Food Oils and Fats: Chemistry & Technology

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Week 1: Course Overview and Introduction

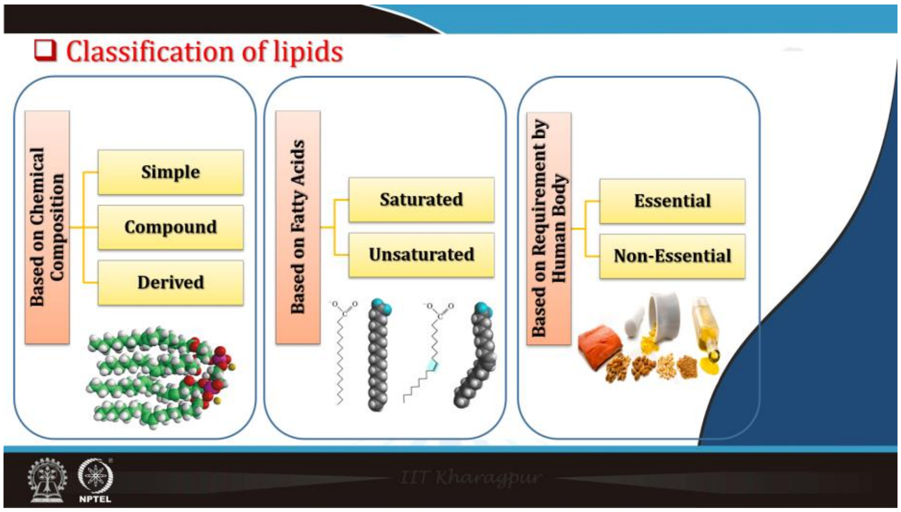
Lecture 6: Lipids and Their Classification

Hi everyone, Namaste. Now we are entering to the second week of the course and this week, the five lectures will be devoted on 'Nature and Occurrences of Food Lipids.' Like in these five lectures, we will discuss various matters or concepts related to that what are the food lipids, what is its nature, how they are found. Today's lecture 6 will talk about 'Lipids and their Classification'.

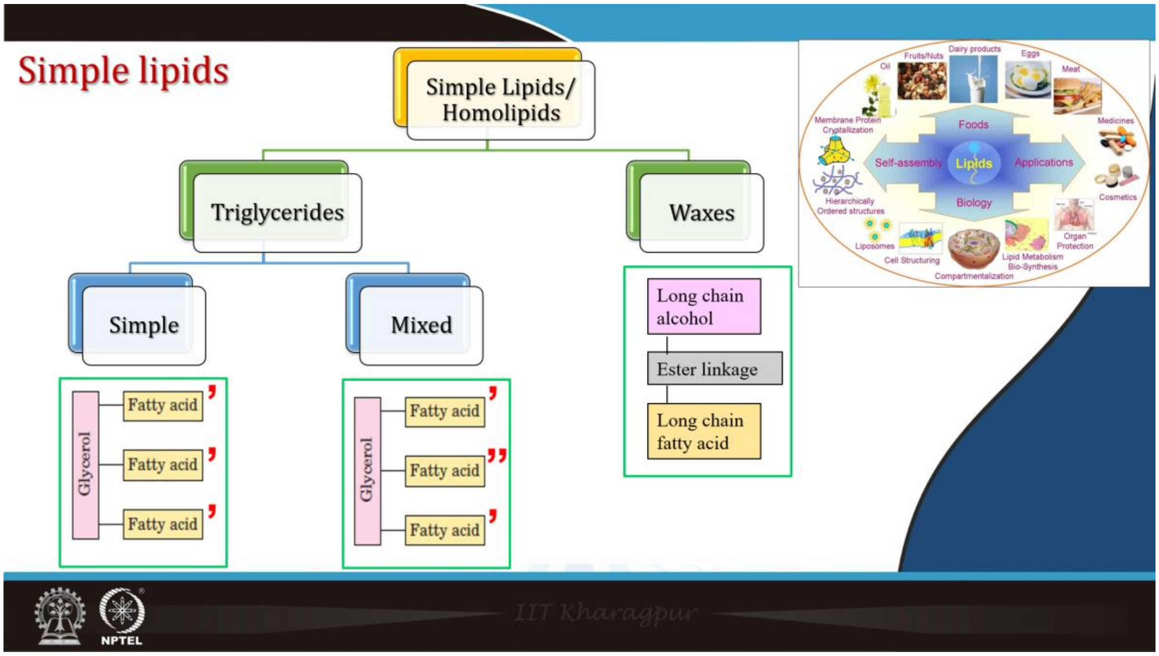
So, we will cover in today's lecture, nature and occurrence of lipids, their classification and what are the different types of lipids like simple lipid, compound lipid and derived lipids. Also, we will throw some light on triglycerides and waxes, phospholipids, sphingolipids and steroids and carotenoids.

Although in earlier classes also we made a small brief mention of all these things, but now we are going towards the deeper side. We will discuss mostly the chemistry etc. what are their constituents, how they are presented.

So, the lipids you have seen earlier also we discussed, they are chemically diverse compounds, which are all soluble in organic solvents. Lipids in the form of triglycerides occur as storage lipids in biological tissues. The triglycerides from plant and animal sources are generally rich in unsaturated and saturated fatty acids, respectively and that is why triglycerides from plant sources are normally liquid at room temperature, triglycerides from animal sources are generally solid at room temperature. Lipids in the form of phospholipids, glycolipids, lipoproteins, sterols etc. occur as membrane lipids in biological systems. Storage lipids are neutral lipids, while the membrane lipids are polar in nature. Other lipids occurring in small quantities also serve crucial functions such as enzyme cofactors, electron carriers, hormones, emulsifying agent in gastrointestinal tracts and so on.



So, the lipids are normally classified in various ways. The three major ways by which we can classify lipid that is on the basis of their chemical composition, that is what are these lipids composed of and accordingly that is on the basis of their chemical composition. Lipids are classified into three groups like simple lipids, compound lipids and derived lipids. We will have details of all these. Then another way of classification is on the basis of type of fatty acids which are present in lipids, that is whether saturated fatty acids are present or unsaturated fatty acids are present. Accordingly, there is the saturated fat or unsaturated fat or solid fat or liquid fat. Then third and the very important classification of the lipid is, that is based on the requirement by the human body, that is, which fat, that is essential fat and non-essential fat. That is essential fat, there are certain particularly some fatty acids etc., which our body cannot desaturate. We do not have the molecular machinery, but the plants do have. So, plant oil, fish oils etc. have those essential fatty acids and these essential fatty acids, because our body, they are required for normal functioning of our body, but our body cannot synthesize them. So, we must take these fatty acids, that is essential fatty acids from the plant sources or fish oil etc. as you discussed in the earlier classes also. So, on the basis of the human body requirement of the fats like essential fat and non-essential fat, the triglycerides or lipids are accordingly classified, that is those who contains more amount of essential fatty acids or which contain non-essential fatty acids. Then let us see little details like the you saw that lipids that is one classification is on the basis of their, that is simple, that is the chemicals compound, their nature like simple lipid, compound lipid and derived lipid.



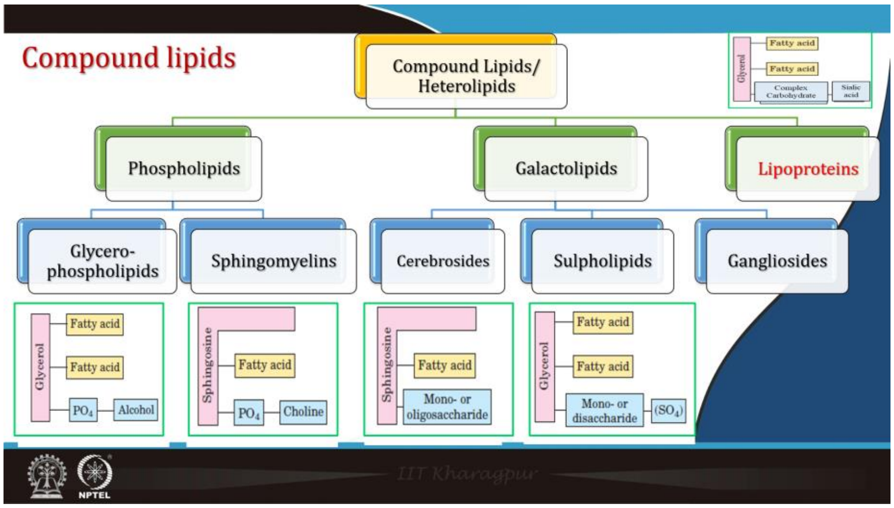
So, let us first discuss simple lipids. Simple lipids are also homolipids called and these are two types. They can be classified. One is the triglyceride; another is the waxes and this triglyceride again there may be a simple triglyceride or mixed triglyceride. Simple triglyceride means in the earlier class we discussed about triglyceride it is glycerol and three fatty acids. So, if all the three fatty acids, which are attached or which are present over the glycerol molecule, they are the same fatty acid like let us say one fatty acid is stearic acid or palmitic acid. If it is in all the three alcohols are esterified with the same fatty acid, then it becomes a simple fatty acid, but the mixed triglycerides that is simple triglyceride. The mixed triglycerides are the one, where different fatty acids may be or two fatty acids might be stearic, one may be palmitic or even one may be oleic, one may be stearic, one may be palmitic. So, these are where, different fatty acids are attached with the same glycerol molecule, then it becomes mixed fatty acid. And mind it most of the fats and oils, they are mixtures of mixed triglycerides.
So, the waxes, they are the esters of long chain alcohols, that is mono hydroxy alcohol and fatty acids, that is here long chain fatty acids and long chain alcohols, they are combined. So, that is the main difference between the triglycerides and waxes. Triglycerides, here these are the glycerol, the three hydroxyl groups and three fatty acids are attached. Whereas, the waxes, one long chain fatty acid and one long chain alcohol, that is mono hydroxy alcohol, these are attached. So, these becomes the waxes.

We will take up the little details of all this more. So, let us see triglycerides that fats and oils. So, as you can see here in this structure, I have shown that the fats and oils earlier also we discussed, they are chemically known as triacylglycerols or triglycerides and they are formed by the reaction between alcohol and fatty acids or reaction of fatty acid with alcohol and when one fatty acid, you see here, that is, it becomes mono glyceride, two fatty acids are joined with the di glyceride and three fatty acids are triglycerides and triglyceride again that is, the I just told you, that is simple triglyceride and mixed triglyceride, you can see here, in the simple triglyceride, where all these R3 fatty acids are the same fatty acids, it becomes simple triglyceride. When these are the different, R1, R2, R3, then it becomes mixed triglyceride.

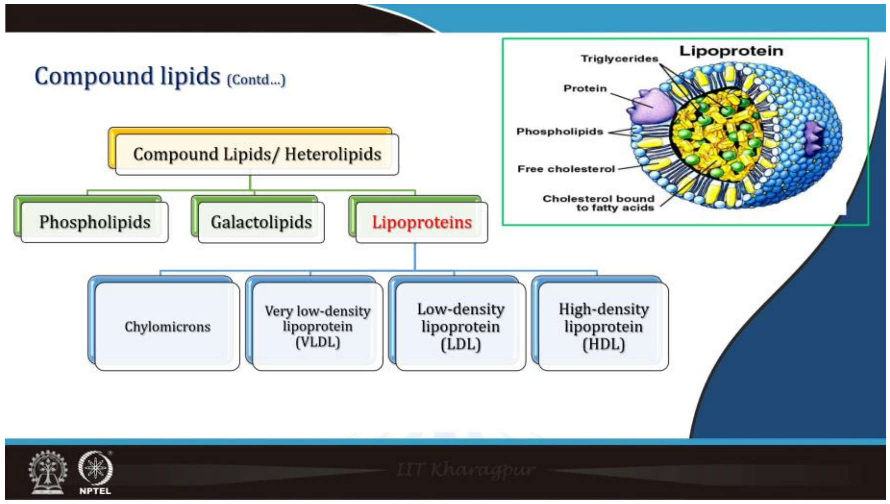
So, mono and diacylglycerols are partially soluble in water, since they have hydroxyl groups. In mono, there are two hydroxyl groups, in di there are one hydroxyl group. So, they are little bit partially soluble with water, but the triacylglycerols, since they do not have any hydroxyl group. So, they are completely non polar, they are only soluble in organic solvents. They are neutral lipids, that is they have no charge. They are more abundant, which constitutes about 98% of all dietary lipids. The differences in texture, appearance, physical properties, functional properties between fats and oils are mainly because of the fatty acids, the differences in the fatty acids, which are attached with the glycerol molecule or in the triglycerides. So, plant and marine triglycerides contain unsaturated fatty acids especially the polyunsaturated fatty acids, while the animal fats are relatively rich in the saturated fatty acids. This we discussed earlier also.

The waxes as I told you they are also commonly called wax esters or mixtures of esters of fatty acids and long chain monohydroxy alcohols. Biological waxes are esters of long chain like C14 to C36 saturated and unsaturated fatty acids with long chain like C16 to C30 alcohols. Their melting points are generally in the range of 60 to 100 degree Celsius and these are generally higher than those of the triacylglycerols. Simple waxes are esters of medium chain fatty acids like 16:0, 18:0, 18:1 and long chain aliphatic alcohols ranging in size from C8 to C18. Simple waxes are found on the surface of animals, plants and insects and they play a role in prevention of water loss. Complex waxes are formed from the diols or from the alcohol acids. So, this triacontanoylpalmitate, the major component of the beeswax is an ester of palmitic acid and trioctanol and a honeycomb constructed of beeswax is formed at around 25 degree celsius and completely impervious to water. In fact, the term ‘wax’ originates in the old English weax, weax meaning the material of honeycomb. So, from w e a x that is from this weax finally, it comes wax.

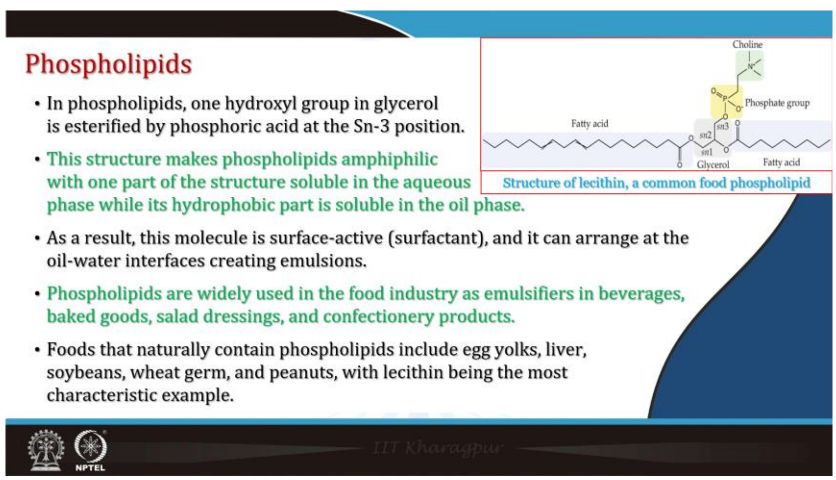
Simple waxes can be named by removing the -ol from the alcohol and replacing it with -yl and replacing the -ic from the acid with -oate. For example, the wax ester of hexadecanol and oleic acid would accordingly be named as hexadecyl oleate or hexadecyl-cis-9-hexadenenoate. So, this is the system of similarly the most of the triglycerides also are named like this. Waxes are found in animal, insect, and plant secretions as protective coatings. Waxes serve as energy sterols and water repellents in biological systems. Carnauba wax, beeswax and candelilla wax are the typical examples of glazing agents and fruit waxing in the food industry. They are generally used for coating over the surface of the fruits to restrict their respiration and increase their shelf life. Now, these were about the simple lipids.



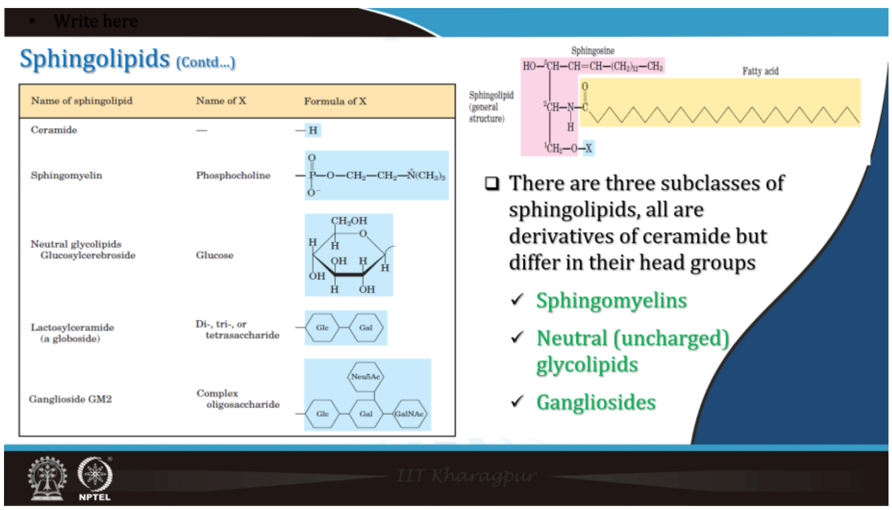
Now, let us talk about the compound lipids or hetero lipids. So, compound lipids they may be of three major categories like phospholipids, galactolipids, and lipoproteins. So, phospholipids are again, they can be further classified into glycero-lipids and sphingomyelins, that is the here. These phospholipids, they are the glycerol molecules, that 2 fatty acids are there and the third fatty acid that is at SN3 position, a phosphoric acid group is joined and which in turn, combined with another moiety that choline, alcohol etc. We will take up little detail further. This sphingomyelin, you can see here, it has at SN2 position fatty acid, SN3 position phosphate and choline and this is a glycerol wax. So, the other galactolipids the other type of the compound lipids they are of two types cerebrosides and sulfolipids. Cerebrosides are that is you can see here that is at SN2 position is a fatty acid and SN2 position are mono or oligosaccharides. In the sulfolipids that is SN1 and SN2 position are fatty acids and SN3 position is mono or disaccharide, which might be further joined with sulfate. and the gangliosides are that is they contain SN1 and SN2, two fatty acids and then SN3 position, there are complex carbohydrate and which may be further tied with the sialic acid. So, this is the gangliosides. Regarding lipoproteins that is the lipoprotein may be further different types, depending upon the various composition derivatives etc. like a chylomicron, very low-density lipoprotein VLDL, low density lipoprotein LDL or high-density lipoprotein HDL.



That is, you can see here in this structure that is how lipoprotein structure of a lipoprotein, there where triglycerides, molecules these green proteins that is phospholipids, free cholesterol or cholesterol bound to fatty acids, they are all present in the cell. But let me tell you, among all these lipids as far as the food processing is concerned. So, simple lipids, that is the fats and oils, that is triglycerides and the phospholipids, that is these two are the phospholipids. These two are the important constituents form from processing point of view and of course, lipoprotein etc. from the nutrition and health point of view, almost all these lipids are important.

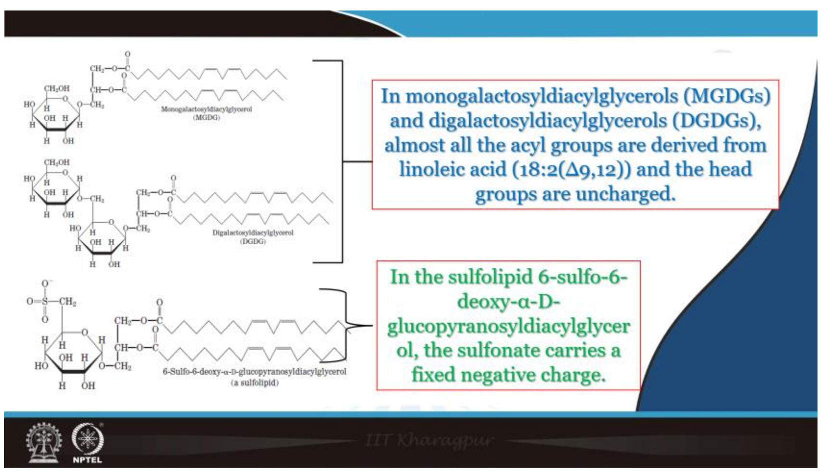


So, let us see phospholipids, that is in the phospholipids, as earlier also, there is one hydroxyl group in glycerol, is esterified by phosphoric acid at SN3 position here. SN1 is fatty acid, SN2 is fatty acid and SN3 is the phosphoric acid and which in turn attached with another moiety which may be choline, which may be some other. So, this structure makes the phospholipid amphiphilic with one part of the structure is soluble in aqueous phase, while it is a hydrophobic part is soluble in the oil phase and that is why these phospholipids, they act as an emulsifier. They keep both oil phase and water phases together and whenever they are present, wherever they are present in the food system and the result, they act as a bridge between them and they keep them in place they do not allow, that is the emulsifiers, which keep two immiscible liquids into a miscible form or stabilized form. As a result, this molecule is surface active and it can arrange at the oil-water interface creating emulsions. Phospholipids are widely used in food industry as emulsifiers in beverages, baked goods, salad dressings, confectionary products etc. and among them lecithin is the one more most important food that naturally contain phospholipid include egg yolk, liver, soybean, wheat germ and peanut and lecithin being the most characteristic example. In fact, in the peanut butter, when the peanut oil the margarine is prepared, we will take up separately in the next class earlier later, that the peanut butter, that is margarine that is in the peanut oil water is added and about it contains as high as 8 to 10 percent of the emulsifier lecithin or some other emulsifier, which keep these water and oil phases mixed together.

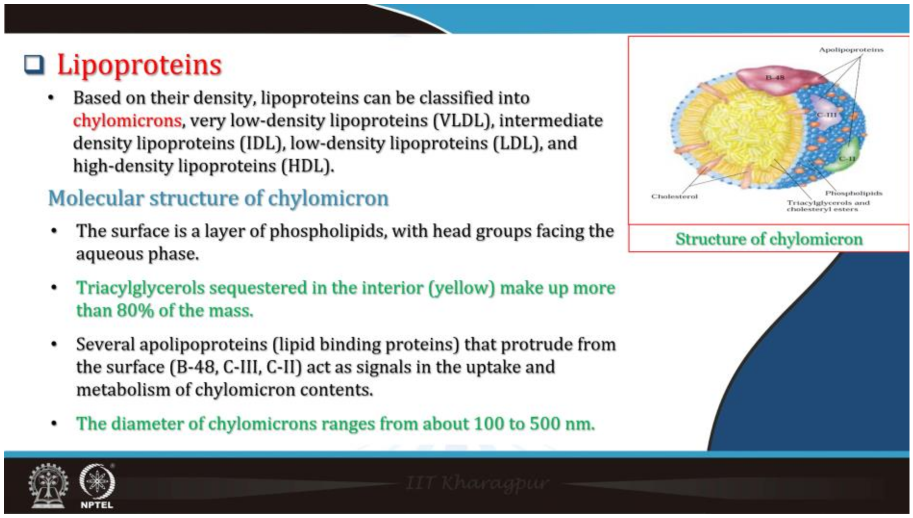


Then sphingolipids, they are class of lipids containing a backbone of sphingoid bases. They are sphingosine is an animal alcohol that form the structural basis of the most important sphingolipids. For example, ceramides are composed of sphingosine with N linked fatty acid at the SN2 position. Derivatives of ceramides may be formed by the reaction between OH group at SN1. For example, sphingomyelin consists of a ceramide with phosphocholine esterified at SN1. When a single sugar residue usually glucose or galactose is attached at SN1, a cerebroside is obtained, whereas, when an oligosaccharide with one or more sialic acid is attached a ganglioside is obtained. These compounds play an important role in signal transduction and cell regulation and although they are not very typically consistent as dietary lipid due to their low concentration, their role is being continuously examined and reevaluated. Foods rich in sphingolipids and their derivatives include dairy, meat, egg, soy and seafoods like mussels, scallops etc. Fruits and vegetables are generally low in their sphingolipid contents. So, here you can see in this picture, there are some major sphingolipids like, this is the structure of a sphingosine as you could see that at SN2 position there is a fatty acid at SN3 position there is a here this is and at SN1 position is a X molecule, which is normally that is X is defined in this table that is when this X is H then it is a ceramide. When X is a phosphocholine, it is become a sphingomyelin, when X is a glucose, it becomes neutral glycolipids, when X is a disaccharide like glucose and galactose or it may be oligosaccharide, di tri etc. etc. it becomes lactoside, ceramide or when X is a complex oligosaccharide, it becomes gangliosides like GM2. So, there are you can summarize that, there are three subclasses of a sphingolipids and that are the derivative of ceramides, but they different mainly in their head group. Here it is SN1 that is head group at SN1 position.

Galactolipids and sulfolipids of course, you see in the earlier structure, the second group of the membrane lipids are those, that predominant in the plant cells or the galactolipids in which one or two galactose residues are conducted by a glycosidic linkage to C3 of 1, 2 diacylglycerols. Galactolipids are localized in thylakoid membranes which are the internal membranes of chloroplast and they make up to 70 to 80% of the total membrane lipids of a vascular plant. They are probably the most abundant membrane lipids in the biosphere. Plant membranes also contain sulfolipids, in which sulfonated glucose residue is joined to a diacylglycerol in glycosidic linkage. In sulfolipids, the sulfonates on the head group bears a fixed negative charge like that of the phosphate group in phospholipids.

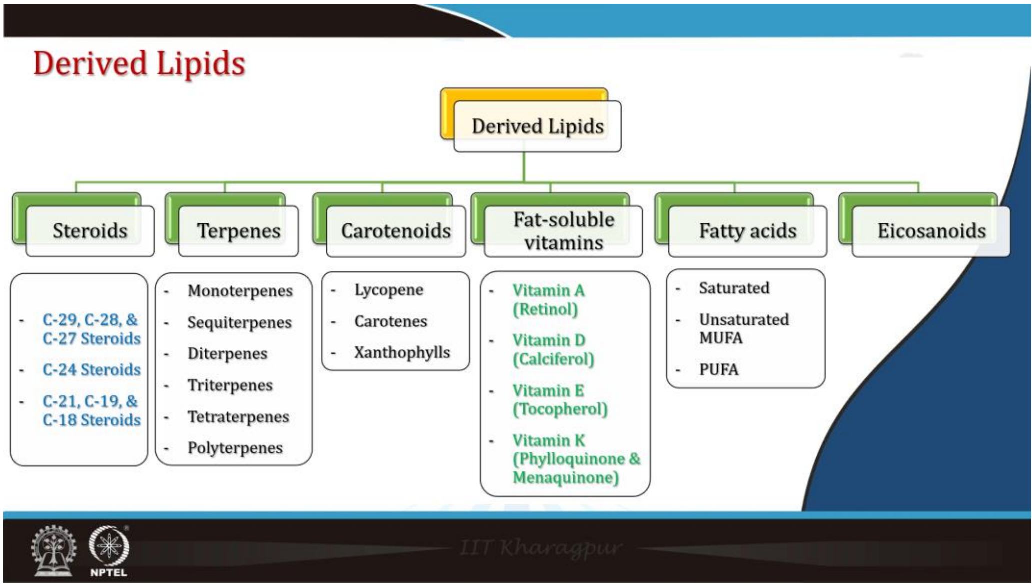


So, because see here, these are the, in monogalactosyl diacylglycerol and digalactosyl diacylglycerol, almost all the acyl groups are derived from linoleic acid, that is 18:2 double bond at 9 and 12 position and the head groups are unchanged. So, these are the mono MGDG and DGDG structures, you can see here. Whereas, in the sulfolipid 6-sulfo 6-deoxy-alpha-D you can see the structure is down that glucopyranosyldiacylglycerol. This is the glucose, but pyranosyl diacyl, third is that group, it is attached and it carries a fixed negative charge. So, these are the structures, we discussed earlier also to make the things more clear.

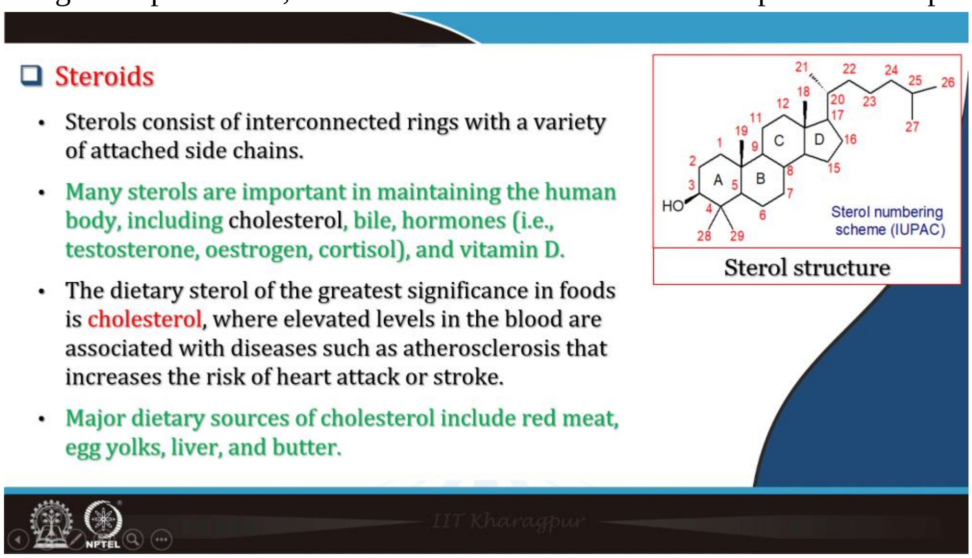


Now, very important from the health point of view lipoproteins, that is these are the compound lipoproteins, that obviously, based on their density lipoproteins can be classified as we discussed earlier also into, that is the chylomicrons and very low-density lipoprotein VLDL, intermediate density lipoprotein IDL, low density lipoprotein and high-density lipoprotein that is HDL. So, here you see that is the molecular structure of chylomicron is shown here, you can see that the surface is a layer of phospholipids particularly this yellow portion you see that is the phospholipids here phospholipids. And with the head group facing the aqueous phase and triacylglycerol sequester in the interior that is they are the yellow portion, triacylglycerol, these yellow portions make up more than 80% of the mass and several apolipoproteins that is lipid binding proteins that is they protrude from the surface B4, C3 and C2 act as signals in the uptake and metabolism of chylomicrons. And the diameter of chylomicrons ranges from about 100 to 500 nanometer even you see that these are the cholesterol also they are attached with it.

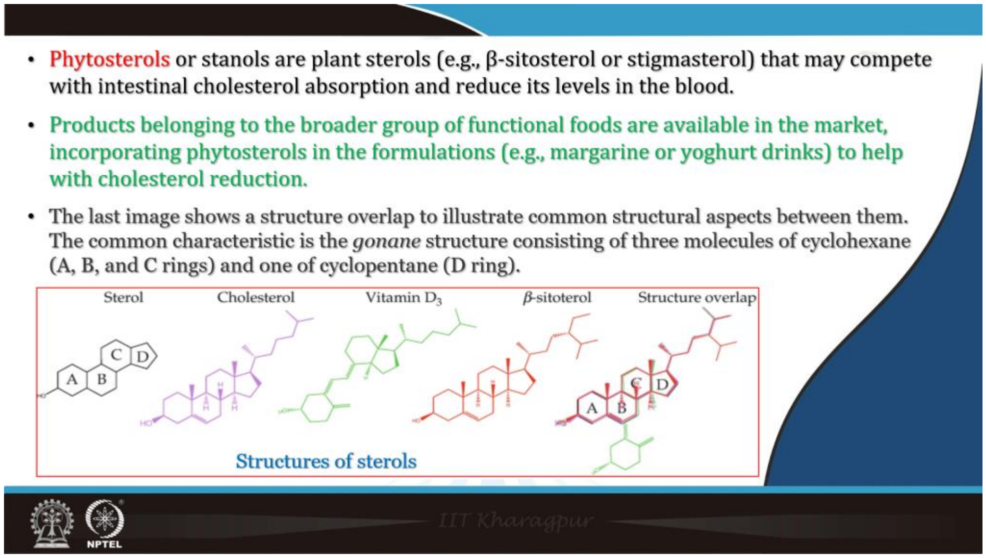
Then apolipoproteins and lipoproteins. Apolipoproteins are lipid binding proteins in the blood, responsible for the transport of triacylglycerols, phospholipids, cholesterol, and cholesteryl esters between organs. Apolipoproteins like apo-mines detached or separate, designating the protein in the lipid free form combined with the lipids to form several classes of lipoprotein practices. Spherical aggregate with hydrophobic lipids and at core and hydrophilic protein side chains and lipid head group at the surface. Various combinations of lipids and proteins produce particles of different densities ranging from chylomicrons and VLDL, VHDL and so on.



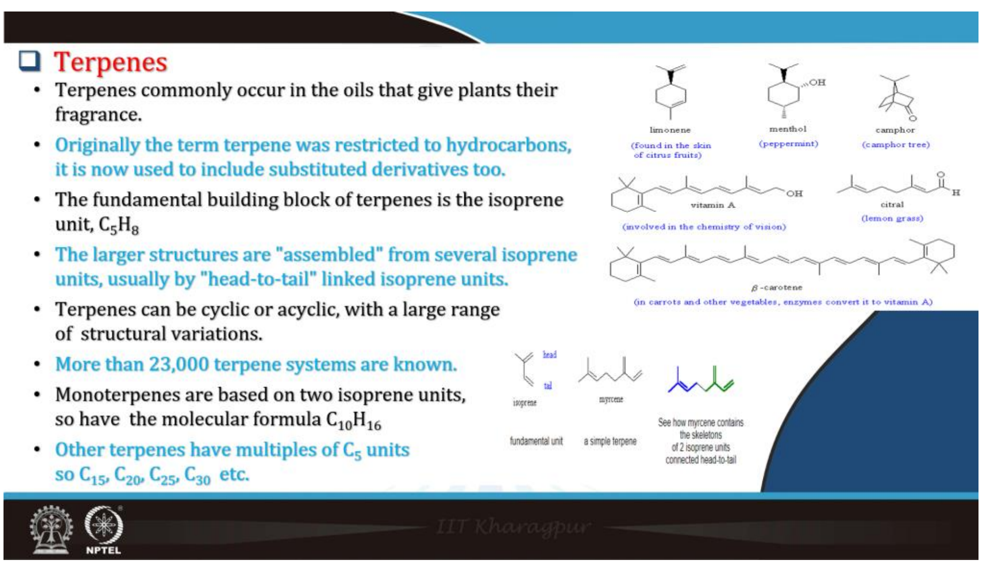
So, derived lipids finally, you see they are steroids, terpenes, carotenoids, fat soluble vitamins, fatty acids, eicosanoids etc. that is steroids that is C-29, C-28, C-27 steroids, and other things diterpenes. So, all these various forms of derived lipids are also present.



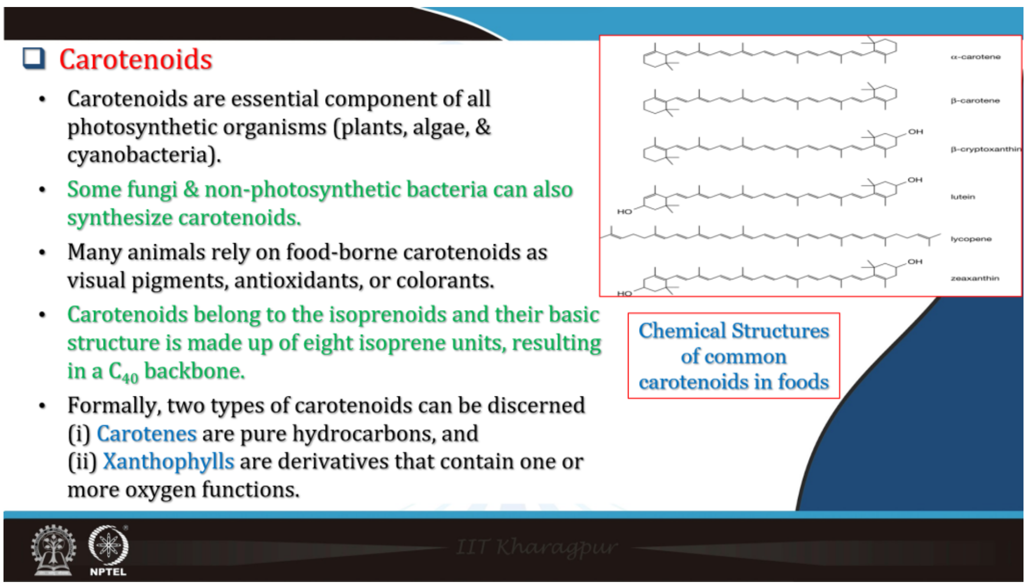
So, we will see that quickly these, that is, steroids they consist of interconnected rings with a variety of attached side chains. You can see here in the steroid structure. Many sterols are important in maintaining the human body including cholesterol, bile, hormones, testosterone, estrogen, cholesterol, and vitamin D. Dietary sterols of the greatest significance in food is cholesterol, where elevated levels of cholesterol in the blood are associated with the diseases, such as atherosclerosis that increases the risk of heart disease, heart attack or stroke etc. And major dietary sources of cholesterol include red beet, egg yolk, liver and butter.



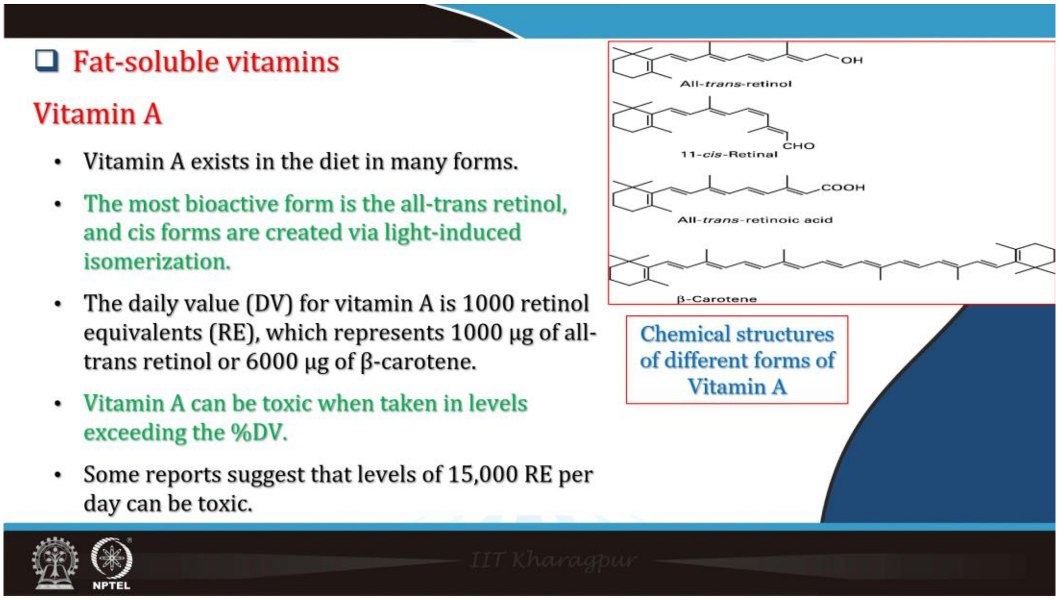
Then phytosterols or the stanlos, they are the plant sterols like beta, sitosterol or stigmasterol and they may compete with intestinal cholesterol absorption and reduce its level in the blood. So, if you are taking more phytosterols, then it becomes beneficial. Products belonging to the broader group of functional foods are available in the market incorporating phytosterols in the formulation like margarine, yogurt drink etc., which help to reduce the cholesterol level in the body. So, here you see some of the sterol structure like sterol, cholesterol, vitamin D 3, beta sitosterol and then there is a structural overlap. So, this image structural overlap is shown, illustrates common structural aspects between the various sterols. And you can see finally, the common characteristic is the gonane structure consisting of there is a last structure consisting of three molecules of cyclohexane, that is A, B and C rings and one cyclopentane like D ring and attached with a side chain.



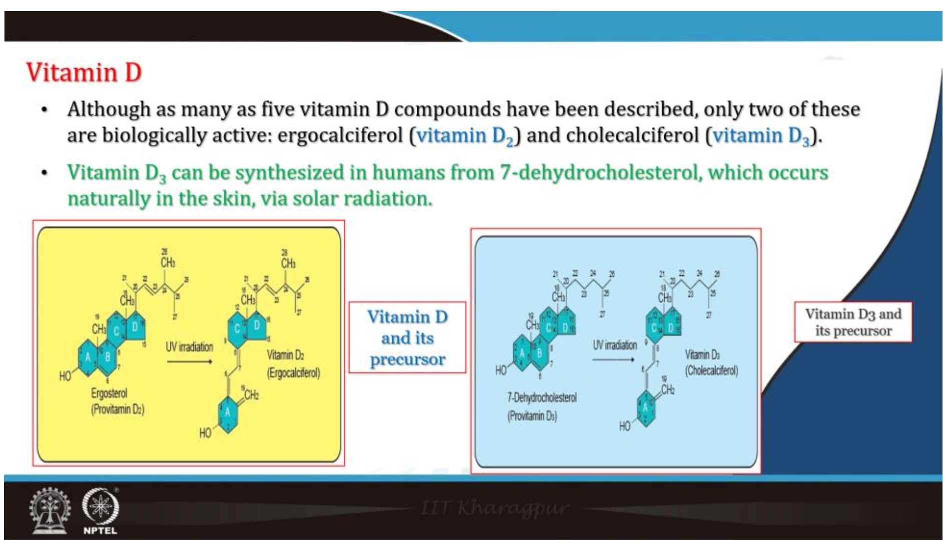
Terpenes, there are large number of terpenes are found, they are commonly occurred in the oil, that give plant their fragrance, particularly many terpenes are the major flavoring materials in the plant sources of the citrus oil, lemon etc. Originally the term terpene was restricted to hydrocarbons. It is now used to include substituted derivatives to the fundamentals building block of the inter terpenes is the isoprene unit that is C5H8. The larger structures are assembled from several isoprene units usually head-to-head or linked isoprene units. Terpenes can be cyclic or acyclic with a larger range of structural variations and more than 23000 terpenes systems are known and mono terpenes are based on two isoprene units. So, have a molecular formula generally C10 H16. Other terpenes have multiple of C5 unit like C15, C20, C25 and major terpene you can see the limonene, menthol, camphor, vitamin A, citral, b-carotene, isoprene, these all, they are present in the various plant sources.



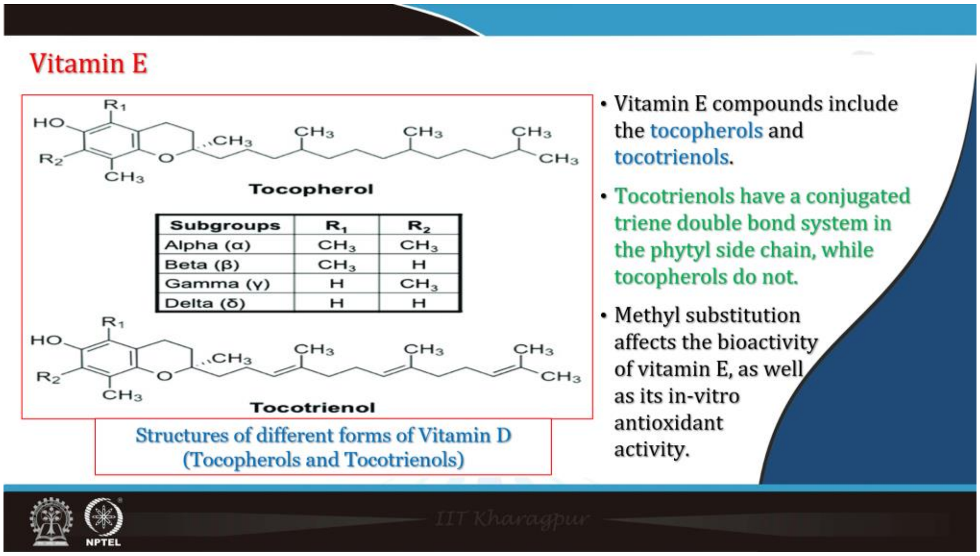
So, then carotenoids, very popular sterol present in the plant sources. They are essential components of all photosynthetic organs like plant, algae, cyanobacteria etc. Some fungi and non-photosynthetic bacteria can also synthesize carotenoids. Many animals rely on the food borne carotenoids as visual pigments antioxidants or colorants. Carotenoids belong to the isoprenoids and their basic structure is made up of eight isoprene units resulting in C40 backbone. Formally, two types of carotenoids can be screened that is the carotene,s which are pure hydrocarbon and the second are the xanthophylls. They are derivatives that contain one or more oxygen functions. You can see different types of carotenes like alpha carotene, beta carotene, beta cryptoxanthin, lutein, lycopene, zeaxanthin. They are all the compounds belonging to the carotene family derived lipids family and then you can see lycopene is the color compound present in tomato and lutein the color compound in aneto that is even this carotene. They are beta carotene is a precursor of vitamin A, that is yellow colored compound present in most of the yellow colored fruits and vegetables.



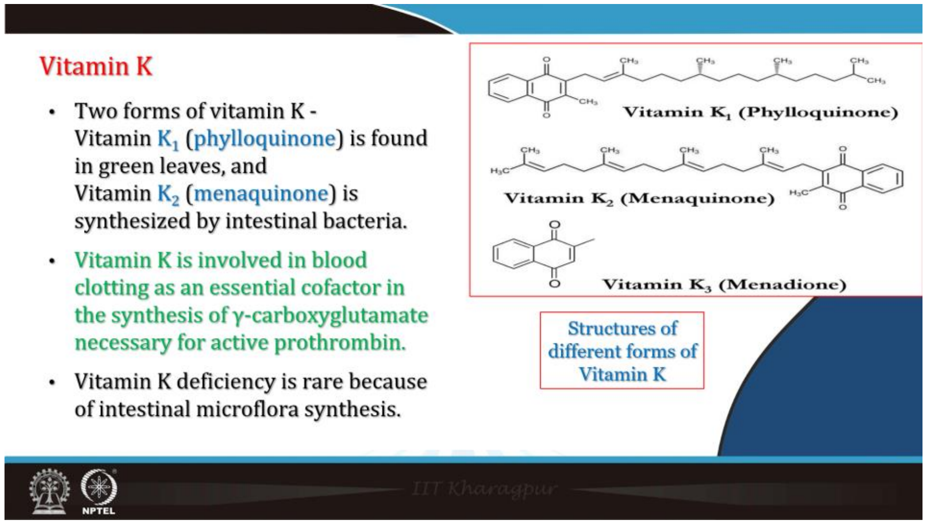
So, these are very important group. Then fat-soluble vitamin like vitamin A, it exists in diet in many farms. The most bioactive form is the all-trans-retinol and cis form that they are created by a light induced isomerization. The daily value of vitamin A is 1000 retinol equivalent which represents 1000 micron of all-trans-retinol equivalent to 6000 micrograms of beta carotene. Vitamin A can be toxic when taken in extra level that is extending to the levels exceeding to the percent daily value. Some reports suggest that level of 15000 RE per day can be toxic.



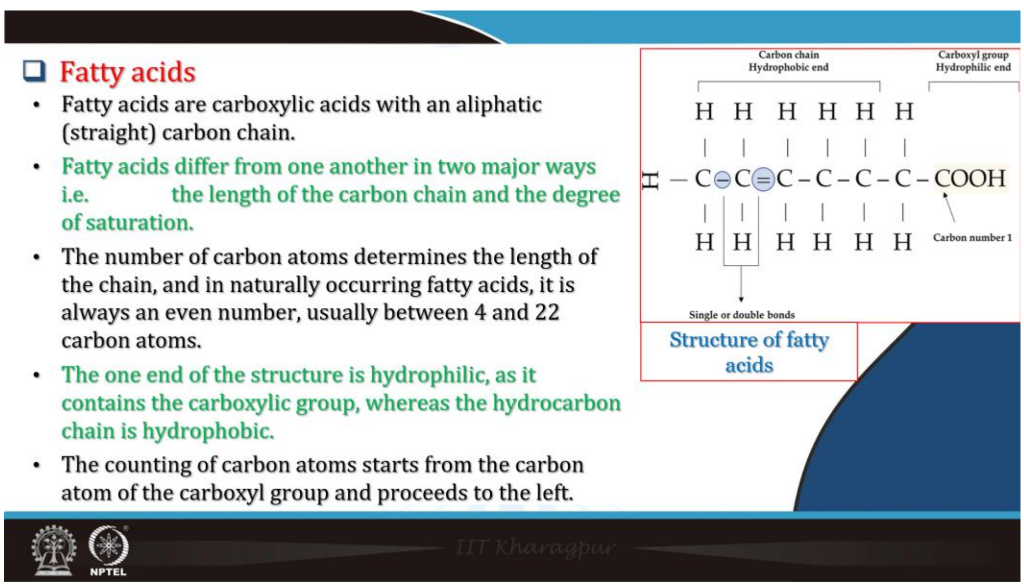
So, you can see here that is the 11 cis-retinol, all-trans-retinol and the beta carotene this structure of the vitamin A. Vitamin D although as many as 5 vitamin D compounds have been described, but only two of these are biologically active and that becomes ergo calciferol, that is vitamin D2 and chole calciferol vitamin D3. Vitamin D3 can be synthesized in human from 7 dehydrocholesterol, which occurs naturally in the skin via solar radiation. That is why for this is a very important vitamin and then exposure to solar radiation is very important, that is the what is that is the ergosterol, which is pro vitamin D2 and then when you with the help of solar radiation UV radiation it is converted into ergocalciferol, that is vitamin D3 or 7 dehydrocholesterol, which is pro vitamin D3 is with the help of solar radiation, UV radiation, it is converted into cholecalciferol, vitamin D3 in our body.



Then vitamin E, these are the compounds which include mainly the tocopherols and tocotrienols. Tocotrienols have a conjugated structure you can see here that is in the structure is the tocopherols and tocotrienols. Only difference in their structure is that is the tocotrienols, they have the conjugated, that is the triene double bond system in their phytol side chain and where it is the single bond saturated phytoside. Even methyl substitution like here you see in the both the cases this affects the bioactivity of vitamin E as well as its in vitro antioxidant activities and both tocopherols and tocotrienols, you can see the structure this R1. So, depending upon whether R1 is a methyl group that is an R2 is a methyl group that is there are R1 and R2 in both. So, if R1 and R2 both are methyl group it becomes alpha tocopherol. If R1 is methyl and R2 is a hydrogen it becomes beta tocopherol. If R1 is H, R2 is CH3 it becomes gamma tocopherol and if both R1 and R2 these are H it becomes delta tocopherol. Then accordingly that four forms of tocotrienol also alpha, beta, gamma, delta are available.

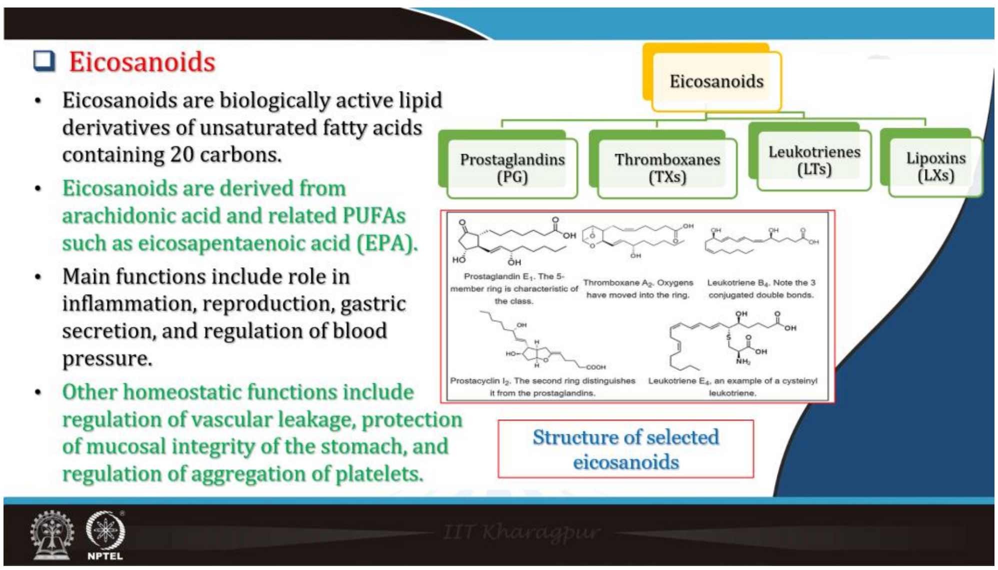


Vitamin K in fact, there are two forms of vitamin K that is vitamin K1 phylloquinone, which is found in green leaves and vitamin K2 menaquinone, which is synthesized in the inside organs by the intestinal microflora. Vitamin K is involved in the blood clotting as an essential cofactor in the synthesis of gamma carboxyglutamate, which is necessary for active prothrombin. Vitamin K deficiency is rare because of the synthesis involved in the intestine and in our body, it is synthesized significant amount and this is here the structure of vitamin K1, K2 and K3 that is phylloquinone, menaquinone and menadione.



Then another derived fatty acid. Fatty acids are carboxylic acids with an aliphatic or a straight carbon atom, you can see here, that is it has one carboxylic end and other is the methyl end. Fatty acids differ from one another in two major ways, that is the length of the carbon chain and degree of saturation also. So, number of carbon atoms determine the length of the chain and naturally occurring fatty acids. It is always an even number especially between 4 and 22 carbon containing. The one end of the structure is a hydrophilic that is methyl end whereas, the other hydrocarbon chain is the hydrophobic that is this hydrocarbon chain. You can see it is a hydrophobic whereas, the carbonyl group is the hydrophilic. The counting of the carbon atoms starts from the carbon atom of the carbonyl group that is 1, 2, 3, 4, 5, 6, 7 and so on and accordingly where this unsaturated linkage that is the numbering is done.

The degree of saturation is determined by the number of double bonds between the carbon atoms in the absence of a carbon-carbon double bond the fatty acid is called saturated fatty acid. Fatty acid with one carbon-carbon double bond is called monounsaturated and the fatty acid with two or more double bonds are called polyunsaturated fatty acid. Saturated fatty acids are primarily found in animal sources such as meat, poultry, butter, egg, lard. Plant sources contain more polyunsaturated fatty acids. However, coconut and palm oil, they contain saturated fatty acids. Major sources of monounsaturated fatty acids are olive and avocado oil as well as peanut butter. PUFA are predominantly found in plants like corn, canola or sunflower or flaxseeds.



Then eicosanoids are other group, that is they are the prostagladins, thromboxanes, leukotrienes and lipoxins. Eicosanoids are biologically active lipids, derivatives of unsaturated fatty acids containing 20 carbons. Eicosanoids are derived from arachidonic acid and related polyunsaturated fatty acids such as EPA, that is Eicosapentaenoic acid. Main functions of this include role in inflammation, reproduction, gastric secretion, and regulation of blood pressure. Other homeostatic functions include regulation of vascular leakage, production of mucosal integrity of stomach and regulation of aggregation of platelets.

Finally, we will summarize this lecture that lipids are the important constituents of human diet. There are different types of lipids like simple lipid, compound lipid and derived lipid. Triacylglycerols or triglycerides are the major components in the vegetable oil as well as the other fats. The different classes of lipids have different structures and perform different biological functions. These are the references which are used in this lecture and finally, thank you all for your patience hearing. Thank you.