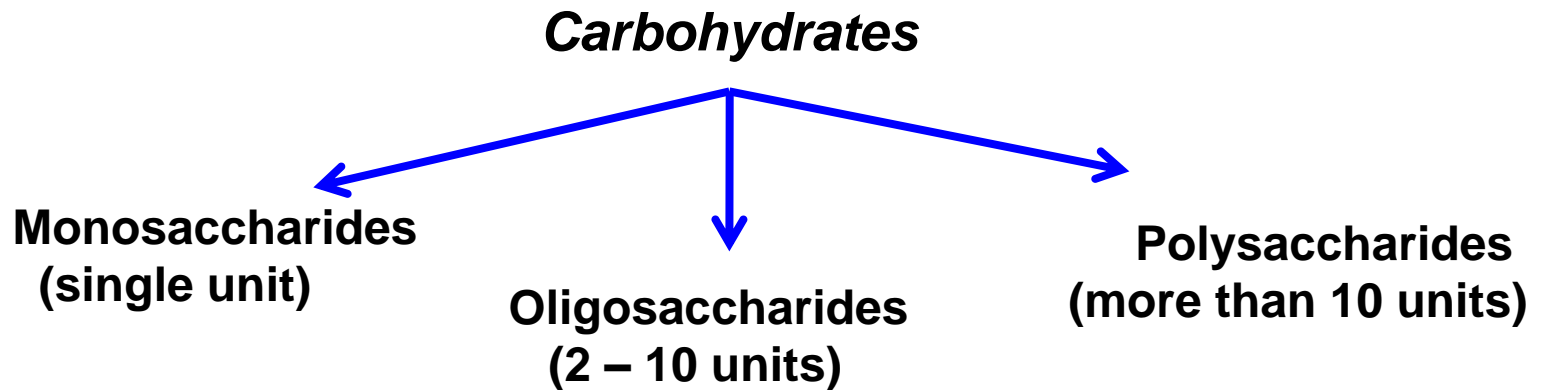
<http://iscamap.chem.polimi.it/citterio/education/course-topics/>



INTRODUCTION.

Carbohydrates : derived from word *kohlenhydrates*, generally known as sugars, are **optically active polyhydroxy aldehydes or ketones** (present either in free, hemiacetal or acetal form), or **substances that hydrolyze to yield polyhydroxy aldehydes or ketones**.

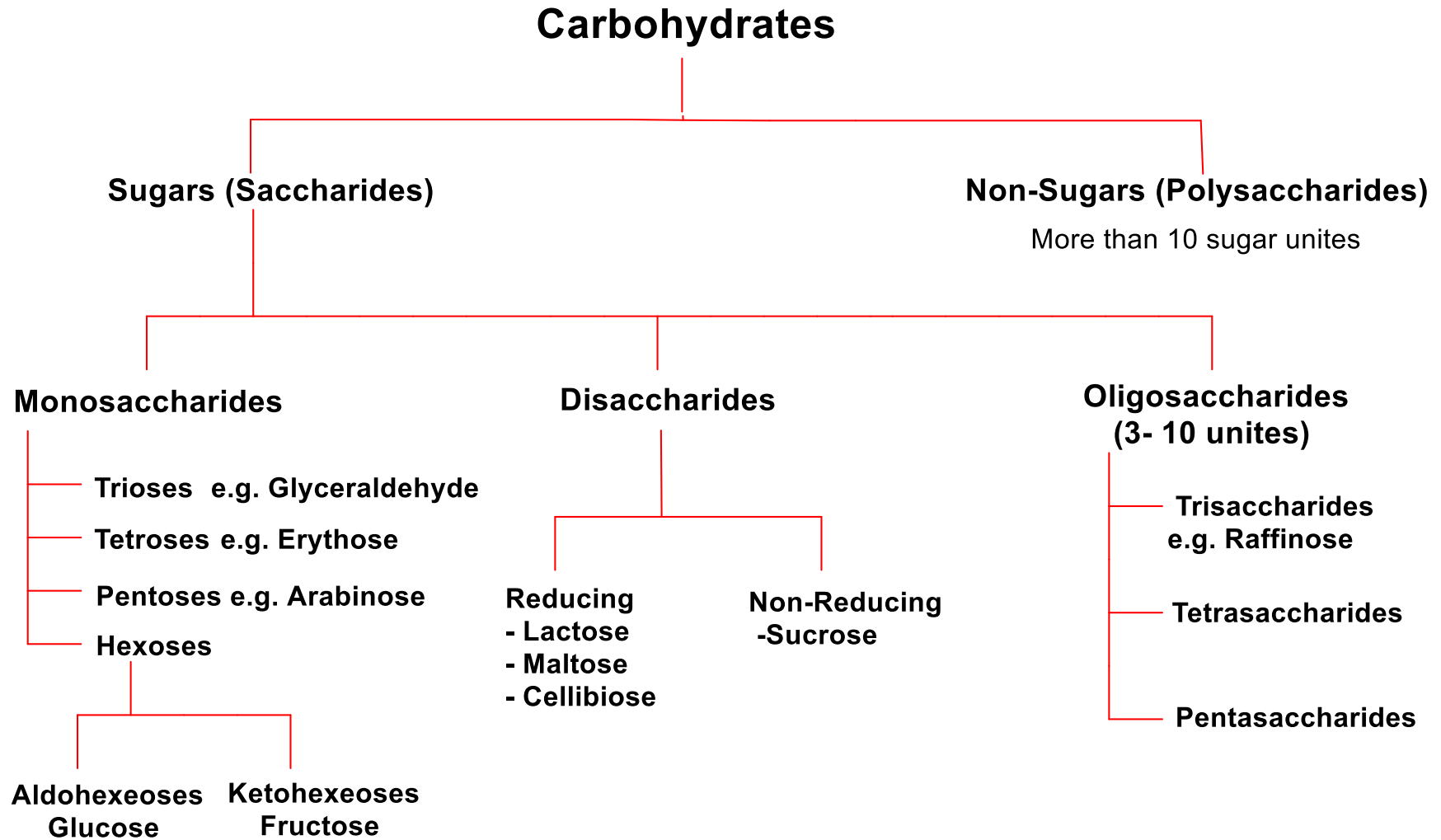
General Classification:



These are regarded as the staff of life for most organisms



Classification of Carbohydrates.

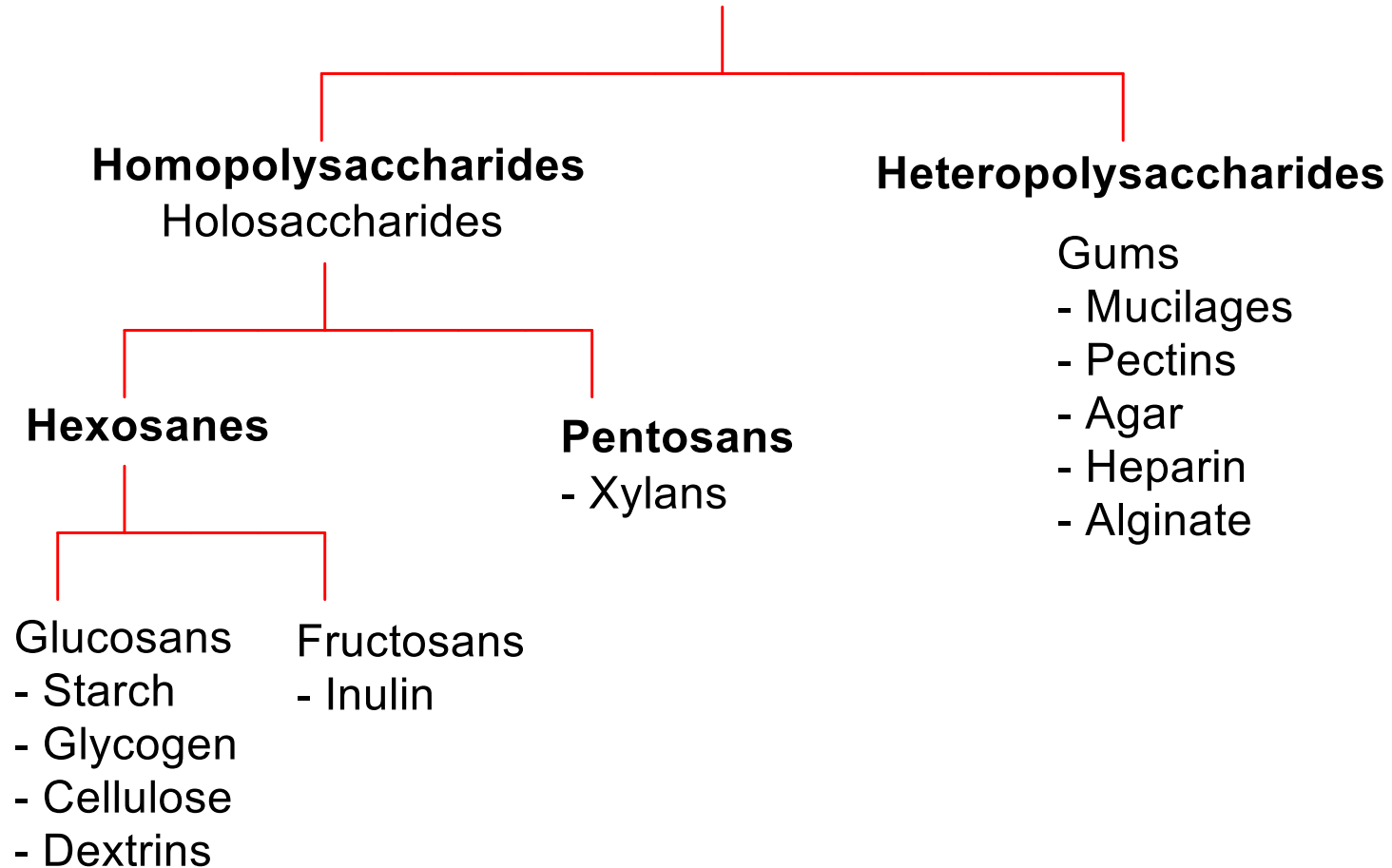




Classification of Polysaccharides.

Non-Sugars (Polysaccharides)

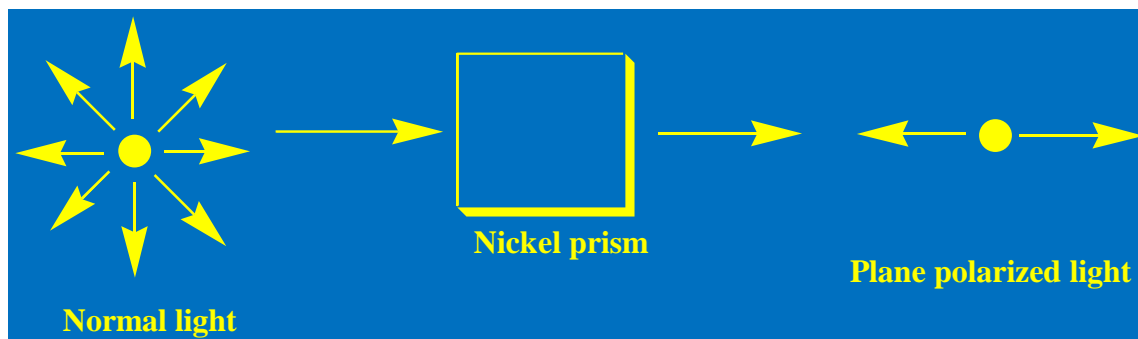
More than 10 sugar units





Optical Activity.

A compound is optically active when, in solution, it is capable to rotate the plane of polarized light either to right (**dextrorotatory**, + or **d**) or to the left (**levorotatory**, - or **l**).



The optical activity of a compound is measured by determination of its specific optical rotation ($[\alpha]_D^t$) using a **polarimeter**, and applying the following equation:

$$[\alpha]_D^{25} = \alpha / (L \cdot C)$$

Where: α = extension of rotation,

L = length of tube (light path) in decimeter,

C = concentration g/ml,

25 = operating temperature (t) in °C,

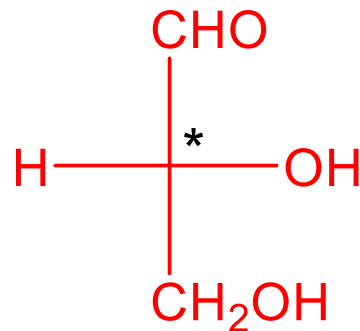
D = line spectrum of sodium light (589 nm).



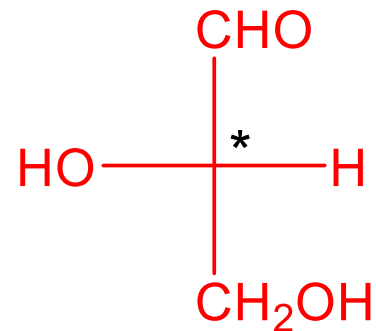
D and L Series in Sugars.

A monosaccharide in which the OH group attached to the carbon atom next to the CH₂OH (farthest asymmetric carbon atom from the carbonyl group) is always to the right is designated as a “D-sugar” and that with the same OH to the left as “L -sugar”.

D and L designations are like (*R*) and (*S*) designations in that they are not necessarily related to the optical rotations of the sugars to which they are applied. Thus, one may encounter sugars that are D (+) or D (-) and others that are L (-) or L (+).



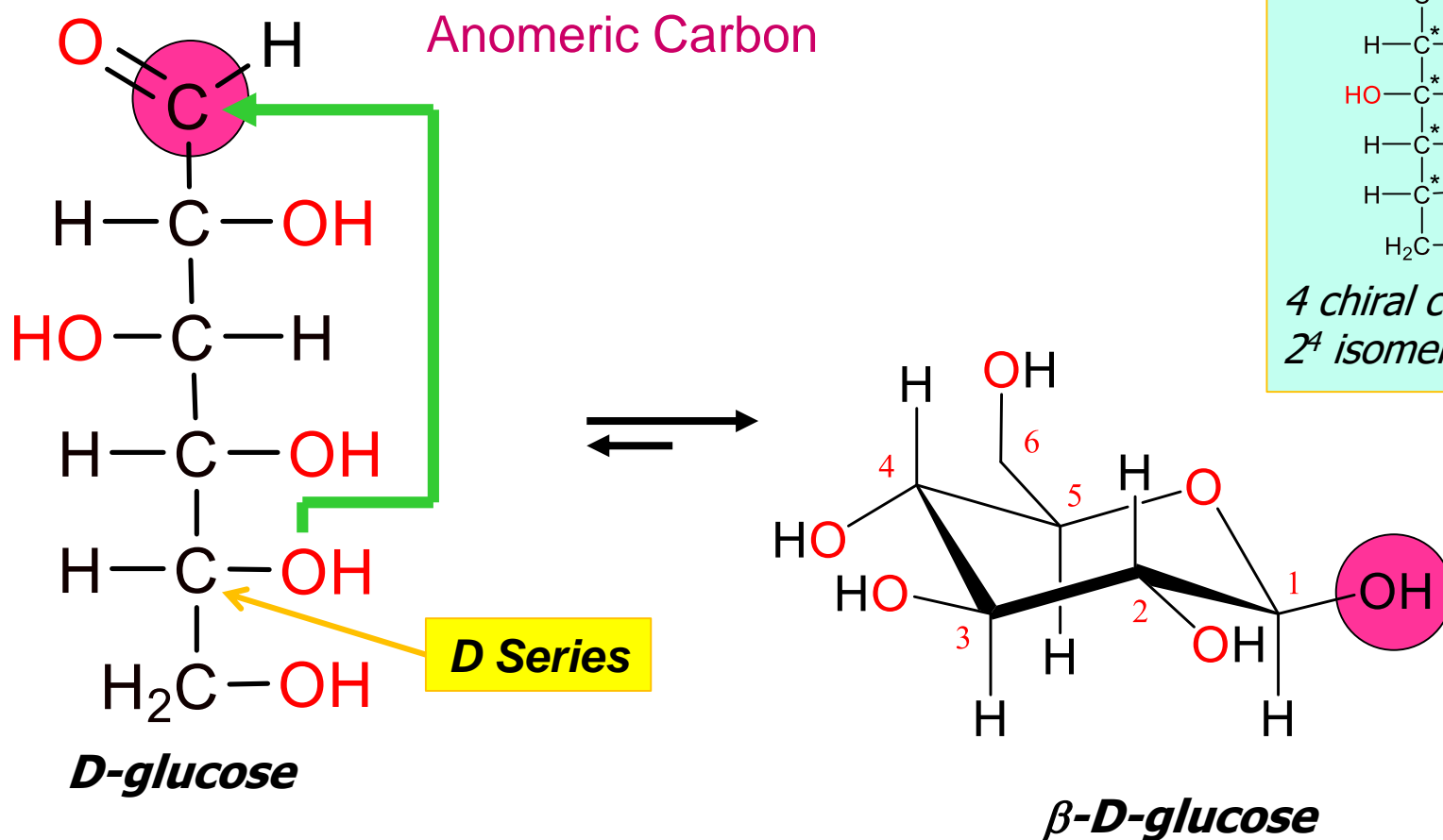
D-Glyceraldehyde



L-Glyceraldehyde



Ring-opening Equilibrium in a Monosaccharide.



Position of anomeric Carbon at **ring closure** decides over formation of α - or β -sugar.

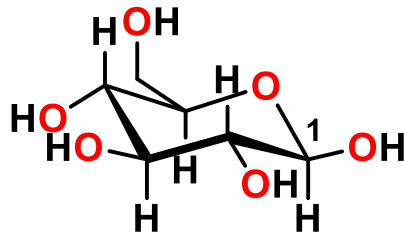


α - and β -Anomers of Glucose: Cellulose and Starch.

Same repetitive unit = Glucose

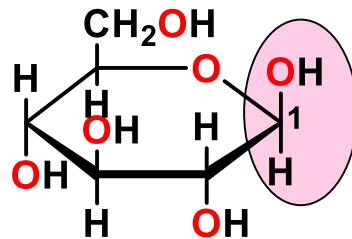
Cellulose

β -D-glucose



β -glucopyranoside

Chair form

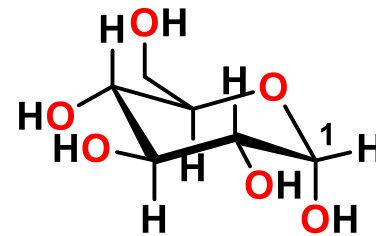


β -glucopyranoside

Haworth formulations

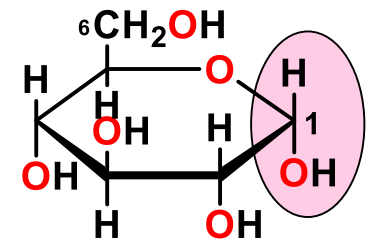
Starch

α -D-glucose



α -glucopyranoside

Chair form



α -glucopyranoside

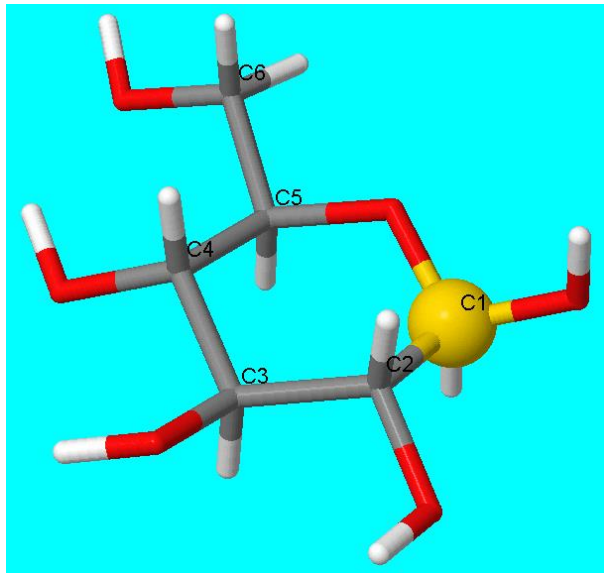
Haworth formulations

Difference:

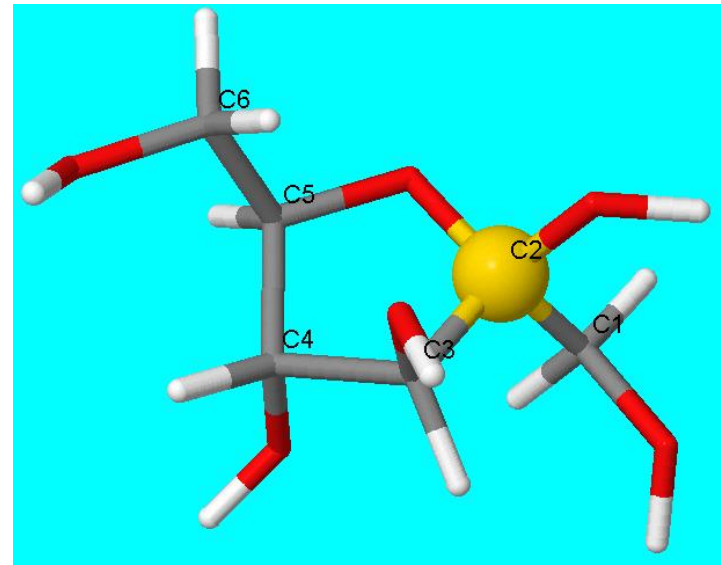
position of Anomeric Carbon in ring closure (upperside – β . downside – α)



Representative C-6 Monosaccharides.



β -D-Glucose

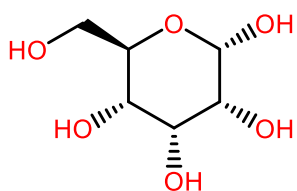


β -D-Fructose

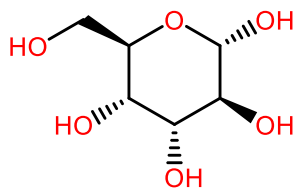
N.B. In yellow are the acetal (Glucose) and ketal (Fructose) **Anomeric Carbons**



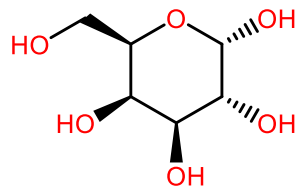
Pyranose Structure of α -D C-5 or C-6 Sugars.



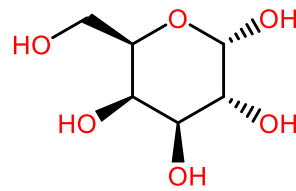
α -D-Allopyranose



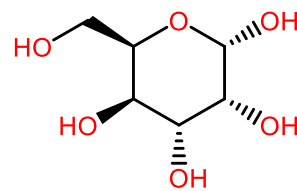
α -D-Altropyranose



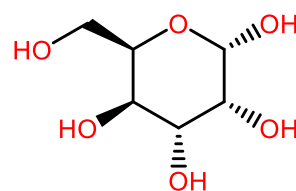
α -D-Galactopyranose



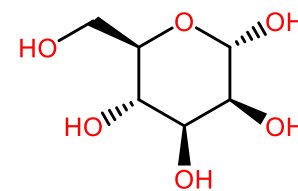
α -D-Glucoopyranose



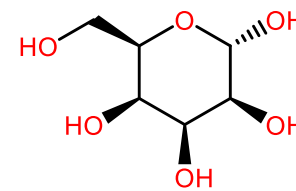
α -D-Gulopyranose



α -D-Idopyranose

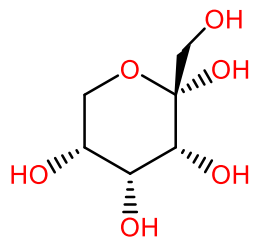


α -D-Mannopyranose

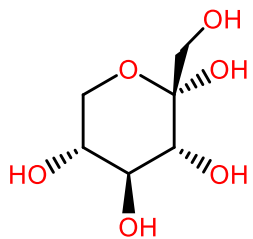


α -D-Talopyranose

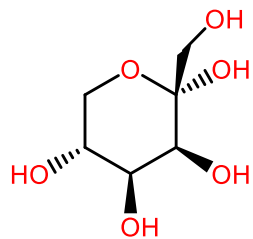
C-6 (CHO)
hemiacetal



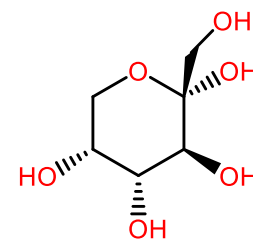
α -D-Psicopyranose



α -D-Sorboypyranose

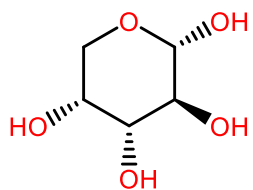


α -D-Tagatopyranose

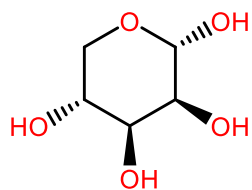


α -D-Fructopyranose

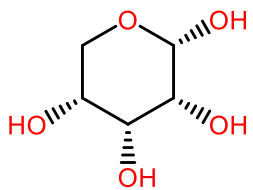
C-6 (CO)
hemiketal



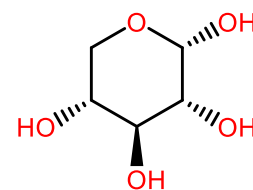
α -D-Arabinopyranose



α -D-Lysopyranose



α -D-Ribopyranose

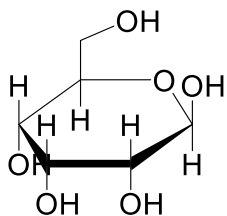


α -D-Xylopyranose

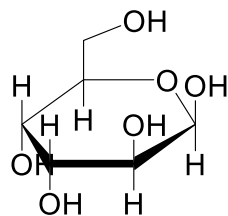
C-5 (CHO)
hemiacetal



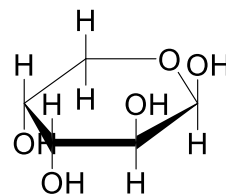
Three-dimensional Vision of β -D Pyranosidic Structures of C-5 and C-6 Sugars.



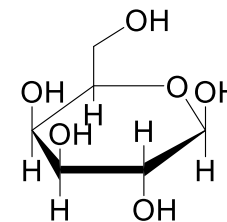
β -D-Allopyranose



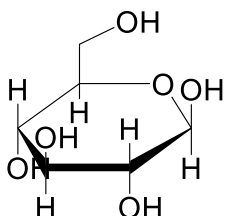
β -D-Altropyranose



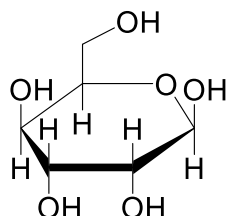
β -D-Arabinopyranose



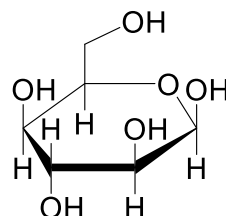
β -D-Galactopyranose



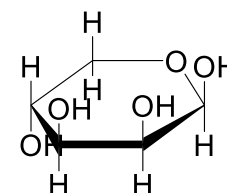
β -D-Glucopyranose



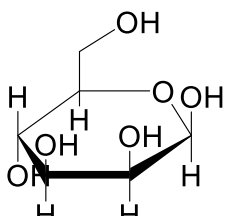
β -D-Gulopyranose



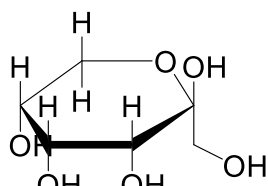
β -D-Idopyranose



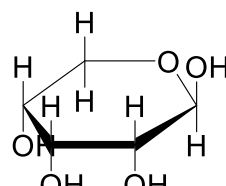
β -D-Lyxopyranose



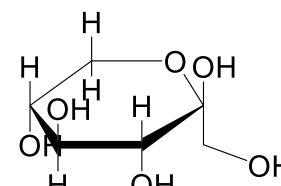
β -D-Mannopyranose



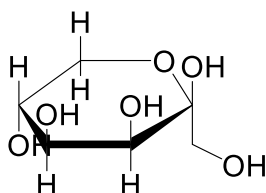
β -D-Psicopyranose



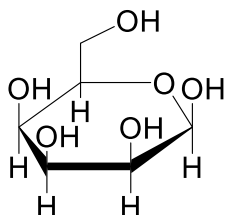
β -D-Ribopyranose



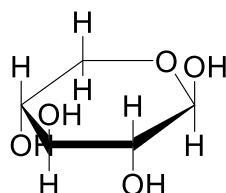
β -D-Sorbopyranose



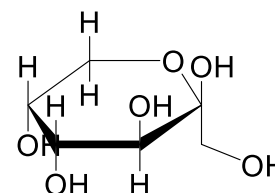
β -D-Tagatopyranose



β -D-Talopyranose



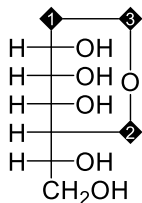
β -D-Xylopyranose



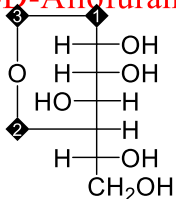
β -D-Fructopyranose



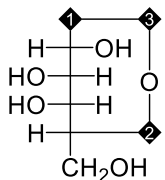
Furanosidic Structures of β -D C-5 and C-6 Sugars.



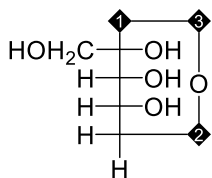
α -D-Allofuranose



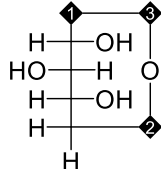
α -D-Galactofuranose



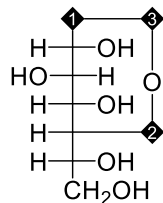
α -D-Lyxofuranose



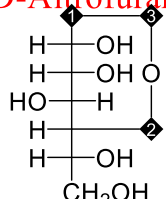
α -D-Ribulofuranose



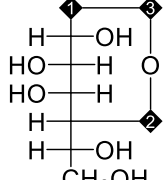
α -D-Threofuranose



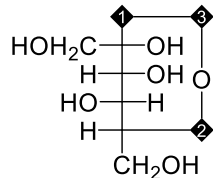
α -D-Altrofuranose



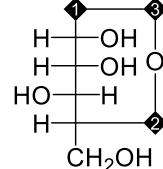
α -D-Glucofuranose



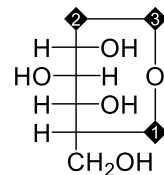
α -D-Mannofuranose



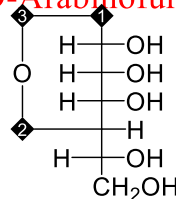
α -D-Sorbofuranose



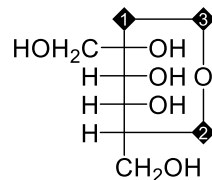
α -D-Xylofuranose



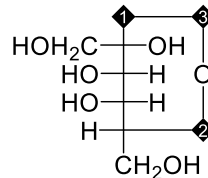
α -D-Arabinofuranose



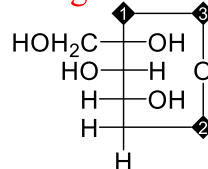
α -D-Gulofuranose



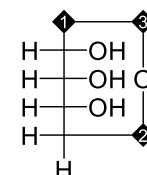
α -D-Psicofuranose



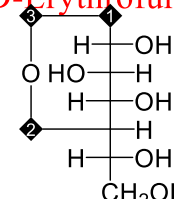
α -D-Tagatofuranose



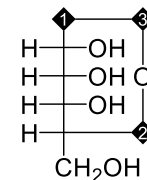
α -D-Xylulofuranose



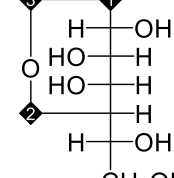
α -D-Erythrofuranoose



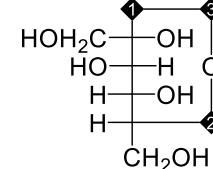
α -D-Idofuranose



α -D-Ribofuranose



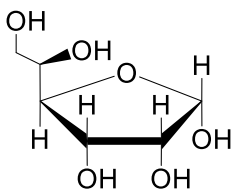
α -D-Talofuranose



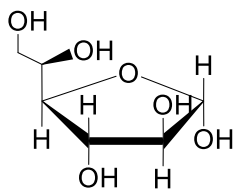
α -D-Fructofuranose



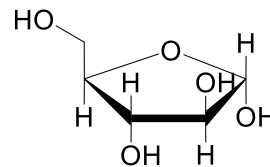
Three-dimensional Vision of α -D Furanosidic Structures of C-5 and C-6 Sugars.



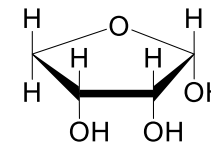
α -D-Allofuranose



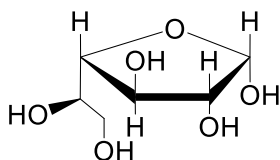
α -D-Altrofuranose



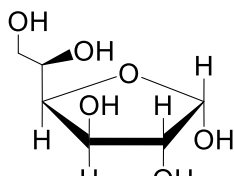
α -D-Arabinofuranose



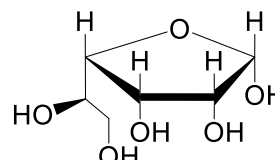
α -D-Erythrofuranose



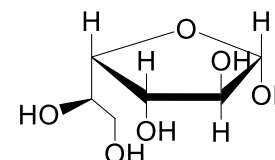
α -D-Galactofuranose



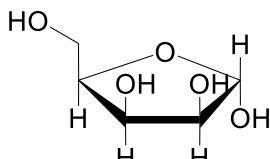
α -D-Glucofuranose



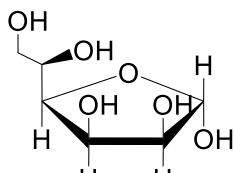
α -D-Gulofuranose



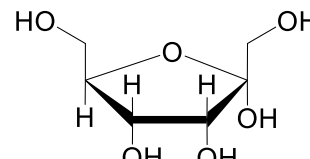
α -D-Idofuranose



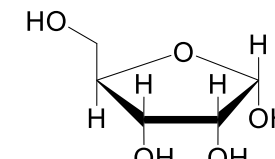
α -D-Lyxofuranose



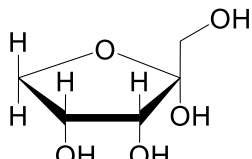
α -D-Mannofuranose



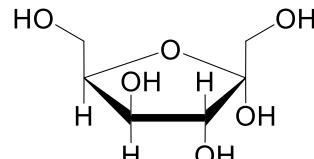
α -D-Psicofuranose



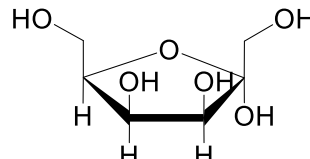
α -D-Ribofuranose



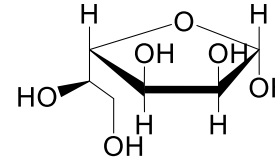
α -D-Ribulofuranose



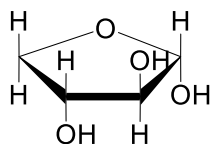
α -D-Sorbofuranose



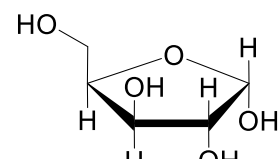
α -D-Tagatofuranose



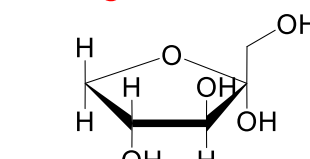
α -D-Talofuranose



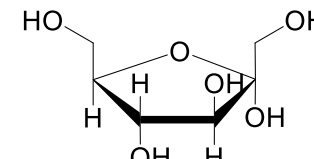
α -D-Threofuranose



α -D-Xylofuranose



α -D-Xylulofuranose



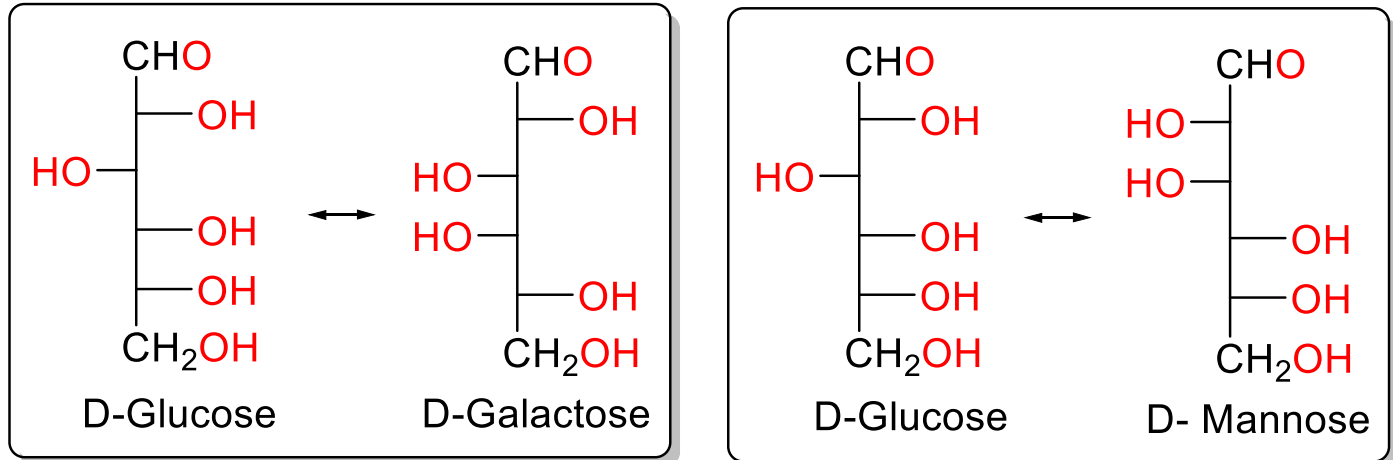
α -D-Fructofuranose



Terms Used to Describe Isomerism: Epimer.

- D-Glucose and D-Galactose are different from each other in the stereochemistry of carbon 4. They are described as “Epimers”.
- D-Glucose and D-Mannose are different from each other in the stereochemistry of carbon 2. They are described as “Epimers”.

Epimers:

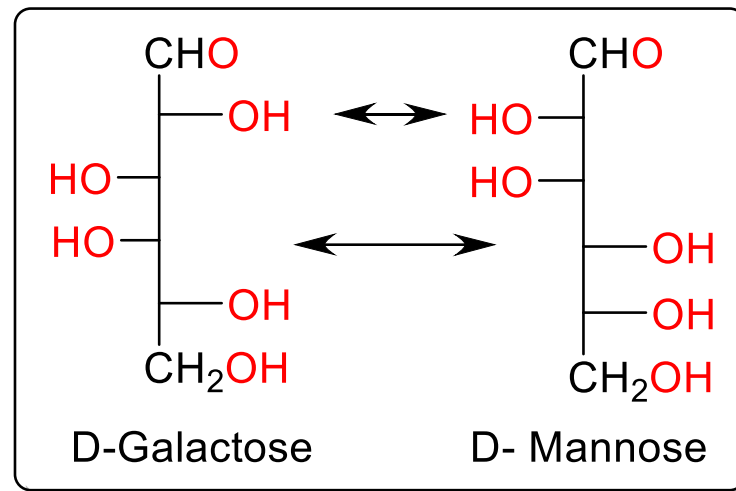




Terms Used to Describe Isomerism: Diastereoisomer.

Galactose and Mannose are different from each other in the stereochemistry of carbons 2 and 4. They are described as “Diastereoisomers””Diastereomers”.

Diastereomers:

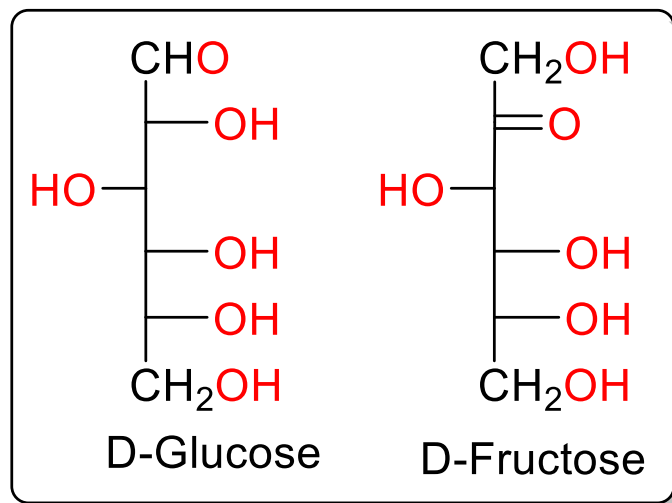




Terms Used to Describe Isomerism: Structural Isomers.

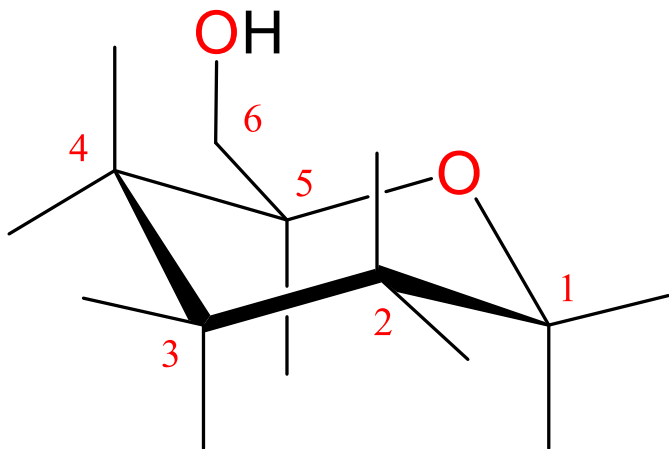
- Glucose and Fructose have the same molecular formula $C_6H_{12}O_6$. They have **different structures with different function groups**. They are described as “Structural Isomers”.

Structural isomers:





Substituted Hexose Saccharides (1 -C=O).



- 6** - CH₂OH
- COOH
- CH₂OSO₃⁻
- COOCH₃
- CH₂-O-COCH₃

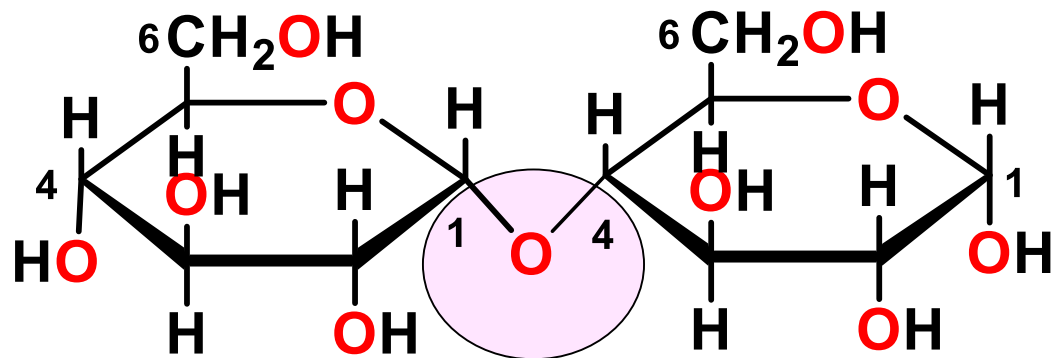
1-4 H, OH

common

2,3,5 OSO₃⁻ ; NH₂, NHCOCH₃

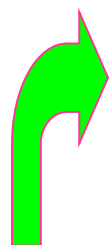


Disaccharides-(α -1,4)



α -glucopyranoside

α -glucopyranoside



Non-reducing end (alcohol)

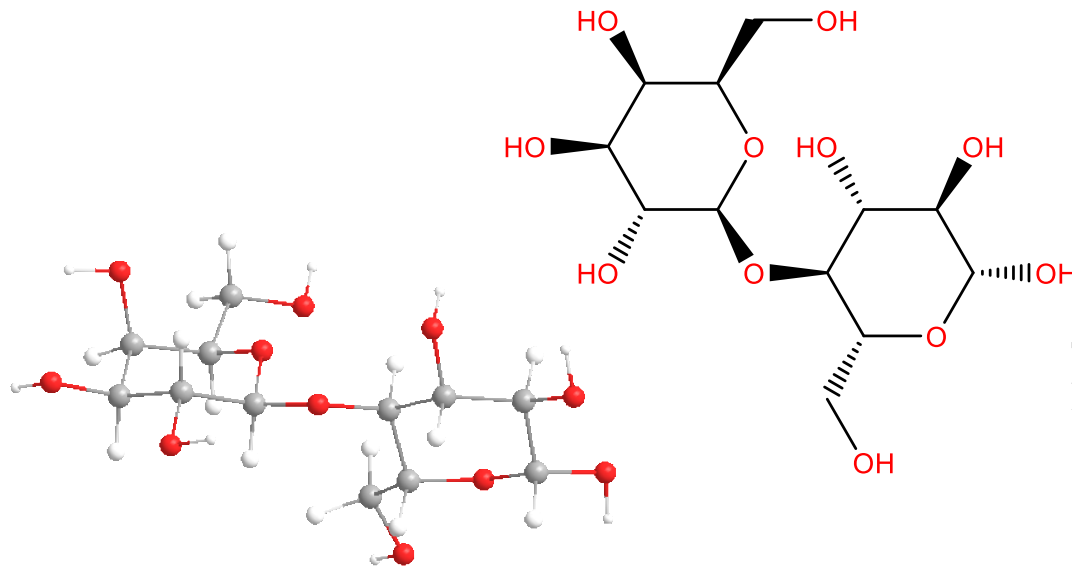


Reducing end (hemiacetal)

Disaccharide, acetal linkage

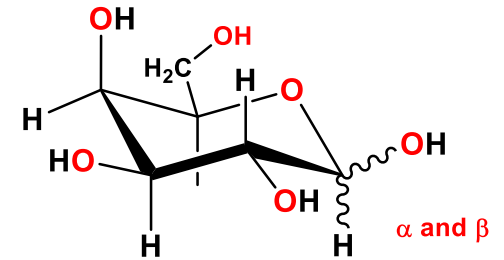
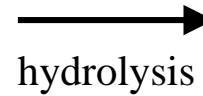


Disaccharides: Lactose.

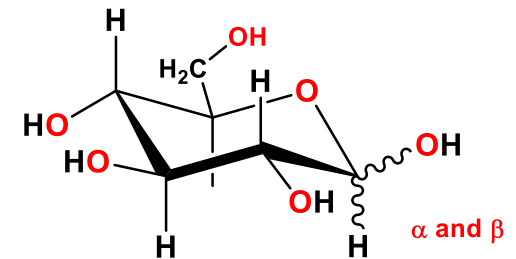


lactose (from milk)

4-O-(β -D-galactopyranosyl)- β (or α)-D-glucopyranose



galactose

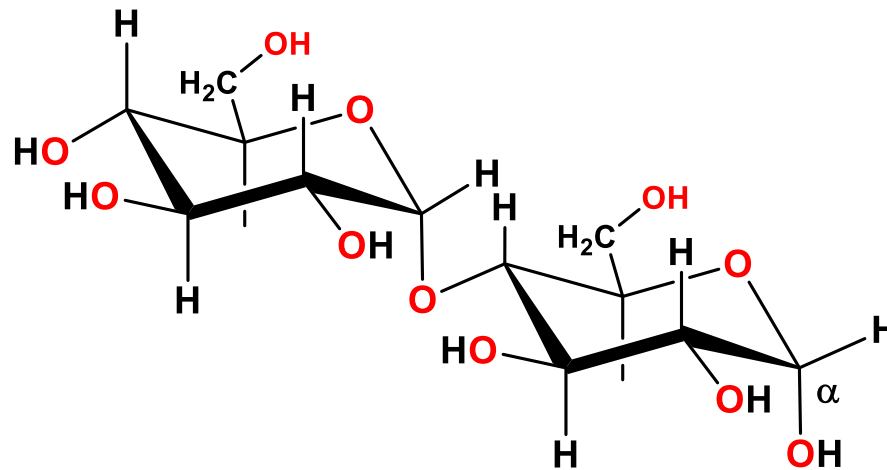


glucose

- a reducing sugar; exhibits mutarotation
- 1,4-acetal linkage between 2 monomeric sugars
- acidic hydrolysis yields galactose and glucose (1:1).



Disaccharide: Maltose.



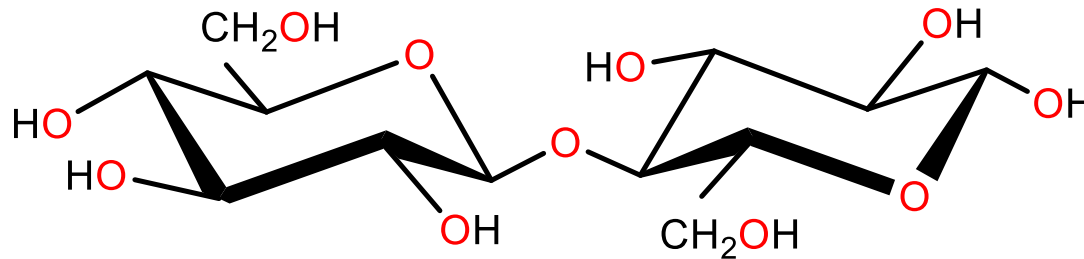
maltose (from partial hydrolysis of starch)

4-O-(α -D-glucopyranosyl)- α (or β)-D-glucopyranose

- a reducing sugar; mutarotates
- acidic hydrolysis yields only glucose
- can be digested by humans & fermented by yeast.



Disaccharide: Cellobiose.



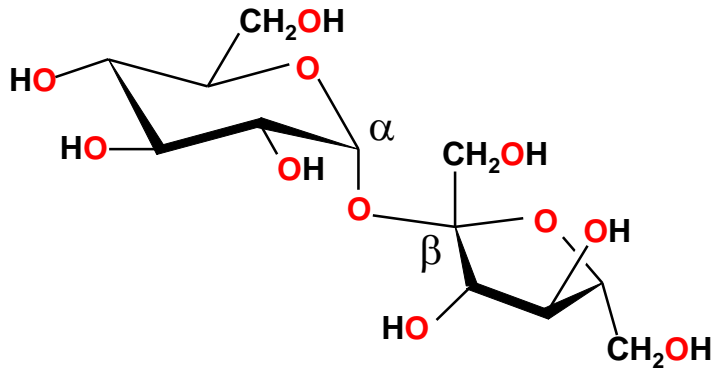
cellobiose (from partial hydrolysis of cellulose)

4-O-(β -D-glucopyranosyl)- β (or α)-D-glucopyranose

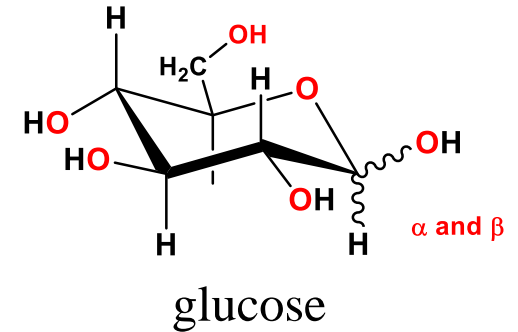
- a reducing sugar; mutarotates
- can NOT be digested by humans nor fermented by yeast; CAN be digested by bacteria in ruminants and termites (which have β -glucosidase enzyme).



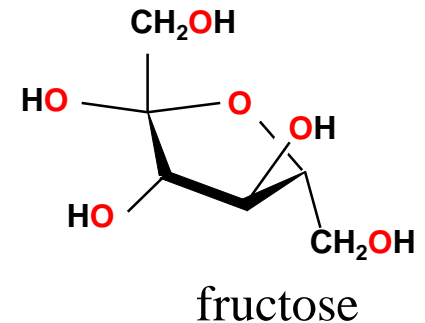
Disaccharide: Sucrose.



hydrolysis



and

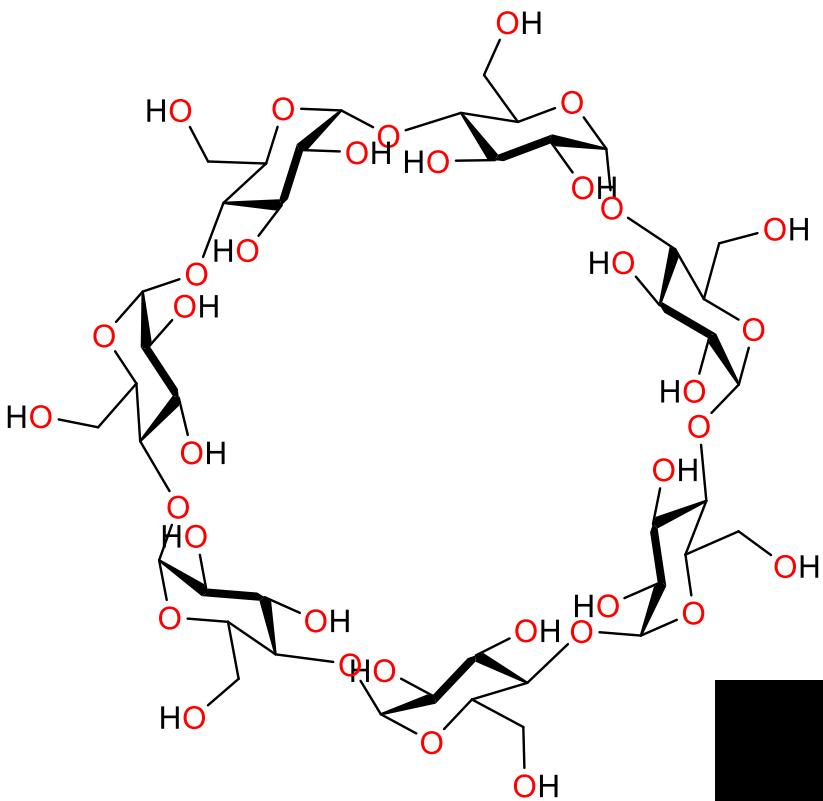


sucrose (from beets and sugar cane)

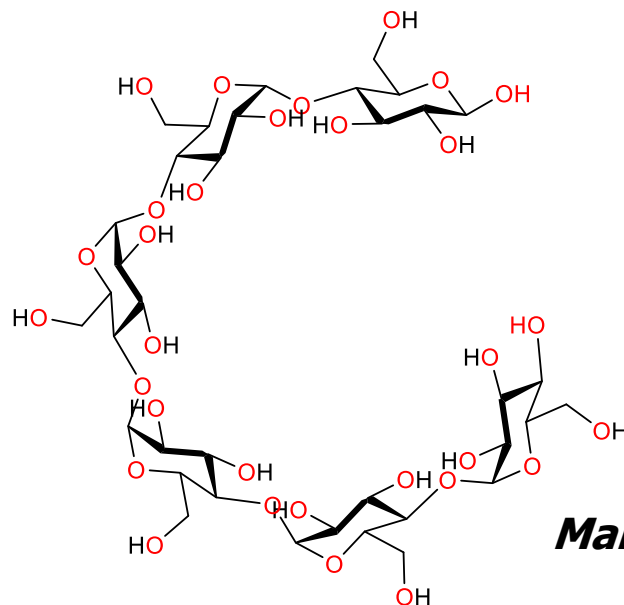
- NOT a reducing sugar; NOT a hemiacetal; does NOT undergo mutarotation
- hydrolysis yields glucose plus fructose (called “invert sugar” because rotation of polarized light changes sign).



Oligosaccharides.



β-Cyclodextrin



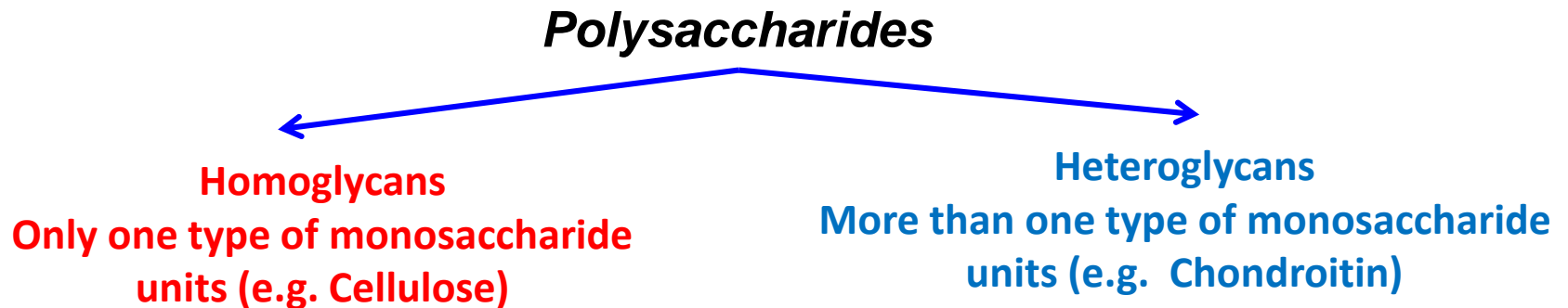
Maltohexaose

	α -CD	β -CD	γ -CD
No. of Glucose Units	6	7	8
Cavity Diameter (nm)	0.47	0.60	0.75
Height of Torus (nm)	0.79	0.79	0.79



POLYSACCHARIDES.

- Polymers formed by condensation of partially oxidised polyalcohols (sugars) at carbons 1,4 or 1,6.
- They are made of long chains of monosaccharide units (> 10) bound together by glycosidic linkages.



These are the most common polymers on earth (mainly based on glucose and its derivatives) and are the most explored polymers, having wide industrial applicability.



Sources and Structure of Polysaccharides.

S. No.	Source	Examples
1.	Plant exudates	Gum karaya, Acacia, Tragacanth
2.	Marine Gums	Carrageenans, Alginates, Agar
3.	Seed endosperms	Guar gum, Locust beans, Plantago Seeds
4.	Plant extracts	Starch, Cellulose, Pectin
5.	Animal sources	Honey, Chitin
6.	Bacteria	Xanthan Gum, Dextran, Gellan

Structure of Polysaccharides

Polysaccharides have a complex structure which is classified, on the basis of monomeric units and on their spatial organization, as:

1. Primary Structure
2. Secondary Structure
3. Tertiary Structure



Cellulose – Starch (the α and β Anomers).

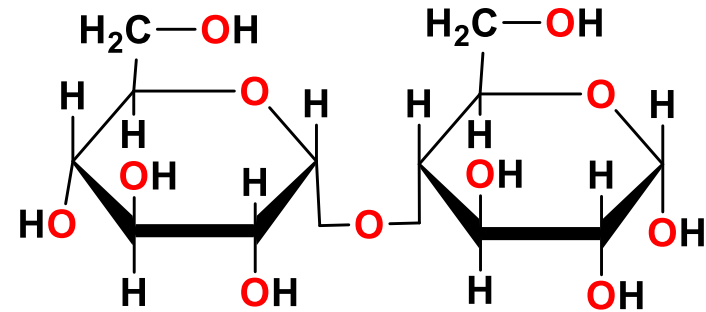
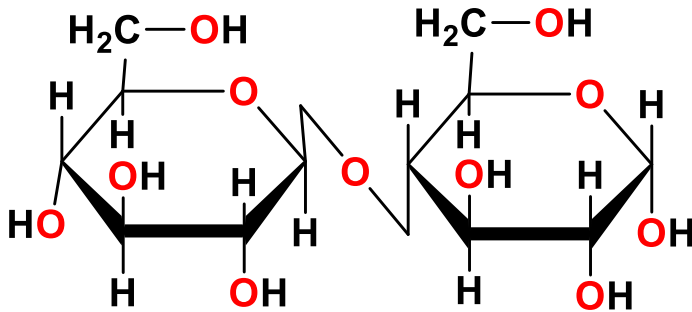


Polymerization



$\beta(1 \rightarrow 4)$ glycosidic bond

$\alpha(1 \rightarrow 4)$ glycosidic bond



Not edible
Linear
Crystalline

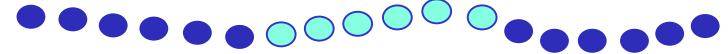
Edible
Branched
Amorphous



Primary Structure: Sequence of Residues.



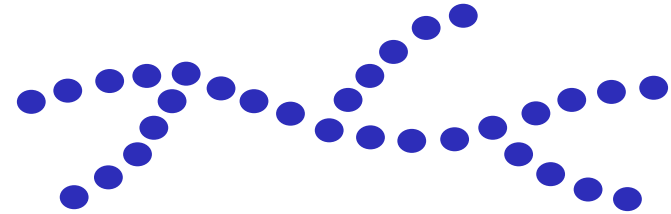
Linear (amylose, cellulose, pullulan)



Block copolymer (alginate)



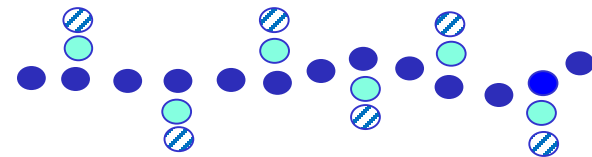
Alternating repeat (agarose, carrageenan)



Branched (dextran, amylopectin, (also lignin))

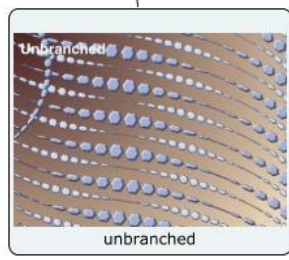
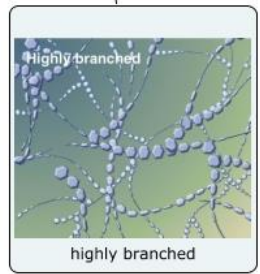
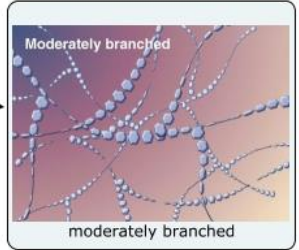
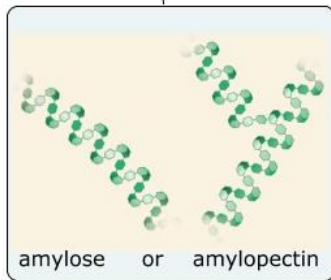
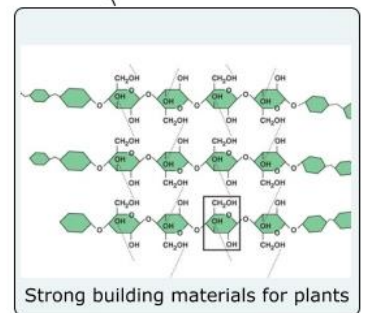
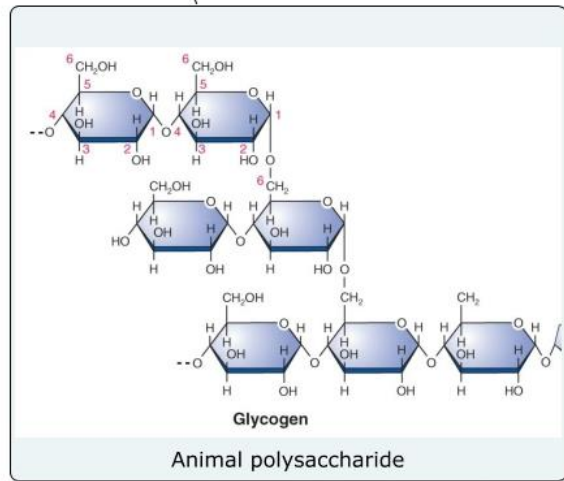
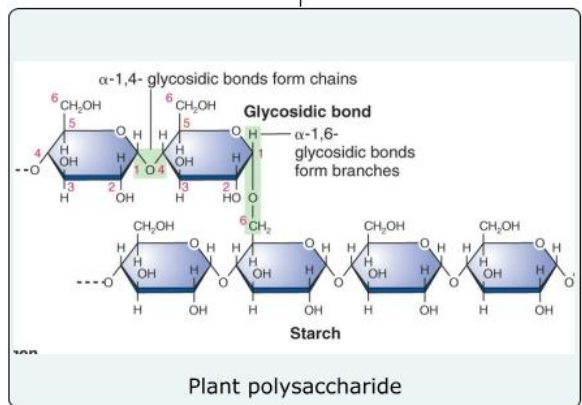
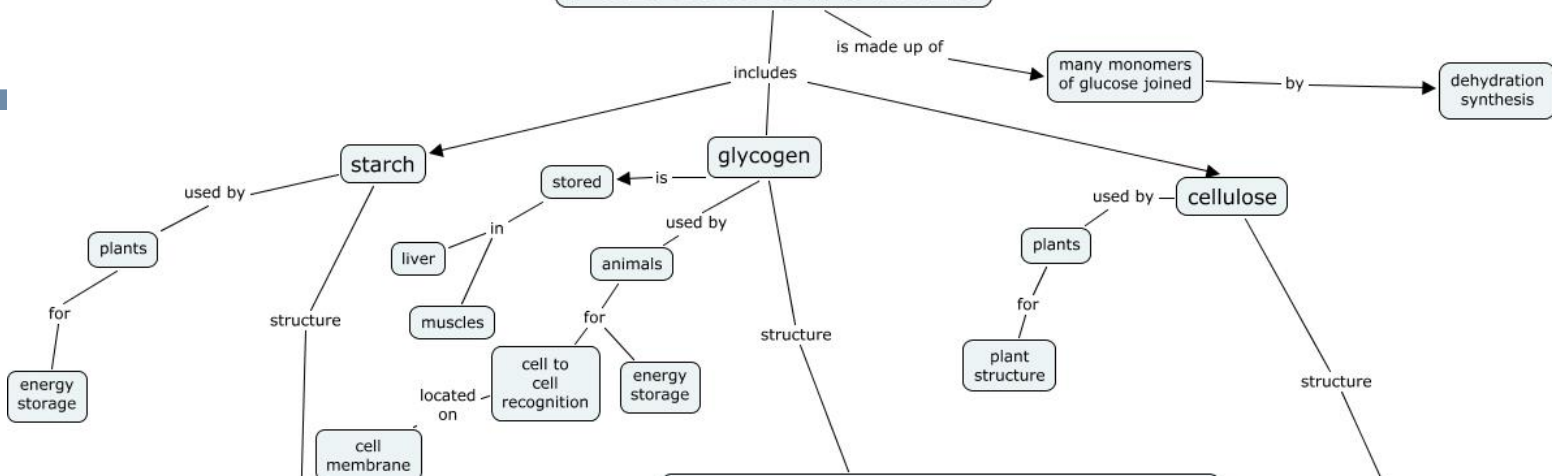


Interrupted repeat (pectin, chitosan, konjac mannan)



Complex repeat (xanthan)

POLYSACCHARIDES

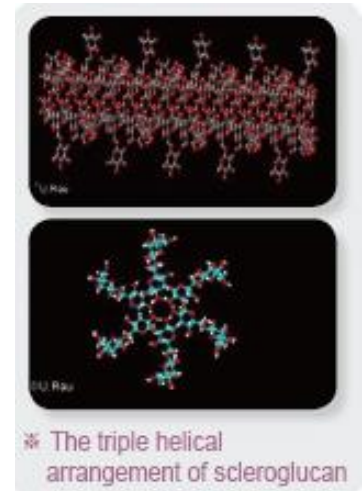




Secondary & Tertiary Structure.

Dependent on:

- rotational freedom
- hydrogen bonding
- oscillations
- local (secondary) and overall (tertiary) random coil helical conformations



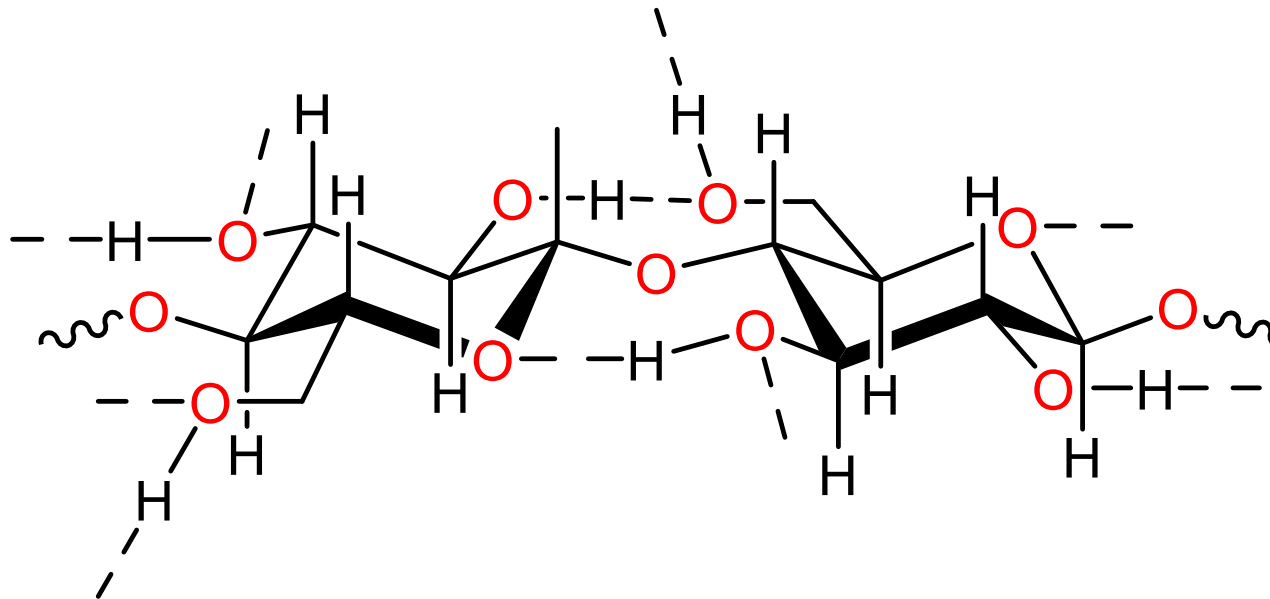
Tertiary structure – sterical/geometrical conformations

- Rule-of-thumb: Overall shape of the chain is determined by geometrical relationship within each monosaccharide unit
- $\beta(1 \rightarrow 4)$ - zig-zag - ribbon like
- $\beta(1 \rightarrow 3)$ & $\alpha(1 \rightarrow 4)$ - U-turn - hollow helix
- $\beta(1 \rightarrow 2)$ - twisted - crumpled
- $(1 \rightarrow 6)$ - no ordered conformation



Example of Tertiary Structure.

Flat ribbon type conformation: **Cellulose** [$\beta(1 \rightarrow 4)$]



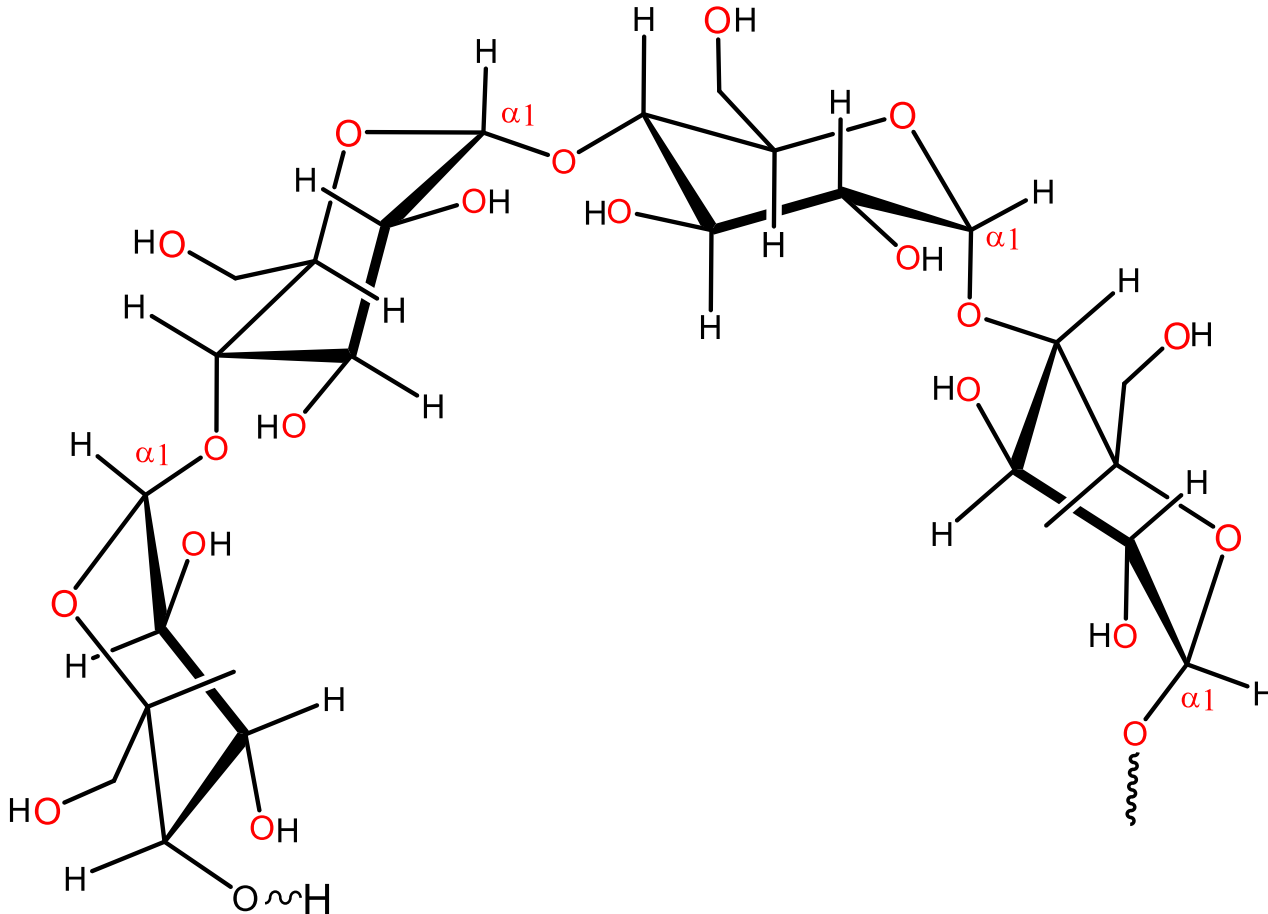
----- Hydrogen bond

Chains can align and pack closely together. Also get hydrogen bonding and interactive forces.



Example of Other Tertiary Structure (Amylose).

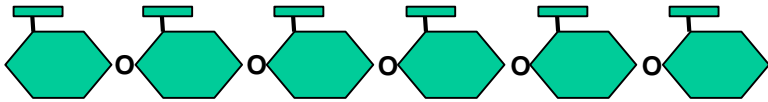
Hollow helix type structures : Amylose forms **inclusion complexes** with iodine, phenol, n-butanol, etc.



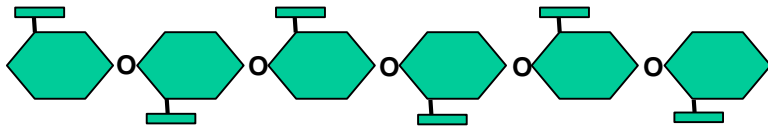


Representative Polysaccharides.

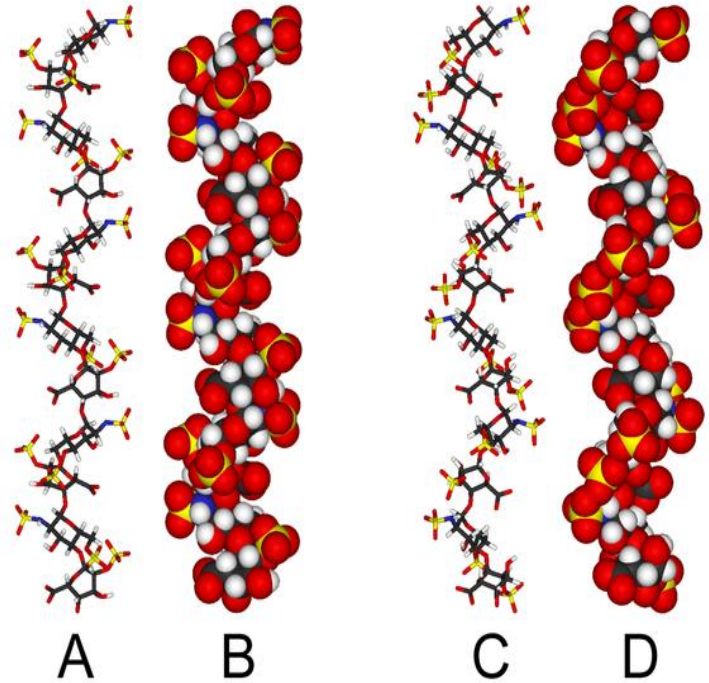
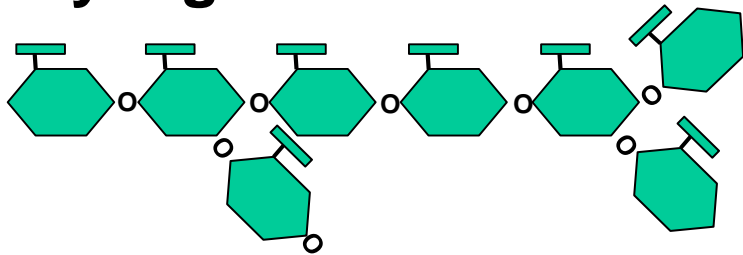
Starch



Cellulose

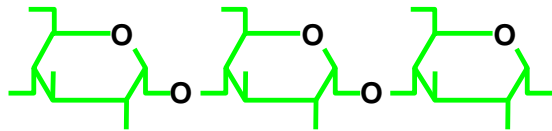
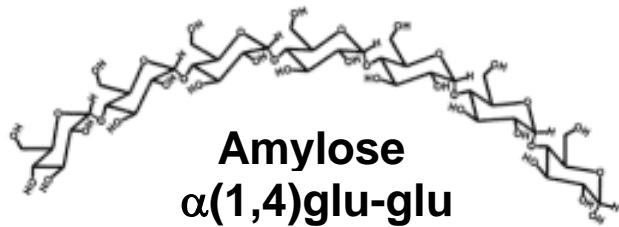


Glycogen

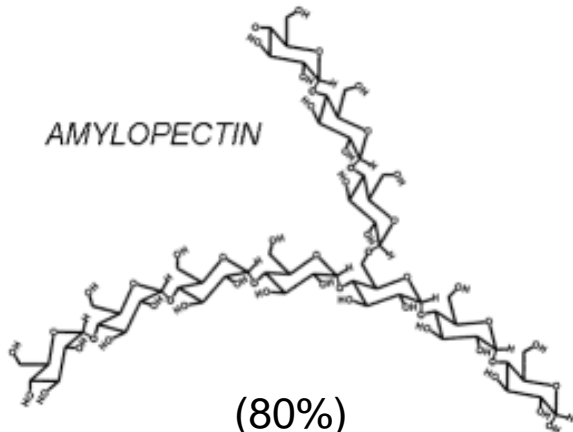




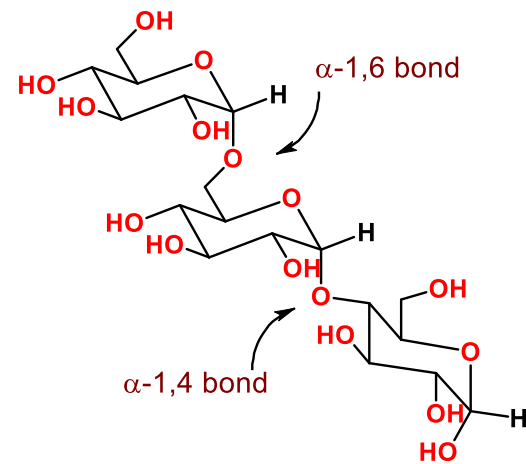
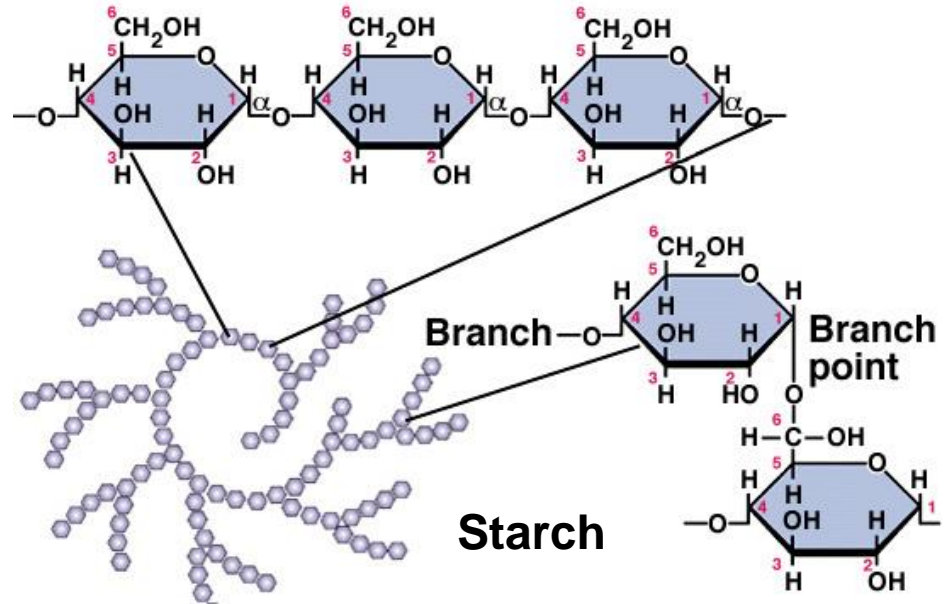
Starch Structure.



(20%)
typically > 200 units

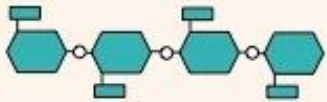
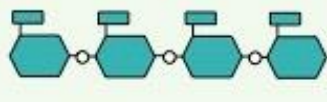
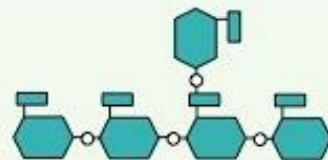
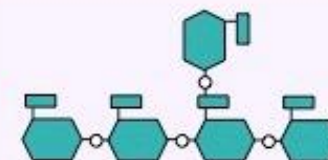
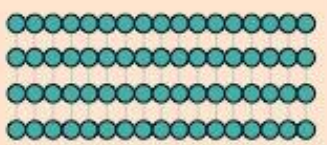


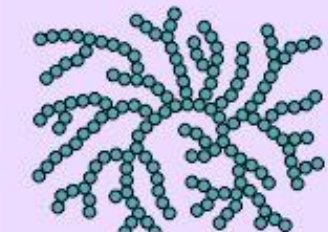


(80%)
branches each ~ 25 units





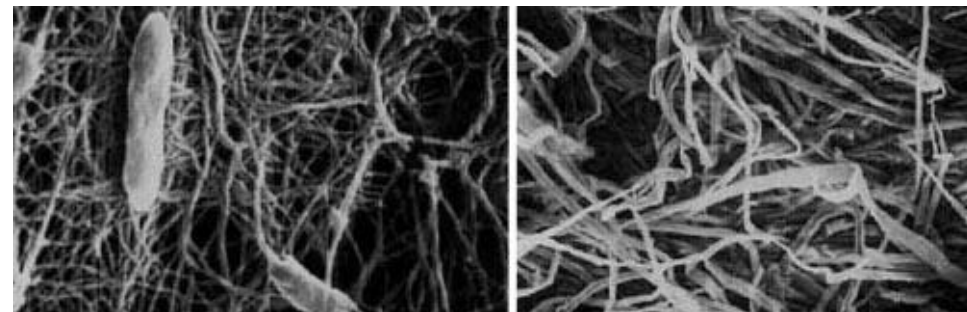
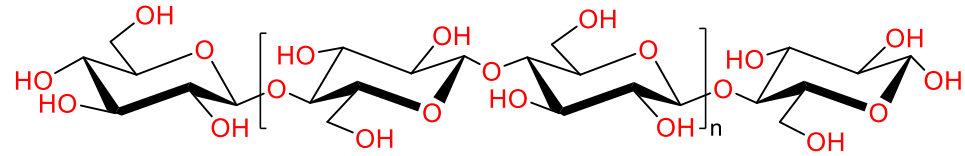
Representative Polysaccharides.

	Cellulose	Starch		Glycogen
		Amylose	Amylopectin	
Source	Plant	Plant	Plant	Animal
Subunit	β -glucose	α -glucose	α -glucose	α -glucose
Bonds	1-4	1-4	1-4 and 1-6	1-4 and 1-6
Branches	No	No	Yes (~per 20 subunits)	Yes (~per 10 subunits)
Diagram				
Shape				



Cellulose.

- Most widely distributed polysaccharide in nature
- Wood & Cotton major source of Cellulose
- Its structure is comprised of chains of D-Glucose units, whereby each unit is joined by a **β -1-4 glycosidic** linkage.
- derivatisation increases solubility (hydroxy-propyl methyl cellulose, carboxymethyl cellulose (CMC), etc.)



Bacterial cellulose ($\times 20,000$)

2 μ m

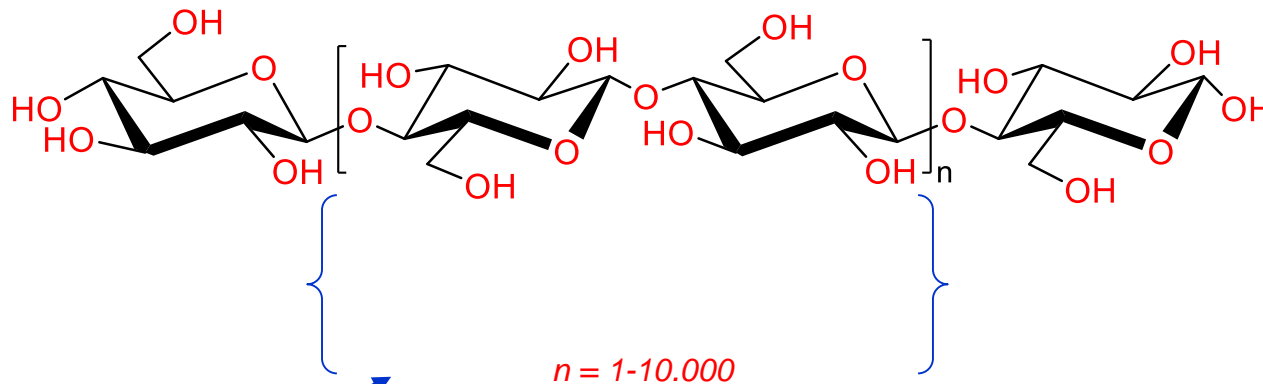
Plant cellulose ($\times 200$)

200 μ m

Fig. 1. Bacterial cellulose and plant cellulose.

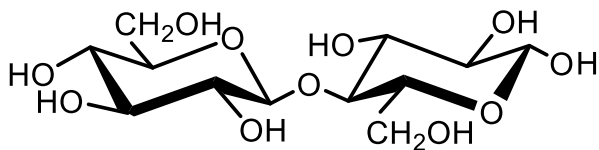


Cellulose - Molecular Structure.



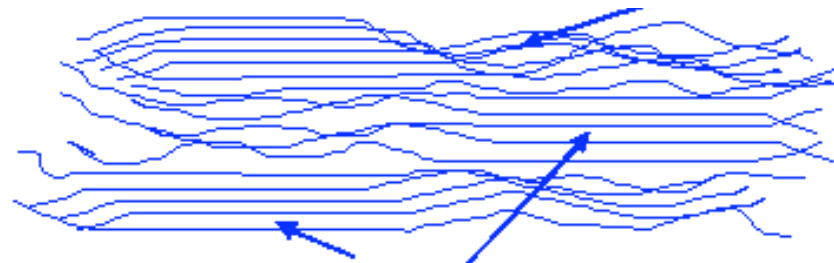
Linear polymer

$n = 1-10.000$



Unit: cellobiose ($n = 2$)

Amorphous Zones (not ordered)



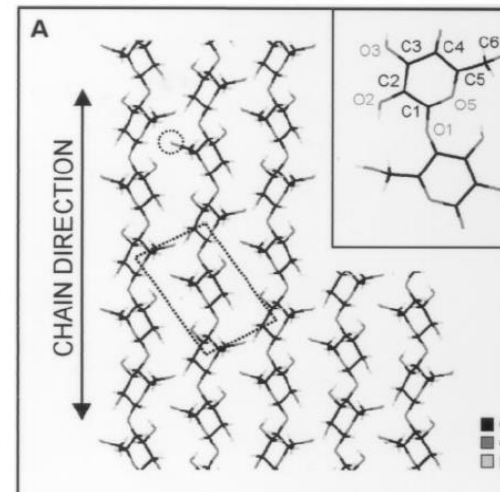
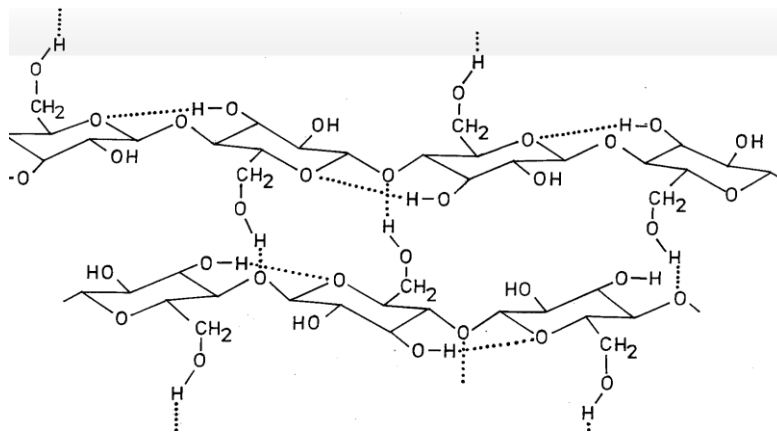
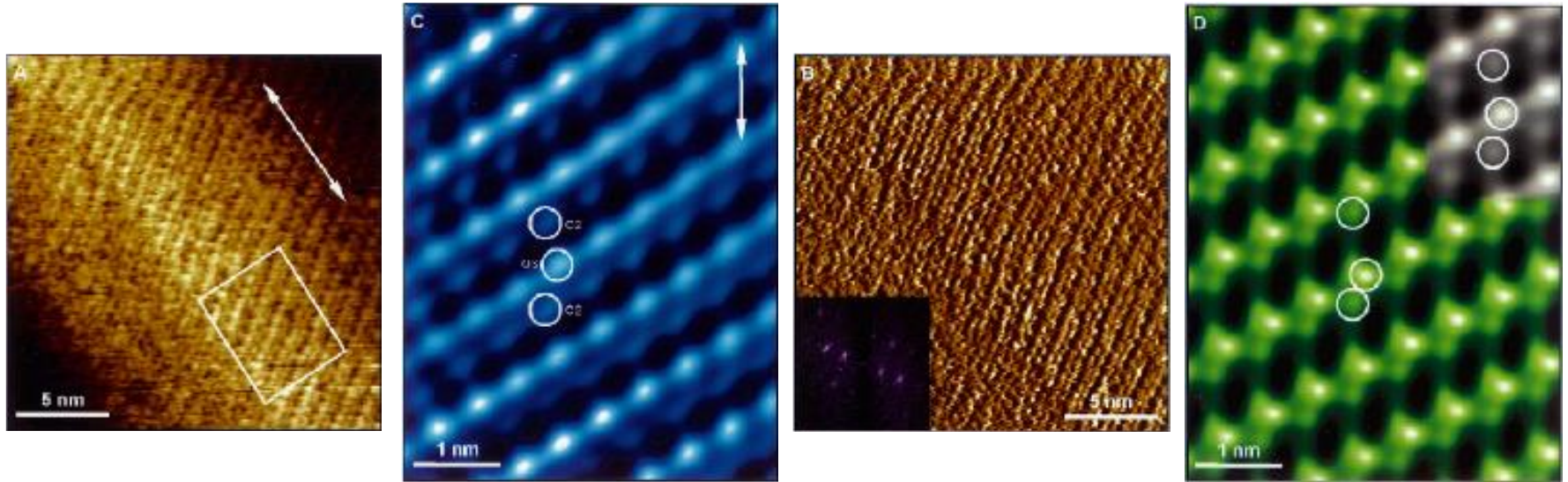
Crystalline island (highly ordered) s)

Cellulose Microfibrils

Partial crystallinity \Rightarrow High resistance

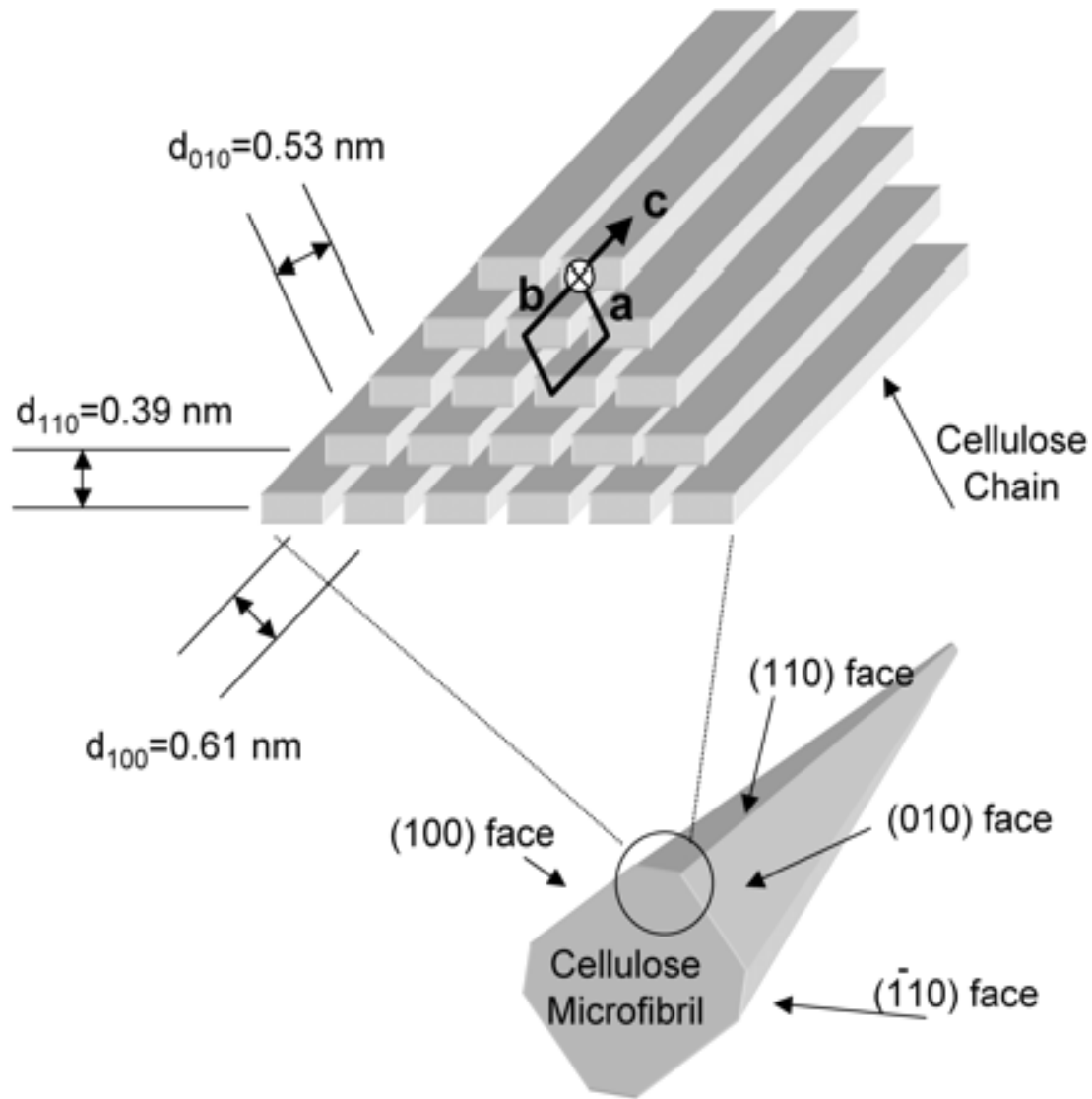


High Resolution AFM Images of Surface of a Cellulose Crystal.





Cellulose crystals of an Algae (Valonia).





Chemistry of Cellulose and Starch.

Reactive Groups :

hydroxy (OH)

Cellulose:

Esterification

nitrate

gun cotton

acetate

fiber

} high DS
~ 2.5

Etherification

methyl cellulose Cell-O-CH₃

Hydroxypropyl cellulose

low DS (1.6 – 2.0) soluble in water

high DS (2.4 – 2.8) soluble in polar solvents

DS = degree of substitution



Cellulose - Starch Chemistry.

Cellulose:

Sulfidizing (CS_2)

Cell-xanthate

rayon fiber

paper

} DS =
1.0 – 1.5

Alkylation

Cross linking

Starch:

Acetylation

Succination

} Low DS
0.01 – 0.2

increase water solubility

reduced gelation

(application in food industry: emulsifier, fat replacement)

15 % of starch produced → food

1/6 of used starch in food is modified



Starch in Biodegradable Plastics.

Intended Use : single use item
garbage bags, mulch film,
fast-food table ware

Starch granules imbedded into: —→ p(ethylene-co-acrylic acid)
(starch < 10%) —→ p(ethylene-co-vinyl alcohol)

★ purpose: enhance disintegration of polyolefin film

Problem: incompatibility of polymers
—→ lack of adhesion
—→ low tensile strength
—→ slow degradation



Starch in Biodegradable Plastics (2).

Starch foams: use water as blowing agent

★ purpose: replace PS foams: captured 15–20% of market

Future: Starch blends with biodegradable polyesters: PLA, PCL
PHA (PHBV)

Advantage: both constituents biodegrade
compostable, complete degradation \longrightarrow $\text{CO}_2 + \text{H}_2\text{O}$

Issues:

- poor adhesion, need of adhesion promoters and compatibility
- poor mechanical stability
- polyester more expensive than polyolefin

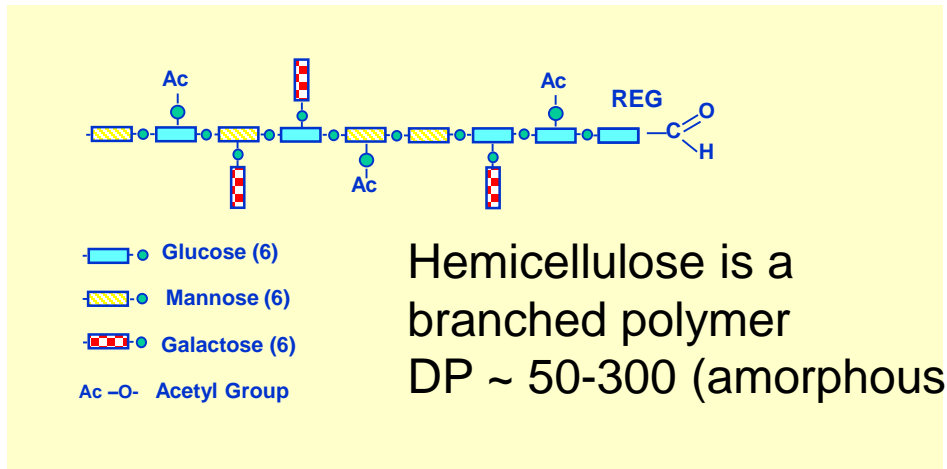


Main Properties of 20 μm Films of Starch Based Bioplastic.

Characteristics	Value		Unit	Method Test
Film size	20 - 100		μm	DIN 53353
Tensile stress - MD (23 °C, 50% r.h.)	near	21	N/mm^2	DIN 53455
Tensile stress - TD (23 °C, 50% r.h.)	near	21	N/mm^2	DIN 53455
Break elongation - MD	near	900	%	DIN 53455
Break elongation - TD	near	720	%	DIN 53455
Water vapor permeability	200		$\text{g}/\text{m}^2 \cdot \text{d}$	DIN 53380
Oxygen permeability, 23 °C, dry	22		$\text{ml}/\text{m}^2 \cdot \text{d} \cdot \text{bar}$	DIN 53380
Oxygen permeability, 23 °C, 85%	330		$\text{ml}/\text{m}^2 \cdot \text{d} \cdot \text{bar}$	DIN 53380
CO_2 permeability, 23 °C, dry	75		$\text{ml}/\text{m}^2 \cdot \text{d} \cdot \text{bar}$	DIN 53380
CO_2 permeability, 23 °C, 85%	1341		$\text{ml}/\text{m}^2 \cdot \text{d} \cdot \text{bar}$	DIN 53380

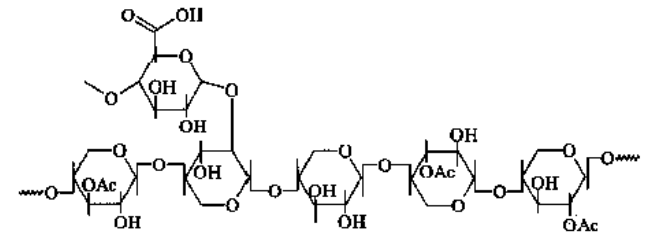


Molecular Structure of Hemicelluloses.

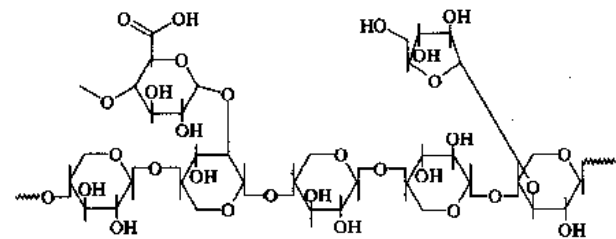


Hemicellulose is more abundant in soft wood = Galactoglucomannanes

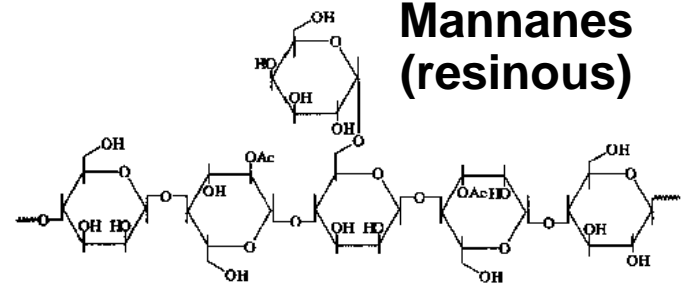
Food additives, thickening, emulsifying, jellifying agents, adhesives



Xylanes

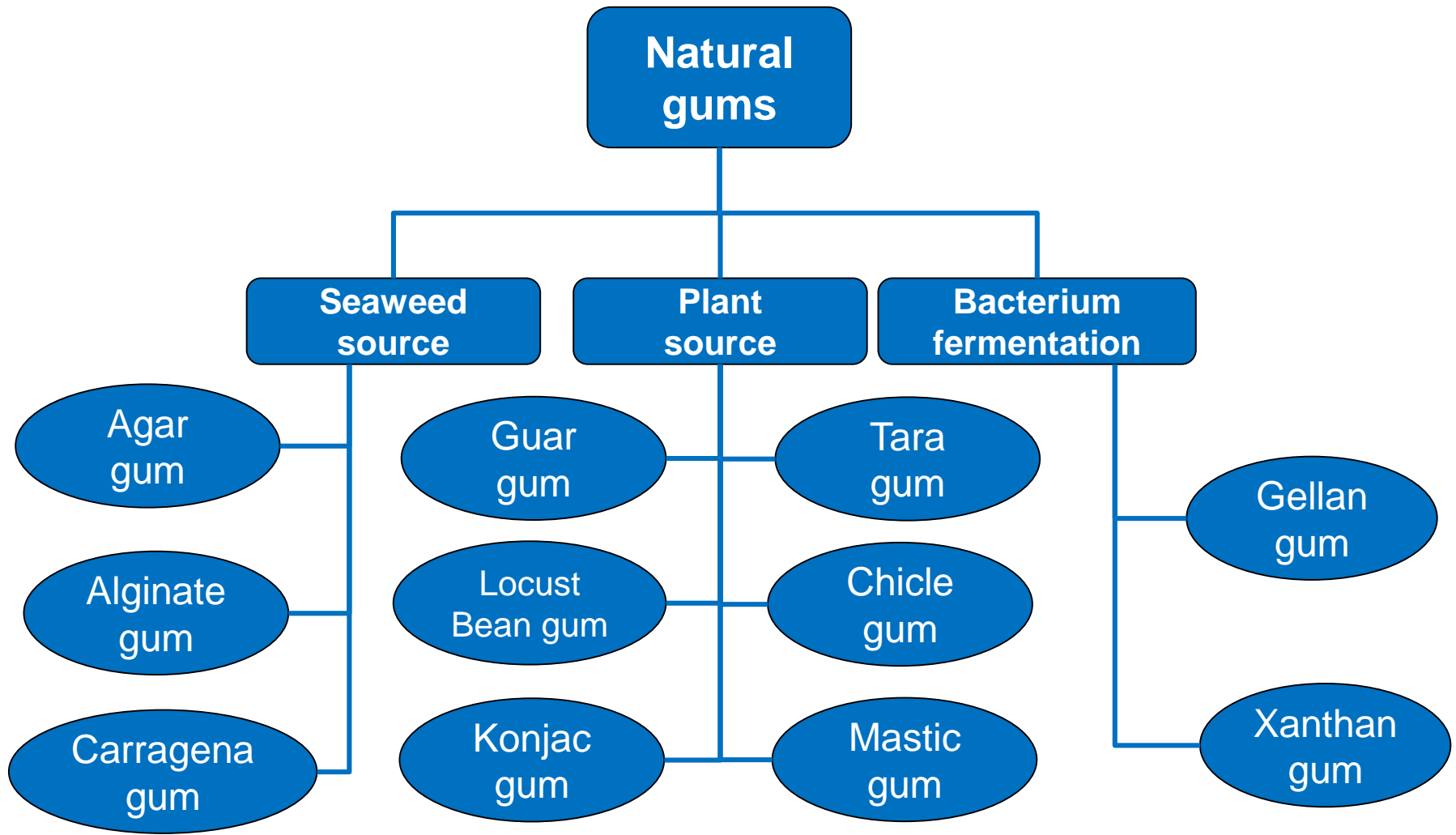


Mannanes (resinous)





Types of Natural Gums.





Sources of Plant Gums – Exudates.

Exudate gums are produced in response to an injury to the plant, and presumably function to seal off opened tissues and help prevent microbial invasions. The production and processing of the major exudate gums still involves considerable hand labor, both in stimulating their production by intentionally injuring the plant as well as in collecting the exuded substances. Nevertheless, these products are ubiquitous components of our processed foods. Major sources of exudate gums are Fabaceae (Leguminosae) or bean family.



Arabic gum,
Acacia senegal

Tragacanth gum,
Astragalus





Sources of Plant Gums – Extractives.

Some gums occur naturally in seeds or wood of certain Fabaceae species, and can be extracted from them. These also involve hand labor, and provide widely used products.



Locust bean gum
Ceratonia siliqua,



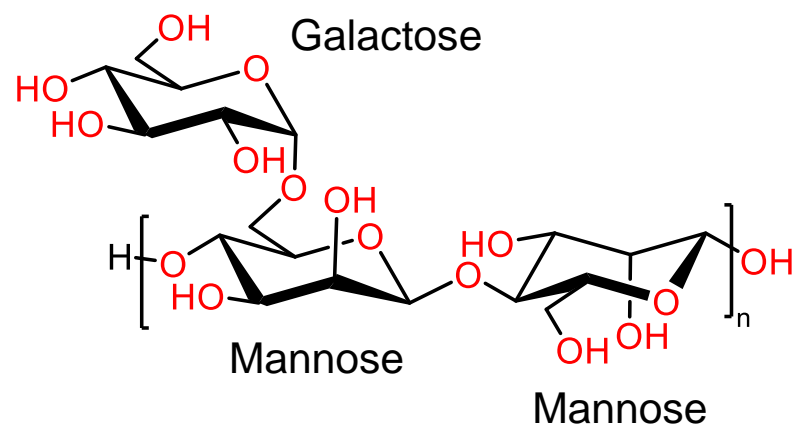
Guar gum
Cyamopsis





Guar Gum.

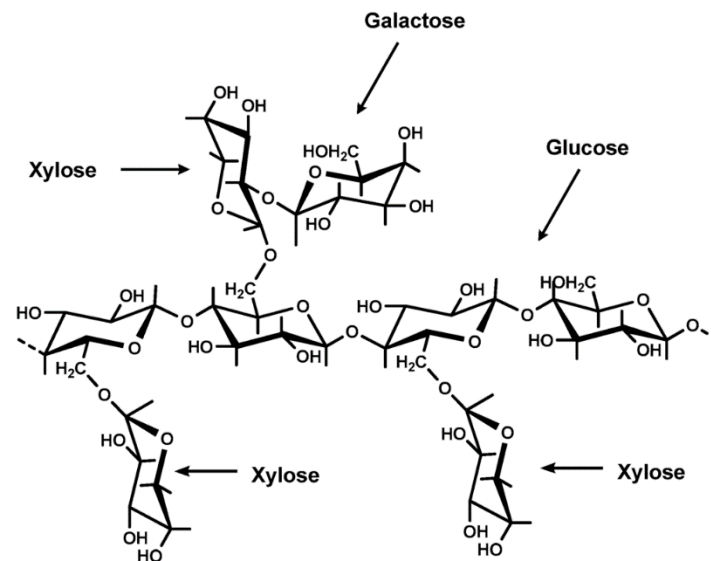
- Obtained from the seed of the legume *Cyamopsis tetragonolobus*
- The structure of the polysaccharide consists of a main chain of (1-4)-linked β -D-mannopyranosyl units with single α -D-galactopyranosyl units linked (1-6) on average to every second main chain unit.
- Guar has a high viscosity in aqueous solution, shows marked pseudoplastic behaviour and forms synergistic gels in the presence of other gums such as carrageenan and xanthan gum.





Tamarind Gum

- Tamarind gum comes from the seed of the tamarind tree *Tamarindus indica*
- It consists of a main chain of β -D-(1-4)-galactopyranosyl unit with a side chain of single xylopyranosyl unit attached to every second, third, and fourth of D-galactopyranosyl unit through α -D-(1-6) linkage
- In application tamarind finds use in the sizing of jute and as a stabilizer and thickener in the food industry.





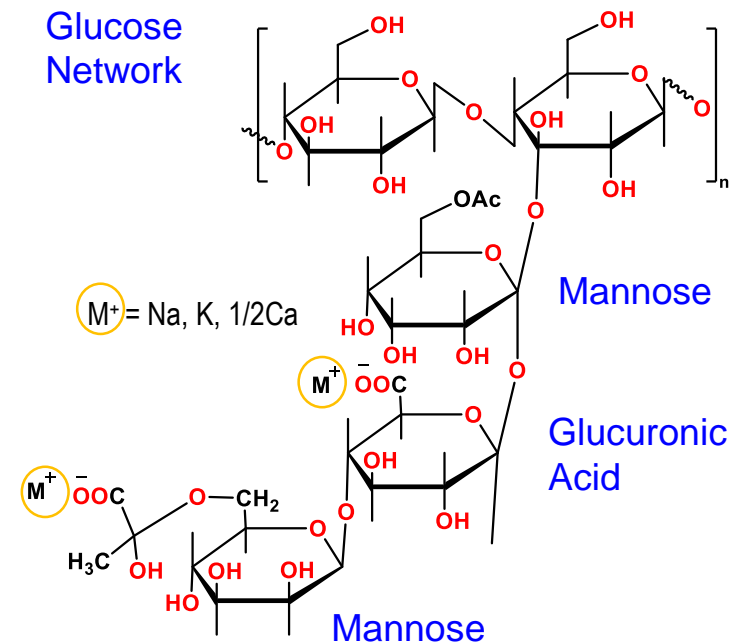
Xanthan Gum

Made by Bacterium *Xanthomonas campestris* through fermentation by using a variety of starting materials, both of plant and animal origin.

Belong to the Polysaccharide family and have a somewhat complex structure, containing glucose main chain and mannose and glucuronic acid in side chain, showing useful physical properties.

Note – can be derived from wheat, so it can contain gluten

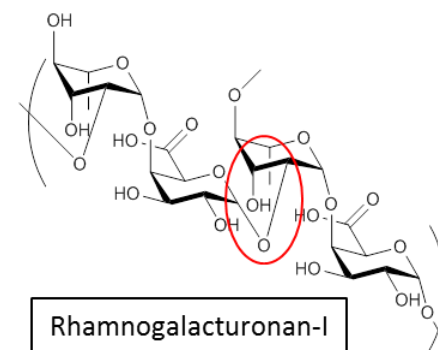
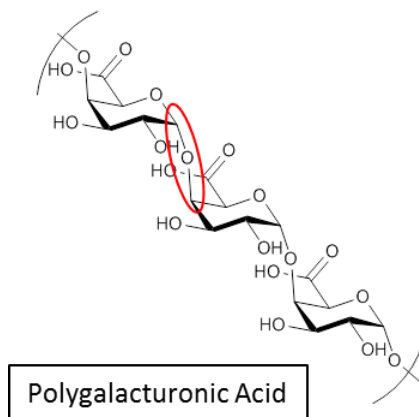
→ Should be avoided by those who are allergic to glutens





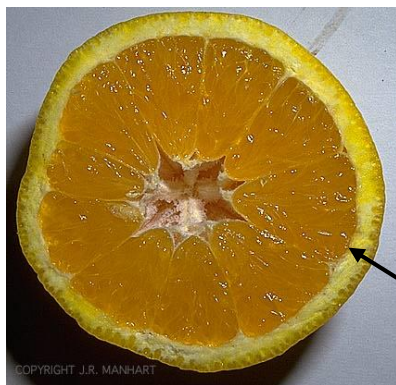
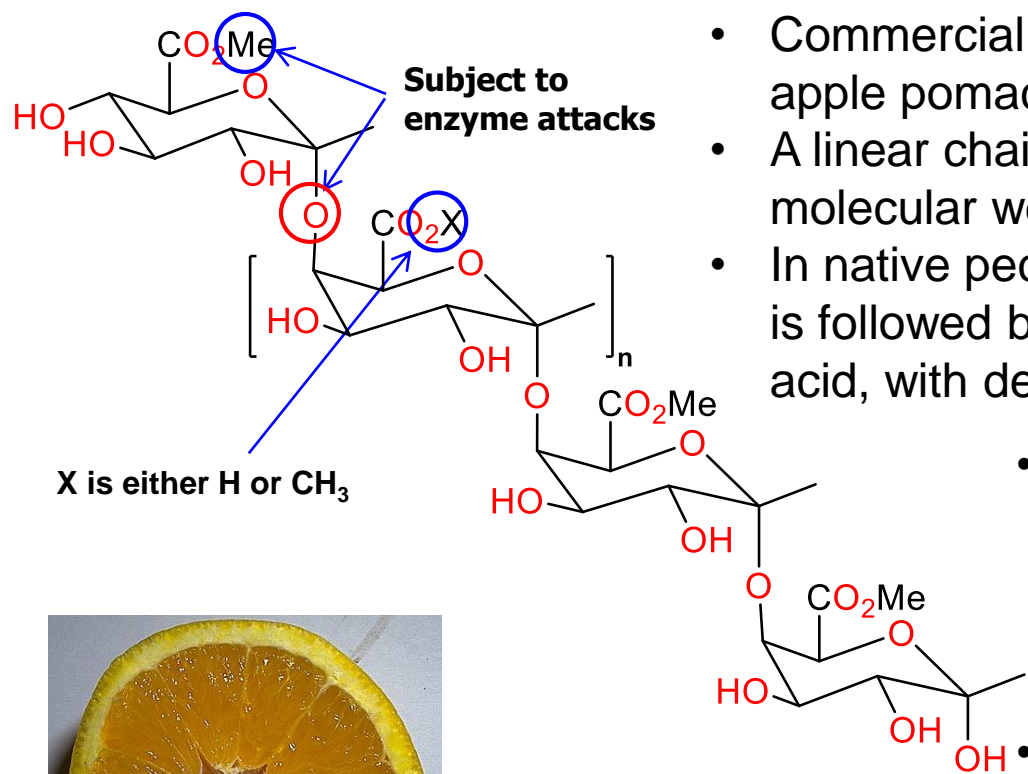
Pectin.

- Found as intracellular substance in the tissues of young plants and are especially abundant in ripe fruits, as apple, guava, pears & citrus fruits.
- Pectin is the methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 galacturonic acid units joined with $1\alpha\rightarrow4$ linkages. Rhamnogalacturonan-I (RG-I) contains a repeating disaccharide subunit of galacturonic acid/methyl ester and rhamnose [$\rightarrow2$]-rhamnose- α -($1\rightarrow4$)-galacturonic acid- α -($1\rightarrow$)].
- Pectin gels - jelly and jams





Pectin.



Pectin-rich mesocarp

- Found in virtually all land-based plant as a structural material in middle lamella of cell wall.
- Commercial pectin extracted from citrus peel, apple pomace, sugar beet, or sunflower heads
- A linear chain of galacturonic acid units with molecular weight about 110,000-150,000
- In native pectin one free galacturonic acid units is followed by 5 methyl esters of galacturonic acid, with degree of esterification (DE) of 83.3%
- DE can be controlled during extraction processing, to obtain low ester (low methoxyl) pectin (DE<50%) or high ester (high methoxyl) pectin (DE>50)
- Low ester pectins gel with calcium and high ester pectins gel with high sugar solids at low pH



Hypothetical Pectin Structure.

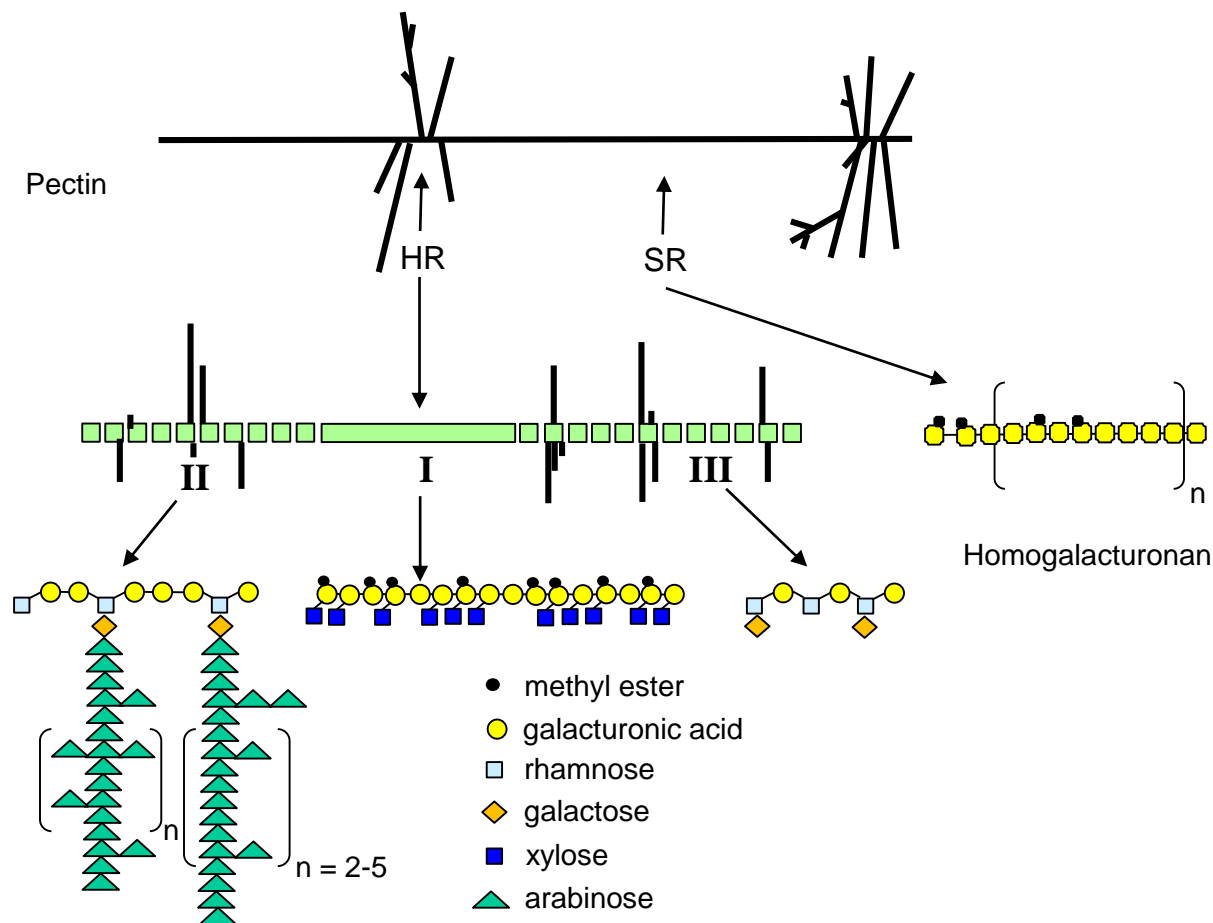


Fig. 10.2 Hypothetical structure of apple pectin showing I xylogalacturonan region, II region with arabinan side chains, III rhamnagalacturonan region making up the 'hairy region'. (From H. Schols *et al.* 'Structural Features of Native and Commercially Extracted Pectins', in *Gums and Stabilisers for the Food Industry 9* ed P. A. Williams and G. O. Phillips, RSC Cambridge, 1998, by permission of the authors.)



Gelation Properties of Pectins (Hydrogels).

❑ Gelation of high methoxyl pectin

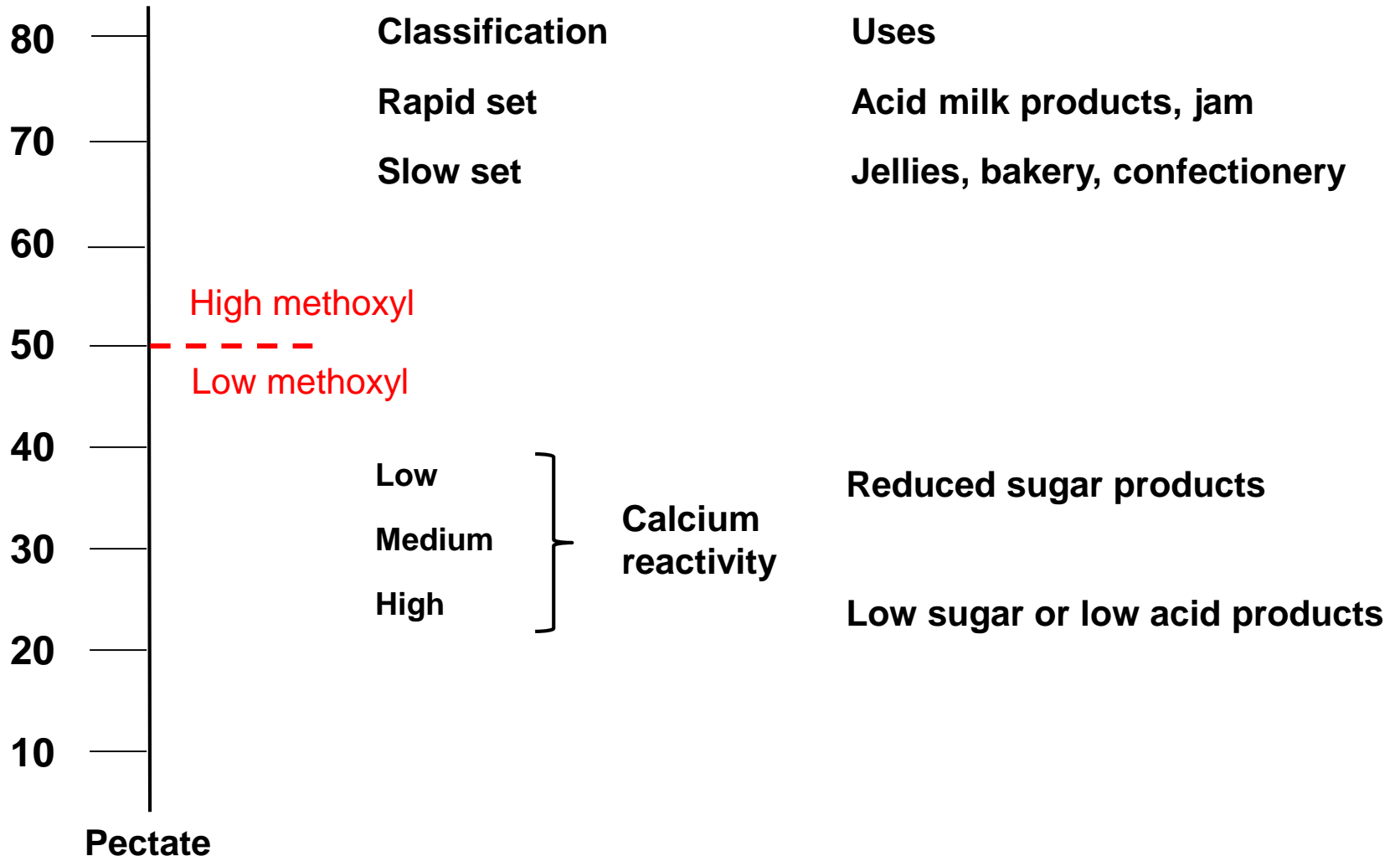
- ❑ The presence of sugars is required
- ❑ At a sufficiently low pH
- ❑ Reduced pH leads to increased gel strength and setting temperature
- ❑ Nature of sugars affects pectin performance (e.g. replacement of sugar by glucose syrup leads to increased setting temperature and pH for gelation, but reduced maximum gel strength)
- ❑ Increased sugar amount leads to increase of setting temperature and optimum pH

❑ Gelation of low methoxyl pectin

- ❑ Governed mainly by interaction between pectin and calcium ions
- ❑ Thus the presence of sequestrant has effects (citrate, di-/poly-phosphate) on gelation, and can be used to produce workable gel system
- ❑ Reactivity increases with decreasing degree of esterification
- ❑ Increased solubles and reduced pH favors gelation



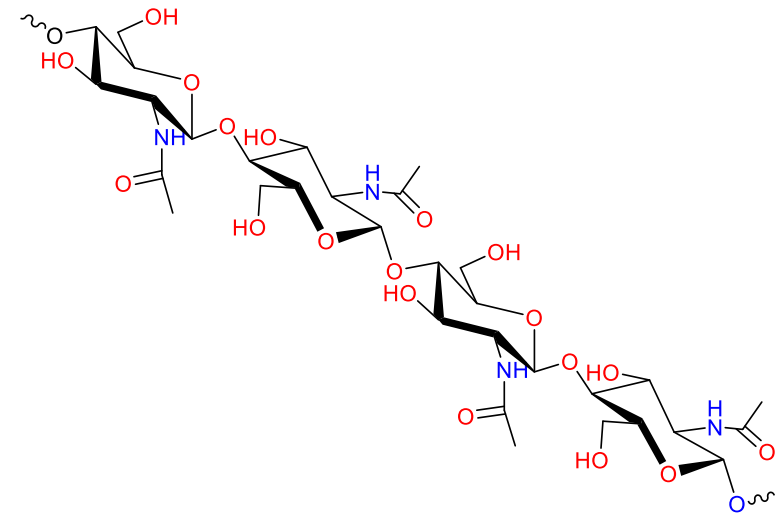
Gelation Properties of Pectins.





Chitin & Chitosan.

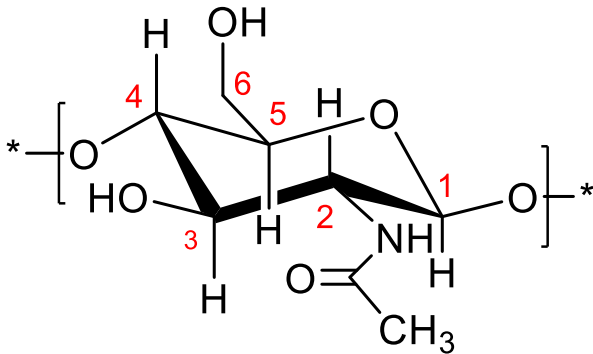
- Functions in a manner similar to collagen in chordates.
- Forms the tough fibrous exoskeletons of insects, crustaceans and other arthropods, and, in addition to its presence in some fungi it occurs in at least one algae.
- The structure of chitin is similar to that of cellulose but with glucose replaced with N-acetyl-D-glucosamine units linked β -D-(1-4) in a linear chain. Chitosan is the deacetylated form of Chitin.
- Today chitin is known as the novel material used in the biomedical, pharmacological and biotechnological fields.





Chitin and Chitosan.

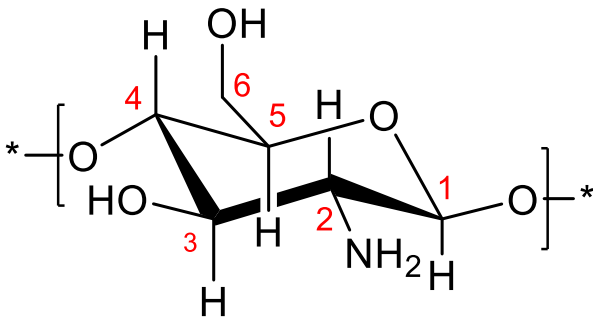
Chitin



2nd most abundant natural polymer after cellulose

2-acetamido-2-deoxy-b-D-glucopyranose

Chitosan



By: (1) alkaline hydrolysis of amido group (synthetic)
(2) by chitin-deacetylase (natural)

2-amino-2-deoxy-b-D-glucopyranose



Chitin and Chitosan (2).

Definitions:

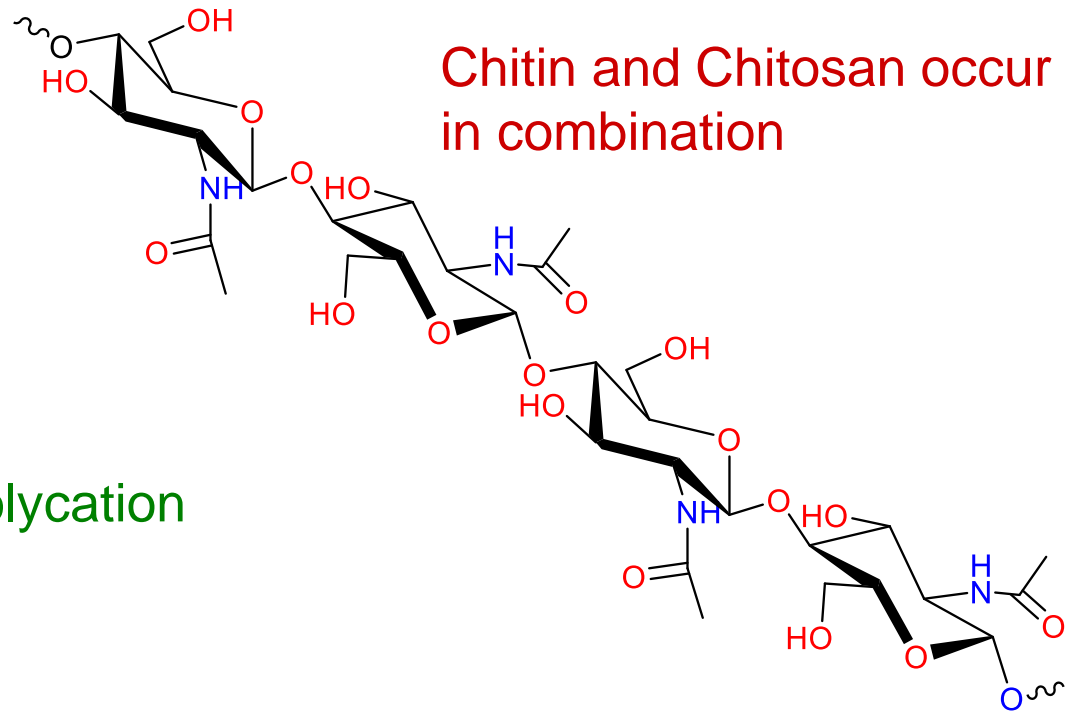
Chitosan:
soluble in dilute acids

↳ formation of polycation

Chitin

insoluble in diluted acids

Chitin and Chitosan occur
in combination



Poly[β -(1 \rightarrow 4)-2-acetamido-deoxy-D-glucopyranose]

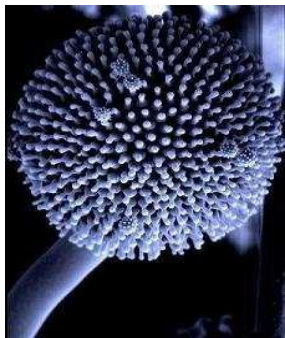
Chitin is considered the parent compound of chitosan, therefore the proportion of glucosamine in chitosan is reported as “degree of N-deacetylation” (DA > 50%)



Sources of Chitin and Chitosan.

2nd most abundant natural polymer after cellulose (50%)

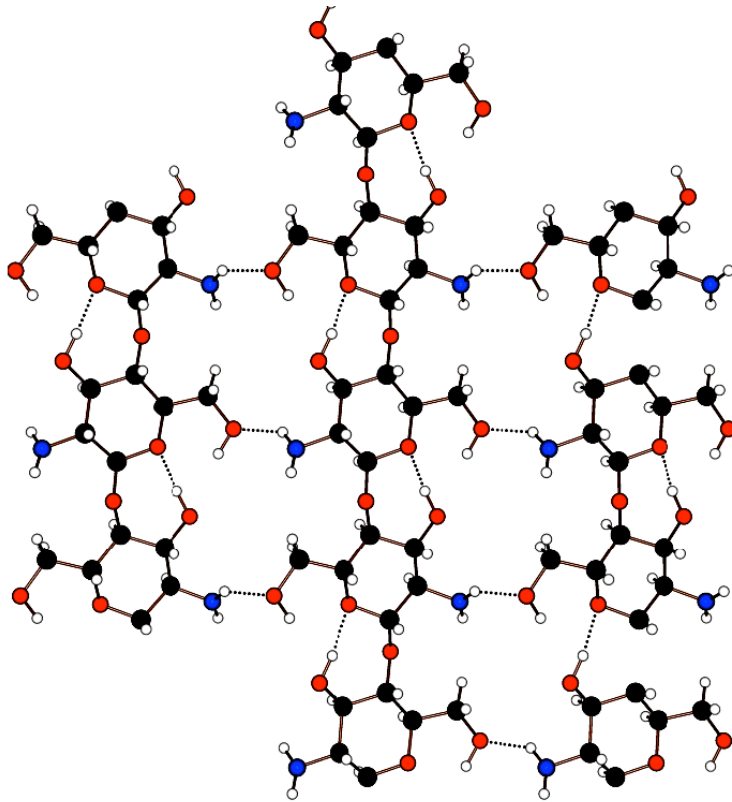
~10 Gt synthesized each year



Sources	Where is found	Chitin (%)
Fungi Ascomicetes Basidiomicetes Ficomycetes	Cellular wall Mycelium Spore	2.9-20.1(*) * in ratio to dry mass of cellular wall
Algae Cloroficee Diatomee	Cellular wall	weak
Cnidars Entozoan Idrozoan	Egg capsule Internal and medium membranes	3-30
Brachiopods Articulated Inarticulated	Cuticles Cuticles and shells	0.2-38
Annelids Polykets	Hairs	Lubricant
Molluscs Poliplacophors Gastropods Cephalopods Lamellibranches	Shells and toots Shells, toots and plaques Shells	6-40
Arthropods Crustaceans Insects Arachnids	Exoskeleton, membranes between segments, cuticle	2-72(*)
Pogonofores	Tubes	33



Properties and Uses of Chitin and Chitosan.



- Waste Treatment (positive charge in acidic media and chelating power) :
 - Metal chelating cationic flocculating agent
 - Sewage effluents
 - Metal finishing/electroplating wastes
 - Paper mills
 - Radioactive wastes
- Protein flocculation for feed market
- Rendering plants, Milk and Vegetable Processing
- Poultry/Egg processing
- Single Cell Protein Recovery
- Film forming properties (food)



Sources of Chitin.

Crustaceans, Insects: exoskeleton



Major source

(currently: shellfish waste: animal feed)

Annual harvest:

$1,700 \times 10^3$ tons shellfish

$18,200 \times 10^3$ tons krill

660×10^3 tons squid

Assumption: extraction of half the waste left from food processing:

96,000 tons chitin



Other Sources of Chitin.

Chitin

Insects

Fungi

Chitosan

Shrimp

Fungi

40% of dry cell wall

Natural occurrence: copolymer
in conjunction with other
polysaccharides, proteins, minerals

$$M_w = 0.1 - 4 \times 10^6$$

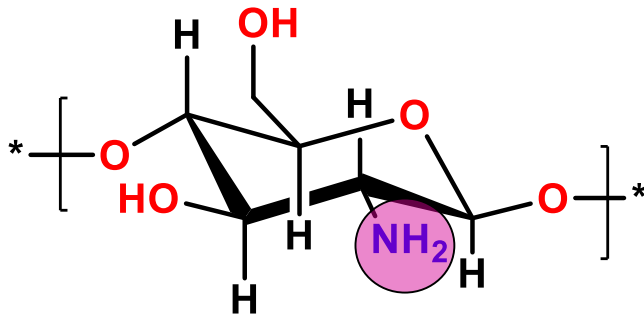
$$M_n = 5 - 8 \times 10^4$$

α , β , γ chitin polymorph

Many occur simultaneously in the same organism



Chemistry of Chitin and Chitosan.

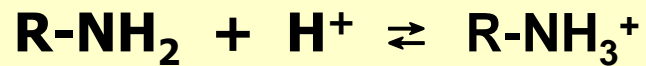


Reactive site

Chemical reaction

- change in solubility
 - absorption affinity
 - hydrolysis ability
- grafting of vinyl polymers
 - surface modification
- formation of Schiff Base

All chemical transformation in solution!



Basic Properties



Fabrication and Application of Chitin and its Derivatives.

Fibres: wet spinning

Direct or via chitin xanthate

LC nature of chitosan

Chitin acetate

Lyotropic, extrusion from HCOOH



Purpose:

medical textiles
sutures

Films: chitosan: excellent film forming capabilities



Purpose:

membranes
wound care
artificial skin
packaging



Fabrication and Application of Chitin and its Derivatives (2).

Beads: uniform size: 50 nm – 2 mm
highly porous
produced by suspension cross-linking
potential coating of beads with polyelectrolytes



Purpose: Metal chelation
Waste water treatment
Drug delivery
Enzyme immobilization



Fabrication and Application of Chitin and its Derivatives (3).

Microcrystalline powders: **by controlled acid hydrolysis**



Purpose:

waste water treatment
pharmaceutical/medical



spray m-crystalline chitin into film
and use as non-woven

Shaped objects:

orthopedics, contact lenses

Solution, gels:

cosmetics, waste water treatment



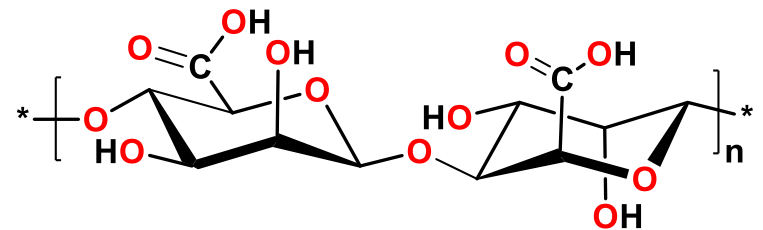
Applications of Chitosan.

Wastewater treatment	Removal of metallic ions; flocculants; coagulants of proteins, dye, amino acids
Food industry	Removal of dye, suspended solids, etc. Preservant; animal food additive color stabilization
Medical	Bandages, skin burn, contact lens blood cholesterol control controlled release of drugs
Biotechnology	enzymes and cell immobilization protein separation; cell recovery, chromatography
Agriculture	seed coating, controlled agrochemical release fertilizer
Cosmetics	Moistening, body creams, lotion
Pulp and paper	Surface treatment, photographic paper



Brown Algae and Alginates (Feoficote = Laminaria).

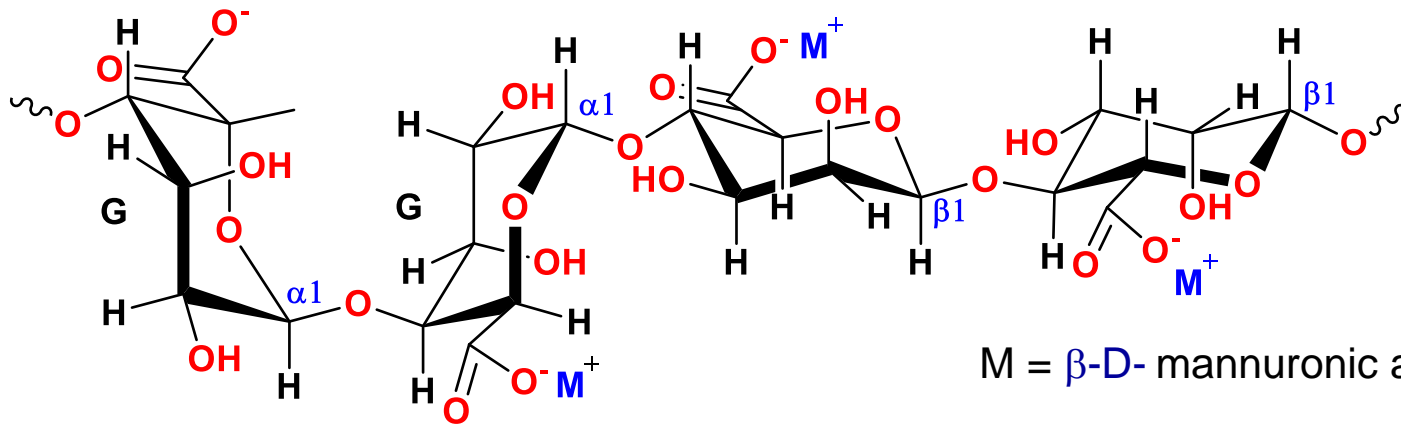
- Alginate is extracted from seaweeds, such as giant kelp (*Macrocystis pyrifera*).
- The chemical constituents of alginate are random sequences of chains of β -D-mannuronic and α -L-glucuronic acids attached with 1 \rightarrow 4 linkages.
- Gauze for wounds (soluble in H₂O/NaCl) Strong affinity for heavy metals
- They are useful as gelling and thickening agents (paper, cosmetics, insecticides)
- Food industry (E400-E404, ice cream, milk shake)





Alginates.

Heteropolysaccharides, often block copolymers



G = β -L-guluronic acid

M = β -D-mannuronic acid

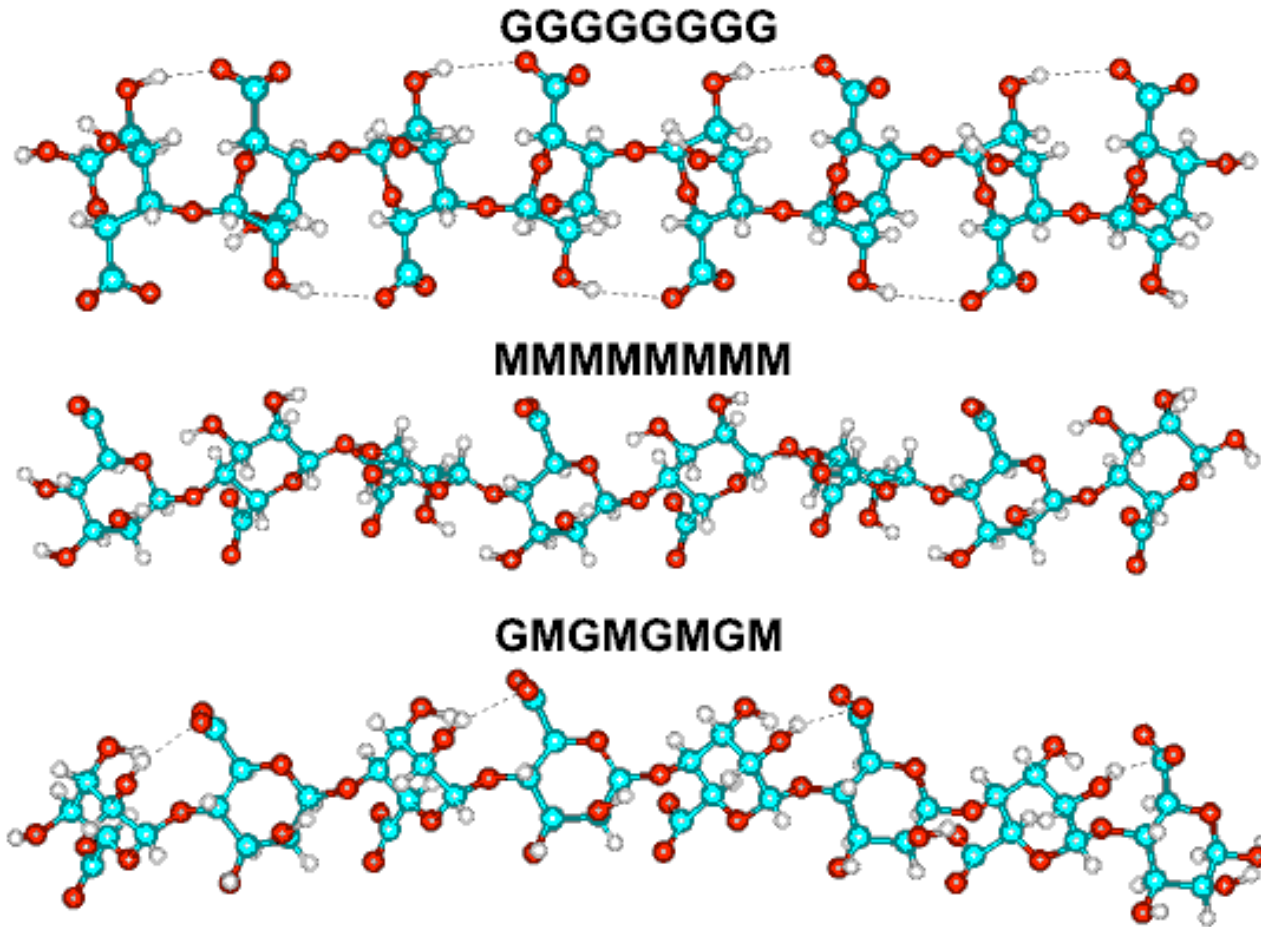
β -1.4 poly(guluronic) acid \longleftrightarrow epimers β -1.4 poly(mannuronic) acid

($0.80 < M/G < 2.1$) linear polymers with 5-100.000 residues

Formation of hydrogels by interchain association via di- and tri-cations, mostly Ca^{2+}



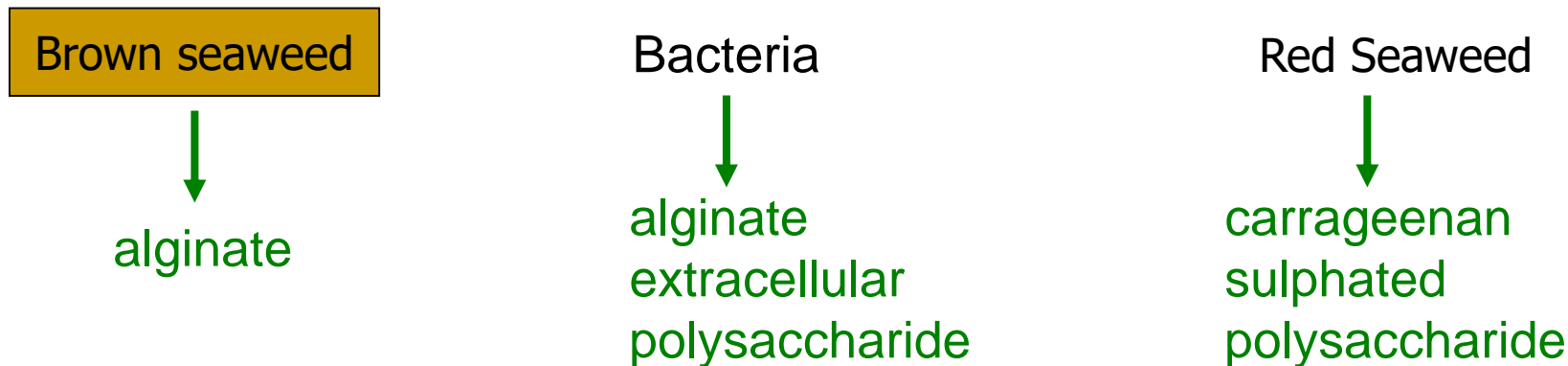
Alginate Structure.



Stabilization of helices through formation of intramolecular hydrogen bridges



Alginate Sources.



Bacterial alginate: structural peculiarity:
controllable mannuronic/guluronic acid ratio

	M_w	M_n
Seaweed alginate	4.7×10^4	1.4×10^4
Bacterial alginate	12.7×10^4	4.3×10^4

Lee, J.W. et al. Carbohydrate Polymers 1996, 29(4) 337-345



Influence of Counter-ions on Alginate Polymer Structure.

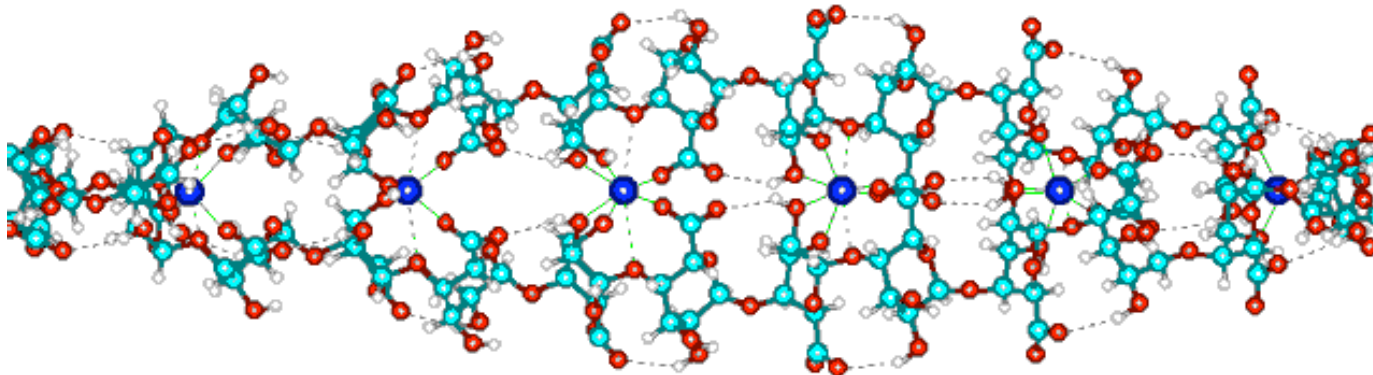
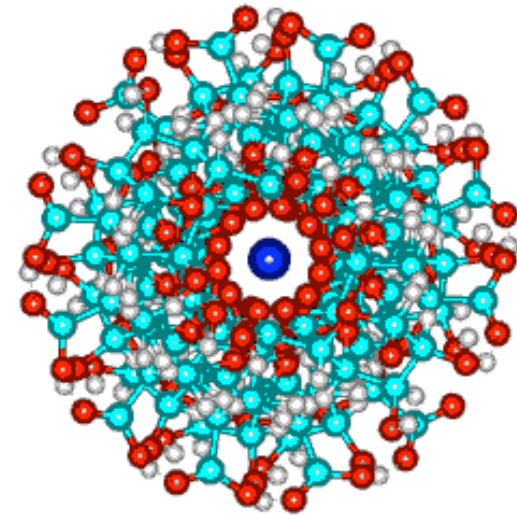
$\text{Na}^+ \rightarrow$ thickening

$\text{Ca}^{++} \rightarrow$ jellifying (fibres)

$\text{Mg}^{2+} \ll \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$

G prevalent \Rightarrow rigid gels

M prevalent \Rightarrow elastic gels





Alginate Isolation.

Seaweed alginate

Culturing under water
harvest 4 × per year



Grinding



Washing



Solubilisation (hot alkali)



Precipitation (CaCl_2)



Neutralize



Alginic acid



Addition of Na_2CO_3



Na-alginate (powder)



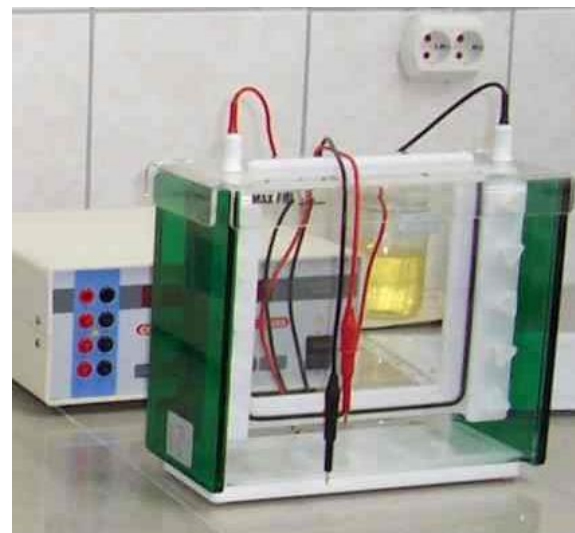
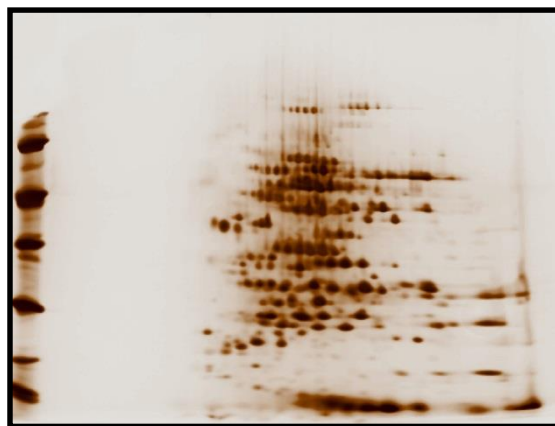
Application of Alginates.

FOOD

Water holding capacity:

- Sacrificing agent, prevents meat dehydration
- Gelling, emulsifying, stabilizing

Gel Electrophoresis !!





Industrial Application of Alginates.

1881: Isolation patented, E.C.C. Stanford

boiler treatment

1929: Kelco Company, Japan: milk soluble alginate

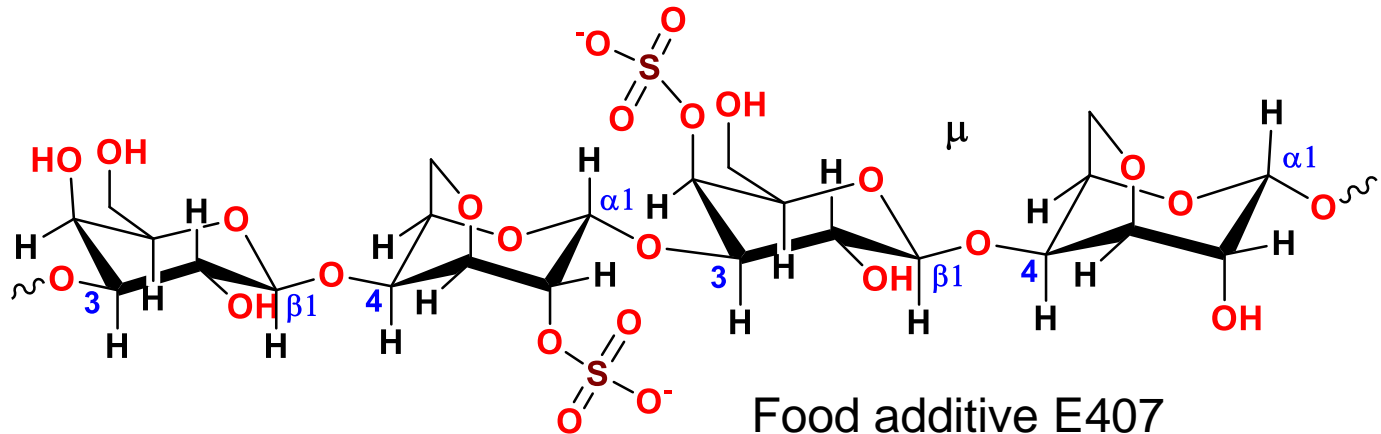
ice cream stabilizer

Property	Application
Water holding	paper industry (coating, rheology control, textile printing
Gelling	Explosives (elastic gels from reaction with borate
Emulsifying	polishes, antifoams, lattices
Stabilizing	cleaners, ceramics

2009 production of alginates was 26,500 tonnes with a value of about US\$318 million (Bixler & Porse 2010). China is said to produce ~ 8-10,000 t of alginates from cultivated *Laminaria japonica*. The main producers are Scotland, Norway, China and the USA, with smaller amounts being produced in Japan, Chile, and France. *Ascophyllum nodosum* and *Laminaria hyperborea* are used in Norway and Scotland.



Carageenans (Red Algae).



Food additive E407
as thickener, stabilizer, texture agent

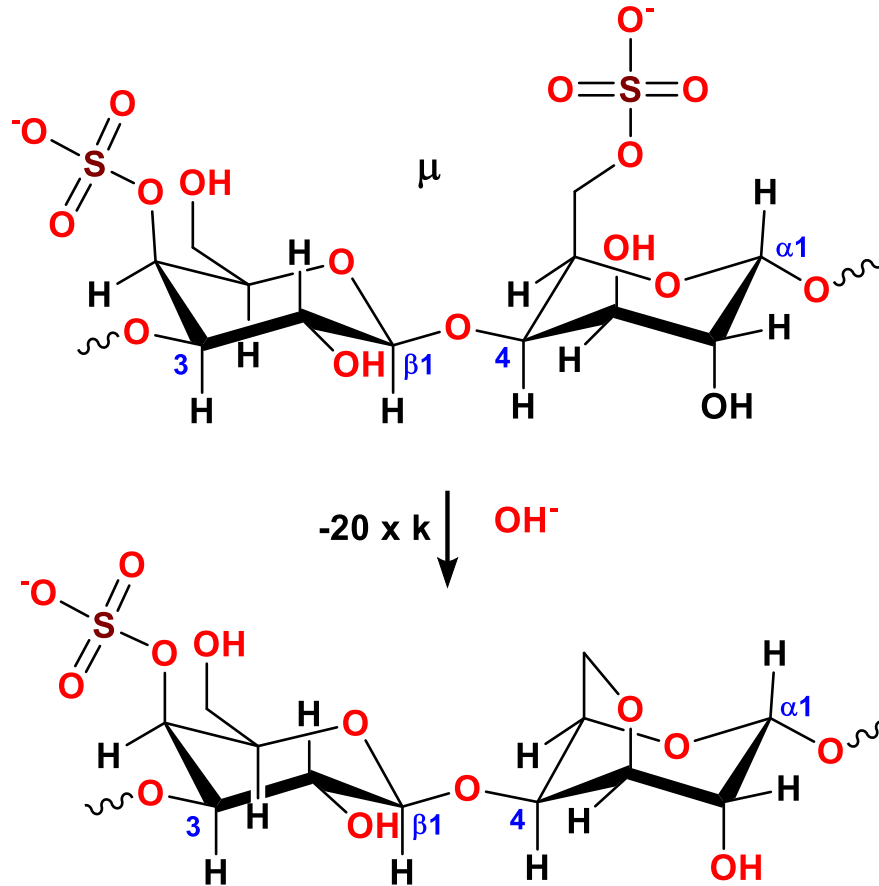
Alternate copolymers of (1→3)-β-D-galactose-4-sulfate and of (1→4)-α-(3,6)anhydro-D or L-galactose-2-sulfate

~ 25.000 residues for chain and various forms (κ, ι, λ)

Only anhydrous forms can jellify via a transition:
coil ⇒ **helix** induced by addition of K⁺ or Ca²⁺ ions
Gained from red seaweed: Kappa, Iota, Lambda



The k-carageenan (*Girgatina Pistillata*, *Hypnea*, *Soleria Girgatina*, *Chondrus*, *Eucheema cottonii*).

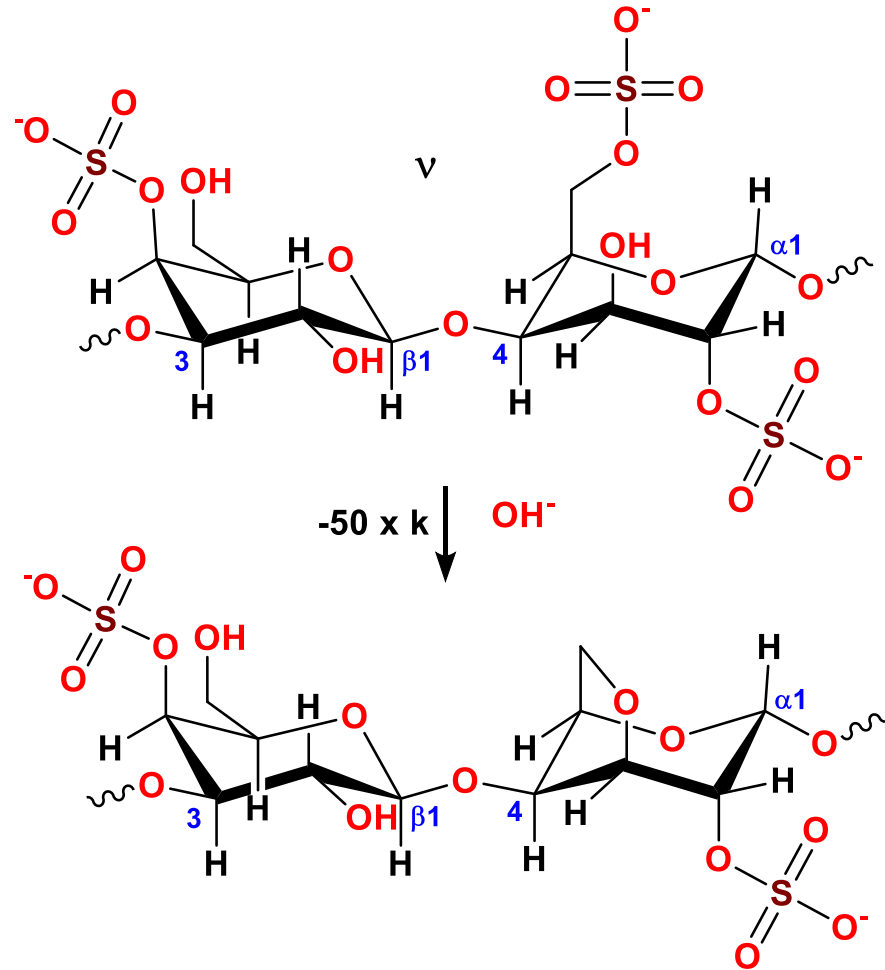


+ cations \Rightarrow rigid and fragmentable gels with sineresis, instable to cold



The λ -carageenans (*Eucheuma Spinosum*).

+ cations \Rightarrow elastic gels
thermo reversible,
stable to cold



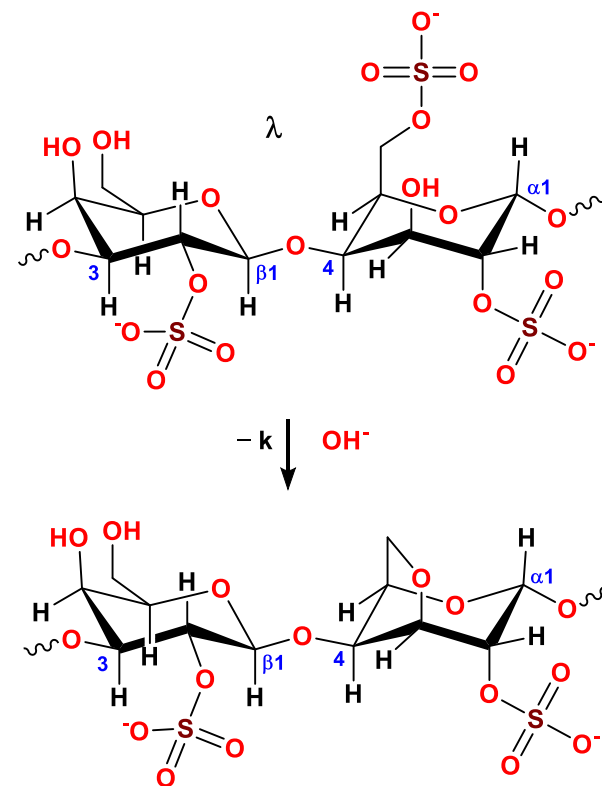


The λ -carageenans (*Gigartina pistillata*, *Chondrus crispus*).

+ cations \Rightarrow no gels

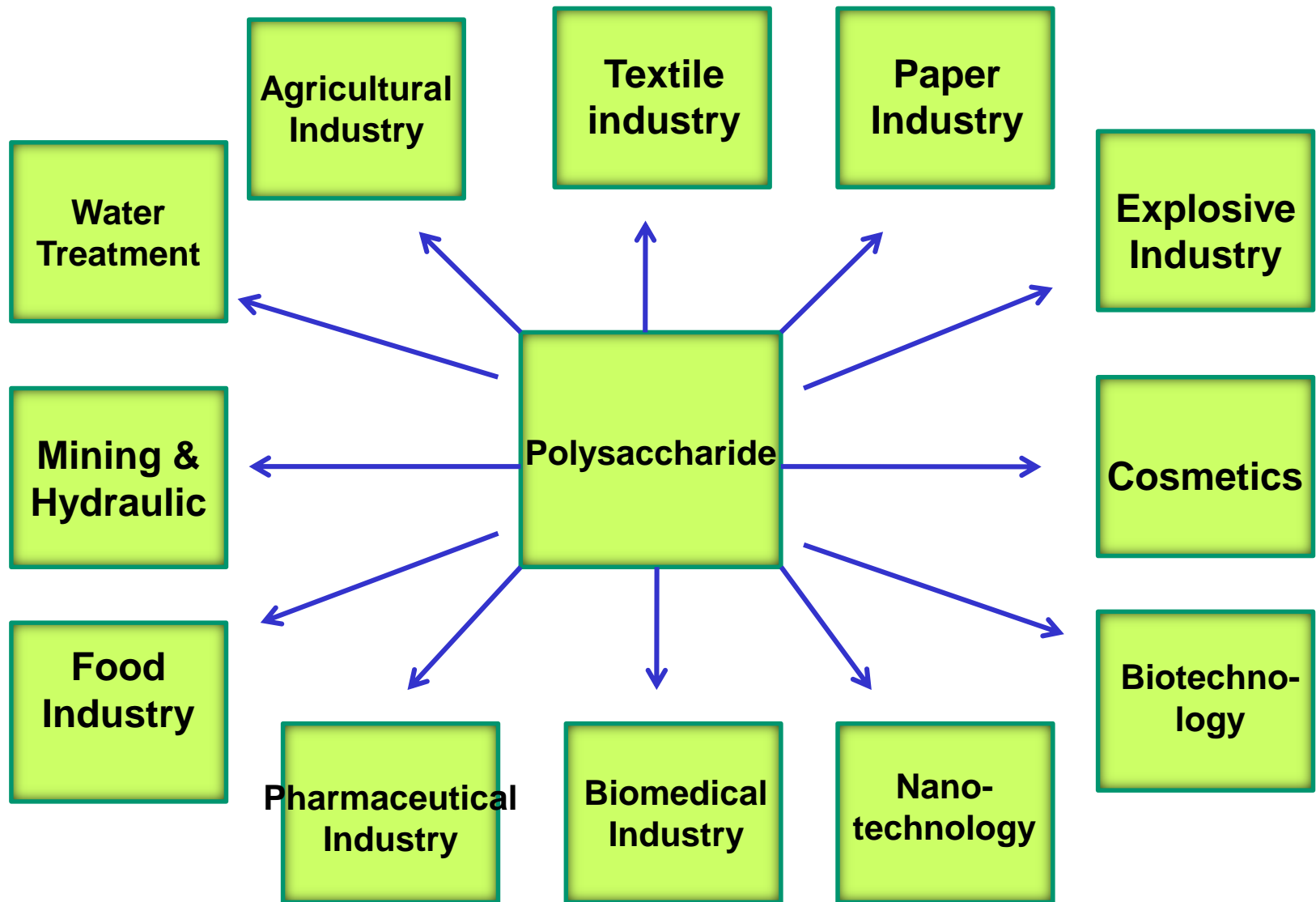
Solubility in water at 20°C

Kappa	Iota	Lamda
Soluble	Na ⁺ salt is soluble	Soluble
Na ⁺ , Ca ⁺⁺ , NH ₄ ⁺ salts swelling	Ca ⁺⁺ salt swelling and forms a thixotropic suspension	
Differences caused by different contents/substitution of sulphate esters		





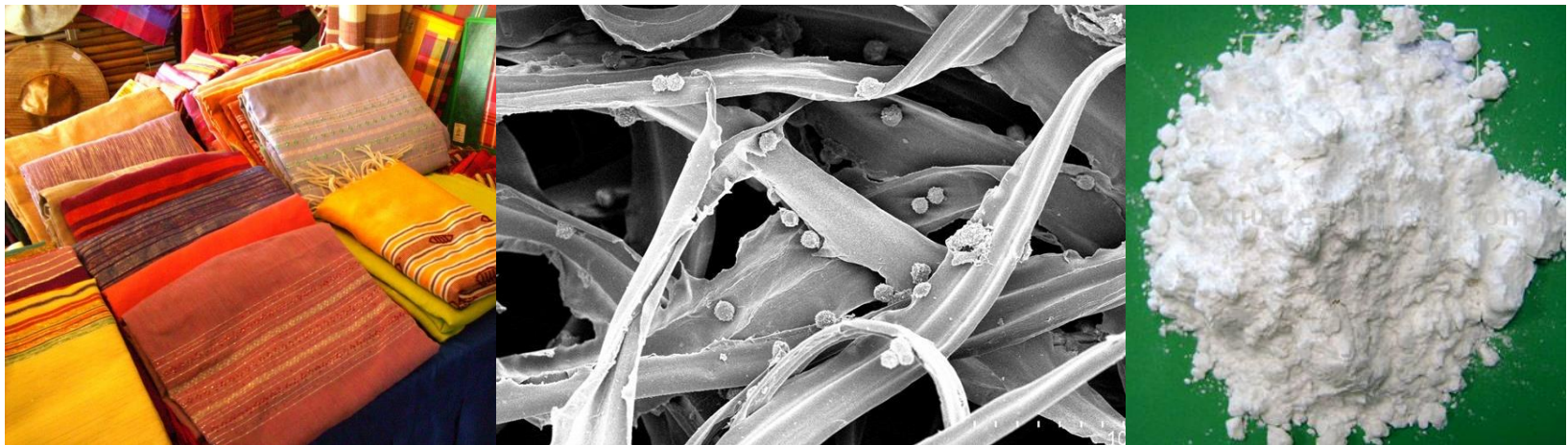
POLYSACCHARIDES IN INDUSTRIES.





TEXTILE INDUSTRY.

- Textile Industry since known: depended on cellulose & starch.
- Cellulose is the major raw material whereas starch is used for sizing yarns, hold colors etc.
- Later on, some polysaccharides replaced starch as:
 - *Alginates: For water proofing and fire proofing fabrics*
 - *Guar gum: For sizing, finishing and printing*
 - *Tamarind gum: Important sizing material for textile*
 - *Chitin: As binder in dyes & fabrics*





New modifications in polysaccharides has improved their applications.

- Chitosan + Monocholoacetic Acid in presence of alkali gives carboxymethylchitosan: A new finishing agent in medical textile possessing antibacterial activity.
- Amphoteric polysaccharides as carboxymethyl hydroxypropyl trimethylammonium chloride galactomannan used in the treatment of textile fibers: prevent color, impart crease resistance or softening





PAPER INDUSTRY.

- Paper made from wood is in turn a cellulose product.
- Starch is used to improve the strength of the sheets.
- Now different polysaccharides along with different combinations & modifications are used to improve the efficiency of paper as:
 - Cellulose + Xyloglucan together → improve performance of paper
 - Chitin: used in processes to size & strengthen paper
 - Modified polysaccharides (such as starches, gums, chitosans, celluloses, alginates, sugars etc.) + amphiphilic hydrocarbons (e.g. surface active agents) → improve softness & enhance surface feel





FOOD INDUSTRY.

- Earlier only a limited number of polysaccharides as starch, plant gums and exudates were used in different food products.
- Maize starch : thickening sauces, pudding and gravies; used for preparing ice cream cones which gives extra strength.
- Now different polysaccharides and their combinations are used in the food industry:
 - Pectin : stabilizer in acidic protein drinks and fat substitute in baked goods.
 - Alginic acid : gelling agent, thickening drinks & ice – creams. Also causes esferification of natural juices & vegetables which ‘explodes’ on tongue.
 - Guar gum : gelling, viscosifying, thickening, clouding, and binding agent as well as used for stabilization, emulsification, preservation, water retention, enhancement of water soluble fibre content etc.





FOOD INDUSTRY (2).

- Liquid glucose and High maltose corn syrup not only prevents sucrose crystallization but also imparts a smoother texture.
- Dextrose Monohydrate is used in jams and jellies and preserves to control sucrose crystallization, body appearance and osmotic pressure.
- Maltodextrin is used in baby foods : readily digested. Also acts as a baking agent, viscosity modifier to control the moisture





EXPLOSIVE INDUSTRY.

- The uses of polysaccharides are diversified.
- Synthetic materials like nitroglycerine and trinitrotoluene are used in the manufacture of explosives.
- Polysaccharides play their role as:
 - Cellulose + nitric acid \rightarrow nitrocellulose or gun cotton : Explosive component of smokeless powder which has a role in mining and hydraulic fracturing.
 - Guar gum acts as a water – proofing agent for explosives when mixed with ammonium nitrate, nitroglycerine etc.



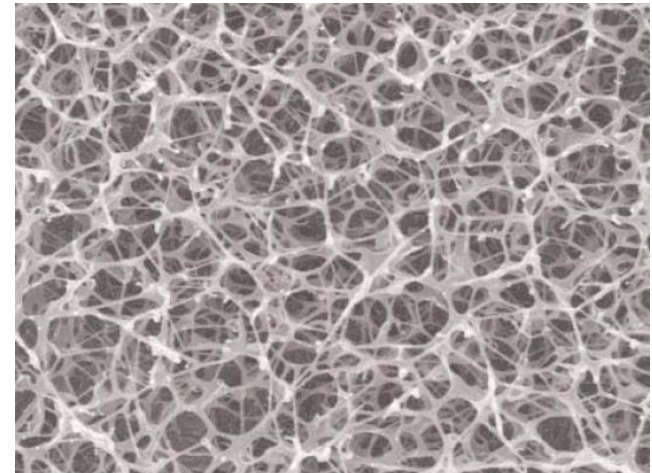


MINING & HYDRAULICS.

- Polysaccharides such as guar gum (i.e. its derivatives 2-hydroxy propyl guar & carboxymethyl guar, xanthan gum, scleroglucan, carboxymethyl cellulose and other galactomannans, such as locust bean gum) induce high viscosity of their aqueous solutions: useful in underground oil well operations for drilling, fracturing, diverting and ground packing.



Cryo SEM micrograph of flask frozen 2% hydroxypropyl guar in deionized water.





WATER TREATMENTS.

- Polysaccharides are now used to treat impure water for its purification.
- Carboxymethylguar → inhibit the formation of mineral scales and also stable to oxidizing biocides.
- Cationic tamarind kernel polysaccharide → flocculant for treatment of textile industry water waste.
- Plantago mucilage → remove dyes from water textile waste water.
- Chitin → manufacture of ion – exchange resins for purification of water.



Industrial cooling tower



COSMETIC INDUSTRY.

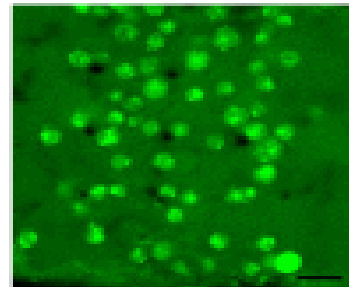
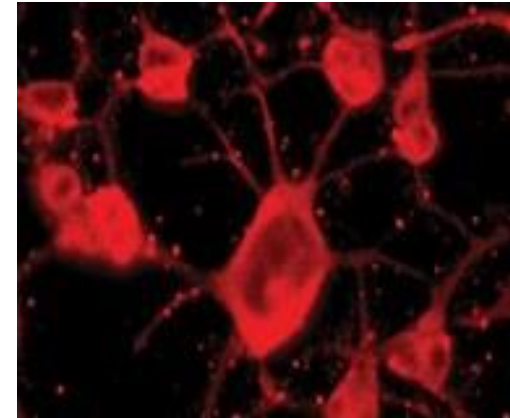
- Different polysaccharides in different cosmetics are now being used as its natural form or as their derivatives.
- Starch → extensively used in the manufacture of powders.
- Carboxymethyl cellulose, carboxymethyl guar (& their other derivatives) & natural gums such as tamarind gum, alginates etc. are used as thickener in tooth-pastes, shampoos, conditioner in shampoos etc.
- Partially nitrated cellulose → pyroxylin → manufacture of plastics, lacquers & nail-polishes.
- Pectin acts as a stabilizer in many cosmetic preparations.





BIOTECHNOLOGY.

- Polysaccharides (Chitin & Alginate) + metal oxide (e.g. iron oxide) → magnetic novel particle conjugates → used in assay for detecting target molecule.
- Starch – based scaffolds for bone – tissue engineering.
- Alginate hydrogels as matrices for tissue engineering e.g. for cell immobilization and entrapment.





Chitosan :

Forms	Uses
Solution	Biostatic agent, Haemostatic agent
Gel	Delivery vehicle, spermicide
Film/Membrane	Dialysis membrane, contact lens, wound healing

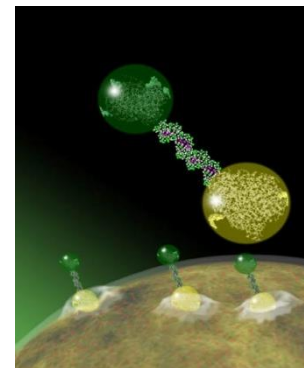
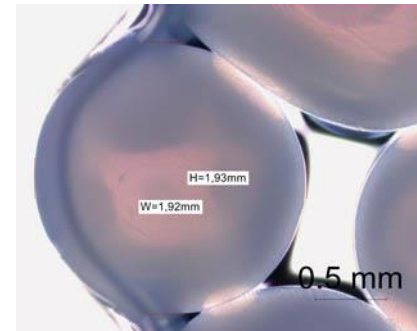
- **High amylose corn starch & glucomannan → new denture adhesive.**
- **Inulin prevents digestive tract infection & support immune system.**
- **Alginate: impression making material in dentistry, prosthetics, life – casting.**



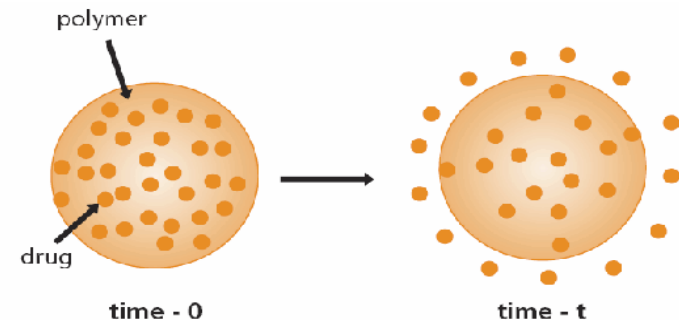


PHARMACEUTICAL INDUSTRY.

- Polysaccharides are primarily used as diluents, binders, disintegrants, adhesives & glidants in conventional dosage forms like tablets and capsules.
- But with the advent of time the role of polysaccharides in pharmaceutical industry is renovated.
- Alginate is used as a metal detoxifier in blood.
- Pullulan, a new polysaccharide → make strong films with high adhesion and oxygen barrier properties → Extensively used in manufacture of capsules.
- Inulin + galactomannans (guar gum) → potential vehicle for colonic drug delivery
- Tamarind seed polysaccharide along with guar gum → high drug holding capacity for sustained – release preparations e.g. verapamil HCl



Pullulan capsules
(www.capsugel.com)





PHARMACEUTICAL INDUSTRY (2).

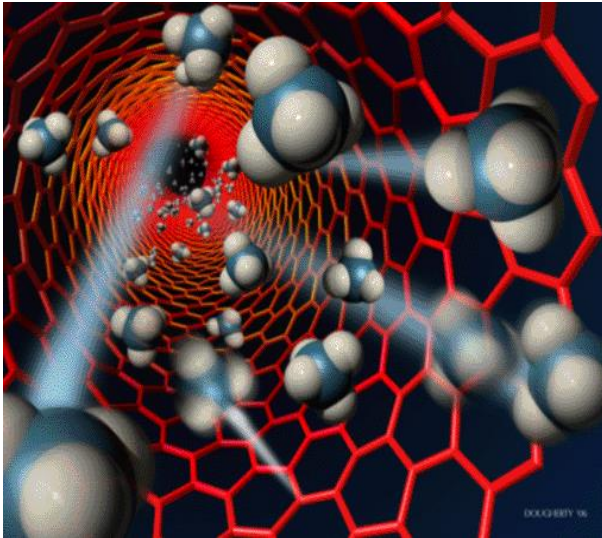
- Pulluans/dextrans/mannans/amylopectin mediate liposomal interaction with targeted cell → drug delivery, targeting & immunization.
- Pectin → prevents constipation & diarrhoea & used in throat lozenges as demulcent.
- Alginic acid acts as appetite suppressant.
- Non-ionic surfactant vesicles (niosomes) appended with o-palmitoylpullulans & cholesteroylpullulans → anchored onto drugs (e.g. propranolol HCl) → NDDS



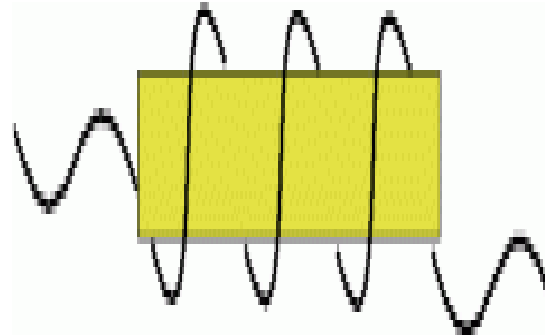


NANOTECHNOLOGY.

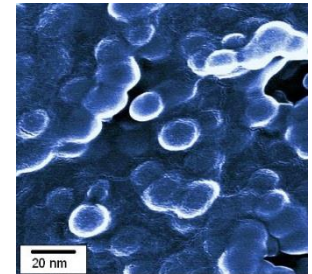
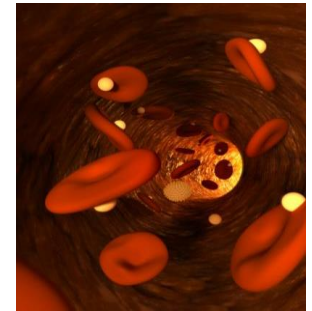
- β -1,3 glucans found in biologically produced polysaccharides as curdlan, schizophyllan & scleroglucan exist in triple – stranded helix structure \rightarrow polysaccharide for nanotubes.



nanotubes



*Triple stranded
helix structure*



nanoparticles



MISCELLANEOUS.

- 1 gram of glucomannan can absorb up to 200 ml of water → absorbant articles → disposable diapers & sanitary napkins.
- Biofuel → glucose from starch can be further fermented to ethanol.
- Chitin → help plants to develop healthy immune responses whereas chitosan → acts as a biocontrol elicitor in agriculture / horticulture.
- Industrial separation membranes & ion exchange resins are made from chitin.





MISCELLANEOUS (2).

- Tamarind kernel powder → good creaming agent for concentration of rubber latex.
- Gum solution of good adhesive strength from tamarind gum & sisal fibers were prepared → false roofing, room partitioning.
- Cellulose triacetate : forms the transparent film which protect the polarizing plate of LCDs (Liquid Crystal Devices)





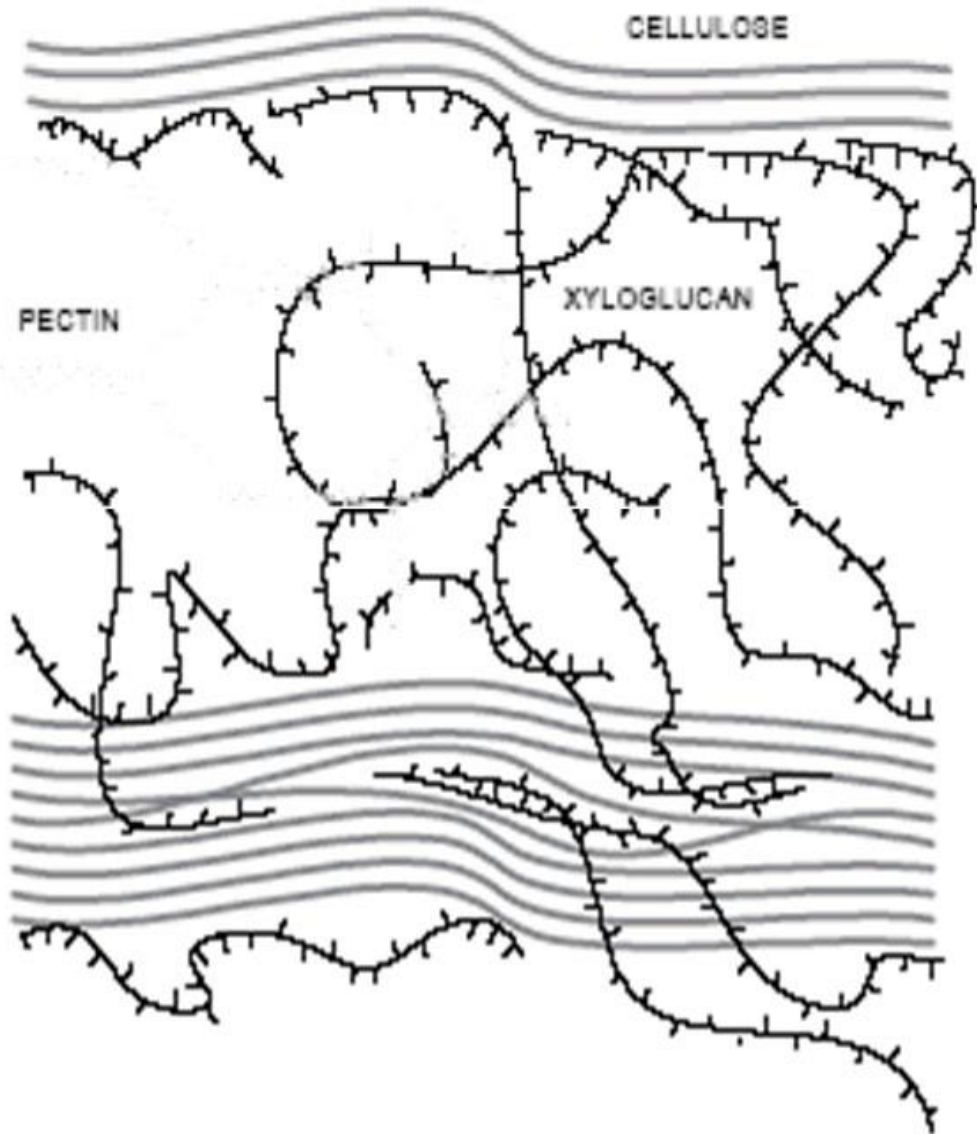
 POLITECNICO DI MILANO



Biological Degradation of Polysaccharides.



Plant Cell Walls.



Cellulose microfibrils contain microcrystalline regions that may be formed by entrapment of **hemicellulose** such as xyloglucan.

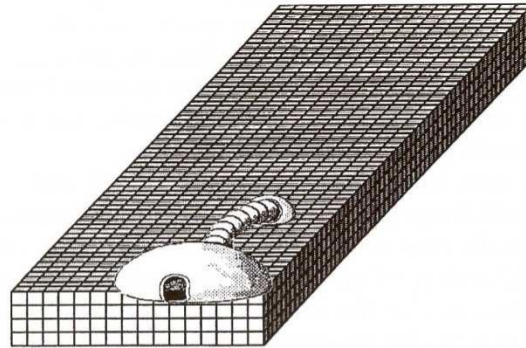
Xyloglucan can also bond to the surface of cellulose and may link two microfibrils together.

Pectins form a space-filled hydrophilic gel between microfibrils.

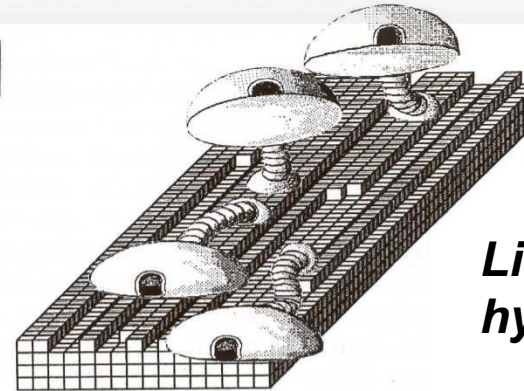


Model for the interaction of an enzyme degrading an insoluble substrate

Adsorption

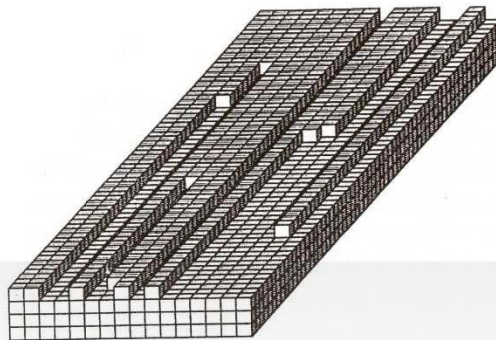


A

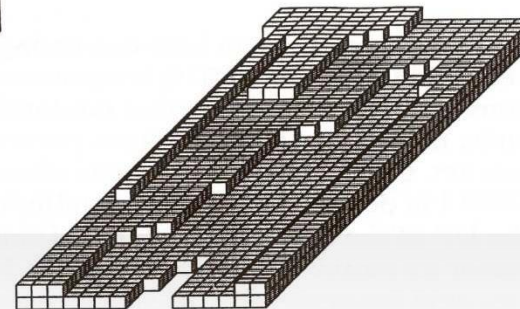


Limited hydrolysis

B



C

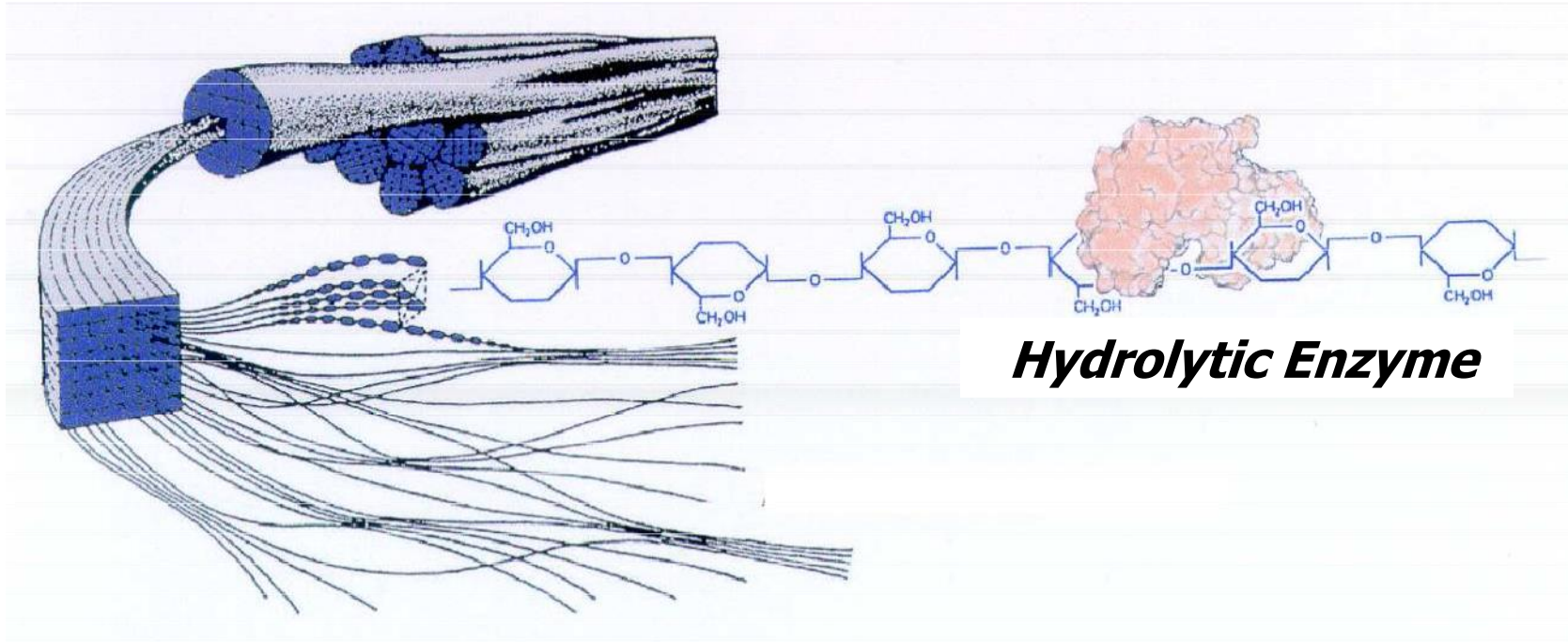


Extention of hydrolysis

D

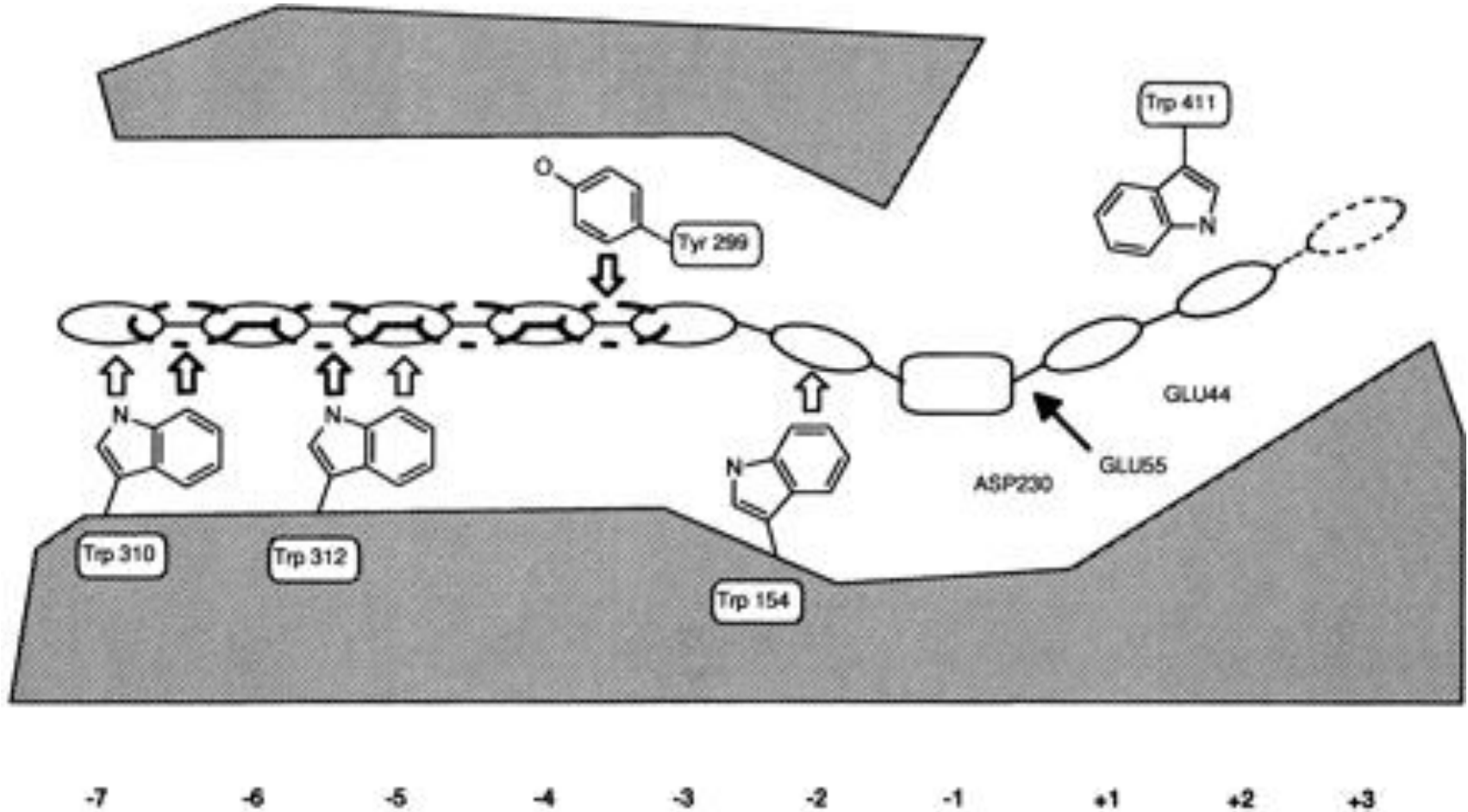


Enzymatic Degradation of Cellulose

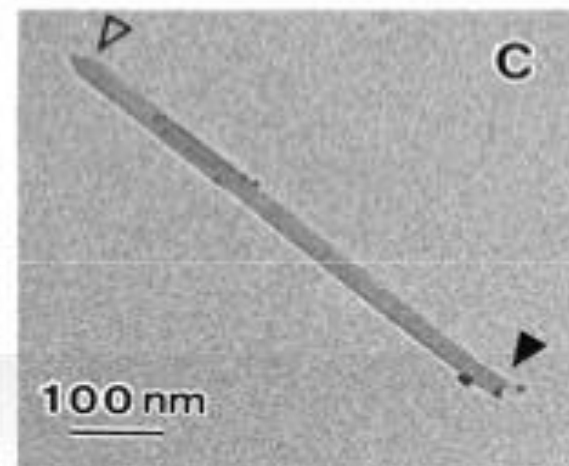
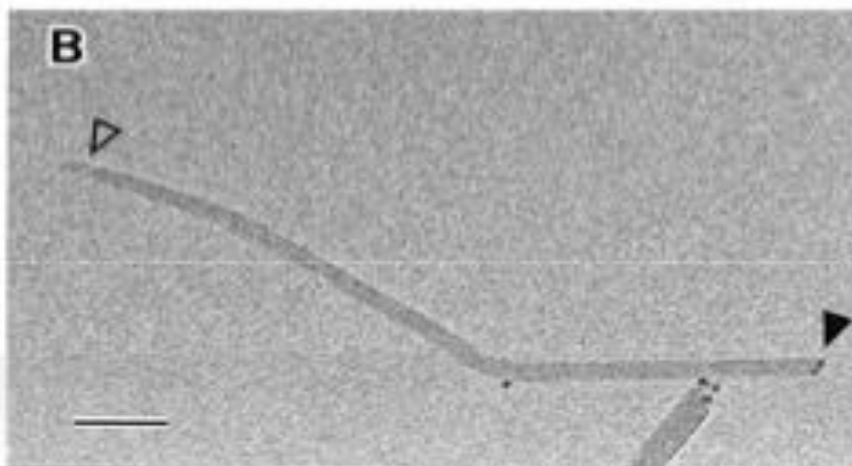
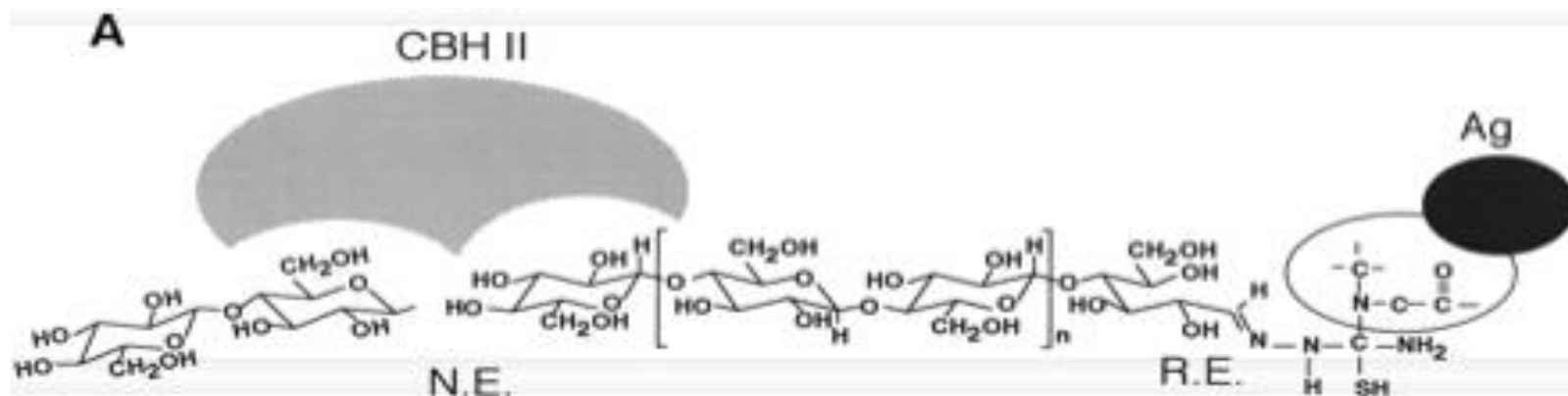




Model for an Enzyme Interacting Cellulose.



Model for an Enzyme Interacting Cellulose (2).



Certain enzymes can recognize and cleave at different ends within a cellulose crystal



The Role of Different Enzyme-Domains.

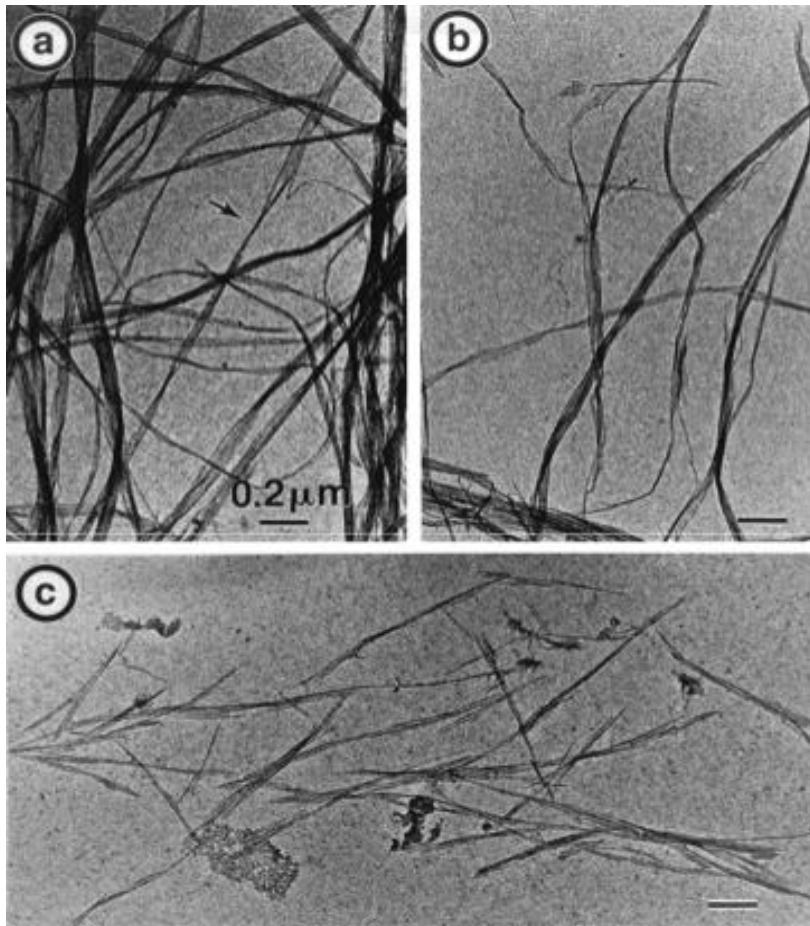


Chains of a polysaccharide

Enzymes acting on insoluble polysaccharides comprise a binding domain linked (via a linker region) with the catalytic domain

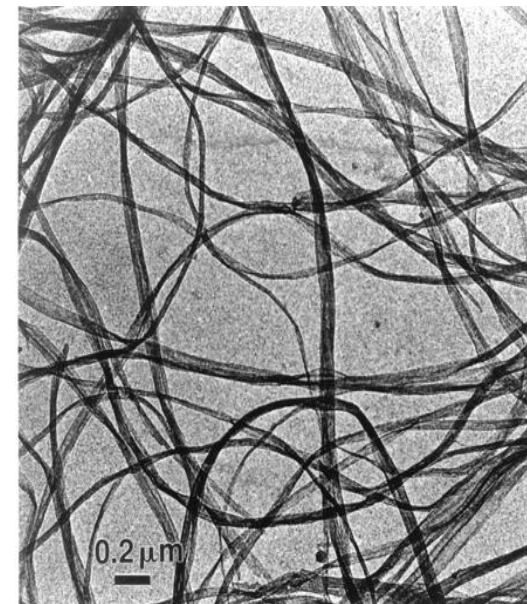


Concerted Action of Enzymes.



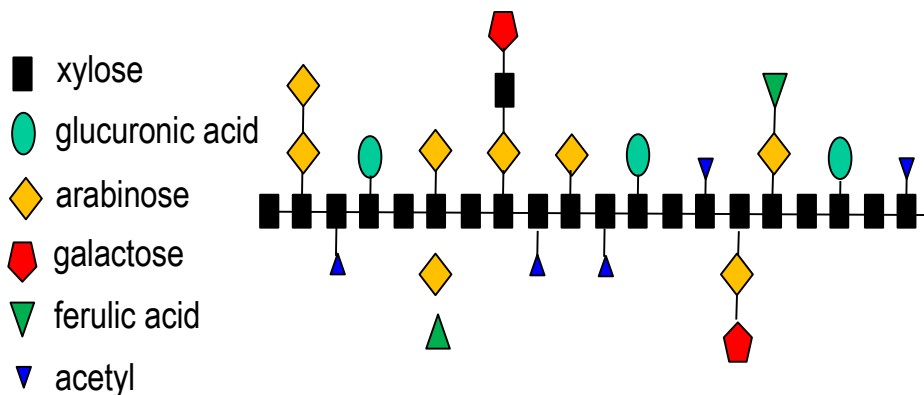
- (a) *Enzyme type 1*
- (b) *Enzyme type 2*
- (c) *Mixture of type 1 and type 2*

Control of the polysaccharide without enzyme

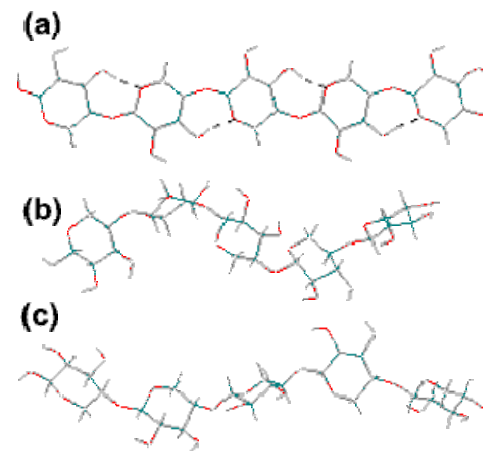




Schematic Presentation of Xylan.

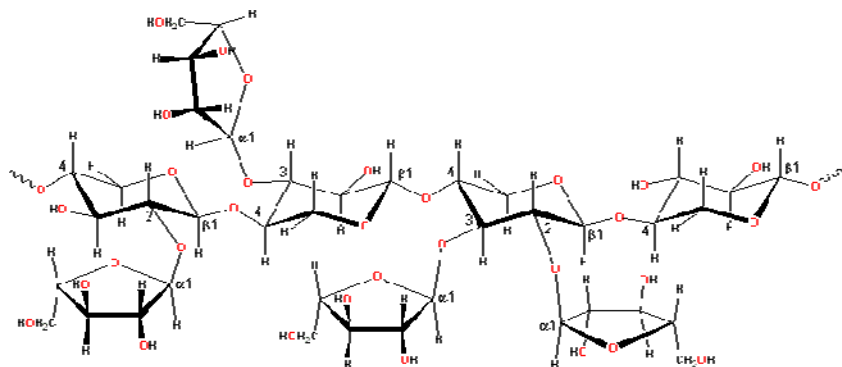


backbone



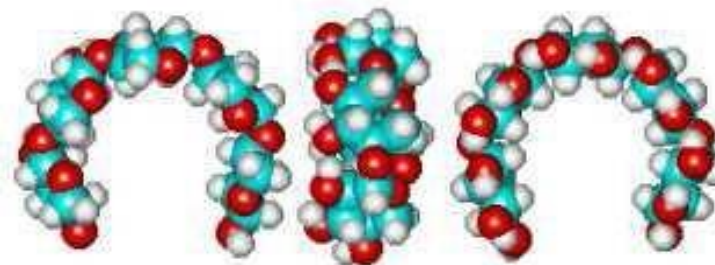
Arabinoxylans

L-arabinofuranose residues attached to **D-xylopyranose** chains



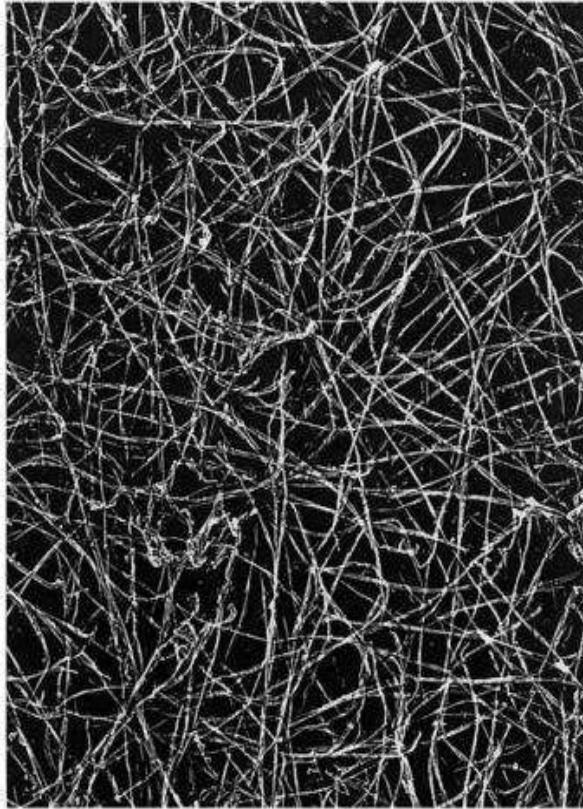
Xylan loop structure

Such structuring will behave similar to the cyclodextrins in binding materials such as aroma compounds.





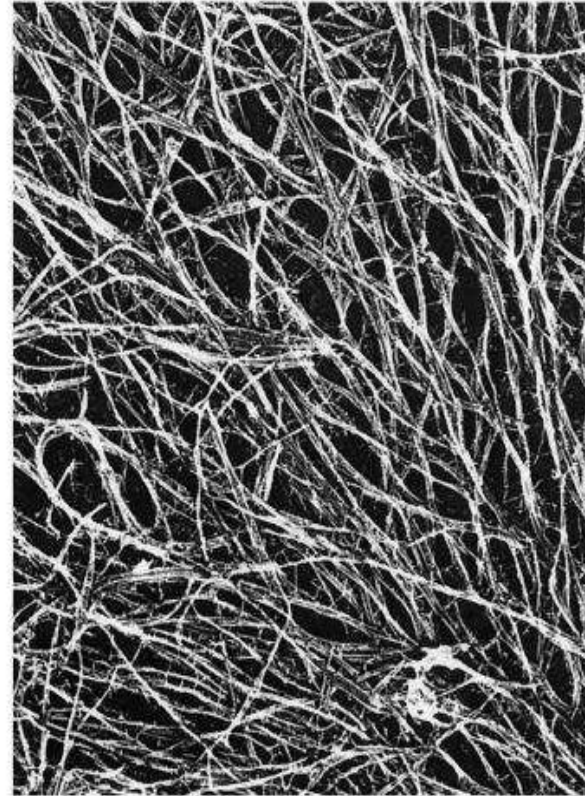
**In plants *xylan* is embedded
in cellulose and glucan.**



A

— 0.5 μm

**Cellulose of plant cell
left after removal
of xylan and glucan**



B

— 0.25 μm

**Cellulose / *Xylan*
Glucan**

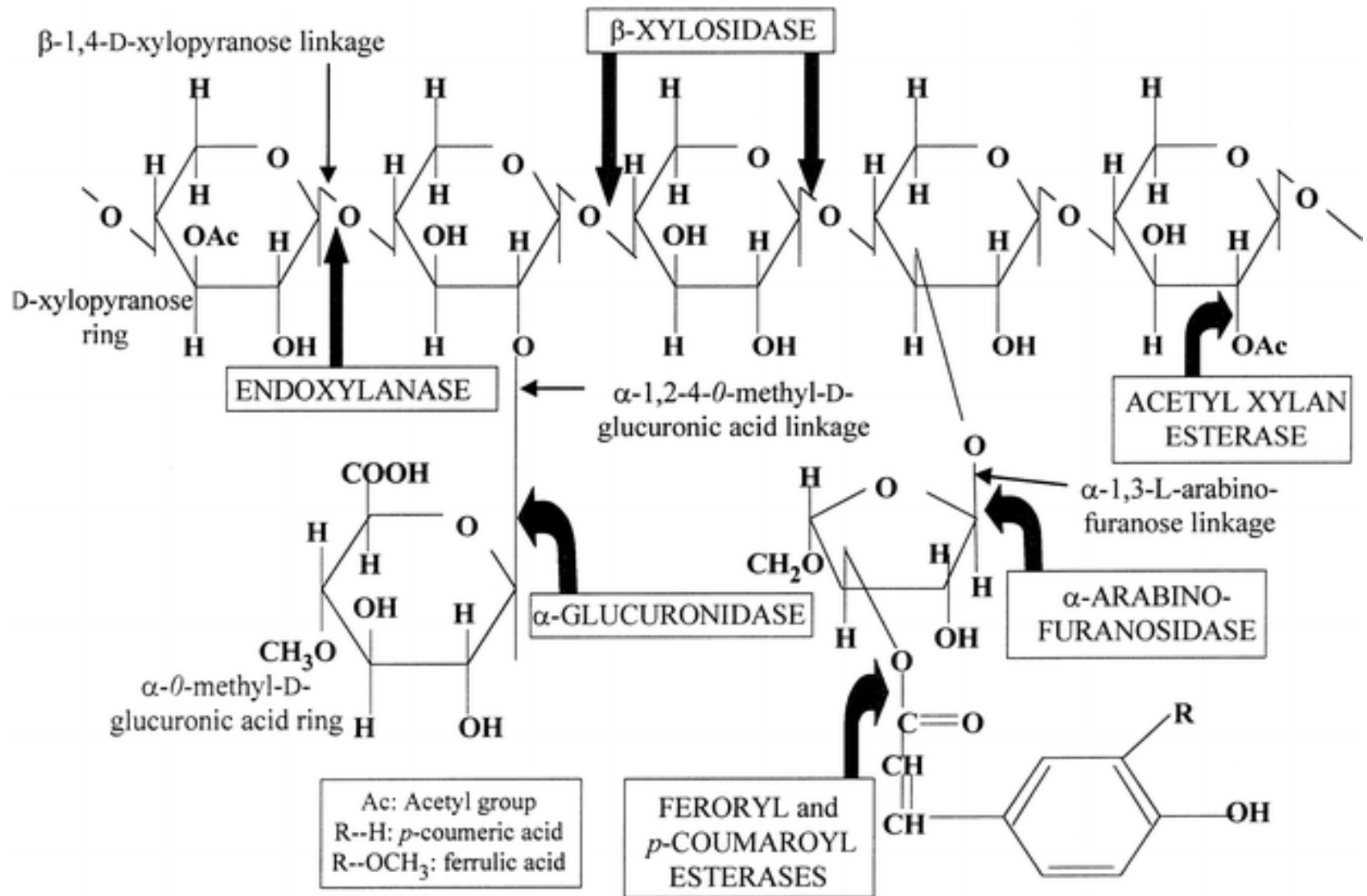


Enzymatic Hydrolysis of Xylans.

- **Multiple enzymes**
- with **different enzymatic activities** are required to **hydrolyze** the
- **backbone and the different side chains of xylans**



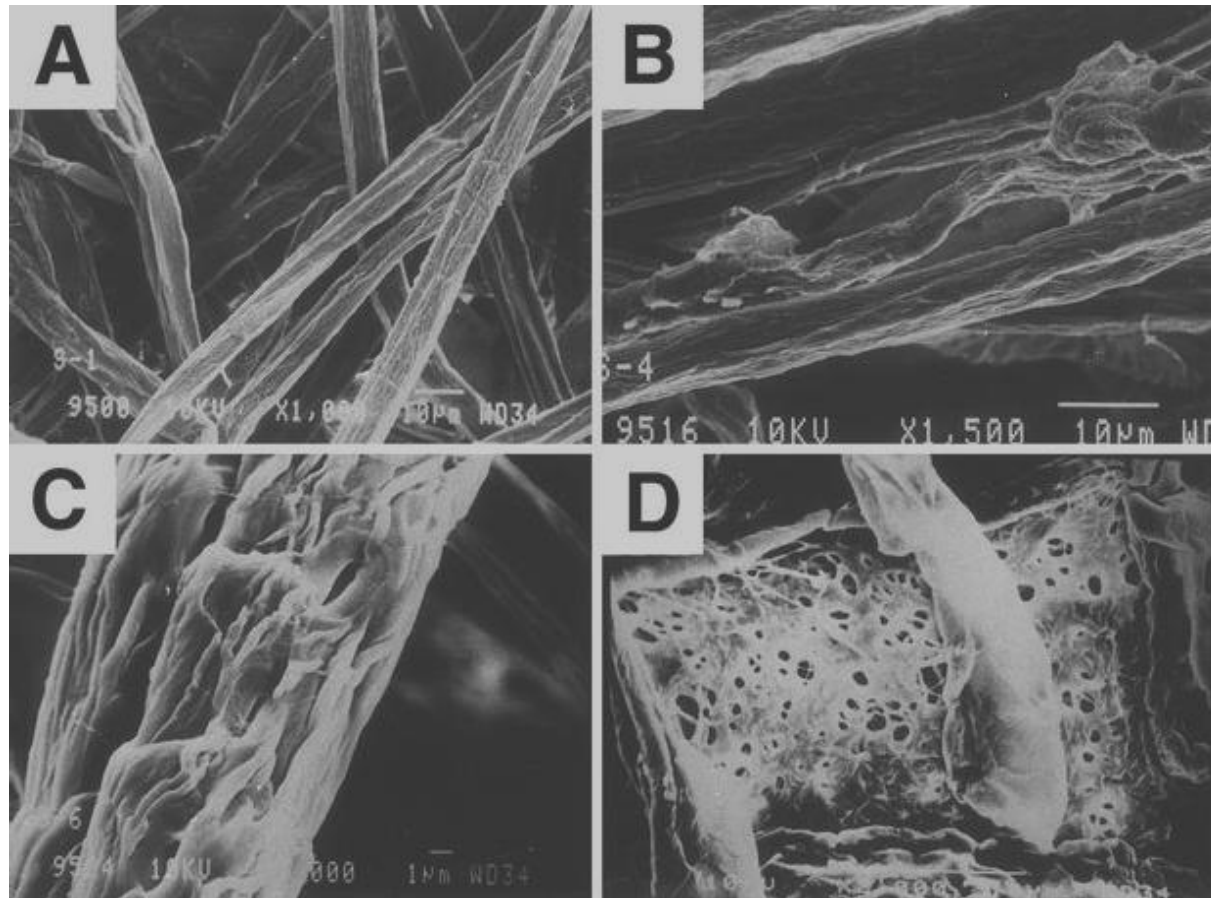
Different Enzymes Acting on Xylan.





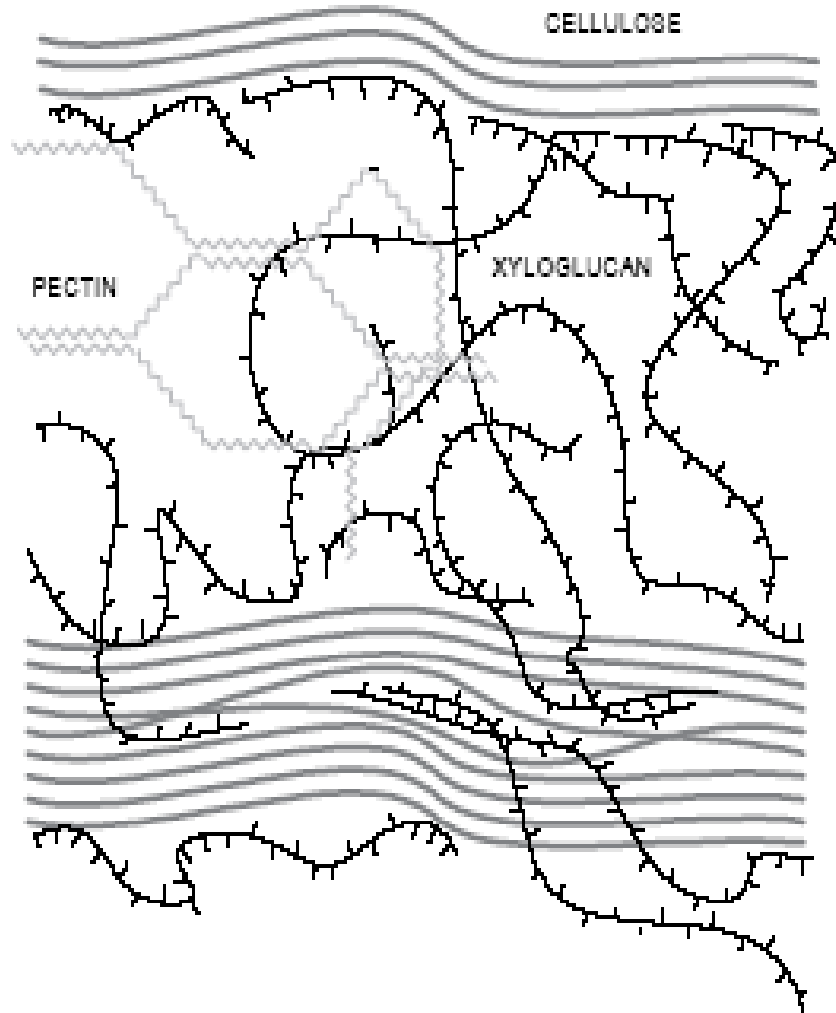
Effects of Different Enzymes on Xylans.

*Viewing (EM) the action of different enzymes acting on the backbone and side sides of **xylan**.*





Pectins.



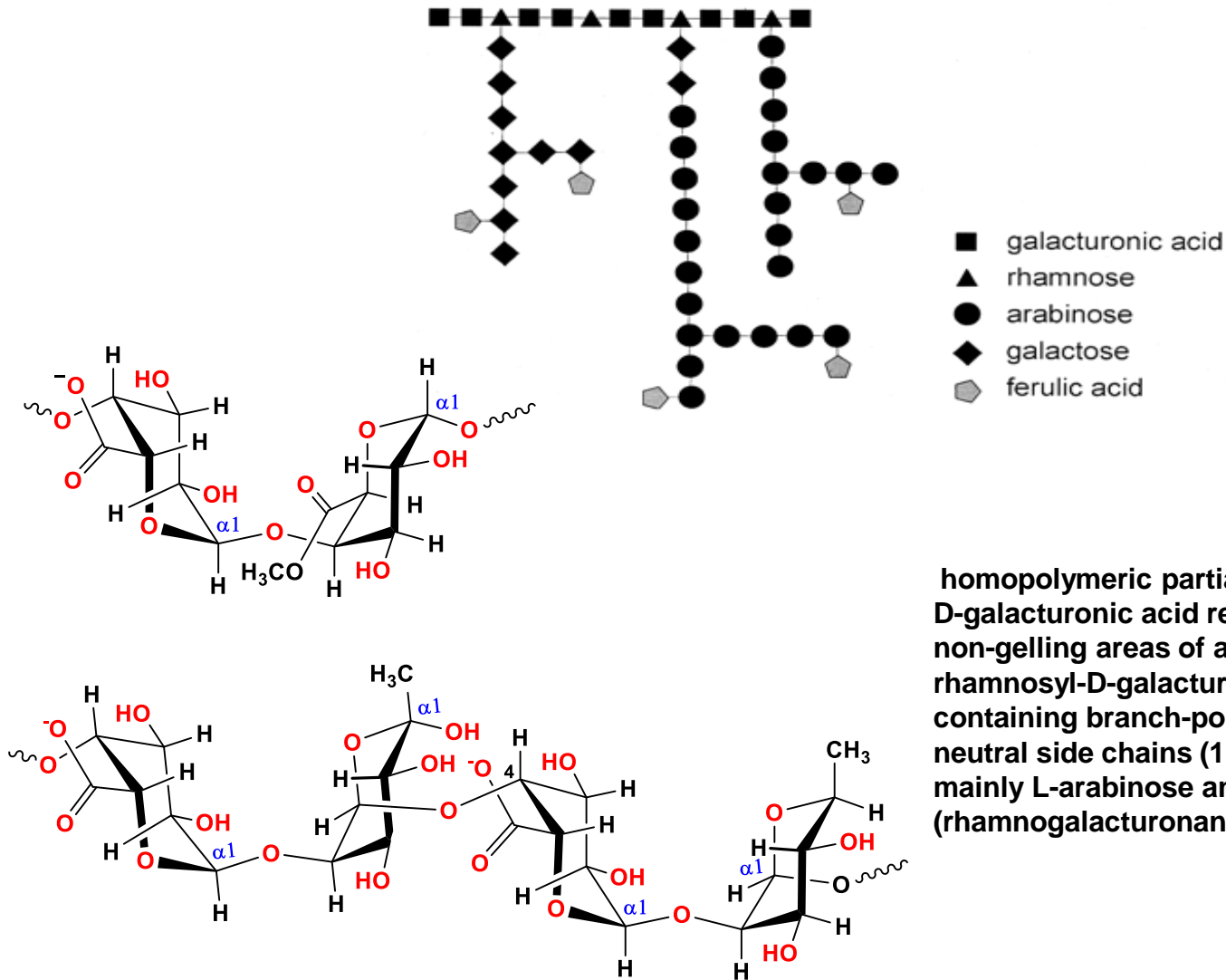
Cellulose microfibrils contain microcrystalline regions that may be formed by entrapment of hemicellulose such as xyloglucan.

Xyloglucan can also bond to the surface of cellulose and may link two microfibrils together.

Pectins form a space-filled hydrophilic gel between microfibrils.



Schematic Presentation of Pectin.



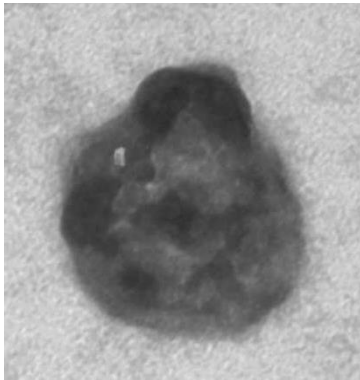


Chitin Synthases.

Membrane proteins

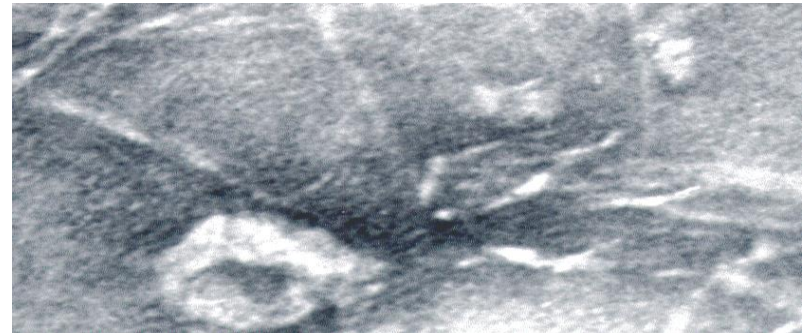


Chitosom



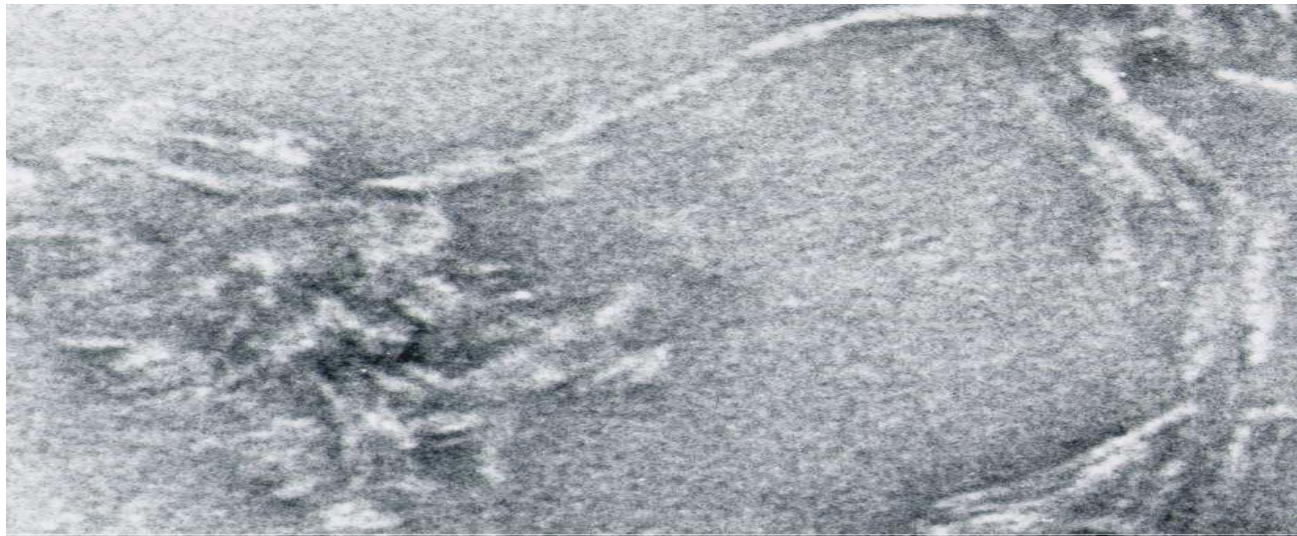
+ *UDP-N-Acetylglucosamine*

Fibers



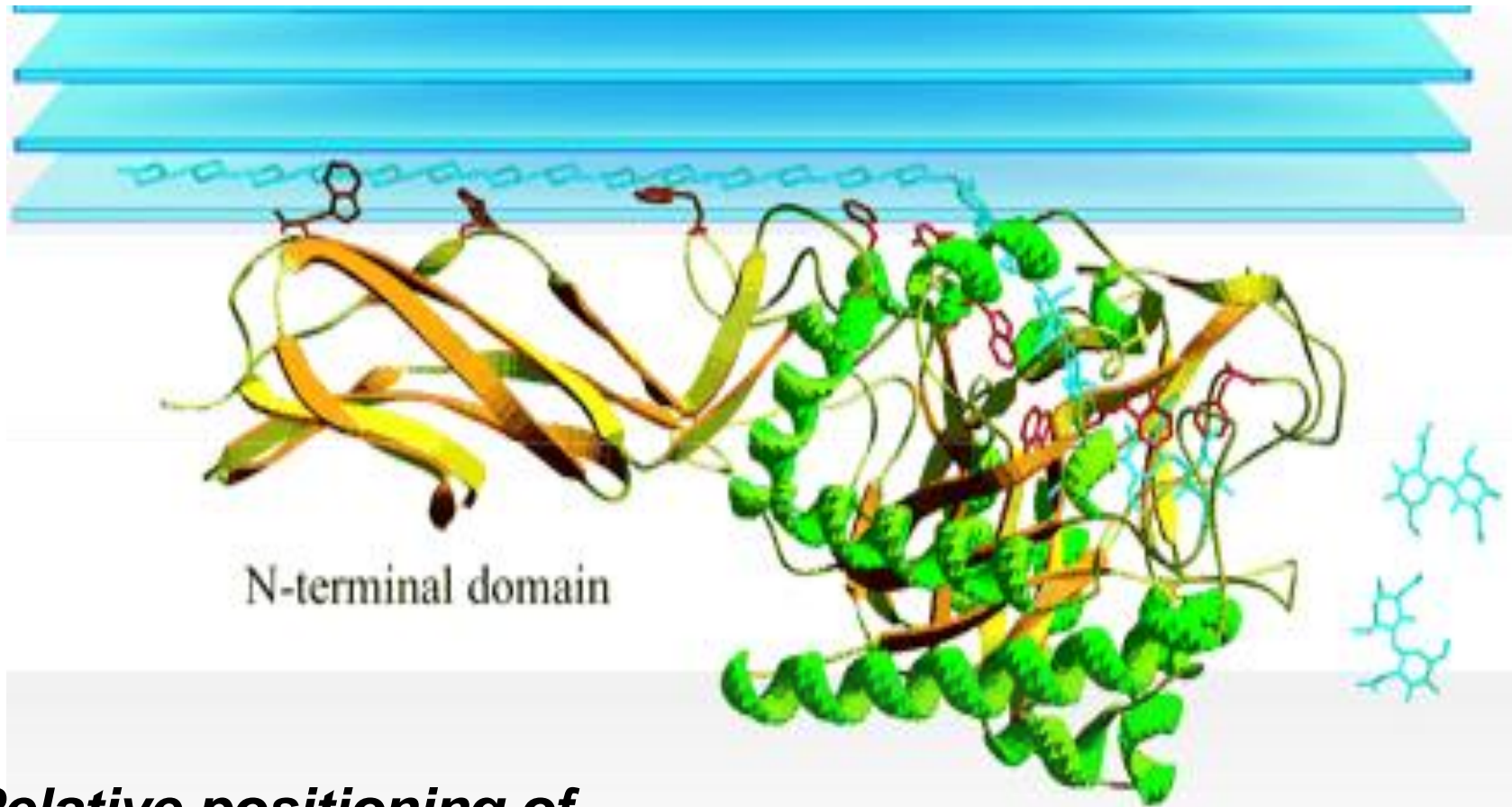


Degradation of Chitin Fibres.





Mechanism of Enzymatic Chitin Hydrolysis.



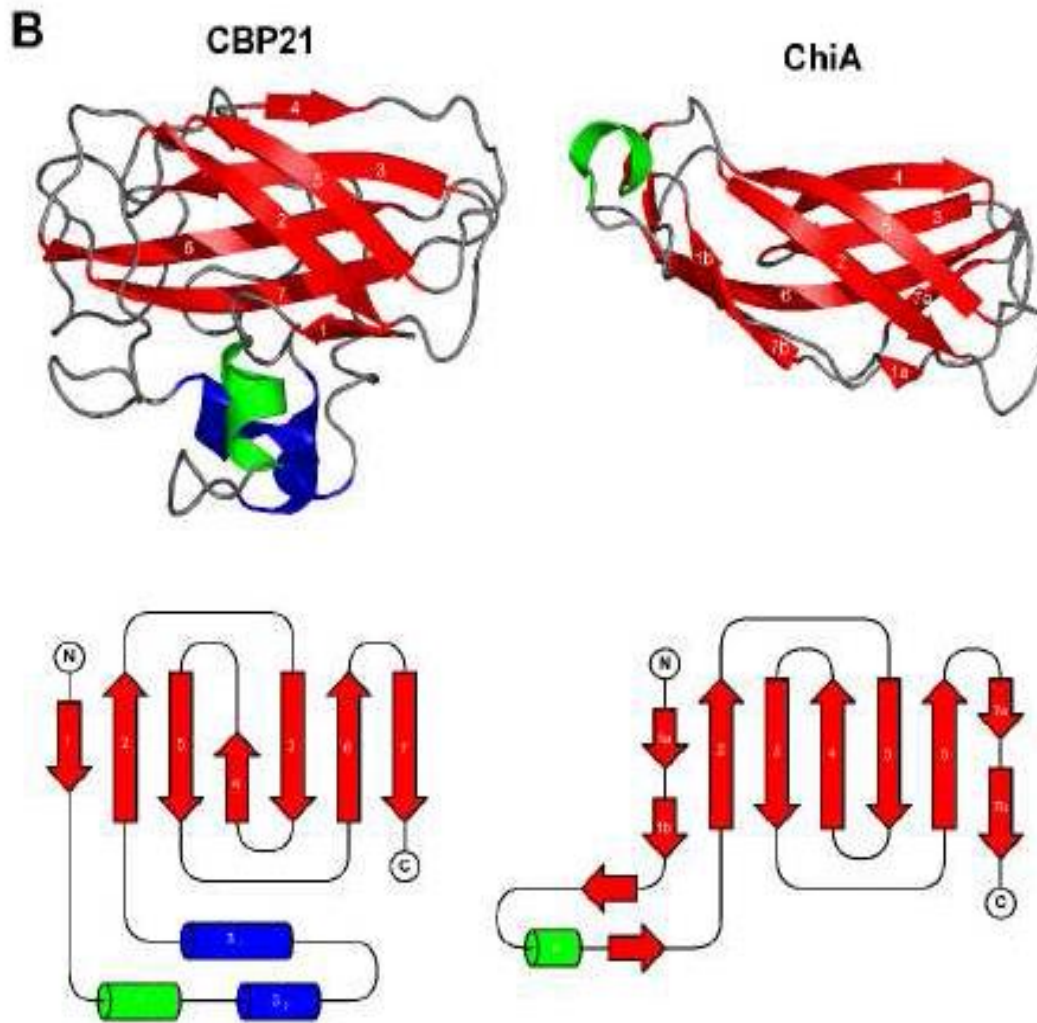
**Relative positioning of
*binding domain***



and catalytic domain



Binding Domain of the Chitinase.





Tools of Recognition, Degradation, Transport and Inhibition.

