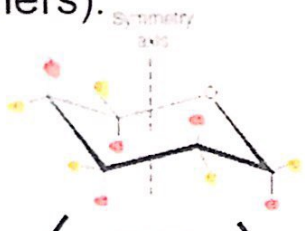
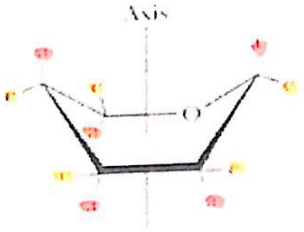
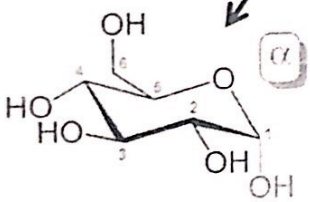
Conformers

- The geometry of the carbon atoms of monosaccharide ring is tetrahedral (bond angles are close to 109.5°), so sugar rings are not actually planar. For example, pyranoses take on either **Chair** or **Boat** conformations (conformational isomers or conformers).

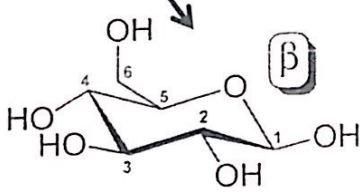


a: axial
e: equatorial

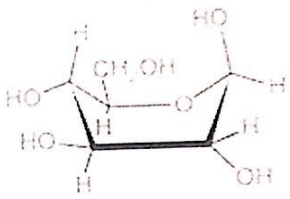




Chair form of α-D-glucose



Chair form of β-D-glucose



Boat form of β-D-glucose

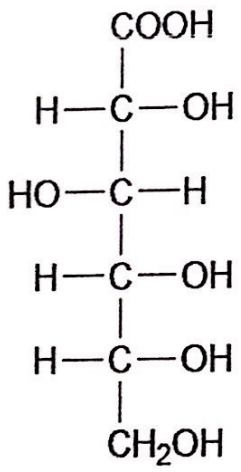
Sugar Modification

Derivitives of monosaccharide

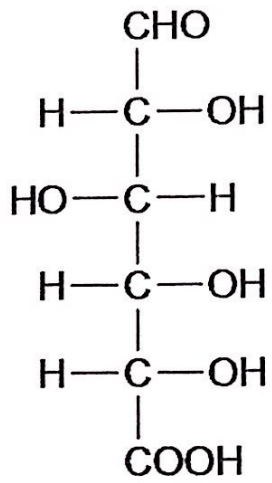
Sugar acids

1. **Aldonic acids** : oxidation of aldehyde (C1) to carboxylic acid; e.g. D-gluconic acid

D-gluconate

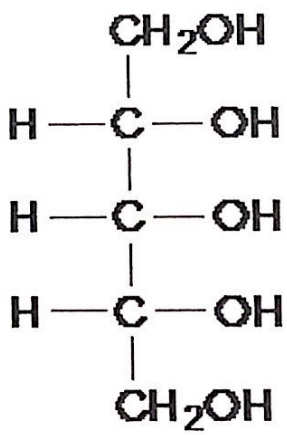


2. **Uronic acids** : oxidation of OH at (C6) to carboxylic acid; e.g. D-glucuronic acid



Sugar alcohols

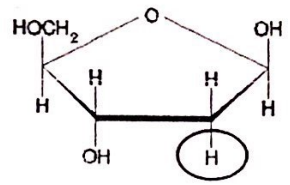
3. **Alditols** : reduction of carbonyl group to alcohol; e.g. D-ribitol and D-glycerol



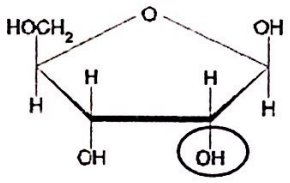
D-ribitol

Sugar Modification

4. **Deoxy sugars** : OH group is replaced by H; e.g. β-D-2-deoxyribose

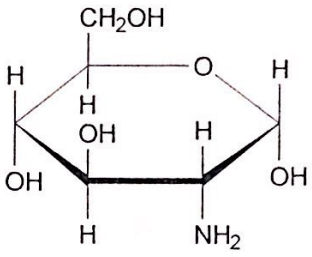


Deoxyribose

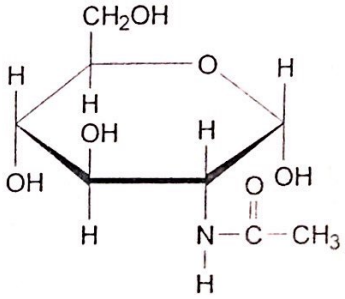


Ribose

4. **Amino sugars** : one or more OH groups are replaced by amino group which is often acetylated; e.g. α-D-glucosamine and α-D-N-acetylglucosamine.



α-D-glucosamine



α-D-*N*-acetylglucosamine

taken as vitamines for cartilage supplement

Alditols : Origin sugar

1) Sorbitol → Glucose
2) Ribitol → Ribose
3) glycerol → Glyceraldehyde
4) mannitol → mannose

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

hollow helix structure → Rapidly mobilized form → energy → easily degraded

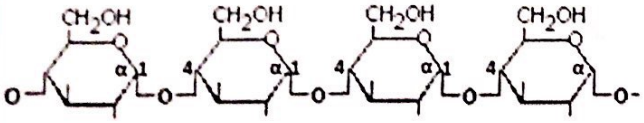
tightly packed → support structure

Storage Polysaccharides

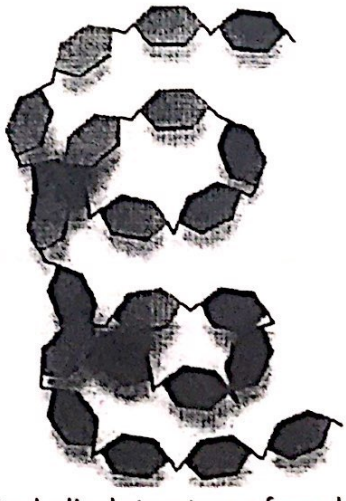
Starch: is the storage polysaccharides in plants.

- Polymer composed of 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

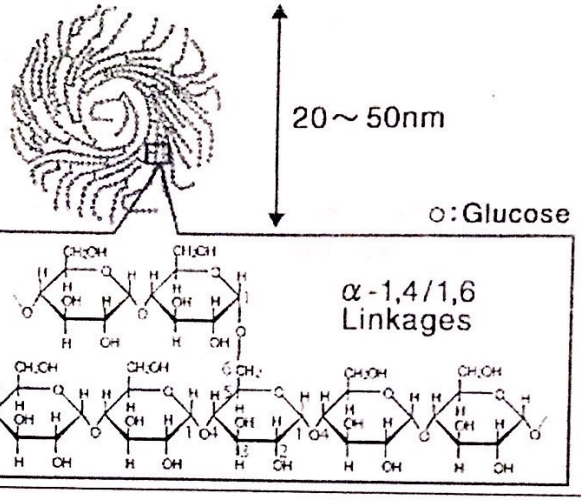
Storage Polysaccharides

Glycogen: is the storage polysaccharide in animal & human

- Polymer composed of glucose units like amylopectin but glycogen is more highly branched with branch points occurring every 8-14 residues
- Mainly found in skeletal muscle (up to 1-2% of muscle mass) and liver cells (up to 10% of liver mass)

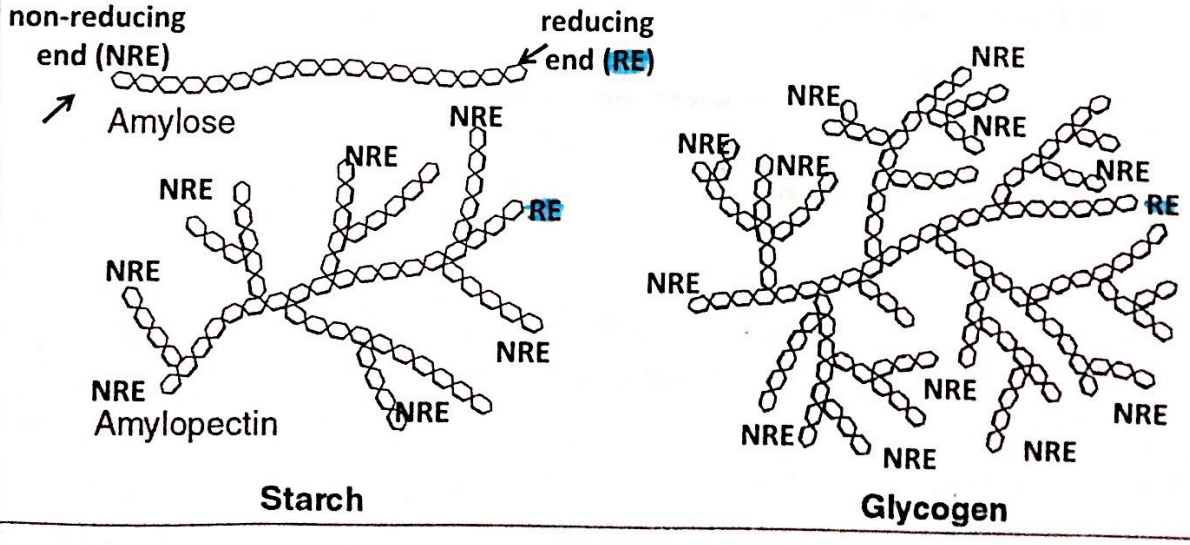
Liver : Store Glycogen For all cells
skeletal muscle : For itself
Brain : For itself
→ can't be share with other cells

Glycogen has a helix hollow shape due to α-glucose



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.



Synthesis & Breakdown of Glycogen

has tiny amount of glycogen

- The brain and other tissues 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

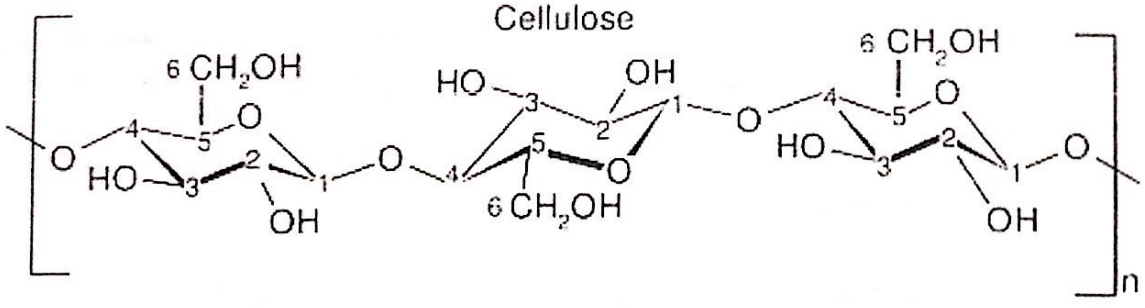
Brain : can only use glucose as source of energy whereas other tissue : can use other things such as lipids, proteins, ... etc
liver : responsible of blood glucose balance

Structural Polysaccharides

support the structure of the cell

Cellulose: the primary structural component of plant cell walls.

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



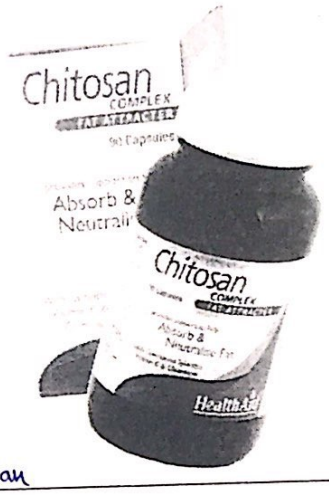
- It is the most abundant organic molecule on the earth. cellulose accounts for over half of the carbon in the biosphere.
- It adopts a very different molecular architecture from that of starch (hollow helix) due to its β-linkages. → Fibrous

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

artificial

Chitosan: is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is produced commercially by deacetylation of chitin (e.g. by treating shrimp shells with the alkali sodium hydroxide).



Medical uses: it is useful in weight loss and obesity treatment plans because it can reduce fat absorption

Proteoglycan: high glycolated protein

Glycoprotein : has less saccharides than proteoglycan

Cell ine { Proteoglycan: Dissacharide chains attached to protein core; present in connective tissue
Glycoprotein: Carbohydrates attached to protein molecule; present on cell surface

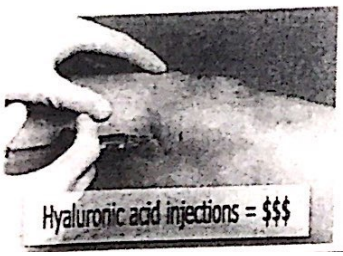
Heteropolysaccharides

usually rarly

- Consist of two or more different monosaccharide units and are closely associated with lipid (glycolipids) or protein (glycoproteins)
- The naturally occurring heteroglycans are mostly found in the connective tissues (such as cartilage, tendon, blood vessel walls,.....etc) Because they are anions → they can attract water

1. Hyaluronic acid (Hyaluronate)

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

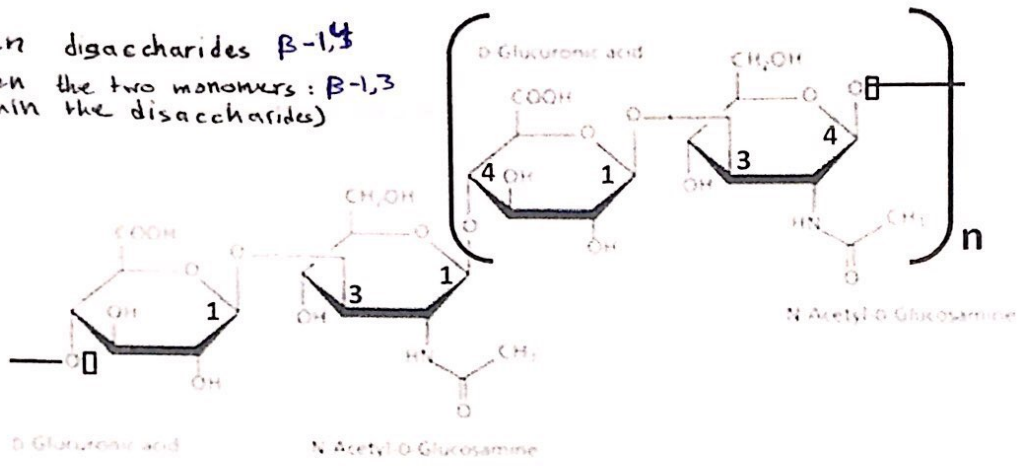


- It is also a major component of skin, where it is involved in tissue repair. Dry and scaly skin such as that caused by eczema may be treated with a prescription skin lotion containing sodium hyaluronate as its active ingredient.

Heteropolysaccharides

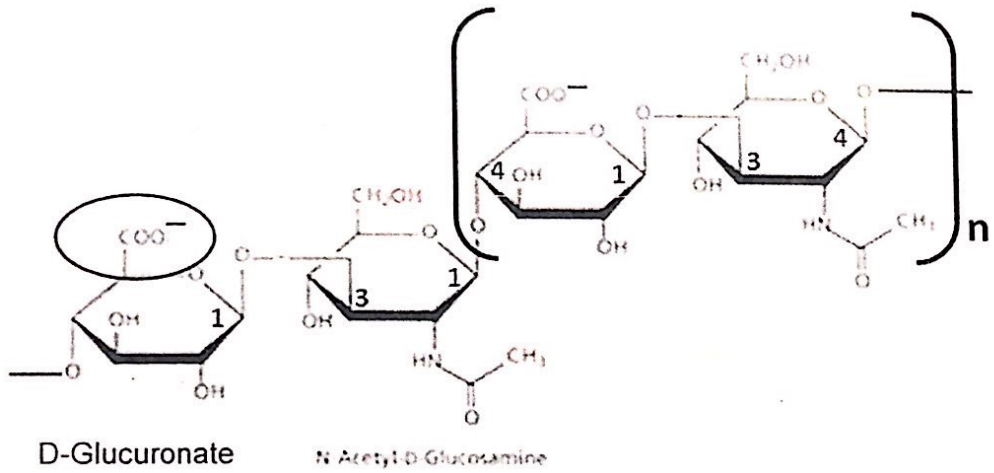
- Hyaluronic acid is a **linear** polymer of the disaccharides " D-glucuronic acid and N-acetyl-D-glucosamine " linked via alternating **β-1,4** and **β-1,3** glycosidic bonds.

between disaccharides β-1,4
between the two monomers : β-1,3
(within the disaccharides)



Hyaluronic Acid

Heteropolysaccharides



D-Glucuronate (anion)

N-Acetyl-D-Glucosamine

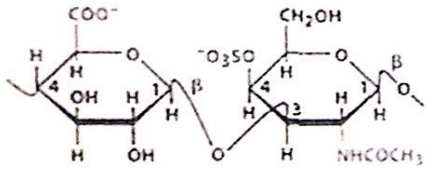
Hyaluronate

Heteropolysaccharides

OSO_3^-

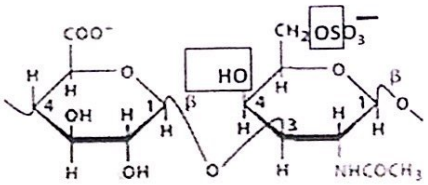
2. **Sulfated heteroglycans** these consist of sulfated disaccharide units such as: chondroitin sulfate, dermatan sulfate, keratan sulfate and heparin

   - **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

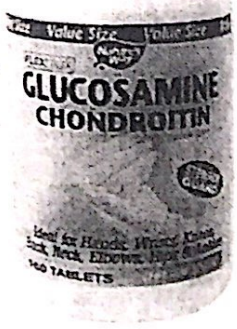
Chondroitin-6-sulfate

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.

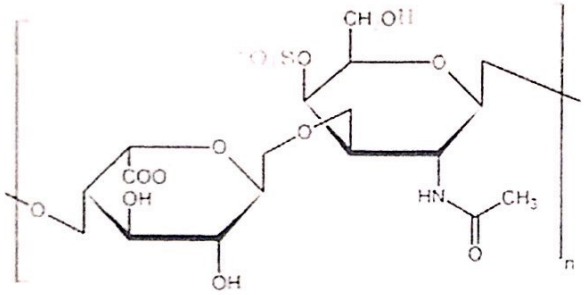
- Chondroitin is used as dietary supplement to treat osteoarthritis. It is commonly sold together with glucosamine

major component of synovial fluid and cartilages



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



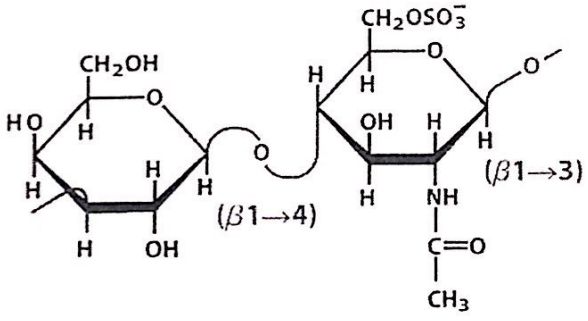
L-Iduronate N-acetyl-D-galactosamine-4-sulfate

Dermatan sulfate

Idose suger: Carbon number 5 Epimer of glucose

Heteropolysaccharides

- Keratan sulfate: is a natural polysaccharide mainly found in the cartilage and bone. It is highly hydrated molecules which in joints 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

Note : Sulfated heteroglycans & hyaluronic acid are mostly found in the connective tissues especially cartilage (synovial Fluid) and act as shock absorbers and lubricating agent Because the are anions thus attract water