Biochemistry –I
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Lecture #17
Carbohydrates II

We have come to our next lecture on carbohydrates. We will be looking at the formation of disaccharide sand the formation of polysaccharides. 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. We learnt in the last class that carbohydrates have the general formula $(CH_2O)_n$. This is something you have studied from probably your school where you know what are starches and cellulose. What we are going to look at now, what is the specific monosaccharide that forms starch, what are the linkages that result in the formation of starch and in the formation of the other polysaccharides and why there will be certain enzymes that do not work for us humans but work animals.

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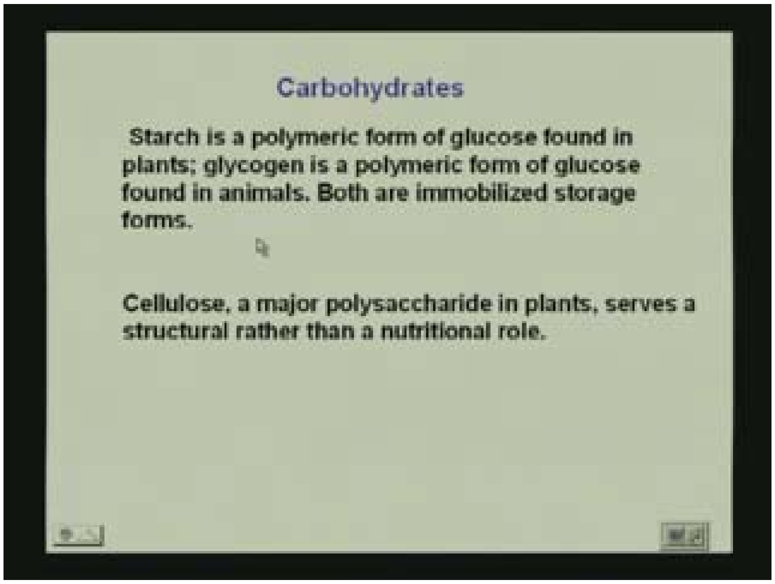

Carbohydrates

Starch is a polymeric form of glucose found in plants; glycogen is a polymeric form of glucose found in animals. Both are immobilized storage forms.

Cellulose, a major polysaccharide in plants, serves a structural rather than a nutritional role.

We have starch that is nothing but a polymeric form of glucose found in plants and glycogen is a polymeric form of glucose that is found in animals. You understand now that 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. How these monosaccharide units are linked with one an other and these are both immobilized. Glycogen is stored in our liver and it is broken down when we require. The glucose breakdown is for metabolism for the energy requirement of our activities. Cellulose is other major polysaccharide in plants that serves rather to be a structural than a nutritional role.

Structure means it forms fibers that helps in its structural build up. What we have here is certain types of bonds that we are actually going to be looking at glycosidic bonds are those bonds that link sugars to one an other. When we consider such as glucose linking with another glucose moiety or glucose linking with galactose or mannose 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 an other in disaccharides 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 N-glycosidic bonds, we know that the nitrogen is involving in the linkage and when you have glycosidic it means that there is a sugar involved. We have nitrogen and sugar. These are the bonds that link sugar 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 ribose sugar to it.

We know the ribose sugar itself contain only carbon, hydrogen and oxygen in the carbohydrate unit. If we have the purines and pyrimidines are actually nitrogen is bases linked to the ribose or the deoxyribose, there is specific N-glycosidic bond linkage that comes into play. When we have O-glycosidic bonds we are basically forming a disaccharide because we have two monosaccharide units linked by an O-glycosidic bond that is going to form a disaccharide.

Similarly, we will have another set of linkages that is 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 the 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.

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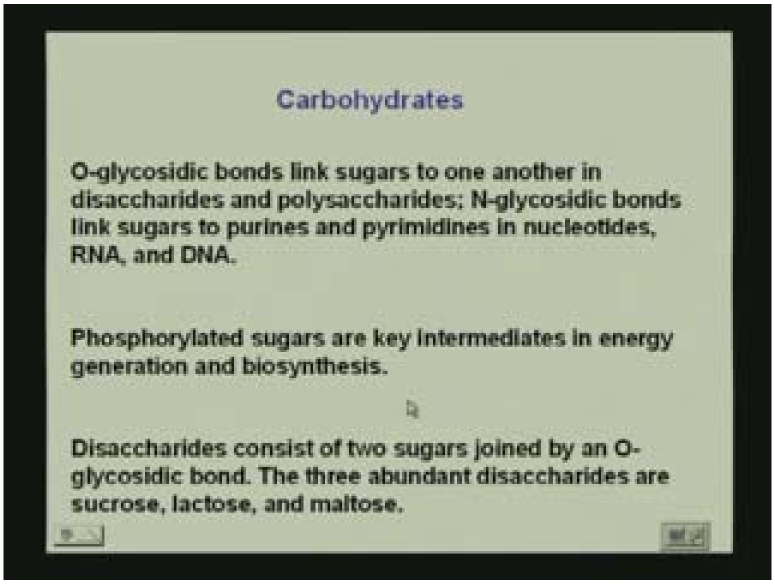

Carbohydrates

O-glycosidic bonds link sugars to one another in disaccharides and polysaccharides; N-glycosidic bonds link sugars to purines and pyrimidines in nucleotides, RNA, and DNA.

Phosphorylated sugars are key intermediates in energy generation and biosynthesis.

Disaccharides consist of two sugars joined by an O-glycosidic bond. The three abundant disaccharides are sucrose, lactose, and maltose.

We have the disaccharides that consist of two monosaccharide units; two sugar units that are joined by an O-glycosidic bond and the three most abundant disaccharides are sucrose, lactose and maltose. These are the ones but we will know how once we know what the linkages how we can actually write out the structures of definitely sucrose, lactose and maltose but also of the other disaccharides. 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 one carbon atom.

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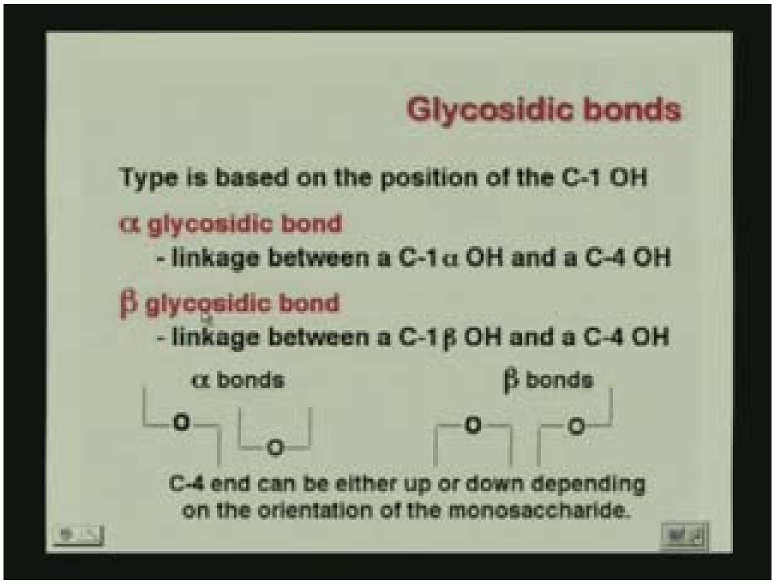

Glycosidic bonds

Type is based on the position of the C-1 OH

α glycosidic bond

- **linkage between a C-1α OH and a C-4 OH**

β glycosidic bond

- **linkage between a C-1β OH and a C-4 OH**

C-4 end can be either up or down depending on the orientation of the monosaccharide.

For example; if the linkage is between a C_1 α OH and a C_4 OH, it does not matter whether what the orientation of the C_4 OH is. If the first carbon is an α, it is called a α glycosidic bond. If it happens to be a, β it is the linkage between a C_1 β OH and C_4 OH. It is called the beta glycosidic bond. 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 cyclized.

When it is cyclized, we had the C=O i.e. the aldehyde part the aldehyde moiety interact in the case of glucose with C_5 OH of carbon atom number 5 into forming a cyclic structure which is the hemiacetal. What happens in this case is you still have an OH available to it. 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 intramolecular cyclization of the glucose forming the cyclized monosaccharide. What was actually formed was an hemiacetal because we had the OH that actually was part of R_1. So this R_2 that we are talking about here is actually the fifth carbon atom of the same structure, so we are cyclizing these whole things into forming what is called a hemiacetal.

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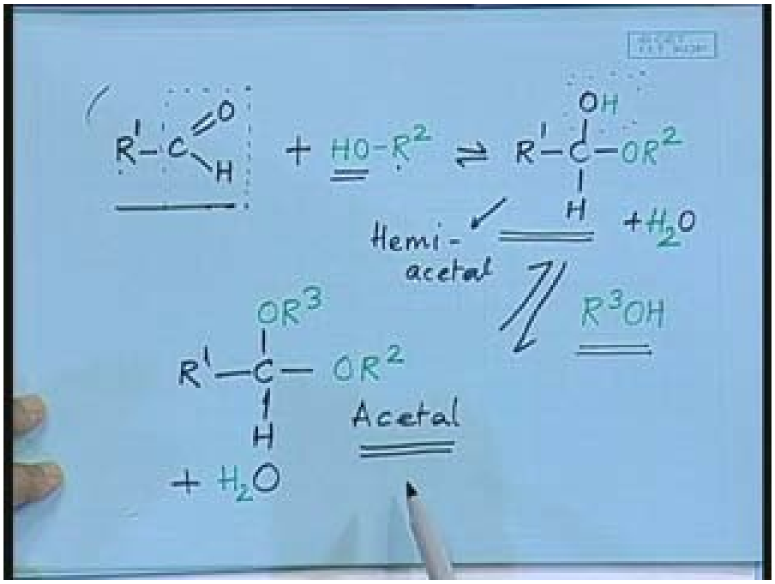

But now if I have another glucose which is also an OH, if have this link with this hemiacetal (refer Slide Time: 08:45), what can I get? I can get an acetal. Depending on cyclic structure, I have either an α or a β form. Let’s just draw one form here or in fact let us draw both forms so we know what we are talking about. These are pyranose rings. We have CH_2 OH. This it is the sixth carbon atom. We have one OH and this OH can be either up or down. If I put it down it becomes α and if I put up it is β. If I form a linkage then the oxygen atom which is going to be linked, suppose we have these two units, if it is in the α form the oxygen is down. So the linkages are going to look like this (Refer Slide Time: 10:19). The oxygen is going to be down. It can be down but the other one that is linking with can be up or down.

This could either be this or it could be this (Refer Slide Time: 10:33). What we are looking at is not, we are looking at monosaccharide unit only. 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 α or β. These are both α forms (Refer Slide Time: 11:11). Why, because in both cases OH is down. This O that is coming from the first monosaccharide unit is trans with respect to the CH_2OH that is why the direction is this way.

If I were to do the same for the β set then in both cases it would be up. What are the two cases I am talking about? We would have an O and another O and other monosaccharide unit that it was linking to, could either be this or this (Refer Slide Time: 12:00). Because what we are looking at now is we are going to get gradually on the structural units but to understand structural units, we have to be very careful about the linkages we are talking about. Because, if you remember, when we did lysozyme we talked about $\beta(1, 4)$ glycosidic linkages. What are these linkages? A β linkage would look like this (Refer Slide Time: 12:26).

In both cases it would begin up why because this is up. This is cis to the CH_2OH. So this would refer to a beta linkage in this case it is down, it is trans to the CH_2OH. This would refer to an α linkage and what it is linking to could be up or down so we have this either looking like this or in the same thing in the β case. That is why we have suppose we have it linking to the C_4 which is the fourth 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 i.e. the case then you would have dependent on the orientation of the monosaccharide either it come down in the α case always has to come down that is what we have to remember because the oxygen of the OH rather it trans to the CH to the OH and it is this that is going to be involved in the acetal formation.

We already have hemiacetal formation. We are now going to have an acetal formation. What is happening is this OH is going to be involved in the reaction that is going to form a glycosidic linkage. When it forms glycosidic linkage in the case of the alpha both of them are going to be down and one that is linking to either C_4 and in this case can be up or down. The same goes with the β. The β will be up initially why because the OH is cis to the CH_2OH and what it is linking to could be either up or down.

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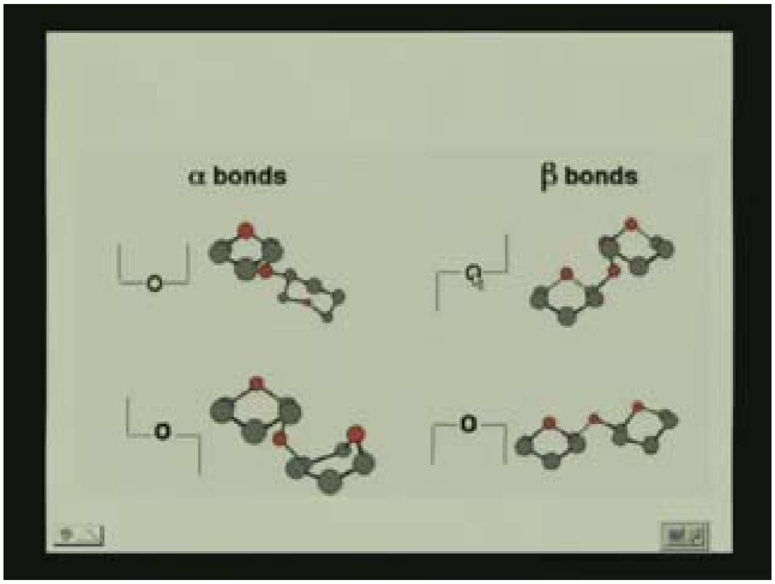

This is what we have. We can have α bonds that look like this (Refer Slide Time: 14:35). You have to remember when the whole look like this is an α linkage when it O comes from towards the top or upward, it is a β bond. So this is what it looks like. Depending on what kind of linkage you have, you see how the structural differences occur that is obvious. It is going to be obviously dependent on how the reaction is talking place. So you could either have α glycosidic linkage or you could have a β glycosidic linkage.

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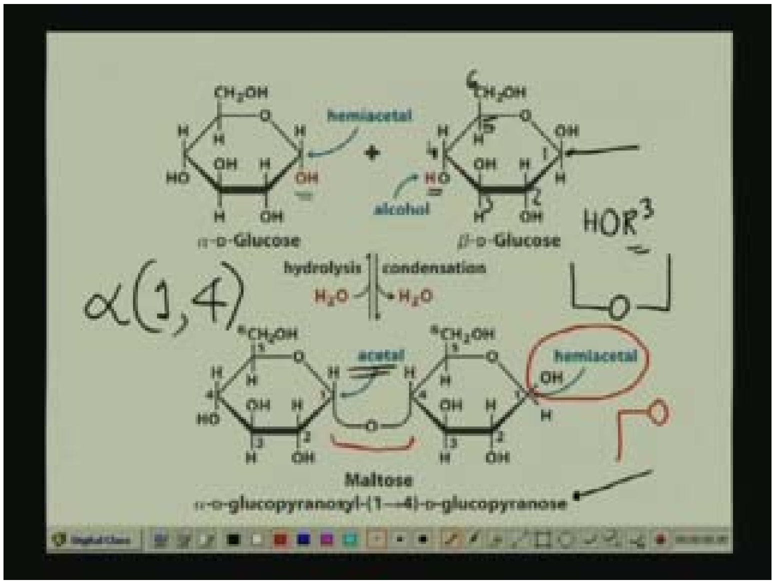

This is what we have. α D-glucose here and a β D-glucose. Follow this very carefully. This is the structure that we did in the last class, what do we have? We have hemiacetal formation where the OH that is of this carbon, C_5 and this is C_1 that originally was an aldehyde. It is now a hemiacetal due to an intramolecular cyclization that has occurred between the 5OH of the fifth carbon and the aldehyde. The OH is trans to the CH_2OH so this is α D glucose. The one on the right here is β D- glucose because the OH is cis to the CH_2OH. This is a hemiacetal. It is still can react with what I showed in the first diagram here, where we have an R_3OH. What is R_3OH? This (Refer Slide Time: 16:34) is the OH on the fourth carbon atom of another glucose moiety, another monosaccharide.

What can it then form?
It can form an acetal when it show initially we had the straight chain which actually linked these two units up together to form a hemiacetal. Once the hemiacetal was formed, this is now linking with another monosaccharide unit to form an acetal. That is exactly what is happening here. We have α D-glucose, the hemiacetal which is linking with carbon number. What we have is, this is (Refer Slide Time: 17:44) carbon number one, this is carbon number two, this is carbon number three, this is carbon number four, this is carbon number five and that is carbon number six.

What is the linking; we are linking this, which is a hemiacetal with the OH here. So we have HOR_3, what is R_3? R_3 is the rest of the molecule. This is the hemiacetal that is going to link with this alcohol to form an α (1, 4) linkage. What it is going to look like in terms? It is going to look like this it has to come down, why because it is α and depending on the OH orientation of the C_4 carbon, this is going to be up or down. In this case, it is up. So what we have is we had glucose. It has cyclized to form the hemiacetal. We now we are linking it with another monosaccharide moiety to form a disaccharide. The linkage is a 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 an O-glycosidic linkage.

We are linking the α of carbon number one to the fourth carbon of the other one. It does not matter whether this is an α or β. The α comes from what is the first one that you are considering. This is alpha carbon number one. So this linkage is an α (1, 4) linkage. It is linking what it is linking this is the actual nomemclauture where you have α D-glucopyranosyl 1, 4 D-glucopyranose. It has now formed an acetal. This is the R 3 moieties. Remember this is our R 3 part. This (Refer Slide Time: 20:56) is the OH part and it has now formed an acetal. This is now a hemiacetal. This can link with another sugar.

We can have a polysaccharide. 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 form because you know the structure of the glucose. You know that if you have two glucopyranose units, it means you have two glucose units and the linkages alpha (1, 4), it forms maltose. We have α D-glucose link with β D-glucose in this case it is β 1 because it is cis. That has nothing to do with the linkages that we concerned with here. When this is going to react with the next R_3 OH or next ROH what is the linkage going to be? It is going to be a beta linkage because the OH in the case of the hemiacetal is up. The linkage is going to be something like this (Refer Slide Time: 22:23). What is going to be the next? It could be either up or down but this is beta and this is alpha. This is about the glycosidic linkages in the formation of disaccharides. Let us look at a few more.

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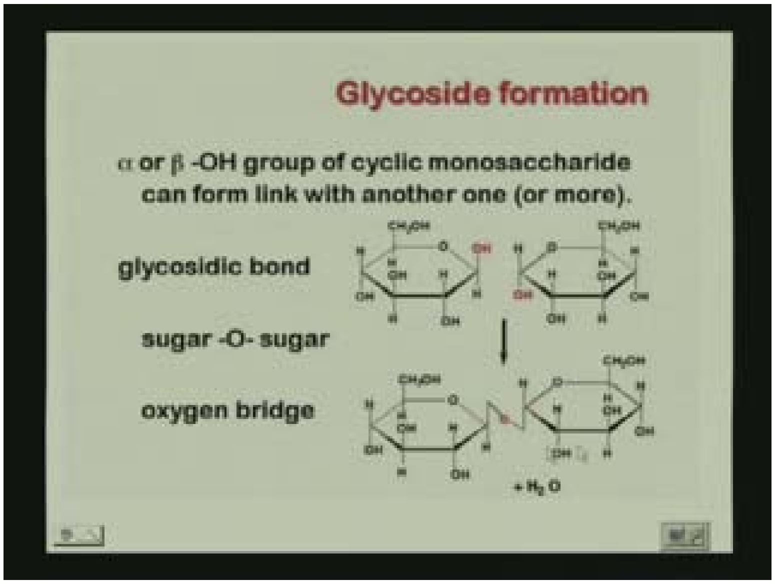

Glycoside formation

α or β -OH group of cyclic monosaccharide can form link with another one (or more).

glycosidic bond

sugar -O- sugar

oxygen bridge

We have this going up. So what is this β ? This is β 11.We have to be careful at what we link because now you formed the completely different disaccharide. You have to know that the numbering this CH_2OH is the number 6, so 6, 5, 4, 3, 2, 1.

We have and this is number one it is going up so it is β so it is β 11. Why O-glycosidic linkage because we have the oxygen the oxygen bridge there that is what exactly happening in the glycosidic formation. Let us look at some examples. So let us look at the rules first. If the alcohol linked to an anomeric carbon is another carbohydrates, obviously the other resulting compound is the dissachride because we have two monosaccharide units. The name of the glycoside specifies the two monosaccharides and the glycosidic linkage which carbons are linked and the configuration about the anomeric carbon, the alpha or the β. We have the either the alpha or the beta and we have to figure out what it is linking to, which carbon it is linking to.

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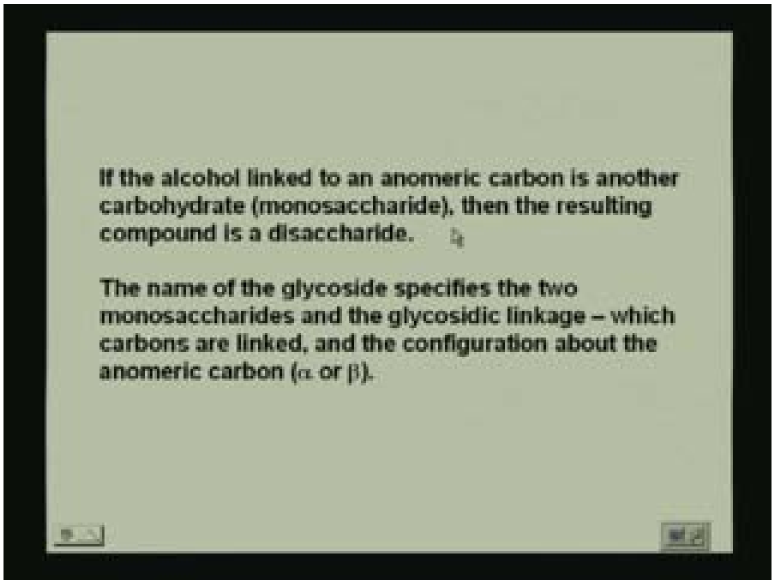

If the alcohol linked to an anomeric carbon is another carbohydrate (monosaccharide), then the resulting compound is a disaccharide.

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).

Now these are some examples. Lactose is galactose β (1, 4) glucose so what we need to know, we need to know the structure of the galactose. We need to know the β anomer of galactose and the structure of glucose and then this is the way written in short form, galactose β (1,4) glucose i.e. lactose.

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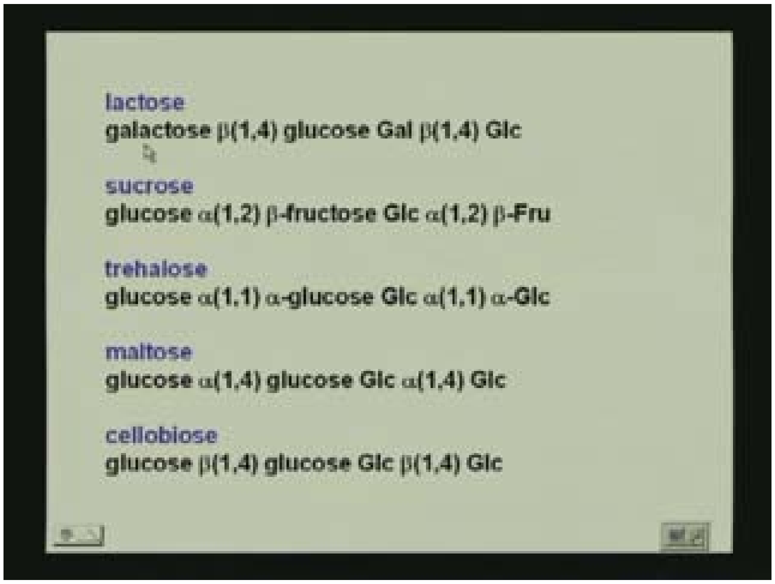

lactose

galactose β(1,4) glucose Gal β(1,4) Glc

sucrose

glucose α(1,2) β-fructose Glc α(1,2) β-Fru

trehalose

glucose α(1,1) α-glucose Glc α(1,1) α-Glc

maltose

glucose α(1,4) glucose Glc α(1,4) Glc

cellobiose

glucose β(1,4) glucose Glc β(1,4) Glc

If we look at sucrose, it is glucose alpha one two beta fructose. All of you know what sucrose is; you can check and see whether this is the right way to write it. We have glucose alpha one two beta fructose. If we look at trehalose, it is glucose α glucose. Maltose is the one that I showed you previously where we have a glucose α (1, 4) linkage. That is what we showed when we are looking at the acetal or hemiacetal. We have cellobiose. Let us do just one of these structures. Let us do trehalose because it is about glucose units and we already looked at maltose.

This is glucose α 1, 1 α . This is what we have and I write this O down. What happens to the other one? How do I write this? I have it linked to number one so my oxygen has to be where? It has to be here and where is my CH_2OH, it is here (Refer Slide Time: 27:19). It has to be linked like that. So this signifies α (Refer Slide Time: 27:55), it is carbon number one. So these two units are glucose and so glucose α (1,1) that gives rise to trehalose.

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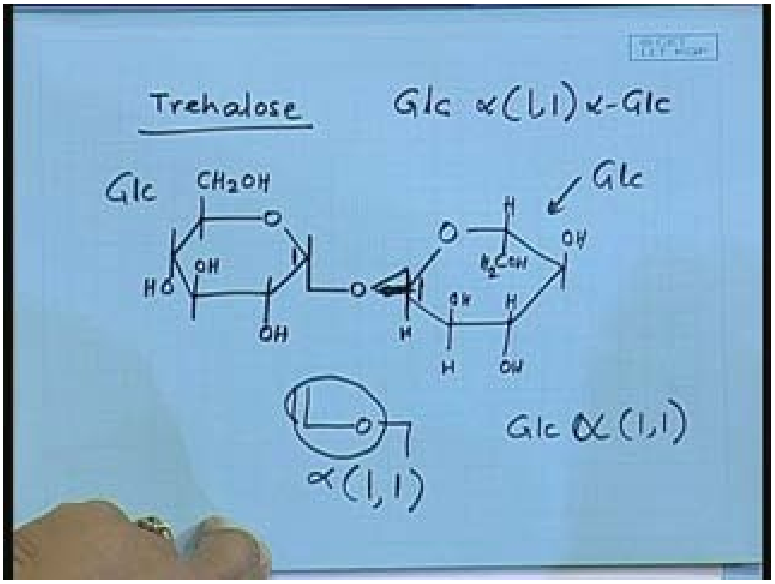

If we look at all the different monosaccharide or disaccharides rather we have here lactose, sucrose, trehalose, maltose and cellobiose. This is lactose. Then what is the linkage. Just look at the linkages, β. But just to figure out that we are linking this is the sixth carbon, this is the fifth carbon and that is the fourth one. So this is β (1, 4) linkage. It is linking galactose and glucose that is lactose. It is the dimer of β D galactose and either the α or β D glucose. so this could be either up or down. This OH because it is linking either the α or β D glucose. We have β (1, 4).

In cellobiose, we have β (1, 4). What is this α (1, 4) (Refer Slide Time: 29:43)? This is maltose. This is the first example that I showed you. Just because this linkages different, we have an enzyme that can break this disaccharide down but do not have an enzyme that can break this (Refer Slide Time: 29:58) disaccharide down. It is that specific. We have an enzyme that can break maltose but not an enzyme that can break cellobiose. The only difference is that this is the β 1 fold linkage and this is the α 1 fold linkage.

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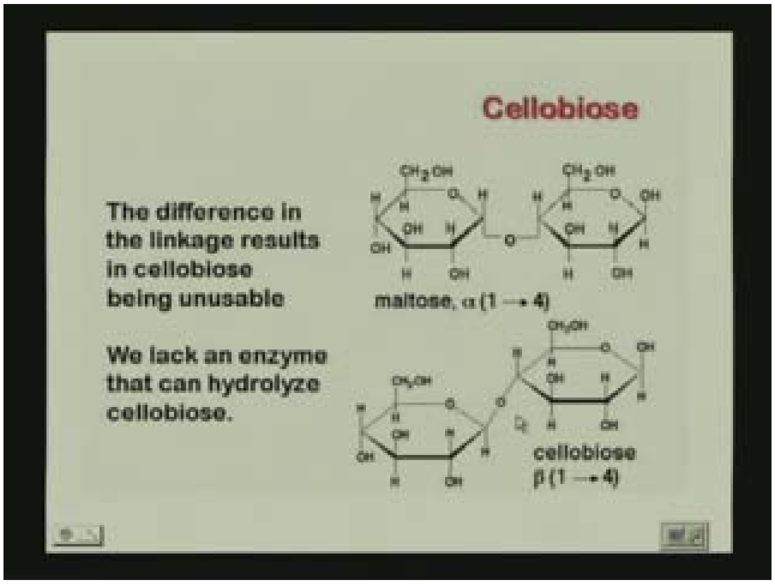

Cellobiose

The difference in the linkage results in cellobiose being unusable

We lack an enzyme that can hydrolyze cellobiose.

maltose, α(1 → 4)

cellobiose
β(1 → 4)

This is actually what it would look like if you go to actually draw it correctly. This would be α (1, 4) linked D-glucose units. What we can have, we can have other units linked together. So the whole structural aspect comes 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 actual chair conformations.

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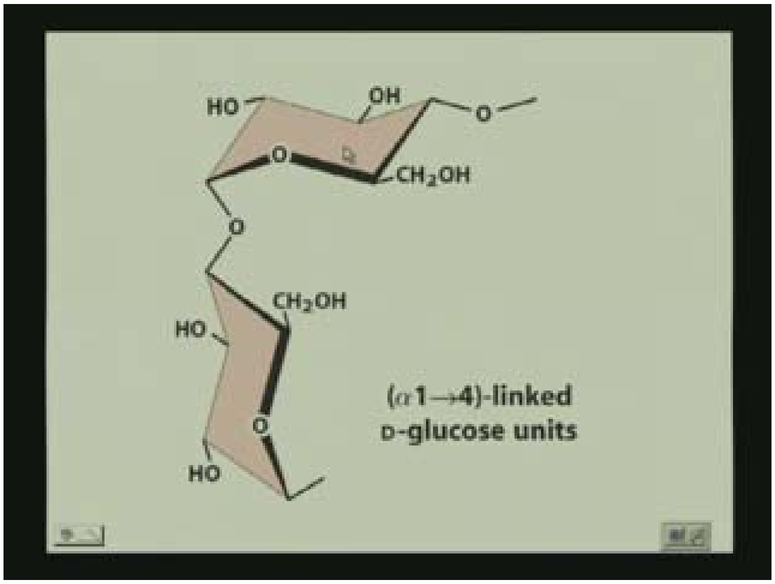

(α1→4)-linked
D-glucose units

When we have the chair conformations, when we know that we have equatorial and axial bonds, then obviously we are going to have the linkages that are going to result in different structural aspects to the whole disaccharide and polysaccharide.

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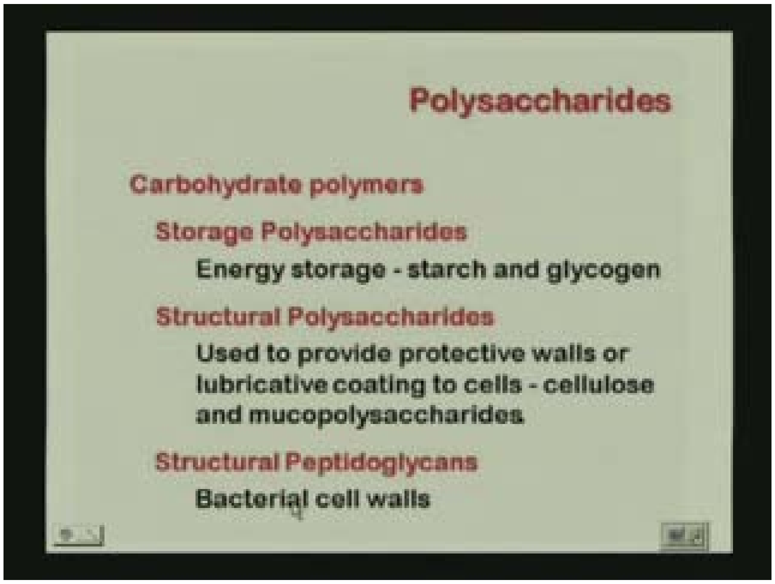

Polysaccharides

Carbohydrate polymers

Storage Polysaccharides

Energy storage - starch and glycogen

Structural Polysaccharides

Used to provide protective walls or lubricative coating to cells - cellulose and mucopolysaccharides

Structural Peptidoglycans

Bacterial cell walls

That is why each of them are going to behave in a different structural fashion. So depending on the linkage it could be starch it could be glycogen it could be amylase, it could be amylopeptin and whatever. That's what we are going to look at the polysaccharides the polysaccharides therefore will be further linkages of what we just learnt. So not only we will be have an α(1,4) we could have α(1,4) α(1,4) α(1,4) β(1,4) and so on and so forth. These polysaccharides are just therefore polymers of the monosaccharides and they could be storage type; a 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 mucopolysaccaharides. We will see an example of each of these as we go along. You also have structural peptidoglycans that actually form bacterial cells walls. And what did learn when we did the lyzosome structure, that it breaks bacterial cell walls.

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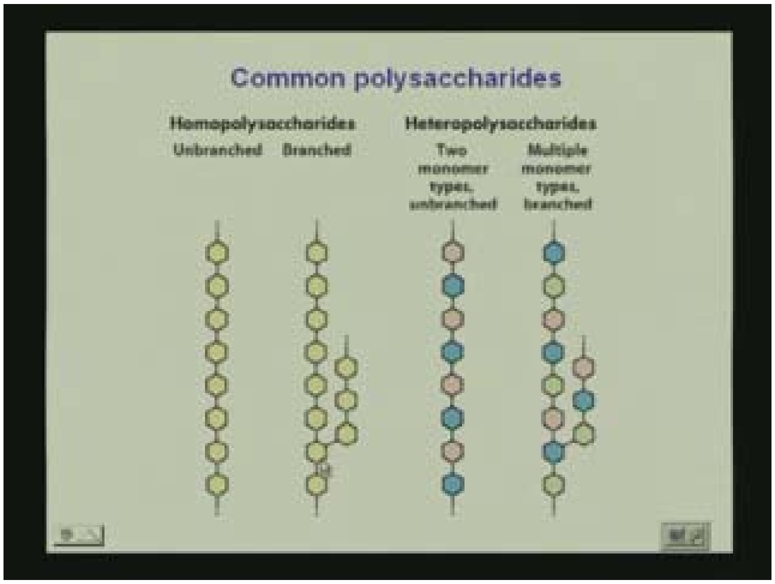

Common polysaccharides

Homopolysaccharides

Unbranched

Branched

Heteropolysaccharides

Two monomer types, unbranched

Multiple monomer types, branched

We can have polysaccharide that looks like this. These would just normal linkages six membered rings. You could have homopolysaccharides where all the sugars are the same. You could have them unbranched or you could have them branched. You would have say α (1, 4) linkage here and say one sixth linkage here or two six linkage there which would form branch to it. You could have heteropolysaccharides where the monomers types are different. You could have them on the unbranched or branched. These would basically be the four types of polysaccharide. We could actually have two types of homopolysaccharides and two types of heteropolysaccharides meaning, they could be unbranched or branched. And each of the monomers units that we studied in the last class and in this class in the disaccharide formation will account for all types of polysaccharides possible.

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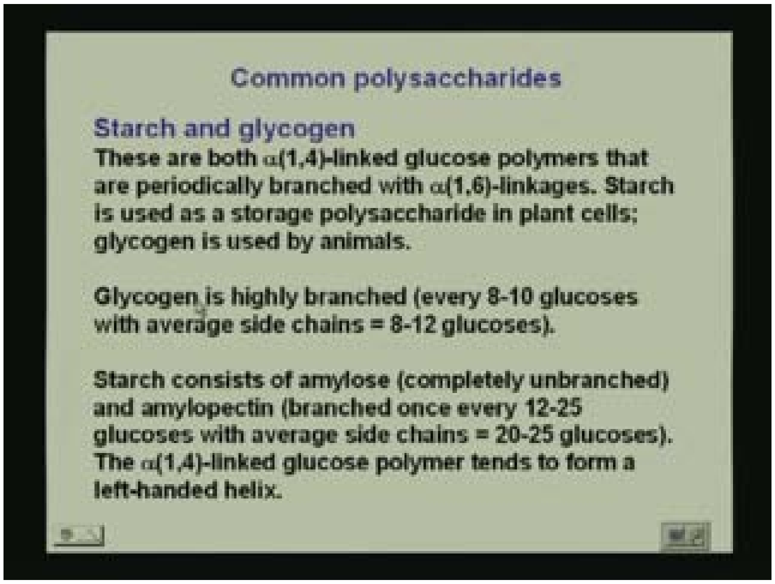

Common polysaccharides

Starch and glycogen

These are both $\alpha(1,4)$-linked glucose polymers that are periodically branched with $\alpha(1,6)$-linkages. Starch is used as a storage polysaccharide in plant cells; glycogen is used by animals.

Glycogen is highly branched (every 8-10 glucoses with average side chains = 8-12 glucoses).

Starch consists of amylose (completely unbranched) and amylopectin (branched once every 12-25 glucoses with average side chains = 20-25 glucoses). The $\alpha(1,4)$-linked glucose polymer tends to form a left-handed helix.

What are these types starch and glycogen are both α (1, 4) linked glucose polymers. You now know what that means α (1, 4) linked glucose polymers. So it is glucose α (1, 4) and another glucose that are periodically branched with α (1, 6) linkages. So you have α (1,4), you can also have α (1,6) that is going to basically make it a branched homopolysaccharide, because you have the same monosaccharide unit glycogen is highly branched. Every 8 to 10 glucoses with average side chains of 8 to 12 glucoses. Means, you have in your previous picture if you look here 8 to 10 here and 8 to 12 branched up then the other set then you have all of it linked together basically to form. You realize now that it is good to form such a compact unit why because they are storage polysaccharide you do not want them to take a lot of space. So you would rather want the storage polysaccharide to be compact which is why starch actually forms granules. For storage purposes it is more convenient to have these now starches we look at the structure in bit more detail.

Starch consists of amylose that is completely unbranched and amylopectin branched once every 12 to 25 glucoses. An unbranched polysaccharide a homopolysaccharide why because it has the same units. Example of an unbranched homopolysaccharide is amylose and these are examples of branched ones. Then the α (1, 4) linked glucose polymer units in amylopectin actually forms something that look like helix.They link in a particular fashion and I will show you in a picture.

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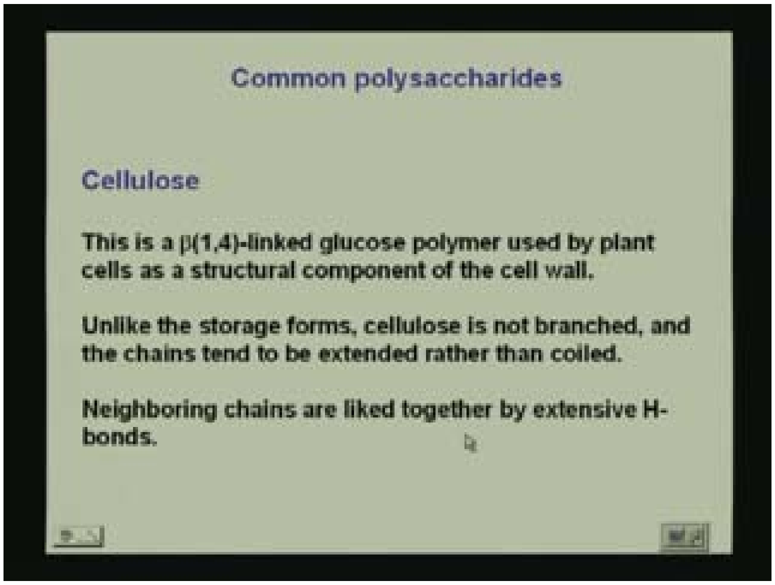

Common polysaccharides

Cellulose

This is a β(1,4)-linked glucose polymer used by plant cells as a structural component of the cell wall.

Unlike the storage forms, cellulose is not branched, and the chains tend to be extended rather than coiled.

Neighboring chains are liked together by extensive H-bonds.

In cellulose you have a β(1, 4) linked glucose 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 structural polysaccharide to be compact. It should be fibrous. If it fibrous it has to be long chain it cannot form a unit. Then the neighboring chains are linked together by hydrogen bonds.

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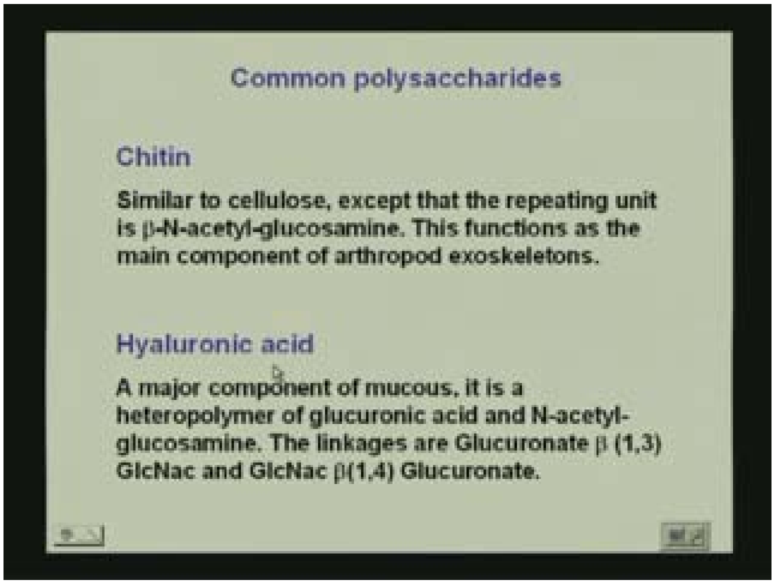

Common polysaccharides

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 mucous, 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.

So then we have other examples which I am not going to do but basically we have chitin and hyluronic 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 lysosome cleavage, how it could actually cleave.

This is basically where it is going to work. This is what it look like we have what sort of linkages this β(1, 4) this is an N-glycosidic. This is the CH_2OH which is 6. If you get confused where the one begins from, go to the CH_2OH. This is six five four so one four linkage this is what it is N-acetyl this is an example of an N-acetal you look at the Ns what are they so what is this this is actually a glucosamine. There is no OH there. It was an NH_2. That has been actylated so it is a glucosamine. This is a β(1, 4) of linkage of a glucosamine. So here you have βN-acetyl-glucosamine. So you now know what it looks like. It is a glucose which had an OH changed to amine, an amine which is actylated that is linked by a β linkage. This is basically what we have. This is now α(1, 4) α(1, 4) one after the other. Then suddenly you have one six. So you see how it looks like a circle. You have like a helix structure. This is amylose starch.

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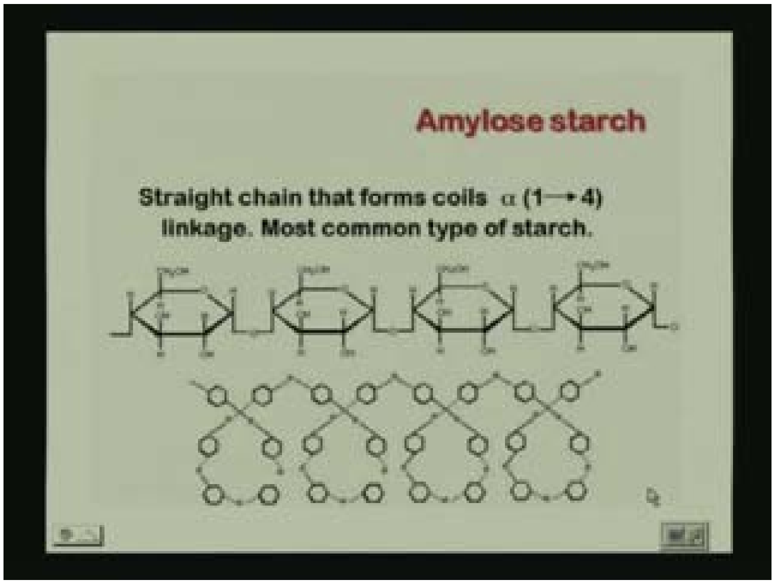

Amylose starch

Straight chain that forms coils α (1→4) linkage. Most common type of starch.

What you need to know is how you can actually form these linkages and α(1, 4) linkage so if you know that the straight chain forms α(1, 4) linkages then branch to form 1, 6. You look at amylopectin. You have what is this linkage a β(1,4) that are the cross link where is the cross link here that is not the cross links where is the cross link the α(1,6) linkages is supposed to be the cross link.

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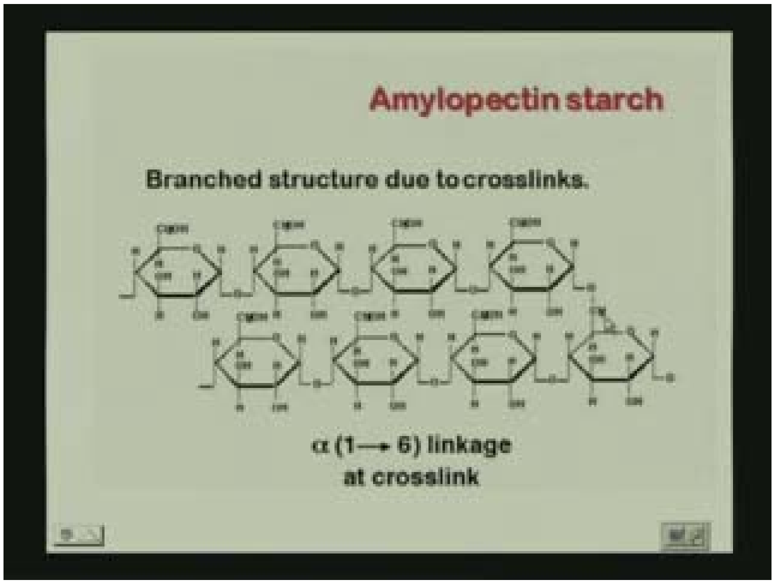

Amylopectin starch

Branched structure due to crosslinks.

α (1→6) linkage
at crosslink

Where will be my cross link? It would be this is the six that is the sixth one. These are basically the different types. Here again you have glycogen that looks like this.

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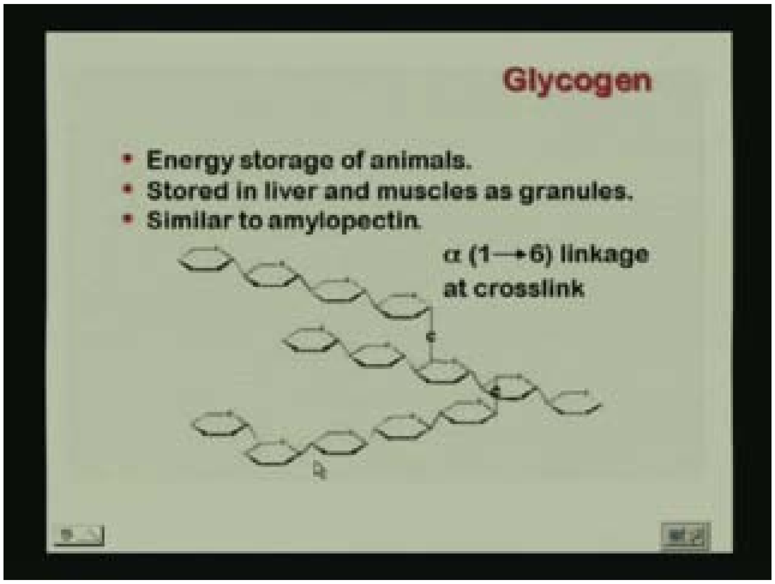

Glycogen

- Energy storage of animals.
- Stored in liver and muscles as granules.
- Similar to amylopectin.

α (1→6) linkage
at crosslink

What we have to remember?
When you are looking at storage polysaccharides, they are stored as granules. That is why they have to be branched polysaccharides. That is an important feature of branched polysaccarides. 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 $\beta(1,4)$. Then we have mucopolysaccharides. What is this unit now the NHCO CH_3? N-acetylglucosamine this is glucuronic acid. What do you mean by glycuronic acid? This is not CH_2OH anymore. It

is COO^- so we have N-acetylglucosamine and glucuronic acid which is what formed in the Fehling's reaction also you have the CO^- instead of CH_2OH at position number 6.

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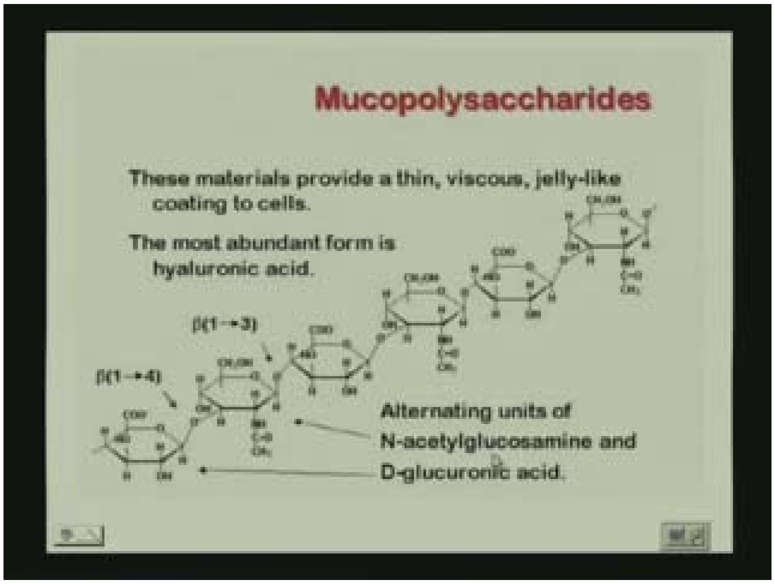

Mucopolysaccharides

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

The most abundant form is hyaluronic acid.

Alternating units of N-acetylglucosamine and D-glucuronic acid.

This is probably something we should be looking at where we have peptide cross links between the polymers trans. The reason we have peptide cross links we saw this in bacterial cell walls.

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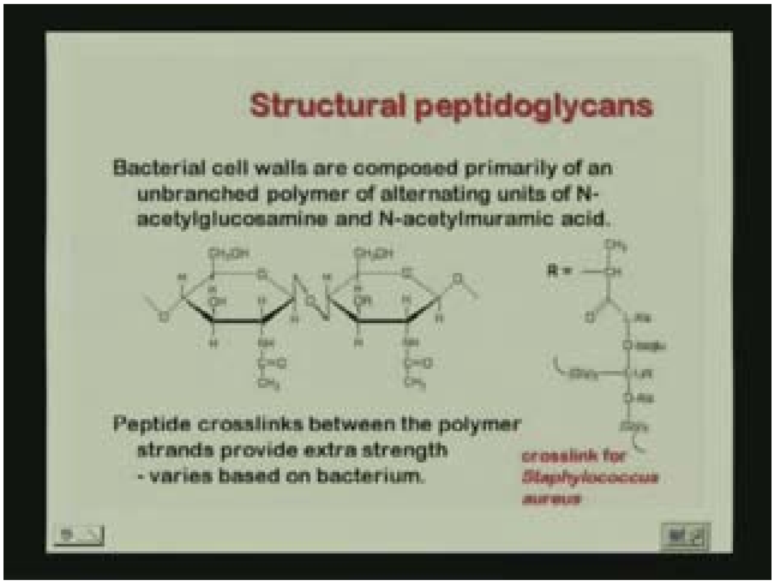

Structural peptidoglycans

Bacterial cell walls are composed primarily of an unbranched polymer of alternating units of N-acetylglucosamine and N-acetylmuramic acid.

Peptide crosslinks between the polymer strands provide extra strength - varies based on bacterium.

crosslink for *Staphylococcus aureus*

When I was just mentioning about lysozyme, we had alternating units of N-acetylglucosamine and N-acetylmuramic acid. We have the muramate and the glucosamine. So what we have is in between these units, we have an R-group; the R-group is actually some alanine, lysine etc. so it has a peptide unit to it. Because of this peptide unit it imparts structural rigidity to the cell wall. It's nothing but having some peptide cross link. Apart from the normal polysaccharide cross links if you have additional peptide cross links, there is going to be extra strength to the bacterium because you do not want it to be broken down. The bacteria obviously does not want it cell wall to be broken down so it has extra cross links.

Now we will be speaking about glycoproteins when we consider lipids and membranes. Now these glycoproteins are proteins that have linked to them covalently sugar units. Now we are going to see where or what the sugar units are and how they are linked to the proteins because we now know the protein structure we know the aminoacids in proteins. We know the monosaccharide; we know something about the carbohydrates so what we are going to look at is how they are linked together. These glycoproteins have important biological functions.

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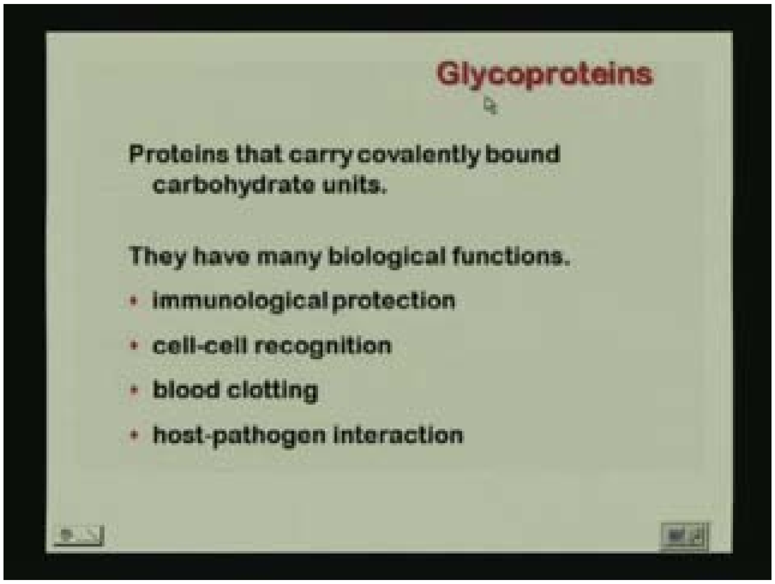

Glycoproteins

Proteins that carry covalently bound carbohydrate units.

They have many biological functions.

- immunological protection
- cell-cell recognition
- blood clotting
- host-pathogen interaction

These are the some of the functions that is listed here. They are immunological protection, cell-cell recognition blood clotting and host pathogen interactions. The carbohydrates account for only 1 to 30 % of the total weight of a glycoprotein. And the most common monosaccharides that actually link up are glucose galactose, manaose, nag and nam. This is N-acetylgalactosamine. We also have muramate sialic acid; these are all the monosaccharide 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. What it is linked by? If this is our polypeptide chain, there are different ways in which these sugars can actually be linked. We learned about O-glycosidic bonds? glycosidic bonds are ones that use the oxygen to link.

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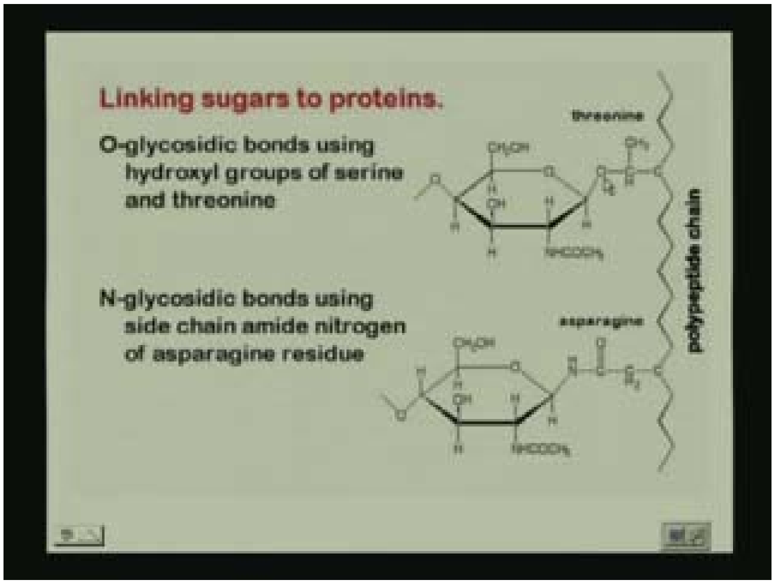

Linking sugars to proteins.

O-glycosidic bonds using hydroxyl groups of serine and threonine

N-glycosidic bonds using side chain amide nitrogen of asparagine residue

In the case of serine and threonine, we know what their side chains are. Serine is OH and threonine is CH_3 and OH. If we have the linking of the sugar to the proteins, this is the polypeptide chain where we have a threonine. This is the CH_3 of the threonine this is the OH. This OH has linked with a saccharide unit. This is an N-acetylglucosamine and what has it formed? If this part of the polypeptide chain, as soon as links up monosaccharide unit to it, forms a glycoprotein. And this again, you realize that this can be linked further.

Hence, these are all the carbohydrates units that we had when we looked at glycoproteins in the lipid membrane in the fluid mosaic model for the membrane. When we are forming N-glycosidic bonds we are using the side chain amide nitrogen. Which two amino acids have amines? They are asparagine and glutamine. So now we have to remember that when we forming a glycoprotein always doing we are doing that linking sugar to the protein now this sugar has to be linked to the polypeptide chain through amino acids because that is what forming the polypeptide chain. When we form these glycoproteins, it is threonine OH that can link to form an O-glycosidic linkage or it is the amide N that can form N-glycosidic linkage.

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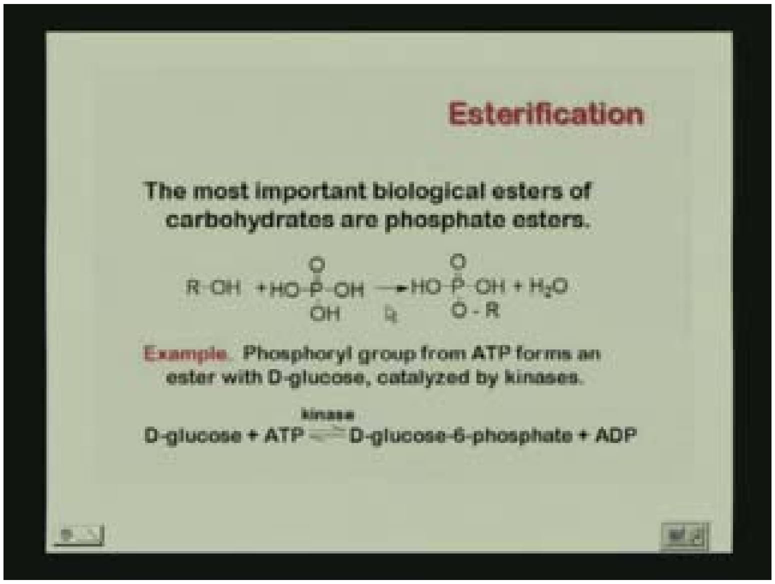

Esterification

The most important biological esters of carbohydrates are phosphate esters.

$$R\text{-}OH + HO\text{-}\overset{O}{\underset{OH}{P}}\text{-}OH \rightarrow HO\text{-}\overset{O}{\underset{O-R}{P}}\text{-}OH + H_2O$$

Example. Phosphoryl group from ATP forms an ester with D-glucose, catalyzed by kinases.

$$\text{D-glucose} + \text{ATP} \xrightleftharpoons{\text{kinase}} \text{D-glucose-6-phosphate} + \text{ADP}$$

Then we can have esterification which 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 six different types of enzymes. Of those enzymes, there was one enzyme called a transferase. One type of enzyme called a transferase but when we have a kinase. It is specific type of transferase that transfers phosphate moieties. We are going to see a lot of these kinases when we do bioenergetics but for now we have an R OH. Now this OH can be part of a monosaccharide unit.

In that case, we have phosphoric acid. We have the formation of an ester; a phosphate ester and a H_2O. When we look at the formation of a biological ester, then the phosphoryal group from ATP, the structure of which we are going to study in detail when we get to it. The ATP will form an ester with D glucose into forming glucose six phosphate which is the first step in the breakdown of the glucose. So we have glucose 6 phosphate and adenosine diphosphate because it’s lost one phosphate to the glucose. This is one sort of reaction we have and these are the amine derivatives which we mentioned before. What are these amino derivatives, whether this is a β glucose you now recognize because the OH and the CH_2OH on the same side. We have β D glucose and this is β D 2 aminoglucose, which is a glucosamine.

It is OH of carbon number two that has been replaced. This is why we have the two amino glucose. We have the beta D-glucose that forms the beta D aminoglucosamine and this can further be actylated to form $NHCOCH_3$. So these are basically the different types of reaction we can have. The uses for these amino sugars actually are for the structural components of bacterial cell walls where again we look at the nag and nam as a component of chitin which is a polymer found in the exoskeleton of insects and crustaceans. This is another amino sugar now the formation of amino sugar actually is important in giving its structural rigidity.

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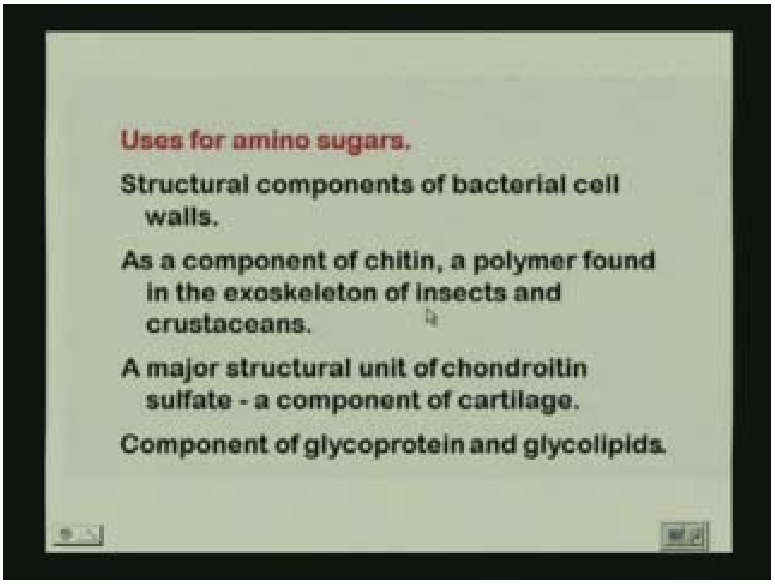

Uses for amino sugars.

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.

That is why it is a sort of hard cell that is found. So basically what happens we have the NH_2 group here, the NH_2 that links with an acetyl group the $NHCOCH_3$ and so on and so forth forming different possible chains that we can have.

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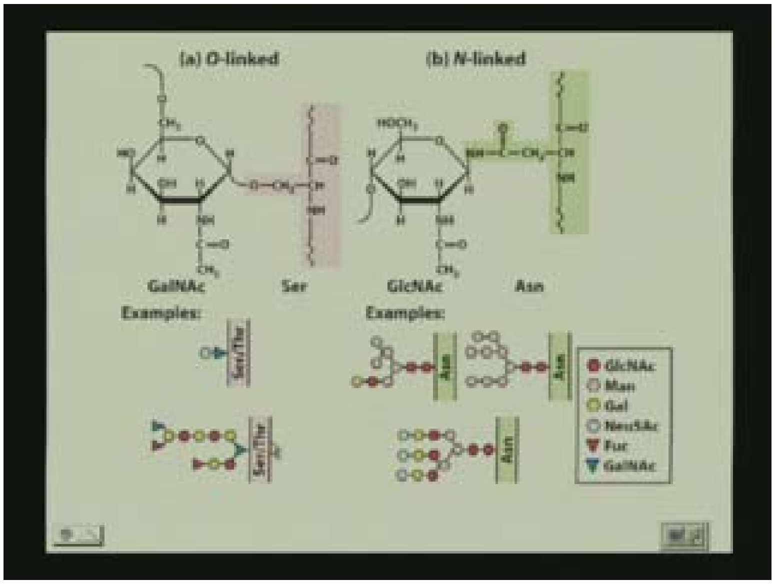

We have different types of oxygen linked and nitrogen linked amino acids or basically glycoproteins what are these when they are linked or when they are over linked they are linked through either serine or threonine. You are linking in this case, it means N-acetyl galactose if you know the structure of galactos,e the usual N-acetylation at position 2. We form originally NH_2 which is the glucosamine or the 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 it forms a glycoprotein.

We have we can have the serine threonine linked basically we can have different functionality different types of groups and so on and so forth. In the N linked case what do we see this is again glucose N acetylated. So its N-acetylated glucose that is nitrogen linked so it means that the amino acids that is linking to is an asparagines. Usually it is asparagines and sometimes it can be glutamine. But in this case we are going to have N-linked and in this case we are going to have O-linked.

In conclusion what we studied was, we looked at all monosaccharide units. Then we looked at the ways we could form the disaccharides. What are these ways? We have specific α and β linkages, glycosidic linkages that we could use to link the monosaccharide units together. Then obviously if we can link two units, we can link multiple units together.

We can have homopolysaccharides and heteropolysaccharides and they can be branched or unbranched depending on how they are utilized what are their actual functions, 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 is unlikely to be cross linked because it would like to be a fiber for structural strength. And then later we went to look at glycoprotein to see how the glycogen other sugar units are actually linked to the proteins they can be linked to the serine or the theronine by the oxygen where they are over linked. They could be either linked to the asparagines where they are end linked. So that completes the lesson on carbohydrates. We will next do vitamins and coenzymes.