ALQUSOUR ACADEMY

أكاديمية القصور

BIOCHEMISTRY

Subject Second Exam - Chapter Sixteen

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CARBOHYDRATES

☒ **Introduction:**

- Carbohydrates are the most abundant molecules in nature. We can classify them into:

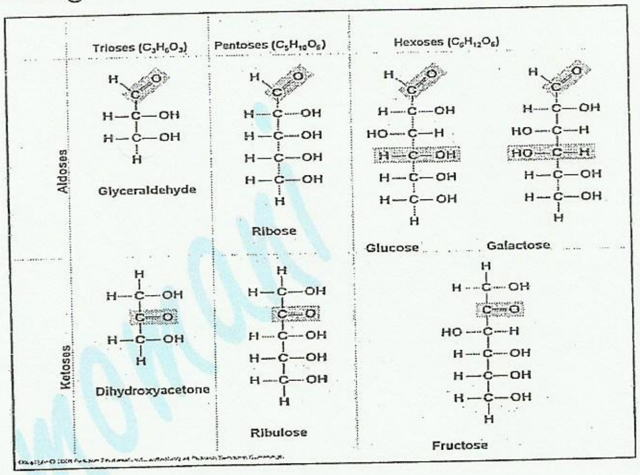
- Simple sugar (**monosaccharides**) fits on the general formula $C_n(H_2O)_n$.
  Examples (glucose, glyceraldehydes, ribose).
- **Oligosaccharides**, are formed when a few monosaccharides are linked together.
- **Polysaccharides**, are formed when many monosaccharides are linked together, (e. g. starch and cellulose in plants, glycogen in animals). The reaction that add monosacchrides units to a growing carbohydrates involves the loss of one H2O for each new link formed.

- **Carbohydrates** play important roles in biochemistry, they are:

- The main source of energy.
- Essential structure component of several classes of organisms (e.g. cellulose in plants).
- Important in the processes take place on the surface of the cell; particularly in cell-cell interactions and immune recognition; (oligosaccharides).

What are the structures and the stereochemistry of monosaccharides?

- Monosaccharides are simple sugar; they are the building block of all carbohydrates.



- Their structure includes carbonyl group and several hydroxyl groups.
- We can classify monosaccharaides in many ways:

1. According to the functional groups:
   - If polyhydroxy aldehyde (**aldose**)
   - If polyhydroxy ketone (**ketose**)
2. According to the number of carbon atoms:

3 carbons	**triose**
4 carbons	**tetrose**
5 carbons	**Pentose**
6 carbons	**Hexose**
7 carbons	**heptose**

	Aldehyde (**aldose**)	Ketone (**ketose**)
3 carbons	Aldotrioses	Ketotrioses
4 carbons	Aldotetroses	Ketotetroses
5 carbons	Aldopentoses	Ketopentoses
6 carbons	Aldohexoses	Ketohexoses
7 carbons	Aldoheptoses	Ketoheptoses

- **Six carbon sugars** are the most abundant in nature.
- **Aldoses** are more common than ketoses.
- The simplest CHO contains 3 carbon atoms (trioses).
- Biochemically important sugars usually contain 5 or 6 carbon atoms.
- 5 carbon sugars (e.g. ribose) are important for the structure of nucleic acids.

Glossary:

- **Stereochemistry**: is the 3 dimensional shape of the molecules.
- **Chiral carbon atom**: is the carbon where there are 4 different groups bounded to it.
- **Stereoisomers:** molecules that differ from each other only in their configuration (3 dimensional shape), also called **optical isomers, the chiral carbon atom is the source of optical isomers.**

- The number of stereoisomer for every molecule = 2^n where (n= number of chiral carbon), half of stereoisomers are D (dextro), and half are L (levus).

<u>E.g.</u> Glyceraldehydes is an aldotriose sugar with 1 chiral carbon, so there are 2 stereoisomers called D-Glyceraldehyde, and L-Glyceraldehyde due to difference in the position of -OH bonded to the central carbon.

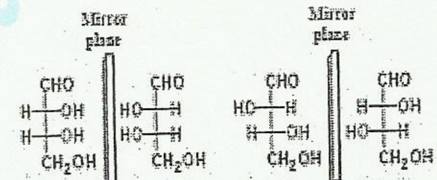
Glyceraldehyde (an aldotriose) Dihydroxyacetone (a ketotriose)

- **D sugars,rather than L sugars, are predominant in nature.**
- **Configuration:** the three-dimensional arrangement of groups around a chiral carbon atom. Stereoisomers differ from each other in configuration.

- **Enantiomers:** mirror-image, non-superimposable stereoisomers. Like L & D seriosomers of glyceraldehyde which is the only possible sterioisomers for 3 carbon CHOs. Number of sterioisomers increase with the increase of number of carbon atoms.

- **Diastereomers:** nonsuperimposable, nonmirror-image stereoisomers; (L-Threose is diastereomer for L- and D- Erythrose).

- **Epimers:-** diastereomers that differ only in configuration around one of several chiral carbon atoms. (e.g. D- Erythrose and D- Threose).

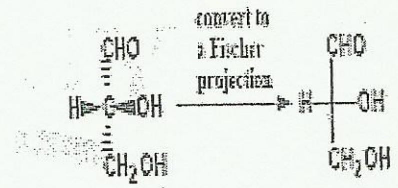


D-Erythrose L-Erythrose D-Threose L-Threose

☒ <u>Fischer projection method</u>:

- A convention used for two-dimension drawing of the three dimensional structures of stereoisomers. **In fisher projection:**

  ✓ Bonds written vertically on the two-dimensional paper represent bonds directed behind the paper in three dimensions, whereas bonds written horizontally represent bonds directed in front of the paper in three dimensions.



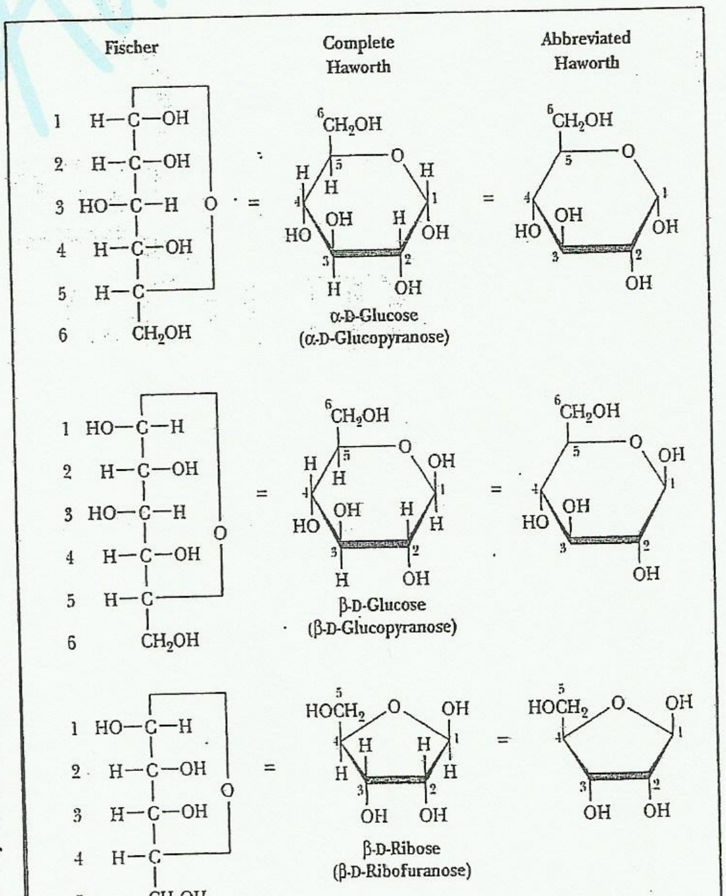
D-Glyceraldehyde D-Glyceraldehyde

  ✓ The carbon atoms are numbered in a sequence from the top, whereas the aldehyde group is C-1, and the ketone group is C-2.

  ✓ The designation of the configuration as L or D depends on the arrangement at the chiral carbon with the highest number, L when the hydroxyle group on the left, and D when it is on the right.

Cyclic structures (anomers):

- Sugars with five or six carbon atoms normally exist as cyclic molecules rather than open chain forms.
- Cyclization takes place as a result of interaction between functional groups on distant carbons to form:
  - **Hemiacetal** (in aldohexose) between C-1 and C-5
  - **Hemiketal** (in ketohexose) between C-2 and C-5
- The cyclization process involves the carbonyl group and give arise to another chiral center (**anomeric carbon**) in addition to the ones already present in the sugar molecule, the two possible cyclic isomers called **anomers**, are designated as α and β.
- In β, the OH group is on the anomeric carbon and the terminal group is on the same side of the ring, while in α, the OH group on the anomeric carbon and the terminal group are on the opposite side of the ring.
- For cyclic sugar fisher projection does not give a realistic picture of the bonding nor do they accurately represent the overall shape of the molecule, so we use the **Haworth projection formulas.**



- **What is the relation between HPF and FPM?**

For D sugar, any group that is written to the right of the carbon in a Fisher projection has a downward direction in a Haworth projection; (α-sugar). Any group that is written to the left in Fisher projection has an upward direction in a Haworth projection; (β-sugar).

- The cyclic sugar is shown as planer five-membered rings called (**furanose**), or six-membered rings called (**pyranose**). The five membared rings of furanose are in reality very nearly planar, but the six membared rings of pyranose actually exist in the solution in chair conformation.

How do monosaccharides react?

1- Oxidation-reduction reactions
2- Esterification reactions
3- Formation of glycosides
4- Others

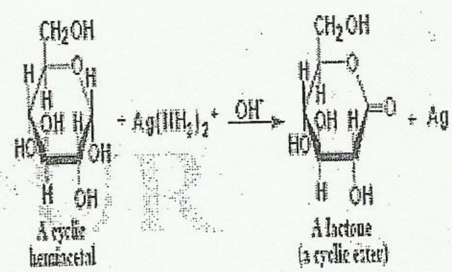
1- Oxidation-reduction reactions:

- Oxidation of sugars provides energy for the organisms.
- Aldehyde, or ketone group of a sugar can be oxidized to a carboxylic group, and this reaction is the basis of a test for the presence of aldose or ketose, so aldose and ketose are called **reducing sugar.**
- **All sugar are reducing sugar except sucrose (has no free aldehyde or ketone groups).**
- The compound result from the oxidation of the aldose called **lactone (cyclic ester).**

☺ **How to detect the reducing sugar in the laboratory??**

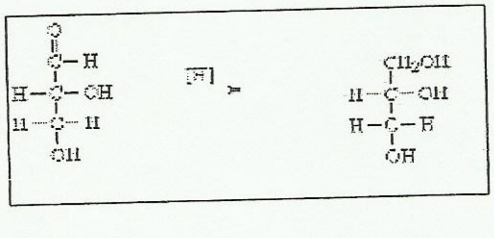
1- By **Tollens reagent**, silver ammonia complex ion [$Ag(NH_3)_2^+$], as oxidizing agent. If reducing sugar are present the silver will deposite on the wall, (Ag ions will be reduced to the free Ag metal).

2- Method which is specific for glucose detection using an enzyme called **glucose oxidase.**



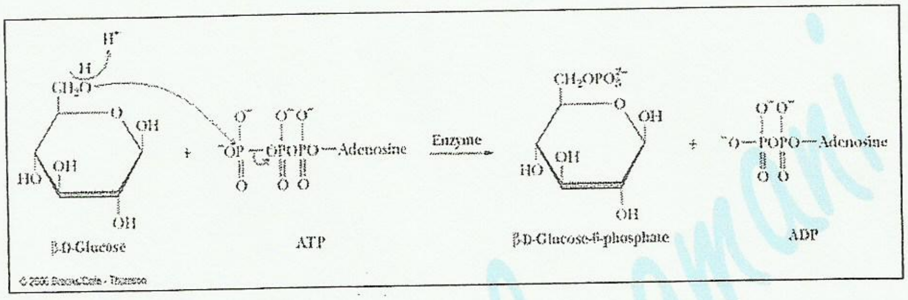
- In addition to oxidized sugars, there are some reduced sugars; in which an H atom is substituted for one of the hydroxyl groups of the sugar (the deoxy sugar, e.g. L-fucose, D-2-deoxyribose). L-fucose presented in ABO blood groups antigens.

- **Alditol (polyhydroxyl alcohol):** is compound result when the carbonyl group of a sugar is reduced to hydroxyl group.



2- Esterification reactions:

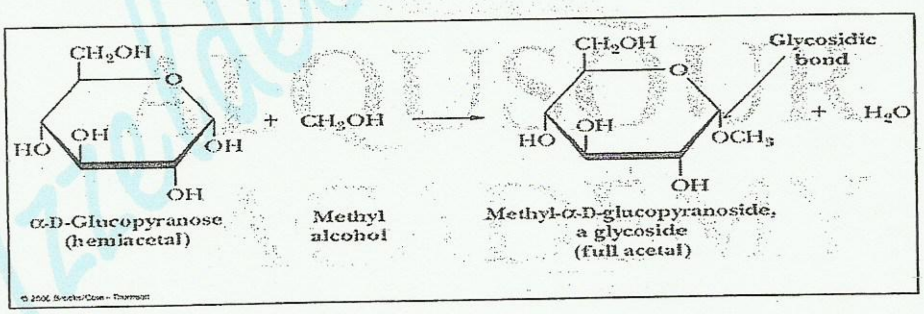
One important example is the esterification of hydroxyl group in a sugar with the phosphate group to give phosphorylated sugar. This reaction plays an important role in the metabolism of sugar.



As represented by the figure; ATP is the phosphate group donor, and the enzyme specifies the interaction with -CH2OH on carbon 6.

3- Formation of glycosides:

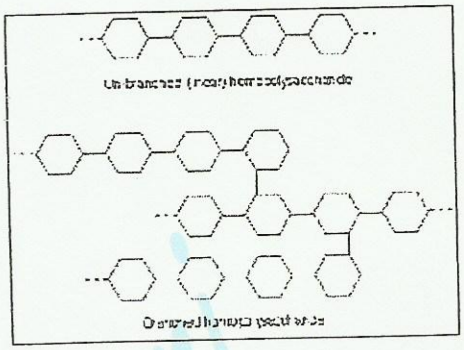
Full acetal which is called Glycoside is a result from binding of hemiacetal with alcohol by glycosidic linkage, if derived from furanoses, called (**furanosiodes**), if derived from pyronoses, called (**pyranosides**).



- Glycosidic bonds between monosaccharids are the basis for the formation of oligosaccharides, and polysaccharides. Glycosidic linkage can take several forms, the anomeric carbon of one sugar can be bonded to any one of the –OH groups on the second sugar.

E.g. α (1→4) means α anomeric carbon C-1 in the monosaccharide molecule is joined by a glycosidic bond to the fourth carbon C-4 in the second monosaccharide molecule.

- The chemical nature of the macromolecules (oligosaccharides, polysaccharides) depends on which monosaccharides are linked together, and on the type of glycosidic linkage.



- Notice that both linear and branched chain polymer can be formed.
- Linear form like amylose, all glycosidic linkages are α (1→4).
- Branched form like amylopectin, and glycogen, all glycosidic linkage along the chain are α (1→4), while at the branched points are α (1→6).
- Sugars with anomeric carbons not involved in glycosidic bonds (e.g. hemiacetal) are reducing sugars, while sugars in which all anomeric carbons are involved in glycosidic bonds (glycosides) are non reducing sugar.

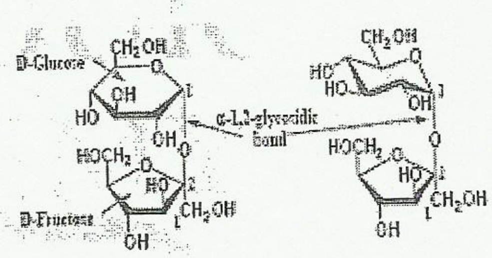
4- **Others derivatives of sugars:**

Amino sugar results when a hydroxyle group in a sugar is replaced by an amino group or one of its derivatives, these compounds are important in the cell wall of bacteria.

What are some important oligosaccharides?

- Oligosaccharides frequently occur as disaccharides.
- **Disaccharides:** linkage of 2 monosaccharides by glycosidic linkage.
- The most important examples are (sucrose, lactose & maltose).

Sucrose:



- The table sugar
- The monosaccharides that make up the sucrose are **α-D-glucose and β-D-fructose**, (Glucose is aldohexose and pyranose, Fructose is ketohexose and furanose).
- The glycosidic linkage between them is **α, ß (1→2).**
- Sucrose is **not a reducing sugar**, because both anomeric groups are involved in glycosidic linkage.
- An excess consumption of sucrose can lead to health problem.

☺ **Other sweetening substitutes are:**

1- **Fructose** itself (can produce the same sweetening effect with fewer caloris).

2- **Sucralose** an artificial sweetener derived from sucrose and does not metabolized by the body so doesn't provide calories)... What are the differents?

- Sucralose (trade name; **splenda**) differs from sucrose in two ways:

  1. 3 of the hydroxyl groups have been replaced by 3 chlorine atoms.

  2. The configuration at carbon atom 4 of the six membered pyranose ring of glucose has been inverted, producing a galactose derivative.

- The 3 chlorine atoms replace the hydroxyl groups in the carbon atom 1 and 6 of the fructose and carbon atom 4 of the galactose moiety.

- Artificial sweeteners synthesized in the lab were found to be harmful:

  1. Saccharin and cyclamate were found to cause cancer in lab animals.

  2. Aspartame is suspected to cause neurological problems especially in individuals who cannot tolerate phenylalanine.

Lactose:

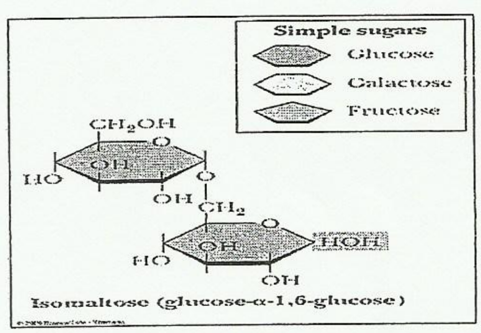
- It is the **milk sugar**.
- It is formed of **β-D-galactose and D-glucose.**
- Galactose is the C4 epimer of glucose. (What does this means?).
- Glyosidic linkage between them is **β (1→4).**

- It is between the the anomeric carbon C1 of the β form of galactose and the C4 carbon of the glucose.

- It is a reducing sugar because the group at the anomeric carbon of the glucose portion is not involved in the glycosidic linkage.

Maltose:

- It is obtained from the hydrolysis of **starch**
- It consist of **2 α-D-glucose**
- The glycosidic linkage is **α (1→4).**



Isomaltose (glucose-α-1,6-glucose)

Cellobiose:

- It is obtained from hydrolysis of **cellulose**
- It consist of 2 **β-D-glucose**
- The glycosidic linkge is **β (1→4)**.
- **Mammals can digest maltose but not cellobiose.**

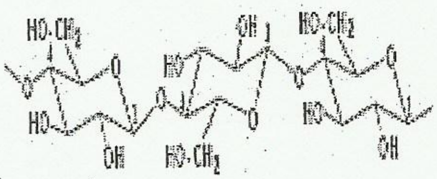
☒ **What are the structures and functions of polysacchrides?**

- Polysaccharides formed in organisms from very few types of monosaccharides component, we classify them into:

1. **Homopolysaccharides**: when polymer consists of only one type of monosaccharides.
2. **Heteropolysaccharides**: when polymer consists of more than one type of monosaccharides. **Glucose is the most common monomer.**

Cellulose:

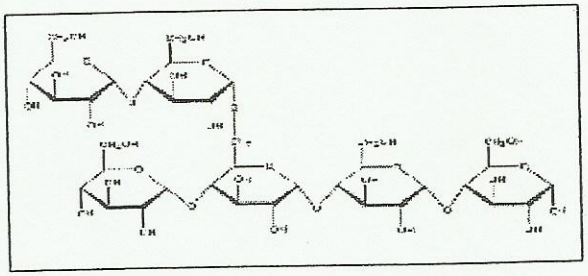
- It is the major structural component in the plants.
- It is a linear homopolysaccharides of **β-D-glucose, linked by β (1→4)**.



- Polysaccharides chains of it are hydrogen bonded together to give plant fiber their mechanical strength.
- ***Cellulase***, the enzyme needed to digest the cellulose to glucose, is not found in animals or human.
- Cellulase found in some **bacteria** which lives in the GIT of some animal like cattle.

Starch:

- It is the energy storage polymer in the plants.
- It is a polymer of **α -D-glucose**, linked by **α (1→4)** and **α (1→6).**
- It presents as **amylose** and **amylopectin.**
- The most usual conformation of amylose is a helix with 6 residues per turn.



- Iodine molecules can fit inside the helix to from a starch-iodine complex which has a dark blue color.

- Both plants and animal contain enzymes that hydrolyze starch (α and β amylase).
- The two enzymes attack α (1→4) glycosidic linkage.
- The ***β-amylase*** is an exoglycosidase that cleave from the non reducing end of the polymer to produce maltose.
- The ***α amylase*** is an endoglycosidase which break the α(1→4) anywhere to produce glucose and maltose.

Amylose	amylopectin
Amylose is a linear polymer with all glucose linked by α(1→4)	Amylopectine is a branched chain polymer
	the branches starting at α(1→6) linkage along the chain of α(1→4)
	The branchs occur at every 25 residues.
Can be completely degraded to glucose and maltose by amylase	Need debranching enzymes to break the α (1→6) linkage.

Glycogen:

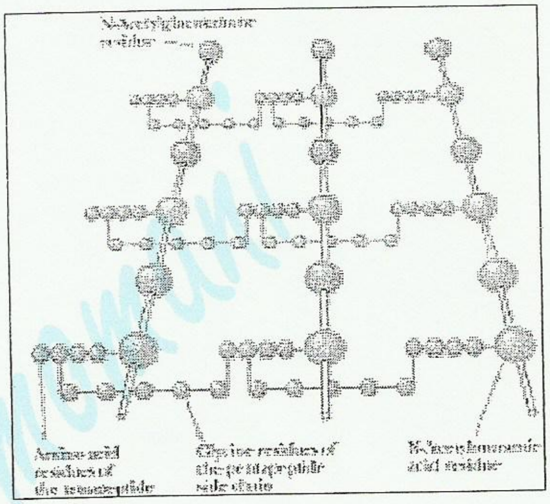
- It is the storage carbohydrates in animal mainly in liver and muscle.
- It is a branched chains polymer of **α-D-glucose**, linked by **α (1→4)**, and **α (1→6)**.
- The main difference between glycogen and amylopectin that the glycogen is **more highly branched.**
- The branch point occur every 10 residues.
- The average chain length is 13 glucose residues.
- In the center of every glycogen there is a protein called **glycogenin.**
- Glycogen is hydrolysed by **debranching** enzymes and by ***glycogen phosphorylase.***
- Glycogen phosphorylase cleaves one glucose at a time from the nonreducing end of a branch to produce glucose -1- phosphate.
- **Glycogen storage disease: caused by lower than normal levels of branching enzymes**; so less branched glycogen become less water soluble and formed into crystals that deposit in liver and muscle.

Chitin:

- It is polysaccharides that is similar to cellulose in both structure and function.
- It is linear polysaccharides, with linkage of β (1→4).
- The monomer is N-acyetyl-β-D-glucosamine.
- It is the major structural component of exoskeleton of the insects.

☒ The role of polysaccharides in the structure of cell wall

Bacterial cell wall:



- Consist of heteropolysaccharides cross-linked by peptides (**peptidoglycan**).
- The repeating unit of the polysaccharides consists of two residues held together by β (1→4).
- The two monomers are **N-acetyl-D-glucosamine**, the other is **N-acetylmuramic acid**.
- The cell wall of bacteria cross-linked by small peptides.
- The best example is ***staphylococcus aureus*** cell wall.
- The tetramer of 4 amino acids (Ala- Gln- Lys- Ala) are linked to N-acetylmuramic acid.
- The tetrapeptides itself are cross-linked by another pentapeptides (five glycine).
- **Peptidoglycan** is both the carbohydrate and the peptide component.

Plant cell wall:

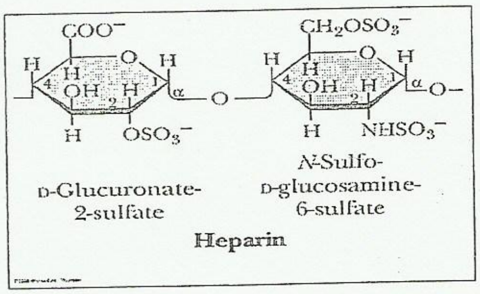
- Consists mainly of cellulose.
- Other important polysaccharides component is **pectin,** polymer made of D-galacturonic acid. It is extracted from plants to be used in the food-processing industry as a gelling agent in yogurt, fruit preserves, jams and jellies.
- **lignin** is a nonpolysaccharide component in the plant cell walls, a polymer of coniferyl alcohol a very tough and durable material.

☒ Glycosaminoglycans:

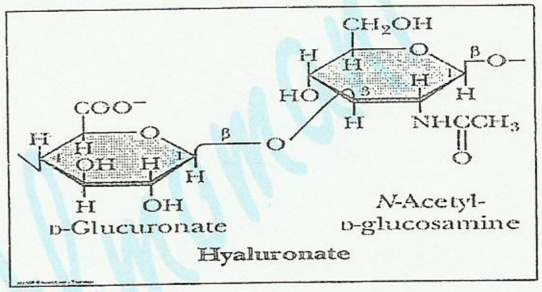
They are type of polysaccharide based on a repeating disaccharide in which one of the sugar is an amino sugar and at least one of them has a negative charge (sulphate group, carboxyl group).

There are many examples of these compounds:

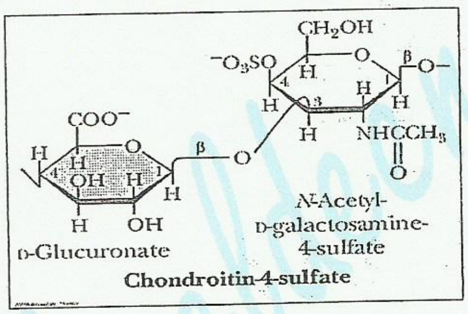
- Heparin ⇒ natural anticoagulant that prevent blood clots.
- Hyaluronic acid ⇒ present in eye as component of vitreous humor and in lubricating fluid of joints.
- Chondroitin sulfate and keratan sulphate ⇒ present in connective tissue.
- The following figures represent the repeated disaccharides in the most common glycosaminoglycans.



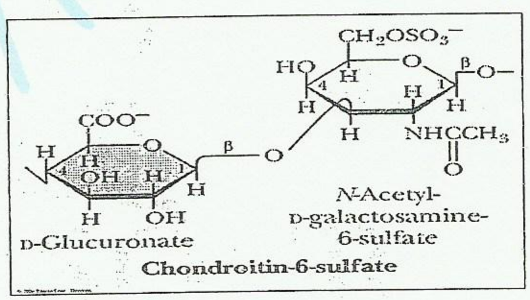
Heparin



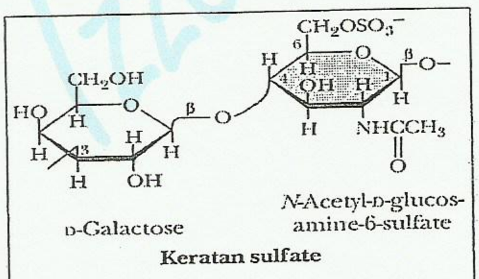
Hyaluronate



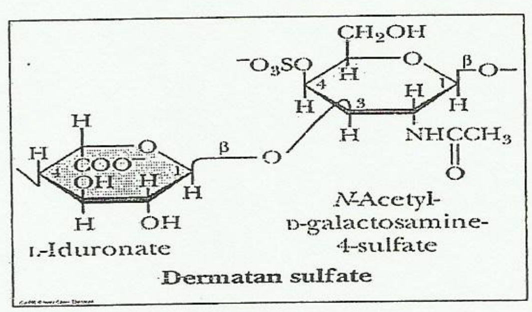
Chondroitin-4-sulfate



Chondroitin-6-sulfate



Keratan sulfate



Dermatan sulfate

What are glycoproteins?

- They are proteins with covalently attached sugar (carbohydrates)
- They occur mostly in eukaryotic cells.
- Almost all secreted and membrane associated proteins are glycoproteins
- Some involved in immunity (antibody as example).

- Also play a key role in **antigenic determinants**. (Human blood group, A, B, AB, O). in antigenic determinants like that presented at the surface of RBCs. All blood groups contains sugar L-fucose.

A ⇒ N-Acetylgalactosamine
B ⇒ α-D-galactose
AB ⇒ both of them
O ⇒ neither of them.

- The glycoprotein with high carbohydrate content (85-95%) called protoglycan.

- **Hurlur`s syndrome**, result from lack of Lysosomal enzymes that hydrolyzed the protoglycan leading to accumulation of them and cause skeletal deformities, severe mental retardation and death in childhood.

Questions:

1- Which of the following is a ketone sugar?
- a- galactose
- b-fructose
- c- glucose
- d-mannose

2- Carbohydrate containing α (1-4) glycosidic bond:
- a- amylose
- b- sucrose
- c- maltose
- d- lactose

3- Lactose is a dimer of :
- a-glucose
- b-fructose
- c-galactose
- d- a and c

4- In carbohydrates which is true:
- a-Glucose and fructose are epimers
- b-Most sugers in the human body are in the L form
- c-α glucose and β galactose are epimers
- d-furanose ring is planar

5- Which of the following is considered as heteropolyscharides
- a- Amylopectin
- b- Bacterial cell wall
- c- Chitin
- d- Glycogen
- e- Cellulose

6- The glycosaminoglycan that contains an α(1→4) linkage is:
- a- chondroitin sulfate
- b- dermatan sulfate
- c- heparin
- d- kertan sulfate

7- Which is a difference between maltose and cellobiose?
- a- One is the repeating unit in cellulose and the other in starch.
- b- One is linear and the other is branched.
- c- The glycosidic bond configuration is different
- d- The subunit sugars are not glucose for both.

8- Reaction of aldehyde with alcohol produces
- a- Hemiketal
- b- Hemiacetal
- c- carboxylic acid
- d- full ketal

Solutions

Q#	Answers
1	B- Fructose
2	C - maltose
3	D- a and c
4	D-furanose ring is planar
5	B- bacterial cell wall
6	C- heparin
7	C- The glycosidic bond configuration is different
8	B- Hemiacetal