Lecture : # 10 - sections 1 , 2 , 3

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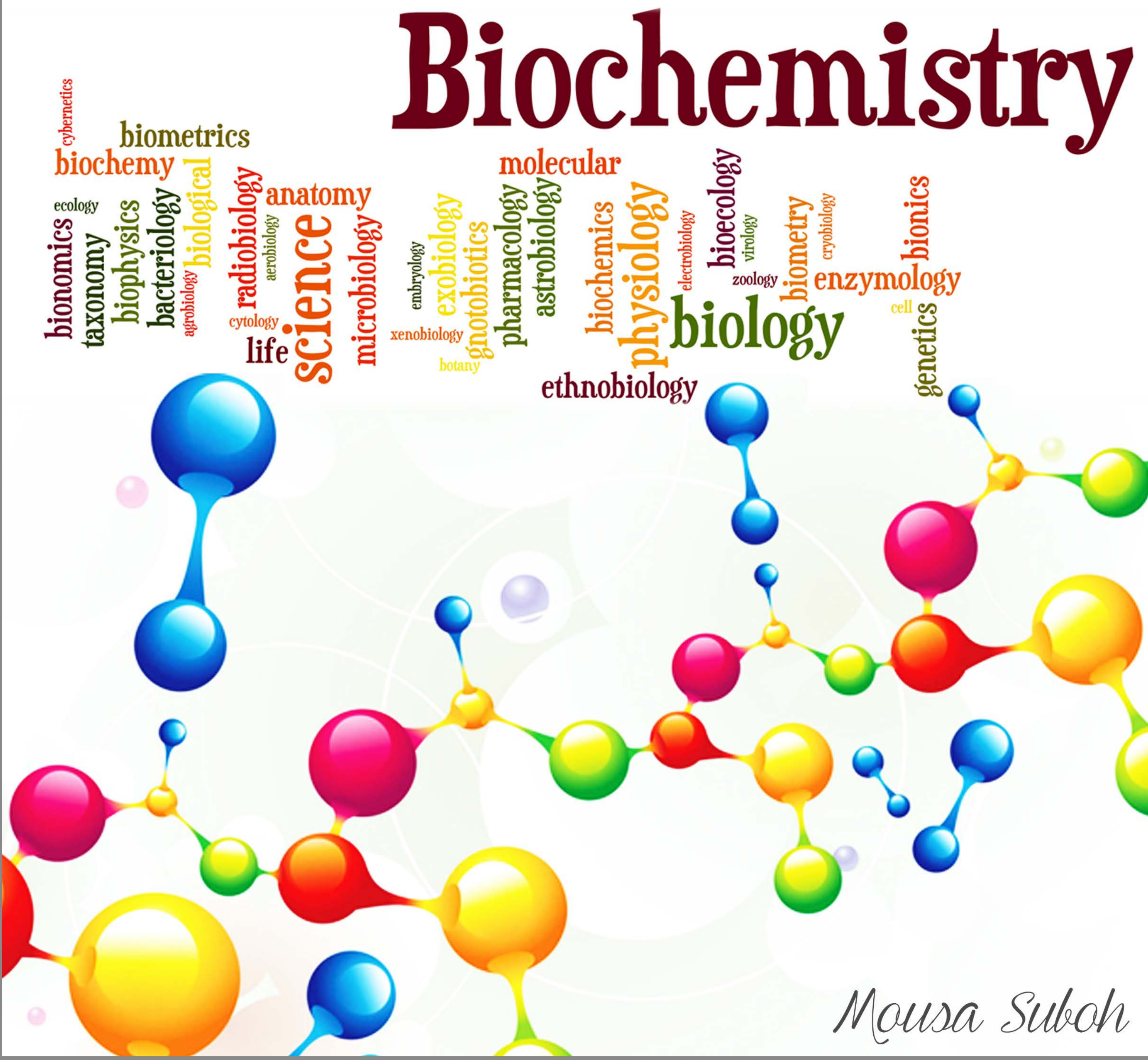
☐ Slide ■ Sheet

Medical Committee
The University of Jordan



Carbohydrates **2**

<u>A study Guide:</u> Kindly,refer to the slide number,look at the structures and read the sheet notes well ,most of the slides content besides all what the doctor said are mentioned here,good luck ☺…..

Revision:

last time we talked about sugars, definition of them, different terms; isomers, stereoisomers, constitutional isomers and enantiomers.

What are enantiomers?

When 2 molecules are mirror images of each other and are not superimposable

why are enantiomers not superimposable ?

Because of the presence of chiral carbons

Which A.A doesn't have an enantiomer ?

Glycine , because the central carbon is achiral

we talked about diastereomers and epimers

What are epimers?

diastereomers that differ in the orientation of the hydroxyl group of just one carbon

Then we talked about the formation of ring structure. We talked about the formation of pyranose (6- membered ring) and furanose (5- membered ring) .

Which one is more stable (pyranose or furanose) ?

Pyranose because the ring is (mb7b7) :D :D >> (the valences are not overlapping)

and we talked about anomers and the anomeric carbons.

What is the anomeric carbon?

The carbon that was either the aldehyde or ketone group. For glucose, it's carbon no.1 and for fructose, it's carbon no.2. and we said that we have 2 anomers, alpha or beta anomers.

What is the difference between alpha anomer and beta anomer?

The orientation or the position of the hydroxyl group in relation to the ring. If it's above the ring then it's beta and if it's below the ring then it's alpha

What is muta-rotation (muta comes from "mutation" so you have difference (a change) in the chain basically) ?

muta- rotation is the process of flipping the hydroxyl group between alpha and beta.

For glucose, you have alpha and beta glucose by looking to carbon no.1 and the same thing for fructose but by looking to carbon no.2.

we can differentiate between glucose and other aldohexoses by looking at carbon no.6 (being out of the ring)

we can tell that this is fructose by having both groups (carbon no.1 and 6) outside the ring .
<u>Remember</u>: All sugars are in the D orientation . **Can you find sugars in L orientation?** Yes, but mainly in D orientation. You can tell if it's D or L by looking to carbon no.6. but we don't care about this a lot because naturally, all sugars are in the D configuration.

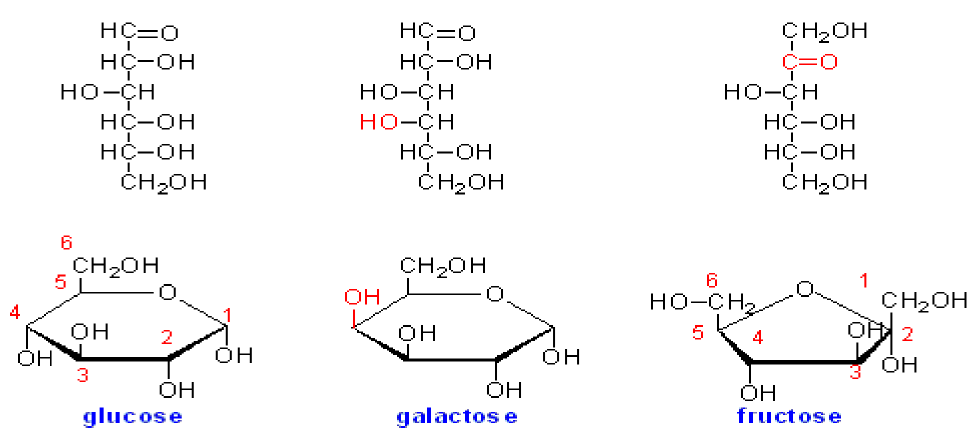
This lecture is based on the slides (25-45)

Slide no.25
you can see the ring structure in Fischer projection. Also, you can see the chain structure of glucose (in the middle) then carbon no.1 reacts with carbon no.5 forming pyranose.

Slide no.26
How can you tell by looking to a certain hydroxyl group in a sugar whether it's below or above the ring?
Simply, if it's (OH group) to the right, then it's below the ring. If it's to the left, it's above the ring. So you can determine the configuration of a sugar molecule like glucose for example by looking to carbon no.1 and determine if the hydroxyl group is to right or to the left.
Look at glucose on the left. **<u>look at carbon no.3, the hydroxyl group is to the left in the chain structure so, it's above the ring as you can see and if it's to the right then it's below the ring.</u>**

What is the structural relationship between glucose and galactose?
Epimers at carbon no.4 (for glucose, it's to the right (so, below the ring) and for galactose, it's to the left (so, above the ring). So you can differentiate between glucose and galactose by looking to the orientation of the hydroxyl group at carbon no.4

what is the structural relationship between glucose and <u>manose</u>?
Epimers at carbon no.2 (for glucose, it's below the ring and <u>for manose</u> it's above the ring)



Slide no.27

These are some of common pyranoses (forget about the last (one) For glucopyranose … it's alpha (look at carbon no.1

Again, the difference between glucose and galactose is at carbon no.4 and the difference between glucose and manose is at carbon no.2

What is the structural relationship between galactose ana manose?
Diastereomers

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Slide no.28
you need to know the structure of furanoses.
You can see the chain and the ring structures. At ring structure, you can have muta-rotation so you are going to have (alpha or beta) ribofuranose.

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Slide no.30
sugars can be involved in many rxns and we will move through these important rxns and their products.
One of them is Oxidation. Sugars can undergo oxidation because all monosaccharides are reducing sugars.

How can any sugar be a reducing sugar?
Any sugar that has at least one free anomeric carbon that's not involved in a covalent bond is a reducing sugar.

Again, what's the anomeric carbon?
It's the carbon that was the aldehyde or ketone group and undergoes muta-rotation of the hydroxyl group (above or below the ring). For glucose, it's carbon no.1

Now, when an aldehyde or alcohol group is oxidized, then you'll have the formation of a carboxylic group.
Look at the oxidized glucose molecules. Notice that when carbon no.1 is oxidized, the ringopens up forming a chain structure and not ring structure. But the same **is not true** for the oxidation of carbon no.6, it's still a ring.

Oxidized glucose at carbon no.6 is known as **glucuronate**. And oxidized glucose at carbon no.1 is known as gluconate (gluconic acid).

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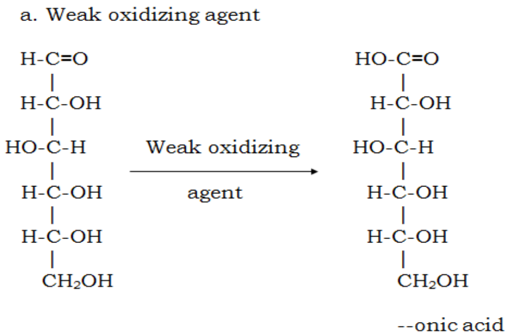
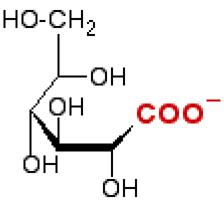
Slide no.31

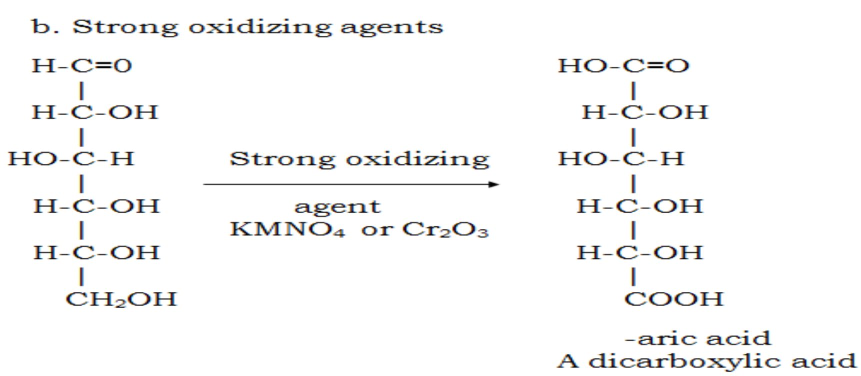
if sugars are oxidized weekly by a week oxidizing agent then the aldehyde group will be oxidized to a carboxylic group forming glucuonate (chain structure)





D-gluconate
(D-gluconic acid, GlcA)
from **oxidation of glucose C1 aldehyde)**

Slide no.32 and 33
if the sugars are oxidized strongly be a strong oxidizing agent then both aldehyde and alcohol groups will be oxidized (carbon no.1 and 6). As in slide 32, oxidation of carbon no.1 and 6 will form a galactaric acid. **As in slide 33, oxidation of carbon no.6 can occur only enzymatically (non-spontaneous).**

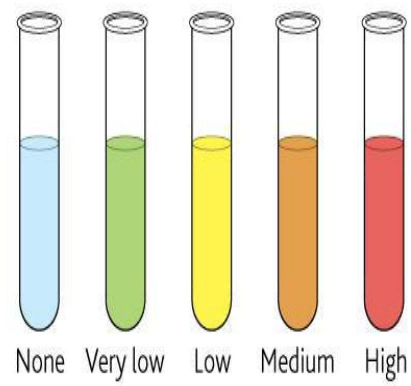


Slide no.34
there is NO OXIDATION for ketone group. So, NO direct oxidation for ketoses. But they can be oxidized indirectly, **how?**
ketose is converted into and aldose, so aldose can be oxidized directly. So, fructose cannot be oxidized directly but it can be oxidized if it's converted into glucose, glucose can be oxidized.

What's the structural relationship between glucose and fructose?
Constitutional isomers (same no. of atoms "C,H,O" but different bond connections).

Slide no.35
there are some tests that can tell if a sample contains a reducing sugar or not (reducing sugar

has a free anomeric carbon).
One of them is **Benedict's test**. In this slide a sample contains glucose (a reducing sugar). Glucose reacts with copper, copper is reduced forming copper oxide and glucose is oxidized forming gluconic acid.
You can determine the amount of reducing sugar the sample contains from the color that appears in the test tube. The more reducing sugar the more red color would appear. As you see in the test tubes, the red one contains more reducing sugar, the blue one has NO reducing sugars.
This test is used sometimes in labs to determine if a person is a diabetic or not. It's a very simple test.



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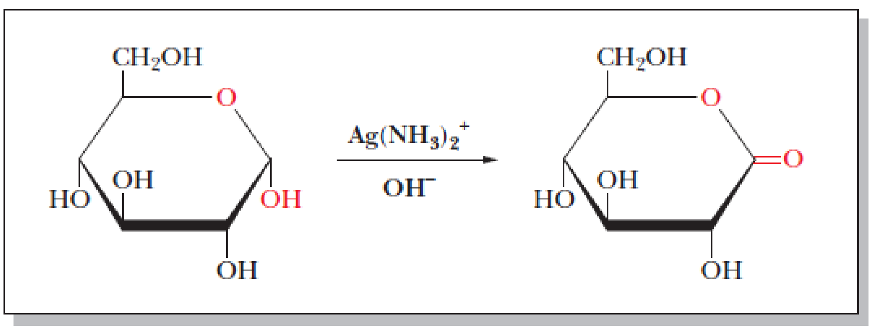
Slide no.36
there are two other tests. One of them is using silver ammonia complex. In this sample, glucose reacts with $Ag(NH_3)^{2+}$ forming Lactone which is a ketone sugar plus a silver product which covers the surface of the test tube.



Another test can be used. This test is enzymatic, so we have the sample and the enzyme glucose oxidase and basically it's a rxn that goes like A+B gives C+D. D can be involved in another rxn giving us another product and we are detecting this final product but we will not care about these details.

Vitamin C deficiency can cause scurvy. Vitamin C can be oxidized with time. So, fresh food has vitamin C, but if it stays for a long time exposed to air, vitamin C will be oxidized. The oxidized vitamin C is not efficient anymore in biological rxns.

Ascorbic acid is a lactone itself and it's unsaturated because of the double bond in its ring structure.

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Slide no.37

sugar samples can be also reduced. In this case, they are the oxidizing molecules.
Examples of reduced sugars include sorbose which is a ketose that can be reduced to sorbitol. Also, xylulose that can be reduced to xylitol.

Whenever you have reduction of an aldehyde, you have the formation of primary alcohol (hydroxyl group). If you have a reduction of a ketone, you will have the formation of secondary alcohol.
You can find sorbitol in the Gum " extra mathalan" because it's so sweet :D.

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Slide no.38
Sugars can be also reduced forming deoxy sugars by removing hydroxyl groups and replacing them with hydrogens.
In this slide, we have a ribose. Carbon no.2 can be reduced forming deoxyribose. Deoxyribose is the sugar that is involved in the formation of DNA. Ribose is involved in the formation of RNA.

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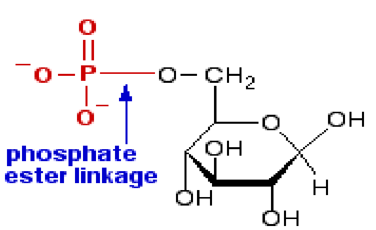
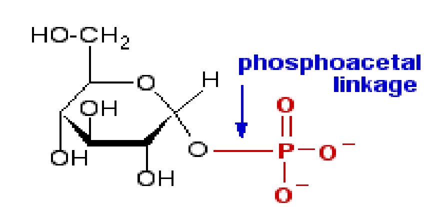
Slide no.39
Esterification is a very important rxn that occurs in the biological system. More specifically, phospho-esterification.
Formation of an ester group of transferring of a phosphate from ATP for example to another molecule, this process is called phosphorylation.
Whenever we have transfer of a phosphate group to a glucose for example, we have the formation of many products.
The esterification of carbon no.1 forms glucose-1-phosphate and the esterification of carbon no.6 forms glucose-6-phosphate.
glycolysis is the metabolism of glucose. The very first rxn involves phosphorylation of glucose



β-D-glucose-6-phosphate
(an ordinary phosphate ester)



α-D-glucose-1-phosphate
(a phosphoacetal)

and formation of glucose-6-phosphate.

Whenever you have a phoshphorylated molecule, this means nearly it is an active molecule. It contains high amount of energy. This is why the first rxn is the phosphorylation of glucose forming glucose-6-phosphate.
Starting from glucose since phosphate, you can go through multiple metabolic pathways. You have the formation of glycogen, the metabolism of glucose, the formation of 5 carbon riboses

and so on.

Slide no.40

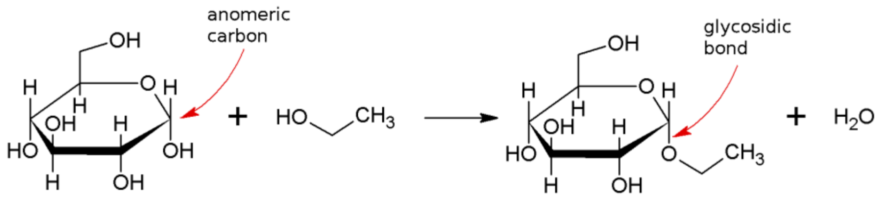
Now, we have a rxn between a sugar and alcohol, the R group of alcohol will be transferred to the anomeric carbon of the sugar forming a new product and the new bond is called glycosidic bond. **So, glycosidic bond is a feature of a rxn between an alcohol molecule with an anomeric carbon.**

In this case, you have the formation of O-glycoside. O-glycoside is the molecule where you have the attachment of R-group to the oxygen of the anomeric carbon.

Once you have the formation of O-glycoside, the ring cannot open up anymore, it's stable.

So, you have two kinds of rings. you have rings that open up forming a chain structure or rings that close down and it's an equilibrium in the ring structure.

Once you have any rxn that involves anomeric carbon then the ring cannot open up, it becomes very stable.This reaction is very important in forming disaccharide .



Slide no.41

we also have the formation of N-glycoside where you have the rxn with amino group . whenever the anomeric carbon is aminated ,again, the ring cannot open up. the bond is called N-glycosidic bond. It's a feature of many molecules such as ATP, ADP and (nucleotides).

Slide no.42

Amino sugars are different from N-glucosides. N-glycosides involve an anomeric carbon but amino sugars involve any other hydroxyl group at any carbon (1,2,3… whatever).

Examples of Amino sugars:

glucoseamine in which carbon no.2 is involved in the bond with the amino group. It can be further modified to N-acetyl-2-glucoseamine where a hydrogen is replaced by acetyl group. N-glucoseamine is used as a drug for knee pain for example because it's thought that it has a role in the formation in cartilage but It doesn't make sense. It's just a business.

Slide no.43

What are disaccharide? Oligosaccharides?

Disaccharides are molecules that are formed by conjugating (linking) two monosaccharides to each other.
we have oligosaccharide by linking 3-10 sugar molecules. If we have more than 10, then it's called polysaccharide.

Hetero- vs. homo-?
Oligosaccharides or even disaccharides can be hetero or homo depending on the sugar molecules. If they are identical then they are homo. If they are different then they are hetero.

What is the type of reaction?
Basically, it's a condensation rxn that involves anomeric carbon of at least one of the sugars.

What is a residue?
Each one of the sugars is known as a residue (like in peptides).
The formation of disaccharides is enzymatic (non-spontaneous). The enzyme is glycosyltransferases

Do they undergo muta-rotation? Are products stable?
Once you have the formation of disaccharides that involves anomeric carbons then these sugars cannot undergo muta-rotation. They are stable.

again, what is muta-rotation?
It's the flipping of the hydroxyl group of the anomeric carbon.

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slide no.44
when we look to a disaccharide or any oligosaccharide, you have to determine of many things:
1- the sugars that make up the disaccharide (glucose, galactose, mannose, fructose… etc.)
2- The stereoconfigurations (D or L)
3- carbons that are involved in the rxn (or in the glycosidic bond). Sometimes carbon no.1 with carbon no.2. Sometimes carbon no.1 with carbon no.4, whatever.
4- You have to order the sugars. So the sugar to the left is no.1 and the one to right is no.2.
5- Configuration of the anomeric carbon (alpha or beta)

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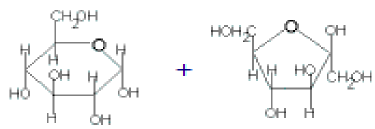
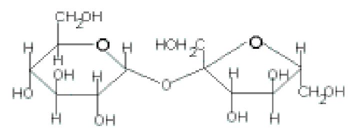
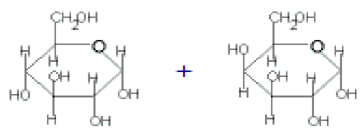
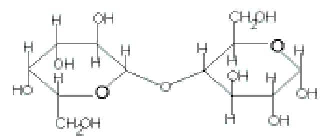
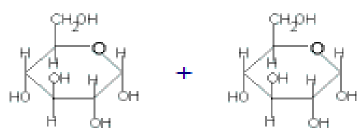
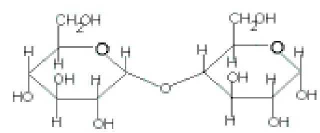
Slide no.45
these are common disaccharides: maltose, lactose and sucrose. These are the common names, they have scientific names as written.

Name	Formula	Formed from	Structure
sucrose	$C_{12}H_{22}O_{11}$	glucose + fructose 	---> sucrose + H_2O 
lactose	$C_{12}H_{22}O_{11}$	glucose + galactose 	---> lactose + H_2O 
maltose	$C_{12}H_{22}O_{11}$	glucose + glucose 	---> maltose + H_2O 

let's look to maltose.

Sugar no.1 with sugar no.2.
sugar no.1 is a pyranose. It's 6 >> hexose. So you say to yourself: it's most probably galactose, manose or glucose. Then to know which is the true you must look to carbon no.4. if it's above or below the ring. It's below the ring, so, it's either glucose or mannose. So you look at carbon no.2 and you can notice that hydroxyl group is below the ring, so it's glucose. Then you have to determine its configuration (alpha or beta). So you look at carbon no.1 (the anomeric carbon). It's below the ring. So it's in alpha configuration. and it's in the D configuration So its name is: α-D-glucopyranose.

the same is for sugar no.2. It's a glucose molecule with alpha configuration. So, its name is: α-D-glucopyranose.

So, we have α-D-glucopyranose links another α-D-glucopyranose by a glycosidic bond. The name of this bond is based on the carbons that are involved in this bond. So, the linkage is between carbon no.1 and carbon no.4. so the whole name of maltose is:
α-D-glucopyranosyl-(1→4)- α-D-glucopyranose

Let's take lactose.

Sugar no.1 with sugar no.2
sugar no.1 : it's a pyranose. It may be glucose, galactose or mannose. Look at carbon no.4. it's

above the ring. You say : it's galactose. Look at carbon no.1. the hydroxyl group is above the ring. So, it's beta. So its name is: β-D-galactopyranose

sugar no.2: it's a pyranose. It may be glucose, galactose or mannose. Look at carbon no.4. it's below the ring. You say: it may be either glucose or mannose. Look at carbon no.2. the hydroxyl group is below the ring. So it's glucose. The you look at carbon no.1. the hydroxyl group is below the ring so it's in the alpha configuration. So it's name is: α-D-glucopyranose

the linkage is between carbon no.1 with carbon no.4 so the sugar's name is:
β-D-galactopyranosyl-(1→4)- α-D-glucopyranose

In brief, let's take sucrose.
Sugar no.1 is α-D-gucopyranose and sugar no.2 is β-D-fructofuranose. The linkage is
: between carbon no.1 and carbon no.2. so its full name is
α-D-glucopyranosyl-(1→2)- β-D- fructofuranose

Now, the question is: which sugars are reducing and which sugars are not?

maltose >>> has at least one free anomeric carbon? Yes >>> it's a reducing sugar.
lactose >>> has at least one free anomeric carbon? Yes >>> it's a reducing sugar.
sucrose >>> has at least one free anomeric carbon? No >>> it's not a reducing sugar.

لن تبلغ المجد حتى تلعق الصبرا

Best Wishes.