Lecture : 11

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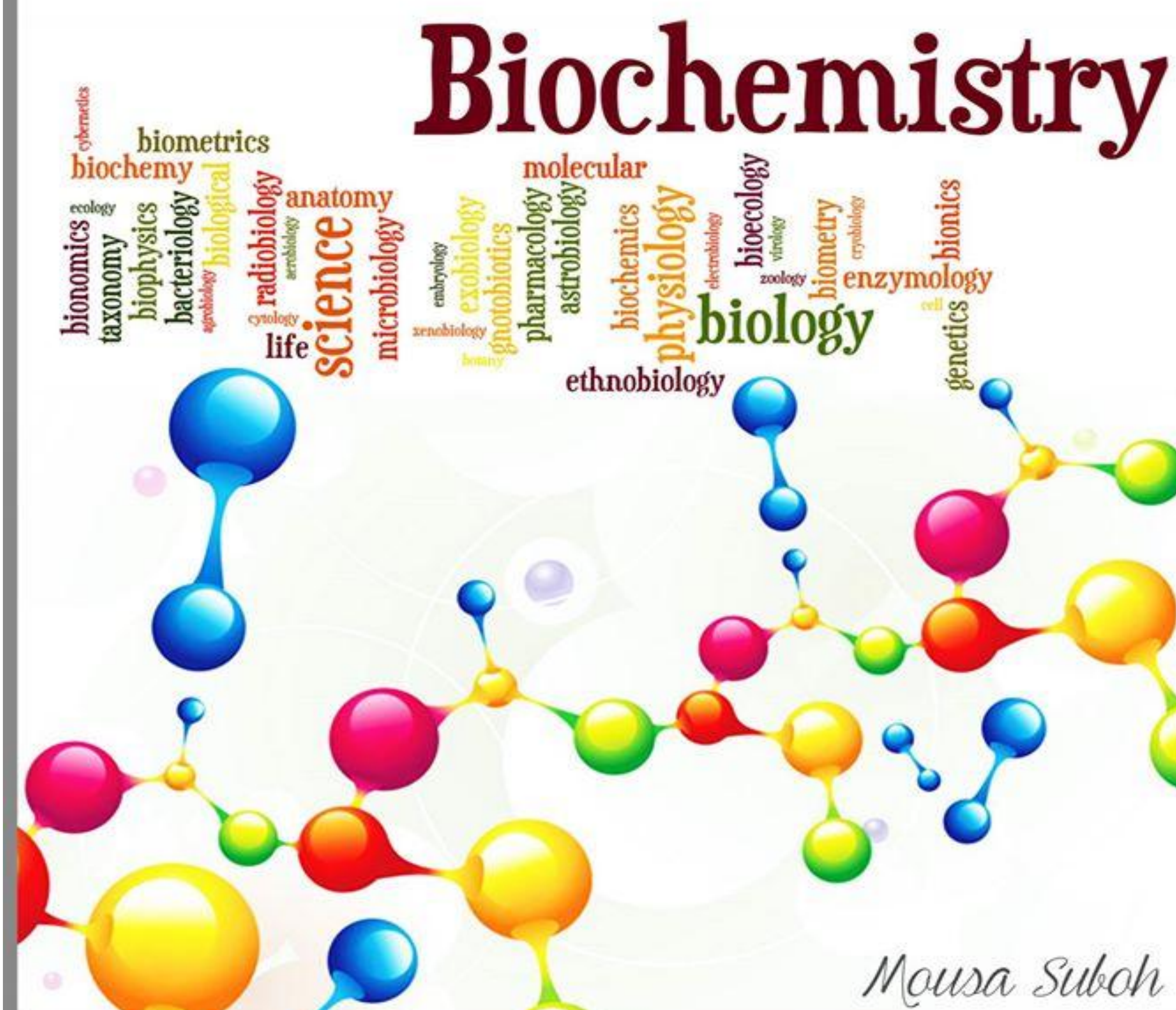
☐ Slide ■ Sheet

Medical Committee
The University of Jordan



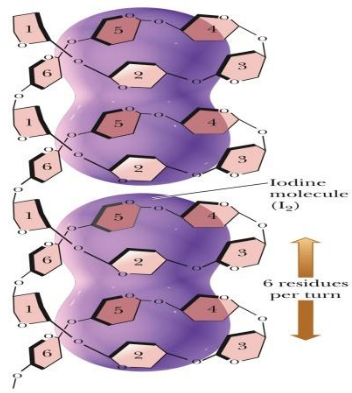
Polysaccharides

Today we're going to complete talking about carbohydrates ..

- Iodine : they use it to test the presence of carbohydrates and if you want to know how much do you have carbohydrates.

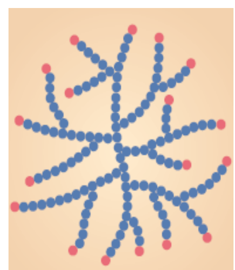
The shape of amylose is spiral with each turn you have 6 monosaccharides, every 6 turns (36 glycosyl residues) you will be able to bind the iodine and test for the presence of carbohydrates.

From knowing much iodine binds with the sample of carbohydrates, we will know the concentration of carbohydrates we have (Every 6 molecules will bind with one iodine molecule).

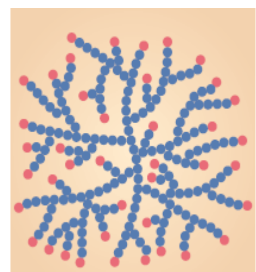


Glycogen: How glycogen is different from starch other than that Glycogen is for animals and starch is for plants?

Glycogen is more highly branched compared to amylopectin in starch. Why as humans would not we have starch instead of glycogen? Would it do the job since it's not as branched as glycogen?



Amylopectin



Glycogen

We as humans we need to move fast suddenly, so we need energy to be immediately elaborated and that needs need a really soluble molecule in water and a molecule that can be hydrolyzed easily; hydrolysis occurs through enzymes, enzymes should work on the small points. so the more small points in the molecule you have to work on the more hydrolysis you achieve.

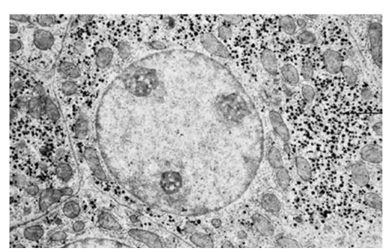
So this is why they differ in branching and this is how it allows enzymes to work on branches.

- Consists of a chain of α(1 → 4) linkages with α(1 → 6) linkages exactly like amylopectin.

The average chain length is 13 glucose residues and branches occur every turn.

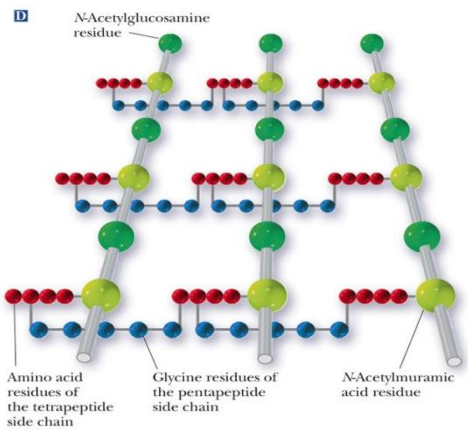
At the heart of every glycogen molecule is a protein named Glycogenin.

glycogen Found in animal cells in granules; if you look at the animal cells you will see these granules as the figure beside. It is found in liver and muscle cells and the amount of glycogen in the whole body is not so large.



- How much glycogen do we have for an adult (70 kg - person)? how much do we store in liver and muscles?

90 grams of glycogen is stored in the liver and that’s not a big quantity.

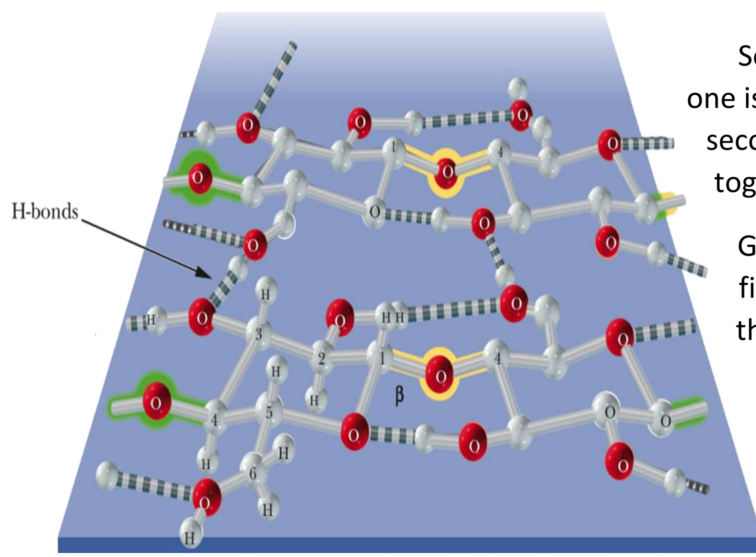


Chitin is the major structural component of the exoskeletons of invertebrates, such as insects, composed of monosaccharide of N-acetyl-β-D-glucosamine (two carbon units attached to Nitrogen which is attached to glucose) joined by β-1,4-glycosidic bonds.

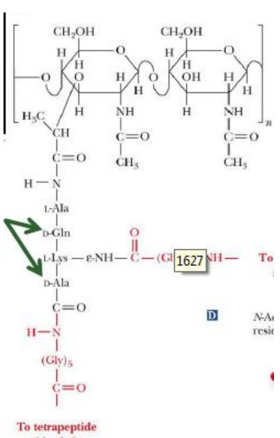
So the function of the chitin is for structural purposes so it should be from the beta type not the alpha, joined through 1-4 carbons so it’s β-1,4-glycosidic bonds.

Bacterial cell walls: repeated disaccharides that consist of two amine sugars; NAM-NAG joined by β-1,4-glycosidic bonds – murmaric acid is similar to glucosamine,but there’s a lactate added on carbon number 3.

*They’re highly cross linked. it’s linked to amino acids, NAM is attached to 4 residues of amino acids, those amino acids are attached and also cross linked between each others. So we have two types of cross cross linking; the first one is which cross links NAM to the amino acids, the second one is which crosses these tetrapeptides together.



There are four amino acids (tetrapeptides): Ala-Gln-Lys-Ala attached to NAM, then a pentapeptide of five Glycine residues attaches these tetrapeptides together.



“The cross linked material of all is named a proteoglycans”

*The amino acids with arrows pointing on them are D-amino acids.

We as humans we don’t posses D-amino acids to be engaged in proteins synthesis. All amino acids are of the L side, we can have them from bacteria or plants but we can't synthesisi them

Glycosaminoglycans

Polysaccharides based on a repeating disaccharide where one of the monomers is an amino sugar (we have a modification on nitrogen in the monosaccahride) and the other has a negative charge due to a sulfate or carboxylate group.

Kinds :

- ✓ Heparin: natural anticoagulant
- ✓ Hyaluronic acid: a component of the vitreous humor of the eye and the lubricating fluid of joints.
- ✓ Chondroitin sulfate and keratan sulfate: components of connective tissue

*All of them should have one residue with amino group and another onw with negative charge.

Sometimes the negative charged residue may have two negative charges, or the one with the amino group may have a negative charge but at least one has an amino group and another one with a negative charge, more things are welcomed.

GAG	Localization	Comments
Hyaluronate	*synovial fluid, vitreous humor,* ECM of loose connective tissue	*the lubricant fluid , shock absorbing* As many as 25,000 disaccharide units
Chondroitin sulfate	*cartilage, bone*, heart valves	*most abundant GAG*
Heparan sulfate	*basement membranes*, components of cell surfaces	contains higher acetylated glucosamine than heparin
Heparin	component of *intracellular granules of mast cells* lining the arteries of the lungs, liver and skin	*A natural anticoagulant*
Dermatan sulfate	*skin, blood vessels*, heart valves	
Keratan sulfate	*cornea, bone, cartilage*	

	aggregated with chondroitin sulfates	

Glycoproteins : Contain carbohydrate units covalently bonded to a polypeptide chain.

Why do we need to attach carbohydrates to proteins?? Cell signal, because carbohydrates work like antigens determining which protein is this .

**one example is the Blood group substances >>ex : o antegin ,,,proteins in the cell membrane ,of red blood cells , are attached to lipids (sphigosine and fatty acids) which is attached to oligosaccharide (glc, gal, galNac ,gal, fuc).

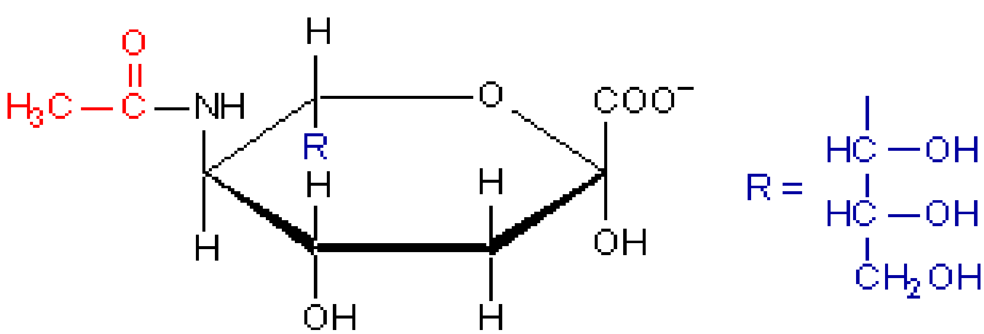
**remember : fue : reduced form of galactose (removed Oxygen)
If A antegin: he will have an extra monosaccharide "galNac" attached to "gal" in the oligosaccharide If B antigen he will have an extra "gal" attached o the original "gal" in the oligoasacride.

If AB antigen, he will have some glycoproteins like those of A antigen and others of B antegin "mixed antigens ".

Sialic Acid

It's the N-acetylneuraminate, (*N*-acetylneuraminic acid, also called sialic acid) is derived from the amino sugar, neuraminic acid.

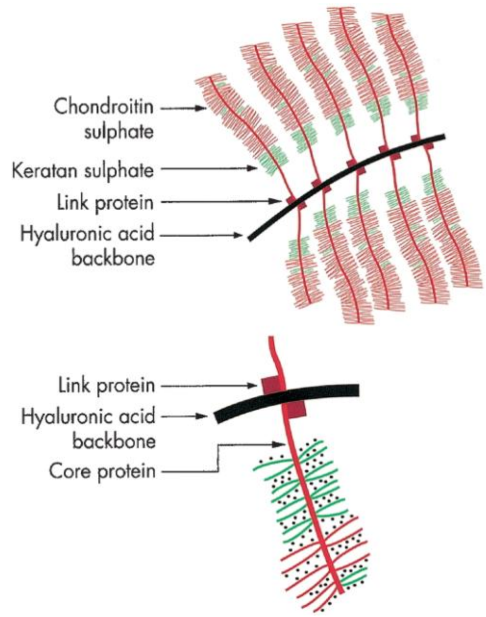
it is often found as a terminal residue of oligosaccharide chains of glycoproteins -(it's massive with an extra –ve charge (look at the image)) giving glycoproteins negative charge and making it work soluble and highly charged .



N-acetylneuraminate (sialic acid)

Proteoglycans

- **Lubricants**
- **Structural components in connective tissue**
- **Mediate adhesion of cells to the extracellular matrix**
- **Bind factors that stimulate cell proliferation**



Revision

The doctor was giving notes about the main concepts in carbohydrates:

- ✓ Always expect any example on carbohydrates, that you will be asked about monomers

You will be given structures and identify them (enantiomers, diasteriomers, epimers...).

- ✓ Any exam about carbohydrates you will get a question about isomerization process and to identify it.
- ✓ Any molecule that you will be given you should be able to identify which carbons are chiral and how will we know which carbon is chiral? $ different groups attached to it.
- ✓ How many stereoisomers? According to the general rule 2^n
- ✓ Expect a question on certain chemical structure related to carbohydrates and to identify how many chiral centers and stereoisomers.
- ✓ HYDROLYISIS VS. CONDENSATION reactions.
- ✓ Carbohydrates are ketoses and aldoses, functions of them.
- ✓ Oligosaccharides
- ✓ Nature of bonds of carbohydrates
- ✓ Classification
- ✓ Common monosaccharides. We talked about carbohydrates in general you know the classification of ten either according to the number of carbons: trioses, tetroses, pentoses and hexoses or according to the functional group.
- ✓ You should memorize trioses which they are:

3 carbon units: **gyceraldehyde** and **manoaldehyde** (if there're D and L).

Dihydroxyacetone is very important in biochemistry we will talk about it more in the next semester and in lipids.

Tetroses : we took **threose** and **erythrose**.

Pentoses : the most common one is **ribose** (RNA and DNA).

Hexoses : **mannose, fructose, glucose and galactose.**

- ✓ You should be familiar and you should be able to recognize the structure of all monosaccharides especially hexoses
.
- ✓ Hexoses :
- Either aliphatic or cyclic.
- Either Fischer projection or Haworth projection, you should be able to identify them.

- ✓ Expect a question as simple as it is: 2 2 2 monosaccharides linked together, identify them.
- ✓ Always remember monosaccharides can differ at their anomeric carbon; OH can be up or can be down and this is what makes them alpha or beta. However, the other OHs can't be different if it's up it's up it can't be down so there are only difference at the anomeric carbon.

- ✓ Galactose is epimer for glucose at carbon number 4.
- ✓ Mannose is an epimer of glucose at carbon number 2.
- ✓ Always when you see a hexagonal ring you directly check OHs on carbon number 2 and 4 so you can decide how they are in relation to glucose.
- ✓ You should be familiar with the structures. They're the key for many questions like: What type of bonds? Which carbon units are there? If you can't identify structures you can't identify which ones are there and if it's alpha or beta? Cis or Trans?

- ✓ Fischer projection: according to it how can I know which one is D and which one is L? I look at the last chiral center (the penultimate carbon).
- ✓ Trioses, tetroses, pentoses, hexoses, glucose isomers are important.

- ✓ Cyclization of sugars : it makes a ring called hemiacetal.

Why hemiacetal? Because the difference between full acetal and hemiacetal that the carbon has an ether bond and a hydroxyl group this is a hemiacetal while 2 ether bonds around the carbon, this is a full acetal.

When I make a ring the anomeric carbon has an OH and also in the other side it's linked to OR (ether bond) so it's hemiacetal.

- ✓ When do l make a full acetal? I have an OH when do I remove the H and link the O with other structure? When I make glycosidic linkages, I link the monosaccharides together (alpha 1,4 and alpha 1,6).

- ✓ Full acetal formation is the basis behind forming polysaccharides and oligosaccharides .

- ✓ Fructose can have a six-memebred ring? Yes
- ✓ Oxidation dehydration reactions on monosaccharides.

When oxidation happen it turns into () and if there's oxidation reaction they should be reducing sugars and all monosaccharides are reducing and all disaccharides are reducing except for sucrose and trehalose, the anomeric carbon is free for oxidation.

- ✓ Polysaccharides are reducing and not at the same time. they are reducing however, chemical wise there's a bond which can be oxidized, the last monosaccharide in the chain has an anomeric carbon and all bonds in polysaccharide are either alpha 1,4 or 1,6 so carbon number 1 from the next monosaccharide is always free (the very first one) so they are reducing. However, we can't detect them so all in all they are not reducing sugars. Chemical wise they can be oxidized but because of the large number monosaccharides involved the lower percentage of reducing monosaccharides vs. non reducing ones makes them non reducing.

Good Luck ☺