Polysaccharides

- Different types of Polysaccharides
- Homopolysaccharides, heteropolysaccharides
- Starch, glycogen, cellulose, chitin
- Glycosaminoglycans, proteoglycans, and glycoproteins, their structure and biological importance

Characteristics of polysaccharides

-polymers (MW from 200,000)
-White and amorphous products (glassy)
-not sweet
-not reducing; do not give the typical aldose or ketose reactions
-form colloidal solutions or suspensions

Polysaccharides

Chemical:

- **Homopolysaccharides/Homoglycans- o**n hydrolysis yields a single type of monosaccharides.

- **Heteropolysaccharides/Heteroglycans-** on hydrolysis yields a mixture of different monosaccharides.

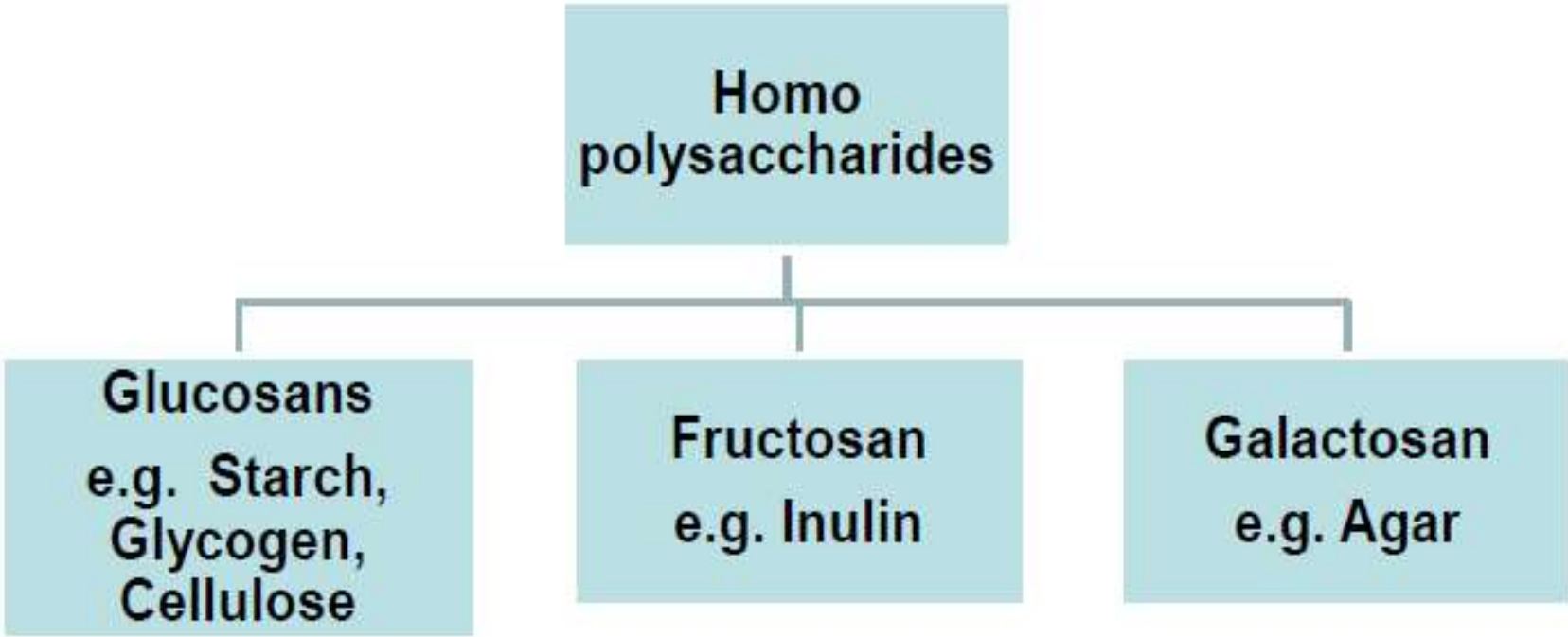
Functional:

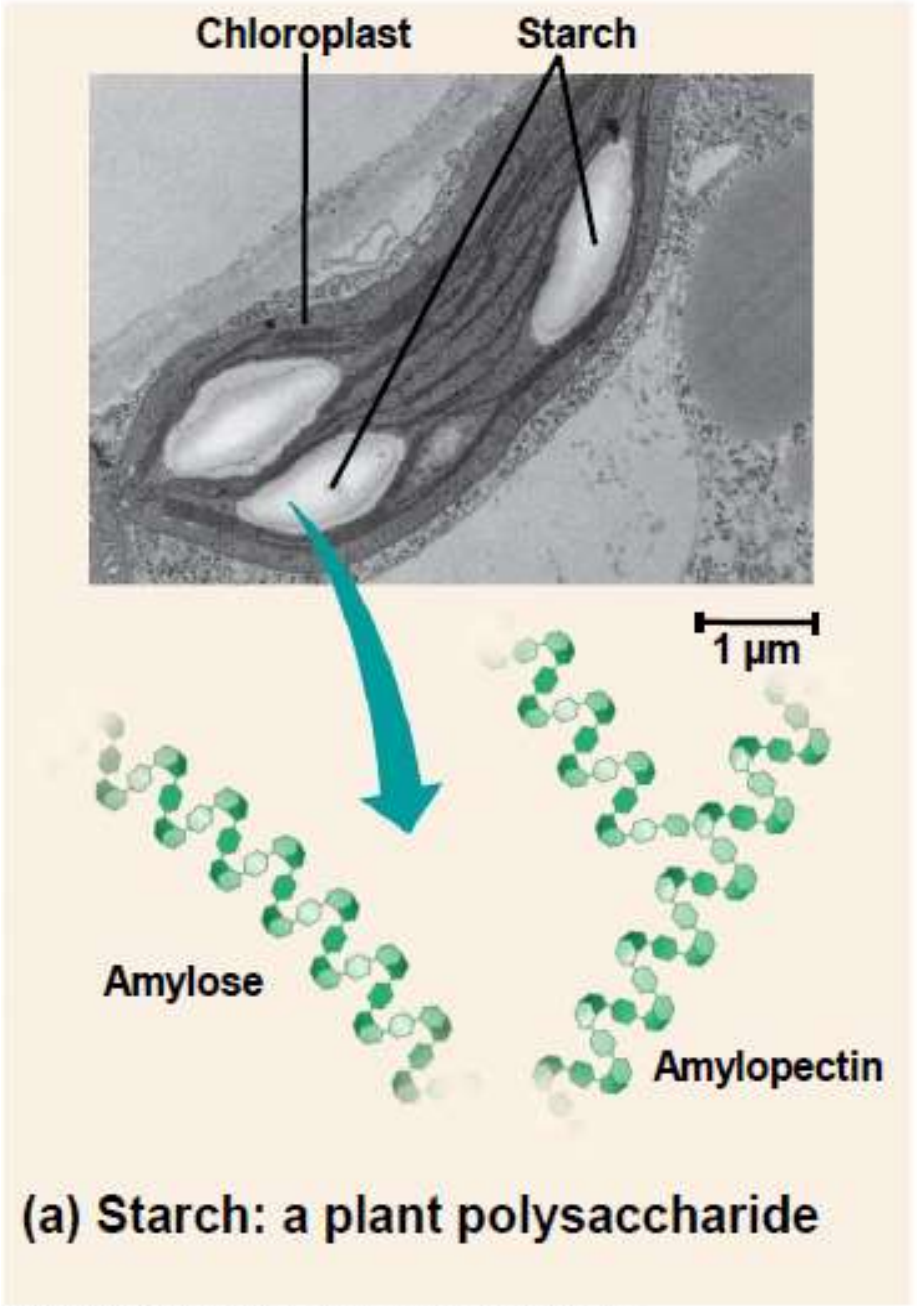
- **Nutrient polysaccharide (digestible)-** metabolic reserves of monosaccharides in plants and animals. **Eg. Starch, glycogen,**

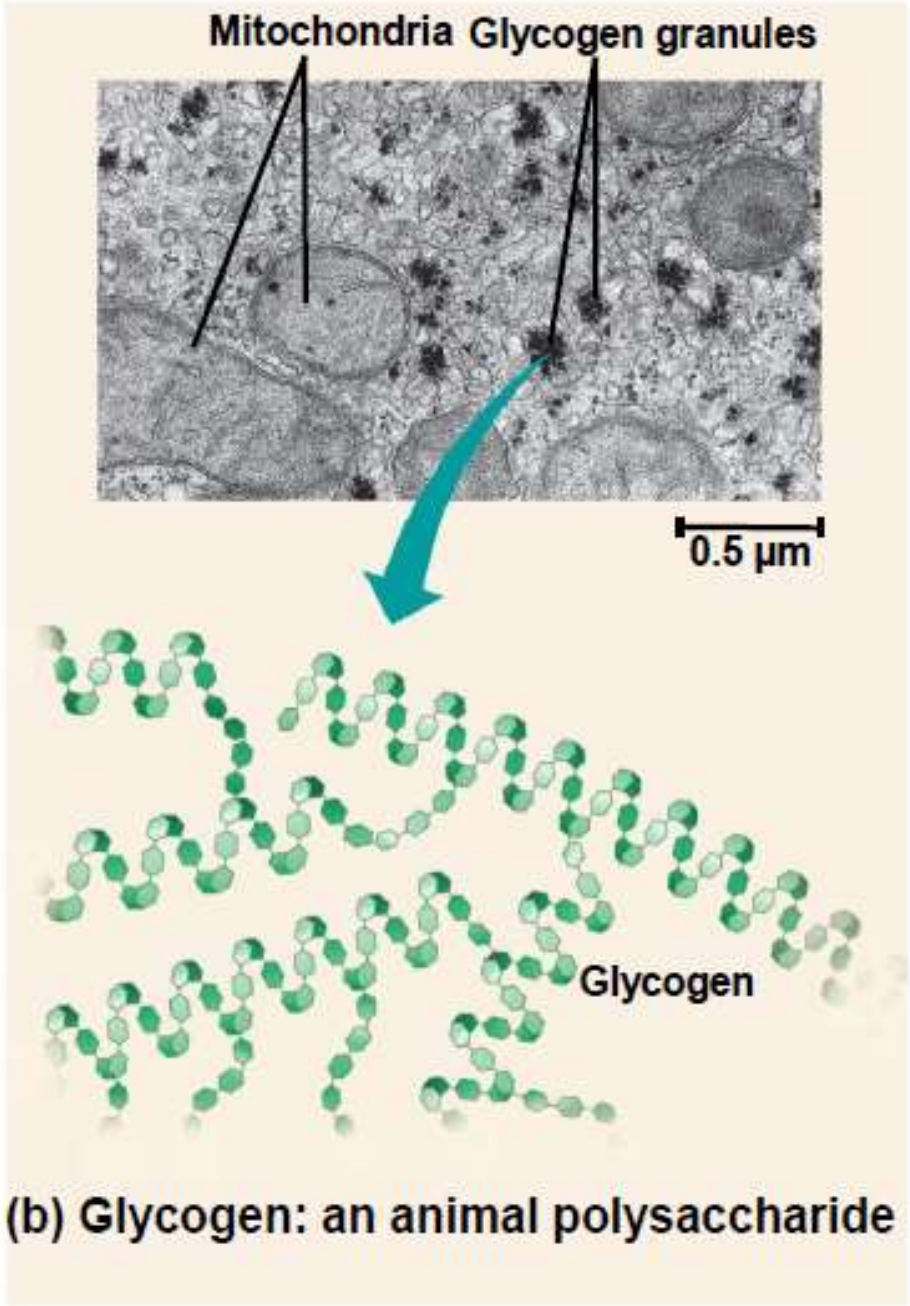
- **Structural polysaccharide (indigestible)-**rigid mechanical structures in plants and animals. **Eg. Cellulose, pectin, chitin**

HOMOPOYSACCHARIDES

• Homopoysaccharides are polymers composed of a single type of sugar monomers







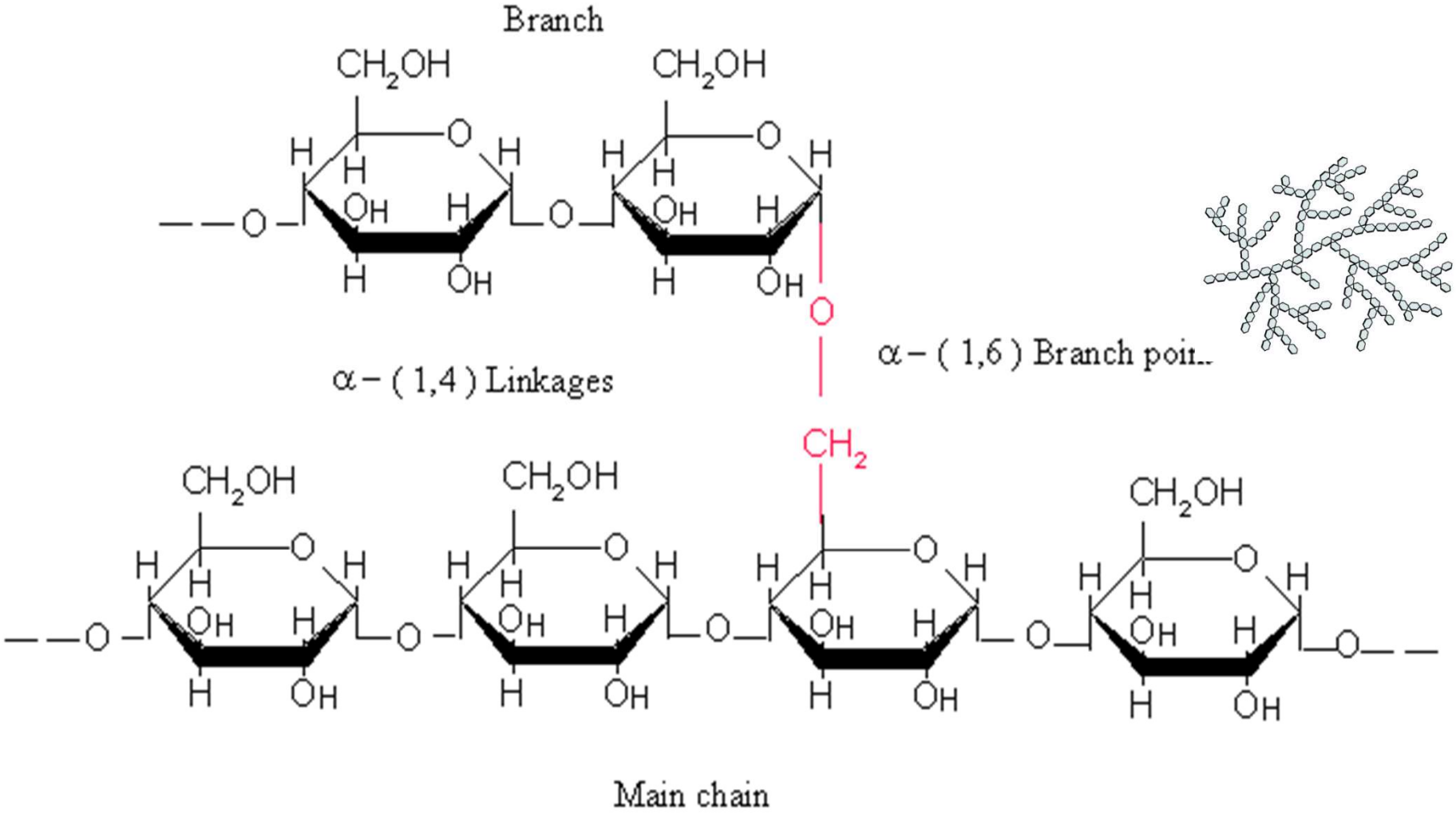
GLUCOSANS /GLUCANS

Glycogen (Storage Polysaccharide) –

- Also known as animal starch.
- Stored in muscle and liver.
- Present in cells as granules (high MW).
- Contains both α (1,4) links and α (1,6) branches at every 8 to 12 glucose unit.
- Complete hydrolysis yields glucose.
- With iodine gives a red-violet color.
- Hydrolyzed by both α and β-amylases

Glycogen

- **Alpha(1,6) branch point every 8-12 residues**



STARCH (STORAGE POLYSACCHARIDE)

- Most common storage polysaccharide in plants.

- Composed of 10 – 30% Amylose and 70-90% amylopectin depending on the source –

  (a) **Amylose** is a linear polymer of α-D-glucose, linked together by α -1→4 glycosidic linkages.

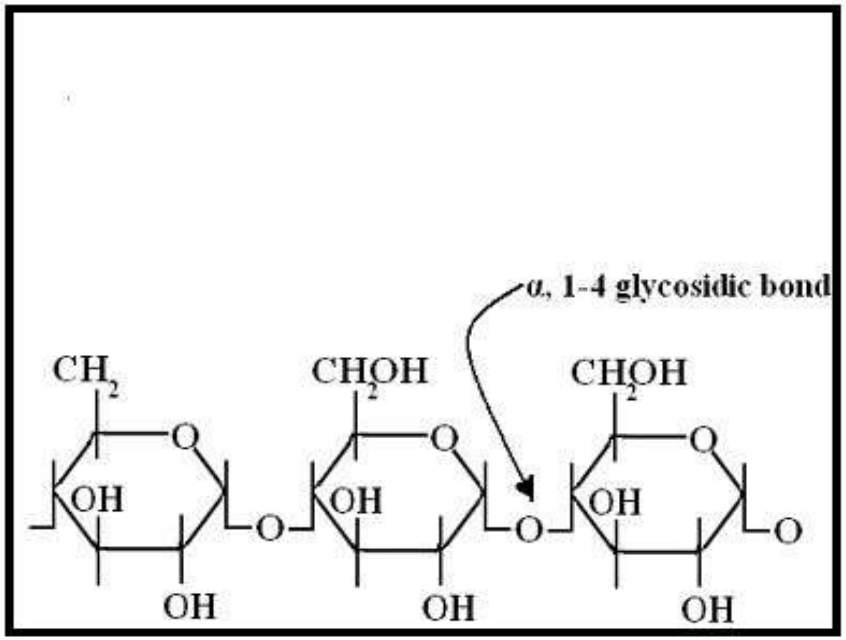
  It is soluble in water, reacts with iodine to give a blue color and the molecular weight of Amylose ranges between 50, 000 – 200, 000.

(b) **Amylopectin** is a highly branched polymer, insoluble in water, reacts with iodine to give a reddish violet color.

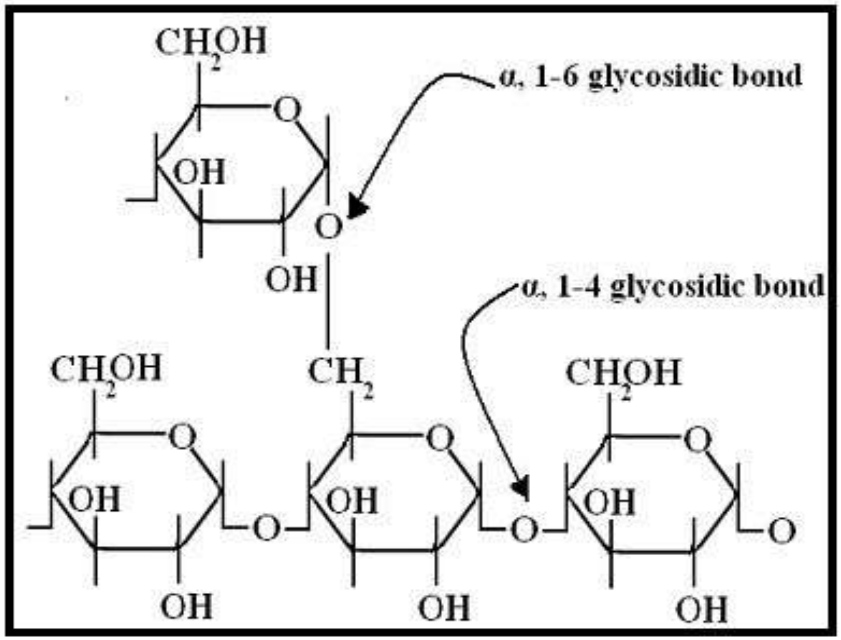
The molecular weight ranges between 70, 000 - 1 000, 000. Branches are composed of 25-30 glucose units linked by α-1→4 glycosidic linkage in the chain and by α-1→6 glycosidic linkage at the branch point.

Starch

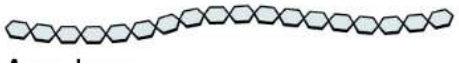
- Alpha(1,6) branch point every 30 residues in amylopectin
- Most starch are 10-30% amylose and 70-90% amylopectin

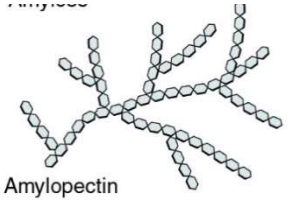


(a) amylose



(b) amylopectin

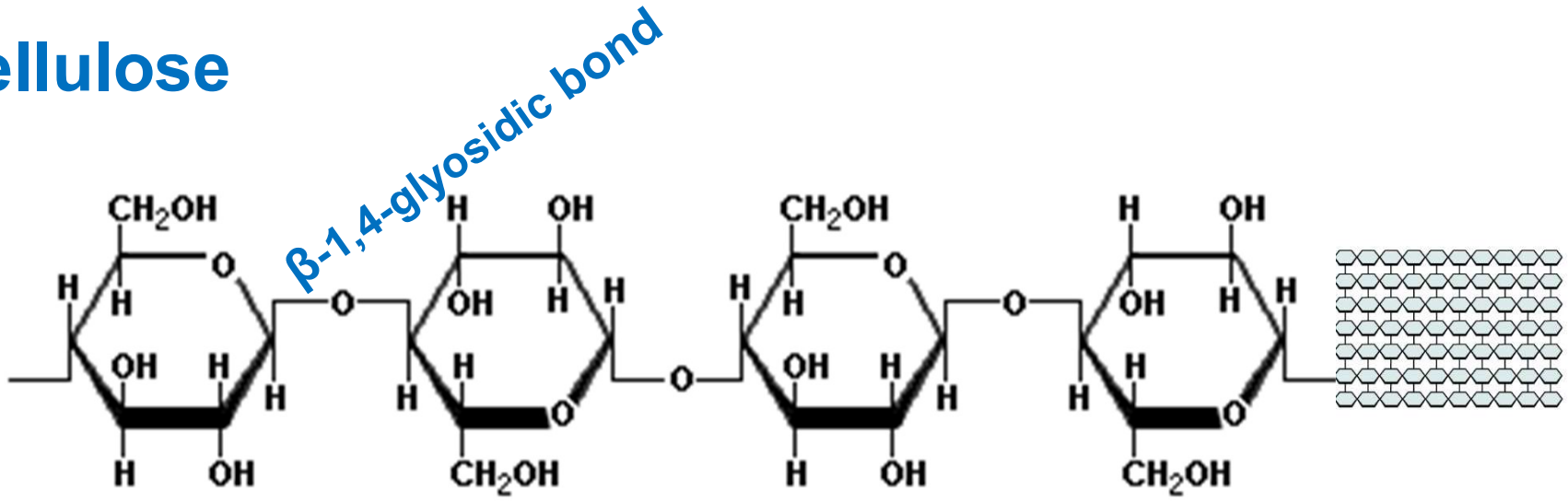




CELLULOSE (STRUCTURAL POLYSACCHARIDE)

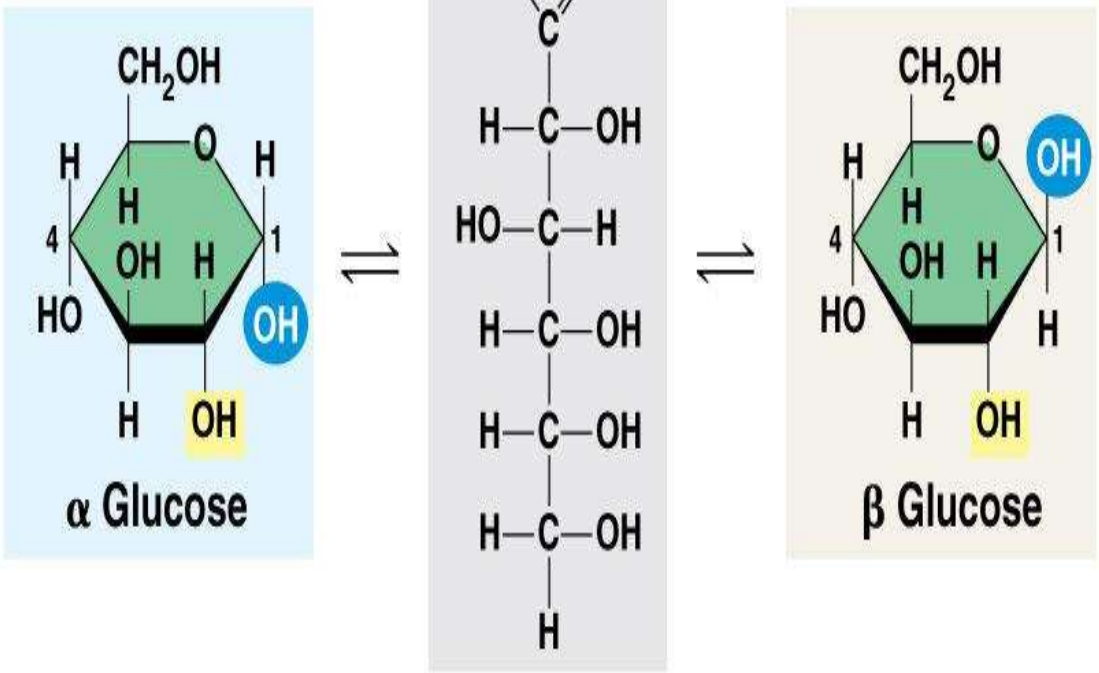
- Polymer of β-D-glucose linked by β(1,4) linkages.
- Yields glucose upon complete hydrolysis.
- Partial hydrolysis yields cellobiose.
- Most abundant of all carbohydrates.
- Gives no color with iodine.
- Cellulose is tasteless, odorless and insoluble in water and most organic solvents.

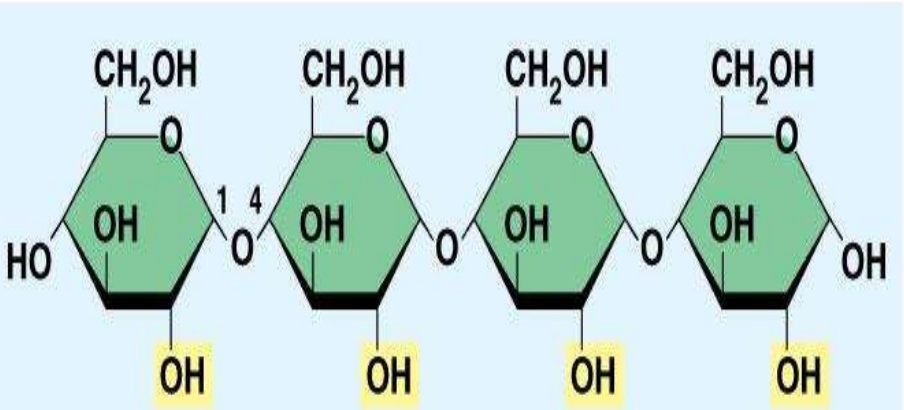
Cellulose



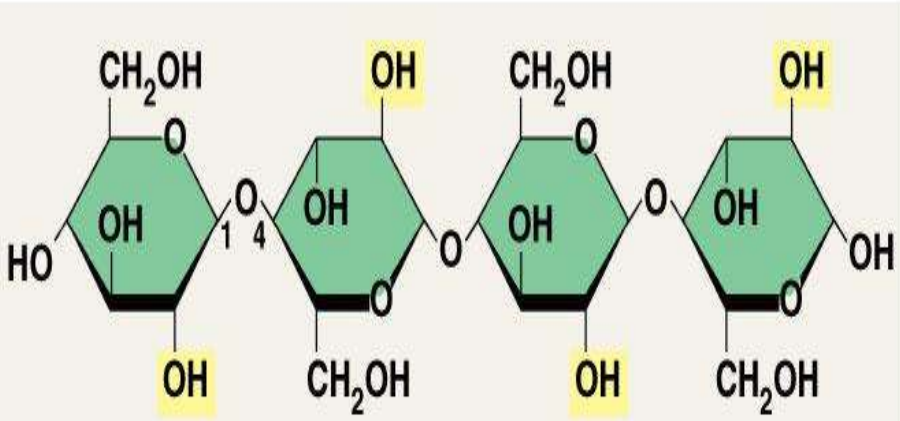
- The **β**-glucose molecules are joined by **condensation**, i.e. the removal of water, forming **β-(1,4) glycosidic linkages**.
- The glucose units are linked into **straight chains** each 100-1000 units long. This gives cellulose a fibre structure with a high tensile strength. Cotton fiber contains 90% cellulose, wood contains approx. 40-50% cellulose.
- Human lacks cellulase enzyme and thus unable to digest cellulose.
- Cellulose act as hydrophilic bulking agent and holds water potentially aiding in defecation.
- Industrial application of cellulose is to use as biofuels.

(a) α and β glucose ring structures

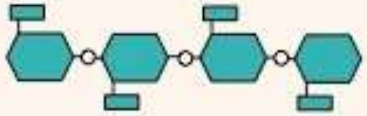
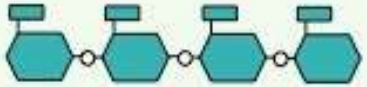
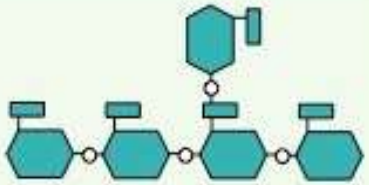
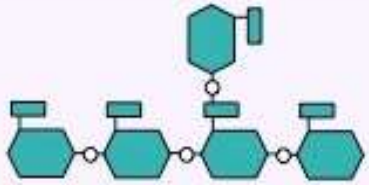
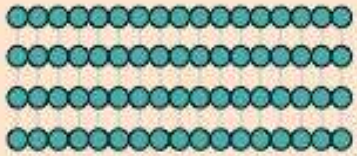
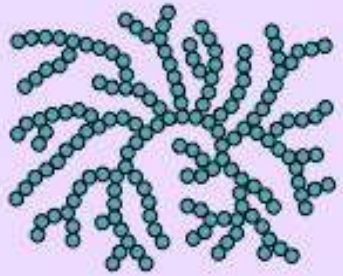




(b) Starch: 1–4 linkage of α glucose monomers

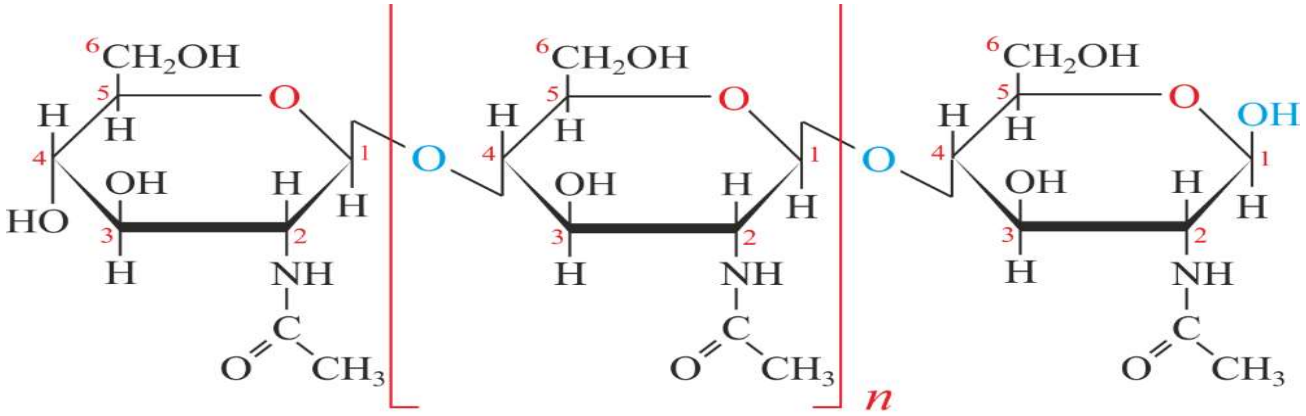


(c) Cellulose: 1–4 linkage of β glucose monomers

	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				

Chitin

- ***Chitin*** makes up the exoskeleton of insects and crustaceans and cell walls of some fungi.
- It is made up of *N*-acetyl glucosamine containing β(1→4) glycosidic bonds.
- It is structurally strong.
- Chitin is used as surgical thread that biodegrades as a wound heals.
- It serves as a protective Exoskeleton in crustacea and insects.
- Chitin is also used to waterproof paper, and in cosmetics and lotions to retain moisture.



β-(1,4)-N-acetyl-D-glucosamine

- **Polymer of N-acetyl-D-glucosamine with β-(1,4) glycosidic linkages**

Dextrins/Dextrans

- Highly branched homoglycan containing Glucose residues in 1-6, 1-4 and 1-3 linkages.
- Produced by microbes.
- Mol. wt:- 1-4 million.
- As large sized, they will not move out of vascular compartment so used as plasma expanders.

Inulin

- D -fructose in β-1,2 linkages.
- Source: Bulbs and tubers chicory, dahlia, dandelion, onions, garlic.
- Not metabolized .
- Not absorbed nor secreted by kidneys so, used to measure GFR.

Heteropolysaccharides

Polymers made from more than one kind of monosaccharides or monosaccharide derivatives.

- Chemically, they are formed mostly of repeated disaccharides units that contain amino sugar (N-acetyl glucosamine or N-acetyl galactosamine) uronic acid (glucuronic acid or its 5 epimer iduronic acid).

3-types

1. **Glycosaminoglycans or mucopolysaccharides (GAGs)**
2. **Proteoglycans**
3. **Glycoproteins**

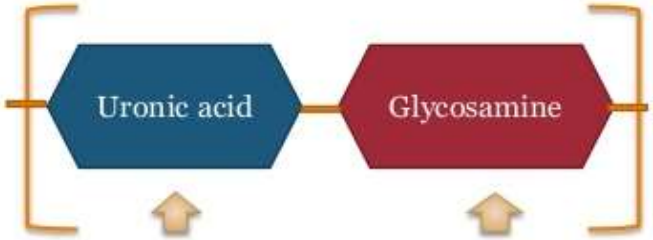
GLYCOSAMINOGLYCANS(GAGs)/MUCOPOLYSACCHARIDES

First isolated from mucin so called mucopolysaccharides

- Long, Unbranched heteropolysaccharide, made of repeating disaccharide units containing uronic acid & amino sugars. These are more commonly known as *Glycosaminoglycans (GAG).*
- Amino sugar – Glucosamine or Galactosamine (Present in there acetylated form)
- Uronic acid – D-Glucuronic acid
- Major components of extracellular matrix of connective tissue, including bone and cartilage, synovial fluid, vitreous humor and secretions of mucus producing cells.

Structure of GAGs

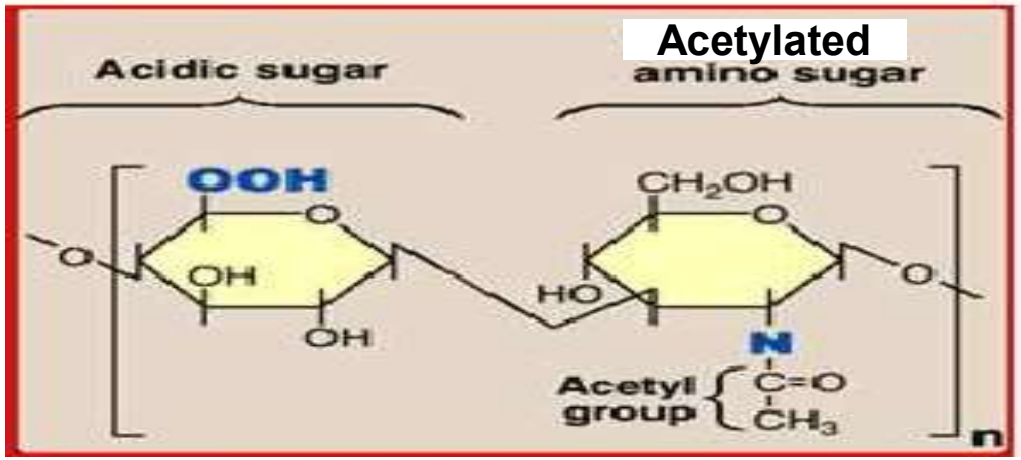
- Linear polymers
- Heteropolysaccharides.... repeating disaccharide units, $(AB)_n$



Repeating unit of glycosaminoglycans

D-glucuronic acid
or
L-iduronic acid
(except in keratan sulfate)

N-acetylglucosamine
Or
N-acetylgalactosamine



One imp. example of GAG is Heparin

- Heparin is clinically useful as an injectable anticoagulant.
- It is a component of intracellular granules of mast cells, lining the arteries of the lungs, liver and skin

Heparin

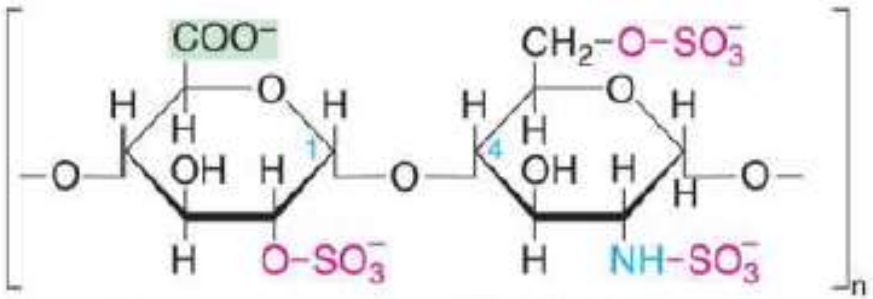
Heparin is a medically important polysaccharide because it prevents clotting in the bloodstream.

It is a highly ionic polysaccharide of repeating disaccharide units of an oxidized monosaccharide and D-glucosamine. Heparin also contains sulfate groups that are negatively charged.

present intracellular: In granules of mast cells and also in lung, liver and skin.

Functions:

- It is an anticoagulant (prevents blood clotting)
- Heparin helps in the release of the enzyme lipoprotein lipase (LPL) which helps to clear the lipidemia after fatty meal – so called *clearing factor.*



D-Glucuronate-2-sulfate N-Sulfoglucosamine 6-sulfate

Heparin

Sulfate free ⟶ **Hyaluronic acid**

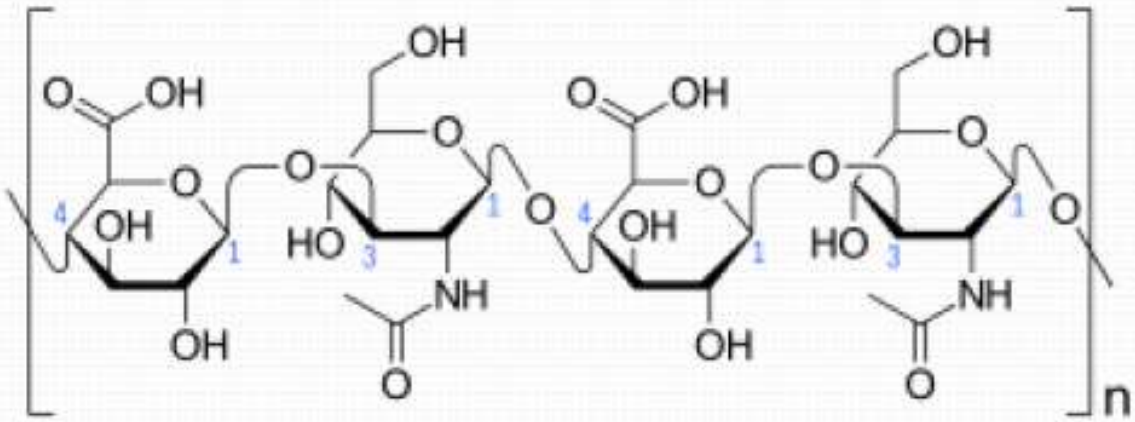
Sulfate containing ⟶ **Chondroitin Sulphate, Dermatan sulphate, keratan sulphate, Heparin, Heparan Sulphate**

Hyaluronic acid

It is the simplest mucopolysaccharide and is a linear polymer of disaccharides which form the repeating unit.

Each disaccharide is linked to the next by β- 1,4 glycosidic bonds. It consists of two alternative units of D-glucuronic acid and N-acetyl D-glucosamine, linked by β-1,3 to give a thread like structure.

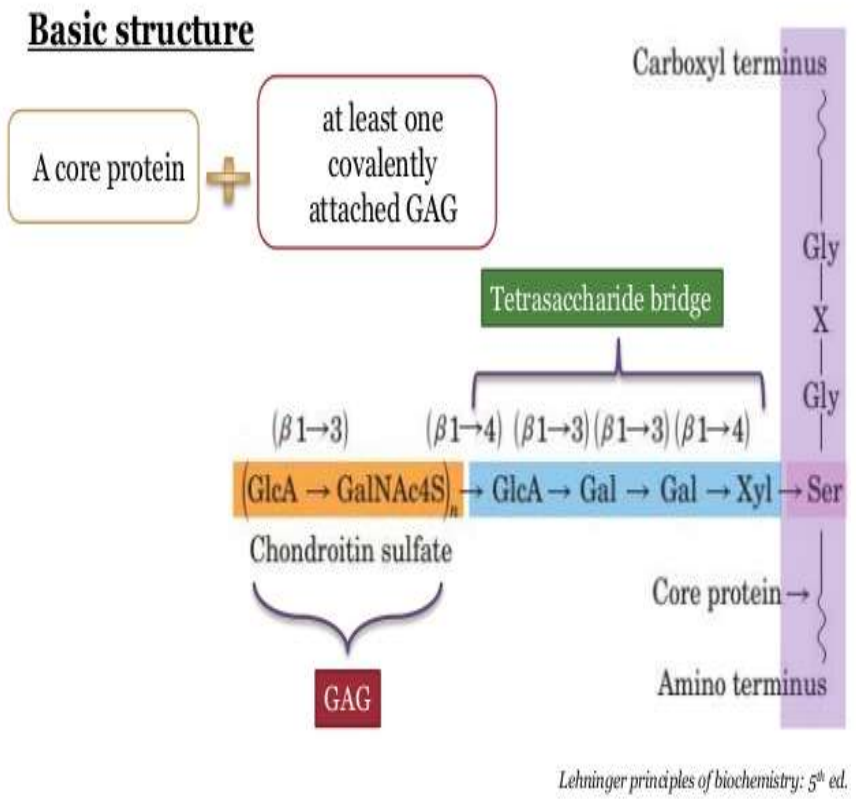
Present in Synovial fluid of joints, vitreous humor, connective tissues and cartilage.



GAGs	Localization	Sugar components and functions
Hyaluronate	synovial fluid, articular cartilage, skin, vitreous humor, ECM of loose connective tissue	**D-Glucuronate and N-acetyl-D-glucosamine (GlcNAc)**; Biological lubricant and high shock absorber
Chondroitin sulfate	cartilage, bone, heart valves	**D-Glucuronate and N-acetyl-D-galctosamine-4-sulphate** most abundant GAG; major component of the extracellular matrix.
Heparin	component of intracellular granules of mast cells, lining the arteries of the lungs, liver and skin	**L-iduronate-2-sulphate and N-sulpho-D-glucosamine-6-sulphate**. clinically useful as an injectable anticoagulant although the precise role in vivo is likely defense against invading bacteria and foreign substances
Dermatan sulfate	skin, blood vessels, heart valves, tendons, lung	**L-iduronate and N-acetyl-D-galactosamine-4-sulphate** wound repair, fibrosis, and infection;
Keratan sulfate	cornea, bone, cartilage aggregated with chondroitin sulfates	**D-galactose and N-acetyl-D-glucosamine-6-sulphate** Component of proteoglycans, occurs in cornea, cartilage bone, and horny structures

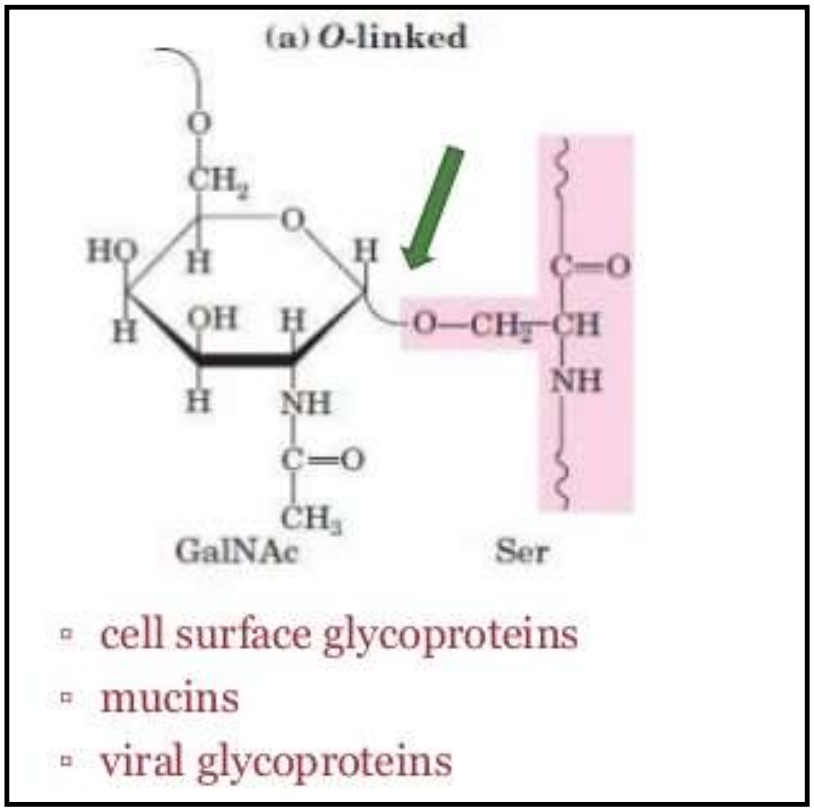
Proteoglycans

- Formed of GAGs covalently attached to core proteins.
- Carbohydrate content is 95% by weight
- **Occurrence:** found in all connective tissues, extracellular matrix (ECM) and on the surface of many cell types.
- Examples: **aggrecan, syndecan**
- **Functions:** role in glomerular filtration in kidney, act as receptors in cell membranes, maintaining in transparency of cornea.

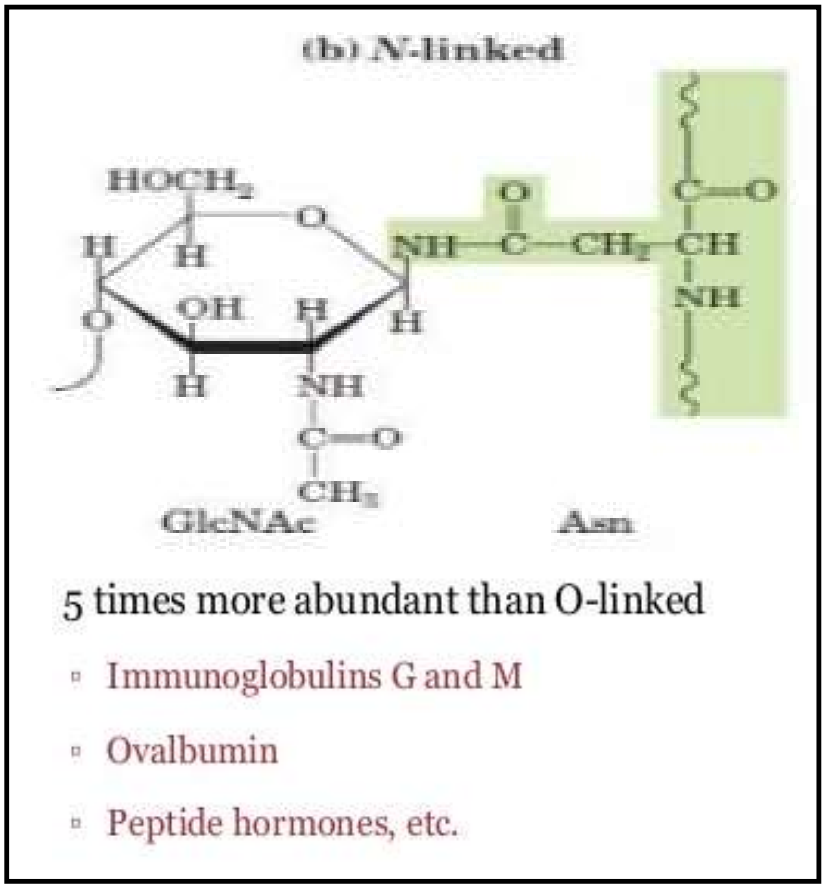


GLYCOPROTEINS

- Covalently attached to proteins with much **smaller percentage of carbohydrate** than protein.
- Carbohydrates can be attached to the amide nitrogen in the side chain of asparagine **(N-linkage)** or to the hydroxyl oxygen of serine or threonine **(O-linkage)**



- cell surface glycoproteins
- mucins
- viral glycoproteins



5 times more abundant than O-linked

- Immunoglobulins G and M
- Ovalbumin
- Peptide hormones, etc.

Functions of glycoproteins

Structural

- receptors on cell surfaces
- strength and support to a matrix
- slime layer of bacteria, and flagella

Protection

- Mucin ... form a highly viscous gel
  - Protect internal epithelial surfaces
- Act as a lubricant
  - Human lacrimal glands produce a glycoprotein which protects the corneal epithelium

Reproduction

- Glycoproteins on surface of sperm cell
  - increase attraction for the egg by altering the electrophoretic mobility of the plasma membrane.
- Hen ovalbumin .... serves as a food storage unit for the embryo.

Adhesion:

- cells to cells ..
  - development of tissues..
    - i.e N-CAM (nerve cell adhesion molecule)
    - on nerve cells and muscle cells... form myoneural junctions
  - Bacterial infection
- cells to substratum
  - cell surface receptors for certain adhesion ligands

SAMPLE QUESTIONS

1. Which of the following monosaccharides is the majority found in the human body?

(a) D-type
(b) L-type
(c) Both L and D-types
(d) None of the above

2. Which of the following is the most abundant biomolecule on the earth?

(a) Lipids
(b) Proteins
(c) Carbohydrates
(d) Nucleic acids.

3. Which of the following is an example of Epimers?

(a) Glucose and Ribose
(b) Glucose and Galactose
(c) Galactose, Mannose and Glucose
(d) Glucose, Ribose and Mannose

4. Class of carbohydrate which cannot be hydrolysed further, is known as?

a) Disaccharides
b) Polysaccharides
c) Proteoglycan
d) Monosaccharide

5. Which class of carbohydrates is considered as non-sugar?

a) Monosaccharides
b) Disaccharides
c) Polysaccharides
d) Oligosaccharides

6. A molecule of amylopectin which contains 1500 glucose residues and is branched after every 30 residues. How many reducing ends are there?

a) 0
b) 1
c) 2
d) 5

7. Which of the following glycosidic linkage found in maltose?

a) Glucose (α-1 – 2β) Fructose
b) Glucose (α1 – 4) Glucose
c) Galactose (β1 – 4) Glucose
d) Glucose (β1 – 4) Glucose

8. Which of the following is also known as invert sugar?

a) Sucrose
b) Fructose
c) Dextrose
d) Glucose

9. Humans are unable to digest

a) starch
b) complex carbohydrates
c) denatured proteins
d) cellulose

10. Which of the following is an analogous to starch?

a) Cellulose
b) Glycogen
c) Sucrose
d) Chitin

11. Non-digestible carbohydrates which serve as dietary fibres.

a) Glucose
b) Fructose
c) Cellulose
d) Maltose

12. When aldoses oxidize under proper conditions, they may form.

a) Aldonic acid
b) Saccharic acids
c) Uronic acid
d) All of these