Biochemistry - I

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Lecture-13
Lipids and membranes - I

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Lipids are non-polar hydrophobic compounds that have a polar head group and a hydrophobic tail. Now we are going to understand how these are organized into membranes and what their functions are. So basically anything that is a non-polar hydrophobic compound soluble in organic solvents is called a lipid.

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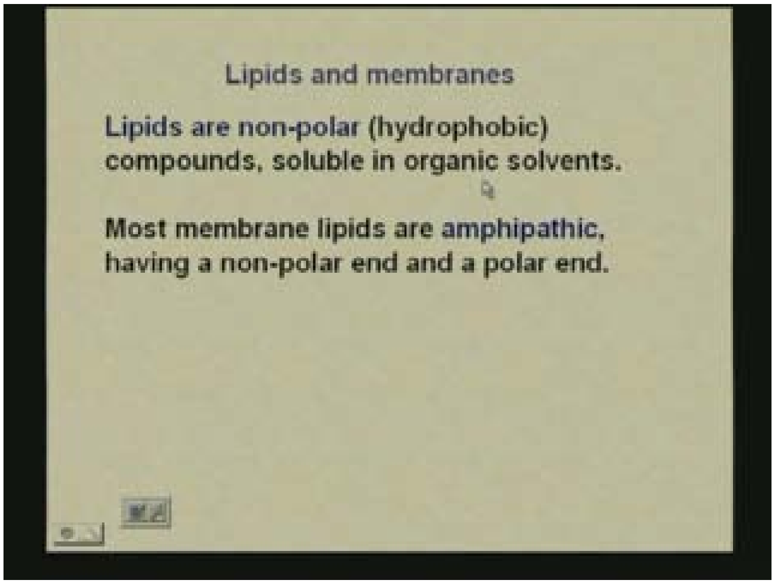

The membrane lipids that we talk about are called amphipathic in nature. Amphipathic means it has both a non-polar end and a polar end to it. The non-polar end arises due to definite chemical moieties, definite groups and polar end again arises due to some other groups that at are present. If we look at the functions of lipids they play a very important role in the biological cells and biological cell membranes and of course membrane transport which will be doing later on. We have steroid hormones, in digestion, as fats and triacylglycerols which give us the fuel for our bodies and the membrane structure. So lipids are involved in all of these activities starting from hormones to digestion elements that are present in the bile. These are all lipids and their components. The fats and triacylglycerols are lipids and in the membrane structures, which is what we will be doing today, we have fatty acids, phospholipids, sphingolipids and cholesterol.

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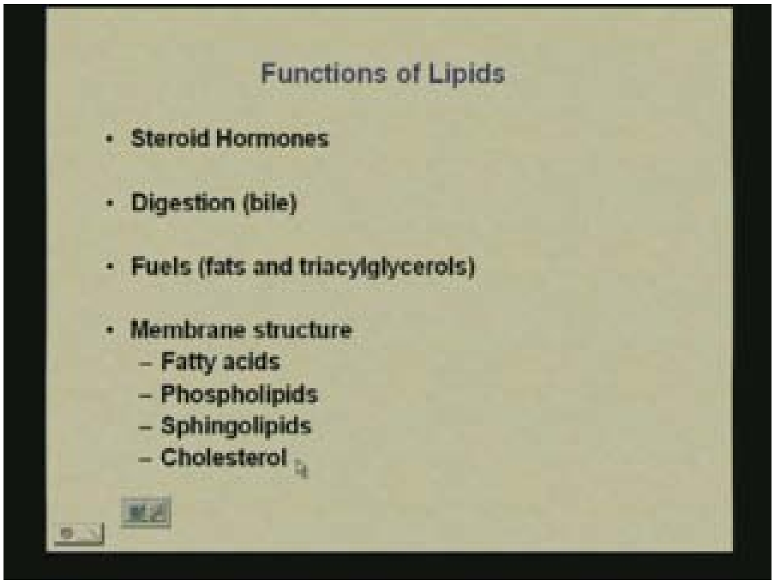

Initially we are going to study the different nomenclature and the different types of fatty acids. A fatty acid is a long chain acid. In the organic carboxylic group that we speak about we speak of a –C=OOH being the acid moiety. Here we have a long chain hydrocarbon with a -COOH attached to it.

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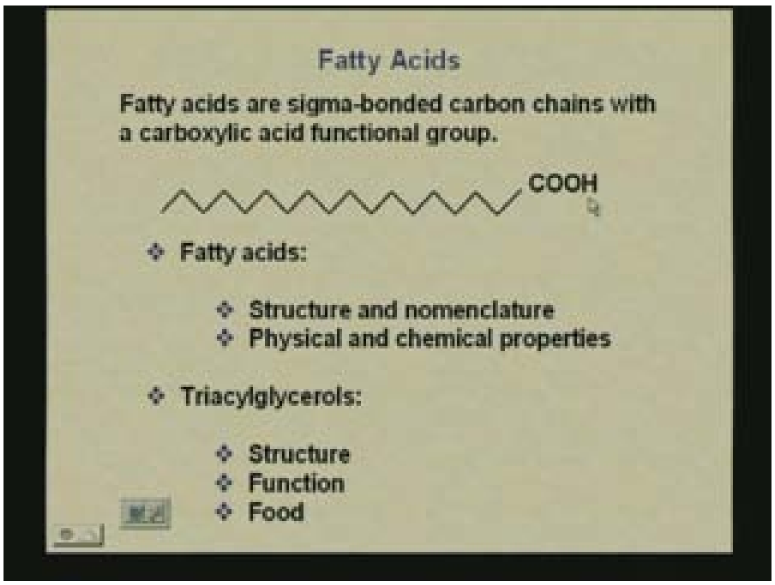

These fatty acids are sigma-bonded carbon chains. Sigma bond mean we have just single bonds here and they have at the end a carboxylic acid moiety, a carboxylic acid functional group. This functional group or this moiety is going to be used in the overall function or overall structure of the lipids that form these membranes. If we consider the fatty acids, the first thing that we are going to look into is their structure and the nomenclature as to how they are identified and then the physical and the chemical properties of the fatty acids. Then we will study about the triacylglycerols and see how they play an important role in the structure and function and the formation of lipid membranes.

The first thing is about the nomenclature. The nomenclature of the fatty acids actually follows two types.

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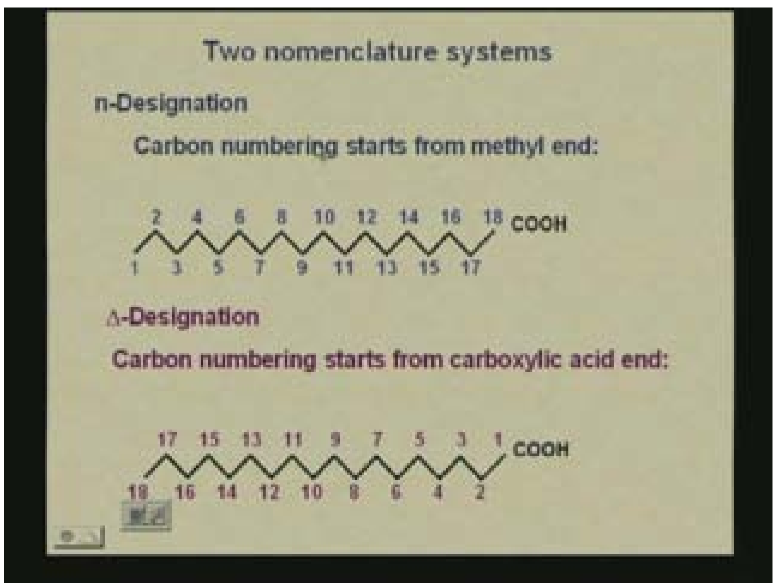

One is called the n-designation and other is called the delta designation. In the n-designation you can straight away see that the numbering is from the extreme end away from the carboxylic acid group. In this case the numbering is from here, 1, 2, 3 and 4. For the delta designation the numbering begins from the carboxylic acid end and it is this nomenclature of this designation that we will be using the delta designation. If you are to write the structure of any particular fatty acid there will be a specific nomenclature that you will follow and that nomenclature will be the delta designation where the numbering will begin from the carboxylic acid end, not the n-designation. How does this help us?

In the next slide we will see as to how we can write the nomenclature. This is a fatty acid in the n-designation and what I have below here is a fatty acid in the delta designation. From this nomenclature you should be able to write the fatty acid. We have to know what each of these numbers mean. The first number that you have here is the carbon chain length. It tells you how many carbon atoms you have. After the colon you see another number. This 20 means that the carbon chain length is 20. The number after the colon designates the number of double bonds present. In this case we have carbon chain length of 20 and the number of double bonds is 4. Now you can tell me that this is actually the position of the double bonds. So the number that we have at the end is the position of the double bonds. The delta 5 means the double bond is between 5 and 6, 8 means it is between 8 and 9, 11 means between 11 and 12 and 14 means between 14 and 15. In the n-designation there is usually just one number put because usually when we form or when the fatty acids are biosynthesized what happens is they form in specific units. If you notice here every double bond is after three carbon atoms. It is 5, 8, 11 and 14.

In the n-designation, only one is specified which tells you that there is going to be another one at 9, 12 and 15 and it is opposite to this because this numbering is opposite to that in the delta designation.

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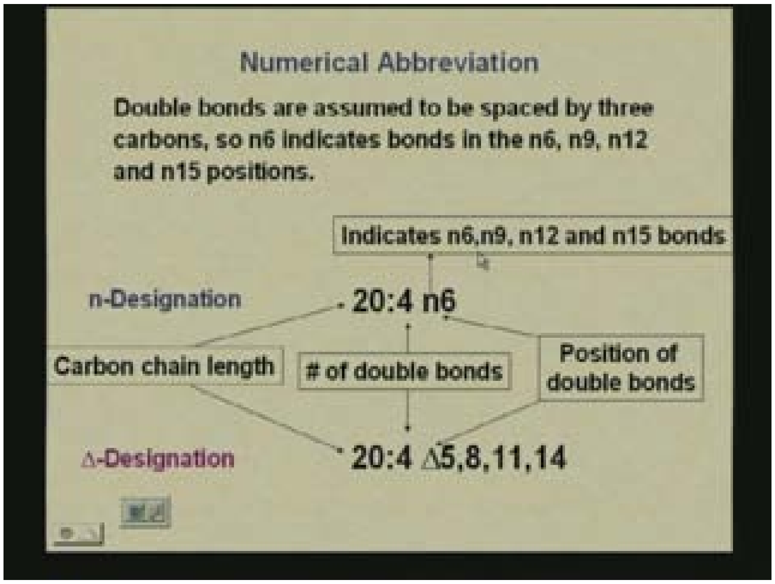

The double bonds are assumed to be spaced by three carbons. So here in the n-designation only end 6 is specified and nothing else. But in the delta designation the position of the double bond is written explicitly where we now know that if this is the nomenclature it means that if you have a carbon chain length of 20 there are 4 double bonds and the position of the double bonds are 5 and 6, 8 and 9, 11 and 12 and 14 and 15. If we look at the set of designations, another thing that we should mention here is that the double that we see in the fatty acid usually have a cis configuration and most naturally occurring fatty acids have an even number of carbon atoms because the way that they are biosynthesized they come in pairs of carbon atoms. If they come in pairs of carbon atoms all of these are usually even numbers. You do not see an odd numbered fatty acid because when fatty acids bio synthesis occurs it comes in pairs of carbon atoms.

If we look at some fatty acid and their common names 14:0 is myristic acid. These are all the delta configurations. So you should be able to write what myristic acid is. What is it?

It’s just a long chain, a hydrocarbon chain with 14 carbon atoms and you do not need numbering in this case because there are no double bonds.

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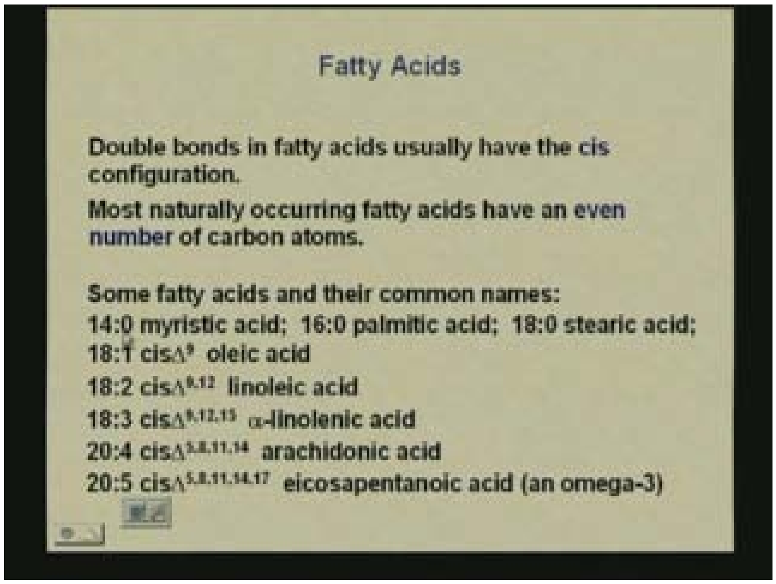

So we have myristic acid, palmitic acid, stearic acid, then we go to oleic acid. It is 18:1 cis. The cis is not usually put in, just delta nine is sufficient because most of them are cis any way. So 18:1delta 9 means that oleic acid is an 18 carbon fatty acid with 1 double bond between 9 and 10. That is as simple as that. The one that I had on the previous page is actually arachidonic acid. It was 20 with 4 double bonds at 5, 8, 11 and 14. Eicosapentanoic acid which is an omega three fatty acid has an additional double bond at position 17. So this nomenclature is sufficient to tell you how to write a fatty acid. This is basically the nomenclature of fatty acids and we are going to see how we can use these fatty acids in forming our lipids.

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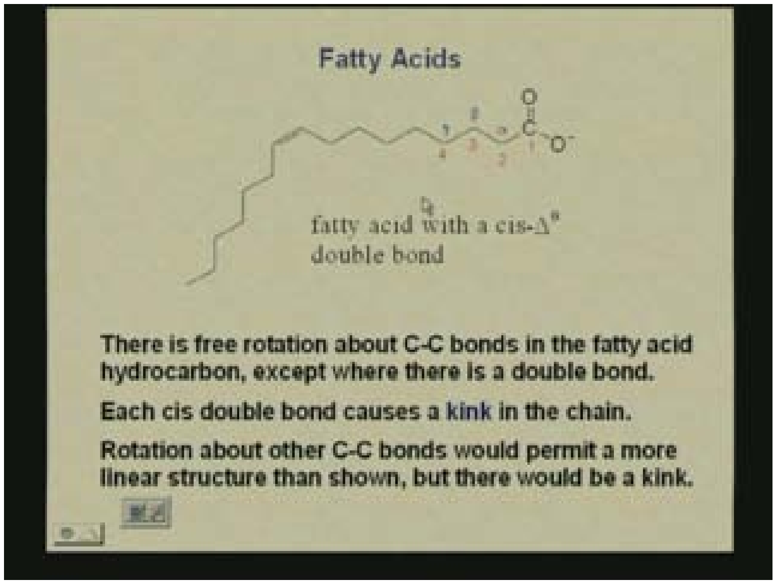

What happens if you have this cis double bond? Here we have a single cis double bond. You see how the carbon chain has now changed direction. If this cis or if this double bond did not exist it would have been a nice straight chain and they could have been rotations about the single bond. But when we have it in the cis configuration then what happens is there is a break in the chain because of the cis configuration. You have what is called a kink in the chain. Instead of having a normal long chain that we would have had and free rotation about the single bond each cis double bond causes a kink in the chain. If I had another cis double bond at this position this part of the fatty acid or this part of the chain would fold back. So I would have a kink in the structure. So I have a kink in the structure due to the fact that I have double bonds in the hydrocarbon chains. When we have these membrane lipids, this is something we are going to study in detail later on, these are my fatty acid chains.

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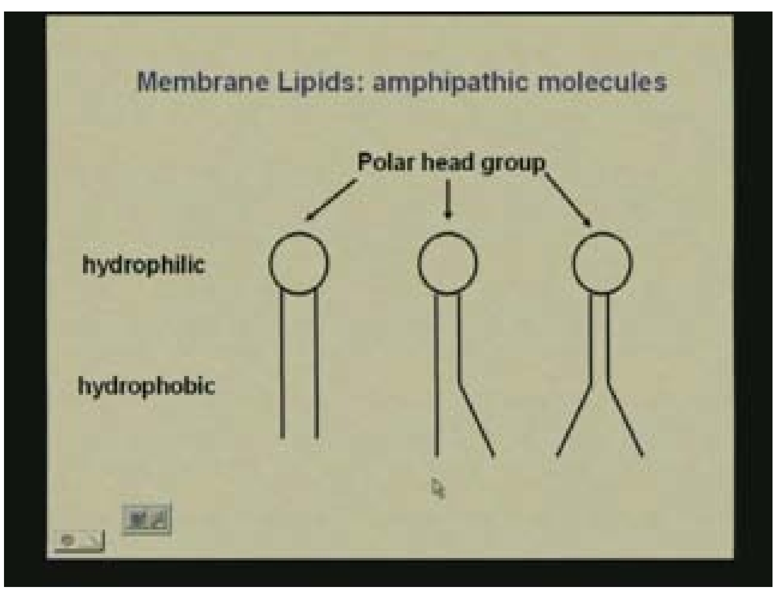

I am going to have a polar head group, we will see what those polar head groups can be, and my hydrophobic tail if it is a straight chain fatty acid it will look like this. If it happens to have one fatty acid that has a kink to it, it is going to be shaped like this. We will see how I am talking about two fatty acids linked to a single polar head group in a moment. But when we are talking about the polar head group and different fatty acids when they link together you see how you can change the structure of the lipids because of the type of fatty acids that is being attached to the polar head group. You are basically changing the structure depending on the choice or the type of the fatty acids that you are considering.

Basically if you look at the fatty acids, this would be the structure where we would have carboxylic group here. This would be the polar part of it and if we have a long chain it would be a smooth long chain, a straight chain. If you happen to have a cis bond here what would happen? The chain would get bend.

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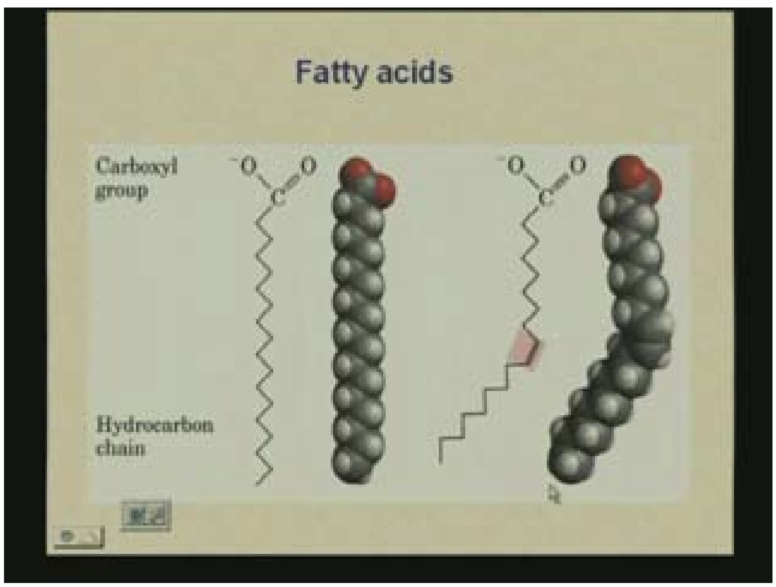

You would have what is called a kink and you recognize that if you had another cis bond here it would twist even more. Here are some physical and chemical properties of fatty acids. Fatty acids are weakly acidic in nature; weakly acidic with a pKa of 4.5 to 5 which means that they are ionized at physiological pH. The physiological pH is 6.7.4.

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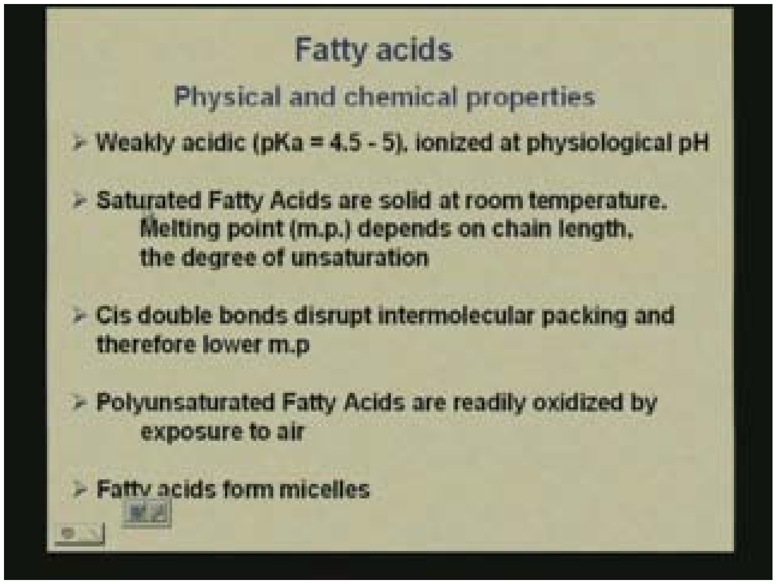

Saturated fatty acids are solids at room temperature. The melting point is going to depend on the chain length and definitely the number of double bonds present; on the degree of unsaturation and we will see how that is going to play an important part in our lipid formation, membrane lipids. So we have weakly acidic fatty acids. The saturated fatty acids are solid at room temperature. The melting point depends up on the chain length and the degree of unsaturation. With the kink in the cis bonds what happens is it disrupts the molecular packing. So it lowers the melting points. If you had straight chain that would normally completely very well organize, you would have a higher melting point. But due to the presence of the cis double bond the intermolecular packing of the hydrophobic chains is disrupted. It is broken and that lowers the melting points. The polyunsaturated fatty acids that you see in a lot of vegetables oils that you consume they say that they are pufa. That is what it is called polyunsaturated fatty acids; they are readily oxidized by exposure to air and these fatty acids can form micelles. You know why they can form micelles? Because they have a hydrocarbon chain and it has a polar head group to it. These are the basic physical and chemical properties of fatty acids. What we have to remember is that they are weakly acids, saturated fatty acids are usually solid at room temperature and the melting point is going to depend up on the number of carbon atoms you have and on the degree of unsaturation and the more the number of cis bonds that you have the lower the melting point is going to be because you are going to disrupt the intermolecular packing between the hydrophobic chains.

Now we are going to come to what are called Glycerophospholipids.

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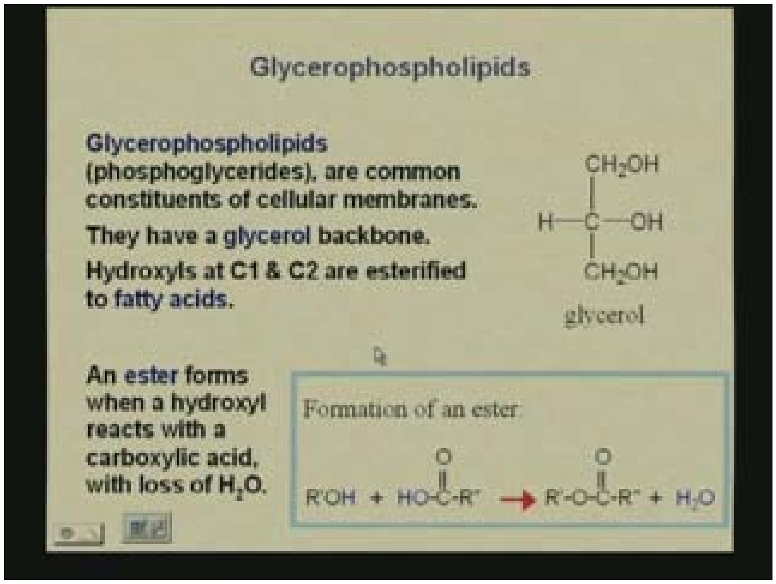

We have glycerol. Glycerol is CH_2OH CHOH-CH_2OH. Glycerophospolipids are what comprise lipid membranes. They form or they are the constituents of cellular membranes. You recognize that these -OH groups that you have here can be esterified by acids. What is an esterfication reaction? We have ROH and RCOOH. With the removal of water, we form a -OCO an ester formation. That means that these H's if they react with fatty acids can be esterified and I can have to this glycerol a long chain attached to either this hydrogen or this hydrogen or this hydrogen. Usually there are two fatty acids attached to it which is why I have two lines sticking out from the polar head groups. We have the hydroxyls at C1 and C2 that are esterified with the fatty acids. We have our glycerol. The one that I show you here is triacylglycerols which is what comprises the fat droplets that we have in cells.

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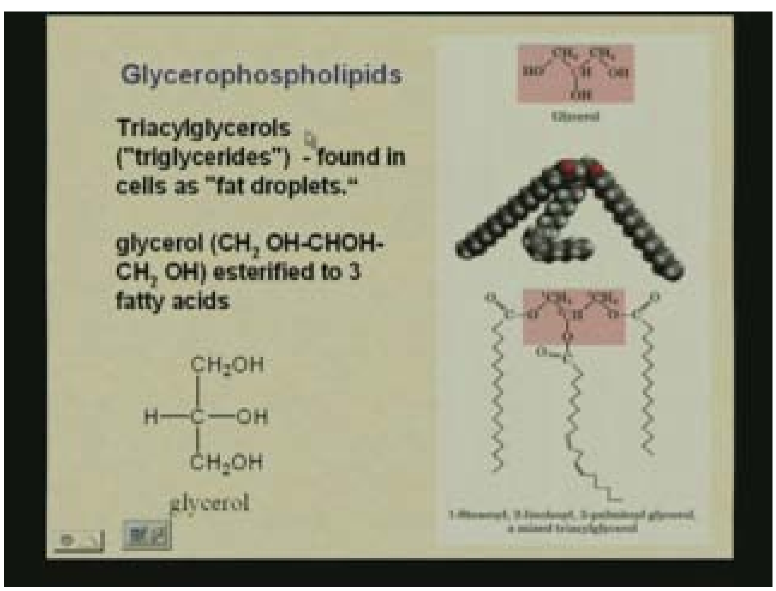

If you see there are triacylglycerols or triglycerides test that have to be performed in blood to see whether you have appropriate triacylglyceride content. If you have more fat droplets then you have fat restricted diet. This is what a triacylglycerol would look like. Here is the structure of glycerol. We have three -OH groups here. If each of them number 1, number 2 and number 3 are each esterified, this is what it is going to look like. So in the first carbon atom and in the third carbon atom we have straight chain fatty acids that have been used to esterify the -OH groups of the glycerol. The extreme -OH groups of the glycerol have been esterified with straight chain fatty acids here. In the middle we straight away know that this has now not only one but it has two cis double bonds which is why it is even bent further than the one I showed you previously. If you look at the structure here this is linolinic acid that has been used. We have one cis bond here and another cis bond here. So it has changed the structure of the hydrocarbon chain into making it more disrupted. It's more kinked in a sense.

We are going to see how we can change the properties of the groups here and then see what the lipids or the glycerophospholipids are actually made of. What we have are called phospholipids. What are these phospholipids? In the two classes of phospholipids that are present these form cell membranes. We have glycerolphospholipids that have a glycerol backbone just like I showed you. We have sphingomyelin that forms from a spingosine backbone and in this case this actually forms a lot of the membranes and these phospholipids are usually refered to as PL.

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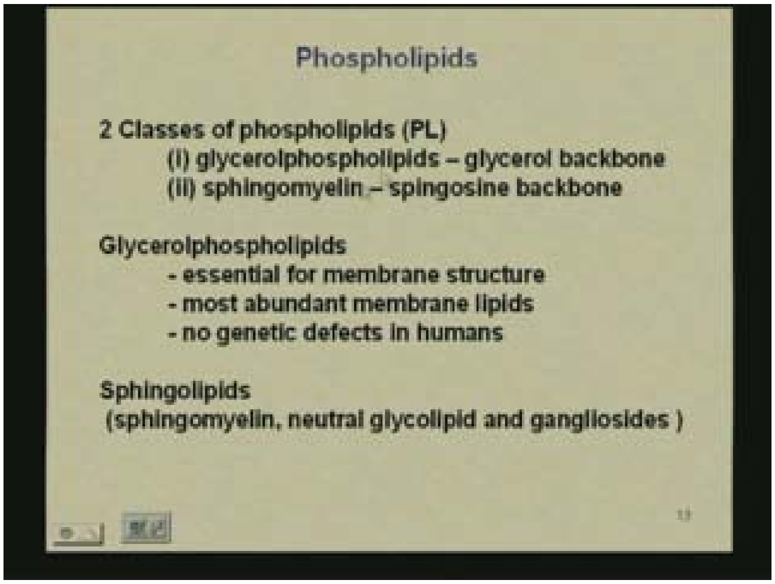

What is essential of these? They are extremely important for membrane structure. They are found in membrane lipids. We will see what these structures actually are. What we need to know is there are two types of phospholipids and they are essential for the membrane structure and they are found in membrane lipids. This is the break up. What we have here is we have storage lipids. Storage lipids like storage in terms of fat droplets.

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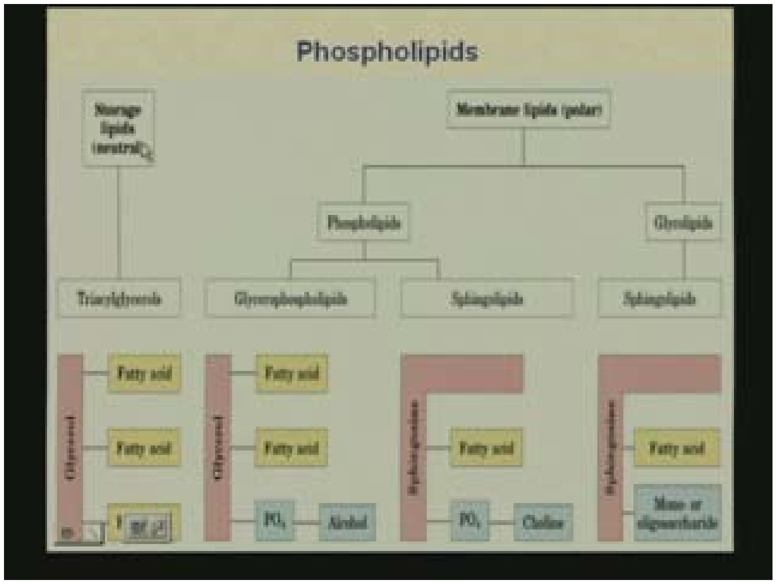

What are the fat droplets? They are triacyl glycerols. We need to know is that the storage lipids which are neutral in nature have three fatty acids attached to the glycerol. We have membrane lipids. In the membrane lipids we have phospholipids and glycolipids. In phospholipids we can have glycerophospholipids or sphingolipids. It is just a break up tree. The membrane lipids are polar in nature because they have a phosphate group attached we will see what that means in a minute. Phospholipids are glycerophospholipids or sphingolipids and glycolipids are other sphingolipids. Glyco means you have sugar. Whenever the word glyco comes in a prefix, glyco means there is sugar present. If we go back to the phospholipids break up we have storage lipids that are triacylglycerols fatty acids. We have membrane lipids that are phospholipids or glycolipids. The breakup of phospholipids is glycerolphospholipids or sphingolipids where the backbone basically different.

Now we will study this in a bit more detail. The black part here is part of glycerol CH_2OH CHOH CH_2OH. What has happened at the first two carbons is the C1 and the C2 have been esterified by fatty acids.

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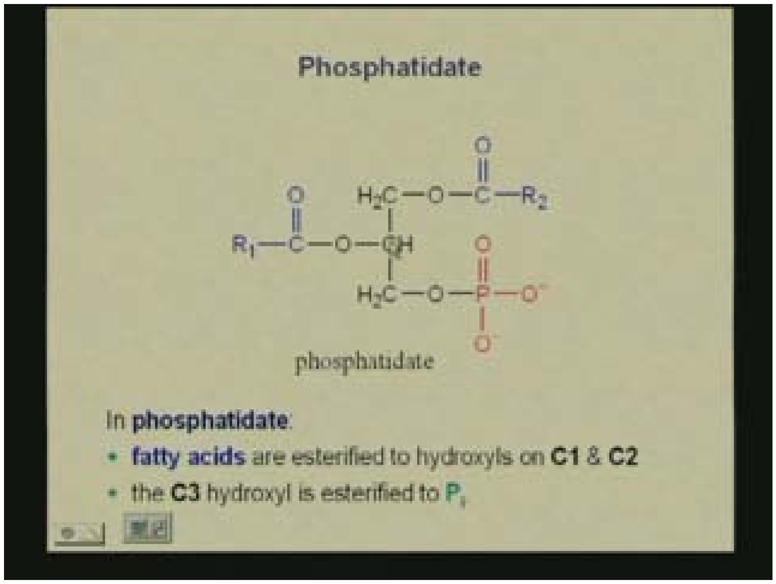

We have long chain fatty acids in both cases. The third carbon has been esterified with the phosphate. Remember that is also an acid. We have two of the carbons esterified with fatty acid chains and one with the phosphate. This is called a phosphatidate. What is the basic structure? The basic structure is glycerol. The two carbons of glycerol have been esterified with two fatty acids and the third with phosphate. We have a glysphosphatidate or otherwise glycerophospholipids. This is what it looks like. We have a fatty acid on the first carbon, we have a fatty acid on the second carbon and we have a phosphate on the third carbon. The phosphate again is esterified. If the phosphate again is esterfied by this X group this is where we can change the type of glycerophospholipids that we have. So where can we make the changes? We have the basic structure of glycerophospholipids that is going to be the glycerol.

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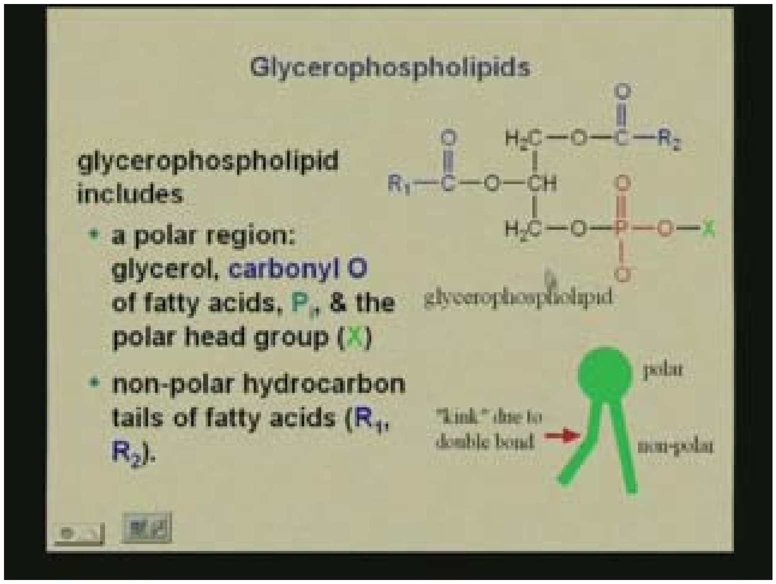

We have one fatty acid linked on the first carbon, a second carbon linking another fatty acid. So we can change the type of fatty acids that we have. As soon as I change the type of fatty acid the type of lipid is going to change. Then I have an esterification on the third carbon atom with phosphate and I have a polar head group here and we will see how that affects it. Where is my polar head group? It is here. Here are all the oxygens and the phosphates and where are my chains? $R_1$and R_2. I have the basic structure of the lipid that is going to look like a polar head, that is this part here, and the R_1 and the R_2 are these chains. You understand what the structure looks like now? We have the overall glycerol, two of the –OH's have been esterified with long chain fatty acids which is why I have two legs to this polar head group and the polar head group forms because of the phosphate esterfication and an additional polar head group. This is the basic structure of a glycerophospholipid. What can I change here? I can change type R_1. I can change $R_{2,}$ I can change X. In that I will be changing the complete type of glycerophospholipid that I have and we are going to see how we can do that.

This is our structure. So we have the P_i-OH. What is happening to this –OH? It has been esterified again. It can be esterified with serine, choline, ethanolamine, glycerol or inositol. There are different groups that can be used to esterify the phosphate in the phospoglyceryl and the two fatty acids that we have R_1 and R_2 are usually not the same. We will see why later.

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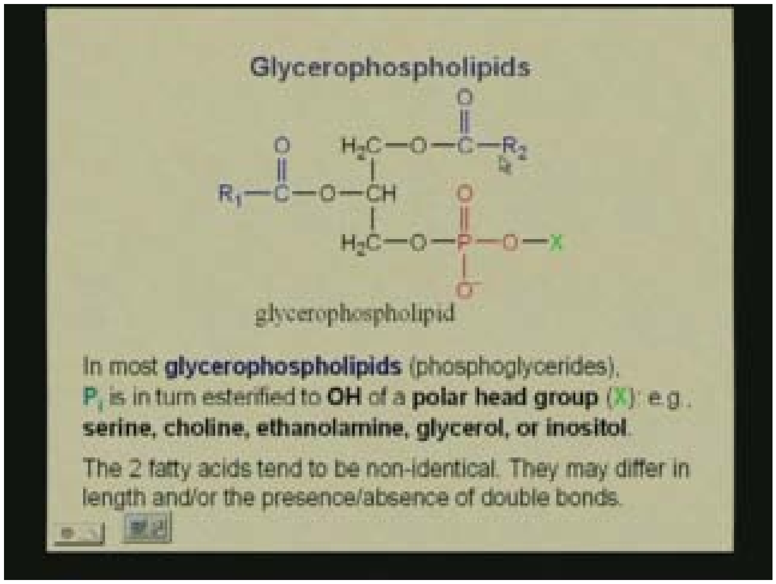

How can they be different? They can be different in their length, they can be different in the number of double bonds and they can be different in the location of these double bonds. That is where we have a difference R_1, R_2, X. So what are the differences? This is phosphatidylinositol.

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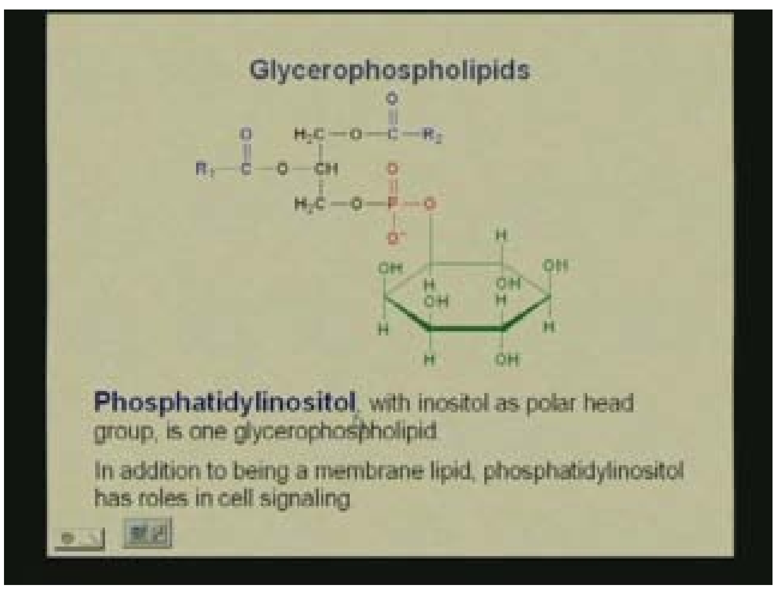

You recognize now the glycerol moiety. Here is a glycerol moiety. So this is one carbon atom, this is the other carbon atom and this is the third carbon atom. What was our glycerol structure? -COH then we have CH-OH and again we have CH_2OH. This has been esterified and this has been esterified. We have long chains here and in this case we have it esterified with the phosphate. Linked to the phosphate again now is another group. This is X that I showed in the previous slide. So it is this group X that in this case is inositol. When you have all this number of OH here and the phosphate here and the negative charge here what does this comprise? It comprises the polar head groups. It is this part that forms the polar head groups and what is R_1 and R_2 forming? The tail. It can be different depending on the type of R_1 and the type R_2.

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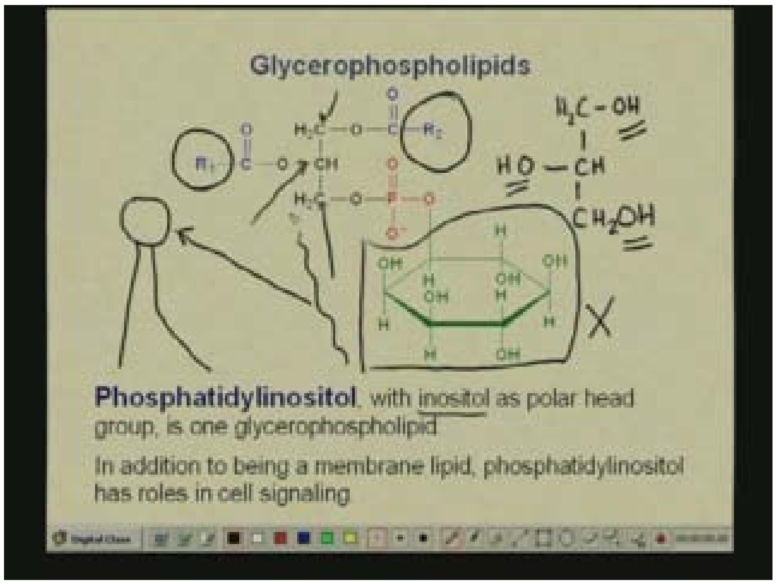

This is the basic structure of a glycerophospholipid. Now what can we change? We can change inositol, make it something else. Let us see what we can change it to. We can make it choline. Again the basic structure is exactly the same. I have R_1, R_2. I have the phosphate. Linked to the phosphate I have another X. What is that X? Choline. So I have instead of phosphatidylinositol I have phosphatidylcholine. I can also have phosphatidylethanolamine. I can have phosphatidylserine. In each of these the difference is going to be just in the X group in this case. We can have identical R_1's and R_2's for phosphatidylchloine, phosphatidylserine and phosphatidylethanolamine.

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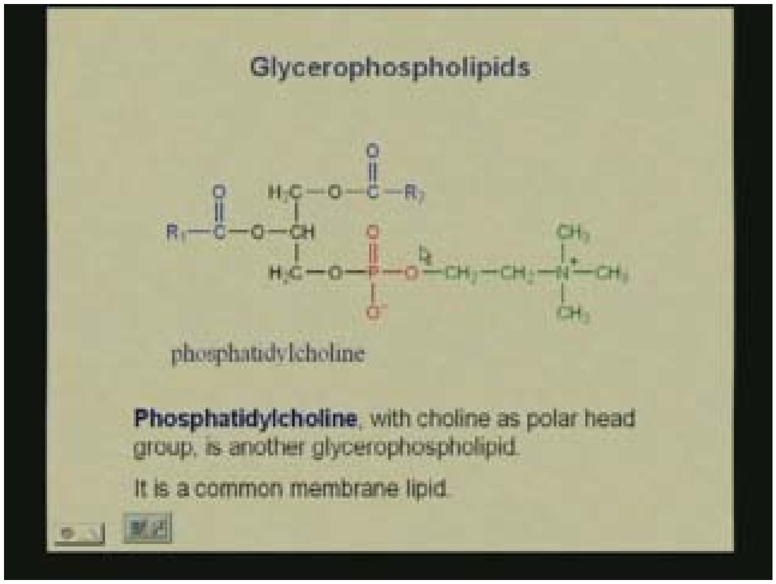

These are the different types of glycerophospholipids that we can have. What you need to remember is the basic structure is a glycerol, you have two fatty acids R_1, R_2, you have a phosphate and the phosphate is linked again to another polar head group that is going to result in a polar head group to your lipid. What is a sphingolipid? This is the structure. It is based on the structure called sphingosine.

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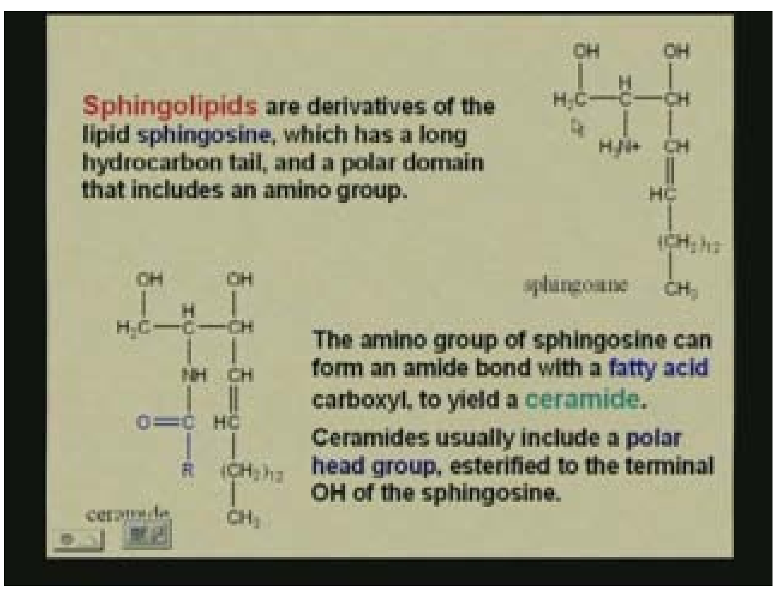

This is the structure of spingosine. You have a $-CH_2OH$. You have in the middle CH-NH_3^+ and in the last carbon you have a –CH-OH to which is linked a long hydrocarbon tail. This is the basic structure of sphingosine. We have a long carbon chain as it is. By default sphingosine comes with a long hydrocarbon chain. It has a polar region here that constitutes an amino group. It has a NH_3^+. What can happen with a NH_3^+ and a fatty acid? It can form an amide. In the part here we have an RC=O-NH. Just like an amino acid linked to NH_3^+would give you an amide, you can have an amide formed here. The amino group of the sphingosine that can form an amide bond with the fatty acid gives you what is called a ceramide. Have you heard the word ceramide before? They sell you shampoos with ceramide in it. If you look at the advertisement of shampoos they will tell you that ceramides are present in it.

This is what a ceramide is. What do you have in a ceramide? You basically have a sphingosine. What is a sphingosine? Sphingolipids are going to be derivatives of this. It has nothing but a long hydrocarbon chain, there is NH_3^+ attached to it and an -OH attached to it. This already has the long hydrocarbon chain attached to it. You can have this NH_3^+ form an amide with another fatty acid. You are going to have two long carbon chains here. We have ceramides that usually include a polar head group and they are esterified to the terminal -OH of the sphingosine. We will see what it is. You recognize the basic structure of the sphingosine now? This is the basic structure of the sphingosine, the one in black. This is the long carbon chain. This is the sphingosine moiety. This is the fatty acid attached to it to form an amide and we had an -OH here. So this can attach to another group forming a sphingomyelin.

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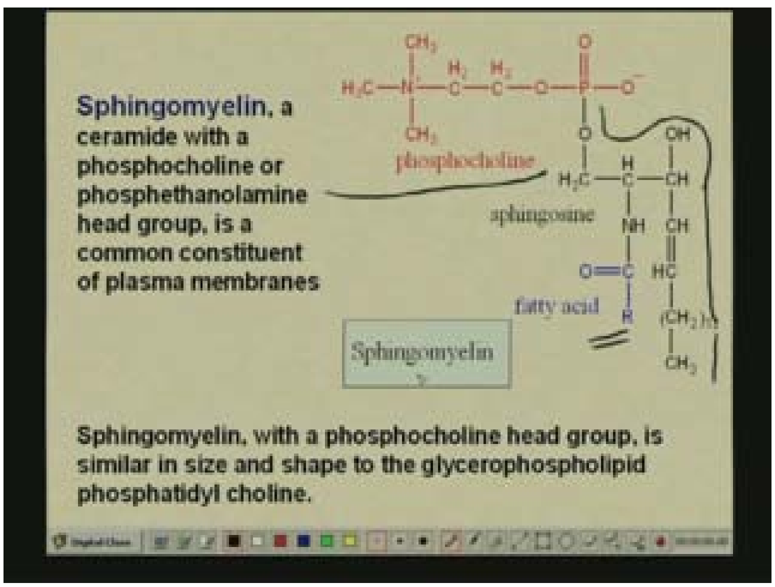

We have what is called a sphingomyelin which is a ceramide with the phosphocholine. What is a ceramide? A ceramide is when you have -OH here and the amide here and the sphingosine as it is. So in the basic structure of the sphingosine if you have the fatty acid linked to form an amide it is called a ceramide. In this case when you have phosphocholine to form a head group here this forms what is called a sphingomyelin. So this is after the formation of a ceramide. So you have an -OH group, initially this was an –OH. This is now linked to phosphocholine to form what is called a sphingomyelin.

There is another thing that we need to know. We remember what a sphingomyelin or what a ceramide is? What is a ceramide? A sphingosine with the fatty acid with –OH.

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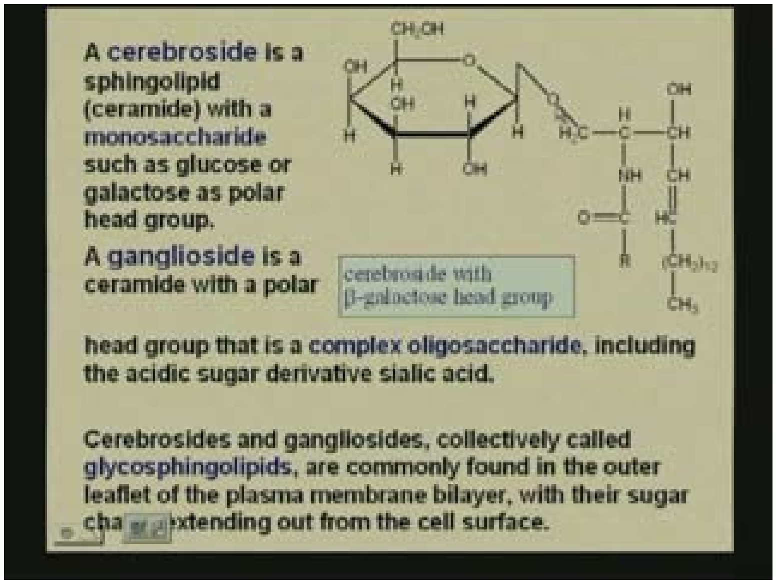

Now you have to recognize that that H can be replaced. If you replace this H with phosphocholine you have sphingomyelin. If you replace it with a sugar you have what is called a cerebroside. It's just nomenclature. All you need to know is you have a glycerol, you have a sphingosine. These are the two backbones. That's it. You have three -OH groups here. If three of them are fatty acids you have a triglyceride. If two of them are fatty acids and one of phosphate you have glycerophospholipids. If that phosphate again is attached with another X, you have series of lipids. In sphingosine you have different types. Basically you have a shape like that. You have a long carbon chain in the structure of sphingosine itself. You have fatty acid attached in forming a ceramide. Then this -OH can be linked to sugar, to form a cerebroside.

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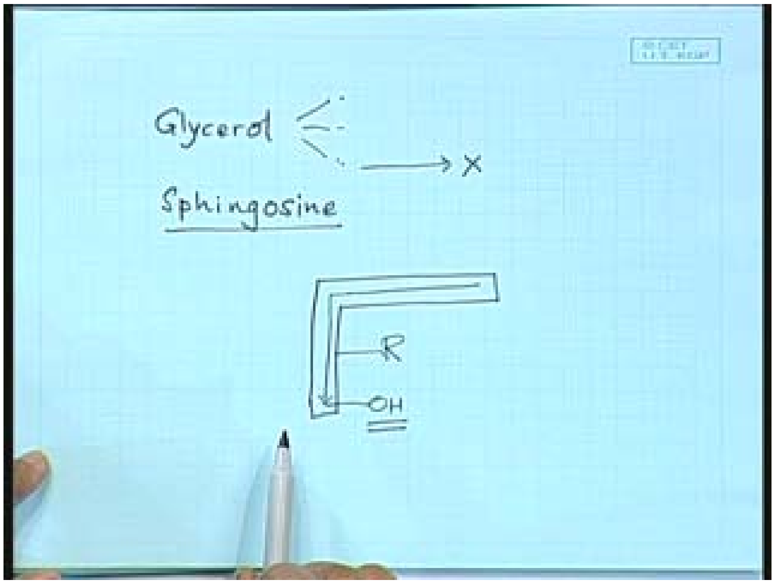

It can be linked to phosphocholine forming a sphingomyelin. That is the basic structure of all these. So we can have a cerebroside if you had just simple sugar or you can have ganglioside when you have complex oligosaccharide attached to it. It's just the nomenclature. They are usually found in the membrane bilayer which is why we have to consider all the different types of possibilities of the sphingolipids of the lipid themselves. If we look at the molecular arrangements of the lipids you know that they can associate with water because the cytosol of the cell itself is embedded in water, embedded in the blood, embedded in the cytosol. The hydrophobic tails will never be in the cytosol.

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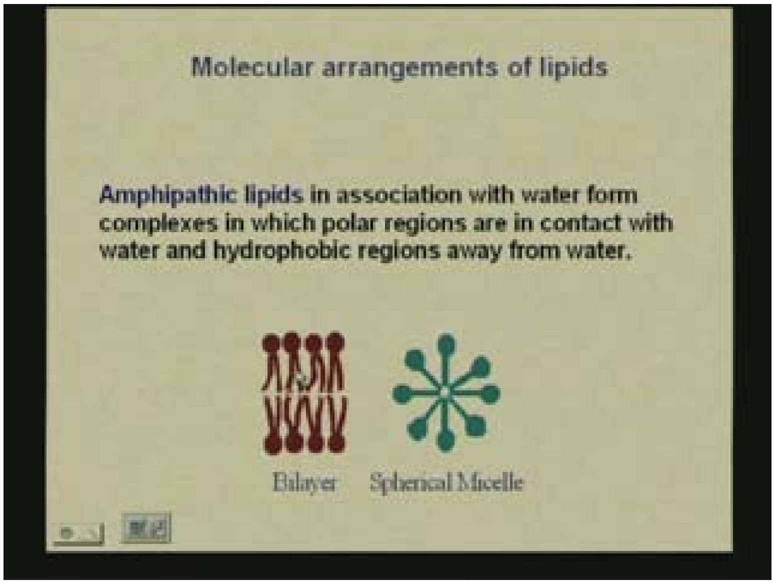

We have to have what is called a bilayer. So it is this polar part that is going to be outside the cell and this polar part that is going to be inside the cell. So we have a bilayer that has polar head groups in either directions. So the amphipathic lipids in association with water will form complexes in which the polar regions are in contact with water and the hydrophobic regions are away from the water. So it is a very smart way of forming the lipids, where you have a strong bilayer which is not going to allow everything in and out of the cell but at the same time it is going to be extremely important in the characterization of the lipid bilayer. There is another way we can organize this. How is that? In a spherical manner, we form what are called spherical micelles. What are these micelles?

These micelles have polar head groups outside and we have the hydrophobic tails inside. We can also have what is called a reverse micelle, where you have the opposite of this. If you put this spherical micelle with the polar head groups in an organic solvent it is going to reverse and the polar head groups are now going to be in the center and the hydrophobic tails are going to be facing the hydrophobic or the organic solvent. So we have what we call the reverse micelles or the normal micelles. When we have a cerebroside or a ganglioside, some structure like this form a micelle then we have a long fatty acid chain at the R group. We have another long hydrocarbon chain in the sphingosine moiety …. because of the sphingosine structure itself. When this forms a micelle we expect this part to be the polar head groups on the surface and these two to be the legs of the structure. The structure that we have here is basically going to be the bilayer with two long chains. In case of a glycerophospholipid both of these are fatty acid chains. But in case of a sphingolipid one part is the hydrocarbon chain that belongs to the sphingosine and this is the ceramide, the amide part that has been linked with the amide of the sphingosine to form an amide. So we have one fatty acid and one sphingosine hydrocarbon chain and the same thing that we would have here. What are the structures that you can have? This is a micelle.

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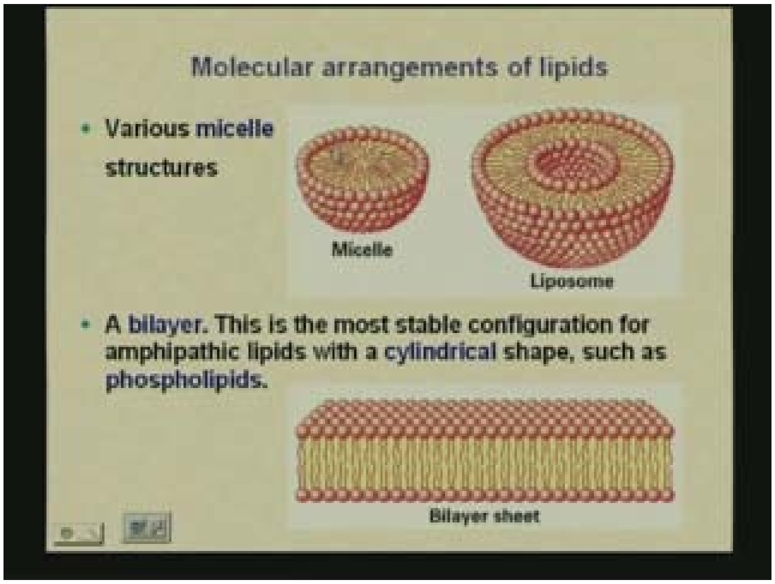

A micelle is not two dimensional it is three dimensional. It actually looks like this. This is just like half of it cut of. We have different types of micelle structures. All these red balls that we see here, red spheres along the surface are all polar head groups and all the chains that are inside are all the hydrophobic chains that we see. Consider a liposome and the way transport of material occur in the body. If you have a micelle and you have a polar ingredient or a polar substance that has to be transported, you understand that it is not going to be possible for this particular micelle to transport it. Why? Because it has a hydrophobic core to it and it would be possible to transfer a hydrophobic component but if it happened to be a polar part it would be difficult to do so. So we have the formation of liposomes. What happens here is you see there is a lipid bilayers sort of a thing that forms the membrane and inside we have a polar center. The reason why I am telling you this is this is used for a lot of drug delivery. When you have drug delivery or when you are creating or making drugs you have to ensure that the drug is water soluble. If you want it to interact with blood plasma you have to have one that is going to be easily solubilized, which is a problem with drugs that they are not easily solubilized.

The transport of a lot of material takes place through these liposomes. You understand that in the center here we can have any polar moiety. Any favorable ionic interaction that might occur will hold the drug in this position and it will transfer it to where it has to go. It will circulate in the blood and then be able to transfer itself. In the case of a bilayer is we have the most stable configuration for amphipathic liquids. This is the possible structure and this is usually used in transport but this is sort of a confined structure. If we have a lipid bilayer then we have the polar groups forming a sheet on one end and the polar group forming the sheet on the other end. We have a lipid bilayer and it is this bilayer that is going to result in all of the transportation, all of the lipids structure, all of the membrane structures that we will be seeing in the next class.

Basically what we have learnt is that we have our glycerol. In the glycerol we have storage lipids. What are storage lipids? Storage lipids are those that are fat droplets. What are these fat droplets? The fat droplets are triacylglycerols or triglycerides. What is the basic structure in this case? We have our three carbon glycerol and we have three –OH. We have this replaced by a fatty acid, this replaced by fatty acid, this esterfied to fatty acid and each of these esterified to fatty acids is going to give our triacylglycerols. They can be esterified by a series of fatty acids and we learnt that if we have such a nomenclature delta 5, 8, 11, 14 we know how we can write this. We have normally a long carbon chain where we have the -COOH attached in a normal fatty acid. When we have a nomenclature in the delta designation we have 18:4. The 18 stands for the number of carbon atoms, the 4 stands for the number of double bonds and these are the positions of the double bonds from 5to 6, 8 to 9, 11 to 12 and 14 to 15.

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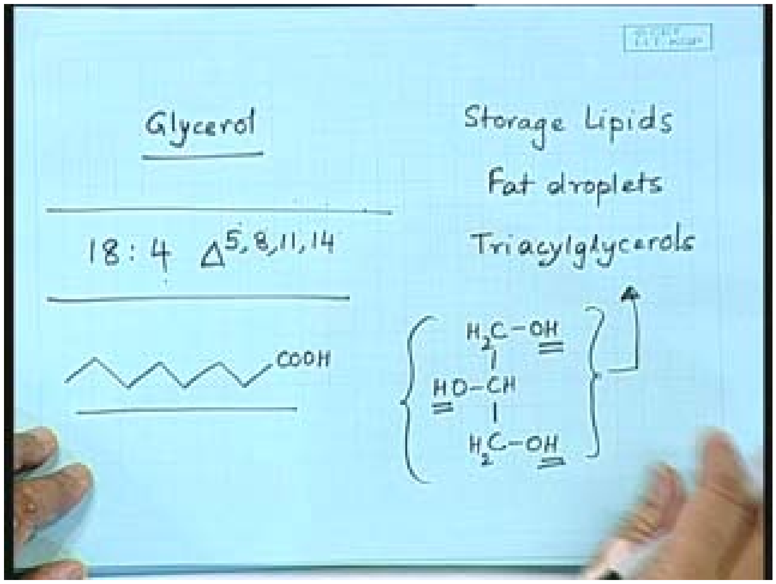

Once we have these fatty acids we can have a cis configuration to the double bond. As soon as we have this in a cis configuration this changes the direction. As soon as this changes the direction then what happens is I have a kink. This gives rise to a kink in the structure and in glycerophospholipid I have H_2, I have R_2 here, I have R_1 here, I have my phosphate and I have to this, linked an X. This is my polar part. What can happen is if this forms R_2 and for R_1 I have straight chain carbon fatty acids and this is my polar head groups. I will have a polar head group that is this part, I will have a long carbon chain which is this part if I happen to have no double bond formation and if I happen to have double bond formation I will bend it like this. I have specific properties of the fatty acids that tell me that the pKa's are around 4.5 to 5 making them or ionizing them at physiological pH and I have specific melting points for these depending on the length of the chain and on the number of the double bonds that we have here.

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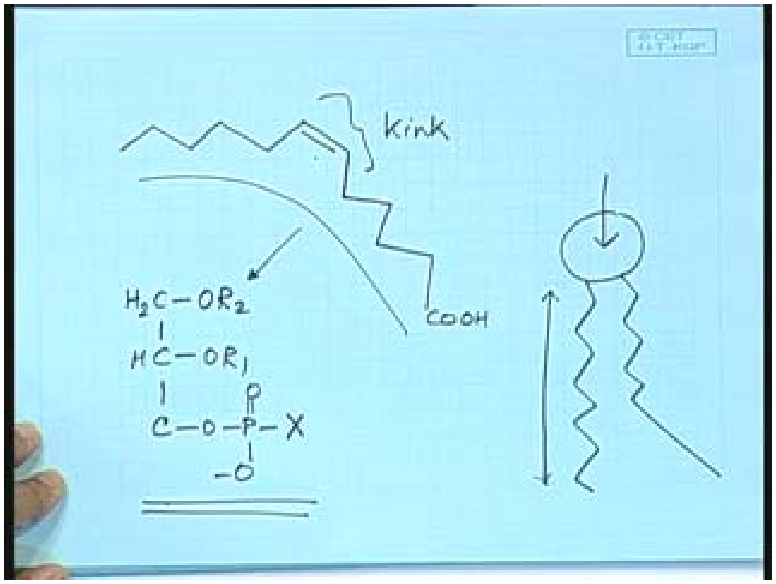

Because the more the number of double bonds, you are disrupting the organized structure that it would have. What would happen if it would look perfect? This is the way they would be organized. But if you had a kink you would have say, one that was shaped like that, one that was disrupted like that. So what would happen to this? This would melt easier than this. So the more the number of double bonds the more the disruption in the structure; you would have lower melting point which is why a saturated fatty acid is solid at room temperature.

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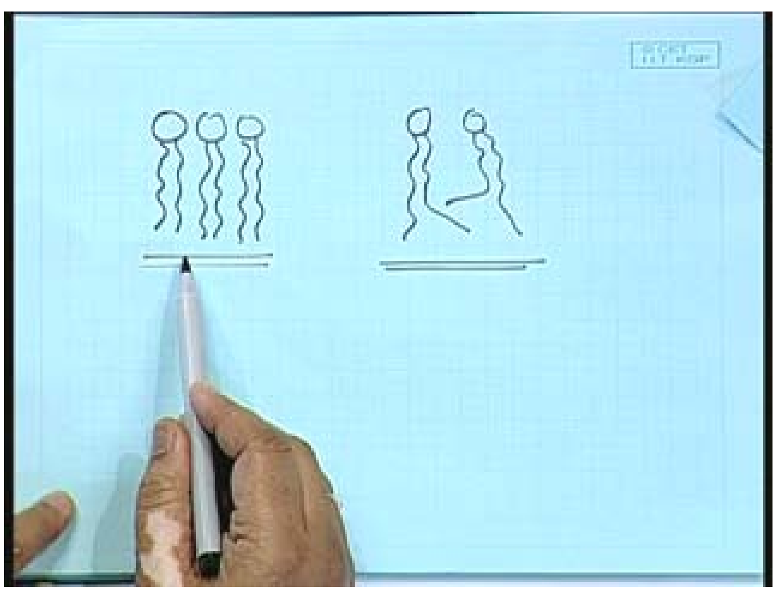

Then we went on to study all the different types of lipids that we could have and these are the different types of molecular arrangements of lipids that we can have and in the next class we will see how we can organize this into an actual lipid bilayer in the protein and we will see how proteins are embedded and how they can help in the transfer of materials inside and outside the cell. Thank you.