CC7_Unit 2.2

Polysaccharides: Homopolysaccharides and Heteropolysaccharides

Polysaccharides (glycans) are long chains of monosaccharides. Each monosaccharide is connected together via glycosidic bonds to form the polymeric structure known as polysaccharide. Polysaccharides are the largest component of biomass. It is estimated that more than 90% of the carbohydrate mass in nature is in the form of polysaccharides.

Generalised functions of polysaccharides:

i) Polysaccharides plays vital role in energy storage and acts as cellular fuel source such as glycogen and starch.

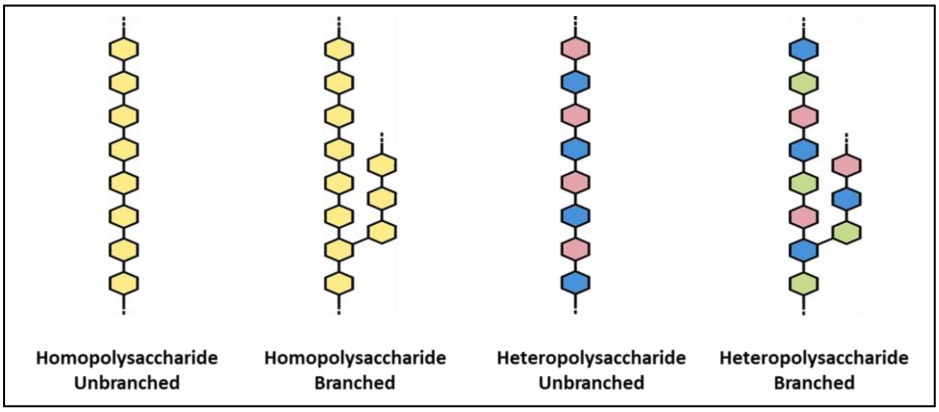
ii) Polysaccharides help to maintain the structural integrity of the organisms such as cellulose helps to maintain structure in plants and chitin is chief component of animal exoskeleton.

iii) Polysaccharides are also present in extracellular space such as in animal tissue that helps in maintain shape, supports cells, tissue and organ.

iv) Polysaccharides are an integral part of cell to cell communication and cellular recognition.

There are two types of polysaccharides: Homopolysaccharides and heteropolysaccharides.

- A typical homopolysaccharides is defined to have only one type of monosaccharide



  units in the chain; whereas, a heteropolysaccharide is composed of two or more types of monosaccharides. In both types of polysaccharide, the monosaccharide can link in a linear fashion or they can branch out into complex formations.

  Unlike proteins, polysaccharides generally do not have a defined molecular weight. This difference is a consequence of the mechanisms of assembly of the polysaccharides. The syntheses of polysaccharides are done without any template and it solely depends on the intrinsic property of enzymes.

Some common polysaccharides are:

- Starch (homopolysaccharides)
- Glycogen (homopolysaccharides)
- Cellulose (homopolysaccharides)
- Chitin (homopolysaccharides)
- Dextran (homopolysaccharides)
- Peptidoglycan (heteropolysaccharides)
- Agarose (heteropolysaccharides)
- Glycosaminoglycans (heteropolysaccharides)

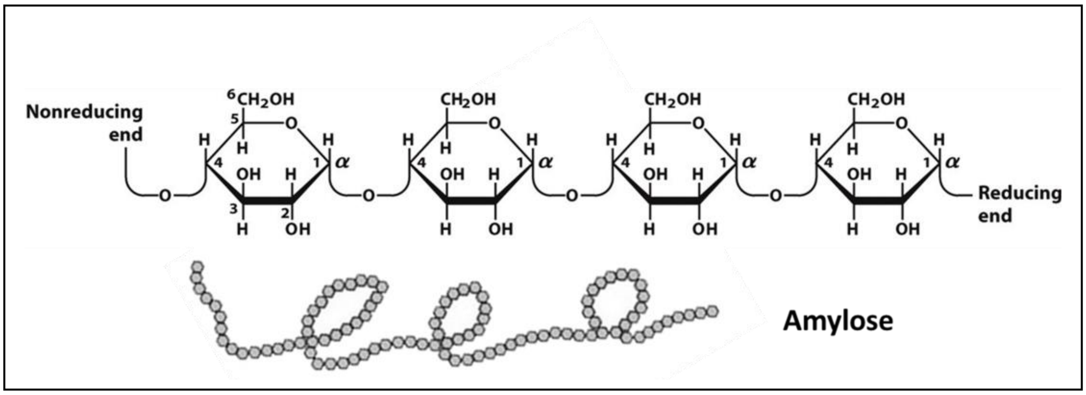
1) Starch (homopolysaccharides):

Starch is a homopolysaccharide comprised of glucose monomer units joined by glycosidic linkage. Starch is the most important storage polysaccharide or nutritional reservoir of plant cells. The starch molecules are present inside the plant cells and exist as large cluster or granules. More than half of the carbohydrates ingested by humans are in the form of starch.

- The starch molecules are heavily hydrated because they have many exposed hydroxyl groups available to make hydrogen bond with water molecule.
- Starch exists in two forms (amylose and amylopectin), both are made up of glucose monomers.

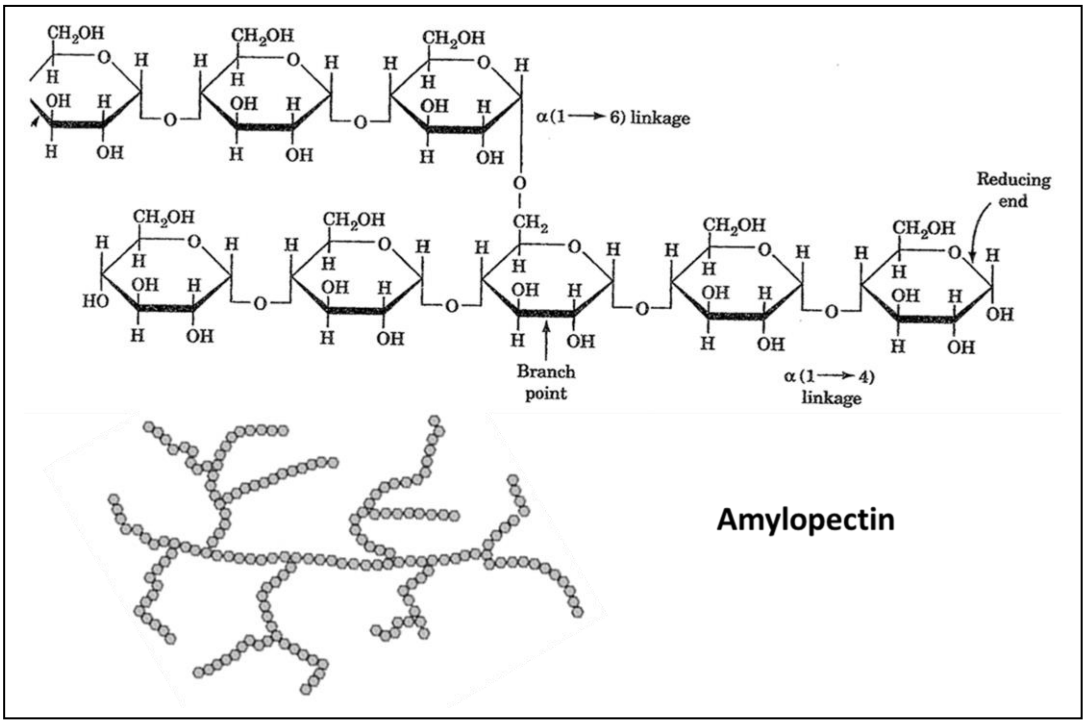
a) Amylose (linear homopolysaccharides):

It is a unbranched type of starch, consists of α-D-glucose monomers joined by α-1,4 glycosidic linkage. Amylose contain is single chain of several thousand D-glucose residues and length of the chain can vary and hence the molecular weight of amylose can be from few thousand to more than a million Daltons (50-5000 units of glucose).



b) Amylopectin (Branched homopolysaccharides):

It is the branched type of starch. The α-D-glucose monomer units are linked in a chain similar to amylose by glycosidic bond (α-1, 4). The branching is originated from the chain by (α-1, 6) glycosidic linkage on an average after every 24-30 residues. The molecular weight of amylopectin can be upto 200 million Daltons or contains upto 10^6 monosaccharide units of α-D-glucose.

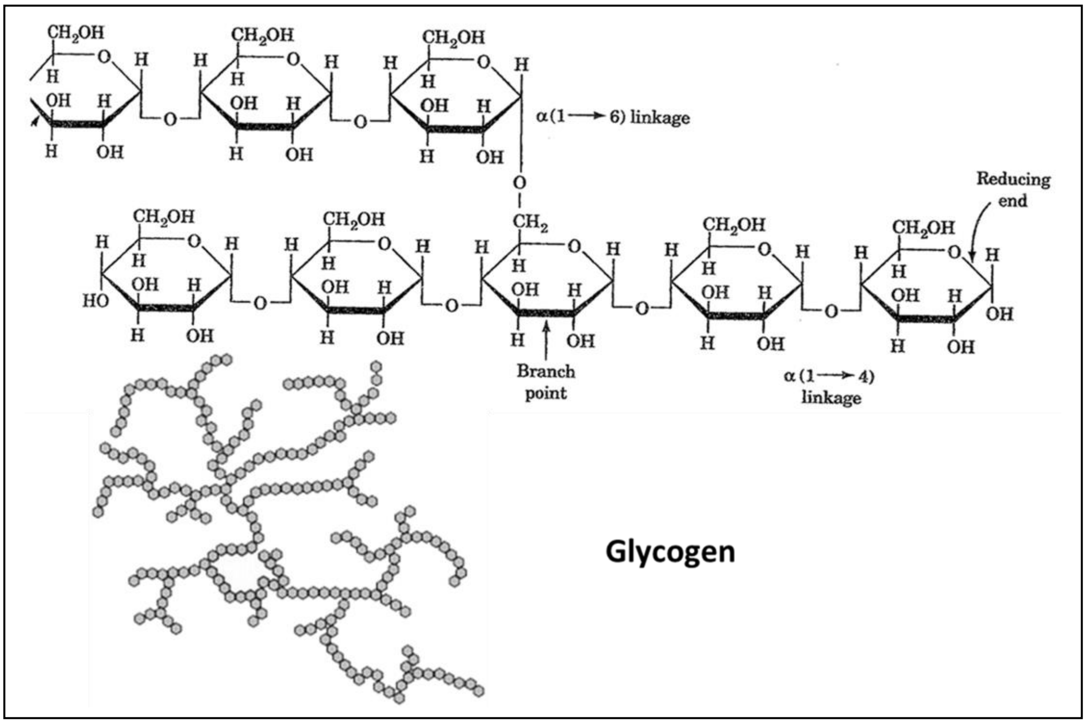


2) <u>Glycogen (Branched homopolysaccharides):</u>

Glycogen is main storage polysaccharide molecule of animal cells.

- Structurally, glycogen is like amylopectin, the only difference between them is the extent of branching. The glycogen is extensively branched compared to amylopectin and with every 8-12 residue the new branch emerges from the glycogen chain.

Glycogen is the polymer of α-D-glucose connected by glycosidic linkage (α-1, 4). The branching point has (α-1, 6) linkage.



- Each glycogen molecule has one reducing end and many non-reducing ends.
- Glycogen is present in all cell types and functions as glucose reserve. Glycogen is abundantly present in liver and muscle cells and stored as large granules. These large granules are comprised of cluster of smaller granules containing glycogen molecules with an average molecular weight of several million Daltons. These granules also contain enzymes responsible for synthesis and degradation of glycogen.

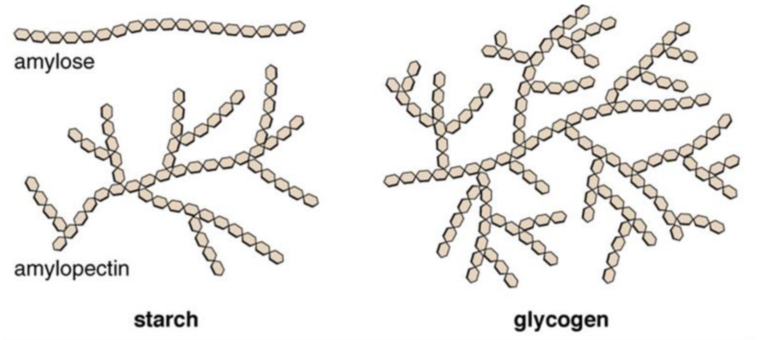
<u>Significance of branching</u>

- Branched sites allow several sites for simultaneous synthesis and degradation.
- Branching speeds up the process of degradation.
- Branching makes glycogen an efficient way to store glucose because it provides compactness as well as the accessibility to enzymes.

Why cells store glucose in polymeric form (glycogen)?

- Because glycogen is insoluble and contributes little to the osmolarity of the cytosol.
- If all glycogen stored in liver cells are converted to glucose the osmolarity will change to 0.4M. At this osmolality the cell will rupture because of osmotic entry of water inside the cell.

- The glucose concentration in blood is approx. 5mM therefore the uptake of glucose inside the cell will be difficult due to higher concentration of glucose inside the cytosol (0.4M). Due to these reasons the glucose is stored inside the cells as glycogen.
- When cells need glucose they enzymatically extract glucose monomers from glycogen without changing the overall osmolality of the cells.

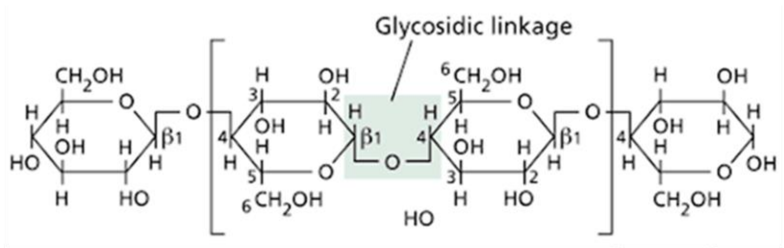


Diagrammatic representation of starch and glycogen. All of them are composed of α-D-glucose and they differ in the level of branching. Amylose is unbranched, amylopectin is moderately branched and glycogen have highest level of branching.

<u>3) Cellulose (linear homopolysaccharides):</u>

Cellulose is one of the most abundant biomaterials on the earth. It is generally synthesized by plants, but it is also produced by some bacteria. Cellulose is a tough, fibrous, and water-insoluble polysaccharide, primarily found in cell walls of plants. It plays an integral role in keeping the structure of plant cell walls stable.

- Cellulose is a homopolymer of β-D-glucose joined by β-1,4 linkages. Like amylose, cellulose molecule is linear, unbranched homopolysaccharide, consists of 10,000-15,000 thousand β-D-glucose units joined by glycosidic linkage.



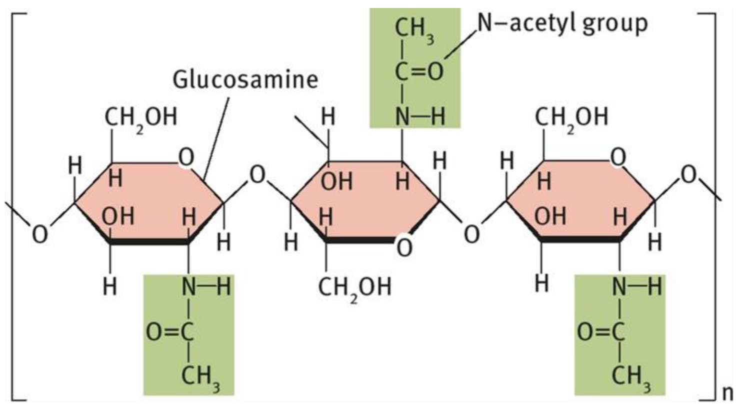
Chemical structure of cellulose: β-D-glucose monomers are linked by glycosidic bond (β-1,4 linkages). The β-D-glucose monomers are linked in such a way that each β-glucose is flipped by 180 degrees with respect to each other. This flipping of monomer unit allows cellulose to form long, straight chains.

- The β configurations of cellulose allow the formation of very long, straight chains which is optimal for construction of fibers having high tensile strength.
- Most animal cannot use cellulose as a fuel source because they lack an enzyme to hydrolyse the β-1,4 linkages. However, cellulose is still an important constituent of our diet as a component of dietary fibers.
- Termites readily digest cellulose (and therefore wood), because their intestinal tract harbours a symbiotic microorganism (Trichonympha), that secretes cellulose, which hudrolyses the β-1,4 linkages. Wood-rot fungi and bacteria also produce cellulose.

4) Chitin (linear homopolysaccharides):

Chitin is one of the most important biopolymers in nature. It is mainly produced by fungi, arthropods and nematodes. Chitin is the principle component of the hard exoskeletons of nearly a million species of arthropods, insects, lobsters and crabs. It is the second most abundant polysaccharides next to cellulose present in the biosphere. In insects, it functions as scaffold material, supporting the cuticles of the epidermis and trachea.

- Chemically, chitin is a linear homopolysaccharide polymer composed of *N*-acetyl-β-D-glucosamine residues as monomer linked by glycosidic bond (β-1,4 linkages).
- The only chemical difference from cellulose is the replacement of the hydroxyl group at C2 position with an acetylated amino group.
- Chitin polymers tend to form microfibrils (also referred to as rods or crystallites) of ~3 nm in diameter that are stabilized by hydrogen bonds formed between the amine and carbonyl groups.



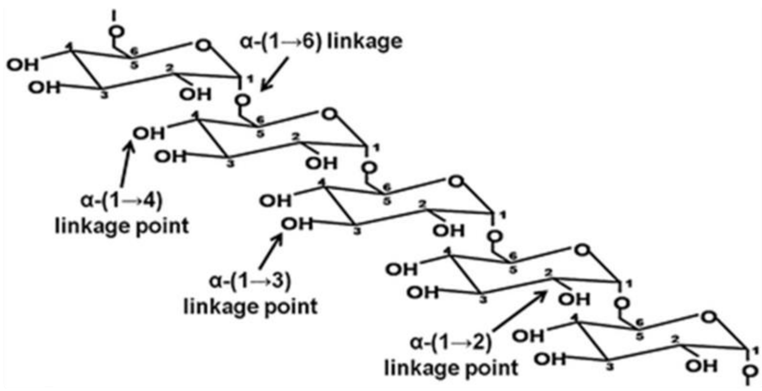
Chemical structure of chitin: *N*-acetyl-β-D-glucosamine monomers linked by glycosidic bond (β-1,4 linkages). Every alternate *N*-acetyl-β-D-glucosamine is rotated 180 degrees and joined by a beta glycosidic bond.

- Chitin forms extended fibers similar to that of cellulose and like cellulose cannot be digested by vertebrates.
- Insect growth and morphogenesis are strictly dependent on the capability to remodel chitin-containing structures by combined action of chitin synthases and chitinolytic enzymes in different tissues.

5) Dextrans (Branched homopolysaccharides)

Dextran, a bacterial homopolysaccharide, was first isolated in 1861, utilizing a bacterial culture of the genus *Leuconostoc.* Several microorganisms produce dextrans with ranges of molecular weights and with structures varying from slightly to highly branched. The dental plaques, formed by bacteria growing on the surface of teeth are rich in dextrans.

- Dextran is a polysaccharide comprised of α-D-glucose repeating units linked through glycosidic linkages. The backbone of the linear polymer (dextran) is comprised of mainly α-1,6 linkages. Dextran also possesses side-chains, stemming mainly from α-1, 3 and occasionally from α-1,4 or α-1,2 branched linkages.
- The molecular weight of dextran ranging from 3 to 2000kDa.



Chemical structure of Dextran: It is composed of linear polymeric backbone consist of *α*-D-glucose monomers linked by glycosidic bond (*α*-1,6 linkages) with linkage point at α-1,2, α-1,3, and α-1,4 positions.

- Synthetic dextrans are used in several commercial products (such as sephadex) are widely used for separation and purification of various products like proteins in research and industry.
- In food industry it is being used as thickener for jam and ice cream as it prevents crystallization of sugar, improves moisture retention, and maintains flavour and appearance of the food stuffs.

Heteropolysaccharides:

Heteropolysaccharides are made up of more than one type of monosaccharide unit. In general, most naturally occurring heteropolysaccharides are attached with peptides, protein and lipids.

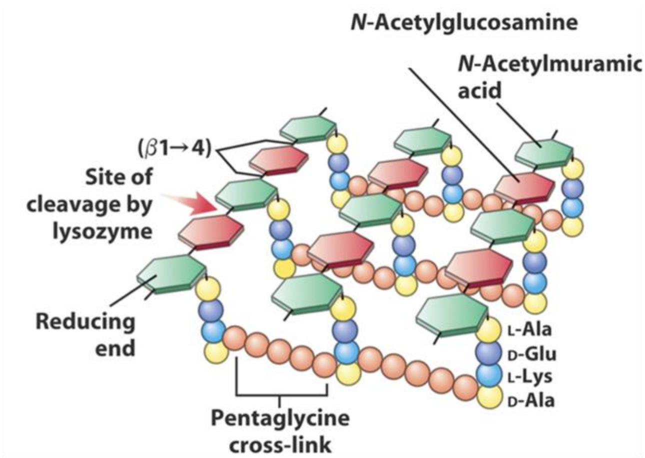
Some of the common heteropolysaccharides are

1) Peptidoglycans
2) Agarose
3) Glycosaminoglycans

1) Peptidoglycans:

Peptidoglycan (murein) is an essential component of the bacterial cell wall found on the outside of the cytoplasmic membrane of almost all bacteria. Its main function is to preserve the cell integrity by withstanding the turgor.

- The main structural features of peptidoglycan are linear polysaccharide strands cross-linked by short peptides.
- The polysaccharide strands are made up of alternating N-acetylglucosamine (GlcNAc) and N-acetylmuramic acid (MurNAc) residues linked by β-1,4 glycosidic linkages. The linear polymer of GlcNAc and MurNAc lie side by side in the cell wall, cross linked by short peptides, the exact structure of which depends on the bacterial species.



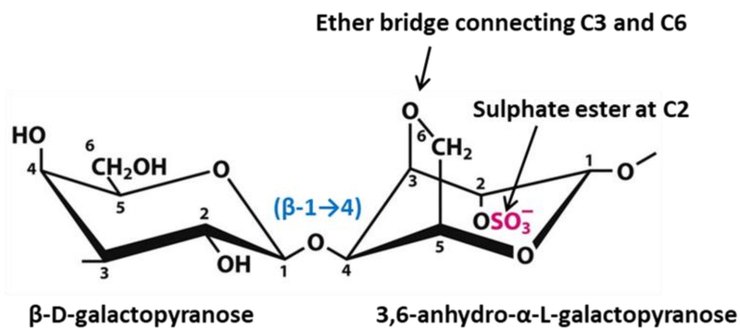
Structure of Peptidoglycan: It is composed of peptide and polysaccharides. The polysaccharide chain consist of alternating N-acetylglucosamine (GlcNAc) and N-acetylmuramic acid (MurNAc) residues linked by β-1,4 glycosidic linkages. The polysaccharide chains are interlinked by peptides.

- The enzyme lysozyme kills bacteria by hydrolysing β-1,4 linkages between GlcNAc and MurNAc. Lysozymes are present in tears as defence mechanism against bacteria.
- Penicillin and related antibiotics kill bacteria by inhibiting synthesis of the cross-links, leaving cell wall too weak to resist osmotic lysis.

2) Agarose:

Agarose is a natural heteropolysaccharide derived from red seaweed and it is a component of their cell wall and provides structural support.

- Agarose is a linear polymer composed of repeating unit of agarbiose. The agarbiose is a disaccharide comprised of D-galactose (β-D-glalctopyranose) and L-galactose derivative (3,6-anhydro-α-L-galactopyranose) linked by β-1,4 glycosidic linkages. The agarbiose units are joined by α-1,3 glycosidic linkage to make a polymer of approx. 600-700 residues long. The 3,6-anhydro-α-L-galactopyranose residue also contain an ether bridge the connect C3 and C6. A small fraction of the 3,6-anhydro-α-L-galactopyranose residues have a sulphate ester at C2 position.



Structure of Agarose (a polymer of agarbiose): Agarbiose unit is composed of D-galactose linked to L-galactose derivative (3,6-anhydro-α-L-galactopyranose) by by β-1,4 glycosidic linkages. The agarbiose dissacharide units are joined by α-1,3 glycosidic linkages to make a linear polymeric chain consist of 600-700 residues.

- Agarose is purified from agar or obtained from agar producing red seaweed. Agar is primarily composed of agarose and agaropectin.
- The remarkable gel-forming property of agarose makes it useful in the biochemistry experiments for the electrophoretic separation of DNA and RNA molecules.

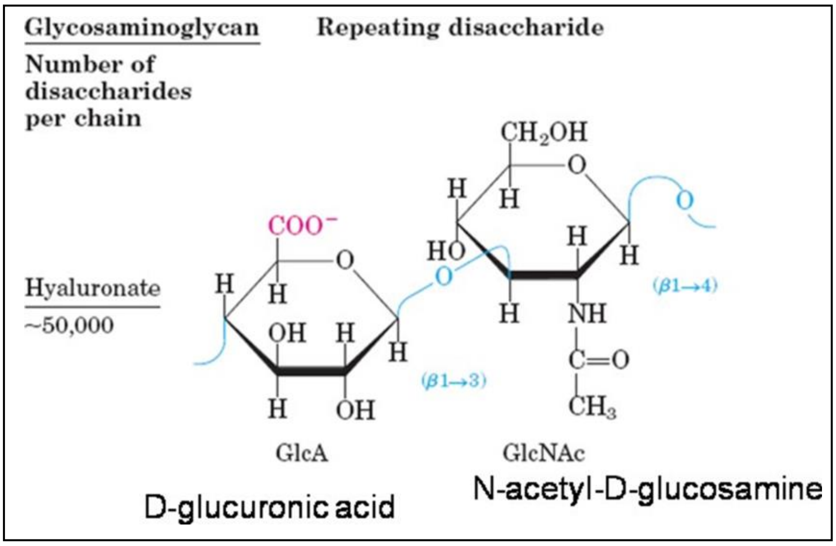
3) Glycosaminoglycans (GAG):

Glycosaminoglycans are heteropolysaccharides unique to animals and bacteria and are not found in plants. In multicellular animals the glycosaminoglycans are present in extracellular matrix (ECM) which holds the cells together in the tissues and provides porous pathway for diffusion of nutrients and oxygen to individual cells.

- Glycosaminoglycans are a family of linear polymers composed of repeating disaccharide units. They are complex carbohydrates containing amino sugars and uronic acids. One of the 2 monosaccharides is N-Acetylglucosamine or N-Acetylgalactosamine and the other is mostly an uronic acid, usually D-glucuronic or L-iduronic acid.
- Some of the examples of glycosaminoglycans are hyaluronic acid, chondroitin sulphate, heparin, dermatan sulphate and keratin sulphate.

a) Hyaluronic acid

- The repeating unit of hyaluronic acid is a disaccharide containing D-Glucuronic acid and N-Acetyl glucosamine held by β-1,3 linkage and repeating disaccharide by β-1,4-linkage.
- Hyaluronic acid contains about 250-50000 disaccharide units held by β-1, 4 glycosidic linkage with a molecular weight up to 4 million Daltons.
- They form clear, highly viscous solutions, which serve as lubricants in the synovial fluids of joints and provide a cushioning effect.

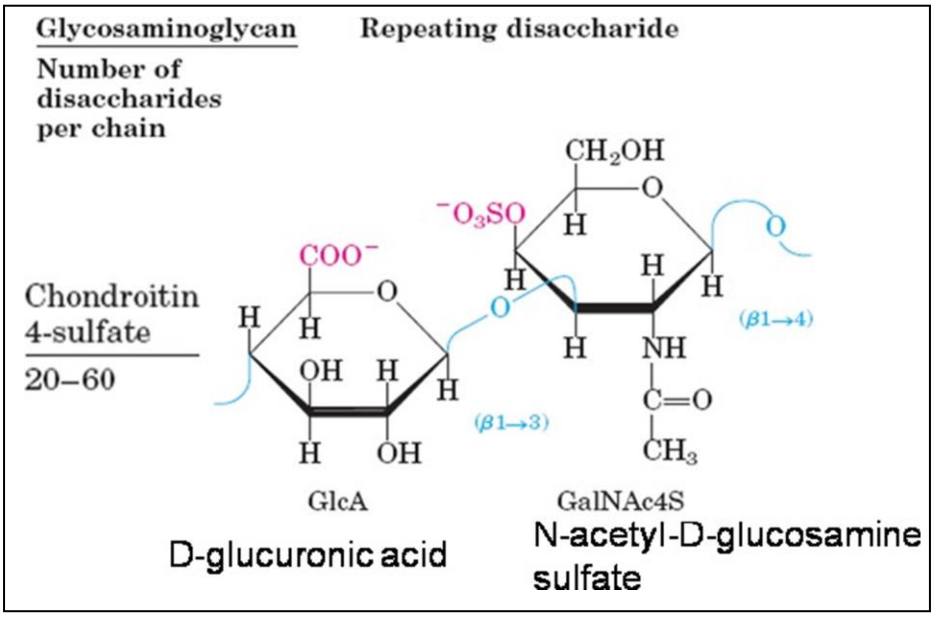


- Hyaluronidase is an enzyme that breaks β-1, 4) glycosidic bond of hyaluronic acid and other GAG. Hyaluronidase also helps in the process of fertilization as this enzyme clears the gel (hyaluronic acid) around the ovum allowing a better penetration of sperm into ovum.

- Hyaluronidase of bacteria helps their invasion into the animal tissues.

b) Chondroitin sulphate:

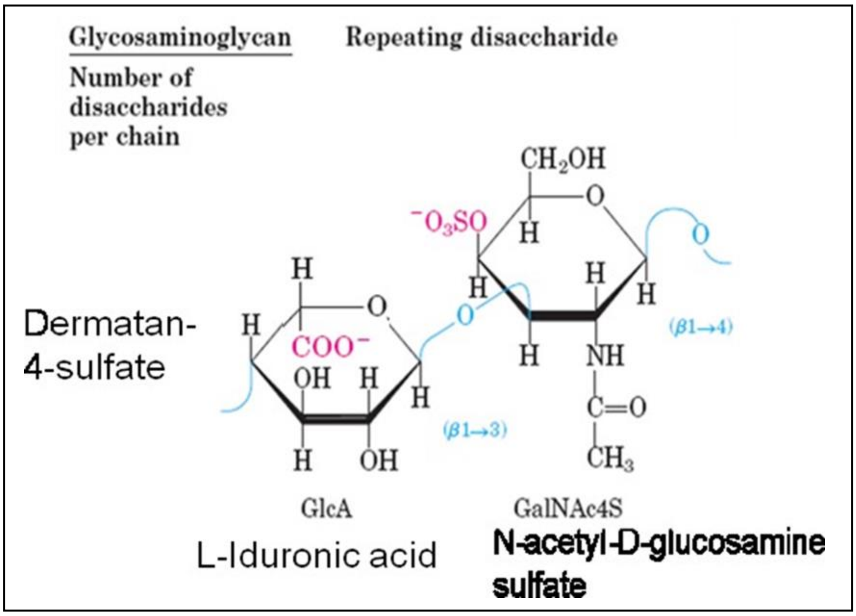
- Chondroitin sulphate or Chondroitin-4-sulphate is a major polysaccharide of cartilage, which contains alternating units of D-Glucuronic acid and N-Acetyl-D-galactosamine.
- The linkage is similar to hyaluronic acid and the N-acetyl galactosamine is sulphated at 4th position.



- Chondroitin-4-sulfate (chondros = cartilage) is a major constituent of various mammalian tissues (bone, cartilage, tendons, heart, valves, skin, cornea etc.).

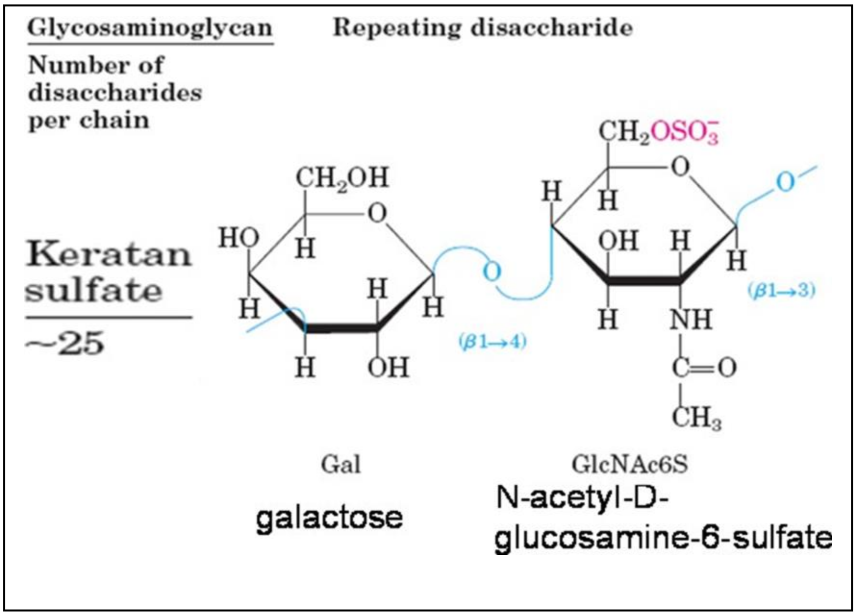
c) Dermatan sulfate:

- The name dermatan sulfate is derived from the fact that this compound mostly occurs in the skin. It is also present in blood vessels and heart valves. It is structurally related to chondroitin-4-sulfate. The only difference is that there is an inversion in the configuration around C5 of D-glucuronic acid to form L-iduronic acid.
- It is composed of alternating units of L- iduronic acid and N- acetyl galactosamine –4 – sulphate linked by β - 1,3 linkage and repeating disaccharide by β - 1,4 linkage.



d) Keratan sulphate:

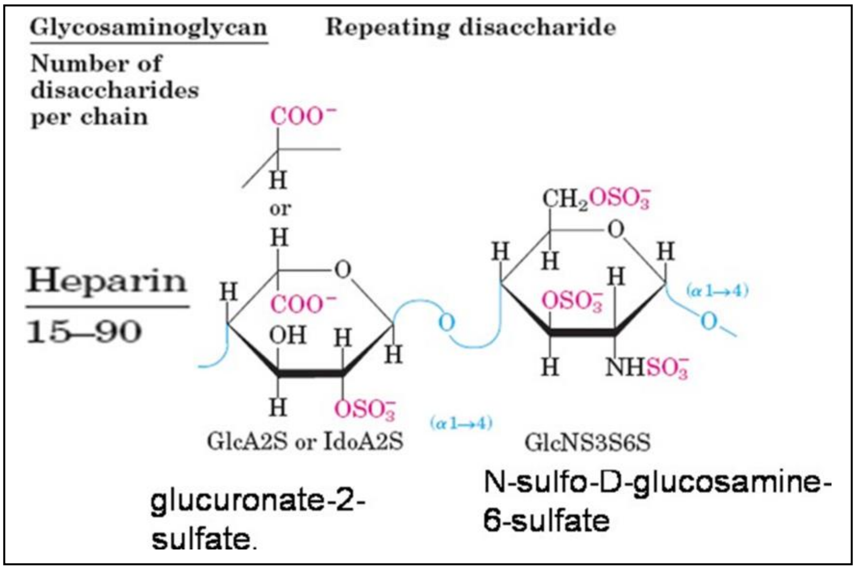
- It is a heterogeneous GAG with variable sulphate content.
- It is made up of repeating units of disaccharides composed of D-galactose and N-acetylglucosamine-6-sulfate linked by β-1, 4 linkages. The disaccharide units are joined together by β-1, 3 linkage.



- They are present in cornea, cartilage, bone and variety of horny structures formed of dead cells: horn, hair, hoofs, nails, and claws.

e) Heparin:

- Heparin is made up of repeating unit of diasaccharide composed of D-glucuronate sulphate / L-idurunote sulphate and N-sulphoglucosamine –6-sulfate linked by α-1,4 glycosidic bonds. The disaccharide units are joined together by α-1,4 linkage.



- It is present in liver, lungs, spleen, monocytes etc. Commercial preparation of heparin is mainly from animal lung tissues.
- It is an anti – coagulant widely used when taking blood in vitro for clinical studies.
- It is also used in vivo to prevent intra vascular coagulation. Heparin binding causes antithrombin to bind to and inhibit thrombin, a protease essential to blood clotting.

Reference:

[1]***Lehninger Principles of biochemistry***

[2]***Lubert Stryer Biochemistry***