



University of Jordan
Faculty of Medicine



Medical Committee
The University of Jordan

Introduction to

BIOCHEMISTRY

Lecture #: (.....2.....)

Sheet Slides Other

Lecturer: Dr. Nafith Abu Tarboush

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Done by: Rana N. Talj

Price:

Review:

Fischer suggested a projection in which the horizontal bonds are projecting towards the viewer and the vertical ones project away from the viewer, and depending on it we can distinguish between D and L isomers => (we look at the last CHIRAL carbon away from the MOST OXIDIZED group , if the -OH attached to it is on the right then the monosaccharide will take the name D , if on the left its named L).

Trioses are the simplest sugars, they contain 3 carbon atoms , glyceraldehydes (simplest aldose) is an example of a triose that have both D and L stereoisomers because it has a chiral carbon , on the other hand dihydroxyacetone (simplest ketose) is a triose > no chiral center > no stereoisomers

Enantiomers : stereoisomers that are mirror images

Diastereomers :stereoisomers that are not mirror images to each other

Epimers : stereoisomers that differ in configuration about only ONE chiral carbon

Anomers: Epimers at carbon no.1

carbohydrates are mainly aldehydes (ketones can interconvert to aldehydes because they are stereoisomers).

Pentoses have 5 carbon atoms >> 3 chiral centers >> $2^3 = 8$ stereoisomers

hexoses have 6 carbon atoms >> 4 chiral centers >> $2^4 = 16$ stereoisomers

these stereoisomers aren't found in nature in the same percentages

for example L-amino acids predominate in nature , oppositely D-sugars predominate in nature (important example : ONLY D-deoxyribose and D-ribose are found in DNA and RNA

respectively).

most of the sugars we encounter in life are pentoses and hexoses
Glucose has 4 chiral centers, therefore it has 16 stereoisomers

Functional groups in the sugar can react with each other and form a cyclic sugar (hydroxyl group on either carbon 5 or 6 will react with the carbonyl group on the functional carbon) .. this projection is called Haworth projection

hydroxyl groups on other carbons can also react but due to steric forces this reaction won't be able to form a cyclic sugar.

aldehyde + alcohol \rightarrow hemiacetal

hemiacetal is any molecule that contains a carbon bonded to an ether group ($-\text{O}-\text{R}$) and to an alcohol group ($-\text{OH}$)

full acetal: is any molecule that contains a carbon bonded to two ether groups

ketone + alcohol \rightarrow hemiketal

in the cyclization process: **the carbonyl carbon becomes a new chiral center in the molecule and is called the anomeric carbon.**

anomers: are stereoisomers in which the configuration differs only at the ANOMERIC carbon, either α or β , other carbon atoms have the same distribution of ($-\text{OH}$) group

i.e. the same monosaccharide with ($-\text{OH}$) group α or β about the anomeric carbon > these are called anomers

Carbon 1 is the anomeric carbon in hemiacetals and they are named α or β based on the position of the hydroxyl group attached to this anomeric carbon; if it is cis with carbon 6 > then the hemiacetal is named β , trans with carbon 6 > hemiacetal is named α (this is the scientific explanation)
(practical way: above the ring: beta, below the ring: alpha)

as we said when functional groups in the sugar react they form a ring structure either 5 or 6 membered ring depending on the type of the sugar (aldose > 6 membered ring , or ketose > 5 membered ring)

five-membered hemiacetal rings are called furanose according to furan and six-membered hemiacetal rings are called pyranose according to pyran

haworth projection is adequate to represent furanoses because five-membered rings are almost planar, but it is not really adequate for pyranoses because six-membered rings are a bit strained so they are more accurately represented as a strain-free chair conformation.

cyclization process happens in glucose , galactose , and fructose
what is the difference between glucose and galactose ?
they are epimers at carbon 4 (if –OH group is projecting upwards then it is galactose , if downwards then it is glucose)

fructose is an hexose (i.e contains 6 carbons) that can form either a 5-membered furanose ring by reaction of the C2 keto group with the –OH on C5 , or a 6-membered pyranose ring by reaction of C2 keto group with the –OH on C6
the most common form of the fructose is furanose with two CH₂OH groups projecting outside the ring

now we're done with the monosaccharides , their structures , their projections , their different isomers
and now we'll talk about the reactions that can occur between these monosaccharides
reactions > additions > not pure monosaccharides anymore > they are now called modified sugars

Reactions of Monosaccharides

1- oxidation – reduction reactions

breaking down molecules is oxidation reaction because breaking bonds means loss of electrons (loss of hydrogen / gain of oxygen) which means oxidation and the reverse is true (i.e. making bonds means gaining electrons (gain of hydrogen / loss of oxygen) is reduction)

glycolysis is an oxidation process in carbohydrates (1 glucose molecule > gives 2 pyruvate molecules > each pyruvate gives acetyl coA > Krebs cycle > gives CO₂ molecules and electrons are carried by NAD and FAD > NADH and FADH₂ > electrons are lost > oxidation)

photosynthesis is a reduction process (building up molecules > means building bonds between molecules > gaining electrons > reduction)

any sugar can either have the ability to be oxidized or don't have it

how can we distinguish if this sugar can be oxidized or not ?
> we look at the anomeric carbon (carbon no1 that's bonding to the oxygen) if it is free (not bonded to other groups) then it can be oxidized

so all monosaccharides have a free anomeric carbon > can be oxidized > reducing agents (sugar)

but for disaccharides , oligosaccharides , and polysaccharides that have bonds in between their monomers , we should check the anomeric carbon and see if its bonded to any other group (if bonded > cant be oxidized > non-reducing agent) (if not bonded (free) > can be oxidized >reducing agent)

oxidation of cyclic hemiacetals gives an acid called lactone

**sucrose is a non-reducing sugar (consists of glucose and

fructose , their anomeric carbons are bonded to each other >> no free anomeric carbons > non-reducing)

ketones can't oxidize to carboxylic acids while aldehydes can , so how can ketoses be reducing sugars ?

ketoses are not reducing sugars although they are monosaccharides but they can flip to aldoses (because they are isomers) and become a reducing sugar.

Test for reducing sugars :

Tollens test : tollens solution (silver ammonia complex ion $\text{Ag}(\text{NH}_3)^{+2}$

If the sugar is reducing > precipitation of silver on the walls of the test tube

non-reducing > no precipitation of $\text{Ag}(\text{NH}_3)^{+2}$

there is another test that is specific for glucose (very common for diabetic patients). the stripe in the device ,used for measuring blood glucose, has two main enzymes peroxidase and glucose oxidase , in air glucose oxidase oxidizes glucose.

in conclusion : glucose oxidase can test only for glucose reducing sugar while tollens solution can test for any reducing sugar

a- **weak** oxidizing agent will cause **oxidation** at **carbon 1** and will convert an aldehyde to an acid (-onic acid) for example : glucose > gluconic acid / galactose >> galactonic acid

b- strong oxidizing agent can oxidize both the aldehyde (carbonyl) and hydroxyl groups (last carbon) to form a dicarboxylic acid (-aric acid) for example : glucose > glucoaric acid / galactose > galactoaric acid

c- oxidation of primary alcohols end in biological systems (carbon 6) the product name will end with (– uronic acid) for example : glucose > glucouronic acid

so when you see the name of the acid you should be able to suspect where did the oxidation happen , at the aldehyde group , alcohol group , or both .

now that we're done with the oxidation part , we'll move on to the reduction process of sugars.

carbonyl group that's present in the monosaccharides can be reduced back to an alcohol , by reduction the monosaccharide is left with only hydroxyl groups , the carbonyl group that used to characterise it is now reduced to a hydroxyl group so the product of reduction is a polyhydroxy compound which is called alditol ,the ending -ol represents that's its an alcohol and according to the sugar's name we remove the (ald) part and replace it with the sugar's name for example : sorbose and xylulose are both sugars when reducing their carbonyl group to alcohol they will be called sorbitol and xylitol (those are very common as sweeteners for commercial applications)

two main examples on readily reduced sugars in human :

Fucose (L-6-deoxygalactose , the oxygen on carbon 6 is removed in galactose to form fucose) it is found on RBCs and it gives the antigenic determinant (ABO) for blood.

Deoxyribose , (oxygen on carbon 2 is removed in ribose to form deoxyribose) it is present in DNA

2- esterification

carboxylic acid + alcohol \rightarrow ester

important esterification that can happen in the body :

modifications to the monosaccharide : when a very negative phosphate group attach to the monosaccharide

for example when glucose reacts with ATP it takes phosphate

group (PO_3^-) from the ATP molecule and get it attached at the CH_2OH after losing hydrogen atom to form glucose-6-phosphate

why is this reaction important for the body ?

Well glucose is present in the bloodstream and as it enters the cell it can exit out, so how can I trap glucose inside the cell? By esterification process, modification on the sugar (adding phosphate to it) now its negatively charged and can't exit the cell.

the most common donor for this phosphate group in the body is ATP, why ?

because it can give an intermediate energy so formation of ATP is easy and can interconvert. On the other hand if we used a molecule that gives higher energy, it will also need high energy for formation.

note: breaking down 1 phosphate group from an ATP gives 7.3 kcal

3- glycosidic bond formation

glycosidic bond is the bond that links two monosaccharides together

so this reaction is the basis for the formation of (di/oligo/poly/) saccharides

glycosidic bond that forms between any two monomers is named according to the monosaccharides that are included in this bond, their type alpha or beta, D or L, and the number of carbons which constitute this bond

glycosides can be linked by :

oxygen \rightarrow (o-glycoside)

nitrogen \rightarrow (glycosylamine) e.g. N-acetylglucosamine

sulfur \rightarrow (thioglycoside)

carbon \rightarrow (c-glycoside) If carbon is activated

why O, N, or S can make modification ? because they have

high electronegativity

Disaccharides : are pairs of monosaccharides , glucose is always one of them

dehydration reaction (condensation) is required to form a disaccharide , we exclude O from one monosaccharide and OH from the other monosaccharide to form glycosidic bond between them

example on disaccharides : maltose , lactose, sucrose

breaking down of starch gives maltose

fermentation of alcohol gives maltose

sucrose is found in sugarcane

lactose is found in milk and milk products.

how do I name the disaccharide ?

there are scientific and common names

maltose , lactose and sucrose are common names

how do I name them scientifically ?

I have two monosaccharides , I should include the things that monosaccharides differ in , D and L , alpha and beta , the position of the glycosidic linkage , pyranose or furanose , and the name of the basic monosaccharide

for example : α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranose

this is the scientific name for sucrose.

Good Luck ☺