# Carbohydrates III

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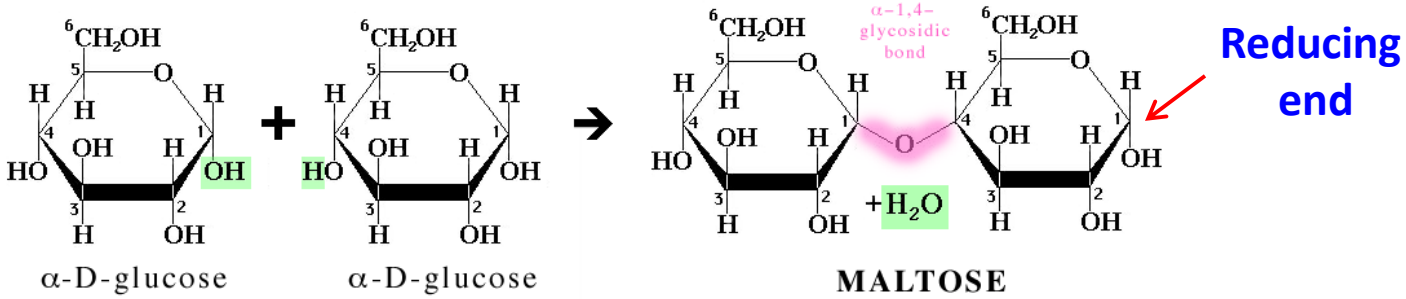
# Disaccharides

- These are two monosaccharides linked together via the glycosidic bond. Three common disaccharides:
  - Maltose "malt sugar" consists of two α-D-glucose units, is a disaccharide released during the hydrolysis of the starch




α-D-glucopyranosyl-(1 ⟶ 4)-α-D-glucopyranose

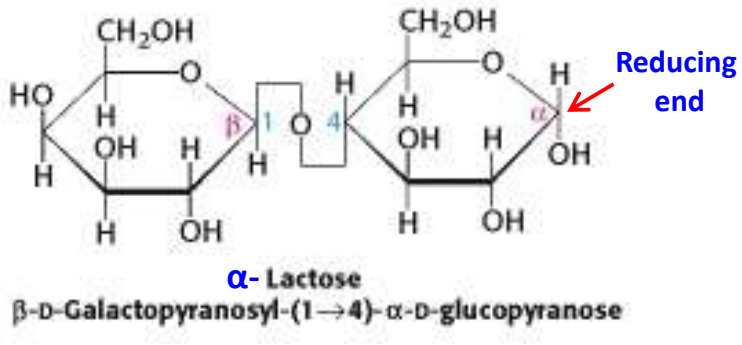

- Barely grains is used for preparation of malt beverage. During the degradation of starch, maltose sugar is produced.

# Glycosidic bond

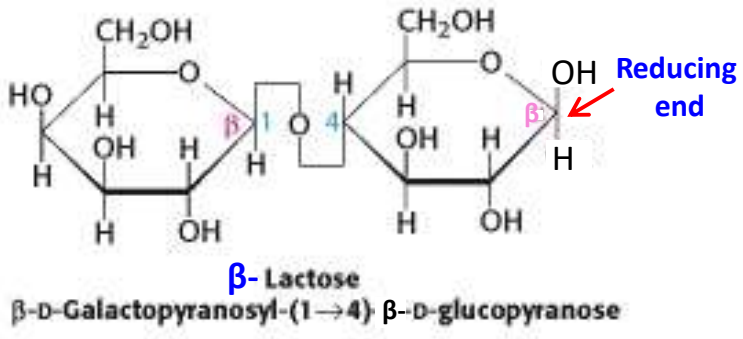
- Glycosidic bond is a type of covalent  bond where the anomeric group of a sugar can **condense** with an alcohol. This type of bond is called O-glycosidic bond (because O atom binds the two carbon atoms together)
- In maltose, the bond will form between C1 of the first unit and C4 of the second unit with a water molecule being released (condensation reaction). This bond is named as α-1-4 O-glycosidic bond
- Maltose is a reducing sugar as it has a free anomeric carbon of the second unit

# Disaccharides

- Lactose “milk sugar” consists of glucose & galactose, is a disaccharide occurs naturally in the milk **(dairy products)**




**α- Lactose**
β-D-Galactopyranosyl-(1→4)-α-D-glucopyranose

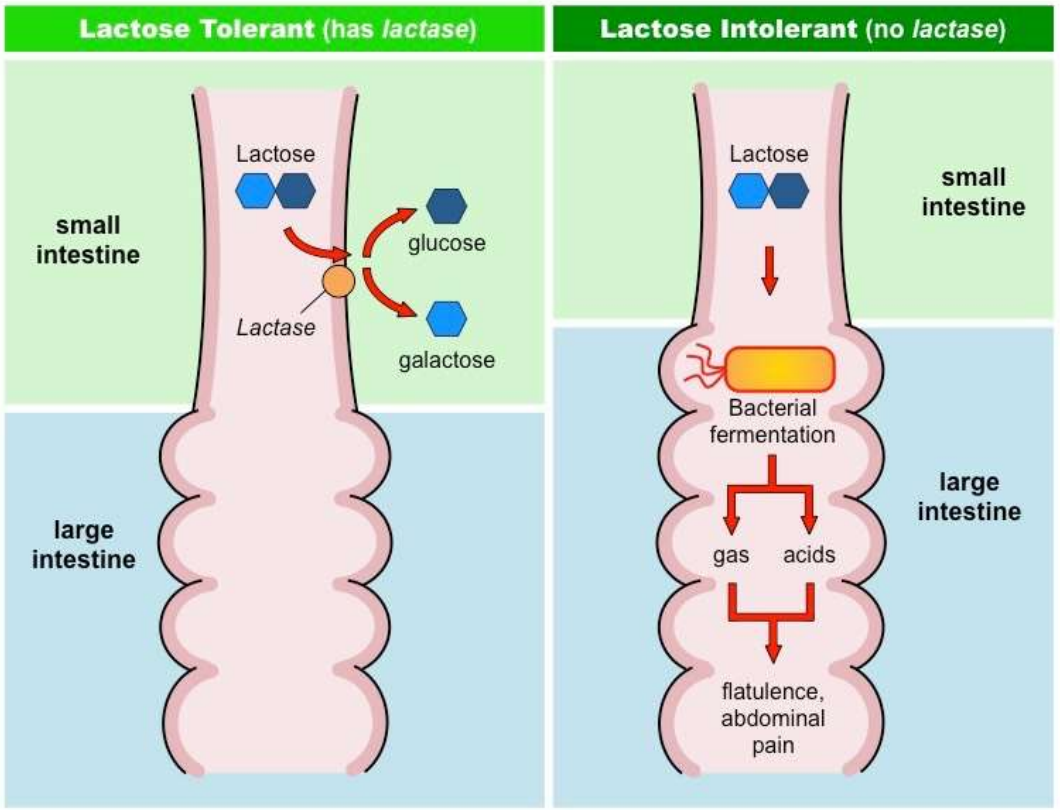



**β- Lactose**
β-D-Galactopyranosyl-(1→4)-β-D-glucopyranose

- Lactose is a reducing sugar as it has a free anomeric carbon of the second unit

# Lactose Intolerance

- Lactose Intolerance: deficiency of lactase enzyme leading to **Gastrointestinal tract (GIT) disturbances such as:** nausea, bloating, abdominal cramps and diarrhea as lactose will reach the colon intact and being digested by bacteria found in colon

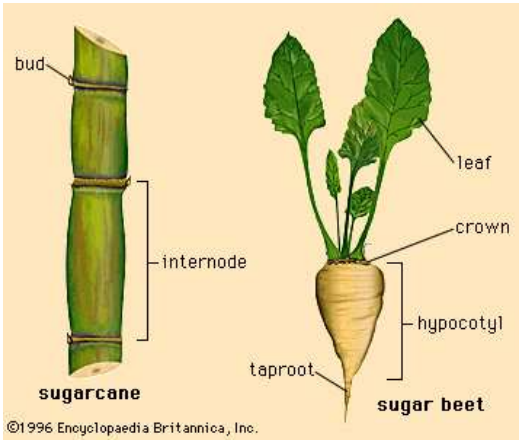


# Lactose Intolerance

- 4 types of Lactose Intolerance : **Primary** (lactase level declines with age), **secondary** (lactase level declines with injury of small intestine due to inflammatory bowel diseases), **congenital** (rare genetic disease, deficiency of lactase at birth) and **developmental** (premature babies).


# Disaccharides

- Sucrose “table sugar” consists of glucose & fructose, is disaccharide obtained commercially from cane or beet.




- Sucrose is not a reducing sugar because the anomeric carbon of the second residue (the reducing end) is not free but involved in the glycosidic bond formation.

# Polysaccharides

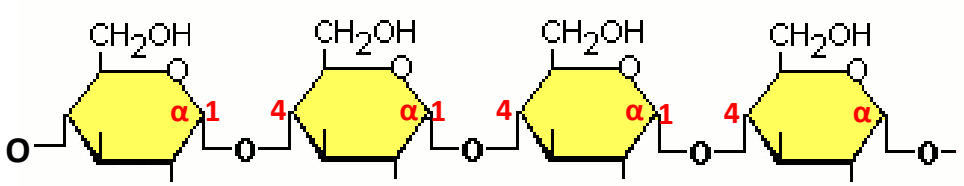
- Polysaccharides “glycans” are polymeric molecules consist of long chains of monosaccharide units bound together via the glycosidic linkages.
- Polysaccharides composed of same type of monosaccharides are called **homopolysaccharides** “homoglycans” and those consisting of more than one type are called **heteropolysaccharides** “heteroglycans” .
- They form branched as well as linear polymers.
- They are classified into:
  1. Storage polysaccharides like starch and glycogen
  2. Structural polysaccharides like cellulose and chitin

# Storage Polysaccharides

Starch: is the storage polysaccharides in plants.

- Polymer composed of **α–D-glucose** monomers
- a mixture of **amylose** (20%, water soluble) and **amylopectin** (80%, water insoluble) stored in plant cells as insoluble granules.

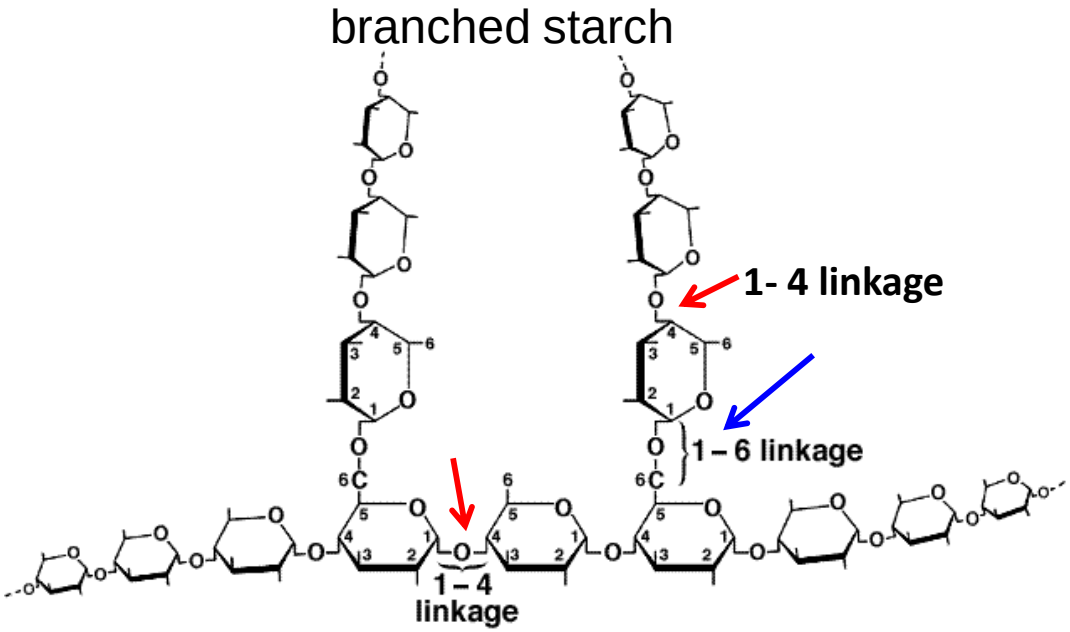
unbranched starch(linear)



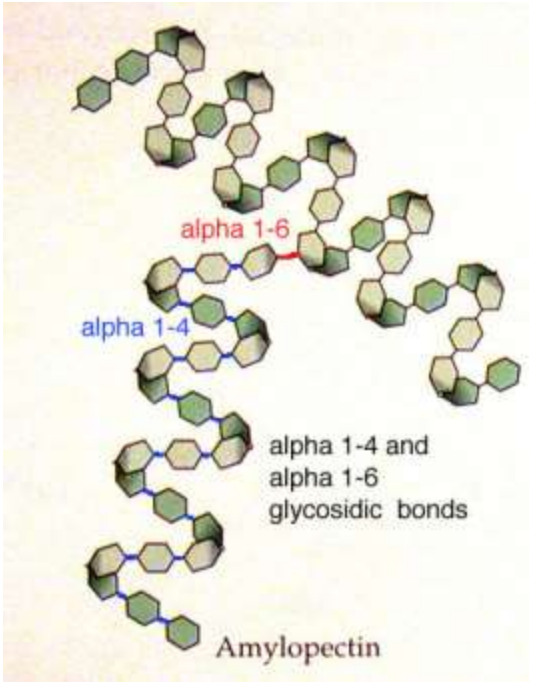

Amylose : α (1 ⟶4) glycosidic bonds

The helical structure of amylose

# Storage Polysaccharides



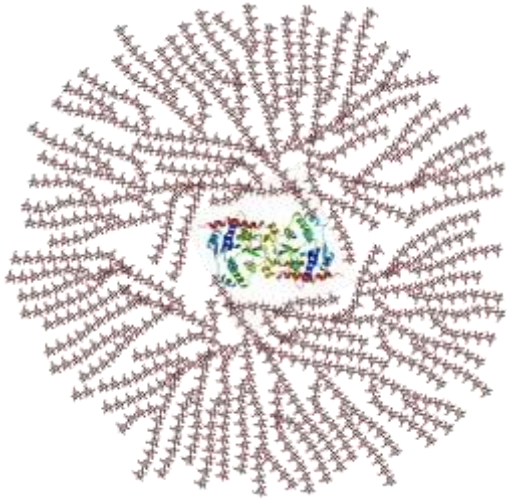

Amylopectin: α (1 ⟶ 4) glycosidic bonds
with α (1 ⟶ 6) branch points (every 24-30 units)

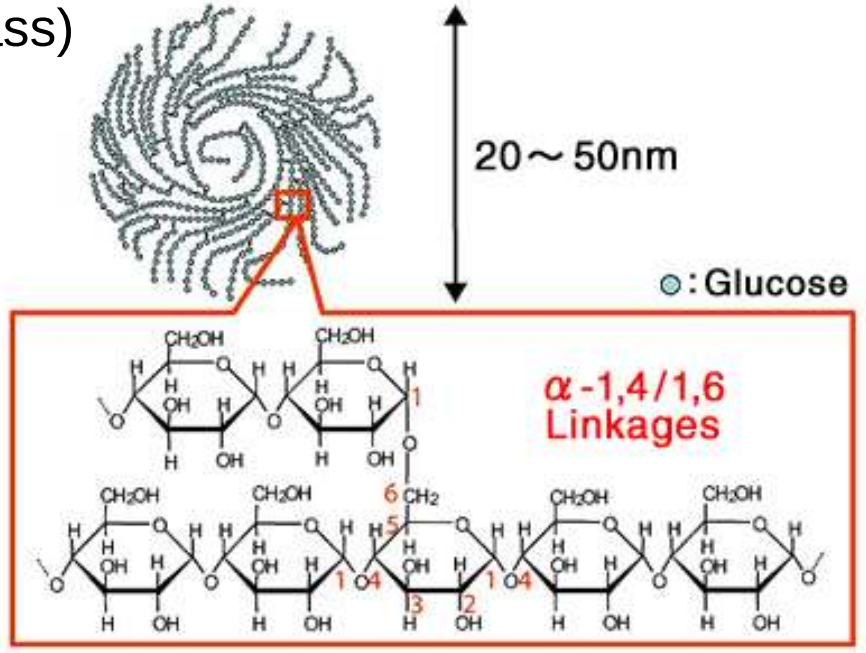


# Storage Polysaccharides

Glycogen: is the storage polysaccharide in animal & human

- Polymer composed of **α–D-glucose** units like amylopectin but glycogen is more highly branched with branch points occurring every 8-14 residues. Due to **α-linkage,** it adopts a helically coiled conformation (similar to starch) to be easily accessible for metabolic enzymes
- Mainly found in skeletal muscle (up to 1-2% of muscle mass) and liver cells (up to 10% of liver mass)



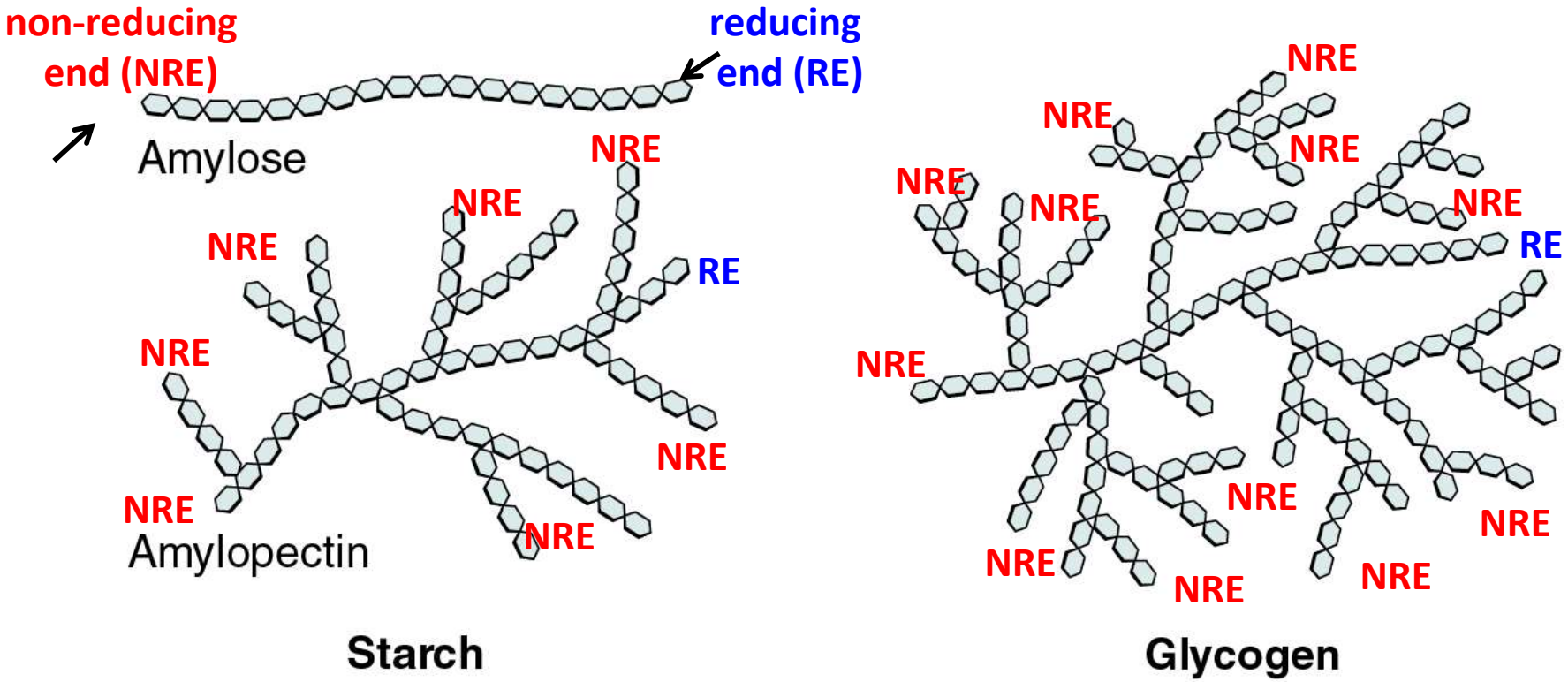


# Synthesis & Breakdown of Glycogen

- Some tissues particularly the brain cells require a constant supply of blood glucose for survival
- Some tissues particularly liver and skeletal muscles store glucose in a form that can be **rapidly mobilized** (i.e. glycogen)
- Glycogen in synthesized (glycogenesis) when blood glucose is high and glycogen is degraded (glycogenolysis) releasing glucose into the blood stream when blood glucose is low (normal blood glucose level is 80-100 mg/dl)
- This balance between the need and availability is called metabolic homeostasis

# Storage Polysaccharides

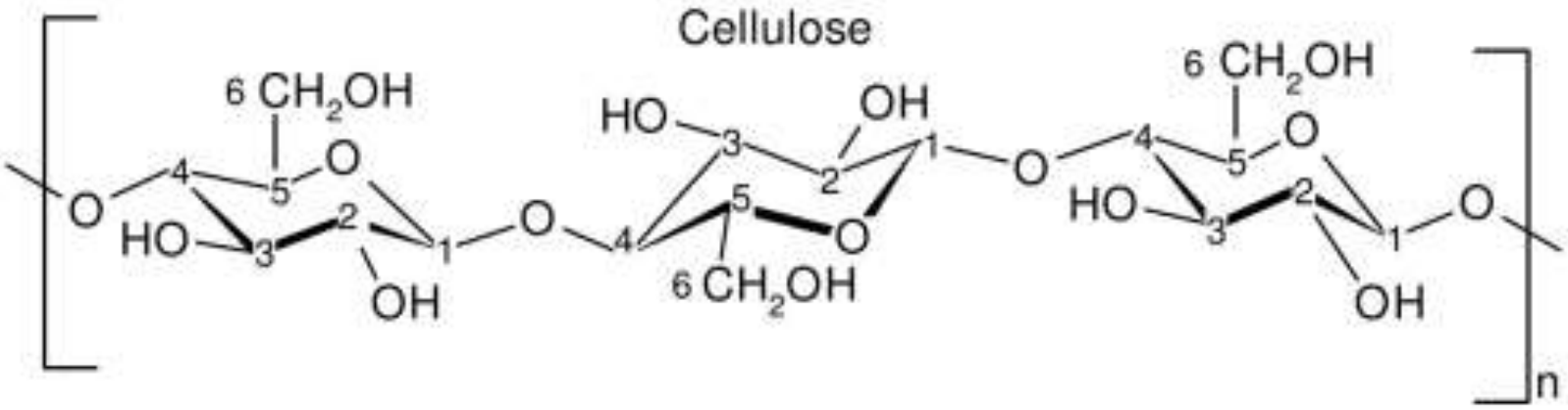
- Starch and glycogen have one reducing end (the molecule end containing a free anomeric carbon C1). On the other hand, the branches ends are all called non-reducing ends and being sites where enzymatic lengthening and degradation occur.



# Structural Polysaccharides

Cellulose: the primary structural component of plant cell walls.

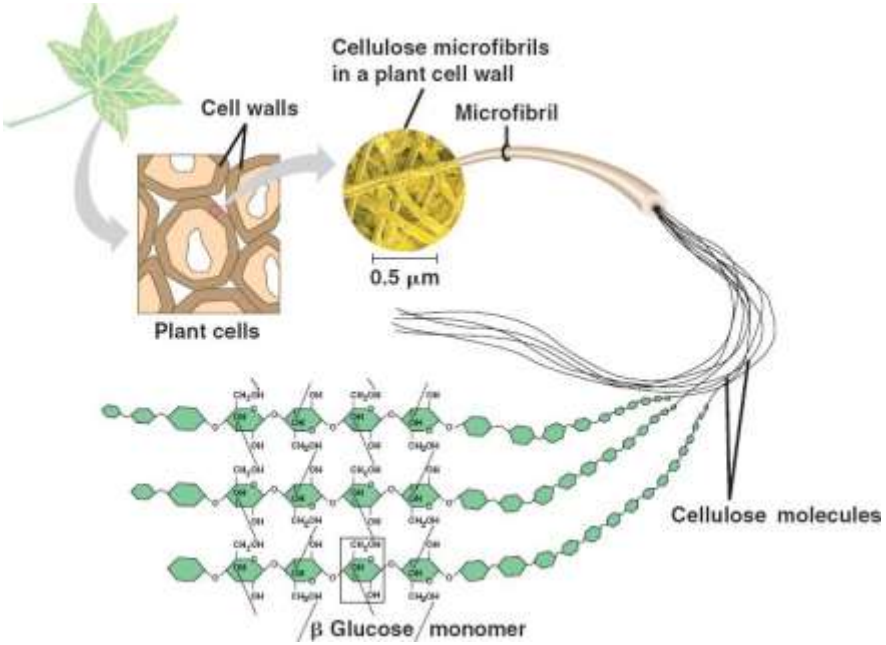
- A **linear** polymer of β-D-glucose residues linked via β-(1-4) glycosidic bonds.

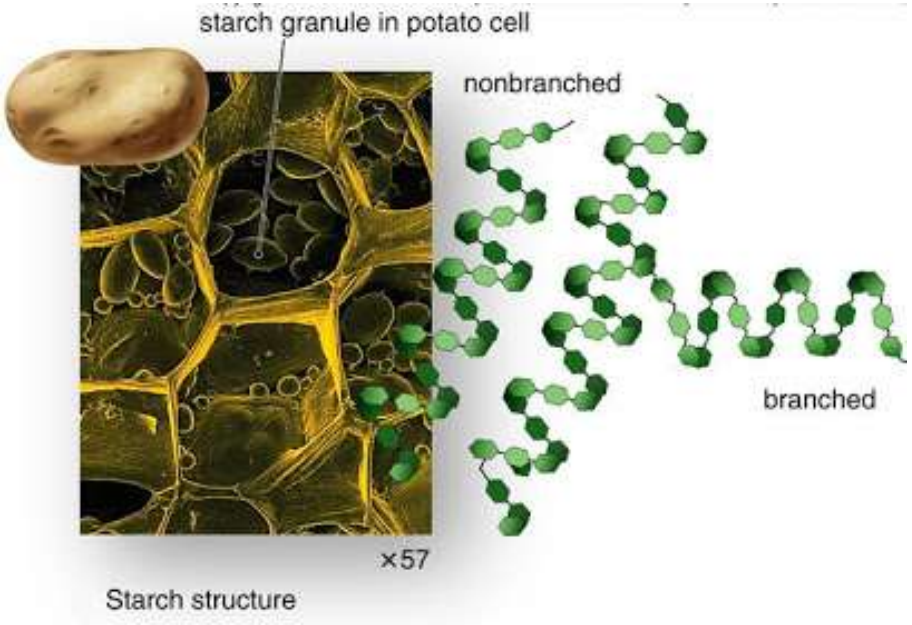



- It adopts a very different molecular architecture from that of starch (hollow helix) due to its β-linkages.

# Structural Polysaccharides

- Cellulose forms very long straight chains. The parallel chains interact with one another through H-bonds. So plant cells are rigid



# Structural Polysaccharides

- Compared to humans, herbivores and termites can digest cellulose because they have cellulases enzymes “enzymes capable of hydrolyzing the β-(1-4) bonds of cellulose ”.

- Cellulose rich food (like vegetables) is used in patients who have constipation by supporting the regular bowel movements.

# Structural Polysaccharides

## Chitin:

- It is the structural component of the exoskeletons of the invertebrates like insects and spiders. Also, it is the main component of the cell walls of fungi.

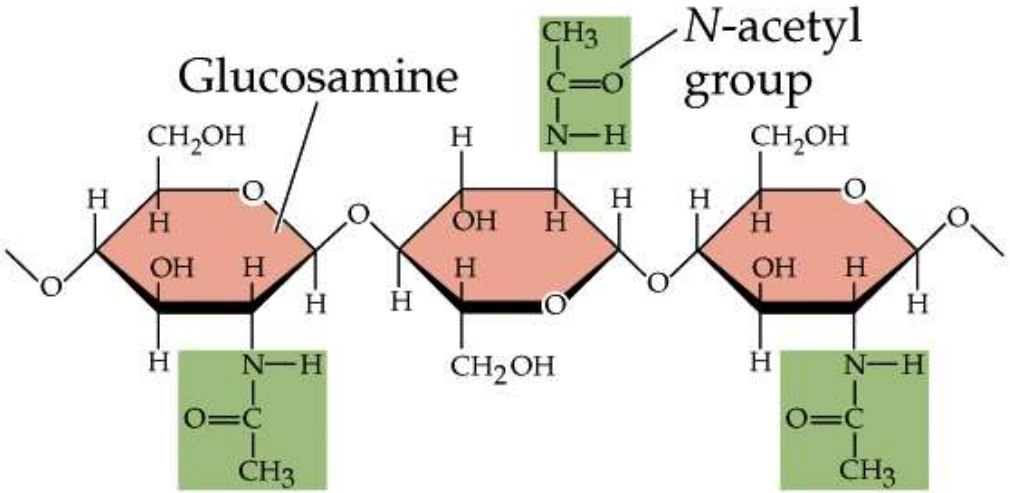
Cockroach

Spider

Shrimp

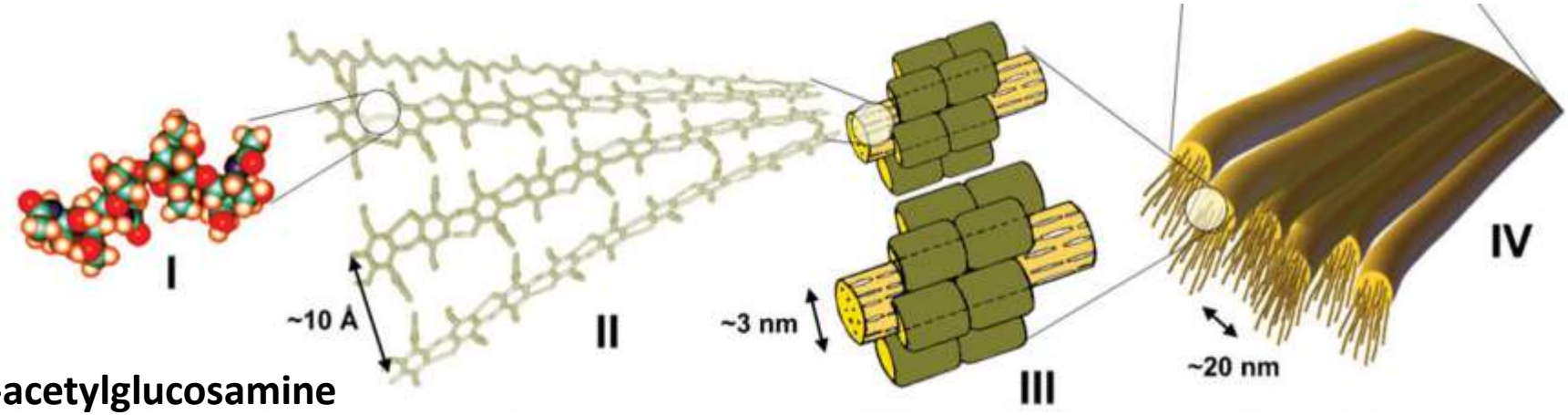
# Structural Polysaccharides

- A long chain polymer of N-acetyl-D-glucosamine residues joined by β-(1-4) bonds.




# Structural Polysaccharides

- It has similar structure to cellulose with the only difference is the replacement of OH at C2 of each monomer with acetyl amine group




**N-acetylglucosamine**

**Parallel long chains with H-bonds**

**Microfibrils**

# Heteropolysaccharides

- Consist of two or more different monosaccharide units and the naturally occurring heteroglycans are mostly found in the connective tissues (such as cartilage, tendon, blood vessel walls,…..etc).

1. **Hyaluronic acid** (Hyaluronate):

- It is the major component of joints fluid (synovial fluid). It acts as a lubricating agent and shock absorber.

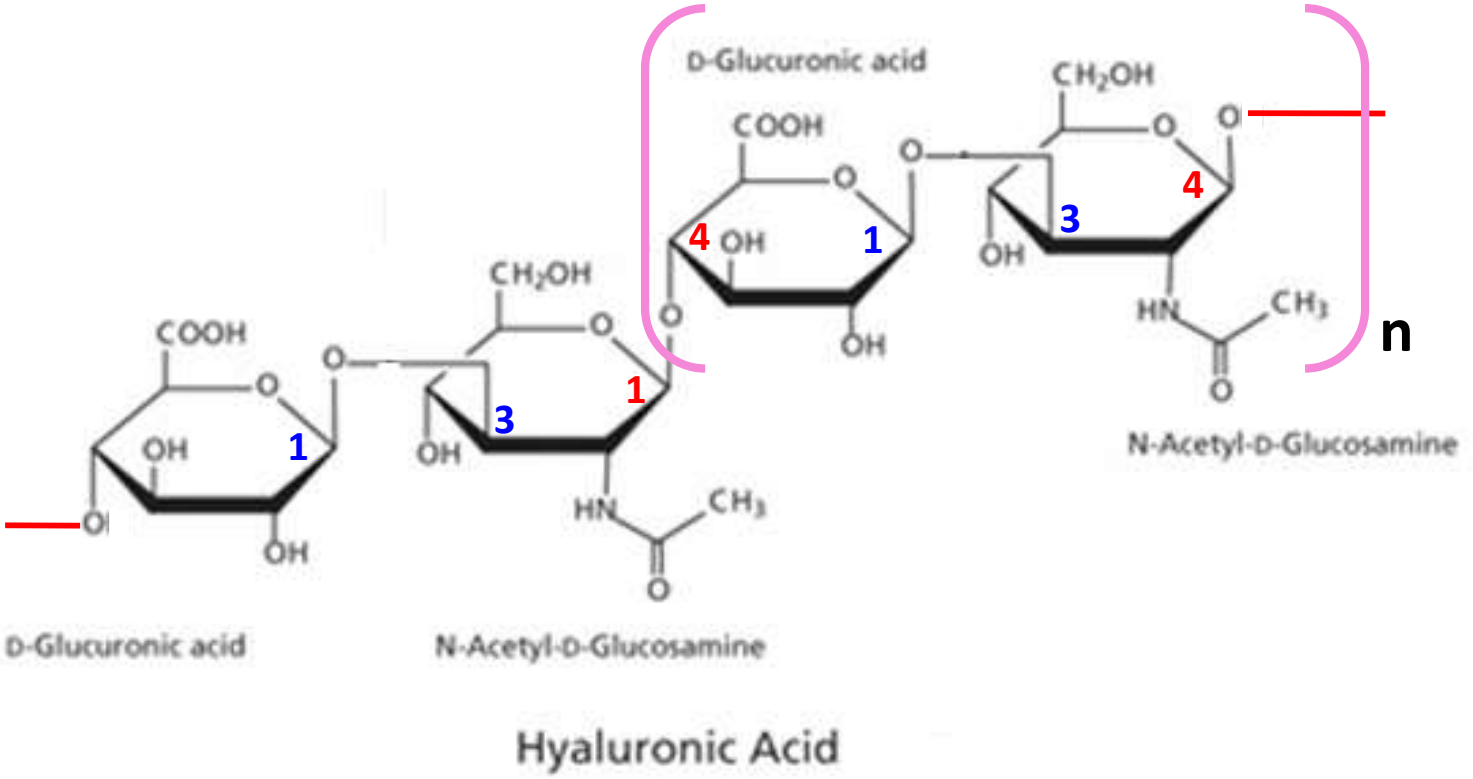


# Hyaluronic acid

- It is also a major component of skin, where it is involved in tissue repair and acts as moisturizing agents. Dry and scaly skin such as that caused by eczema may be treated with a prescription of skin lotion containing sodium hyaluronate as its active ingredient.

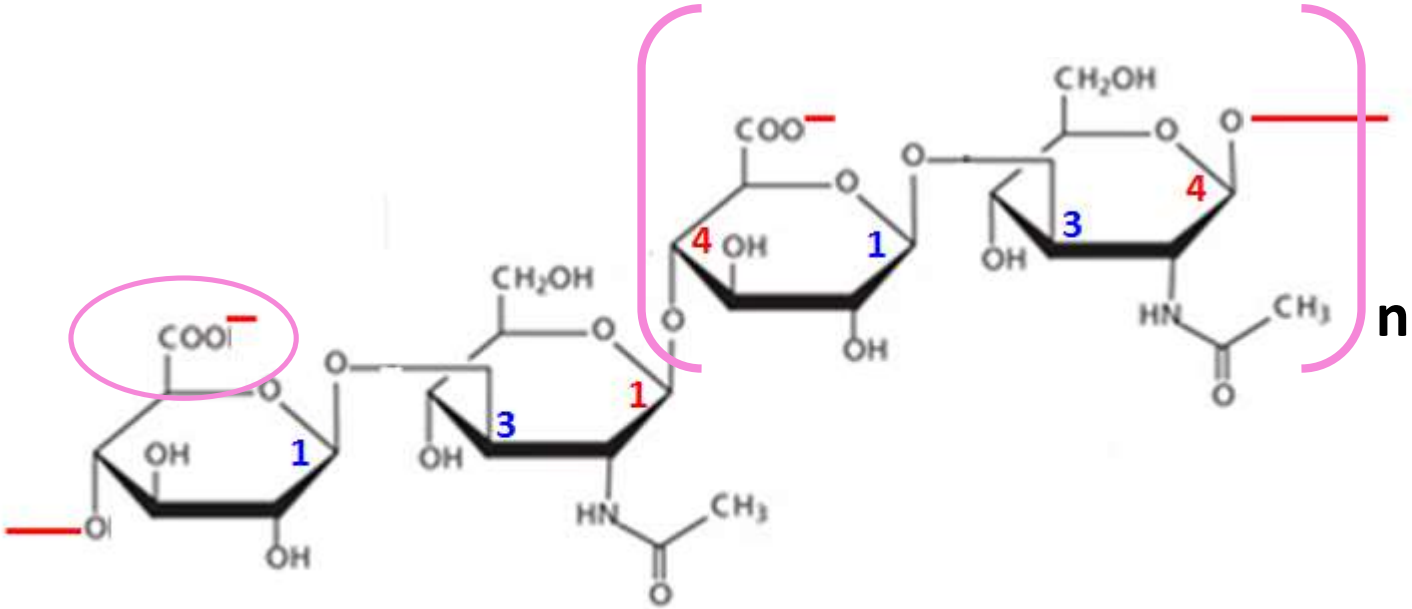

# Hyaluronic acid

- Hyaluronic acid is a **linear** polymer of the disaccharides " D-glucuronic acid and N-acetyl-D-glucosamine "




Hyaluronic Acid

# Hyaluronic acid




D-Glucuronate
(**anion**)

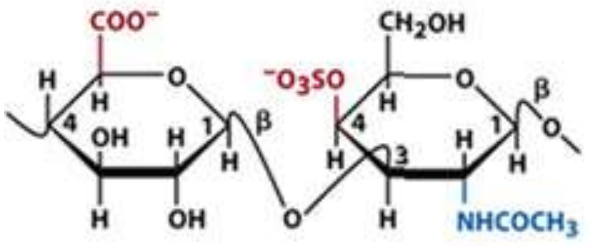
N-Acetyl-D-Glucosamine

**Hyaluronate (anionic polymer)**

# Heteropolysaccharides

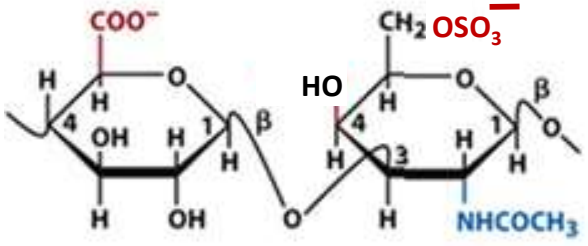
2. **Sulfated heteroglycans** these consist of sulfated disaccharide units such as: chondroitin sulfate, dermatan sulfate, keratan sulfate and heparin

   - **Chondroitin-4-sulfate & Chondroitin-6-sulfate** are unbranched polymers containing the disaccharide " D-glucuronic acid and N-acetyl-D-galactosamine " with the N-acetyl-D-galactosamine OH groups at position 4 and 6 being sulfated, respectively.




D-Glucuronate N-acetyl-D-galactosamine-4-sulfate

**Chondroitin-4-sulfate**




D-Glucuronate N-acetyl-D-galactosamine-6-sulfate

**Chondroitin-6-sulfate**

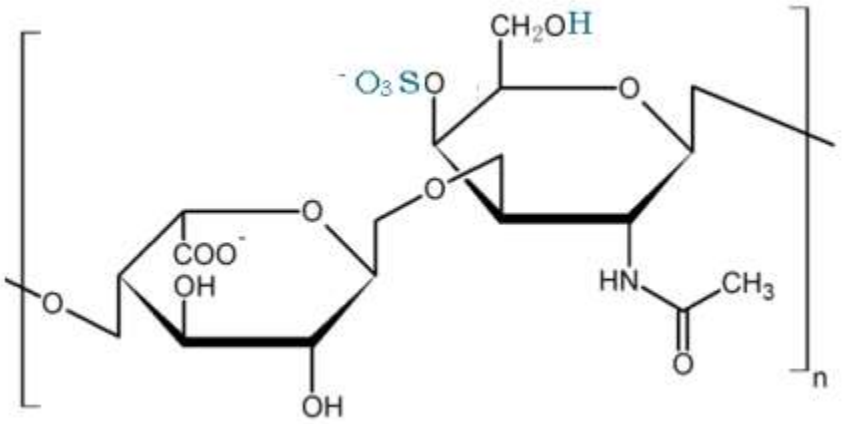
# Heteropolysaccharides

- Chondroitin sulfate is a major component of cartilages. They provide them with resistance to compression. Loss of chondroitin sulfate from the cartilage is a major cause of osteoarthritis.

- Chondroitin is used as dietary supplement to treat osteoarthritis. It is commonly sold together with glucosamine


# Heteropolysaccharides

- Dermatan sulfate: is a natural polysaccharide found mostly in the skin. It is a linear polymer of a disaccharide containing L-Iduronic acid (modified L-Idose sugar) and N-acetyl-D-galactosamine-4-sulfate

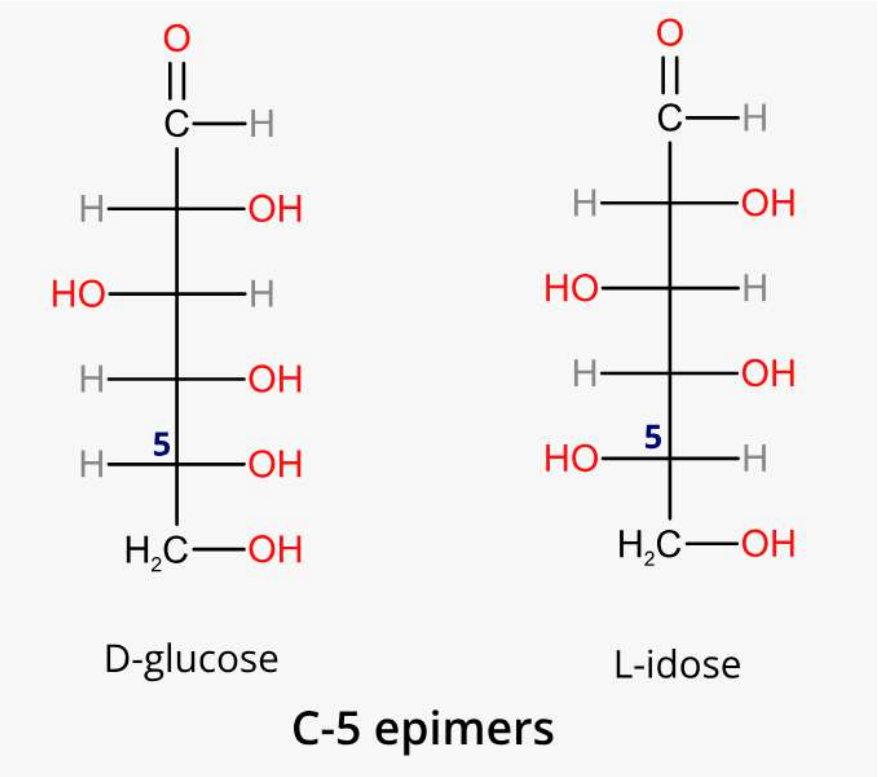



L-Iduronate N-acetyl-D-galactosamine-4-sulfate

**Dermatan sulfate**

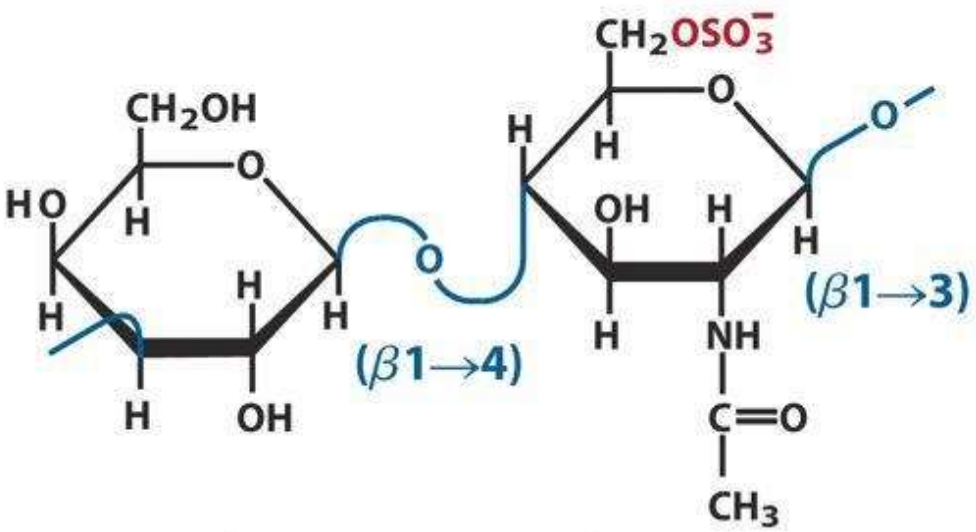
# Heteropolysaccharides

- L-Idose is hexoaldose sugar. It is C5 epimer of D-glucose. It is not found in nature but its modified uronic acid (L-Iduronic acid) is a major component 0f dermatan sulfate and heparin.



# Heteropolysaccharides

- Keratan sulfate: is a natural polysaccharide mainly found in the cartilage and bone. In joints, it can act as a cushion to absorb mechanical shock.This linear polymer is consisting of repeating disaccharide unit containing D-galactose and N-acetyl-D-glucosamine-6-sulfate

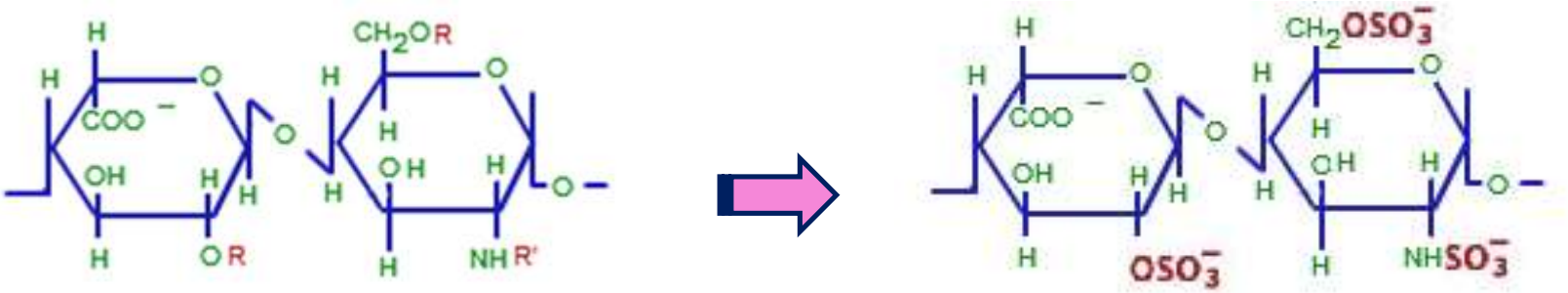



D-galactose N-acetyl-D-glucosamine-6-sulfate

**Keratan sulfate**

# Heteropolysaccharides

- Heparin: is the most highly charged polymer of any known biological molecule. Heparin is a complex mixture of linear polysaccharide and it varies in the degree of sulphation of its sugar units. One example is the sulfated disaccharide unit containing L-Iduronate-2-sulfate and N-sulfo-D-glucosamine-6-sulfate



L-Iduronic acid D-glucosamine L-Iduronate-2-sulfate N-sulfo-D-glucosamine-6-sulfate

**Heparin**

# Heteropolysaccharides

- Heparin is stored almost exclusively within the secretory granules of mast cells and it inhibits blood clotting. So, heparin is widely used as an injectable anticoagulant (e.g. postsurgical patients)