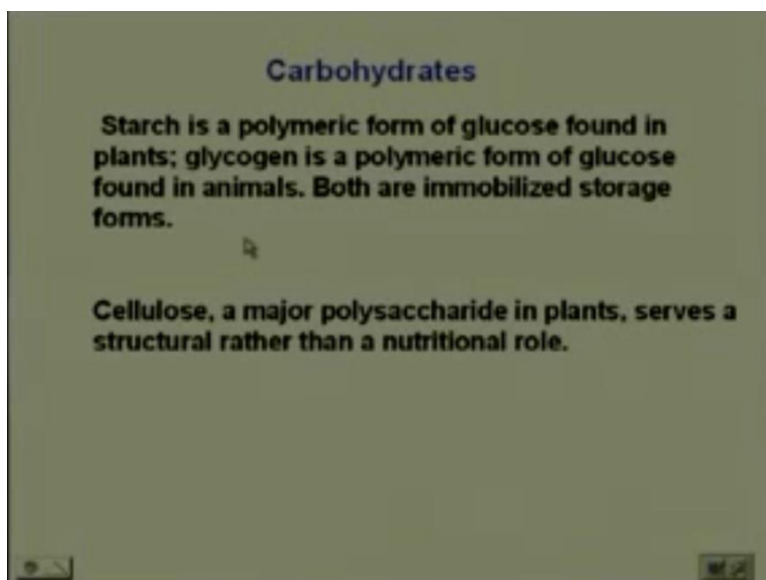


Biochemistry
Prof. S. Dasgupta
Department of Chemistry
Indian Institute of Technology – Kharagpur

Lecture - 22
Carbohydrates- II

We come to our next lecture on carbohydrates and here we will be looking at the formation of disaccharides and formation of polysaccharides and how they actually help or where they are found and what linkages they actually have. So, before we get into that we will look at what these carbohydrates are.

(Refer Slide Time: 00:35)



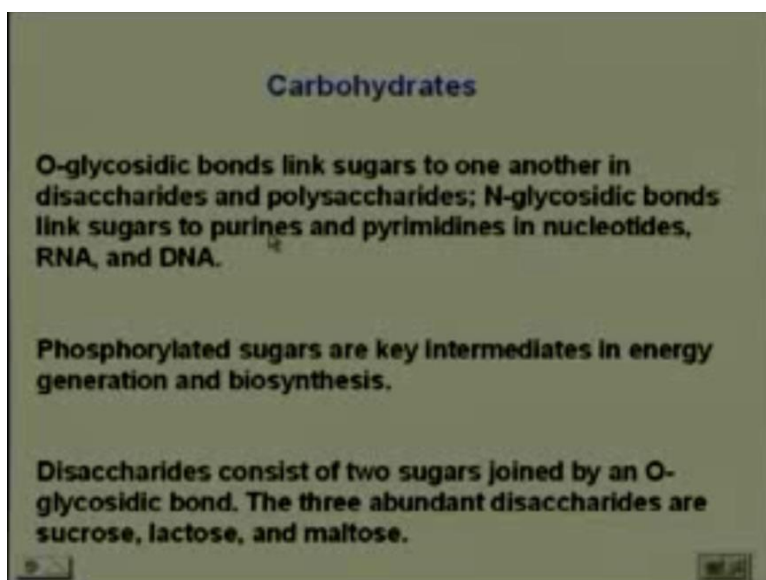
We learnt in the last class that carbohydrates have the general formula CH_2O whole N. Now, this is something you have studied from probably your school, where you know what starch is and what cellulose is and things like that. But, what we are going to look at now is what are the specific monosaccharaides that form starch, what are the linkages that result in the formation of starch and in the formation of the other polysaccharides and why for example there will be certain enzymes that do not work for humans but work for animals.

So, we have starch that is nothing but a polymeric form of glucose. So, since you understand now since the basic unit is glucose, it would be the linking that would be different because now that is exactly what we are going to consider is how these glucose units, these monosaccharide units are linked with one another and these are both immobilized glycogenis

stored in our liver and it is broken down when we require the glucose breakdown for metabolism for the energy requirement of our activities.

Cellulose is another major polysaccharide in plants that serves rather to be a structural rather than a nutritional role. Structural means it forms fibers that help in its structural build up.

(Refer Slide Time: 02:13)



Now, what we have here is certain types of bonds that we are actually are going to be looking at. Glycosidic bonds are those bonds that link sugars to one another. Now, when we consider, say, just glucose linking with another glucose moiety or glucose linking with galactose or manose or where we have just O- glycosidic linkages, we are going to form disaccharides and polysaccharides.

So, the O-glycosidic bonds that link sugars to one another in disaccharide's and polysaccharides. When we speak of N- glycosidic bonds, we know that in the O-glycosidic bonds, we have the oxygen that is involved in the linkage. When we have an N-glycosidic bonds we know that the nitrogen is involved in the linkage and when you have glycosidic, it means there is a sugar involved.

So, we have nitrogen and sugar. These are the bonds that link sugars to the purines and pyrimidines in nucleotides. This we will study in much more detail when we consider the nucleic acids and their specific components. But for now, what we studied in the last class, when we look at ribonucleic acid, it has a ribose sugar to it. Now to the ribose sugar, we

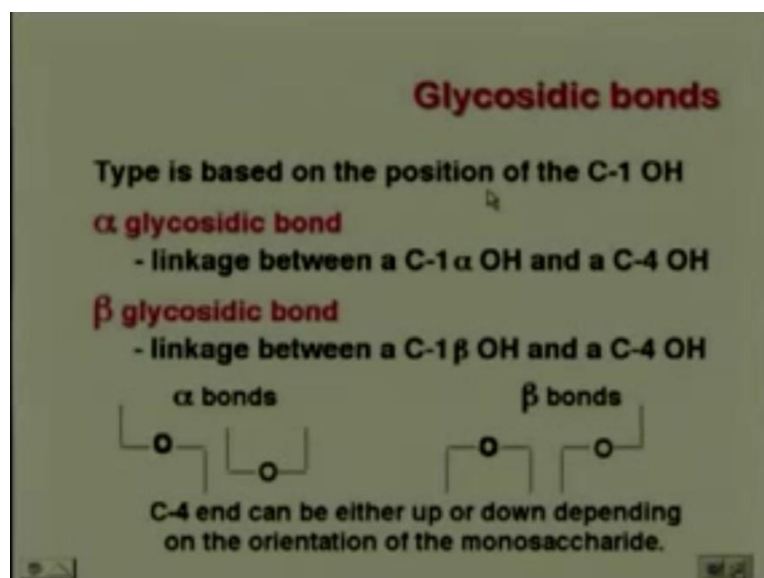
know that the ribose sugar itself contained only carbon, hydrogen and oxygen in the carbohydrate unit that it was.

Now, if we have the purines and the pyrimidines that are actually nitrogenous bases linked to the ribose or the deoxyribose there is a specific N-glycosidic bond linkage that comes into play. So, when we have an O-glycosidic bond, we are basically forming a disaccharide because we have 2 monosaccharide units linked by an O-glycosidic bond that is going to form a disaccharide.

And similarly we will have another set of linkages that are going to result in the formation of polysaccharides. In case of N-glycosidic bonds, we are going to have the linking of the sugars, the ribose or the deoxyribose to the basis purines and pyrimidines. Another important part is phosphorylated sugar. What does that mean? It means that when you have a ribose sugar you can have phosphate attached to it which we will see when we consider adenosine triphosphate, where we have phosphorylated sugars that are key intermediates in energy generation and biosynthesis.

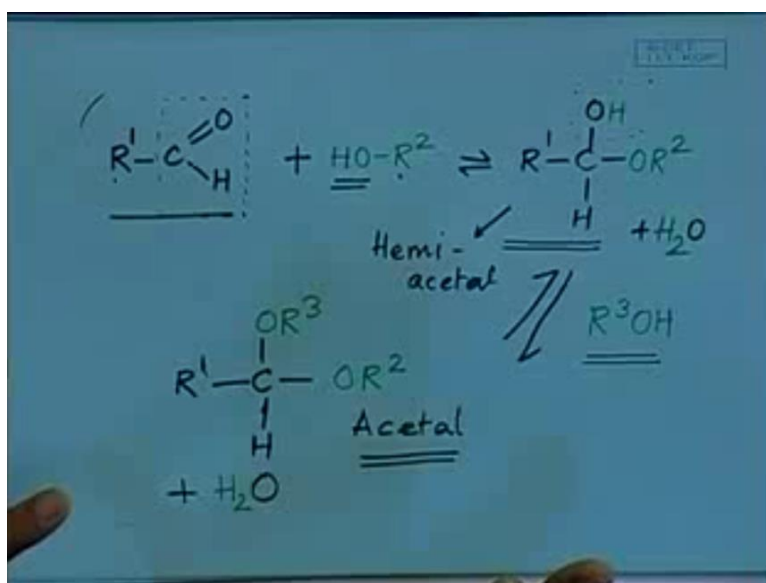
We have the disaccharides that consist of 2 monosaccharide units, 2 sugar units that are joined by O-glycosidic bond and the 3 most abundant disaccharides are sucrose, lactose and maltose. These are the ones, but we will know how, once if we know what the linkages are, how we can actually write out the structures of sucrose, lactose and maltose and also of other disaccharides.

(Refer Slide Time: 05:40)



Now, this is something that I was mentioning in the last class. We are concerned here by the type of glycosidic linkage we have. Now, in forming a glycosidic linkage we have a linkage depending on what the first monosaccharide has a disposition of the C-1 carbon atom. For example, if the linkage is between a C-1 alpha OH and a C-4 OH, it does not matter what the orientation of this C-4 OH is. If the first carbon is an alpha, it is called an alpha glycosidic bond. If it happens to be a beta, it is the linkage between a C-1 beta OH and a C-4 OH, it is called the beta glycosidic bond.

(Refer Slide Time: 06:48)



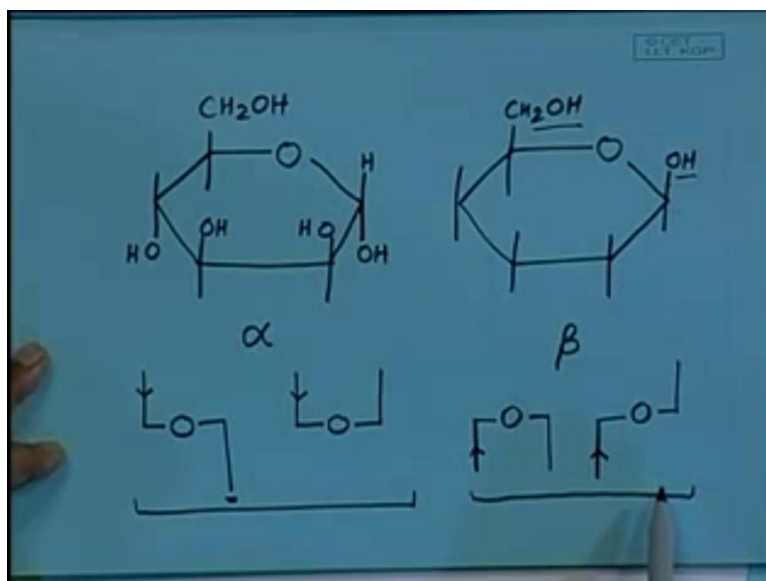
Let us just go here and just look at how we had hemiacetal formation. This is something that we did in the last class. This was our aldehyde molecule. When we have the aldehyde molecule, we know that it is cyclised. Now, when it's cyclized, we had C double bond O, that's the aldehyde part, the aldehyde moiety, interact in the case of glucose with the OH of carbon atom number 5 into forming a cyclic structure which is the hemiacetal.

Now, what happens in this case is you still have an OH available to it. And now, what can happen is we can have another unit come and link up with the hemiacetal into forming an acetal. Now, this unit which has an OH group could be another sugar. It could be another sugar also. So we are going to form an acetal. In the intra molecular cyclisation of the glucose forming the cyclised monosaccharide, what was actually formed was a hemiacetal because we had the OH that actually was part of R1.

So, this R2 that we are talking about here is actually the 5th carbon atom of the same structure here. So, we are cyclizing the whole thing into forming what is called a hemiacetal.

But now, if I have another glucose which is also an OH, it has an OH to it, if I have this link with this hemiacetal, what can I get? I can get an acetal.

(Refer Slide Time: 08:56)



Now, depending on my cyclic structure I have either an alpha form or a beta form. Let us just draw 1 form here or in fact let us draw the forms so that we can know what we are talking about. We have two forms here. What are these? These are pyranose rings. Which carbon atom is this? It is the 6th carbon atom. We have our OH here. One OH here. One OH here. And this OH can be either up or down.

If I put it down it becomes alpha. If I put it up it is beta. I am not drawing the other one. So, this is our beta and this is our alpha. Now, if I form a linkage then the oxygen atom which is going to be linked, suppose we have these 2 units. If it is in the alpha form, the oxygen is where? It is down. So, the linkage is going to look like this. The oxygen is going to be down. It can be down. But, the other one that it's linking with can be up or down. So, this could either be this or it could be this.

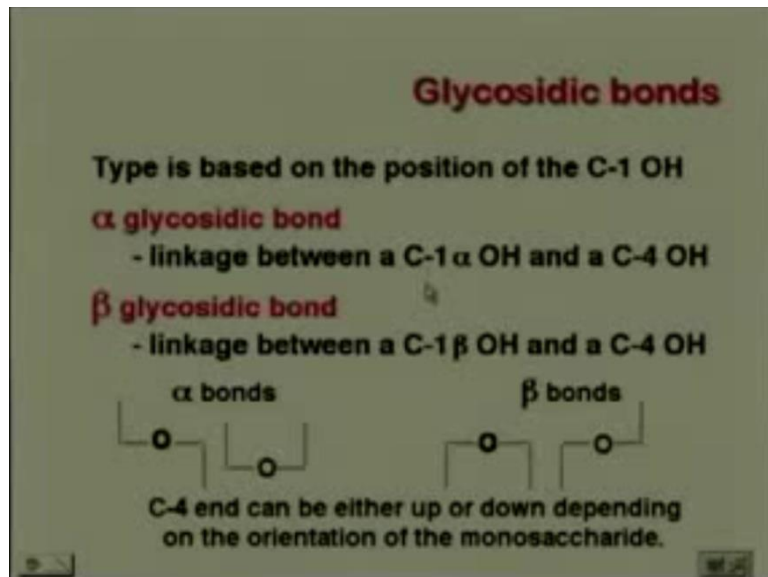
What we are looking at is we are not looking at our monosaccharide unit only anymore. We are going to link this monosaccharide unit with another monosaccharide unit into forming a glycosidic linkage. In the formation of the glycosidic linkage, we have to look at the disposition of the OH with respect to the CH_2OH that is going to determine whether this is alpha or beta.

Now, these are both alpha forms, why? because in both cases my OH is down. This O that is coming from the first monosaccharide unit is Trans with respect to CH₂OH. That's why the direction is this way. If I were to do the same for the beta set, then in both cases, it would be up. What are the both cases I am talking about? We would have an O and an O and the other monosaccharide unit that it would be linking to could either be this or this. Because what we are looking at now is we are going to gradually get on to structural units.

To understand the structural units, we have to be very careful about the linkages that we are talking about because if you remember when we did lysosine, we talked about beta (1, 4) glycosidic linkages. What are these linkages? A beta linkage would look like this. Now in both cases it would begin up, why? because this is up. This is cis to this CH₂OH. So this would refer to a beta linkage. In this case, it's down.

It's Trans to CH₂OH. So, this would refer to an alpha linkage and what it's linking to could be up or down. So, we have it either looking like this or like this, the same thing in the beta case.

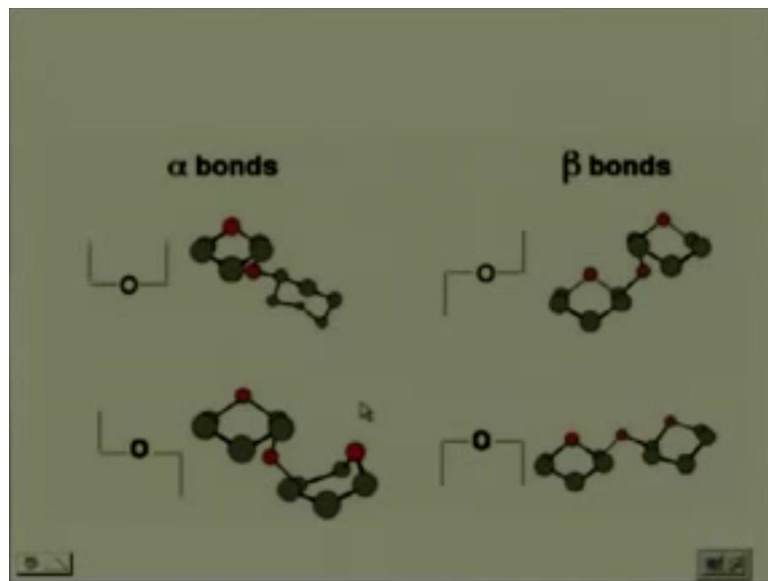
(Refer Slide Time: 13:13)



Suppose, we have it linking to C-4, which is the 4th carbon of the next monosaccharide unit, then the C-4 end could have the oxygen, where? up or down, depending on what unit you are considering. Now, that is the case, then you would have dependent on the orientation of the monosaccharide either it comes down in the alpha case or it always has to come down. That's what you have to remember because the oxygen or rather OH is Trans to CH₂OH and it is this that is going to be involved in the acetal formation.

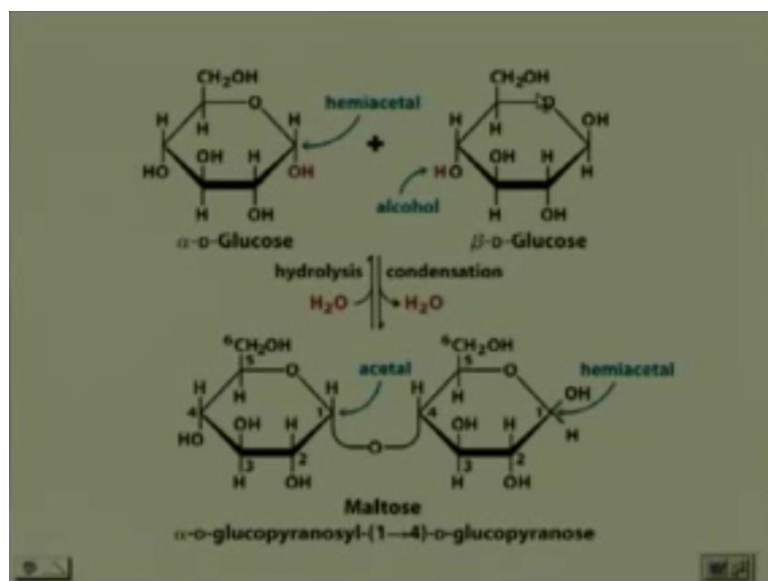
We already have a hemiacetal formation. We are now going to have an acetal formation. So, what is happening is this OH is going to be involved in a reaction that is going to form a glycosidic linkage. Now, when it forms this glycosidic linkage in the case of alpha both of them are going to be down and the one that's linking to say C-4 in this case can be up or down. The same goes with the beta. The beta will be up initially, why? because the OH is cis to CH₂OH and what it's linking to could be either up or down.

(Refer Slide Time: 14:32)



So, this is what we have. We can have alpha bonds that look like this. You have to remember when the O looks like this, and then this is an alpha linkage. When O comes towards the top or upward it is a beta bond. So, this is what it looks like. So depending on what kind of linkage you have you see how the structural differences occur. That is obvious. It is going to be obviously dependent on how the reaction is taking place. So, you could either have an alpha glycosidic linkage or you could have a beta glycosidic linkage.

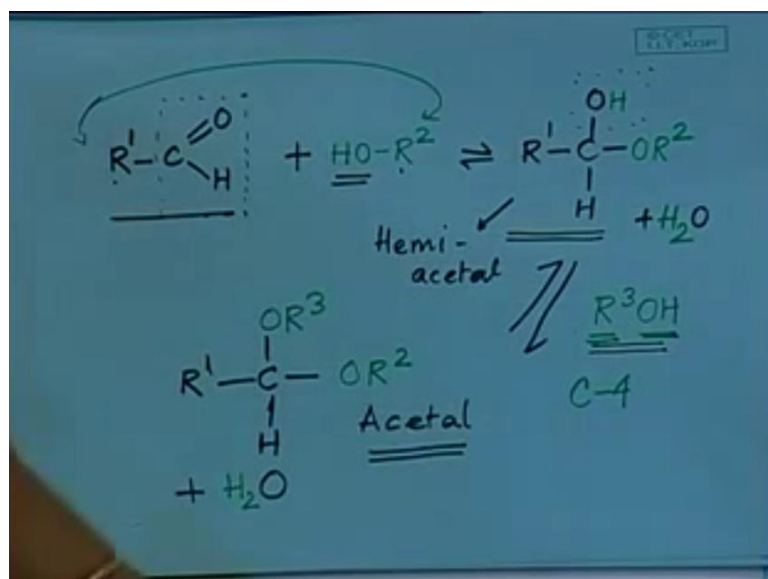
(Refer Slide Time: 15:13)



So, let us see what it is? So, this is what we have. We have an alpha D glucose here and a beta D glucose. Now follow this very carefully. This is the structure that we did in our last class. What do we have? We have hemiacetal formation where the OH of this carbon, what carbon is this? carbon number 5 and this is carbon number 1 that originally was an aldehyde. It is now a hemiacetal due to an intermolecular cyclisation that has occurred between the OH of the 5th carbon and the aldehyde.

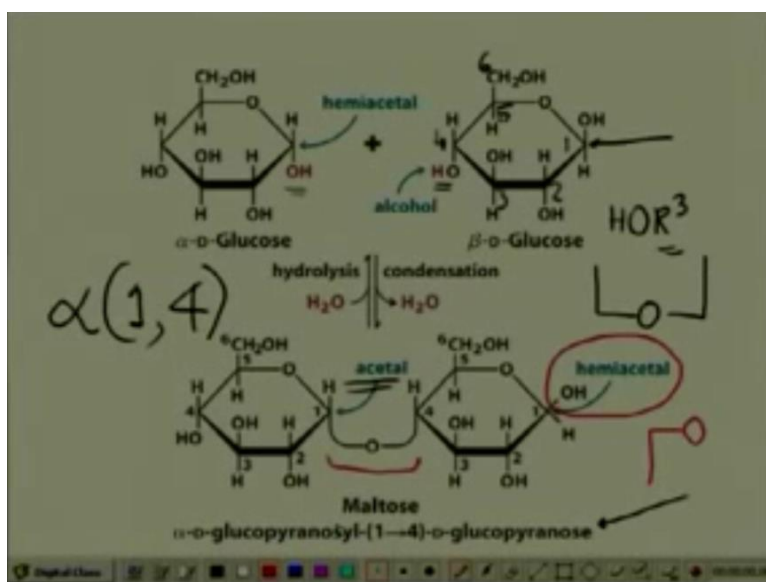
The OH is Trans to the CH₂OH. So, this is alpha D- glucose. The one on the right here is beta D- glucose why? because the OH is cis to the CH₂OH. This is a hemiacetal. It still can react with what I showed in the first diagram here where we have an R₃OH. So what is our R₃OH?

(Refer Slide Time: 16:27)



This is our R₃OH. Which OH is this? This is the OH on the 4th carbon atom of another glucose moiety, another monosaccharide. So, what can it then form? It can form an acetal. So, initially we had the straight chain which actually linked these 2 units up together to form an hemiacetal. Once the hemiacetal was formed, this is now linking with another monosaccharide unit to form an acetal. So, that's exactly what is happening here.

(Refer Slide Time: 17:10)



We have alpha D- glucose, the hemiacetal which is linking with, what number carbon is this? It's carbon number 4. This is carbon number 1, 2, 3, and 4. Let us get this straight here. What is this carbon number? It's 1. This is carbon number 1. This is carbon number 2. This is carbon number 3. This is carbon number 4. This is carbon number 5. And that's carbon number 6.

So, what is that we are linking? We are linking this one, which is a hemiacetal with the OH here. So, we have HOR₃. What is R₃, R₃ in the rest of the molecule? So, this is our hemiacetal now that is going to link with this alcohol to form an alpha (1, 4) linkage. Why alpha? That's because this is alpha. So what is it going to look like? It is going to look like this. It has to come down, why? because it's alpha and depending on the OH orientation of the C4 carbon this is going to be up or down. In this case, it is up.

So, what we have is, we had our glucose. It has cyclized to form the hemiacetal. We are now linking it with another monosaccharide moiety to form a disaccharide. The linkage is glycosidic linkage because we are linking sugars. It is an O glycosidic linkage, because the linkage is between the sugars by oxygen. The linkage to the sugar is by the oxygen. So, this is

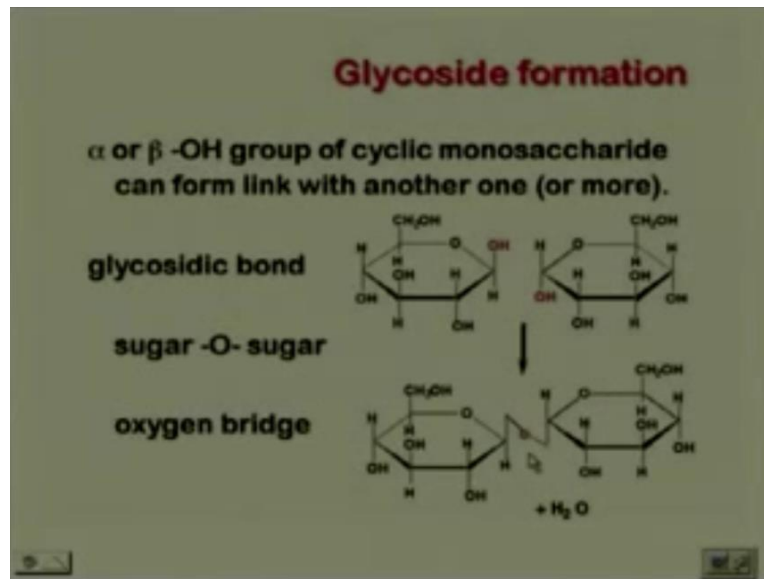
an O- glycosidic linkage. We are linking the alpha of carbon number 1 to the 4th carbon of the other one. It does not matter whether this is an alpha or a beta.

The alpha comes from what is the first one that you are considering. This is alpha, carbon number 1. So, this linkage is an alpha (1, 4) linkage. What it is linking? It is linking, this is the actual nomenclature where you have alpha D- glucopyranosyl- (1, 4)- D- glucopyranose. What is it formed now? It has formed an acetal. This is the R3 moiety. This is our R3 part and this is the OH part. It has now formed an acetal. This is now hemiacetal. What can happen? This can link with another sugar. So, we can have a polysaccharide.

So, this is the formation of a disaccharide and we are going to look at specific linkages because if this name is given to you, you should be able to draw the structure of the disaccharide formed because you know the structure of glucose. You know that if you have 2 glucopyranose units, it means you have 2 glucose units and if the linkage is alpha (1 4), it forms maltose. So we have alpha- D- glucose linked with beta D- glucose.

In this case it's beta, why? because it's the cis that has nothing to do with the linkage that we are concerned with here. When this is going to react with the next R3OH or next ROH, what is the linkage going to be? It is going to be a beta linkage, because the OH in this case of the hemiacetal is up. So, the linkage is going to be something like this and we don't know what is going to be the other one. So it could be either up or down. But, this is beta. This is alpha. This is about the glycosidic linkages and the formation of disaccharides. Let us look at a few more.

(Refer Slide Time: 22:46)



So, what do we have? We have this going up. So, what is this? It's beta. It is linking with the 4th carbon. Is this the 4th carbon? This is O and this is 1, 2, 3, 4, 5, and 6. So what linkage is this? It is a beta (1, 1). So, we have to be careful at what we link because now you formed a completely different disaccharide. So, because you have to know that the numbering, this CH₂OH is number 6. So, 6, 5, 4, 3, 2, and 1. And this is number 1, which is going up. So it's beta. So it's a beta (1, 1) O- glycosidic linkage because we have the oxygen bridge there. That's exactly what is happening in the glycoside formation. Now Let us look at some examples.

(Refer Slide Time: 24:04)

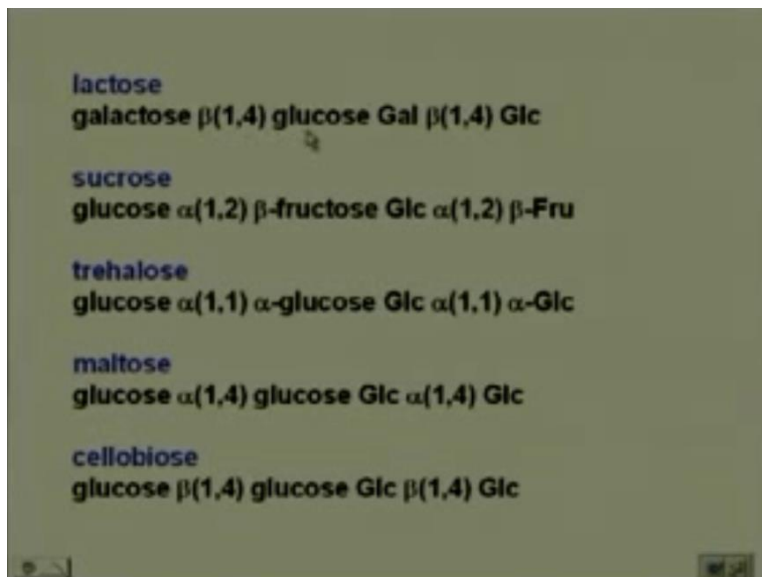
If the alcohol linked to an anomeric carbon is another carbohydrate (monosaccharide), then the resulting compound is a disaccharide.

The name of the glycoside specifies the two monosaccharides and the glycosidic linkage – which carbons are linked, and the configuration about the anomeric carbon (α or β).

So, let us look at the rules first. If the alcohol linked to anomeric carbon is another carbohydrate, then obviously the resulting compound is a disaccharide because we have 2 monosaccharide units. The name of the glycoside specifies the 2 monosaccharides and the

glycosidic linkage which carbons are linked and the configuration about the anomeric carbon, the alpha or the beta. So, we have either the alpha or the beta and we have to figure out what it is linking to or which carbon it is linking to.

(Refer Slide Time: 24:40)

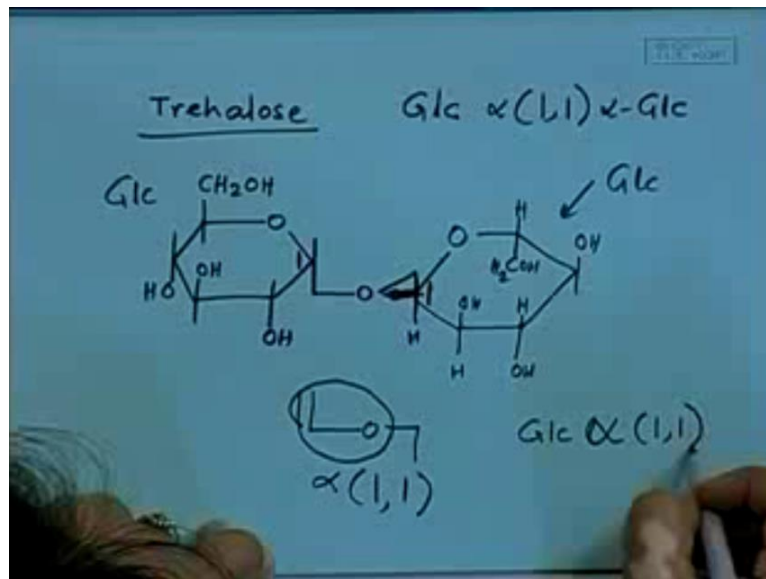


lactose	galactose $\beta(1,4)$ glucose Gal $\beta(1,4)$ Glc
sucrose	glucose $\alpha(1,2)$ β -fructose Glc $\alpha(1,2)$ β -Fru
trehalose	glucose $\alpha(1,1)$ α -glucose Glc $\alpha(1,1)$ α -Glc
maltose	glucose $\alpha(1,4)$ glucose Glc $\alpha(1,4)$ Glc
cellobiose	glucose $\beta(1,4)$ glucose Glc $\beta(1,4)$ Glc

Now these are some examples. Lactose is galactose beta (1, 4) glucose. So, what do we need to know for this? We need to know the structure of galactose, we need to know the beta anomer of galactose and the structure of glucose. And, then this is the way it is written in short form, Galactose beta (1, 4) Glucose. That is lactose. If we look at sucrose, it is Glucose alpha (1, 2) Beta-Fructose. All of you know what sucrose is.

So, you can check and see whether this is the right way to write it. So, we have Glc alpha (1, 2) beta- Fru. If we looked at trehalose it is glucose alpha (1, 1) alpha- glucose. Maltose is the one that I showed you previously, where we have glucose alpha (1, 4) glucose. That's what I have shown while looking at the acetal and hemiacetal. We have cellobiose. Let us do just one of these structures. Let us do trehalose because it's both glucose units and we already looked at maltose.

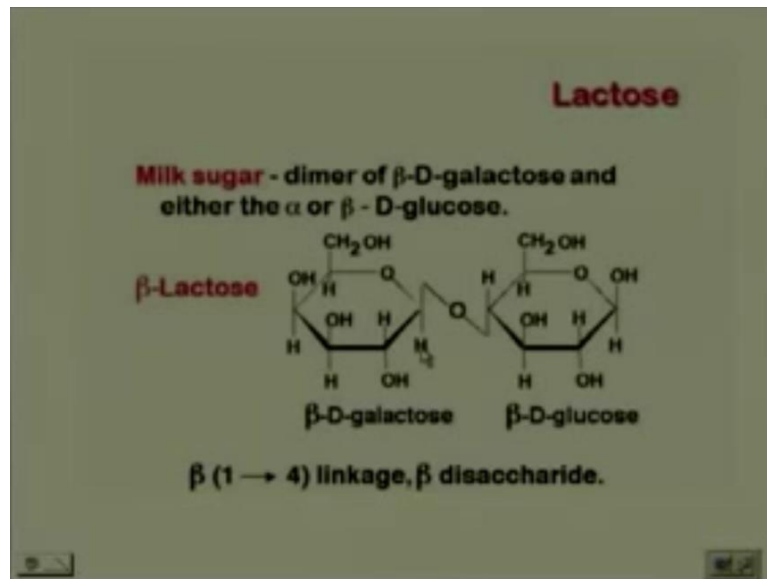
(Refer Slide Time: 25:54)



What is this? This is glucose alpha (1, 1) alpha- glucose which means that the other glucose is also an alpha. So, this is what I have when I write this. How will I write the O? It's down. now, what happens to the other one? How do I write this? Now, I have it linked to number 1. Where my oxygen has to be? It has to be here. And where is my CH₂OH? It is here. It has to be linked like that.

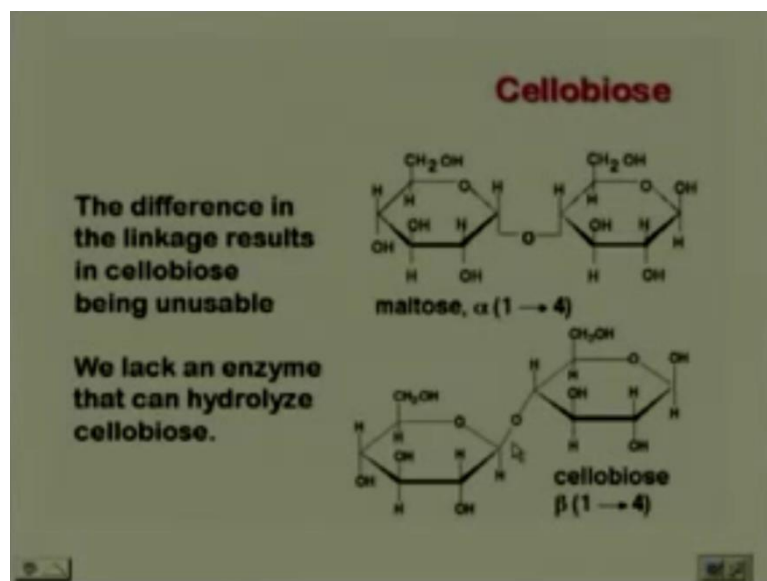
Actually, the link is like this. I could not draw it correctly here. But that is what your structure is going to look like where the H is going to be here. So, what do we have here? What does this signify? That's alpha. It is carbon number 1. This is carbon number 1. These 2 units are glucose and glucose. So, it is glucose alpha (1, 1). That gives rise to trehalose. If we look at the monosaccharaides and disaccharides we have here, we have lactose, sucrose, trehalose, maltose and cellobiose.

(Refer Slide Time: 28:33)



This is lactose then. What is the linkage? Let us just look at the linkages now. Try not to look at the answer. This is the 6th carbon, this is the 5th carbon and that is the 4th one. So, it is beta (1, 4) linkage. It is linking galactose and glucose that is lactose. So, it is the dimer of Beta- D- galactose and either the alpha or beta- D- glucose. So, this OH could be either up or down because it is linking either the alpha or beta- D- glucose. So we have beta (1 4).

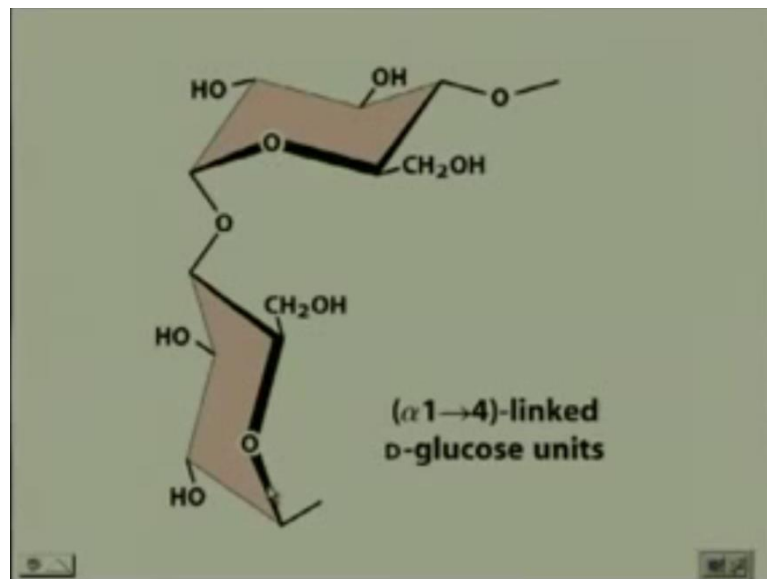
(Refer Slide Time: 29:25)



In cellobiose, we have, this is also beta (1 4). What is this? It is alpha (1 4). This is maltose and this is the first example that I showed you. Now just because this linkage is different, we have an enzyme that can break this disaccharide down but we do not have an enzyme that can break this disaccharide down. It is that specific, all the enzymes that break down sugars, which we will see later on. We have an enzyme that can break maltose but not an enzyme

that can break cellobiose. The only difference is that this is the beta 1 4 linkages and this is the alpha 1 4 linkages.

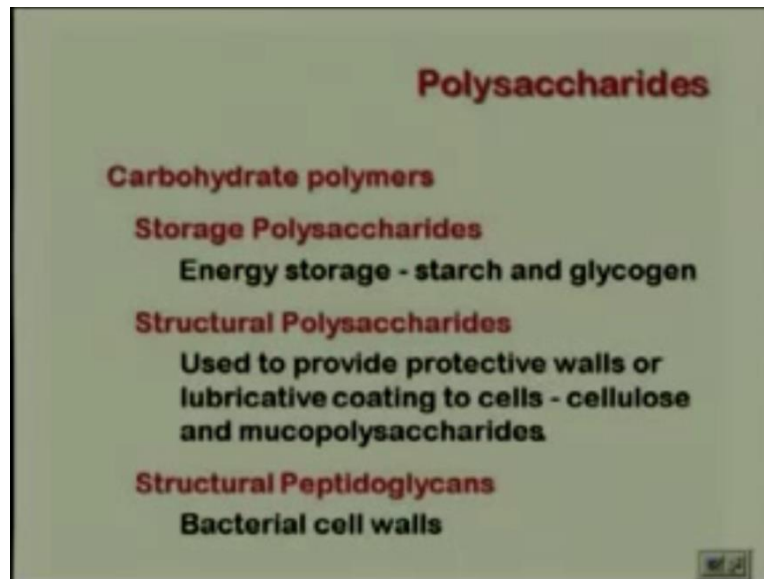
(Refer Slide Time: 30:18)



This is what it actually would look like if you were to actually draw it correctly. This would be alpha 1 4 linked D-glucose units. So what can we have? We can have other units linked together. So, the whole structural aspects come into the picture now, as to because we are actually not going to have those projections that we are drawing but we are going to have the actual chair conformations.

Now, when we have the chair conformations and we know that we have equatorial and axial bonds then obviously we are going to have linkages that are going to result in different structural aspects to the whole disaccharides and polysaccharides. That's why each of them is going to behave in a different structural fashion. Depending on the linkage it could be starch or glycogen or amylose or amylopectin and whatever, that's what we are going to look at.

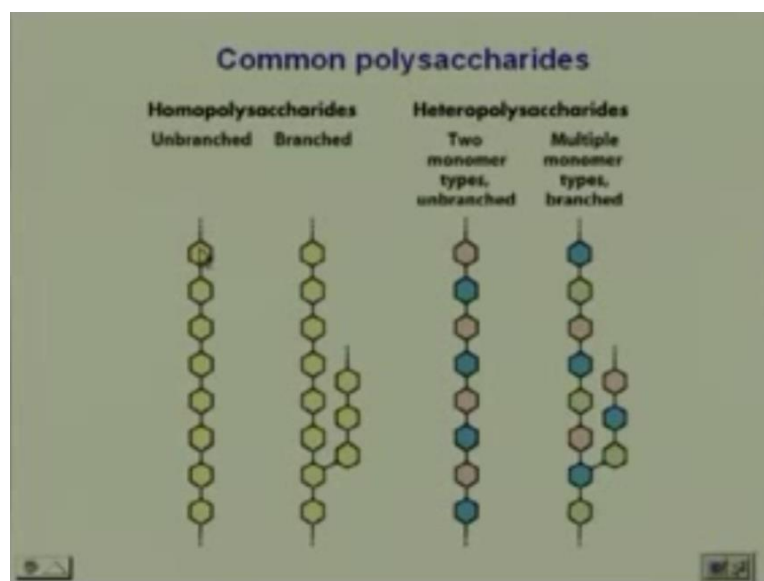
(Refer Slide Time: 31:15)



The polysaccharides therefore will be of further linkages of what we just learnt. So, not only will we have alpha 1 4 we could have alpha 1 4, alpha 1 4, alpha 1 4, beta 1 4 and so on and so forth. These polysaccharides are just therefore polymers of the monosaccharaides and they could be storage type. The storage types are starch and glycogen. They could be structural, where they are used to provide protective walls or lubricative coating to the cells.

This is like cellulose and muco polysaccharides. We will see example of each of these as we go along. You also have structural peptidoglycans that actually form bacterial cell walls. And what did we learn when we did the lysosine structure? That it breaks bacterial cell walls.

(Refer Slide Time: 32:15)

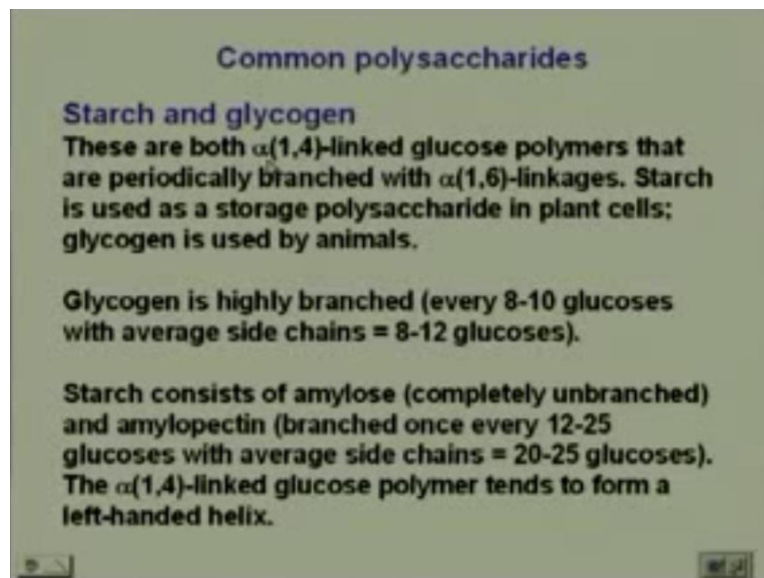


So, we can have polysaccharides that look like this. So, these would be just normal linkages 6 member rings. You could have homopolysaccharides where all the sugars are the same. You

could have them unbranched or you could have them branched. So you have, say an alpha 1 4 linkage here and say a 1 6 linkages here or a 2 6 linkages there, which would form a branch to it? You could have heteropolysaccharides where the monomer types are different. You could also have them unbranched or branched.

So, these are basically 4 types of polysaccharides that you could actually have. 2 types of homopolysaccharides and 2 types of heteropolysaccharides meaning they could be unbranched or branched. And each of the monomer units that we studied in the last class and this class in the disaccharide formation will come for all the polysaccharides possible. So, what are these types?

(Refer Slide Time: 33:19)



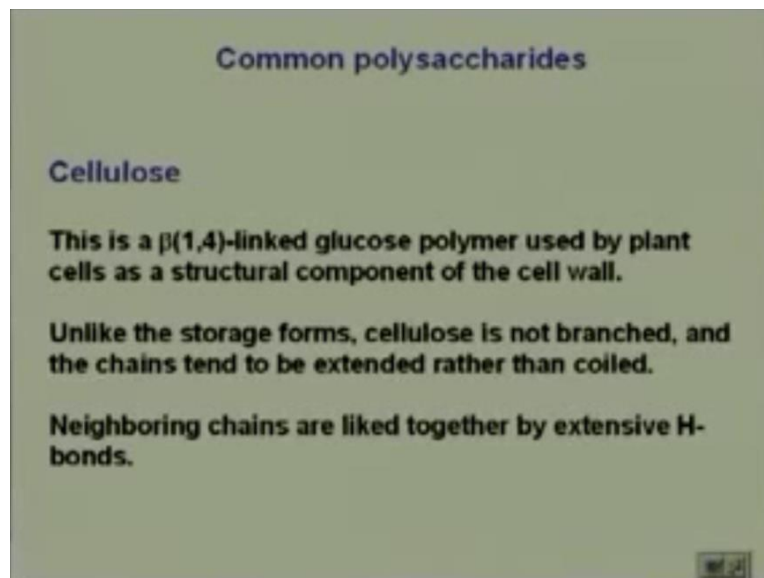
Starch and glycogen are both alpha (1, 4) linked glucose polymers. You now know what that means. Alpha (1,4) linked glucose polymers. So it's glucose alpha (1, 4) and another glucose that are periodically branched with alpha (1, 6) linkages. So, you have alpha (1, 4) and you can also have alpha (1, 6) that is going to basically make it a branched homopolysaccharides because you have the same monosaccharide unit.

Glycogen is highly branched every 8-10 glucoses with average side chains of 8-12 glucoses. Means, in the previous picture, if you look, you have 8-10 here and 8-12 branched on another set. So, you have all of it linked together basically and you realize that is good to form such a compact unit, why? because they are storage polysaccharides. You don't want them to take a lot of space.

You would rather want the storage polysaccharides to be compact which is why starch actually form granules. For storage purposes it is more convenient to have these. Now, we will look at the structure in a bit more detail. Starch consists of amylose that is completely unbranched and amylopectin that is branched once every 12-25 glucoses. So, an unbranched polysaccharide is a homopolysaccharide, why? Because, it has same units.

An example of unbranched homopolysaccharide is amylose and these are the examples of branched one. Then, the alpha (1, 4) linked glucose polymer units in amylopectin actually forms something that looks like a helix, because they are linked like this. I'll show you in a picture.

(Refer Slide Time: 35:50)



In cellulose you have a beta (1, 4) linked polymer that is used by plant cells. Unlike the storage forms which I was mentioning cellulose is not branched because it would not be useful to have something fibrous that is going to be a structural polysaccharide to be compact. So, if it is fibrous it has to be a long chain. It cannot form a unit. Then the neighboring chains are linked together by hydrogen bonds.

(Refer Slide Time: 36:30)

Common polysaccharides

Chitin

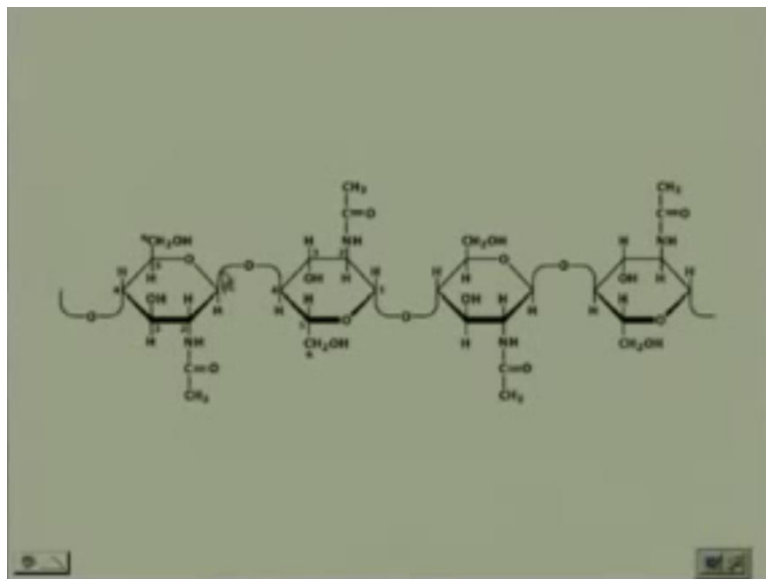
Similar to cellulose, except that the repeating unit is β -N-acetyl-glucosamine. This functions as the main component of arthropod exoskeletons.

Hyaluronic acid

A major component of mucus, it is a heteropolymer of glucuronic acid and N-acetyl-glucosamine. The linkages are Glucuronate β (1,3) GlcNac and GlcNac β (1,4) Glucuronate.

Then we have other examples which I am not going to go into, but basically we have chitin and hyaluronic acid, which actually have linkages of that N-acetyl-glucosamine. If you remember we did N-acetyl-glucosamine and N-acetyl-muramate, the NAG and the NAM when we consider the lysozyme cleavage of how it actually could cleave. This is basically where it is going to work.

(Refer Slide Time: 36:59)



This is what it actually looks like. What sort of a linkage is this? It is beta (1, 4) and this is a N-glycosidic. This is CH_2OH which is 6. If you get confused from where one begins from, go to CH_2OH . This is 6, 5, 4. So it is (1, 4) linkage. This is what an N-acetyl is. This is an example of an N-acetyl. You look at the ends. What are they? So what is this? This is actually a glucosamine. There's no OH there.

What is it? It is NH₂ that has been acetylated. So it is a glucosamine and this is the beta (1, 4) linkage of a glucosamine. So what is it?

(Refer Slide Time: 38:09)

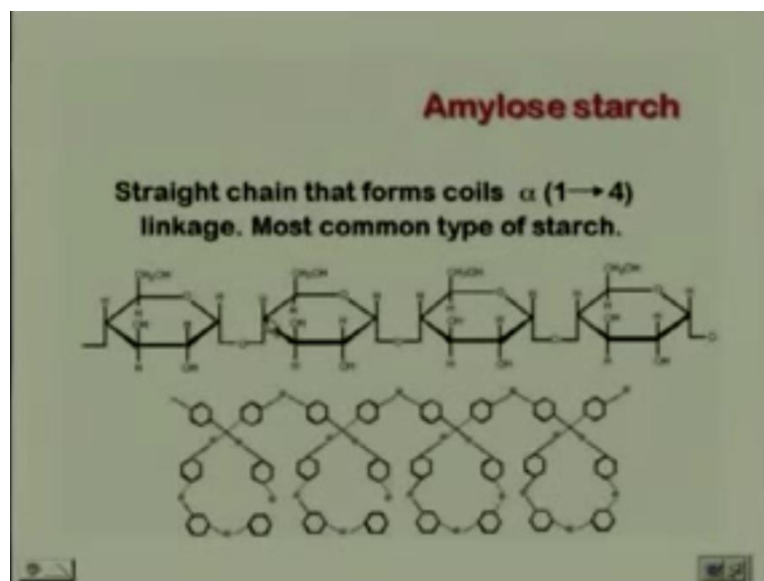
Common polysaccharides

Chitin
Similar to cellulose, except that the repeating unit is β -N-acetyl-glucosamine. This functions as the main component of arthropod exoskeletons.

Hyaluronic acid
A major component of mucus, it is a heteropolymer of glucuronic acid and N-acetyl-glucosamine. The linkages are Glucuronate β (1,3) GlcNac and GlcNac β (1,4) Glucuronate.

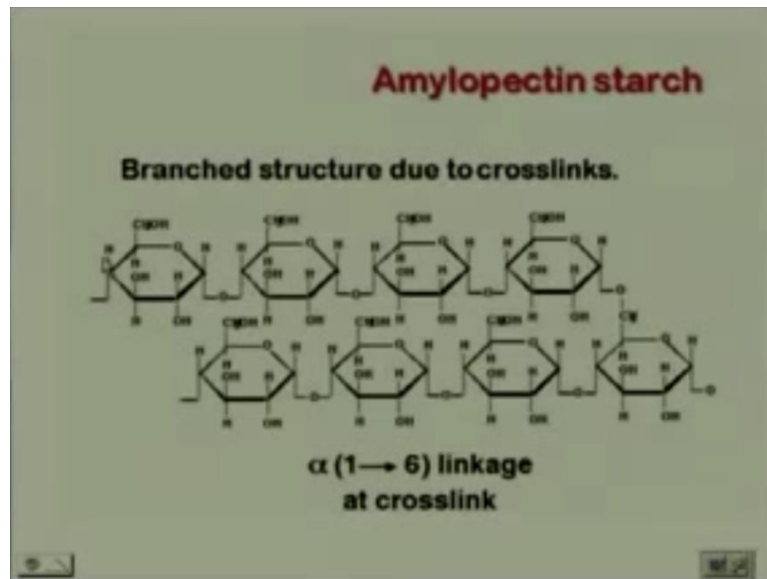
You have Beta-N-acetyl-glucosamine. So, you now know what it looks like. It is a glucose which had an OH chain to an amine, which is acetylated that is linked by a beta linkage.

(Refer Slide Time: 38:27)



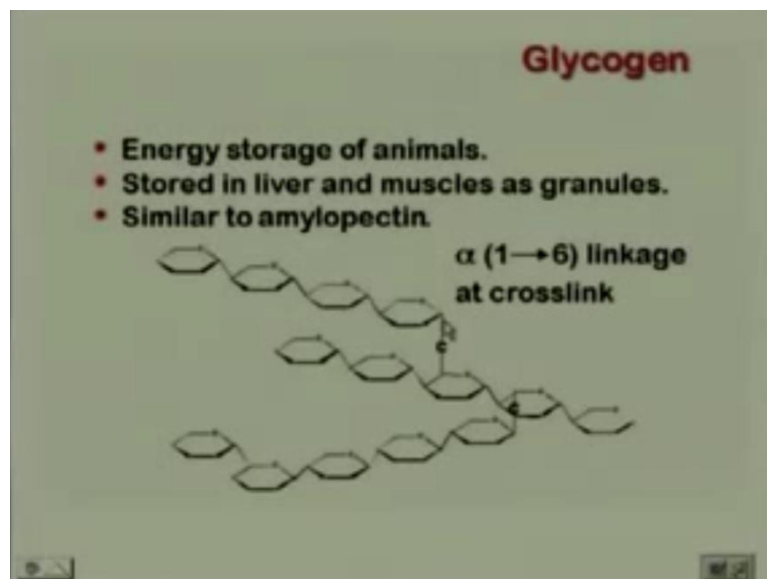
This is basically what we have here. What is this now? It is alpha (1 4) one after the other then suddenly you have some (1, 6). So you see how it looks like a circle like that. So you have like a helix structure. This is amylose starch. What you need to know is how you can actually form these linkages, an alpha (1, 4) linkage. So if you know that the straight chain forms alpha (1, 4) linkages and then branch of to form (1, 6) it looks like that.

(Refer Slide Time: 39:02)



If you look at amylopectin you have, what is this linkage? It is beta (1 4). Where is the crosslink? It is here, no that is not the crosslink. Where is the crosslink? The alpha (1 6) linkage is supposed to be the crosslink. So where will be my crosslink? It will be this. It is the 6 and that will be the sixth one.

(Refer Slide Time: 39:39)

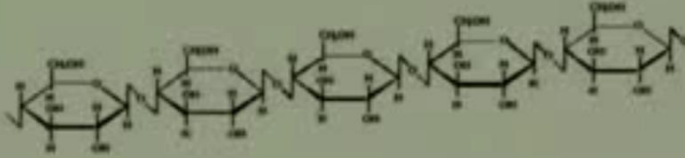


These are basically the different types. Here again you have glycogen that looks like this and what we have to remember is when you are looking at the storage polysaccharides they are stored as granules. That is why they have to be branched polysaccharides. That is an important feature of branched polysaccharides.

(Refer Slide Time: 39:58)

Cellulose

- Most abundant polysaccharide.
- β (1 $\rightarrow$ 4) glycosidic linkages.
- Result in long fibers - for plant structure.



The diagram illustrates the chemical structure of cellulose, a linear polysaccharide composed of glucose units. Each glucose unit is in its cyclic Haworth projection. The units are connected by β (1 $\rightarrow$ 4) glycosidic linkages, where the C1 of one glucose unit is linked to the C4 of the next glucose unit. This results in a long, unbranched chain of fibers.

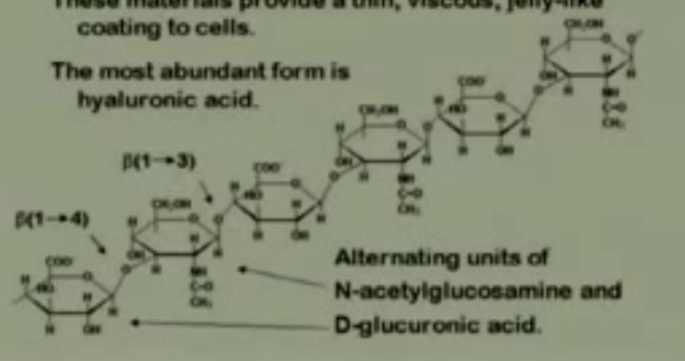
Again, we have cellulose. Cellulose does not have to be branched. In fact, it should not be branched. It should be long fibrous for the plant structure. So, this is basically the most abundant polysaccharide and this is beta (1 4).

(Refer Slide Time: 40:19)

Mucopolysaccharides

These materials provide a thin, viscous, jelly-like coating to cells.

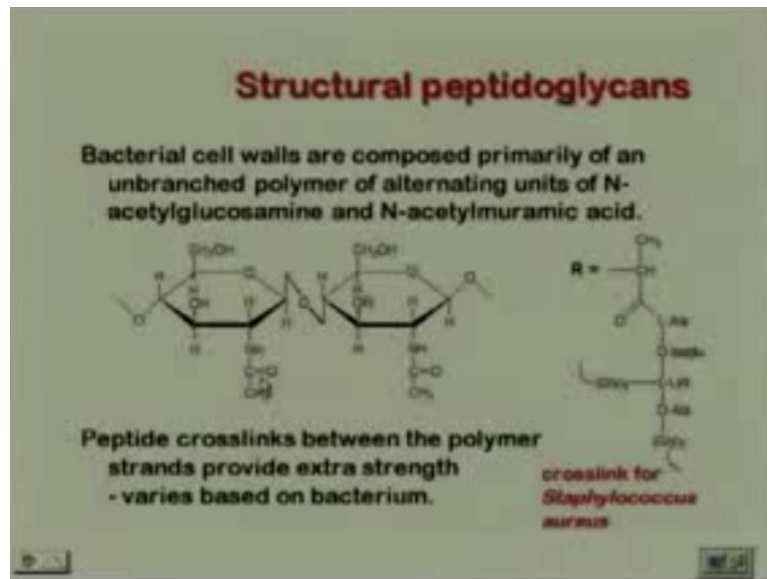
The most abundant form is hyaluronic acid.



The diagram shows the chemical structure of mucopolysaccharides, specifically hyaluronic acid. It consists of alternating units of N-acetylglucosamine (NAG) and D-glucuronic acid (GlcA). The NAG units are linked to the GlcA units via β (1 $\rightarrow$ 3) glycosidic linkages, while the GlcA units are linked to the next NAG unit via β (1 $\rightarrow$ 4) glycosidic linkages. The GlcA units have a carboxylate group (COO-) at the C6 position instead of a hydroxymethyl group (CH₂OH).

Then, we have mucopolysaccharides. What do we have, what is this? The unit is NHCOCH₃ N-acetylglucosamine and this is glucuronic acid. What do we mean by glucuronic acid? This is not CH₂OH anymore. It is COO-. So, we have N-acetylglucosamine and glucuronic acid, which is what formed in the felling's reaction also. You have COO- instead of CH₂OH at position number 6.

(Refer Slide Time: 40:58)

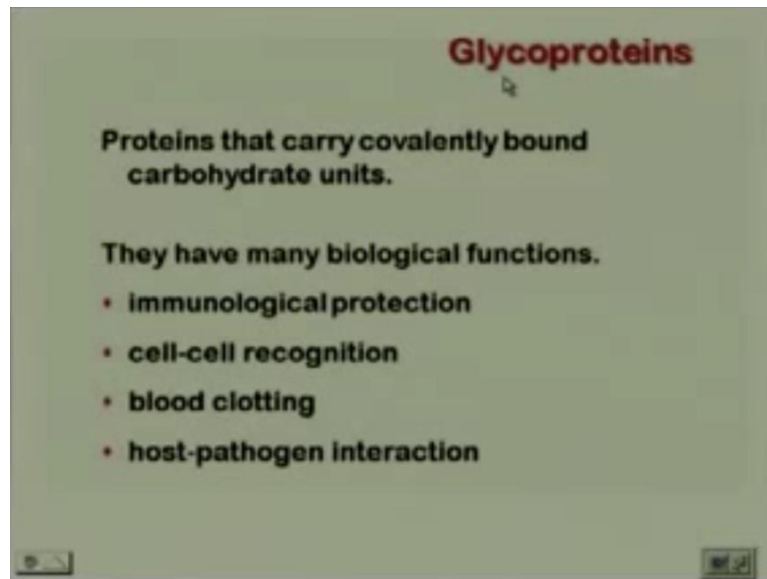


This is probably something we should be looking at, where we have peptide crosslinks between the polymer strands. Now, the reason we have peptide crosslinks is, we have seen it in bacterial cell walls when I was just mentioning about lysozyme. We had alternating units of N-acetylglucosamine and N-acetylmuramic acid. Remember we have muramate and glucosamine.

So what we have is, in between these units where we have an R group, this is the R group. This R group is some alanine, lysine. So, it has a peptide unit to it. Now, because of this peptide unit, it imparts structural rigidity to the cell wall. So, it's nothing but having some peptide crosslinks. Apart from the normal polysaccharide crosslinks if you have additional peptide crosslinks there is going to be extra strength to the bacterium because you don't want it to be broken down.

The bacterial obviously doesn't want its cell wall to be broken down. So, it has extra crosslinks.

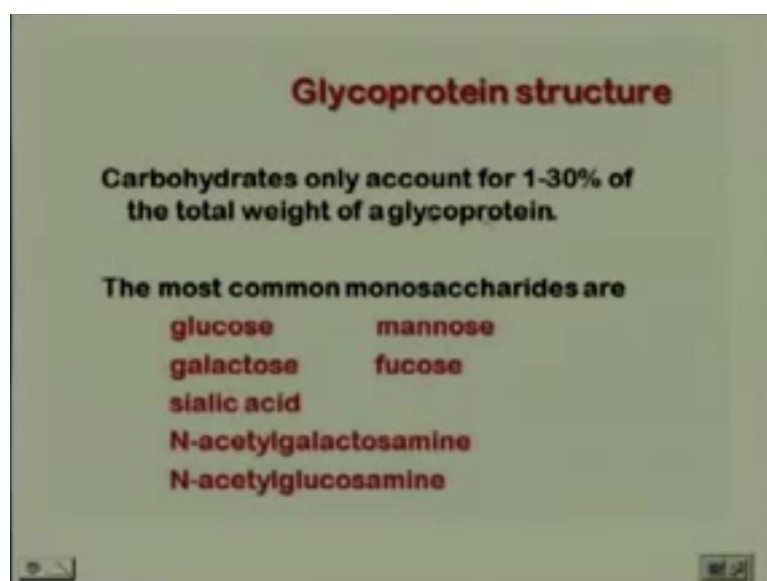
(Refer Slide Time: 42:13)



Now we've been speaking about glycoproteins, when we considered lipids and membranes. Now, these glycoproteins are the proteins that have linked to them covalently sugar units. Now, we are going to see where or what these sugar units are and how they are linked to the proteins because we now know the protein structure. We know the amino acids and proteins. We know the monosaccharides now.

We know something about the carbohydrates now. So, what we are going to look is how they are linked together. These glycoproteins have important biological functions. These are some of the functions that are listed here. They are immunological protection, cell-cell recognition and blood clotting and host-pathogen interactions.

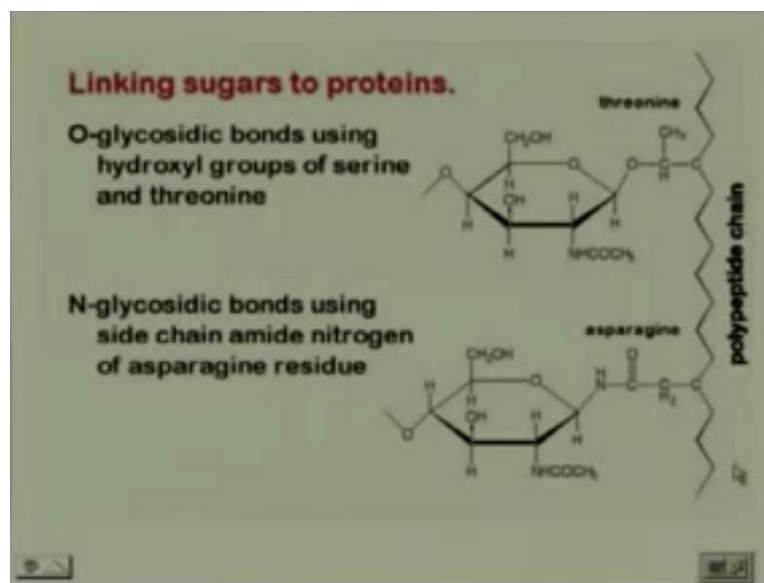
(Refer Slide Time: 43:09)



So, usually the carbohydrates account for only 1 - 30% of the total weight of a glycoprotein. And the most common monosaccharides that actually link up are glucose, galactose, mannose, NAG and NAM. This is N-acetylgalactosamine and N-acetylglucosamine and we also have muramase, sialic acid. These are all the monosaccharides that link with the proteins. But where do they link? It means they have to link to specific amino acids.

If they are to be formed, if they have to be glycoproteins, it means there has to be a sugar unit that is linked to the protein. So what is it linked by?

(Refer Slide Time: 43:52)



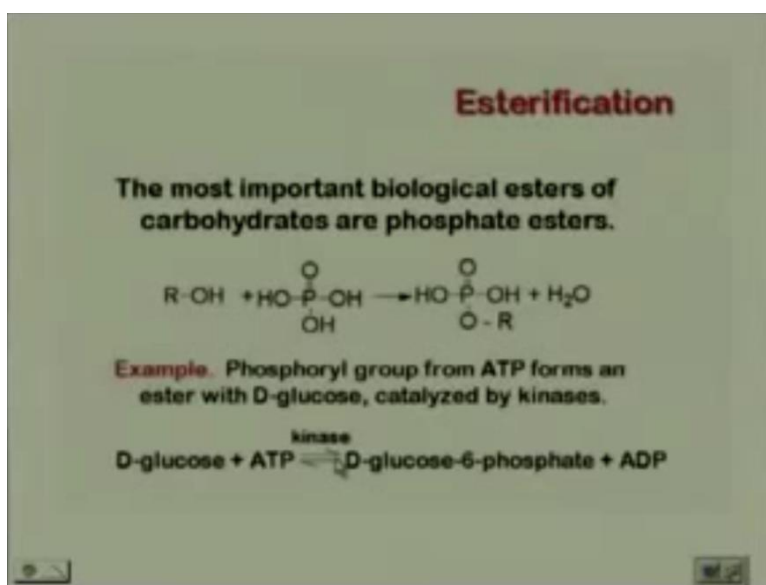
If this is our polypeptide chain, there are different ways in which these sugars can actually link. We learnt about O- glycosidic bonds. What are O- glycosidic bonds? Glycosidic bonds that use the oxygen to link. Now, in the case of serine and threonine we know what their side chains are. Serine is OH and threonine is CH₃ and OH. If we have the linking of the sugar to the proteins this is the polypeptide chain, where we have threonine.

This is the CH₃ of the threonine and this is the OH. This OH has linked with the saccharide unit. It is an N- acetylglucosamine and what does it form. If this is a part of the polypeptide chain as soon as it links up the monosaccharide unit to it, it forms a glycoprotein. And this again you can realize that this can be linked further. So, these are all the carbohydrate units that we had when we looked at glycoproteins in the lipid membrane, the fluid mosaic model for the membrane.

When we are forming N- glycosidic bonds we are using the side chain amide nitrogen. Which 2 amino acids have amides? Asparagine and glutamine. So, now we have to remember that when we are forming a glycoprotein all we were doing is we are linking the sugar to the protein. Now, this sugar has to be linked to the polypeptide chain through amino acids, because that's what is forming the polypeptide chain.

So, when we form these glycoproteins, it is the threonine OH that can link to form a O- glycosidic linkage or it is the amide N nitrogen that can form a N- glycosidic linkage.

(Refer Slide Time: 46:20)

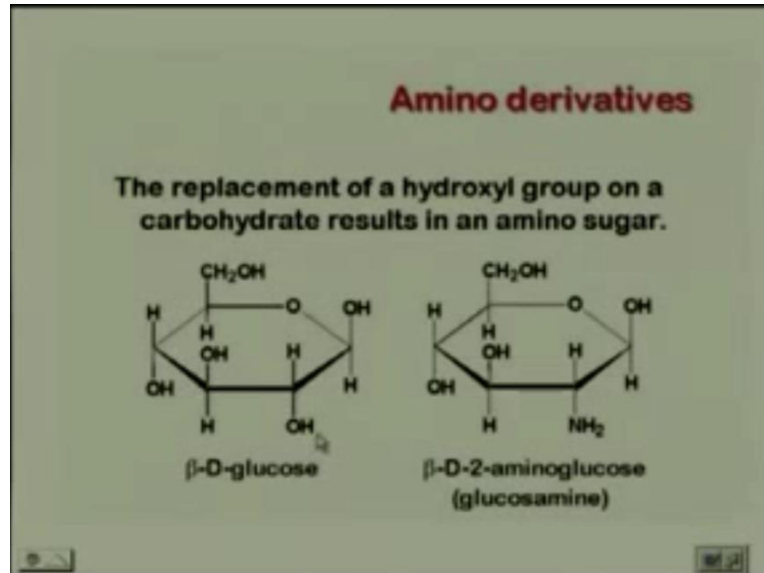


Then we can have esterification, which is probably one of the most important biological esters that are formed, where we have a specific enzyme. Remember I mentioned kinases as being a type of transferase. We have 6 different types of enzymes. Of those enzymes there was one enzyme called transferase. It is one type of enzyme. But, when we have a kinase, it is a specific type of transferase that transfers phosphate moieties.

We are going to see a lot of these kinase when we are doing bioenergetics. But for now, we have an ROH. This OH can be part of a monosaccharide unit. The OH that we have here can be part of monosaccharide unit. In that case, what do we have here? We have phosphoric acid and we have the formation of a phosphate ester and H₂O. When we look at a biological system, the formation of a biological ester then the phosphorile group from ATP the structure of which we are going to study in a bit detail when we get to it.

The ATP then will form an ester with D- glucose into forming glucose-6- phosphate, which is the first step in the breakdown of glucose. So, we have glucose-6- phosphate and adenosine diphosphate, because it lost 1 phosphate to the glucose. So, this is one sort of reaction.

(Refer Slide Time: 48:11)



These are the amine derivatives which we mentioned before. What are these amino derivatives? This is a beta glucose, you now recognize because the OH and CH₂OH on the same side. We have beta D- glucose and this is beta D- 2- amino glucose which is a glucosamine. It is the OH of carbon number 2 that has been replaced. This is why we have the 2 here. The 2 amino glucose.

So, we have the beta- D- glucose that forms the Beta-D- amino glucosamine and this can further be acetylated to form NHCOCH₃. These are basically the different types of reactions we can have.

(Refer Slide Time: 49:11)

Uses for amino sugars.

Structural components of bacterial cell walls.

As a component of chitin, a polymer found in the exoskeleton of insects and crustaceans.

A major structural unit of chondroitin sulfate - a component of cartilage.

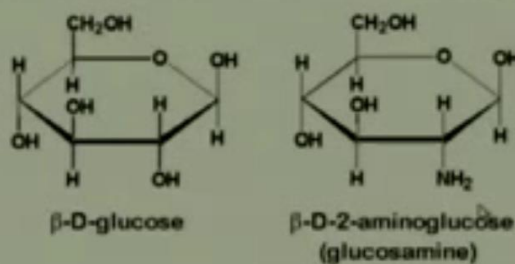
Component of glycoprotein and glycolipids.

Now the uses for these amino sugars actually are for the structural components of the bacterial cell walls, where again we looked at the NAG and the NAM. As a component of chitin which is a polymer found in the exoskeleton of insects and crustaceans. So, this is another amino sugar. Now, the formation of amino sugar is actually important in giving it a structural rigidity. So, that's why it is a sort of a hard shell that is found.

(Refer Slide Time: 49:57)

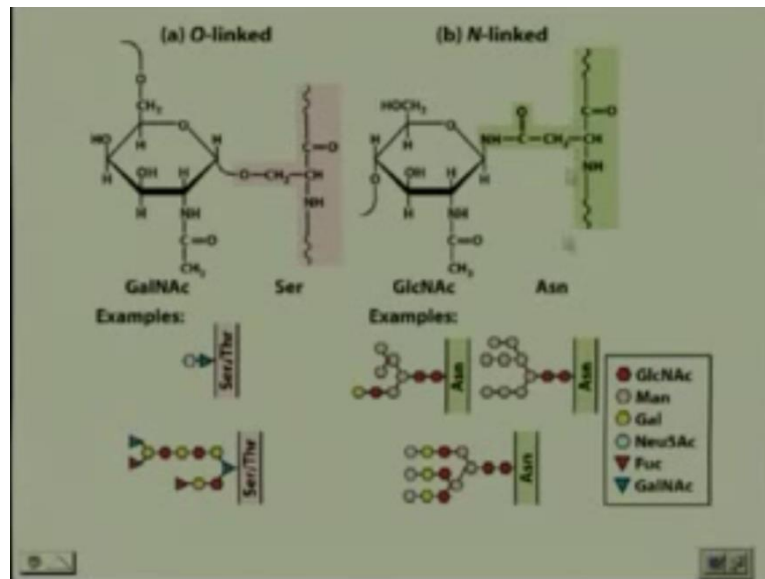
Amino derivatives

The replacement of a hydroxyl group on a carbohydrate results in an amino sugar.



So basically what happens is we have NH₂ group here. We have NH₂ that links with an acetyl group, the NHCOH₃ and so on and so forth forming the different possible chains that we can have.

(Refer Slide Time: 50:07)



So, we have different types of oxygen linked and nitrogen linked amino acids or basically glycoproteins. What are these? When they are linked or when they are O-linked, they are linked through either serine or threonine. What are you linking? In this case, if I say GalNAC, what does it mean? It is N-acetyl galactose. If you know the structure of the galactose, the usual N acetylation is at position 2.

We form originally NH_2 which is the glucosamine or galactosamine in this case. If you have galactosamine that is acetylated you have galactose N acetylated that is linked to the serine of the peptide chain. So, what does this form? It forms a glycoprotein. So, we can have a serine threonine linked basically. We can have different functionalities and different types of groups and so on and so forth. What do we see in the N-linked case?

This is again glucose N acetylated. So, it is N acetylated glucose that is nitrogen linked, so it means that the amino acid that it is linking to is an asparagine. Usually, it is asparagine and sometimes it can be glutamine. But in this case, we are going to have an N linked and in this case we are going to have an O linked. In conclusion, what we studied was we looked at all the monosaccharide units then we looked at the ways we could form the disaccharides.

What are these ways? We have specific alpha and beta linkages and glycosidic linkages that we could use to link the monosaccharide units together. Then obviously if you can link 2 units, you can link multiple units together. We can have homopolysaccharides, we can have heteropolysaccharides and they can be branched or unbranched and depending on how they are utilized or what their actual functions are, they are either cross linked or not cross linked.

For example, when we have storage polysaccharides like starch and glycogen, they are most likely to be cross linked. But, if we have cellulose, then it's unlikely to be cross linked because it would like to be a fiber for structural strength. And then we later went on to look at glycoproteins to see how the glycogen or the sugar units are actually linked to the proteins. They can be linked to the serine or the threonine via the oxygen, where they are O linked.

They could be linked to asparagine, where they are N linked. So that completes our lesson on carbohydrate. We will next do vitamins and coenzymes. Thank you.