

# FOOD SCIENCE AND TECHNOLOGY

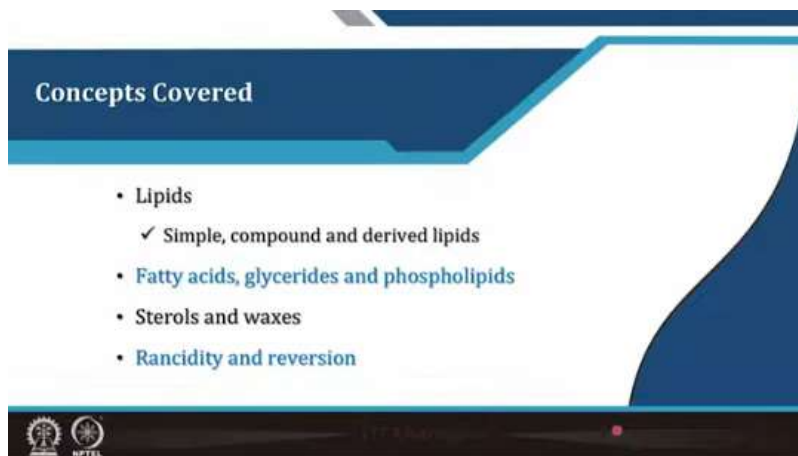
## Lecture25

### Lecture 25: Triglycerides and Phospholipids

Hello everyone.



Namaste. Now, in this 25th lecture today, we will talk about triglycerides and phospholipids.

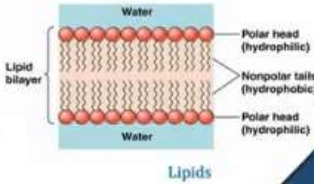


So, these triglycerides and phospholipids are basically called lipids. So, we will discuss what lipids are. There are different types of lipids, like simple lipids, compound lipids, and

derived lipids. Also, we will talk about how these lipids are formed—that is, what the components of lipids are, like fatty acids, then glycerides and phospholipids. We will also discuss sterols and waxes. Finally, we will discuss major phenomena in food fats and oils, such as rancidity and reversion.

### Lipids

- Lipids are a broad group of chemically diverse compounds that are soluble in organic solvents and insoluble in polar solvents.
- Polymers of fatty acids that contain a long, non-polar hydrocarbon chain with a small polar region containing oxygen.
- They are present in or derived from living organisms.
- Function as energy storage molecules and as structural components of membranes.

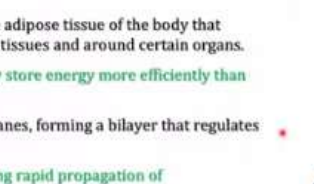


Dr. Khanna

Lipids are a broad group of chemically diverse compounds that are soluble in organic solvents. They are not soluble in polar solvents. So, polymers of fatty acids contain a long-chain, non-polar hydrocarbon chain with a small polar region containing oxygen. You can see here that these are the polar heads hydrophobic. That is the lipid bilayer and the waters. The polar head and, in between the middle, are the nonpolar tail, which is the hydrophobic tail. They are present in or derived from living organisms. These lipids function as energy storage molecules and as structural components of membranes.

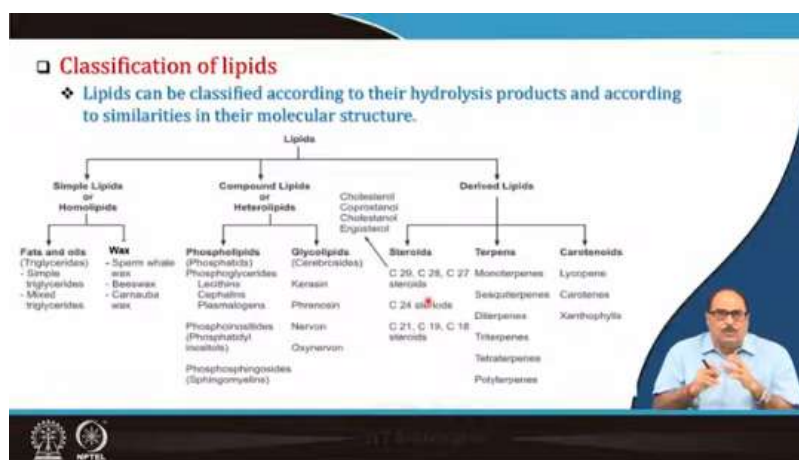
### Significance of lipids

- They are greasy nonpolar molecules, stored in the adipose tissue of the body that serves as a thermal insulator in the subcutaneous tissues and around certain organs.
- Provide energy for different life processes, as they store energy more efficiently than carbohydrates.
- Phospholipids are key components of cell membranes, forming a bilayer that regulates the entry and exit of molecules.
- Nonpolar lipids act as electrical insulators, allowing rapid propagation of depolarization waves along myelinated nerves.
- Lipids, such as steroid hormones (e.g. estrogen, testosterone), act as signaling molecules that regulate various physiological processes like growth, metabolism, and reproduction.
- Combinations of lipid and protein (lipoproteins) are key components of cell membranes and mitochondria and play a vital role in transporting lipids through the blood.



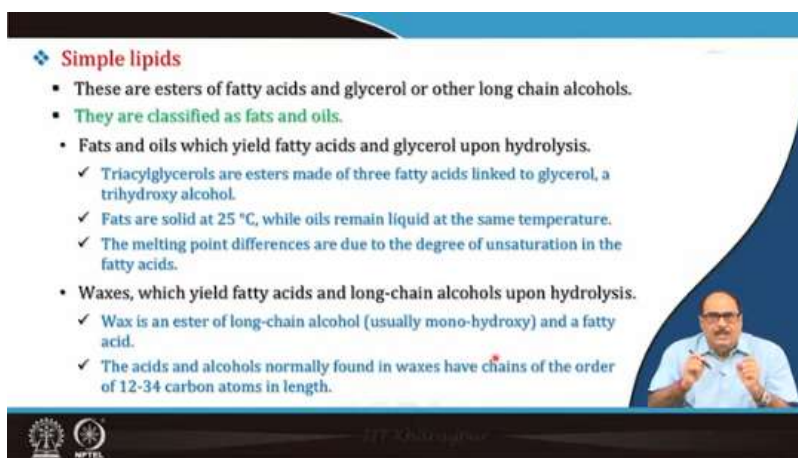
Dr. Khanna

Lipids have a very important role in food and biological systems, as well as being essential for our normal body functioning for doing daily work, etc., as energy molecules. They are greasy, nonpolar molecules stored in the body's adipose tissues and serve as thermal insulators in the subcutaneous tissue and around certain organs. If you see any cut in the skin, etc., a white layer of wax is found. So, these provide thermal insulation in the tissue. Also, they provide energy for different life processes as they store energy. More efficiently than carbohydrates. They are more anhydrous, which is why they have almost double the energy of carbohydrates and proteins. Phospholipids are the key components of cell membranes, forming a bilayer that regulates the entry and exit of molecules. Non-polar lipids act as electrical insulators, allowing rapid propagation of depolarization waves along myelinated nerves. Lipids such as steroid hormones like estrogen and testosterone act as signaling molecules that regulate various physiological processes like growth, metabolism, and reproduction. So, combinations of lipids and proteins, like lipoproteins, are key components of cell membranes and mitochondria, and they play a very vital role in transporting lipids through the blood. So, they have a very important role to play in our nutrition as well as in the food system.



So, lipids can be classified into different categories; they are of three types mainly depending on their structure, hydrolysis products, or similarity in their molecular structure, etc. So, there are three categories of lipids: simple lipids or homolipids, then compound lipids or heterolipids, and finally derived lipids. So, simple lipids have two subdivisions again: either fats or oils, which are mainly triglycerides like simple triglycerides or mixed triglycerides. Then, waxes, such as sperm wax, bee wax, carnauba wax, etc. So, these fats, oils and waxes are categorized as simple lipids or homolipids. Phospholipids and glycolipids come under the category of compound lipids, meaning that the lipid moiety is

connected with another non-lipid component, like glycolipids. Here, that non-lipid component is the glyco, meaning there are sugar compounds or phospholipids or lipoproteins; these are all examples of the compound lipids or heterolipids. Then come the derived lipids, which are the lipid decomposition products like sterols, terpenes, carotenoids, and so on. Carotenoids include lycopene, carotenes, and xanthophylls. Similarly, there are monoterpenes, diterpenes, tetraterpenes, and various ethylides. These derived lipids are found in many food materials, etc. They serve either as flavouring components or have many other biochemical or bioactive roles to play.



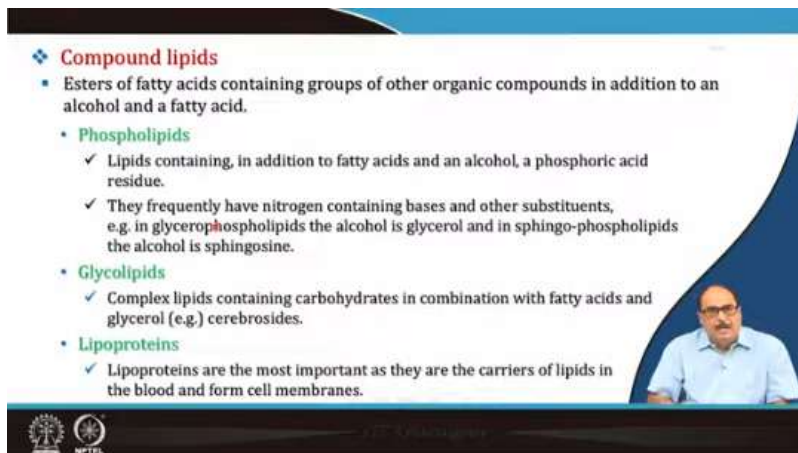
**Simple lipids**

- These are esters of fatty acids and glycerol or other long chain alcohols.
- They are classified as fats and oils.
- Fats and oils which yield fatty acids and glycerol upon hydrolysis.
  - ✓ Triacylglycerols are esters made of three fatty acids linked to glycerol, a trihydroxy alcohol.
  - ✓ Fats are solid at 25 °C, while oils remain liquid at the same temperature.
  - ✓ The melting point differences are due to the degree of unsaturation in the fatty acids.
- Waxes, which yield fatty acids and long-chain alcohols upon hydrolysis.
  - ✓ Wax is an ester of long-chain alcohol (usually mono-hydroxy) and a fatty acid.
  - ✓ The acids and alcohols normally found in waxes have chains of the order of 12-34 carbon atoms in length.

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So, having discussed these, let us now examine simple lipids, which are basically esters of fatty acids and glycerol or other long-chain alcohols. These are the simple lipids. These are the esters of fatty acids, such as triglycerides, which are trihydroxy alcohols or even long-chain alcohols. When there is a long-chain monohydroxy alcohol, it becomes wax. Otherwise, when it is a trihydroxy alcohol or polyhydroxy alcohol and fatty acids, these become fats and oils. So, as mentioned, simple lipids are classified as fats and oils. Fats and oils yield fatty acids and glycerol upon hydrolysis, meaning these fats and oils are composed of glycerol. That is the glycerol and fatty acids. So triacylglycerols are esters made of three fatty acids linked to glycerol. That is a trihydroxy alcohol. The fats are normally solid at 25 degrees Celsius, whereas the oils remain liquid at that temperature. At room temperature, oils are generally liquid. The melting point differences are mainly due to the degree of unsaturation of the fatty acid, that is, the type of fatty acid that is connected to the glycerol molecule and differentiates fats from oils. The fats normally contain saturated fatty acids, which is why they are solid at room temperature. The fatty acids are either unsaturated or polyunsaturated. Their melting point is lower, so they are liquid at room temperature. The waxes, as I told you, yield fatty acids and long-chain alcohols upon

hydrolysis. That is, they are the esters of long-chain alcohols, usually monohydroxy alcohols and fatty acids. The acid and alcohol normally found in waxes have chains of the order of 12 to 34 carbon atoms in length.



**Compound lipids**

- Esters of fatty acids containing groups of other organic compounds in addition to an alcohol and a fatty acid.
- **Phospholipids**
  - ✓ Lipids containing, in addition to fatty acids and an alcohol, a phosphoric acid residue.
  - ✓ They frequently have nitrogen containing bases and other substituents, e.g. in glycerophospholipids the alcohol is glycerol and in sphingo-phospholipids the alcohol is sphingosine.
- **Glycolipids**
  - ✓ Complex lipids containing carbohydrates in combination with fatty acids and glycerol (e.g.) cerebrosides.
- **Lipoproteins**
  - ✓ Lipoproteins are the most important as they are the carriers of lipids in the blood and form cell membranes.

The compound lipids, that is, the esters of fatty acids, contain groups of other organic compounds in addition to an alcohol and a fatty acid. As I told you, there is a lipid that, in addition to the lipid component, has some non-lipid moiety also associated with them, like phospholipids, that is, the lipids containing, in addition to the fatty acid and alcohol, a phosphoric group a phosphoric acid residue attached with that is, the phosphoric acid phospholipids. They frequently have nitrogen-containing bases and other substituents, like the glycerophospholipids, where the alcohol is glycerol. And in sphingo-phospholipids, the alcohol is sphingosine, etcetera. So, these phospholipids that is, where the phosphoric acid group is present, we will see later in the lecture that the phosphoric acid group is further attached with another moiety, and on the basis of that, there are even different types of differentiations in the phospholipids as well. Another type of glycolipids can be compound lipids; glycolipids are complex lipids containing carbohydrates in combination with fatty acids and glycerol, like cerebrosides. Similarly, lipoproteins are the most important, as they are the carriers of lipids in the blood and from the cell membrane.

Derived lipids, like the substances that are liberated during hydrolysis of simple and compound lipids, still retain their properties. These include fatty acids, glycerol, steroids and other alcohols, fatty aldehydes, ketone bodies, hydrocarbons, lipid-soluble vitamins, hormones, etc.

### Derived lipids

- These are substances liberated during hydrolysis of simple and compound lipids which still retain the properties of lipids.
- These include fatty acids, glycerol, steroids, other alcohols, fatty aldehydes, and ketone bodies, hydrocarbons, lipid-soluble vitamins, and hormones.
- Because they are uncharged, acylglycerols (glycerides), cholesterol, and cholesterol esters are termed neutral lipids.
- ✓ **Steroids:** Contain no fatty acids and unlike fats, are non-saponifiable.
- ✓ **Cholesterol:** An important component of cell membranes and plasma lipoproteins and important precursor of many biologically important substances like bile acids and steroid hormones.
- ✓ **Terpenes:** Large group of volatile unsaturated hydrocarbons.
- ✓ **Carotenoids:** Class of mainly yellow, orange, or red fat-soluble pigments.



So, because they are uncharged, acylglycerols, cholesterol, and cholesterol esters are termed neutral lipids. So, they are basically neutral lipids, which are uncharged. So, steroids contain no fatty acids, and like fats, they are non-saponifiable. Similarly, cholesterol is an important component of cell membranes and plasma lipoproteins, and they are important precursors of many biologically important substances like bile acids, steroid hormones, etc. Terpenes form a large group of volatile unsaturated hydrocarbons, and they are a main source of the essence or flavours, etc., in citrus fruits and all citrus oils. Carotenoids are a class of many yellow, orange, and red fat-soluble pigments which contribute to the flavour of many yellow-coloured vegetables, etc. For example, lycopene is an important carotenoid that gives a yellow colour or gives the colour of the tomato.

Now, let's talk about triglycerides. Triglycerides are a type of lipid which is an ester of three fatty acids with glycerol. You can see a glycerol molecule here, that is, glycerol.

### Triglycerides

- Triglycerides are a type of lipid which is an ester of three fatty acids with glycerol.



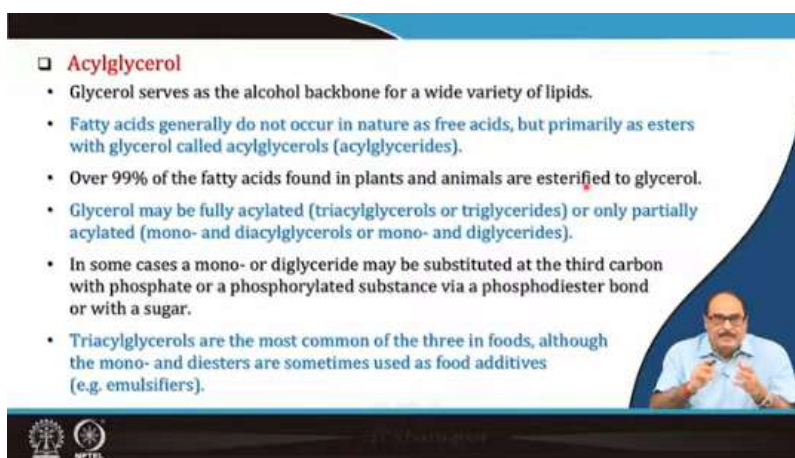
- Triglycerides are the main constituents of body fat in humans, other vertebrates, and vegetable fats.
- They are the most common lipid in the foods and dietary supplements.
- Fatty acids are found in triglycerides in nature.
- Triglycerides provide energy, serve as the body's main energy storage, insulate and protect organs, and assist in the absorption and transport of fat-soluble vitamins.



There are three hydroxyl groups. So, the glycerol with these three molecules of fatty acid



are connected, and the linkage again is  $\text{CHOOH}$ , and this fatty acid carboxyl group is  $\text{OH}$ . So, in this case, at least one molecule of water will be removed. So, when glycerol combines with three fatty acids, three molecules of water are liberated, and the resulting compound is called a triglyceride. So, triglycerides are the main constituents of body fat in humans, other vertebrates, and vegetable fats. They are the most common lipids in food and in dietary supplements. Fatty acids are found in triglycerides. Fatty acids are not found free in nature. They are found in the form of triglycerides. Also, these triglycerides, which provide energy, serve as the body's main energy storage. A molecule insulates and protects organs and assists in the absorption and transport of fat-soluble vitamins.

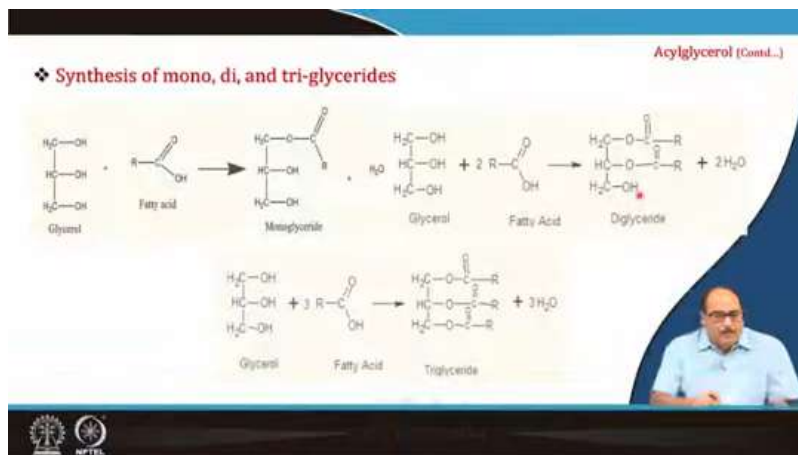


**Acylglycerol**

- Glycerol serves as the alcohol backbone for a wide variety of lipids.
- Fatty acids generally do not occur in nature as free acids, but primarily as esters with glycerol called acylglycerols (acylglycerides).
- Over 99% of the fatty acids found in plants and animals are esterified to glycerol.
- Glycerol may be fully acylated (triacylglycerols or triglycerides) or only partially acylated (mono- and diacylglycerols or mono- and diglycerides).
- In some cases a mono- or diglyceride may be substituted at the third carbon with phosphate or a phosphorylated substance via a phosphodiester bond or with a sugar.
- Triacylglycerols are the most common of the three in foods, although the mono- and diesters are sometimes used as food additives (e.g. emulsifiers).

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Acylglycerols, that is glycerol, serve as the alcohol backbone of a wide variety of lipids. So, fatty acids generally do not occur in nature, as I told you, in free form, but primarily, They are found as esters with glycerol and acylglycerol. That is the glycerides; that is the ester linkage here. You have seen earlier in the monosaccharides when there are various polymer forms, it is the glycosidic linkage. In the protein, you saw it is the peptide linkage. So, here in these lipids, when the fatty acids and the glycerol combine together, the formed linkage is known as ester linkage. Over 99 percent of the fatty acids found in plants and animals are esterified to glycerol. Glycerol may be fully acetylated, that is, either as triacylglycerols or triglycerides or only partially acetylated, sometimes as monoglycerides, mono- or diglycerides, diacylglycerides, etcetera, are also there. Only one alcoholic group or two alcoholic groups might be attached to one or two fatty acids. So, in some cases, a mono- or diglyceride may be substituted at the third carbon with a phosphate or phosphorylated substance by a phosphodiester bond or with a sugar. So, triacylglycerols are the most common of the three compounds. Three in the foods, although monoglycerides or diglycerides, etc. It is also sometimes used as a food additive or emulsifier, etc.



Then, if you see the synthesis of mono-, di-, and triglycerides like glycerol plus fatty acids if one fatty acid is connected, it will give monoglyceride and one molecule of  $\text{H}_2\text{O}$  will be released. When two fatty acids are connected with the two hydroxyl groups of glycerol, it gives a diglyceride.  $\text{H}_2\text{O}$ , and then glycerol and three molecules of fatty acids combine; three water molecules are released, and triglyceride and triacyl glyceride are formed. So, these are how monoglyceride, diglyceride, and triglyceride are formed and similarly, when triglyceride is hydrolyzed, it may give a free fatty acid and a mixture of diglyceride, monoglyceride, and even some triglyceride, etc., might also be there. So, it releases; it gives the free fatty acid. Upon complete hydrolysis, it will give free fatty acid plus glycerol. So, these fatty acids are the backbone, the main constituent that forms the triglycerides, which we call fats and oils.

**Fatty acids**

- Fatty acids are organic molecules that are long-chained carboxylic acids with 4 - 36 carbon atoms.
- These are molecules with a formula  $\text{R}-\text{COOH}$  where R is a hydrocarbon chain.

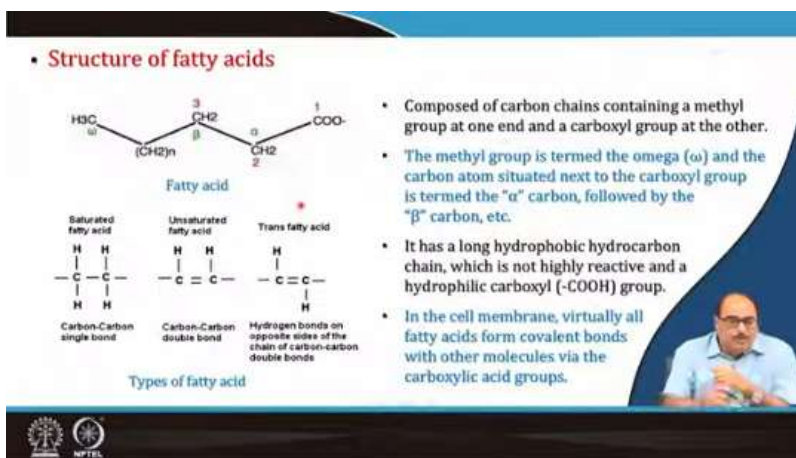
The diagram shows the structure of a fatty acid molecule. It consists of a carboxyl group (labeled "Carboxyl group") and a hydrocarbon chain (labeled "Hydrocarbon chain"). The carboxyl group is represented as  $\text{HO}-\text{C}(=\text{O})-\text{R}$ . The hydrocarbon chain is represented as a zigzag line, indicating it can be saturated or unsaturated.

- Hydrocarbon chains are either saturated or unsaturated, depending on the bonds between the carbon atoms.
- Naturally occurring fatty acids are mostly unbranched, and these occur in three main classes of lipids; triglycerides, phospholipids, and cholesterol esters.
- Fatty acids are stored as an energy reserve (fat) through an ester linkage to glycerol to form triglycerides.

So, fatty acids are basically Organic molecules that are long-chained carboxylic acids with carbon atoms ranging from 4 to 36 in number. You can see these are molecules with a

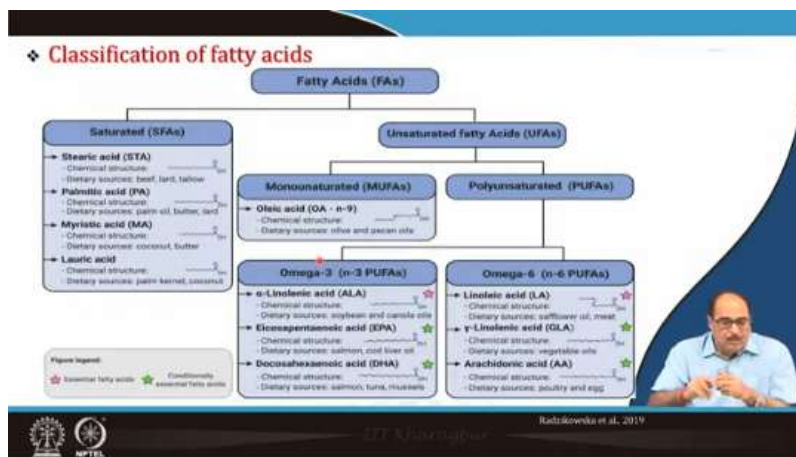


formula, the general formula of  $R\text{-COOH}$ . You can see here  $R$  is a hydrocarbon chain. You can see this is a hydrocarbon chain and this is the carboxylic group. So, hydrocarbon chains are either saturated or unsaturated depending upon the bonds between the carbon atoms. Naturally occurring fatty acids are mostly unbranched, and these occur in three main classes of lipids: triglycerides, phospholipids and cholesterol esters. So fatty acids are stored as an energy reserve through an ester linkage to the glyceride to form triglycerides and most food triglycerides or a mixture of mixed triglycerides there will be triglycerides also there may be two types of mixed triglycerides simple triglyceride means when all three fatty acids attaching with the glycerol molecule are the same it is a mixed simple triglyceride when there are different like two fatty acids or three different fatty acids are attached to the So, glycerol gives a mixed triglyceride, and most of the food fats and oils are mixtures of mixed triglycerides.



So, the structure of a fatty acid is basically  $RCOH$ . So, here you can say they are composed of a carbon chain containing a methyl group at the end, which is called the omega end, and there is a carboxyl group at the end carboxyl group, and in between there is a carbon chain hydrocarbon chain that is the  $CH_2$  types. So, this is the alpha group, beta group, and omega end. As I told you, the methyl group is termed the omega group in the carbon atom, which is next to the carboxyl group. Then, the carbon atom situated next to the carboxyl group is termed alpha carbon, followed by beta carbon, and methyl carbon is the omega carbon. So, it has a long hydrophobic hydrocarbon chain that is not highly reactive, and a hydrophilic carboxyl group is attached. So, in the cell membrane, virtually all fatty acids form covalent bonds with other molecules via carboxylic acid groups. Now, these fatty acids, again, there may be, depending upon how the balances of the carbons are satisfied or substituted, how many hydrogen atoms are attached with suppose in the carbon, all the balances are satisfied

if they are all bonds with four valences so it becomes a saturated fatty acid. That is, there are always single bonds, such as the carbon-carbon single bond. But if there are some carbon-carbon double bonds, as you can see here two hydrogens, it becomes unsaturated fatty acids. Similarly, in unsaturated fatty acids, normally, there are two hydrogens on the same side of the molecule. It becomes cis, and most of the natural fatty acids are in the cis form. But when these fatty acid triglycerides are given heat treatment during the extraction process, refining process, frying, cooking, etcetera, the position of the hydrogen changes. It changes from trans from cis to trans acid, and the fatty acid resulting from fatty acid is known as trans fatty acids.



So, the classification of the fatty acids further, as I told you, the saturated fatty acids, may be further depending upon the chain length, number of carbon atoms, etcetera. They may be stearic acid, palmitic acid, myristic acid, lauric acid or some other fatty acid. They are all, however, they are all carbon balances saturated, and they are normally like stearic acid is found in beef, lard, tallow, etc. Palmitic acid in palm oil, butter, and lard. Myristic acid in coconut butter. Lauric acid is found in palm oil, kernel, and coconut. So, these are the plant and animal sources of the saturated fatty acids. Accordingly, you can say saturated fats. Then comes the unsaturated fatty acids, which is where carbon balances are not satisfied. They have double bonds. So, depending upon the number of double bonds, it becomes monounsaturated fatty acid if there is only one double bond. If there is more than one double bond in the hydrocarbon chain, then it becomes a polyunsaturated fatty acid. Like a monounsaturated fatty acid, oleic acid, where there is one double bond at the omega position, which is the 9th position from the omega end, and olive oil and bacon oil are the major dietary sources, and finally, palmitic acid is a C18 carbonate. Palmitic acid may finally get desaturated into oleic acid, palmitic, stearic, palmitic, and oleic acid. Then come

the polyunsaturated fatty acids. The omega-3 and omega-6 fatty acids, that is, omega-3, which is n-3 PUFA, alpha-linoleic acid, eicosatetraenoic acid, and docosahexaenoic acid and they normally contain double bonds. Their omega-6 fatty acids are similar to linoleic acid, linoleic acid, and arachidonic acid. Most of these omega-3 and omega-6 fatty acids, as you can see that is, the red stars or pink stars, are mainly essential fatty acids that our human system cannot digest. Desaturate these saturated fatty acids like stearic acid, acting on carbon fatty acids into oleic acid, oleic acid to linoleic acid, linoleic acid to linolenic acid, etc. These plants can desaturate. So, plants can contain all these monounsaturated fatty acids, polyunsaturated fatty acids, and so on. However, the human system cannot desaturate oleic acid into linoleic acid. But they are highly essential for our brain formation and other functions. So, they must be taken from food sources. So, basically, this omega-3, linoleic acid, which is an essential fatty acid, is sourced from soybean oil and canola oil. Similarly, linolenic acid is a source of sunflower oil, meat, etc. Similarly, eicosatetraenoic acid, docosahexaenoic acid, gamma-linolenic acid, or arachidonic acid are also sometimes conditionally essential fatty acids for certain functions required in the body. So, we can take these things accordingly, such as a balance of the oils, etc. So that we get the desired amount of essential fatty acids.

**Saturated fatty acid**

- Saturated fatty acids are simple, unbranched chains of  $\text{CH}_2$  groups linked by single carbon-carbon bonds, ending with a carboxylic acid group.
- "Saturated" denotes that each 'C' atom is fully bonded to 'H' atoms.
- The general formula for these acids is  $\text{C}_n\text{H}_{2n}\text{COOH}$ .
- Saturated fatty acids have higher melting points, which is why they stay solid at room temperature.

Brown et al., 2015

- Fatty acids from animal sources are even-numbered, saturated, and solid, found in products like butter, meat, and whole milk.
- Coconut oil and palm oil are plant sources of saturated fat.


Saturated fatty acids like capric acid, caprylic acid, lauric acid, myristic acid, palmitic acid and stearic acid depend upon the number of carbon atoms present. Saturated denotes that all the carbon balances are fulfilled. They have a structural formula  $\text{C}_n\text{H}_{2n}\text{COOH}$ . These saturated fatty acids have generally higher melting points, which is why they remain solid at room temperature. So, fatty acids from animal sources are generally even-numbered; they are saturated and solid, and they are generally found in products like butter, meat,

whole milk, etc. Whereas the coconut oil in the plant sources, coconut oil as well as palm oil are the major sources of saturated fats.

❖ **Nomenclature of saturated fatty acids**

| Systematic name | Common name | Numerical abbreviation |
|-----------------|-------------|------------------------|
| Hexanoic        | Caproic     | 6:0                    |
| Octanoic        | Caprylic    | 8:0                    |
| Decanoic        | Capric      | 10:0                   |
| Tetradecanoic   | Myristic    | 14:0                   |
| Hexadecanoic    | Palmitic    | 16:0                   |
| Octadecanoic    | Stearic     | 18:0                   |
| Dodecanoic      | Lauric      | 12:0                   |

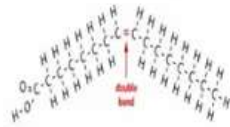

- The IUPAC system names the parent hydrocarbon of the fatty acid based on the number of carbons (e.g. Ten carbons would be Decane).
- Since fatty acids contain a carboxylic acid group, the terminal 'e' in the hydrocarbon's name is replaced by 'oic' (e.g. Decanoic).
- A numerical system can be used for abbreviated names.
- The first number designates the number of carbons in the fatty acids while the second number designates the number of double bonds (e.g. Hexadecanoic = Palmitic = 16:0).
- This second number will always be zero for the saturated fatty acids.



Then the fatty acids, saturated fatty acids in the IUPAC systems of naming the parent hydrocarbon of the fatty acids are based on the number of the carbon. If there are 10 carbon atoms, it will be decane. Similarly, there are octane, tetradecane, hexadecane, and so on. Since fatty acids contain a carboxylic acid group, the terminal 'e' in the hydrocarbon's name is replaced with 'oic'. So, it becomes decanoic acid, octanoic acid, or hexanoic acid. A numbering system is used to give the abbreviated form. The first number designates the number of carbons, as seen here in the numerical abbreviation. These are the systematic names: hexanoic, decanoic, octanoic, tetradecanoic. The common name for hexanoic acid is caproic acid. This means it contains 6 carbon atoms and no double bonds. There are no double bonds. Similarly, hexadecanoic acid is also called palmitic acid. It has 16 carbons and no double bonds. Octadecanoic acid, or stearic acid, has 18 carbons and no double bonds. This stearic acid is actually the most commonly found, and it is desaturated into oleic, linoleic, etc. All of those are unsaturated fatty acids. So, upon hydrogenation, when we hydrogenate vegetable oils, etcetera, they are finally converted into stearic acid, an 18-carbon-containing saturated fat, etcetera.

❑ **Unsaturated fatty acid**

- They are more complex fatty acids with bent hydrocarbon chains linked together by one or more carbon-carbon double bonds with a terminal carboxylic acids group.
- Term 'unsaturated' indicates that the 'C' atoms do not have the maximum possible 'H' atoms.
- Due to the presence of double bonds, the **cis** and **trans** conformation of these molecules are important.
- The unsaturated fatty acids found in the human body exist in the **cis** conformation.
- Have a lower melting point as compared to saturated fatty acids, and thus they exist in the liquid state at room temperatures.
- Most vegetable oils and fish oils are some of the important sources of unsaturated fatty acids.





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Then, unsaturated fatty acids, as we earlier saw, are here where all the valences are not satisfied. There will be some double bonds present. The unsaturated fatty acids found in the human body mostly exist in the cis conformation. However, they also have a lower melting point compared to saturated fatty acids, and thus they exist in a liquid state at room temperature. Most vegetable oils and fish oils are some of the important sources of unsaturated fatty acids, such as vegetable oils and fish oil, which are key sources of unsaturated fatty acids, cod liver oil, etc. and fish liver oil—all these things are very good materials. Most plant oils like sunflower oil, soybean oil, rapeseed oil, or you can say safflower oil, groundnut oil, and sesame oil are very good sources of unsaturated fatty acids, particularly polyunsaturated fatty acids.

❖ **Nomenclature of unsaturated fatty acids**

- In the IUPAC system, the anionic designation is changed to enoic to designate the presence of a double bond.
- On the basis of the number of double bonds, the terms di-, tri-, tetra-, and so on are added.
- The numerical abbreviation system is similar to the saturated fatty acids with the second number indicating the number of double bonds (e.g., octadecadienoic = 18:2).
- The positions of the double bonds in the IUPAC system are numbered by the delta ( $\Delta$ ) system that indicates the position of the double bonds from the carboxylic acid end of the fatty acid.
- An alternative numbering system that indicates the position of the double bonds from the methyl end of the fatty acids is known as the omega ( $\omega$ ) system (sometimes given a shorthand notation of "n").



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So here, in the nomenclature of the IUPAC system, the 'anoic' designation is changed to 'enoic,' that is, 'decanoic' becomes 'decenoic.' This means 'enoic' designates that there is a double bond. The position of a double bond. So, based on the number of double bonds,




then again, 'dienoic,' 'trienoic,' 'tetraenoic,' etc., means 1 double bond, 2 double bonds, or 3 double bonds, and so on. The numerical abbreviation system is similar to saturated fatty acids, with the second number indicating the number of double bonds. For example, 'octadecadienoic acid' means it will be 18:2; 18 means 18 carbon atoms, and there are 2 double bonds in it. Similarly, the position of the double bond in the IUPAC system is numbered by delta. It indicates the position of the double bond from the carboxylic end, and this is the delta. It is the carboxylic end, and if the number is given omega, then it is from the numbering from the methyl end. So, methyl end is the omega or N; also sometimes it is called N, N3, omega 3, N6, and omega six fatty acids.


Nomenclature of unsaturated fatty acids (Contd..)

| Systematic name  | Common name | Numerical abbreviation |
|--|-------------|------------------------|
| <i>cis</i> -9-Octadecenoic   | Oleic       | 18:1 Δ <sup>9</sup>    |
| <i>cis</i> -9, <i>cis</i> -12-Octadecadienoic  | Linoleic    | 18:2 Δ <sup>9</sup>    |
| <i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic   | Linolenic   | 18:3 Δ <sup>9</sup>    |
| <i>cis</i> -5, <i>cis</i> -8, <i>cis</i> -11, <i>cis</i> -14-Eicosatetraenoic                                | Arachidonic | 20:4 Δ <sup>5</sup>    |
| <i>cis</i> -5, <i>cis</i> -8, <i>cis</i> -11, <i>cis</i> -14, <i>cis</i> -17-Eicosapentaenoic                | EPA         | 20:5 Δ <sup>5</sup>    |
| <i>cis</i> -4, <i>cis</i> -7, <i>cis</i> -10, <i>cis</i> -13, <i>cis</i> -16, <i>cis</i> -19-Docosahexaenoic | DHA         | 22:6 Δ <sup>4</sup>    |



omega numbering system: Δ<sup>9</sup>-6  
delta numbering system: Δ<sup>9</sup>,12



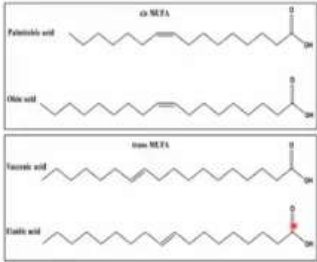


Dr. N. V. Subrahmanya


So, here you can see there are some systematic names like *cis*-9-deca- octadecanoic acid means it is basically oleic acid. Carbon atoms are there, and one double bond is there. This triangle indicates the number of positions, the position of the double bond, and, let us say, the 9th from the carboxylic end. Similarly, *cis* 5, *cis* 8, *cis* 11, *cis* 14, eicosatetraenoic, is arachidonic acid, which means it has 20 carbon atoms in it, there are 4 double bonds, and the double bond starts at 5, which means at the 5, then 8, then 11, then 14. You will find that if you look at the retail structure, there will be a difference of 3. Like if they start as 9, like here, linoleic acid has 2, that is, double bonds, 18 and 2, and it starts from position 9. So that will be 9 and then 12. And the 3, it is the 9, 12, 15. Then 5, 8, 11, 14. then 25 again 5, 11, 14 and 17 like that. So, there is always a gap that is 5, 8, 11, 15, 9, 12, 15, and there is a regularity in the position of the double bond. So, see the number as shown here from the end, which is the delta end or triangle, or methyl end, which is the omega end; it is taken one. So, here this becomes omega 6 fatty acids whereas, if it is taken from this bond, it becomes carboglycan that is carboglycan 9 and then 10, 9, 12 positional double bonds.

So, these are the in the IOPC system, and how very systematic the name of nomenclature of this is given.

❖ **Monounsaturated fatty acids**



- Contain one double bond between adjacent carbon atoms.
- General formula is  $C_nH_{(2n-2)}O_2$ .
- Double bond is at a number of locations along the carbon chain, resulting monoene isomers e.g. 16:1 (n-9) and 16:1 (n-11).
- All double bonds in FA are generally of cis geometry; converted into trans geometry when lipids are exposed to heating (cooking, frying, etc.).




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Then monounsaturated fatty acids like palmitoleic acid or it is also basically the oleic acid from the palmitoleic acid or oleic acid or even transmuffa may be basilic acid or elastic acid. This carbon all contains monounsaturated fatty acid, which means they contain one double bond between adjacent carbon atoms. The general formula is  $C_nH_{2n}$  minus two and  $O_2$ . Double bond is at a number of locations along the carbon chain resulting from monoene isomers like 16:1(n-9), 16:1 (n-11) and so on. All double bonds in the fatty acids are generally of cis geometry, and they are converted into trans. Then the lipids are exposed to heat.

❑ **Polyunsaturated fatty acids**

- These are the fatty acids that contain more than one double bond in their structure.
- Widely known as essential fatty acids since they cannot be synthesized in the human body and must be obtained from diet.
- These fatty acids are essential for maintaining normal growth and development, including that of the brain, and are important components of all cell membranes in the body.
- There are two types of PUFAs,  $\omega$ -3 and  $\omega$ -6
- The main  $\omega$ -3 fatty acid is  $\alpha$ -linolenic acid (ALA), and the main  $\omega$ -6 fatty acid is linoleic acid (LA).
- ALA is a precursor of the longer chain  $\omega$ -3 fatty acids eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA).
- LA is a precursor of the longer chain  $\omega$ -6 fatty acids  $\gamma$ -linolenic acid (GLA), dihomo  $\gamma$ -linolenic acid (DGLA), and arachidonic acid (AA).















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Polyunsaturated fatty acids contain more than one double bond. They are widely known as essential fatty acids. These fatty acids are essential for maintaining normal growth and development. There are two types of polyunsaturated fatty acids omega-3 and omega-6.

The main omega-3 fatty acids are alpha-linolenic acids, and the main omega-6 fatty acid is linoleic acid. This alpha-linolenic acid is a precursor of the longer-chain omega-3 fatty acid, eicosapentaenoic acid and docosahexaenoic acid. Meanwhile, linoleic acid is the precursor of the longer-chain omega-6 fatty acids, and gamma-linolenic acid, dihomo-gamma-linolenic acid, and arachidonic acid.

Polyunsaturated fatty acids (Contd.)

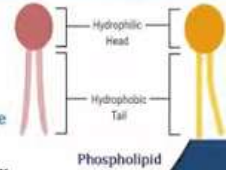
| Plant and animal sources  | Typical PUFA  | Microbial sources  |
|---|---|--|
| <br><b>Borage</b><br><br><b>Animal tissue</b><br><br><b>Antarctic krill</b><br><br><b>Deep sea fish</b> | $\gamma$ -Linolenic acid (C18:3, n-6)<br><br>Arachidonic acid (C20:4, n-6)<br><br>Eicosapentaenoic acid (C20:5, n-3)<br><br>Docosahexaenoic acid (C22:6, n-3)<br> | <br><b>Filamentous fungus</b><br><br><b>Algae</b><br><br><b>Oleaginous yeast</b><br><br><b>Marine fungus</b><br><i>Trends in Biotechnology</i><br>J. & Huang, 2019 |

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So, these are some of the sources like epicalin and gamma-linolenic acid in the plant sources and animal sources where they can be found. Arachidonic acid is found in algae and only in animal tissues, etc. Eicosapentaenoic acid is again in the Antarctic krill and then in the East, etc. So, these are the various typical polyunsaturated fatty acids; essential fatty acids are mostly found in some plant sources as well as microbial sources, etc.

### Phospholipids

- Phospholipids or phosphoglycerides are modifications of triacylglycerols where phosphate groups are typically found in the Sn-3 position.
- Phospholipid bilayer forms an important part of the cell membrane for the selective transport of molecules in and out of the cell.
- The phosphate group forms the hydrophilic head, whereas the fatty acids form the hydrophobic tails.
- The head and tail regions in phospholipids are joined by a glycerol molecule.
- The hydrophobic and hydrophilic interaction between different molecules and the lipid bilayer enables the passage of biomolecules.
- These interactions make the cell membrane amphipathic.



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Then, the phospholipids, you see that the phospholipids here are the phosphoglycerides, modifications of the glyceride triacylglycerol, particularly at the Sn-3 position. Phospholipids, while here, form an important part of the cell membrane for the selective

transport of molecules in and out of the cell. The phosphate group forms the hydrophilic head, whereas the fatty acid forms the hydrophobic tail. You see hydrophilic head and hydrophobic tail. So, this is the fat acid, etcetera, that is the form of the phospholipids. So, it contains both hydrophobic and hydrophilic groups. The head and tail regions of the phospholipids are joined by the glycerol molecule, and the hydrophobic and hydrophilic interaction between different molecules and the lipid bilayer enables the passage of biomolecules, and these interactions make the cell membrane that is amphipathic.

### Structure of phospholipids

❖ Phospholipids, like triglycerides, have a glycerol backbone but are attached to two fatty acids and a phosphate group.

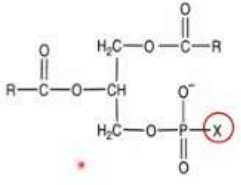
- Hydrophilic (polar) phosphate heads**
  - ✓ The hydrophilic head contains a negatively charged phosphate group with an alkyl group.
  - ✓ These heads face outward, interacting with the aqueous environment inside and outside the cell.
- Hydrophobic (non-polar) fatty acid tails**
  - ✓ The hydrophobic part of the phospholipid bilayer, (fatty acid tails), interacts with other hydrophobic molecules.
  - ✓ These tails are tucked inside the membrane, creating a barrier that prevents polar compounds from easily crossing the membrane.


So, now you see the structure of a phospholipid. Like here, phospholipids like triglycerides have a glycerol backbone but are attached to the two fatty acids only. These are attached to two fatty acids, where it has generally been seen that one fatty acid may be saturated and the other fatty acid may be unsaturated. The third fatty acid, carbonation, is replaced with a phosphoric group, which is again attached to another moiety X, which is hydrophobic heat contained in a reactively charged phosphate group. with an alkyl group and these heads face towards interacting with the aqueous environment inside and outside the cell. These are the hydrophilic polar groups. Hydrophobic non-polar fatty acids are parts of the phospholipid bilayer that interact with other phospholipid molecules, and these tails are placed inside the membrane, creating a barrier that prevents polar compounds from easily crossing the membrane.

So, these are the structures of phospholipids. You can say that these are the two fatty acids, and this is the phosphoric group, which is again connected with the X and this X may be either phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl serine or phosphatidyl inositol.

Structure of phospholipids (Contd...)

❖ Structures of phospholipids commonly found in foods



$X = OH$  = Phosphatidic acid  
 $X = O-CH_2-CH_2-NH_2$  = Phosphatidylethanolamine  
 $X = O-CH_2-CH_2-N^+(CH_3)_3$  = Phosphatidylcholine  
 $X = O-CH_2-CH(NH_2)-COOH$  = Phosphatidylserine  
 $X =$   = Phosphatidylinositol

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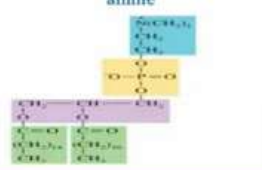
So, this means X is the inositol, serine, choline, ethanolamine or anything or OH. Then, accordingly, these are the major phospholipids. This phosphatidylcholine basically is the main constituent. This is a very important phospholipid, a major component of lecithin, and it is the one lecithin that is found in milk naturally. It keeps the butter phases and water phases. Water in the emulsion form does not allow the fat to separate, and the lecithin is commercially obtained from the sludge after that as a byproduct of the oil refining process, and this is used as an emulsifier in many food products.

❑ Classification of phospholipids

- Phospholipids are classified according to their alcohol content.

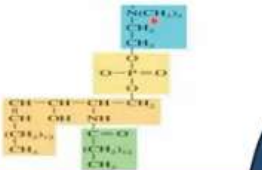
❖ **Glycerophospholipids**

Glycerophospholipids composed of glycerol, two fatty acids, phosphate group and alcohol amine



❖ **Sphingophospholipids**

Sphingophospholipids composed of sphingosine alcohol + one fatty acid + phosphate + choline



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Then, the phospholipids can be classified as glycerophospholipids or sphingophospholipids. Glycerophospholipids are composed of glycerol, 2 fatty acids, phosphate group and alcohol amine. Whereas a sphingophospholipid consists of composed of sphingosine alcohol, 1 fatty acid, phosphate and choline.

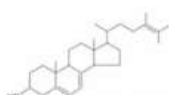


## Sterols

- Sterols are derivatives of steroids.
- These nonpolar lipids have three six-carbon rings and a five carbon ring that is attached to an aliphatic chain.
- They have a hydroxyl group attached to carbon 3 of the A ring.
- Sterol esters are sterols with a fatty acid esterified onto the hydroxyl group at carbon 3.



The four-member cyclopentano-perhydrophenanthrene ring



Ergosterol



Cholesterol



Then sterols see they are again derivatives of the steroids. These nonpolar lipids have 6 carbon rings at a position that is 6 carbon rings and attached to an aliphatic chain carbon. They have a hydroxyl group attached to the carbon 3, the ring A. Sterol esters and sterols with a fatty acid esterified into the hydroxyl group at the carbon 3. They may be the 4 number cyclopentane parenteral hydroxyl real. This ergosterol, cholesterol is a very important group among the sterols.

## Sterols (Contd...)

- Sterols vary in composition based on the organism and environment due to different biosynthetic pathways in plants, fungi, and animals.
- The most important and familiar type of sterol is cholesterol which plays an essential role in cell membrane structure and functions.
- Cholesterol acts as a precursor to fat-soluble vitamins like Vitamin D and hormones.

### ❖ Classification of sterols

| Sterol      | Source         | Examples                             |
|-------------|----------------|--------------------------------------|
| Zoosterol   | Animals        | Cholesterol, coprostanol             |
| Phytosterol | Plants         | Ergosterol, stigmasterol, sitosterol |
| Mycosterol  | Yeast or Fungi | Ergosterol                           |



Sterols vary in composition based on the organism and the environment due to the different biosynthetic pathways in plants, fungi, animals, etc. The most important and familiar type of sterol is cholesterol, which plays an essential role in cell structure and function. Cholesterol acts as a precursor for fat-soluble vitamins like vitamin D and other hormones. So, you can say that sterol sources and their examples, like zoosterol, are found in animals, such as cholesterol and coprostanol. Phytosterols are found in plants, like ergosterol, stigmasterol, and sitosterol. Then, mycosterols are found in yeast and fungi, such as ergosterols.

## Waxes

- It is an ester of a long-chain acid and a long-chain alcohol.
- In reality, industrial and food waxes are a combination of chemical classes including wax esters, sterol esters, ketones, aldehydes, alcohols, hydrocarbons, and sterols.
- They can be classified according to their origin as animal (beeswax), plant (carnauba wax), and mineral (petroleum waxes).
- Found on the surface of plant and animal tissues to inhibit water loss or to repel water.
- Are commonly added to the surface of fruits to slow dehydration during storage.



Dr. K. S. Narayana

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Waxes are mainly long-chain fatty acids and long-chain monohydroxy alcohols. In reality, industrial and food waxes are combinations of chemical classes, including wax esters, sterol esters, ketones, aldehydes, alcohols, and so on. They can be classified according to origin: animal (like beeswax), plant (carnauba wax), and mineral (petroleum waxes). They are found on the surface of plant and animal tissues to inhibit water loss and to repel water. They are commonly added to the surface of fruits to slow dehydration during storage, etc.

## Rancidity

- Rancidity is the natural process of decomposition of fats or oils leading to the development of undesirable flavour & odour by either hydrolysis or oxidation, or both.

### Types of rancidity

| Types of rancidity | Main substances producing rancidity                    | Types of chemical reaction                     | Materials subject to the type of rancidity |
|--------------------|--|--|--|
| Lipolytic          | Low fatty acids, medium chain fatty acids              | Enzymic hydrolysis                             | Milk fat, palm seed oils                   |
| Oxidative          | Lower aldehydes and ketones                            | Autooxidation, enzymic oxidation               | Polyunsaturated edible oil                 |
| Flavor reversion   | Oxygen substituted cleavage and rearrangement products | Oxidation cleavage, and rearrangement          | Soybean oil                                |
| Ketonic            | 2-Alkanones (methyl ketones)                           | $\beta$ -oxidation and enzymic decarboxylation | Milk fat, palm seed oils                   |



Dr. K. S. Narayana

Now, we talk about rancidity. There is the rancidity; although these details of all these rancidity reversions, etcetera, we have discussed these fats and lipids we have discussed in my other NPTEL course, which is Food Oils and Fats Chemistry and Technology and here I have, because obviously of the time constraint, very briefly discussed. So, rancidity generally is a natural process of decomposition of fats or oils leading to the development of undesirable flavour and odour by either hydrolysis or oxidation. There will be different types of rancidity, like lipolytic rancidity. Oxidative rancidity, flavour reversion, or ketonic

rancidity may be present. So, normally, lipolytic rancidity gives the fatty acid as the main product, substituents producing rancidity: fatty acid and medium-chain fatty acid; the types of it may be chemical, physical agents may cause, that is basically hydrolysis. Then, oxidative, which is auto-oxidation or enzymatic oxidation, is used. So basically, these are the various flavor reversions that are oxidative cleavage and rearrangement. Ketonic oxidation, where beta-oxidation and enzymatic decarboxylation reactions take place, and various products are formed, ultimately causes the change in the flavour of the oil, which is called rancidity.

**Rancidity (Contd...)**

- ❖ **Hydrolytic rancidity**
  - ✓ If the liberation of free fatty acids from the glycerol backbone results in the development of off-flavors (e.g. volatile short-chain free fatty acids that form off-aromas or long-chain fatty acids that form soapy tastes), this is known as hydrolytic rancidity.
- ❖ **Oxidative rancidity**
  - ✓ Fats react with oxygen producing products with undesirable characteristics, known as oxidative rancidity.
  - Oxidation
    - Photo-oxidation
    - Autooxidation
    - Enzymatic oxidation

Like hydrolytic rancidity and oxidative rancidity. Hydrolytic rancidity, basically, is the release of free fatty acids. So, the undesirable flavour is mainly because of acidity. The free fatty flavour of the free fatty acids of flavour. Meanwhile, in oxidative acidity, the fat reacts with oxygen and produces byproducts or undesirable characteristics. It may be photo-oxidation, auto-oxidation, enzymatic oxidation, and the various decomposition products, carbonyl compounds, etc., form here, which may sometimes even be toxic and have an undesirable flavor. The objectionable flavor, in this case, is because of the various carbonyl compounds.


Then, there is reversion; the reversion is the change in the flavor of fats again, but it is before the onset of rancidity. The refined material develops an objectionable flavor as the edible fats become inedible. Flavor reversion is more prominent in some fats like soybean, particularly those oils which have more polyunsaturated fat.

**❑ Reversion**

- Flavor reversion is the change in the flavour of fats prior to rancidity.
- The refined material develops an objectionable flavour and the edible fats become inedible.
- Flavor reversion is more prominent in some fats like-Soybean oil has a tendency to have 'beany', 'haylike' and eventually 'fishy' off flavours.
- Prevention- the addition of sequester ants such as EDTA.

❖ The reasons attributed to these changes are:

- ✓ Exposure of ultra violet and visible light.
- ✓ Heating of the fat.
- ✓ The presence of oxygen for the reaction to occur.
- ✓ Triglycerides containing linolenic acid are precursors to flavour reversion reaction.
- ✓ Traces of Fe and Cu which catalyse the reactions and act as pro-oxidants.




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So, they have more tendency to develop undesirable flavours, like soybean has a beany flavour, hay-like flavour. And they eventually develop fishy flavors, etc. So, the prevention and addition of sequestrants such as EDTA can be used to prevent this reversion. So, the reasons attributing to these changes in reversion are mainly exposure to ultraviolet or invisible light, heating of the fat, presence of oxygen for the reaction to occur, or triglycerides containing linolenic acid, which are the precursors of flavour reversion reactions. So, traces of metals like ferrous and cupric or copper ions, which catalyze the reactions, act as pro-oxidants.

**Summary**

- Lipids are hydrophobic molecules like fats, oils, and waxes, essential for cell membranes, energy storage, and signalling.
- Glycerides, formed by combining fatty acids with glycerol, are key components of fats and oils, while phospholipids, containing fatty acids and a phosphate group, are crucial for cell membranes.
- Sterols support cell membrane structure and hormone synthesis, and waxes provide protective coatings for plants and animals.
- Rancidity is the oxidation of fats and oils, leading to unpleasant odors and flavors, while reversion refers to off-flavors in unsaturated fats, like soybean oil, before rancidity fully occurs.



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So, finally, I will summarize this lecture by saying that lipids are hydrophobic molecules like fats, oils, and waxes, which are essential oils. These glycerols and glycerides are formed by combining fatty acids with glycerol, etcetera. Sterols support cell membranes, and rancidity reversion is the major problem. That oxidative rancidity; generally, in most

plant oils, it is a major problem, and this is prevented by adding antioxidants, etcetera, into it so that it is and it should be packed nicely so that its flavour remains intact.

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These are the references which were used in this class.

Thank you very much.