



University of Jordan
Faculty of Medicine



Medical Committee
The University of Jordan

Introduction to
BIOCHEMISTRY

Lecture #: (.....3.....)



Sheet



Slides



Other

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Date: June - 23th - 2013.....

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Price:

Carbohydrates, last lecture

-A question of a classmate: how can we differentiate between L and D in cyclic monosaccharides?

The answer is that we define D and L by the last chiral carbon (the first carbon we start with in numbering is the most oxidized), in hexoses for example no. 1 is “-CHO” and no. 5 is the last chiral one. Now in the cyclic form the oxygen in “-OH” of carbon no. 5 is already engaged in the ring, so we can't know it. However, all cyclic monosaccharides we talk about are D sugars for they are the common in nature.

Oligosaccharides

These polymers contain few monosaccharides linked together. A good example is **Raffinose** which is composed of 3 monosaccharides; galactose, fructose, and glucose. This can be found in peas and beans. Oligosaccharides also include **streptomycin** (3 monosaccharide connected to special amino groups- an antibiotic drug for bacteria infections), **doxorubicin** (a monosaccharide connected to a large cyclic ring - anticancer generally for breast), **erythromycin A** (2 monosaccharides connected separately to a large cyclic ring), **digoxin** (3 monosaccharides connected to a cyclic ring -used to treat heart failure), and others.

Polysaccharides

They are either **homopolysaccharides** that are composed of one type of monosaccharides and they are most common in nature, or **heteropolysaccharides** that are of more than one type. Usually heteropolysaccharides are repetitive disaccharide-units. A lot of glucose is found in disaccharides and polysaccharides.

Know that: β - glycosidic linkages in general are tough and hard so wherever we see them we expect the structural role out this polysaccharide. α -linkages are more resilient; providing free movement so these are for storage purposes.

So polysaccharides function as structural materials such as cellulose and chitin. And they also serve as carbohydrate storage polymers such as starch in plants and glycogen in animals.

- *Cellulose:*

It's the basic building block of plants especially wood and fibers. It's a unbranched linear polymer produced by β -1,4-glycosidic bonding of approximately 2800 D-glucose units. Intra and intermolecular hydrogen bondings between cellulose chains give them stability and strength. Although humans ingest cellulose, they lack the enzymes that digest it. Recall that in cows for example some bacteria in their intestines are producing cellulase that is responsible for cellulose breaking down.

- *Starch*

It's an energy store in plants. It consists of α -D-glucose units. Starch contains two types of molecules:

1. Amylose: unbranched continuous chain made up of 4000 α -D-glucose units that are joined by α -1,4-glycosidic bonds.
2. Amylopectin: a highly branched polymer in which 24 to 30 D-glucose units are joined by α -1,4-glycosidic bonds, and branches are linked with α -1,6-glycosidic bonds.

Starch is broken down to monomers by two types of enzymes: **amylases** that catalyse the hydrolysis α -1,4-glycosidic bonds, and **debranching enzymes** that catalyse the hydrolysis of α -1,6-glycosidic bonds. Amylase can be either **β -amylase** that works from the non-reducing end (exoglycosidase: attacks the starch molecule from its non reducing end by chopping the last monosaccharide), or **α -amylase** that catalyses the hydrolysis of glycosidic linkage within the chain producing glucose and maltose (endoglycosidase: it cuts in between D-glucose units).

Question: will we have a full degradation of amylose and amylopectin if we put them in a mixture of **α -amylase** and **β -amylase**?

amylase will have complete degradation because amylases work on α -1,4-glycosidic bonds, but amylopectin won't ; because of the branching (α -1,6-glycosidic bonds) and breaking these bonds is the role of debranching enzymes.

Iodine test is used to check if the sample contains starch or doesn't. Amylose is found in helical chain with six glycosyl residues per turn. When iodine molecules are fit in the axis of six turns of the helix (36 residues,) the formed complex is responsible for the blue color.

- *Glycogen*

It's a branched polysaccharide of α -D-glucose molecules (a branch each 10 glucoses) so it's much more branched than amylopectin (where one branch each 25 glucoses). $\alpha(1\rightarrow4)$ linkages are within the same chain and Branches are linked to the chains $\alpha(1\rightarrow6)$ linkages. A protein called **glycogenin** is needed to initiate the synthesis of glycogen, an amino acid (tyrosine) in its structure makes it as starting point where further glucose molecules are added.

Glycogen granules are found in liver and skeletal muscle cells, rarely excess quantities in blood are then stored in other cell types.

Multiple enzymes can break glycogen: **glycogen phosphorylase** which chops the first glucose molecule from the nonreducing end and adds a phosphate group on order not to go back to glycogen. And **debranching enzymes** also here catalyse the hydrolysis of α -1,6-glycosidic bonds.

Glycogen is more branched than any other polysaccharide, this adds some properties such as higher water solubility (since it's less ordered and higher surface area so higher H-bonding and thus higher solubility), also higher potential targets for enzymes (more heads to bind during random collision so more availability of glycogen for the enzyme and faster binding in animals). Remember the doctor's term for branching: "3afshaga".

- *Chitin*

Naturally this polysaccharide is found in cell walls of algae, fungi, and yeast. Also It's the major component of the exoskeletons of invertebrates like insects, So since it has a major role in stability it must have β linkages! It's a chain of N-acetyl- β -D-glucosamine (glucose with nitrogen and acetate group) linked with β -1,4-glycosidic bonds.

- *Bacterial cell walls*

In prokaryotic cell walls there are polysaccharides that play a structural role. They are formed of repetitive 2 monosaccharides "N-acetylmuramic acid and N-acetylglucosamine" disaccharide-units through β -1,4-glycosidic bonds. N-acetylmuramic acid is modified, there are four amino acids (alanine, glutamine, lysine, and alanine) glycine residues connect alanine and lysine of different NAM molecules and this gives strength to the bacterial cell wall.

- *Glycosaminoglycans*

They are polysaccharides that are formed of repeating disaccharides. One of the disaccharides is modified by an amino group (a nitrogen atom replaces a hydrogen one). The other monosaccharide is modified by having a negatively charged group either a sulfate or carboxylate one. Examples on them are in the table go there and while reading:

- Hyaluronate= hyaluronic acid, it's mainly found in joints.
- Synovial fluid: fluid found in joints (السائل الزليلي)
 - Vitreous humor of the eye: the clear gel that fills the space between the lens and the retina of the eyeball.
- "chondro-": cartilage, "derm-": skin
- In allergy and inflammation the person looks flushing because heparin (by mast cells) prevents clotting of blood.

Glycoproteins

They are proteins that are connected to carbohydrates. Good examples are antibodies and those on the cell membrane of red blood cells. The oligosaccharide part is an antigenic determinant and this is the case of grouping blood in ABO system. The RB cell's membrane's protein is connected to a fatty acid and to an oligosaccharide (composed of glucose, galactose, *N*-Acetylglucosamine, galactose and then fucose). Now if the structure of the oligosaccharide isn't modified blood is of **type O**, if extra *N*-Acetylglucosamine is added to the galactose blood is of **type A**, if extra galactose is added to the galactose blood is of **type B**, and if both antigenic determinants are on the protein then blood's type will be **AB**.

Sialic acid

it's a modified monosaccharide. It's found mainly in the oligosaccharides of the glycoproteins, adding one negative charge which changes their properties.

And finally, proteoglycans

They are glycoproteins however they are heavily glycosylated (much more carbohydrate contact). They work as lubricants because high H-bonding between carbohydrates means high viscosity, proteoglycans on cell membranes are responsible of adhesion with the extracellular matrix. **All the best**