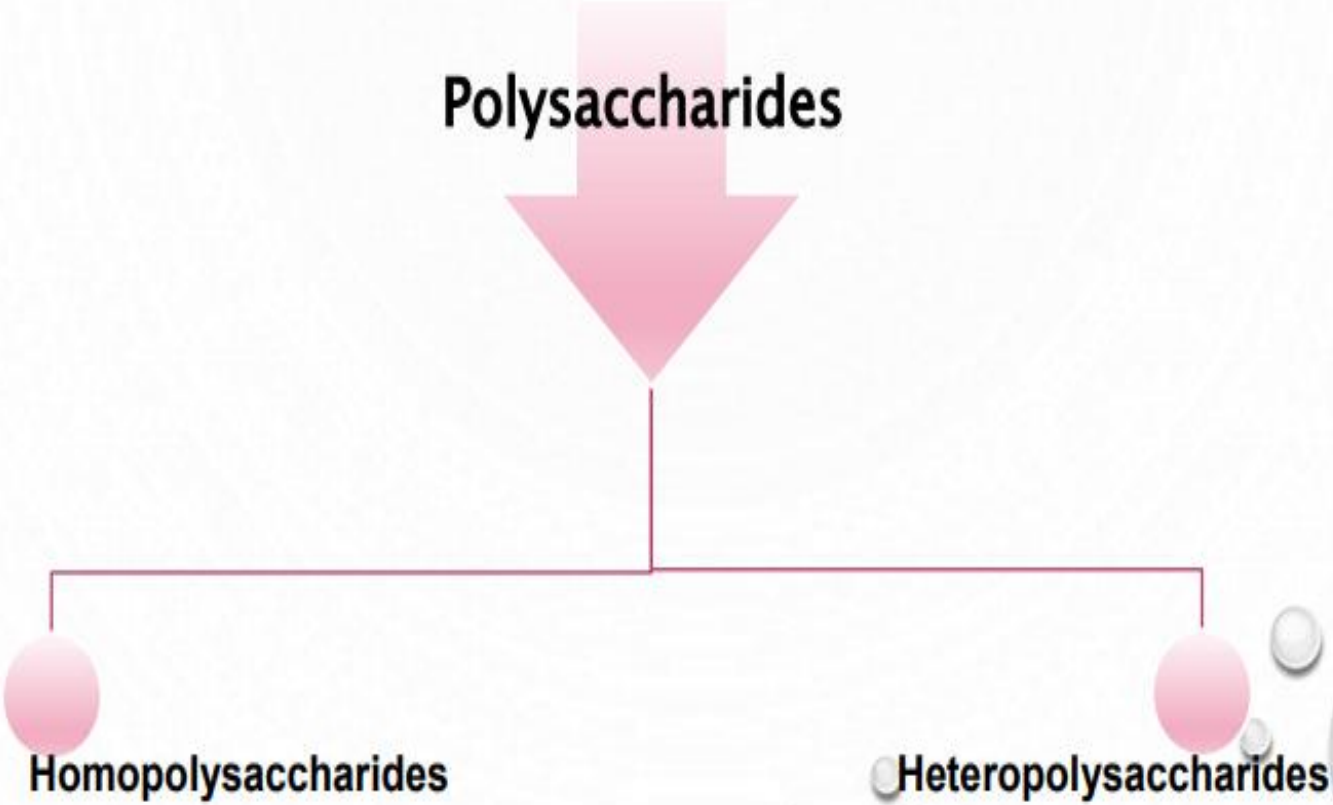
Polysaccharides

POLYSACCHARIDES

Definition:

- polysaccharides (greek: poly-many) are polymers of monosaccharide units with high molecular weight .
- Polysaccharides (or simply **glycans**) consist of repeat units of monosaccharides or their derivatives, held together by glycosidic bonds.
- They are usually tasteless (non-sugars) and form colloids with water.

Classification of polysaccharides



Polysaccharides

Chemical:

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

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

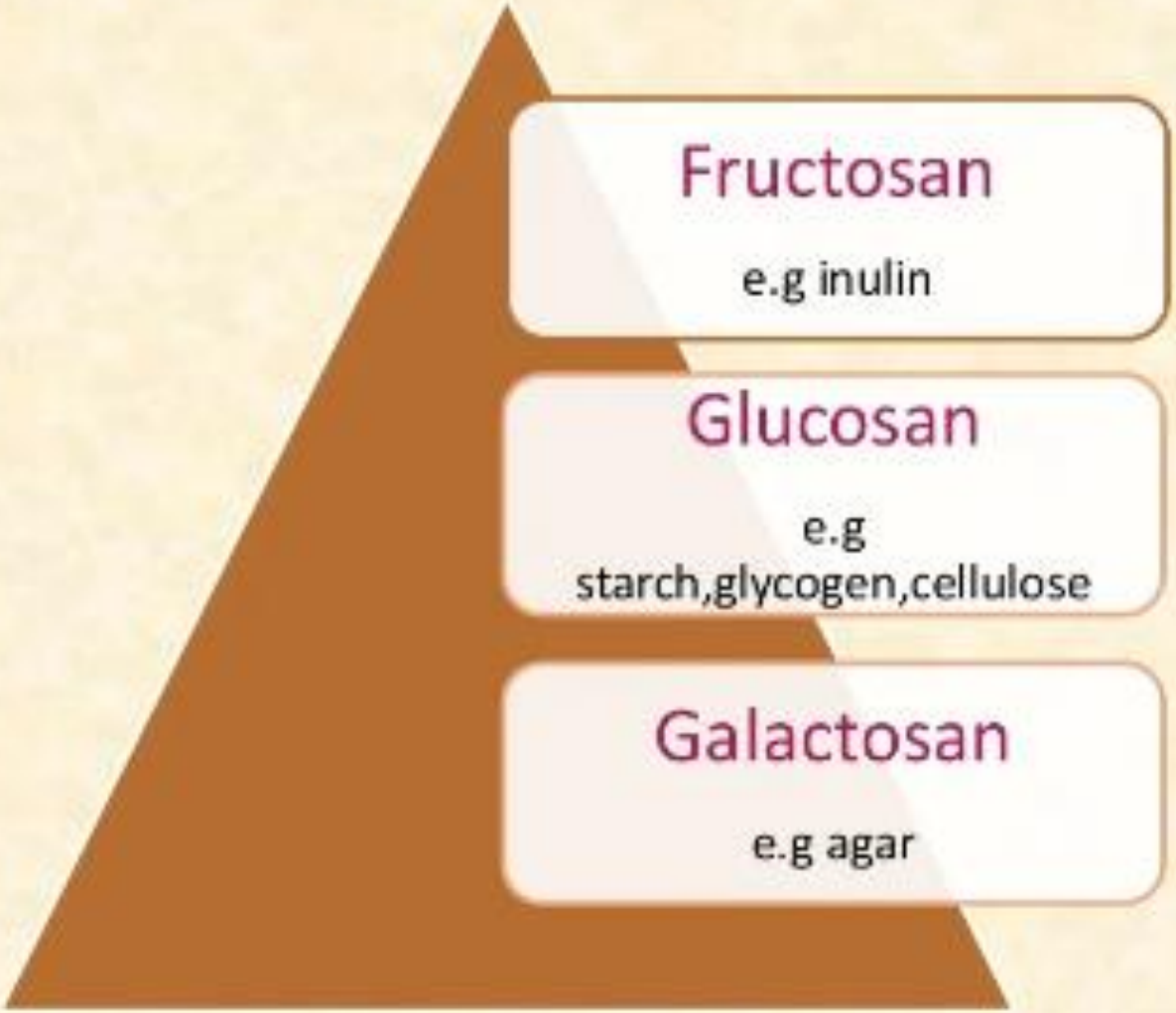
Functional:

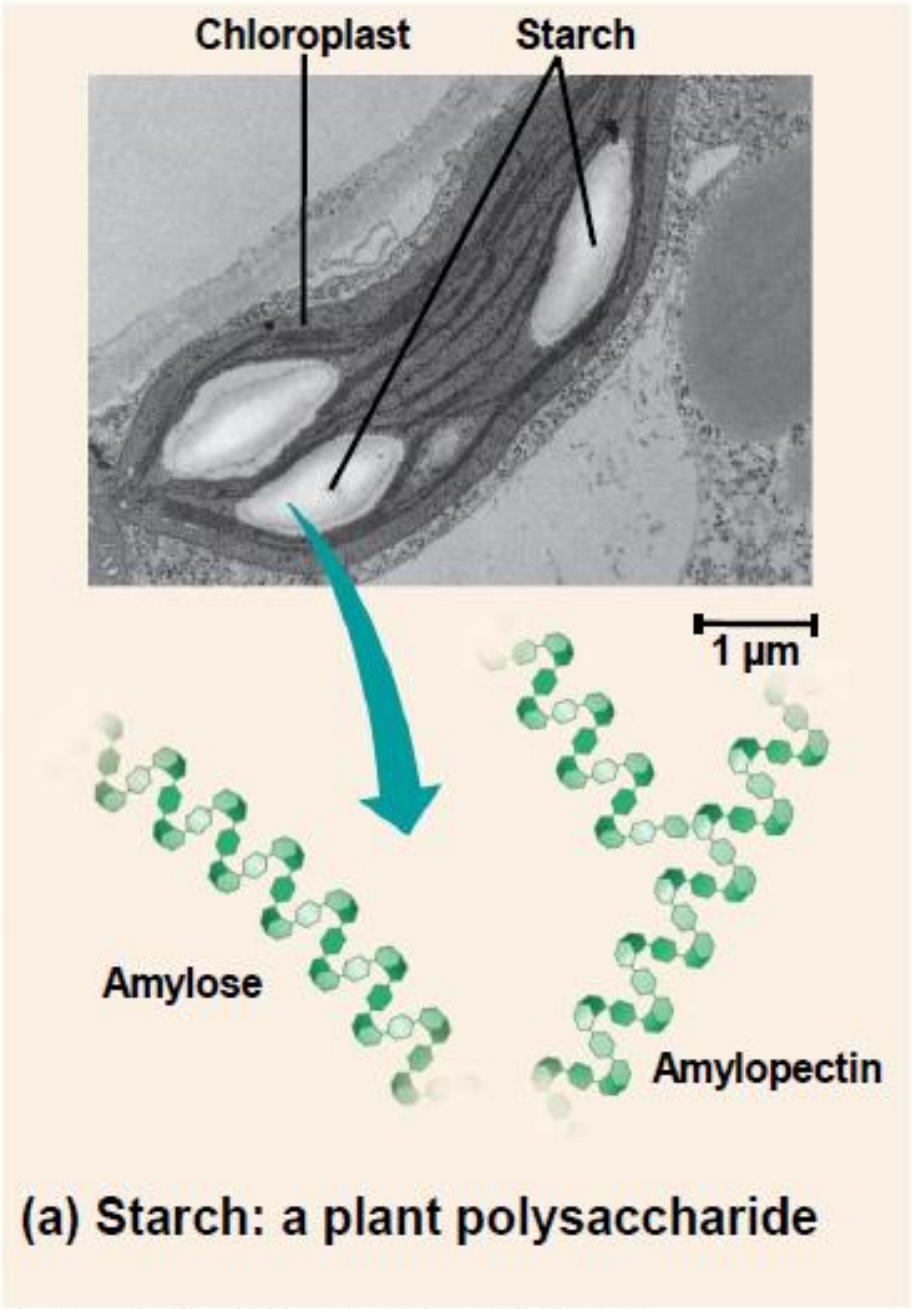
- **Nutrient polysaccharide (digestible)-** metabolic reserves of monosaccharides in plants and animals. **Eg. Starch, glycogen,**

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

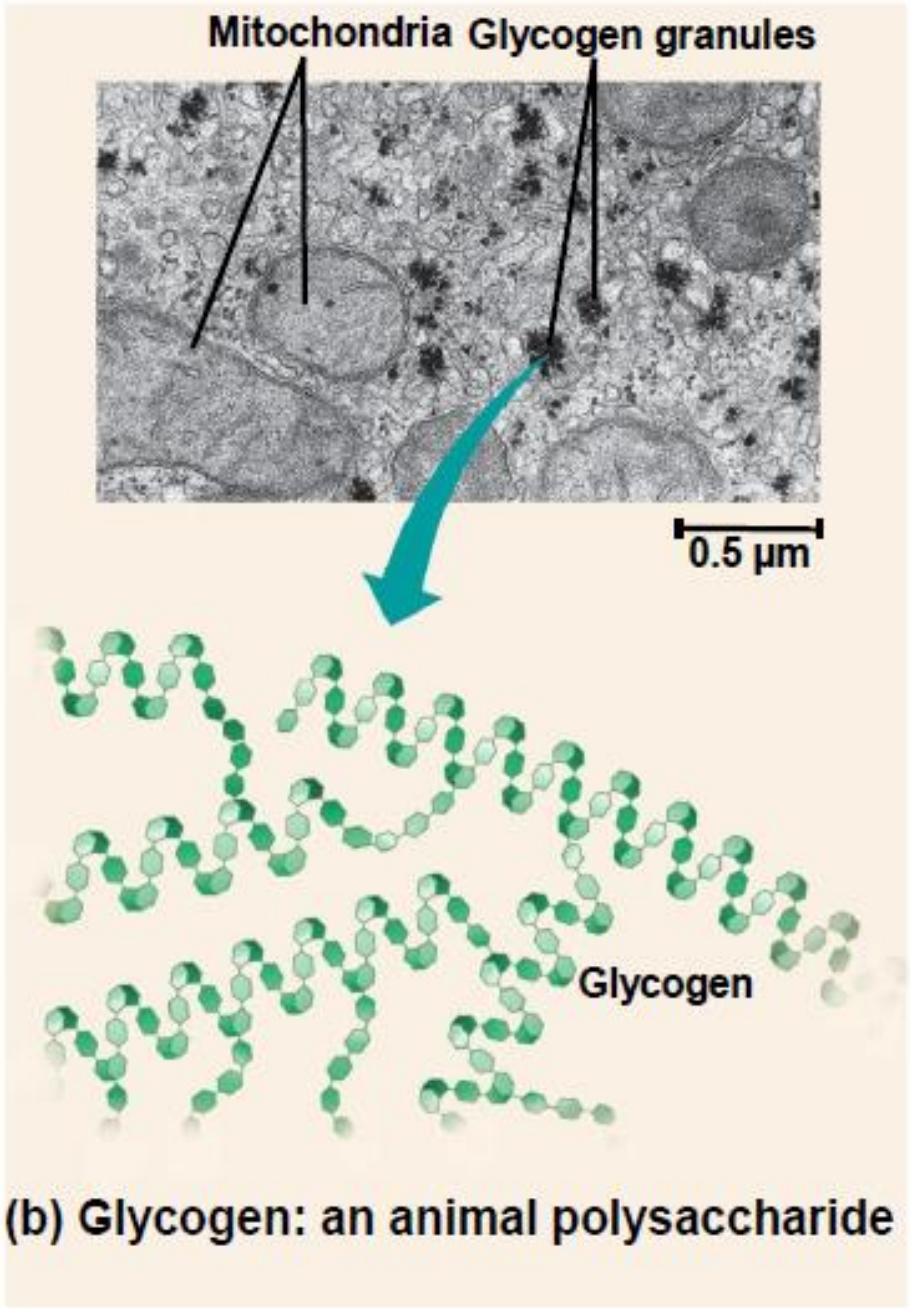
1.HOMOPOLYSACCHARIDES

Homopolysaccharides are polymers composed of single type of sugar units.





(a) Starch: a plant polysaccharide



(b) Glycogen: an animal polysaccharide

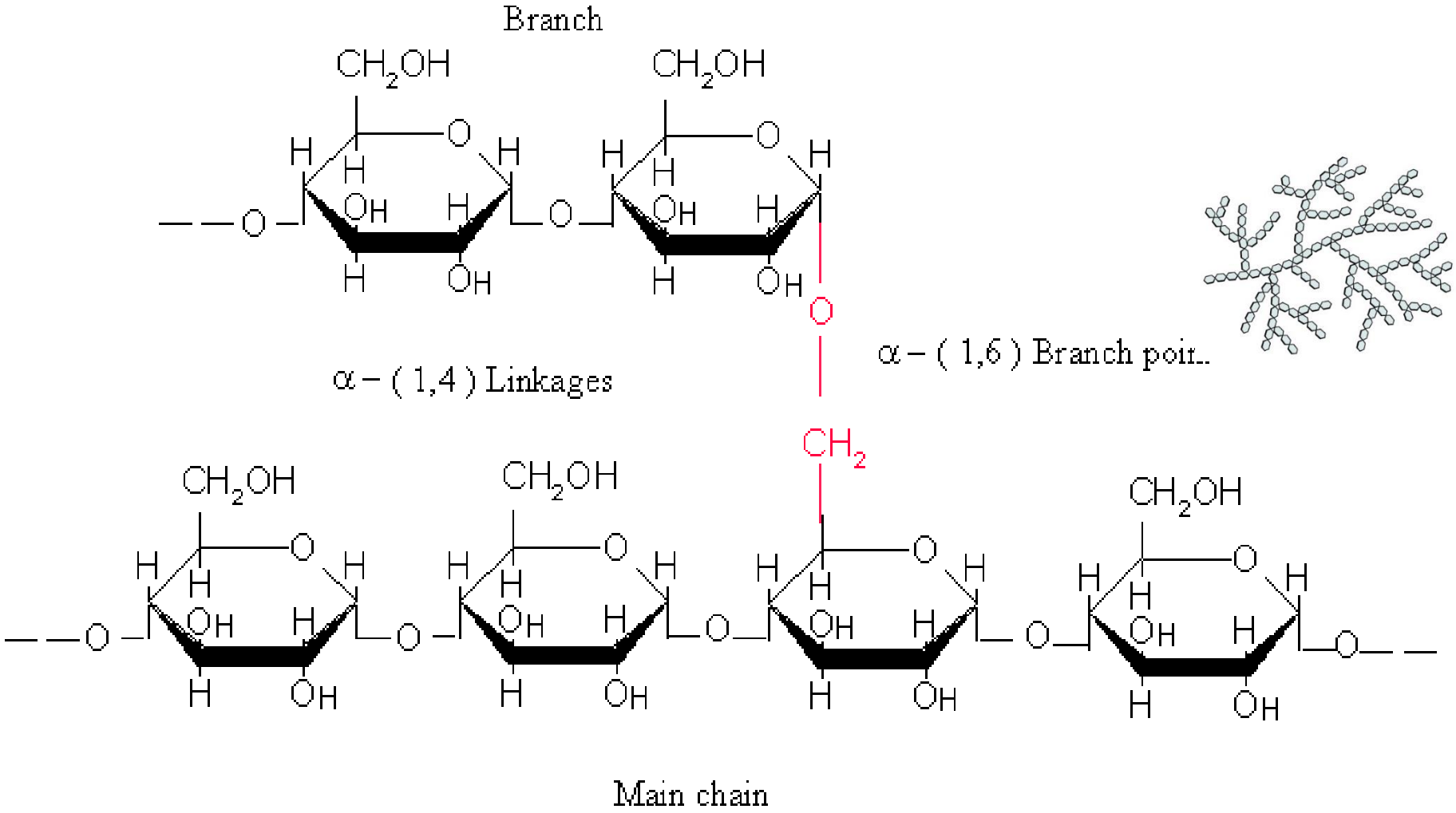
GLUCOSANS /GLUCANS

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.

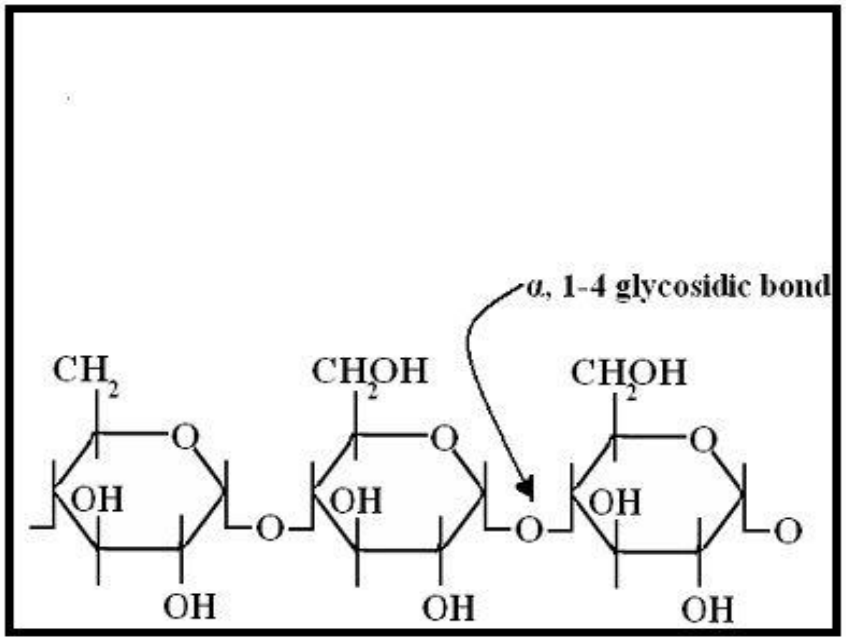
  It is soluble in water, reacts with iodine to give a blue color and the molecular weight of Amylose ranges between 50, 000 – 200, 000.

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

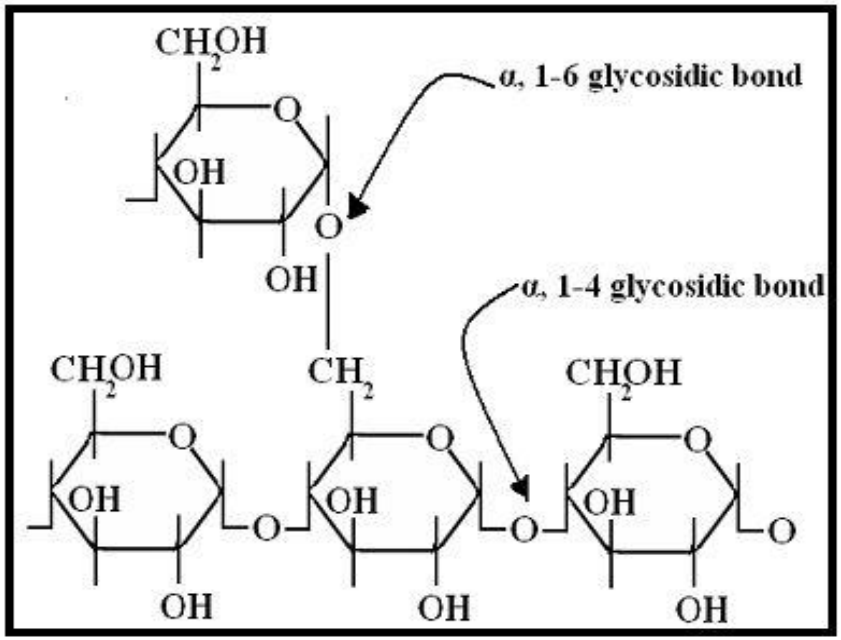
The molecular weight ranges between 70, 000 - 1 000, 000. Branches are composed of 25-30 glucose units linked by α-1→4 glycosidic linkage in the chain and by α-1→6 glycosidic linkage at the branch point.

Starch

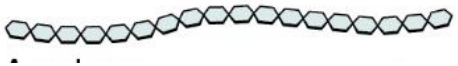
- **Alpha(1,6) branch point every 30 residues in amylopectin**
- **Most starch are 10-30% amylose and 70-90% amylopectin**

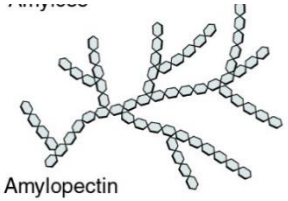


(a) amylose



(b) amylopectin





Amylose

1) Soluble in water

2)Gives Blue colour with dilute iodine solution

3)Structure –unbranched

4)250 to 300 D-glucose units linked by alpha 1→4 linkages

5)Mol. wt approx.60000

6)Occurs at the extent of 15 to 20%

Amylopectin

1)Insoluble in water

2)Gives reddish colour with iodine solution

3)Structure – highly branched

4)Units joined together by Alpha 1→4glycosidic bond and at branch point with alpha 1→6 glycosidic linkages

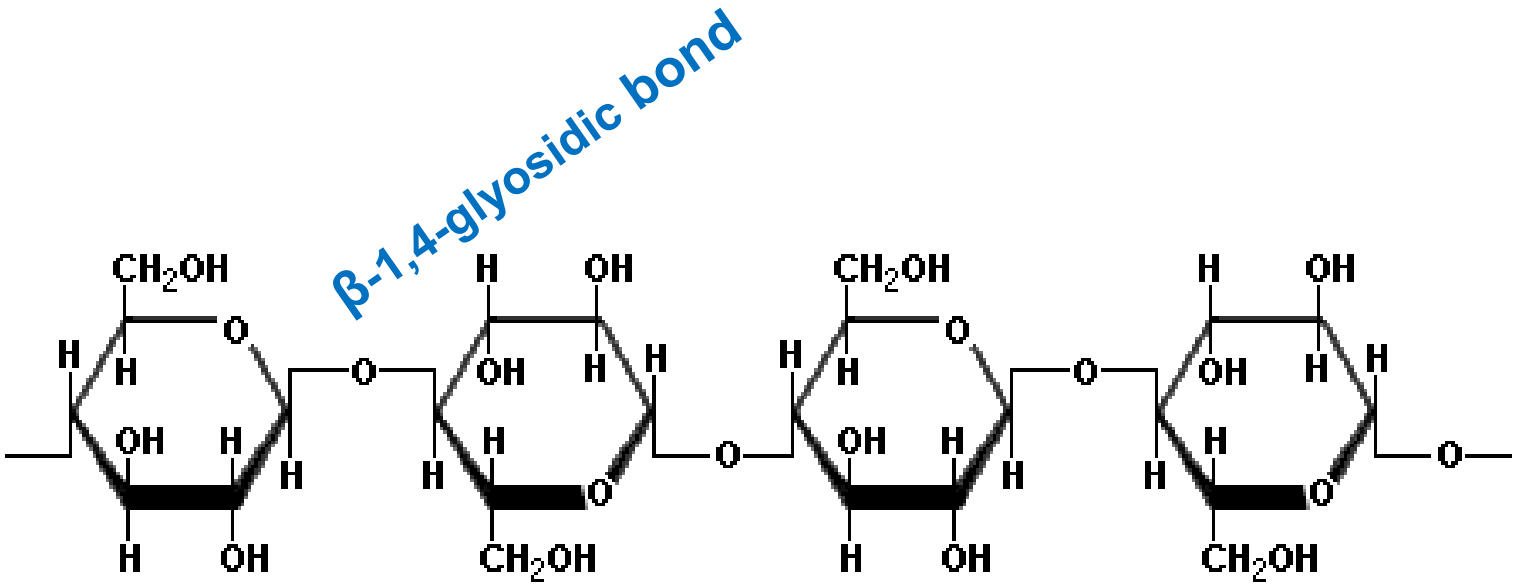
5)Mol. wt. approx 500000

6)0ccurs at 80 to 85%

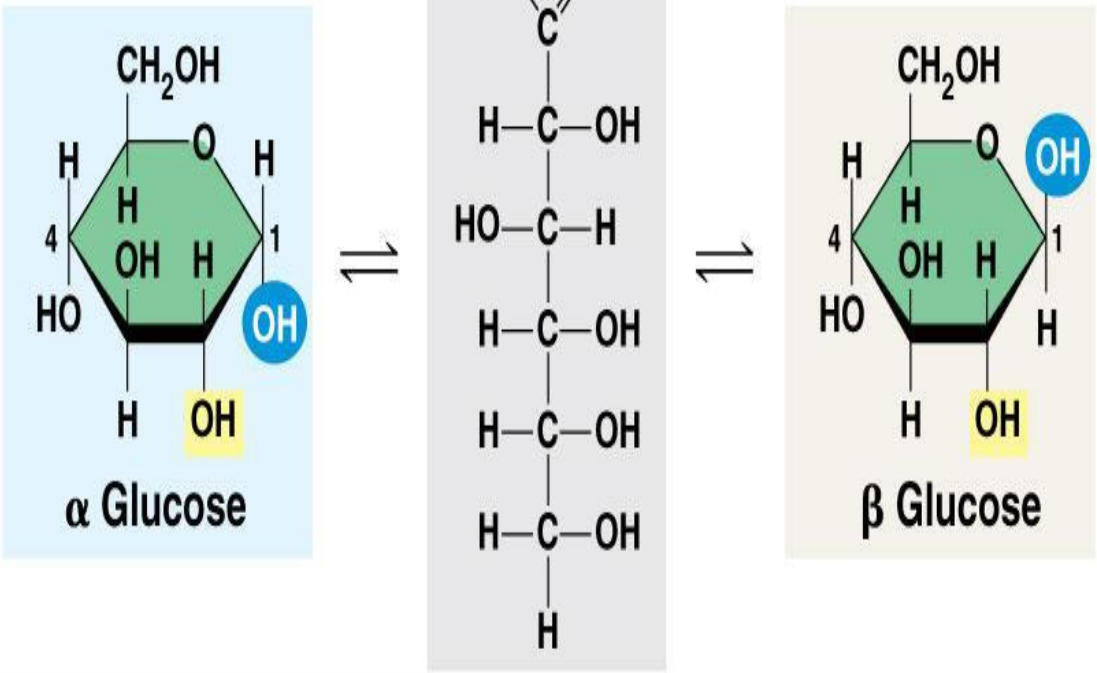
CELLULOSE (STRUCTURAL POLYSACCHARIDE)

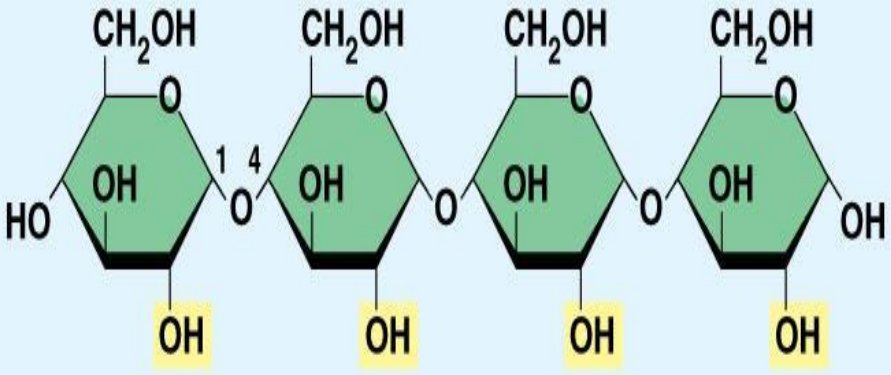
- Polymer of β-D-glucose linked by β(1,4) linkages.
- Yields glucose upon complete hydrolysis.
- Partial hydrolysis yields cellobiose.
- Most abundant of all carbohydrates.
- Gives no color with iodine.
- Cellulose is tasteless, odorless and insoluble in water and most organic solvents.

- Herbivorous animals utilise cellulose with the help of bacteria.
- Human beings lack any enzyme that hydrolyzes the β (1→ 4) bonds, and so cannot digest cellulose. It is an important source of "bulk" in the diet, and the major component of dietary fiber stimulating peristalsis and elimination of indigestible food residues.

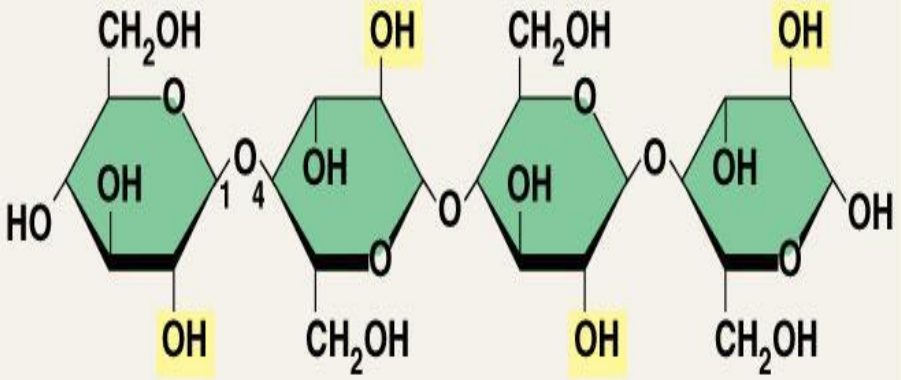


(a) α and β glucose ring structures

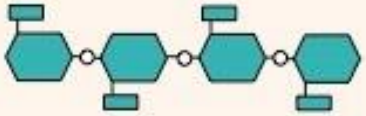
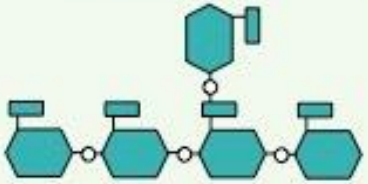
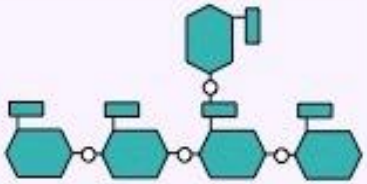
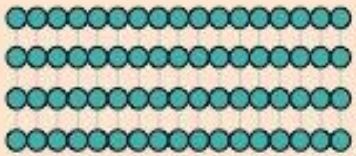
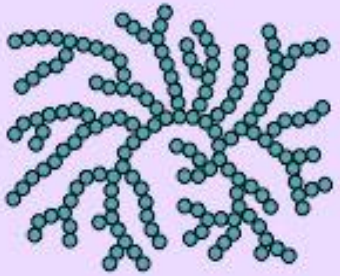




(b) Starch: 1–4 linkage of α glucose monomers

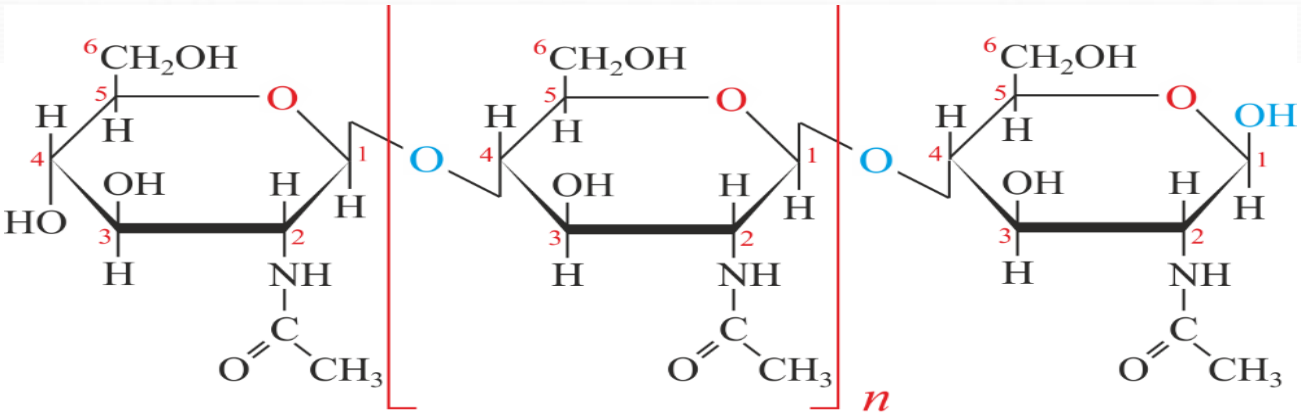


(c) Cellulose: 1–4 linkage of β glucose monomers

	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 is the second most abundant carbohydrate polymer
- Like cellulose, chitin is a structural polymer
- present in the cell wall of fungi and in the exoskeletons of crustaceans, insects and spiders
- Consists of N-acetyl-D-glucosamine units joined by β(1→4) glycosidic linkages



β-(1,4)-N-acetyl-D-glucosamine

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

Dextrans

- Products of the reaction of glucose and the enzyme transglucosidase from *Leuconostoc mesenteroides*.
- contains a (1,4), a (1,6) a (1,3) and a (1,2) linkages.
- MW: 4,000,000
- It is used in some eye drops as a lubricant.
- also used as molecular sieves to separate proteins and other large molecules (gel filtration chromatography)
- component of dental plaques.

FRUCTOSANS

Inulin

- β-(1,2) linked fructofuranoses
- linear only; no branching
- lower molecular weight than starch
- hydrolysis yields fructose
- sources include onions, garlic etc.
- used as diagnostic agent for the evaluation of glomerular filtration rate (renal function test)

GALACTOSANS

❖AGAR:-

- Agar is a galactose polymer.
- Obtained from the cell walls of some species of red algae (*Sphaerococcus Euchema*) and species of Gelidium.
- Dissolved in hot water and cooled, agar becomes gelatinous.
- Used in microbiology .

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).

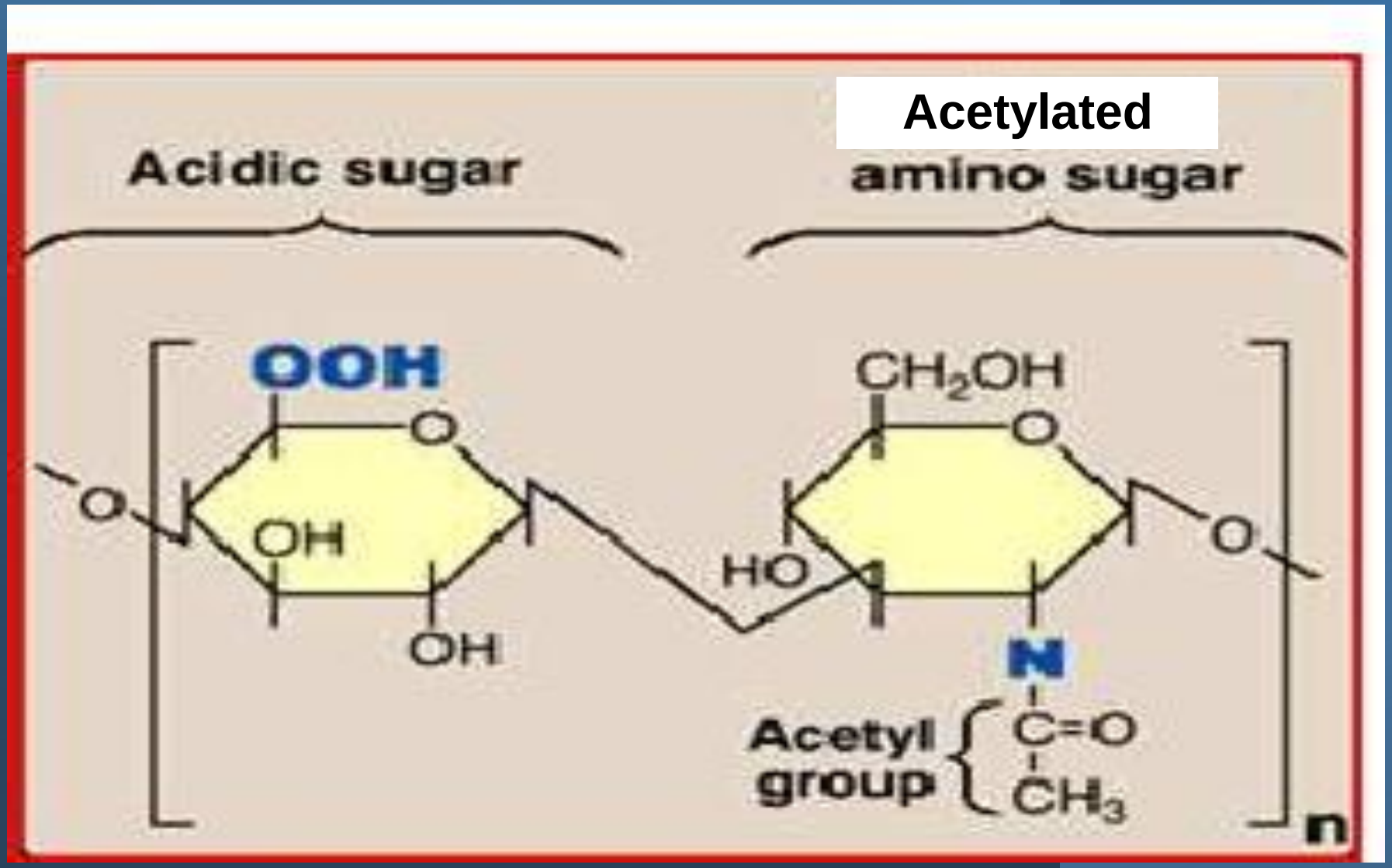
3-types

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.


Acetylated
Acidic sugar
amino sugar
COOH
O
O
OH
OH
CH2OH
O
O
HO
N
Acetyl group
C=O
CH3
n

Heparin

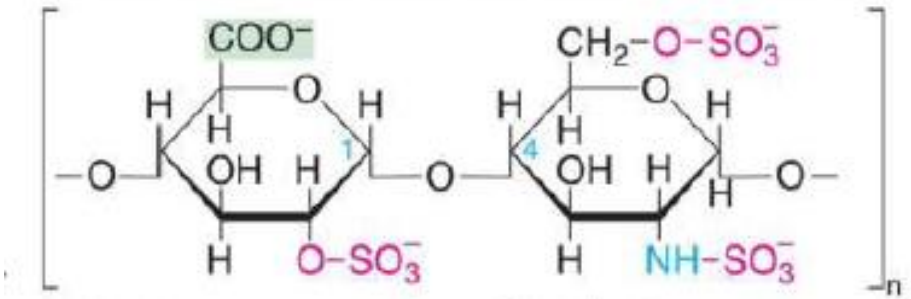
Heparin is a medically important polysaccharide because it prevents clotting in the bloodstream.

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**

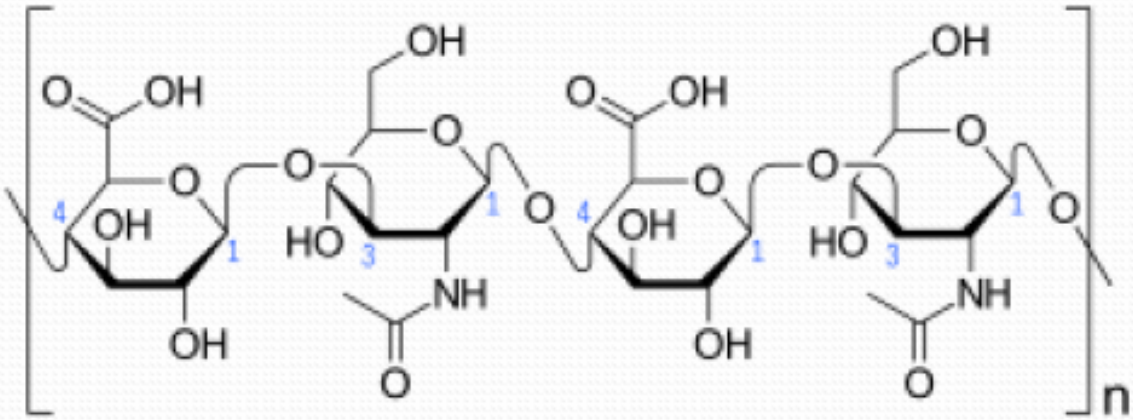
Sulfate containing ⟶ **Chondroitin Sulphate, Dermatan sulphate, keratan sulphate, Heparin, Heparan Sulphate**

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.

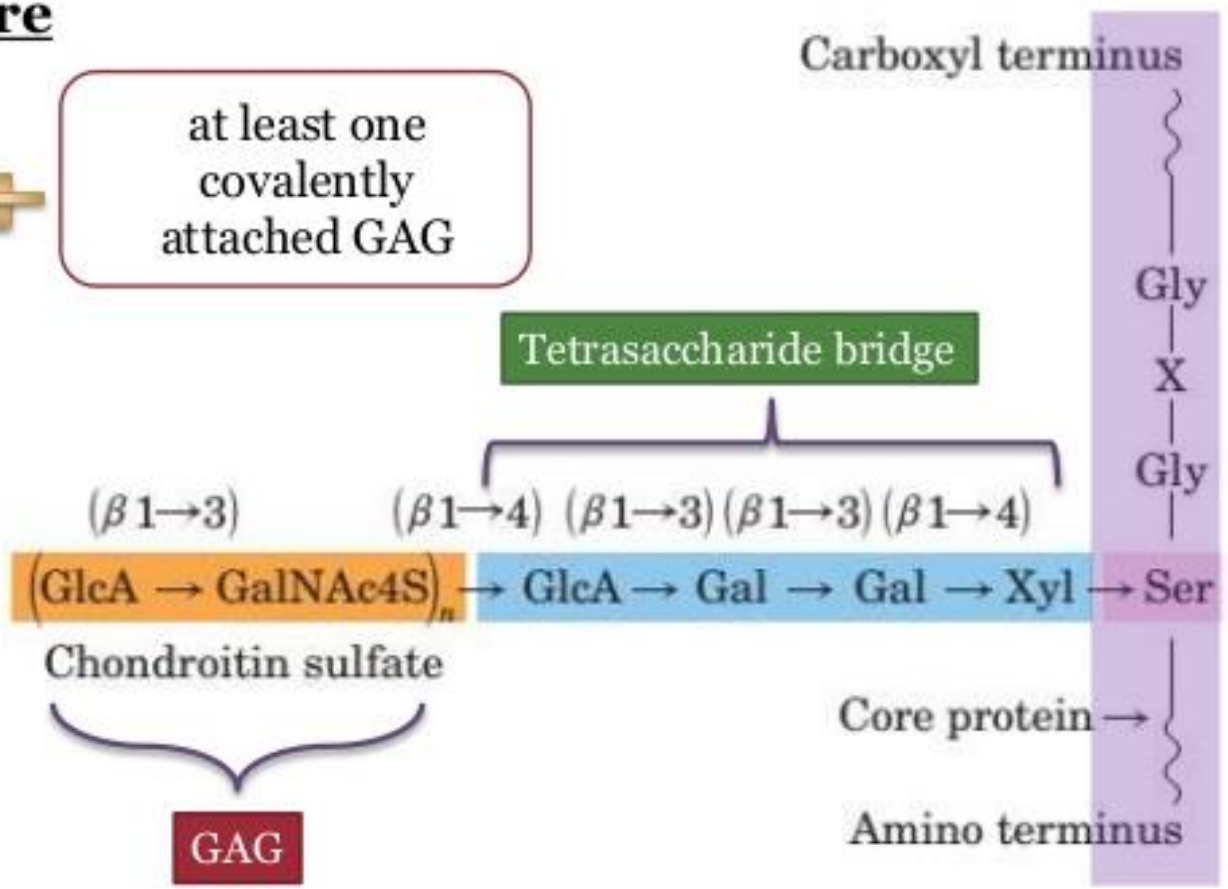
Proteoglycans

- 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.

Basic structure

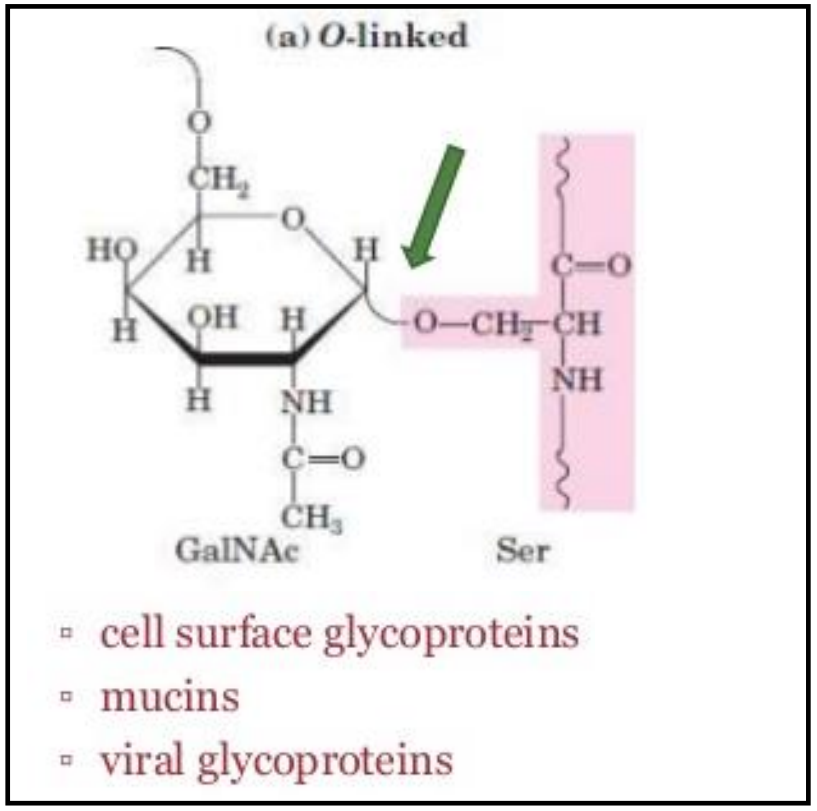
A core protein + at least one covalently attached GAG



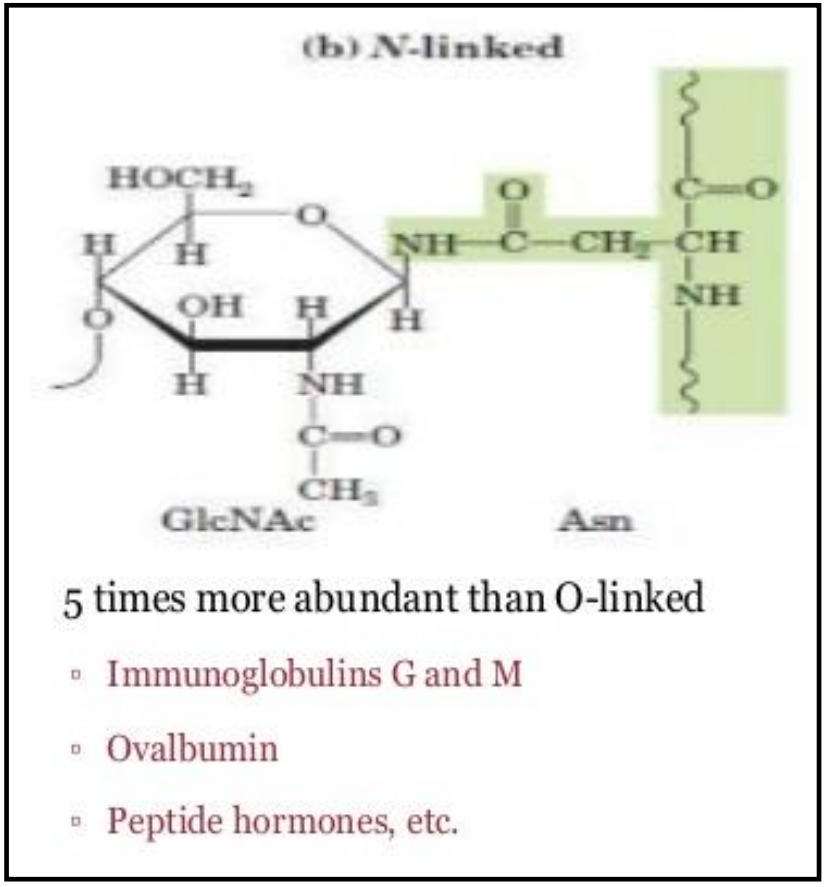
Lehninger principles of biochemistry: 5th ed.

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