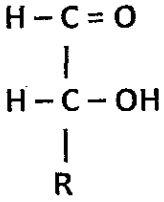
Carbohydrates Chemistry

❖ **Definition:** - are organic substances composed of carbon, hydrogen, and oxygen.

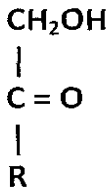
Or - are simple sugar (polyhydroxy aldehyde or ketone) or its derivatives.

الكربوهيدرات هي : السكر البسيط وأي من مشتقاته

السكر البسيط هو :الألدهيدات أو الكيتونات عديدة الهيدروكسيل



Polyhydroxyaldehydes



Polyhydroxyketones

❖ **Classification of carbohydrates: according to the hydrolysis (تحلل مائي) products**

1. Monosaccharides	Contain 1 sugar unit. (Can't be Hydrolyzed)
2. Disaccharides	Contain 2 sugar units.
3. Oligosaccharide	Contain 3-10 sugar units.
4. Polysaccharides	Contain more than 10 sugar units.

N.B. Usually the ratio between Carbon & H2O is 1. Hence the name carbohydrate.

Monosaccharide's (glycoses)

❖ **Definition: They are the simplest units of carbohydrate containing one sugar unit.**

General formula is: $C_n(H_2O)_n$.

❖ **Naming of monosaccharide's:**

A. According to the Functional group:

1. **Aldoses: monosaccharide's containing aldehyde group (-CHO).**
2. **Ketoses: monosaccharide's containing ketone group (-C=O).**

B. According to the No. of Carbon atoms:

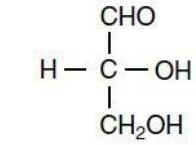
Sugar	No. of Carbons	Includes
Trioses	3	Aldotrioses and ketotrioses
Tetroses	4	Aldotetroses and ketotetroses
Pentoses	5	Aldopentoses and ketopentoses
Hexoses	6	Aldohexoses and ketohexoses

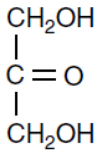
❖ Classification of monosaccharide's:

1. Trioses: monosaccharide's containing 3 carbons.

a. Aldotrioses: Glyceraldehyde "glycerose".

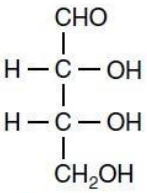
b. Ketotrioses: Dihydroxyacetone.

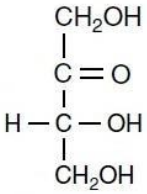

D-Glycerose
(D-glyceraldehyde)


Dihydroxyacetone

2. Tetroses: monosaccharide's containing 4 carbon atoms:

a. Note: The suffix —ulose means Keto group.

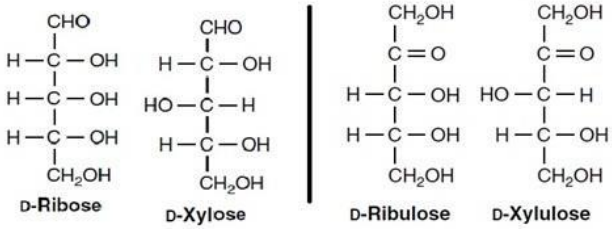

D-Erythrose


D-Erythrulose

3. Pentoses: monosaccharide's containing 5 carbon atoms.

a. Aldopentoses: Ribose, arabinose, xylose and Lyxose.

b. Ketopentoses: Ribulose and xylulose.


D-Ribose D-Xylose D-Ribulose D-Xylulose

c. Importance (functions) of pentoses:

- **Ribose:**

- Enter in the structure of nucleic acids (RNA and DNA.)

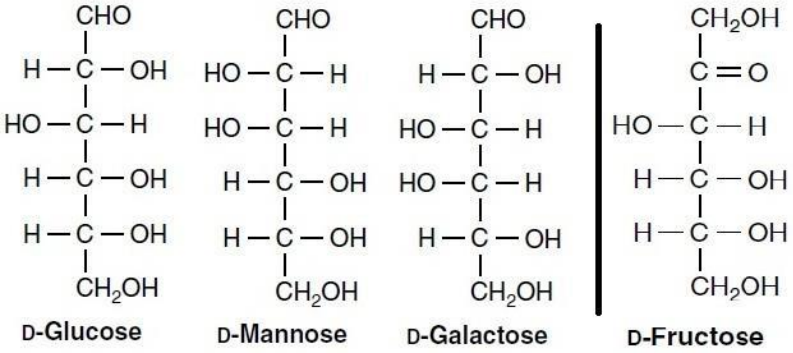
- Enters in the structure of ATP, GTP .

- Enters in the structure of coenzymes NAD, NADP and FAD.

4. Hexoses: monosaccharides containing 6 carbon atoms.

a. Aldohexoses: glucose, mannose, and galactose.

b. Ketohexose: fructose



c. Importance (functions) of Hexoses:

1- Glucose: "grape sugar" is the most important sugar of carbohydrate:

- Glucose is the main sugar in blood

- Glucose is one of major sources of energy in the body.

- In the liver and other tissues, glucose is converted to all carbohydrates in the body e.g. glycogen, galactose,

2- Galactose:

- It can be converted into glucose in the liver.

- It is synthesized in mammary gland to make the lactose of milk (milk sugar)

3- Fructose: "fruit sugar":

- It can be converted into glucose in the liver.

- It is the main sugar of semen.

4- Mannose: A constituent of many glycoproteins.

❖ Properties of monosaccharides:

- **Ring (cyclic) structure of sugars:**

a) This Cyclic form is due to: reaction between C=O (carbonyl) of aldehyde group in Aldoses or of Ketol group in Ketoses with an alcoholic hydroxyl group to form

- **Furanose → 4 Carbon ring**
- **Pyranose → 5 Carbon ring**

b) If the remaining —OH is on the right side, it is α— sugar.

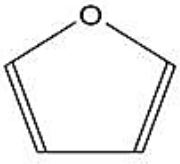
If the remaining —OH is on the left side, it is β — sugar.

c) Pyranose and furanose:

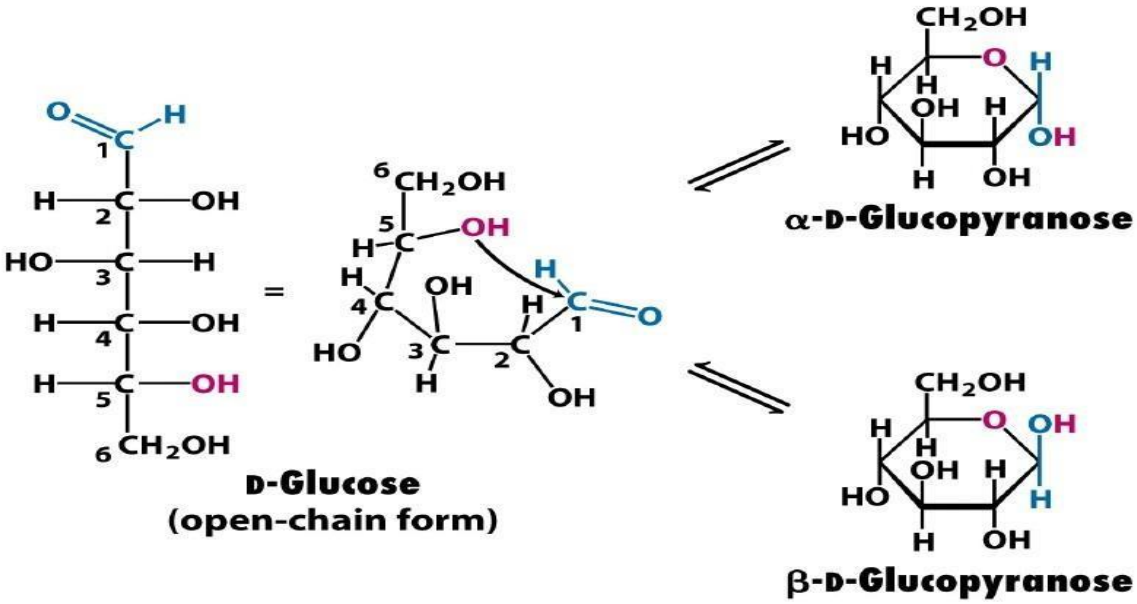
- The 1-5 ring form is called pyranose as it resembles an Organic compound called pyran e.g. α and β glucopyranose.

- The 1-4 ring form is called furanose as it resembles an Organic compound called furan e.g. α and β glucofuranose.

Pyran



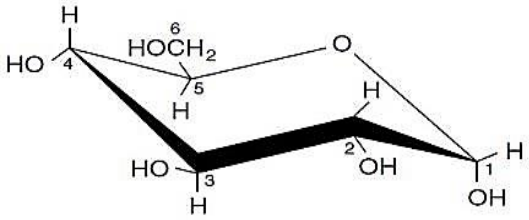
Furan



d) Haworth and chair forms:

i. Cyclic structure of sugars may be present in the form of Haworth or chair forms. as follows:

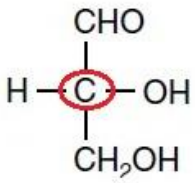
- **All the -OH groups on the right side in old ring structure are written downwards in Haworth formula.**
- **All the -OH groups on the left side in old ring structure are written upwards in Haworth formula.**
- **These rules are reversed at CH2-OH groups e.g. last carbon atom of glucose that attached to oxygen i.e. c4 in furanose and C5 in pyranose**



D-Glucose. A: straight chain form.

Asymmetric carbon atom:

Is the carbon atom to which 4 different groups or atoms are attached.



Any substance containing asymmetric carbon atom shows 2 Properties,

Optical activity and Optical isomerism.

a. Optical activity: It is the ability of substance to rotate plane polarized light either to the right or to the left.

1- If the substance rotates plane polarized light to the right so it is called:

dextrorotatory or d or (+).

2- If it rotates it to the left so it is called: levorotatory or I or (-).

3- Glucose contains 4 asymmetric carbon atoms. It is dextrorotatory, so it is sometimes named dextrose.

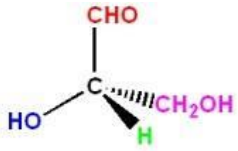
4- Fructose contains 3 asymmetric carbon atoms. It is levorotatory. so it is sometimes called: LevuIose

b. Optical isomerism: It is the ability of substance to present in more than one form (isomer).

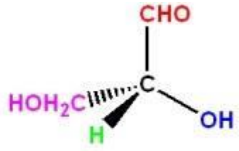
- Substance containing one asymmetric carbon atom has 2 isomers.

1- Configuration (Enantiomers): لازم كل الكربونات تكون معكوسة وانظر على قبل الاخيرة

a. The simplest carbohydrate is Glyceraldehyde that has one asymmetric carbon atom. So it has 2 optically active forms.



L-Glyceraldehyde

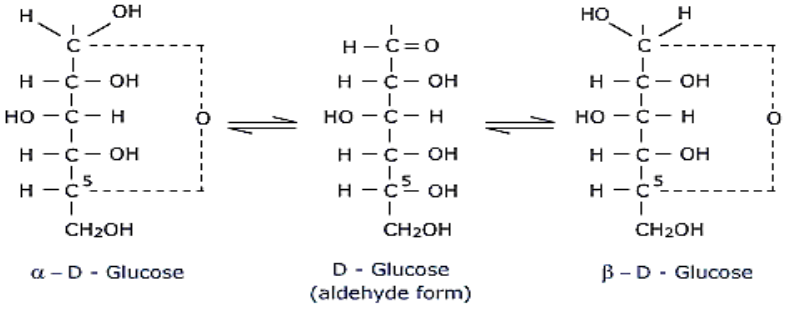


D-Glyceraldehyde

2- Anomeric carbons & anomers: ring structure لازم السكر يكون في ال

a. Anomeric carbon: is the asymmetric carbon atom obtained from active carbonyl sugar group: C1 in aldoses and C2 in ketoses.

b. Anomers: These are isomers obtained from the change of position of hydroxyl group attached to the anomeric carbon e.g. α and β glucose are 2 anomers. Also α and β fructose are 2 anomers.



3- Aldose-Ketose isomerism (functional group isomerism): Have the same molecular formula but differs in functional group.

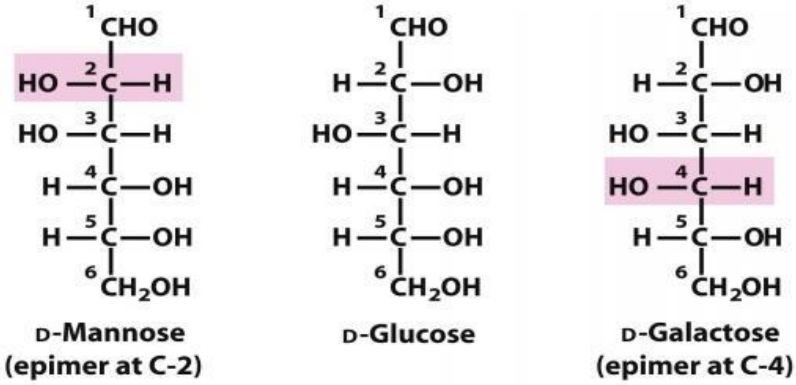
EX: Fructose & glucose One contains Ketone group (C=O) and the other contains aldehyde group (-CHO). Both are isomers.

4- Epimers: كربونه واحده بس هب المختلفة

A. Epimers are isomers having more than asymmetric carbon, all are same except only one is different.

a. Glucose & Mannose are epimers at carbons 2.

b. Glucose & Galactose are epimers at carbons 4

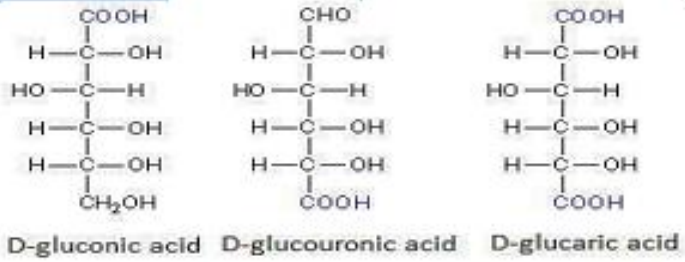


Sugar derivatives

1- Sugar acids:

- Are produced by oxidation of carbonyl carbon, last carbon or both.

Carbonyl carbon	Aldonic acid	e.g. glucose	gluconic acid.
Last hydroxyl carbon	uronic acid	Glucose	glucuronic acid
BOTH	Aldaric acids	Glucose	glucaric (saccharic) acid



D-gluconic acid D-glucouronic acid D-glucaric acid

- L-Ascorbic acid (vitamin C) is an important sugar acid.

2- Sugar alcohols:

- Are produced by Reduction of carbonyl carbon

sugar	Sugar alcohols	function
Glucose	sorbitol	
Mannose	Mannitol	
galactose	Dulcitol	
Glyceraldehyde dihydroxyacetone	glycerol	Structure of Triacylglecerol (TAG) & phospholipid
Ribose	ribitol	Structure of riboflavin (vitamin B_2)
Inositol	Myoinositol Cyclic alcohol	Structure of phospholipid It acts as precursor of 2nd messenger
Fructose	mannitol and sorbitol	

3- Deoxysugars:

1. Are produced by replacement of hydroxyl groups by hydrogen atom i.e. one oxygen is missed.
2. Occurring in nucleic acid DNA Ribose De-oxy ribose.
3. L-Fucose (6-deoxyL-galactose): enters in BL.group AG.

4- Amino sugars: in these sugars, the hydroxyl group attached to C2 is replaced by an amino or an acetyl-amino group.

1) Amino sugars enter in glycoproteins.
2) Examples:
   a) Glucosamine: It enters in heparin and hyaluronic acid.
   b) Galactosamine: It enters in chondroitin sulphate.
   c) Mannosamine: It enters in neuraminic and sialic acids.

5- Amino sugar acids:

1. Formed by addition of amino sugars and some acids.
2. Examples:
   1- Neuraminic acid = Mannosamine + pyruvic acid. 9C
   2- Sialic acid or N-acetylneuraminic acid (NANA) enters in glycolipid.

6- Glycosidic bond and glycosides:

A. Glycosidic bond: It is the bond between a carbohydrate and another Compound to form a complex carbohydrate.

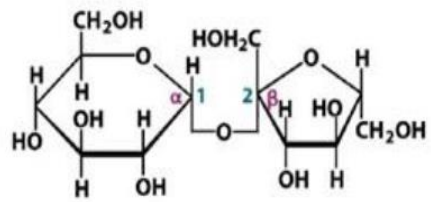
1. This bond is between the hydroxyl group of anomeric carbon of monosaccharide and another compound which may be:
   a) Another monosaccharide to form **disaccharide**.
   b) A glycone i.e. non-carbohydrate to form **glycoside**.
2. N and O-glycoside bond:

B. Examples of gilycosides:

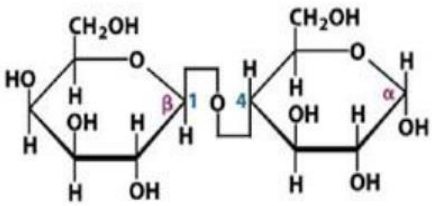
1. **Disaccharides:** discussed later.
2. **Sugar nucleotide** as ATP, GTP and other nucleotides: aglycone here is purines And pyrimidines.
3. **Cardiac glycosides:**
   a) Aglycone here is steroid.
   b) Cardiac glycosides such as digitalis.
   C) used in treatment of cardiac disease.

DISACCHARIDES

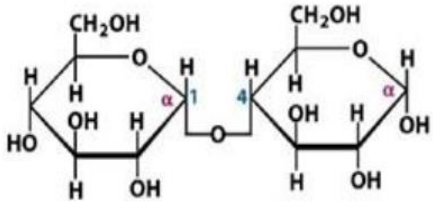
- **The most important disaccharides are:**
  - {α-glucose + α-glucose} : → α (1-1) glycosidic bond → trehalose
    → α (1-4) glycosidic bond → Maltose
    → α (1-6) glycosidic bond → Isomaltose
  - { α-glucose + β-fructose} : → (α1-β2) glycosidic bond or (β2-1 fructosidic b) → Sucrose
  - {β-glucose + β-galactose} : → β (1-4) galactosidic bond → Lactose
- **Properties:** all disaccharide except (trehalose & Sucrose) showing the following characters :
  - It is a reducing agent (can reduce Benedict's reagent).
  - It can be present in α and β forms.
  - It can form characteristic osazone crystals.



Sucrose
(α-D-Glucopyranosyl-(1 → 2)-β-D-fructofuranose



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



Maltose
(α-D-Glucopyranosyl-(1 → 4)-α-D-glucopyranose

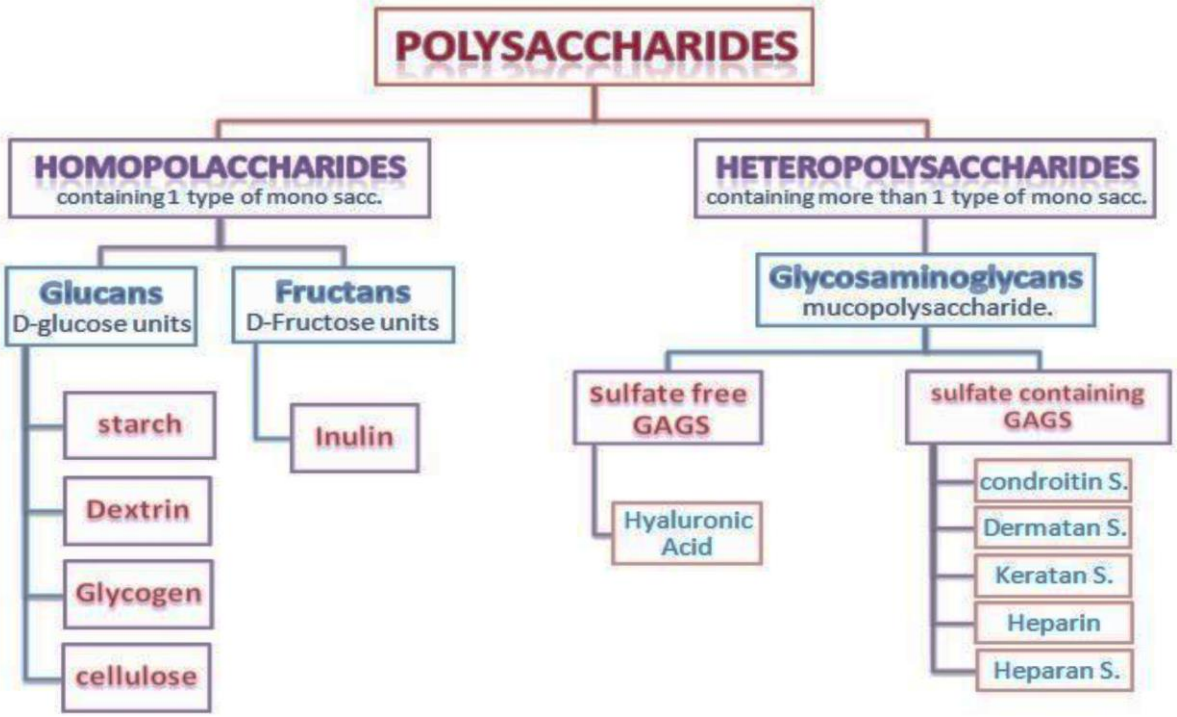
Sugar	Source
Maltose	a) Malt. b) **Maltose** is produced during digestion of starch by **amylase** enzyme.
Isomaltose	**Isomaltose** is produced during digestion of starch and glycogen by **amylase** enzyme
Lactose	a) Milk. - **Non-fermentable** sugar.
Sucrose	a) cane and beet sugar (table sugar) b) Pineapple and carrot.

• invert Sugar :

- **Structure: It is a sugar that contains equal number of both glucose and fructose molecules (unbound).**
- **Sources: a) Bee honey**
  b) By hydrolysis of sucrose by sucrase (invertase) enzyme
- **Properties: levorotatory sugar due to strong levorotatory of fructose invert the previous dextro-rotatory action of sucrose.**

POLYSACCHARIDES

- Thy are polymer of more than 10 unit of monosaccharides or their derivatives e.g.(aminosugar and uronic acid).



HOMOPOLYSACCHARIDES

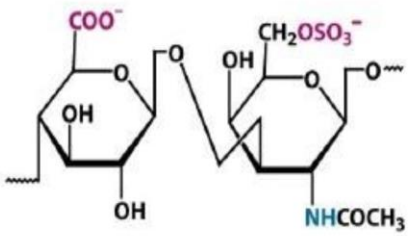
GLUCANS	Starch	Starch granule is formed of: 1) **Inner layer:** called **amylose. It** constitutes 15-20% of the granule and formed of non-branching helical structure of glucose units linked together by α 1 — 4 glycosidic bond. 2) **Outer layer:** called **amylopectin** constitutes 80-85% of the granule and formed of branched chain. Each chain is composed of 24-30 glucose units linked together by α 1 — 4 glycosidic bond and a 1 — 6 glycosidic bond at branching points.	- cereals, potatoes, legumes and other vegetables - In plants it synthesized by photosynthesis.	1) Starch gives blue color with iodine. Amylopectin gives red color with iodine. 2) Partial hydrolysis (digestion) by amylase enzyme gives various forms of dextrins
	Dextrins	- amylodextrin, erythrodextrin and achrodextrin.	- By hydrolysis of starch.	- They give red color with iodine.
	Glycogen	- Highly branched chain - Each branch is composed of 12-14 glucose units. - Similar to amylopectin	- The storage form of CHO in human and animals - in liver, muscles	- gives reddish violet color with iodine
	Cellulose	- long linear chains of (β-D-glucopyranose) linked together by β 1-4 glycosidic bond **- The presence of cellulose in diet is important because it:** - increases the bulk of stool. - This stimulates intestinal movement and prevents constipation.	- plants: vegetables, cotton	- give NO color with iodine - insoluble in water - **Cannot** be digested due to absence of digestive hydrolase enzyme that attacks **β**-linkage.
Fructans	Inulin	- Repeated units of fructose linked together by β1-2 bonds.	- Root of artichokes and other plants.	- Inulin clearance is one of diagnostic tests for investigation of GFR.

Heteropolysaccharides

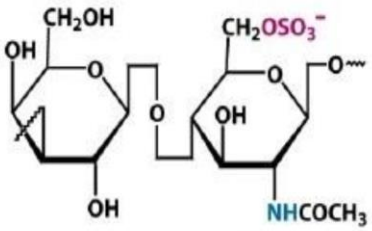
- **Glycosaminoglycans, GAGs (mucopolysaccharide):**

Introduction:

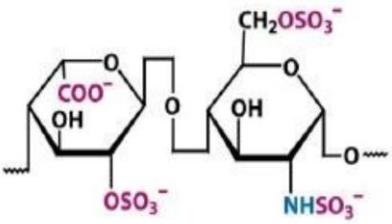
1. They are formed of repeating disaccharide units **(Acidic sugar- Amino sugar)n**
   - **a-**The acidic sugar is either D-glucuronic acid or its epimer, L-induronic acid.
   - **b-**Amino sugar is either D-glucosamine or D-Galactosamine in which the amino group is usually acetylated. The amino sugar may also be sulfated at carbon 4 or 6.
2. GAGs often contain sulfate group. The uronic acid and sulfate residues cause them to be very negatively charged.
3. They are unbranched and contain no N-acetyl neuraminic acid.
4. Most of GAGs are present extracellularly except heparin.
5. Most of them form the structural components of connective tissue such as bone, elastin and collagen.
6. They act as Lubricants and cushion for other tissues because they have the property of holding large quantities of water.
7. When a solution of glycosaminoglycans is compressed, the water is "squeezed out" and the glycosaminoglycans are forced to occupy a smaller volume, when the compression is released, the glycosaminoglycans return to their original hydrated volume because of the repulsion of their negative charges. This property is the cause of resilience of synovial fluid and the vitreous humor of the eye.



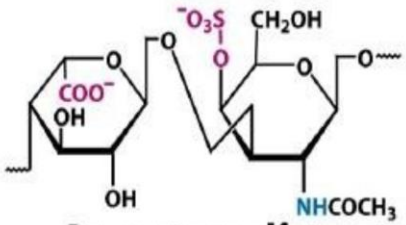
Chondroitin 6-sulfate



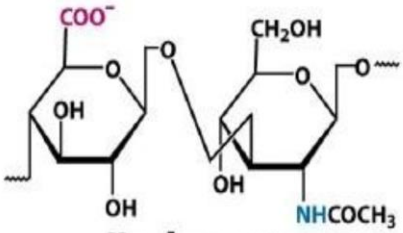
Keratan sulfate



Heparin



Dermatan sulfate



Hyaluronate

Type	Structure	Site	Functions
Hyaluronic acid	Glucuronic acid	Cartilage	lubricant in joints
		Synovial fluid	makes cartilage **compressible**
	N-acetyl glucosamine NO Sulfate	Connective tissue	cell migration during **wound repair**
		Vitreous humor of the eye	cell migration during **morphogenesis**
Chondroitin 4- and 6 sulfate	Glucuronic acid	sage, tendons, ligaments and bones	Have role in compressibility of cartilage in weight bearing
	N-acetylgalactosamine with sulfate on either C4 or C6	Aorta, skin, cornea, umblical cord and in certain neurons	it binds collagen and hold fibers in strong network
Keratan sulfate	Galactose (no uronic acid), with sulfate on C6	Cornea	corneal transparency
	N-acetyl glucosamine with sulfate on C6	Found in Cartilage	
Dramatan sulfate	L-Induronic acid	Cornea	corneal transparency
	N-acetylgalactosamine with sulfate on C6	Sclera. Skin, blood vessels and heart valves	Maintaining the shape of the eye.
Heparin	Induronic acid with sulfate on C2	mast cells (intracellular compound) in the wall of blood vessels	anticoagulant
	Glucosamine with sulfate on C2 and C6		
Heparan sulfate		cell membrane	- act as receptors - cell adhesion and cell-cell interaction
		basement membrane of the kidney	Determining the charge selectiveness of glomerular filtration.

	Glycoproteins	proteoglycans
Definition	Are proteins that contain oligosaccharide chains.	chains of glycosaminoglycans attached to protein molecule
1- Structure	Oligosaccharide units.	Glycosaminoglycans.
CHO component		
Ptn component	Protein core	Protein
Types of sugar	Contain no uronic acid	Contain uronic acid
	Pentoses: as arabinose and xylose.	Sugaramines as glucosamines.
	Methylpentoses: L-fucose	
Sulfate group	Contain no sulfate	Contain sulfate.
Size of CHO component	2-15 units.	More than 50 units.
Repeating structure	Little or non.	Repeating disaccharides.
Shape	Usually branched	Linear, unbranched.
2- Function	- Extracellular matrix. - Mucin. - Blood group antigens e.g. A, B and AB. - Cell receptors. - Glycophorins. - Plasma proteins. - Some hormones. - Enzymes. - Antibodies.	- ground substance and support tissues as cartilage, bone and tendons - cell membrane