Biochemistry - I

Prof. S. Dasgupta

Department of Chemistry

Indian Institute of Technology, Kharagpur

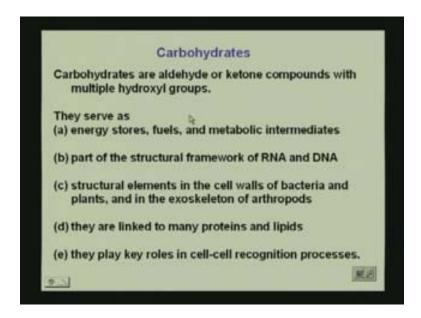
Lecture #16 Carbohydrates

We begin our lecture on carbohydrates today. We will have two lectures on carbohydrates. We will see how important they are in the process as we go on especially when we do bioenergetics where we will be studying metabolism of these carbohydrates.

The first thing that we want to know is what are carbohydrates? Carbohydrates are actually aldehyde or ketone compounds with multiple hydroxyl groups. They have a lot of functions in our body. The first one which is the most important is as energy stores in the body as fuel and metabolic intermediates that give us our basic energetic, the energy we need actually to get along. The next important thing is that they form the part of the structural framework of RNA and DNA, the essential molecules for life. When we consider the central dogma of biology, it was to go from DNA to RNA to protein. These carbohydrates actually form the basic structural framework of RNA and DNA and when we do the structures of nucleic acids and their components, we will see how this actually comes into the picture. They also form the structural elements in the cell walls of bacteria and plants and in the exoskeleton of arthropods.

This is what forms the chit in which you would have probably heard about the exoskeleton of these arthropods like cockroaches and it's that hard shell that is formed. That is also a polysaccharide which is basically a carbohydrate. They are also linked to many proteins and lipids and when we study lipids and the fluid mosaic membrane of lipids, we found out there were proteins which we called glycoprotein that adds sugar attached to the lipid moieties that was part of the fluid mosaic membrane that allowed the transfer of material from the inside to the outside of the cell.

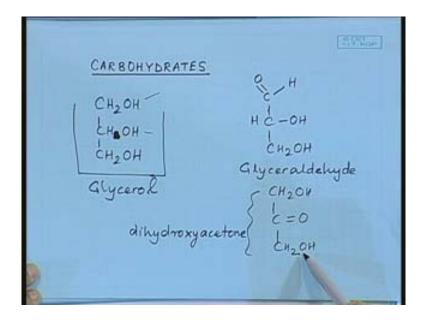
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They also play a key role in cell-cell recognition processes. So these are the major function of these carbohydrates that are basically aldehyde or ketone compound that are multiple hydroxyl groups. Basically these polyhydroxy alcohols, as you probably might all know they have the general formula $(CH_2O)_n$ and n is the number of carbon atoms that are present. For example; glycerol which was something we also used in the lipids can be considered to be the parent compound even though itself it is not a carbohydrate.

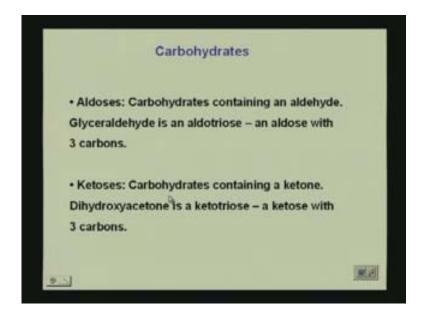
What can happen to this glycerol is it can be oxidized to form an aldehyde or a ketone and these actually form the basis for all carbohydrates. If we go look at structure of the glycerol, this is what glycerol is CH₂OH CHOH CH₂OH. When we study the fatty acids and lipids, we found that these were linked to fatty acids forming an ester and then we had a phosphate linkage and then some extra linkages. That actually gave us the polar head groups and the two hydrophobic tails of our lipid molecule. When we come to carbohydrates again, we see that glycerol again here is the parent compound. What is happening here is there is oxidization to form glyceraldehydes. We can also form CH₂OHC=OCH₂OH which is called dihydroxyacetone.

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We know that acetone is CH₃COCH₃. This is dihydroxyacetone. We have again the parent compound being glycerol and from this we can get these two aldehyde and ketone components that actually form the basis for all carbohydrates. We have carbohydrates that contain an aldehyde like glyceraldehyde that are called aldoses. Glycerolaldehyde is an aldotriose because it has three carbon atoms and aldose with three carbon atoms.

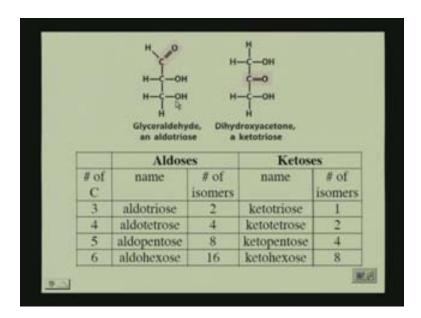
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We have ketoses like the one I just drew, dihydroxyacetone where the carbohydrate contains a ketone. It is a ketotriose. It is a ketose with three carbon atoms. This is just nomenclature that you would look at. So you have an aldose. In this case glyceraldehyde is an aldotriose. We have ketoses. Dihydroxyacetone is it ketotriose. These are the structures that we just looked at. We have our glyceraldehyde and aldotriose. We have dihydroxyacetone, a ketotriose. If we look at the carbon atoms here, this carbon atom the one that in centre here (Refer Slide Time: 07:11) is an asymmetric carbon atom because it has four different groups attached to it. We can form therefore isomers of glyceraldehydes if the OH is on the other side. If the OH is on the left, then we form an isomer. That is not true in the case of the ketotriose. We do not have a chiral center here because we have identical groups; there is no carbon atom that has four different groups attached to it.

When we look at aldoses and ketoses, the numbers of isomers are different depending on the number of carbon atoms present. If we have three carbon atoms like in this aldotriose, there is a possibility of two isomers being formed because this OH can flip from the right to the left. Whereas, for the ketotriose, this is the only possible isomer. When we have an aldotetrose, we have four carbon atoms and four isomers possible. Similarly when we have a ketotetrose ,which is a ketone with four carbon atoms, in that case you could have a possibility of two isomers depending on the number of chiral carbon atoms that you would have and where you could place the OH in 3D structure.

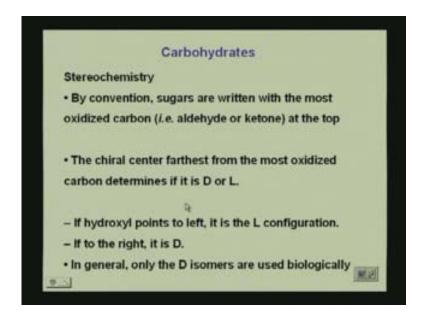
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If we look at glyceraldehyde once more, we have these four different groups attached to it. It means there are two such stereoisomers of glyceraldehyde possible. One is D-glyceradehyde and the other is L-glyceradehyde. In L-glyceradehyde the OH is on the

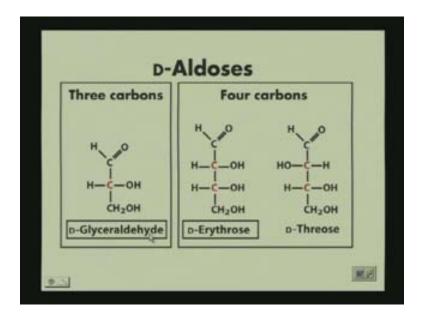
left D- glyceradehyde the OH group is on the right. So this is the stereochemistry that is followed by convention for all carbohydrates. By convention the sugars are written in such a manner that the most oxidized carbon, that is the aldehyde or the ketone is written to the top of the structure. The chiral centre that is farthest from the oxidized group is the one that decides whether D or L, not any other OH group. We have the sugars written with the most oxidized carbon i.e. the aldehyde or the ketone at the top. The chiral center that is farthest from the oxidized carbon will determine whether it is D or L. If the hydroxyl group is to the left, it is the L configuration, if it is to the right it is the D configuration. In general, we mostly use D isomers in biological components.

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We have some other aldoses that we can consider here. This is three carbon atoms. We have D-glyceraldehyde. When we look at four carbons, we have D-erythrose, the D because the most oxidized carbon is at the top.

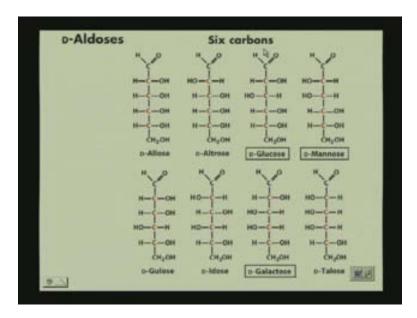
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The carbon atom that is chiral that is farthest away from the oxidized carbon has the OH to the right which means this is D-erythrose. This is also D-threose because the OH attached to the chiral carbon farthest away from the oxidized carbon is on the right i.e. your nomenclature. In D-ketoses we have the three carbons, you have dihydroxyacetone. When we are looking at four carbons again, we have carbohydric called erythrulose where we have ketotetrose .It has four carbon atoms. It is a ketose. We have now the oxidized carbon as for the top is possible. We have the chiral carbon with the OH to the right. So it is a D-erythrulose.

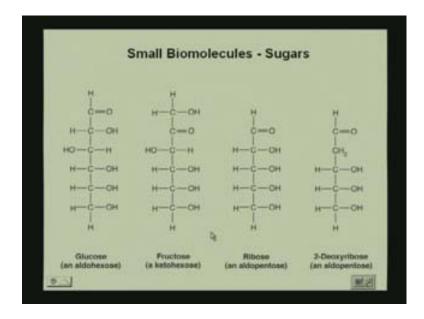
The other types of D-aldoses, where we look at 6 carbons that are going to consider, we have allose, altrose, glucose, mannose, gulose, idose, galactose and talose. What we need to know is it what is important for most biological carbohydrates is glucose, mannose and galactose.

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We see all these are actually D structures that have been drawn here. The most oxidized carbon is at the top. The farthest chiral centre away from the oxidized carbon has the OH on the right, so this is the D glucose. The glucose one is the one that we are going to be most interested in and we look at the structure in much more detail as we go along.

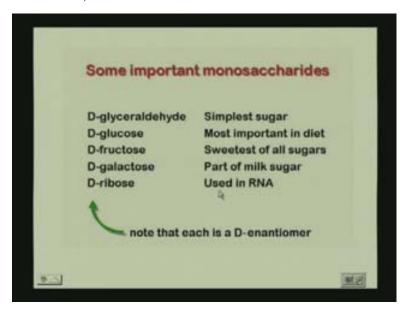
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These are other sugars that these structures are important now for all of the sugars that we are going to do later. Glucose is an aldohexose why because it has aldehyde group and it has six carbon atoms. So it is an aldohexose. Fructose is a ketohexose. It has six carbon atoms and it has the ketone group to it. Ribose which forms the basis of the ribonucleate acid, the basic sugar in ribonucleic acid is an aldopentose and the sugar that forms the basis for all DNA molecules is 2 deoxyribose where the numbering begins from always the most oxidized carbon atom. So this (Refer Slide Time: 13:53) is number 1, this is number two. The deoxy means it has lost this. It is now CH₂ so this is deoxyribose. What we have for ribose that is going to form the basis for ribonucleic acid is the ribose sugar which is an aldopentose for deoxyribo nucleic acid; the basis is two deoxyribose which is missing and OH. We will see how important this is in a lot of structures. For example, when we did the mechanism of ribonuclease, we found out that the ribonuclease because it acts on this two prime OH could not act on DNA and cleave DNA.

It could only cleave ribonucleic acid, if you remember when we did enzyme mechanism. So these are the small bio molecules that are extremely important or probably the most important ones where we have glucose, fructose, ribose, and 2 deoxyribose.

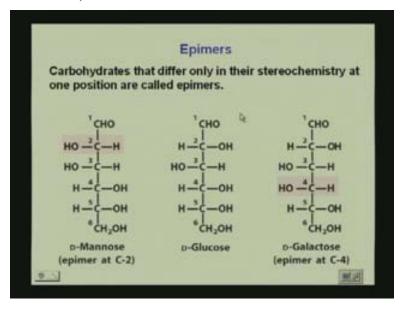
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These are some other important monosaccharides. D-glyceraldehyde is simplest of sugars. D-glucose is the most important one in the diet. We will see how this is also stored and how it is even broken down in the body. Then we have D-fructose which happens to be the sweetest of all sugars. We have the D-galactose that forms of part of milk sugar. And as I said, D-ribose is used in RNA. And deoxyribose is used in DNA and all of these you see are D-enantiomers. When we looked at proteins, we found that most of them were L-amino acids.

Now this is what we mean by something called epimers. First of all, let us look at the numbering of glucose. If we look at the numbering of glucose, we find that it is basically an aldohexose.

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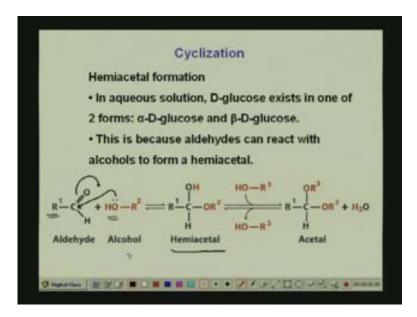
The aldohexose has an aldehyde group on the top. This is the way it is written and the rest of the molecules follow. The chiral carbon that is number 5 here which is the farthest away from the oxidized carbon will determine whether it is D or L. This is on the right so it is D-glucose. We have now two other aldohexoses is here; D-mannose and D-galactose. What we have here is, if we look at the structures carefully, in this case the change in the orientation of the OH is on carbon number 2. The rest is the same. We have the OH on the left in mannose and on the right in glucose.

However for carbon number 3, 4 and 5, the OH directions are exactly the same. The only change that you see is in carbon number 2 between D-glucose and D-mannose. What you say is when you have the difference in the stereochemistry at only one carbon atom; it is referred to as what is called an epimer. So you would call this an epimer at C_2 meaning that at carbon number 2 this would be an epimer of D-glucose at carbon number 2. Since we all have to remember the structure of the D-glucose and if it what to be mentioned that, you know the structure of the D-glucose and you know that you have D-mannose which is an epimer of D-glucose at carbon number two, you would know the stereochemistry carbon number 2 is the only one that is different. Instead of having OH on the right you would write the OH on the left. If I say now that there is another epimer of glucose that is an epimer at C_4 that is called D-galactose.

Now since we know the structure of glucose, the only stereochemistry of the carbon that is going to change the stereochemistry is going to be at carbon number 4. In carbon

number 4, instead of having the OH on the right I am going to have the OH on the left. So that would be the epimer at C_4 which is D-galactose. All we would have to remember actually is the structure of glucose and then know that D-galactose is an epimer of glucose at C_4 and D-mannose is an epimer of glucose at C_2 .

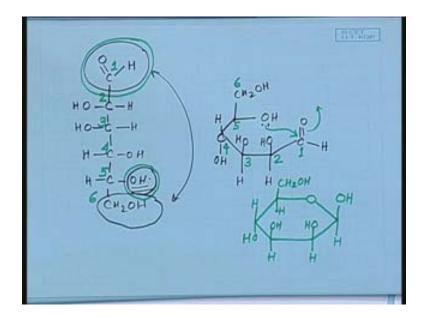
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Let's look at other structures of glucose. We have what is called hemiacetal formation. This is some thing that you probably studied before also but nevertheless we go through it because it is going to be important in the understanding of what goes on later on in terms of its breakage and cleavage. We have an aldehyde. An aldehyde reacts with an alcohol. When it reacts with this alcohol, it can form what is called a hemiacetal. What is this hemiacetal? It has an OH and an OR₂. What is attached here is the rest of the chain. We have the aldehyde group and an alcohol group here. What happens here is this OR₂, the lone pair on the oxygen is going to attack this carbon. So what happens here is this goes and takes up this proton. So it forms you see this proton is marked in red which is actually coming from the alcohol and the OR₂ is now linked to the carbon to form what is called a hemiacetal.

We can also form an acetal. What is going to happen to acetal? We are going to have again this attack on the carbon here and what is going to be released now. The OH is going to take up this H and form H_2O and an acetal. This is extremely important in the cyclization of glucose which will see in a moment. We have two such forms of glucose called an α and a β form. Basically what is happening is, in the glucose structure, we have not only an aldehyde group but also an alcohol group. What does it is actually look like? We not only have an aldehyde group. We can write this actually in a different fashion. Our aldehyde is sitting here and our alcohol is here (Refer Slide Time: 22:28). So what can actually happen? I can have cyclization.

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We write this in a manner that is going to be like this actually it's not the one that actually react this alcohol. We have OH CH₂OH COH, this would be apparent when I show you the slide also but you should draw it yourself once. We have an H also sticking here. We just number the carbon. Let us be careful in numbering. We have this carbon number 1, 2, 3, 4, 5 and 6. Which is the alcohol that is actually forming the hemiacetal? It is this alcohol with this (Refer Slide Time: 22:56) aldehyde because this CH₂OH is up 3 numbers 6. So the numbering is 1, 2,3,4,5 and 6.

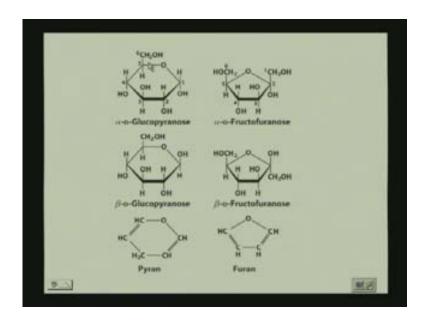
If we have the same reaction going on, what is going to happen is, the oxygen is going to come here. What is this going to do? It is going to take up this proton. What have we actually done, if we go back to the hemiacetal formation, we have the aldehyde with the alcohol forming an hemiacetal.

If we look at the this is, what is happening we have the cyclization where is this OH attached to five that is doing what participating with the aldehyde so the hydroxyl oxygen and the aldehyde of carbon number one is going to cyclize and we will get a six membered ring. One of the member is going to be the oxygen, a six membered ring with the CH₂OH being the sixth carbon. We can also five membered rings because we can also have the cyclization of D-fructose.

We will look at what those ring look like in a moment so six membered rings resemble pyran, they are called pyranosides. So glucose is also called glucopyranoside. Furanoside are five membered rings with oxygen because they resemble furan.We usually have them drawn as Haworth projection as shown before. We have six membered rings and five membered rings that resemble pyran and furan so they are also called pyranosides and furanosides. This is what we have. You should try and work out the structure for the case of furanose and see what it look likes. You should get a five membered ring in that case because we have the C=O. We have a CH₂OH attached to it.

If we look at the α -D glucopyranose, we will see what the α is in a moment. but for now we have to know that we have a six membered ring and the oxygen resembling the structure of a pyran, so we have glucopyranose. The five membered ring in case of fructose which is the ketohexose is forming a fructofuranose. There are somethings that we can notice here especially at carbon atom number one. In the first diagram, we have the OH that is trans to the CH₂OH.

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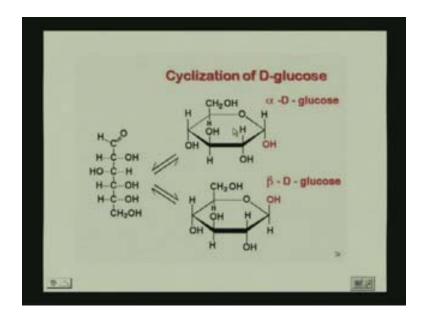


In the second diagram, we have the OH cis to the CH_2OH which is the sixth carbon. What do we have, what is called an α anomer and β anomer. You form anomers of glucose only when you have the closed ring structure. In this case the OH on carbon atom number one that we have to take care of, if this OH is trans to the CH_2OH . It is called an α anomer. If it is cis to the CH_2OH , it is known as a β anomer. The same goes with fructofuranose, the CH_2OH if it cis to other CH_2OH . It is the α , if it is trans then it is the β form. This is what the anomers are. The different stereoisomers α and β are called anomers. We have the aldehyde or ketone carbon which will give us or decide whether we have the anomeric in the β position or in the α position. You have

to remember that this is only possible when there is cyclization. So we have the α OH down compare to CH₂OH, that's trans. If the β OH group is up compared to CH₂OH, it is basically a cis conformation when it is β and when we have the α . We will see how this is going to help us in all the glycosidic linkages that we will talk about later.

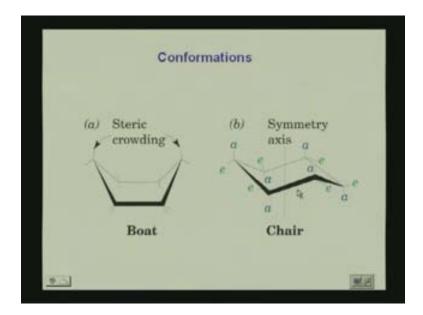
We have glucose here, we have the cyclization. What is the cyclization leading us to, when we have the OH trans to the CH_2OH , we have α D glucose, when we have the OH cis to the CH_2OH , it is beta D glucose. When we have the ketose sugar, in this case they shown the OH trans to the CH_2OH and the OH cis to the CH_2OH .

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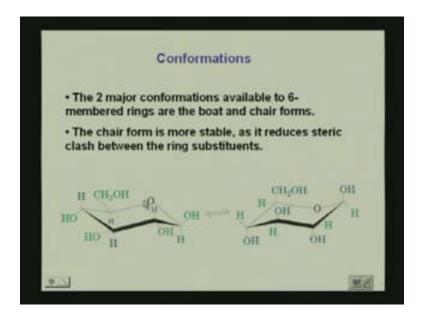
We have six membered rings for R glucose which means that we can have either a boat conformation or a chair conformation. This is something you already know with six membered ring and what do we have is we can have axial bonds or equilateral bonds depending on the disposition. This shape is because this carbon atom is sp three hybridized. So it has a tetrahedral disposition conformation to it which means that you can have an axial path and an equatorial path. We also know the chair conformation is favored over the boat conformations because in this case we have steric crowding.

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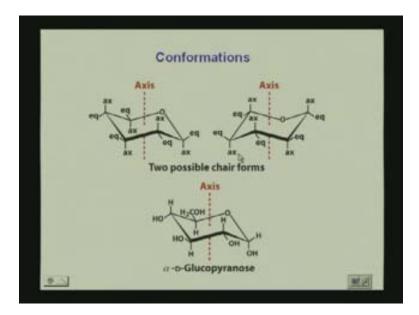
Of these two major conformations that are available, this would be the structure of glucose. We have the six membered rings which is our pyranose ring because we have the oxygen sitting here. We have the OH and we have the OH in this case it is in the equatorial form here it is in the axial form. We have the stable chair conformations because it is obviously going to reduce the steric clash between the ring substitutents, This is something you know already.

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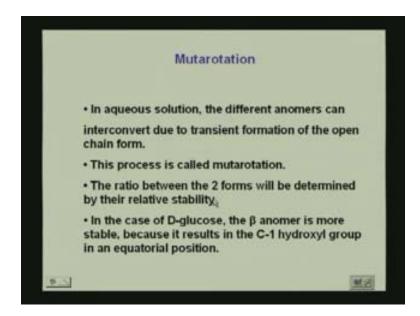
We have here the axial and the equatorial axis. There are two possible chair conformations where we have the oxygen. What we can have here, this is α D glycopyranose. We have to look at the name carefully pyranose means it has a six membered ring with oxygen unit. We have the OH trans to the CH₂OH. It is α . Why is it D? It is D because the last chiral carbon atom away from the most oxidize carbon atom is having the OH on the right. It is α D glucopyranose. Another thing we have to consider is in aqueous solution, the different anomers can actually interconvert between themselves.

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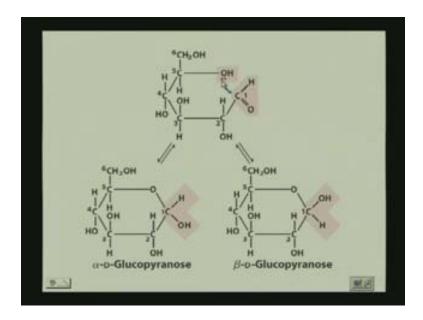
This inter conversion actually gives us a transient formation of the open chain form because you realize that once it goes through the reaction there is going to be certain intermediate that is going to have the alpha chain in the open conformation. When it has it in the open conformation, when it closes again the OH could either be up or down i.e. cis or trans to the CH₂OH that's on the sixth carbon atom.

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What can happen is in aqueous solution, when we have the different anomers that can actually interconvert due to the transient formation of the open chain form. this process is known as mutarotation. The ratio of the two forms is actually determined by the relative stability and in the case of D-glucose; the β anomer is more stable because it results in the C_1 hydroxyl group in the equatorial position. Between the boat and chair, we know that the chair conformation is more stable. When we are looking at the chair conformation if you want to look at which of the chair conformations are stable. We have to look at the chair conformation which has the most bulkiest substituent at the equatorial positions. That is exactly in the case of the β anomer whether hydroxyl group is in the equatorial position and that will make it the stable form for D-glucose.

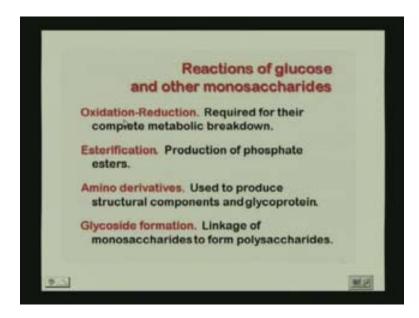
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This is what we have in looking at the structure of glucose. We have aldehyde group and the OH that is attached to the carbon number 5. We have the formation of the basically have our cyclization. In this cyclization, it is possible that the OH either goes trans to the CH₂OH or it goes cis to the CH₂OH. We usually refer to this as a pyranoses. It is based on pyran and then we also know that when we look at the chair conformation of this, it would be more convenient to have the OH group at an equatorial position so that there will not be any bulky groups at axial position would be unfavorable.

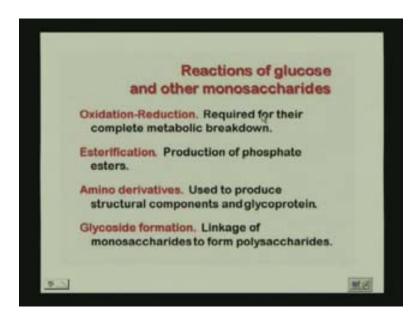
Let us look at the reactions of the glucose and other monosaccharides. There are certain reactions of glucose that are important for the metabolic breakdown of glucose.

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There is oxidation and reduction that can occur. Oxidation and reduction required for the complete metabolic breakdown of glucose, this is extremely important and another important about glucose is storage. It is not stored as glucose because glucose breaks down. There is a metabolic breakdown of glucose so when it is stored it is stored as a glycogen. We will see in the next class what the different types of methodologies are or the different types of linkages are and how we can actually store them. We have our different reactions one is oxidation reduction. What is the oxidation reduction? We will see later on when we do bioenergetics and consider metabolism of carbohydrates how this is important there.

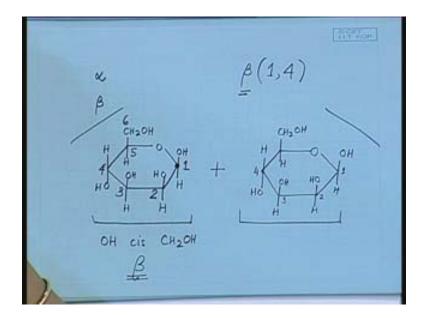
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We have esterification where we have the production of phosphate esters. We have amino derivatives where we have the use to produce structural component and glycoprotein. Glycoproteins are those that have glucose linked to the protein. We will see how they are actually linked to the protein. Then the most important thing that we will be considering for disaccharide formation of polysaccharide formation is glycosidic linkages. When we consider glycoside formation, we will understand what these linkages actually are in their formation. For example; when we consider that we have an α form we know that we have a β form.

Now if we just look at the structure of glucose in different forms, consider the beta form. Why is it the β form because the OH is cis to the CH₂? So it is β . When we talk of these linkages, we have to first of all remember the numbering of the carbon. What is the number of this carbon? It is number 1, 2, 3, 4, 5 and 6. What happened here? We had hemi acetal formation because we have the aldehyde and the OH of C₅ link together.

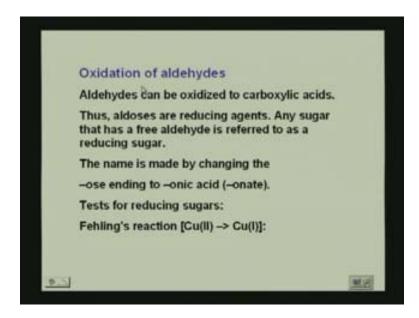
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When we have glycosidic linkages, we will see in the next class, we are forming now from one unit we are going to link in another unit. in the linkage of the other unit, we are going to first of all look at whether this carbon is α or β , then we are going to determine what it is linked into or which two carbon atoms are linked. If you link one and four and the first carbon atom that you are linking is in the beta form, this forms what is called beta one four linkage. If I were to write another β form of this, I have to number them again. I have 1, 2, 3 and 4. If I have a link between the carbon atom at 1 and the carbon atom at 4 in the other monosaccharide, this is one monosaccharide and this is the other one, if I link these (Refer Slide Time: 41:30) two together, at 1 and 4, I would have a 1,4 glycosidic linkage. Depending on whether the first monosaccharide being linked to the second one was in the α or β position, I would have the numbering as β (1, 4).

We will look at this in bit more detail when we do the next lecture. What are the reactions of these glucose? These are the specific reactions that can actually go on. We look how we can actually have glycosidic formation? What is this glycosidic formation? If we go back to the slides here, we have the linkage of the monosaccharides in this case what we looked at was the formation of a possible disaccharide. If we keep on linking in this fashion, if we have a series of say β 1, 4 linkages, then obviously I am going to form what is the polysaccharide. We will look at the different linkage as I said in the next class.

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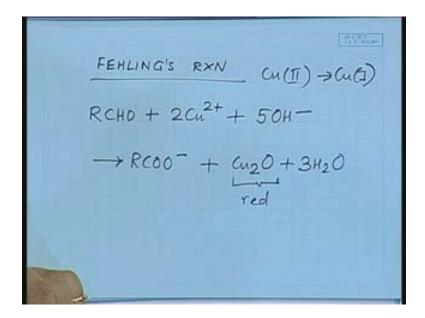


Now one of the reactions that is extremely important when we consider aldehydes is their oxidation to carboxylic acids. In their oxidation, the sugar that has a free aldehyde is usually referred to as reducing sugar. Sugar with free aldehyde for example; like glucose which is the sugar that has the free aldehyde. So, all aldoses are sugars with free aldehyde groups.

All these aldoses are reducing sugar and what happens is actually, when you have the suffix ose, it is referred to as sugar whether it is a ketose or aldoses. It has the ose and aldose is where you would have the sugar in the aldehyde form a ketose is where would have it in the ketone form. The name basically is made by changing the ose ending i.e. ose the end of the ose to onate. So if you have glucose it would become gluconate. The test for reducing sugar is something called Fehling's reaction. What happens here is you have a reduction of Cu(II) to Cu(I).

The basic reaction for reducing sugar for aldehydes is Fehling's Reaction. It is a very common reaction that is used in the determination of whether you have glucose. For example; it can be quantitative even when you have say, pathological test or biochemical test. In this case we are looking at glucose. It works for any reducing sugar. So reducing sugar would be one that would have an aldehyde to it.

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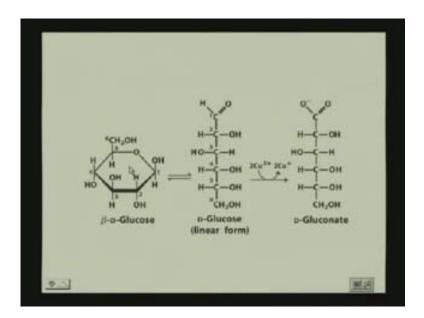


What would be an aldehyde with a sugar and aldose in this case? We are looking at glucose which is an aldohexose. That is basically all the nomenclature that we would know for a monosaccharide what is basically happening. Fehling's reaction that are going from Cu(II) to Cu(I).

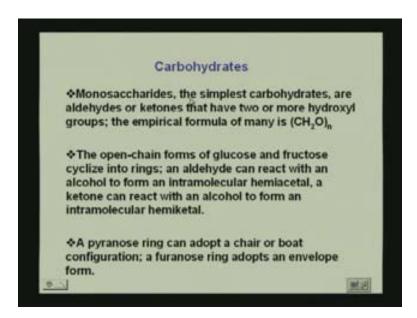
What happens is you have RCHO + 2 Cu^{2+} + 5OH^- ? Is basically an alkaline medium where this goes to RCOO $^-$ so what we have formed gluconate We have Cu₂O as well. Then what happens here is this actually gives you a red coloration to your experiment.

What we have in this case here, in β D glucose, now you recognize this is beta D glucose. So any structure given to it should be recognizable in terms of where the OH is, where this CH₂OH is and whether it is fructose or a furanose or a pyranose. We have a linear and a cyclized form. So we have β D glucose in the linear form forming the gluconate.

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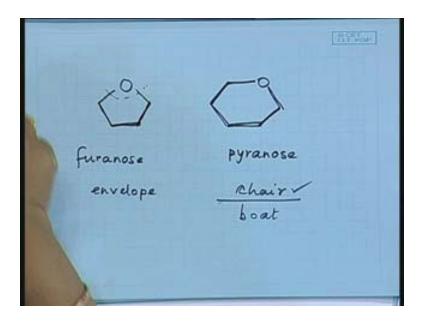


The monosaccharides are the simplest carbohydrates. We found out that they are all formed from glyceraldehydes. The basic form is glycerol, and then from glycerol, we form glyceroldehyde. We know that we have two forms of glyceroldehyde; D-glyceroldehyde and L-glyceroldehyde. It is the disposition of the OH at the chiral carbon that determines whether it is D or L. If it is on the left it is L glyceroldehyde if it is on the right it is D-glyceroldehyde. Then we have the aldehydes or ketones that

would have two or more hydroxyl groups attached to it. Basically that would be the carbohydrates and the empirical formula is $(CH_2O)_n$, where n is the number of carbon atoms present. We have aldoses and ketoses depending on whether we have the oxidized carbon in the aldehyde form or in the ketone form.

The open chain forms of glucose and fructose cyclize into rings. We looked at that also where the aldehyde can react with an alcohol to form an intramolecular hemiacetal. We looked at reaction, where it is possible for the aldehyde and the alcohol to form a hemiacetal. In this case, we have the aldehyde and alcohol both in the same molecule. Since they are both in the same molecule we form an intramolecular hemiacetal and then a ketone can react with an alcohol to form an intermolecular hemiketal.

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When we form these structures, we form either a pyranose depending on whether we have a six membered ring or we form a furanose if we have a five membered ring. For the fructose case we will have a furanose and for the glucose case we have a pyranose. Then we also looked at how the pyranose ring can actually adopt either a chair conformation or a boat conformation and the furanose actually adapts what is called an envelope conformation. What is this envelope conformation? I am sure all of you are aware of this.

We have the furanose it looks like (Refer Slide Time: 51:38) this and when we have the pyranose it looks like this right so this would be a pyranose and this would be a furanose. What happens in this case is it is these parts that are level and in this case we have either the chair or boat conformation but in this case we have what is known as an envelope conformation what is the envelope conformation. The oxygen is slightly lifted

up from the rest of the carbon atoms like flap of an envelope. This would adapt an envelope conformation. This would adapt a chair or boat conformation. What did we find out? We know that this is going to adapt a chair conformation why because the boat conformation would give it some steric hindrances. Then we also found out that the β conformation would be more stable for glucose. Then we looked at certain reaction that could go on different reaction at glucose can actually have.