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# Carbohydrates;

Also called saccharides; most abundant molecules on earth. Most are produced by photosynthesis.

Uses: Yield energy (ATP) to drive metabolic processes.
Energy- storage molecules (e.g. glycogen and starch).
Structural - cell walls and exoskeletons of some organisms.
Carbohydrate derivatives found in coenzymes (FAD) and nucleic acids.
Can be described by the number of monomers they contain:

1) **Monosaccharide** - $(CH_2O)_n$ where n = 3-6; one sugar molecule
2) **Oligosaccharide** - polymers from 2-10
3) **Polysaccharide** - polymers of greater than 10 sugar residues

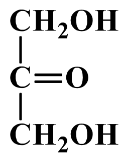
## 1- Monosaccharides

Also known as poly hydroxy aldehydes or ketones. Classified based upon type of carbonyl group (C=O) and number of carbon atoms.

**Aldose** - sugar with aldehyde group
**ketose** - sugar with ketone group

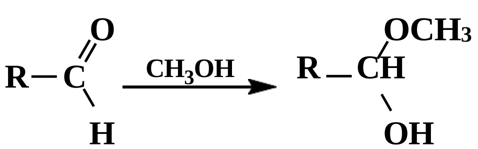
There are two important trioses:
glyceraldehyde (Aldotriose) and dihydroxyacetone (ketotriose)


**Glyceraldehyde (Aldotriose)**

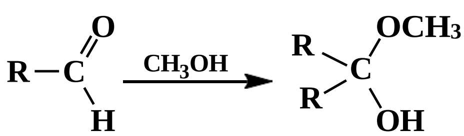



**Dihyoxyacetone (ketotriose)**

Both aldoses and ketoses engage in intramolecular cyclization
Alcohol + Aldehyde = **Hemiacetal**
Alcohol + ketone = **Hemiketal**

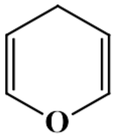



**hemi-acetal**

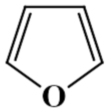



**hemi-Ketal**

Monosaccharides can form two types of rings
5-membered = **Furanose**
6-membered = **Pyranose**



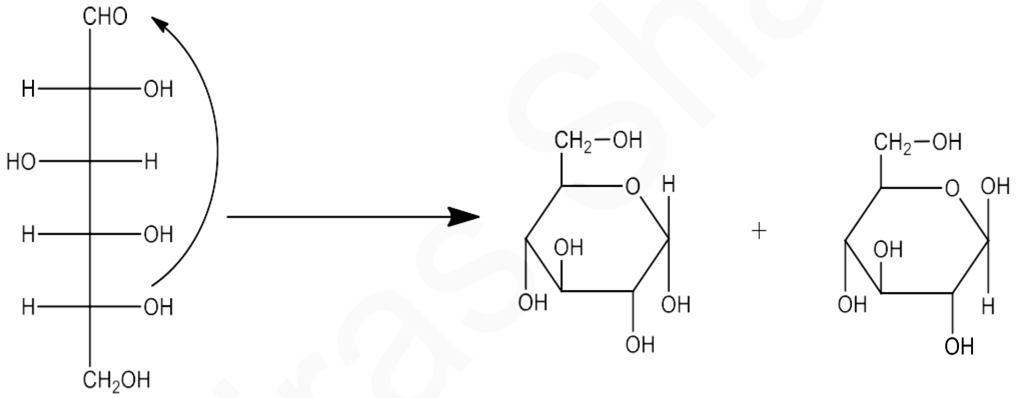

**Pyran**




**Furan**

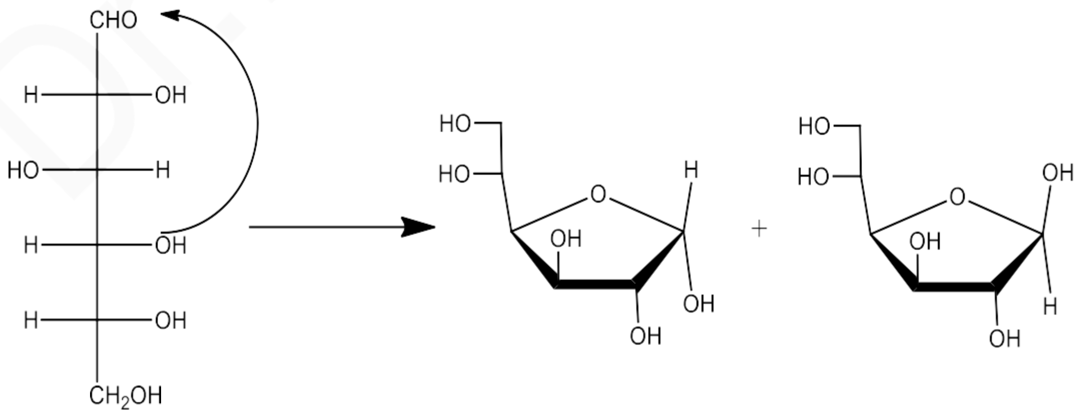
## Cyclazation of sugars

Pentoses and hexoses can cyclize, as the aldehyde or keto group reacts with a hydroxyl on one of the distal carbons. e.g., glucose forms an intra-molecular hemiacetal by reaction of the aldehyde on C1 with the hydroxyl on C5, forming a six-member pyranose ring, named after the compound pyran.




**D-Glucose** **$\alpha$-D-Glucopyranose** **$\beta$-D-Glucopyranose**

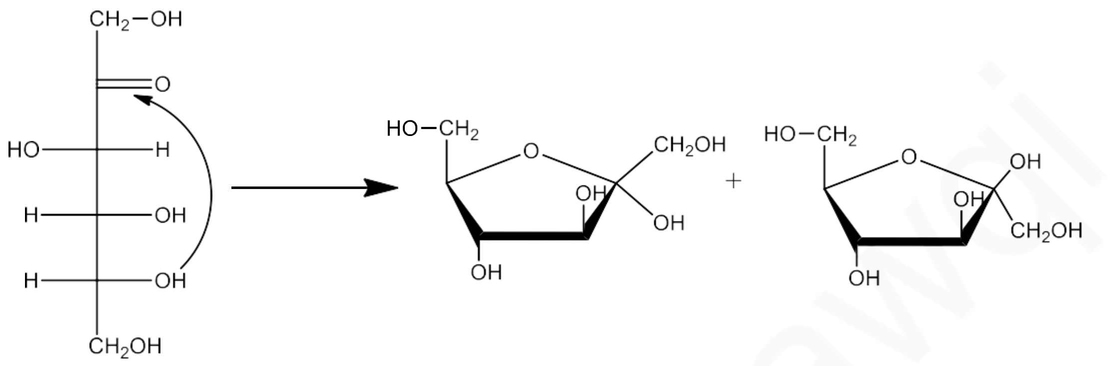
It can also be a form a 5 member ring as a result of the reaction of an aldehyde group with a hydroxyl group on C-4 and it is called a furan ring.




**D-Glucose** **$\alpha$-D-Glucofuranose** **$\beta$-D-Glucofuranose**

Cyclization of glucose produces a new asymmetric center at C-1, with the two stereoisomers called **Anomers**, ***α*** and ***β***.

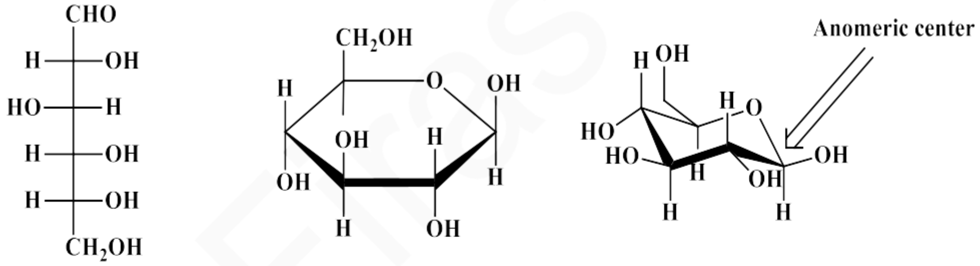
Fructose can form either: 5-member **furanose** ring, by reaction of the C-2 (keto group) with the hydroxyl on C-5



**D-Frucose** ***α*-D-Fructofuranose** ***β*-D-Fructofuranose**

-Aldoses and ketoses equilibrate between cyclic and open forms.

-Most oxidized carbon (C-1; attached to 2 oxygen atoms) is known as an **Anomeric** carbon.

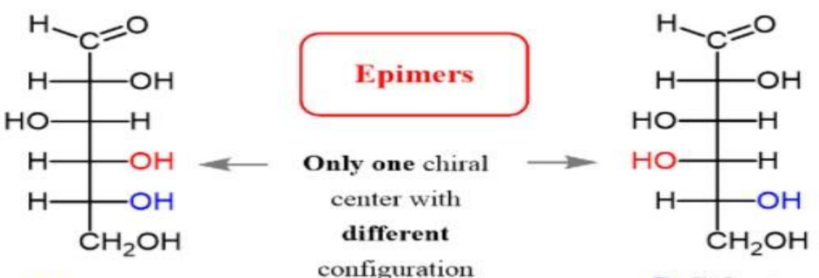



D-Glucose β-D-Glucopyranose (β-D-Glucose)

## Epimers

Epimers are carbohydrates that differ in the location of the -OH group in one location.

**D-glucose and D-galactose are epimeric at carbon-4**

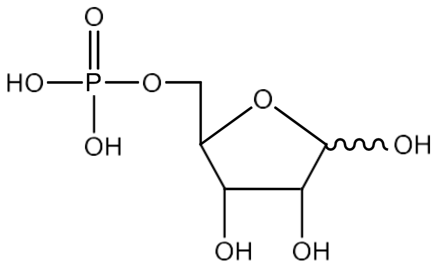



**D-Glucose** **D-Galactose**

# Derivatives of monosaccharides:

**1) Sugar phosphates**

Metabolized as phosphate esters

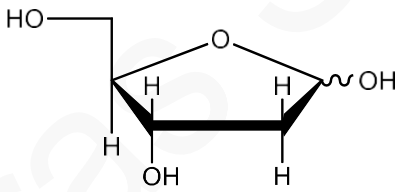



**5-phosphate-D-ribofuranose**

**2) Deoxy sugars**

Hydrogen atoms replaces -OH group on C-2.

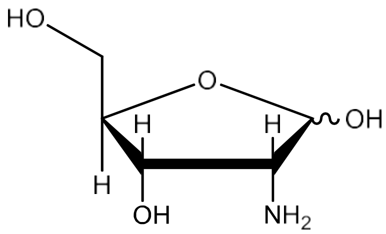
It is one of the important compounds as it enters the synthesis of nucleic acids (DNA)




**2-Deoxy-D-ribosfuranose**

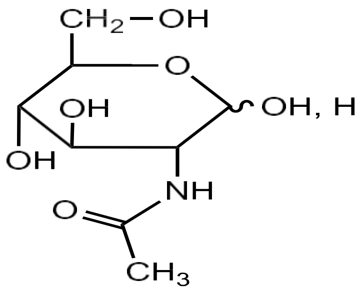
**3) Amino sugars**

Amino group (-NH) substituted for -OH group in monosaccharide.




**2-Amino-D-ribofuranose**

More than 60 amino sugars are known, with one of the most abundant being N-Acetyl-d-glucosamine, which is the main component of **chitin**.

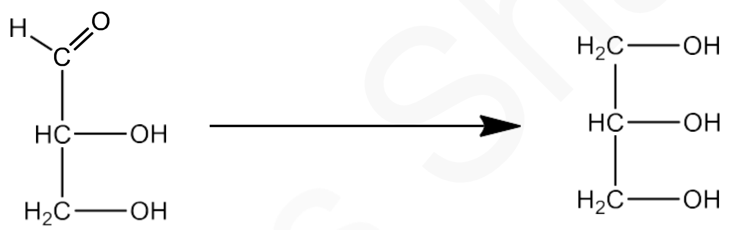



**N-Acetyl-D-Glucoseamine**

### 4) Sugar alcohols

Replace carbonyl oxygen to form polyhydroxy alcohols

e.g. glyceraldehyde --> glycerol




**D-Glyceraldehyde** **Glycerol**

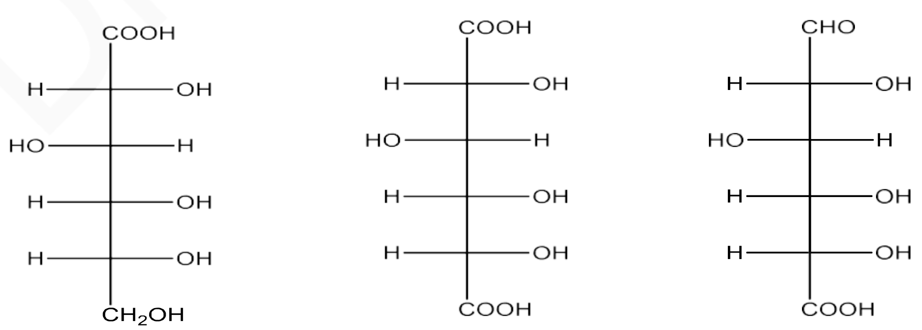
Replace "-ose" with "-itol".

Ribose ⟶ ribitol

### 5) Sugar acids

Oxidation of carbonyl carbon or highest carbon.

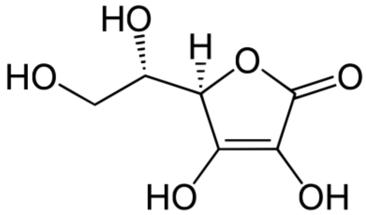
glucose --> gluconic acid or Glucaric acid or glucuronic acid




**D-Gluconic acid** **D-Glucaric acid** **D-Glucuronic acid**

**6) L-Ascorbic acid**

Derived from D-glucose.




**L-Ascorbic acid**

## 2- Disaccharides

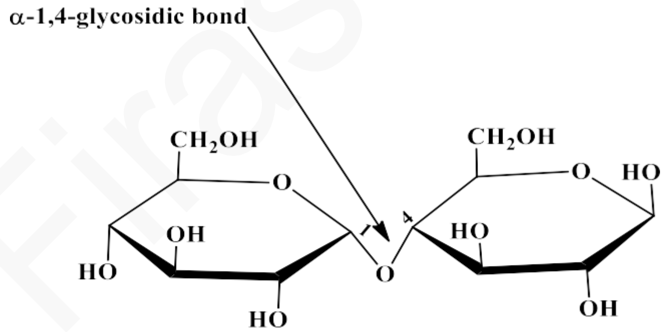
Two monosaccharides joined by covalent bond called a **glycosidic linkage** via a condensation reaction. Bond is created between the C-1 of one sugar and the -OH of another carbon

Examples:

**1- Maltose**

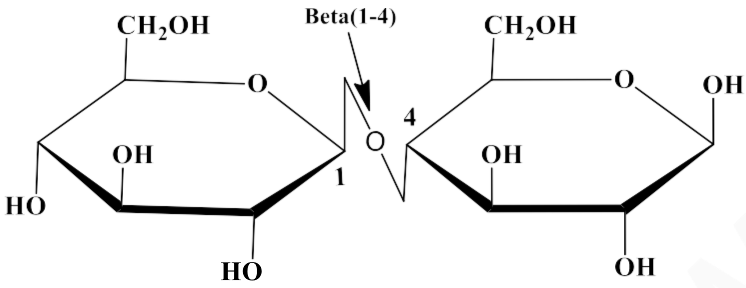
Maltose derives its name from its presence in malt, the juice from sprouted barley and other cereal grains (from which beer is brewed).

Maltose consists of two molecules of D-glucopyranose joined by an α(1,4) glycosidic bond between carbon 1 (the anomeric carbon) of one unit and carbon 4 of the other unit. Following are representations for fl-maltose, so named because the OH on the anomeric carbon of the glucose unit on the right is beta.



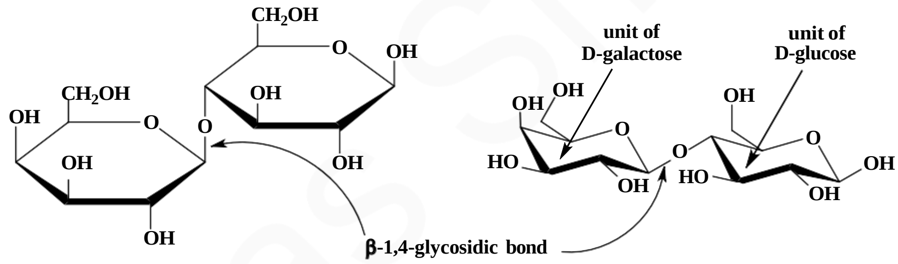

**Maltose**

**2- Cellobiose** 2 glucoses joined by beta(1-4)-glycosidic bond; plant polysaccharide

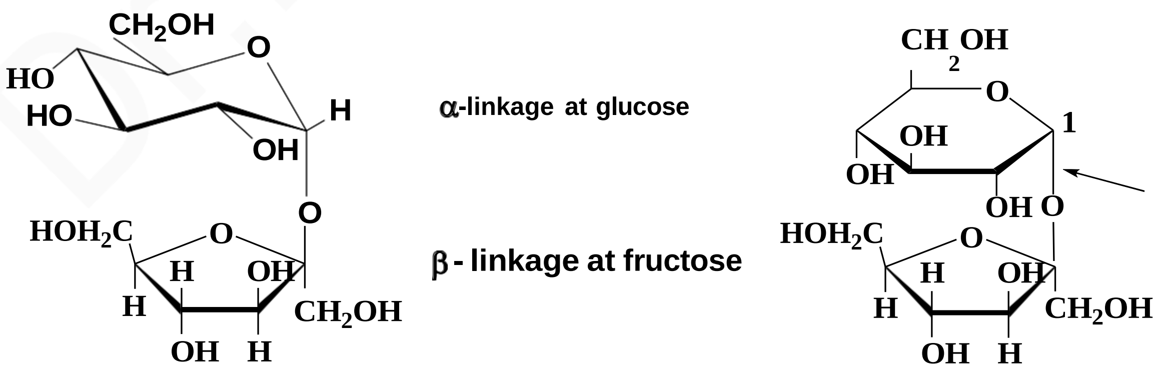



**Cellobiose**

**3) Lactose -** Lactose is the principal sugar present in milk. It makes up about 5-8% of human milk and 4-6% of cow's milk. It consists of D-galactopyranose bonded by a β-1-4-glycosidic bond to carbon 4 of D-glucopyranose. Lactose is a reducing sugar.




**4) Sucrose** –(**nonreducing sugar**) is the most abundant disaccharide in the biological world. It is obtained principally from the juice of sugar cane and sugar beets. In sucrose, carbon 1 of α-D-glucopyranose is joined to carbon 2 of β-D-fructofuranose by an α-1,2-glycosidic bond.




(+)-sucrose or α -D- glucopyranosyl-β -D-fructofuranoside

**Reducing and nonreducing sugars**

-Some monosaccharides and most disaccharides have a reactive carbonyl group or anomeric carbon that can be oxidized.

Examples: glucose, maltose, cellobiose, lactose

-Nonreducing sugars have both anomeric carbons in a glycosidic bond (e.g. sucrose).

## 3- <u>Polysaccharides</u>

Divided in two two classes:

1) **homoglycans** (homopolysaccharides): composed on one monosaccharide
2) **heteroglycans** (heteropolysaccharides): made of more than one type of monosaccharide

Often classified according to their biological role:

**1) Starch and glycogen** - storage polysaccharides

Both are homoglycans.
Starch is storage form in plants and fungi.
Glycogen is storage form in animals.
Bacteria contain both.

**Starch** - mixture of **amylose** and **amylopectin**

-**Amylose** is an unbranched polymer of 100-1000 D-glucose in an α-(1-4) glycosidic linkage.

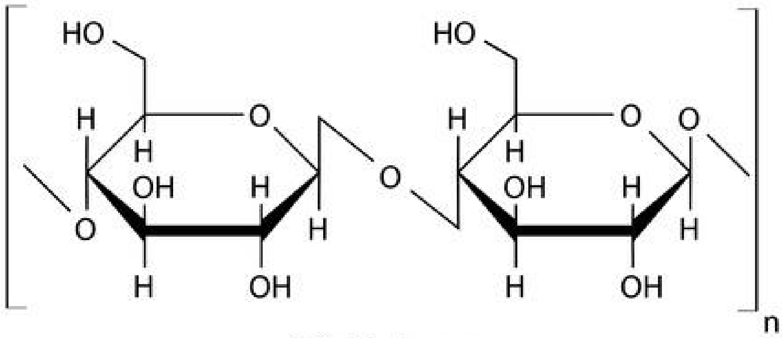
-**Amylopectin** is a branched polymer α-(1- 6) branches of residues in an α-(1-4) linkage; overall between 300-6000 glucose residues, with branches once every 25-30 residues; side chains are 12 residues long

**Glycogen** - branched polymer of glucose residues with branches every 8-12 residues with branches containing as many as 50,000 glucose residues

**2) Cellulose and Chitin** - structural polysaccharides

### -Cellulose

Cellulose, the most widely distributed plant skeletal polysaccharide, constitutes almost half of the cell waft material of wood. Cotton is almost pure cellulose, Cellulose is a linear polysaccharide of D-glucose units joined by β-(1-4) glycosidic bonds. It has an average molecular weight of 400,000 g/mol, corresponding



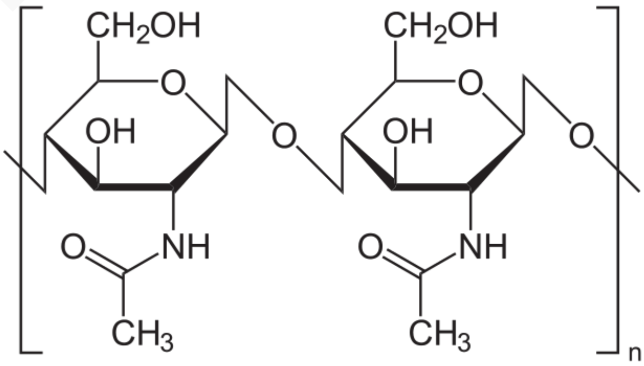
Cellulose

To approximately 2200 glucose units per molecule. Cellulose molecules act very much like stiff rods, a feature that enables them to align themselves side by side into well- organized water-insoluble fibers in which the OH groups form numerous intermolecular hydrogen bonds. This arrangement of parallel chains in bundles gives cellulose fibers their high mechanical strength. It is also the reason cellulose is insoluble in water.

Humans and other animals cannot use cellulose as food because our digestive systems do not contain β-glucosidases, enzymes that catalyze the hydrolysis of β-glucosidic bonds. Instead, we have only α-glucosidases; hence, the polysaccharides we use as sources of glucose are starch and glycogen. On the other hand, many bacteria and microorganisms do contain β-glucosidases and so can digest cellulose.

## -Chitin

Chitin is a polymer of *N*-acetyl-D-glucosamine (or, as it is known systematically, 2-acetamido-2-deoxy-D-glucose .)Residues of this carbohydrate are connected by β-1,4-glucosidic linkages within the chitin polymer.



**Chitin**

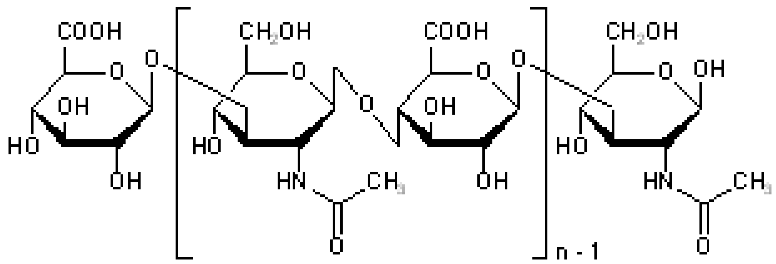
**3- Acidic Polysaccharides:**

Acidic polysaccharides a group of polysaccharides that contain carboxyl groups and/or sulfuric ester groups play important roles in the structure and function of connective tissues. There is no single general type of connective tissue. Rather, there are a large number of highly specialized forms, such as cartilage, bone, skin, tendons, blood vessels, and cornea.

Most connective tissues are made up of collagen, a structural protein, in combination with a variety of acidic polysaccharides that interact with collagen to form tight or loose networks.

**1. Hyaluronic Acid**

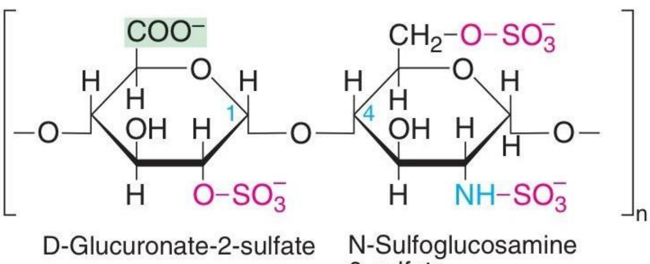
Hyaluronic acid is the simplest acidic polysaccharide present in connective tissue. It has contains from 3000 to 100,000 repeating units, depending on the organ in which it occurs. The repealing disaccharide unit in hyaluronic acid is D-glucuronic acid linked by β-1,3-glycosidic bond between glucuronic acid and *N*-acetyl-D-glucosamine.



**2. Heparin**

Heparin is a heterogeneous mixture of variably sulfonated polysaccharide chains, ranging in molecular weight front 6000 to 30,000 g/mol. This acidic polysaccharide is synthesized and stored in mast cells of various tissues, particularly the liver, lungs, and gut. Heparin has many biological functions, the best known and understood of which is its anticoagulant activity. It binds strongly to antithrombin III, a plasma protein involved in terminating the clotting process.

The repeating monosaccharide units of heparin (one of its kind) are N-sulfoglucosamine-6-sulfate, and D-Glucuronate-2-sulfate, bonded by a combination of α-(1,4) glycosidic bonds.




**Heparin**