

**Food Oils and Fats: Chemistry & Technology**  
**Professor H N Mishra**  
**Agricultural and Food Engineering Department**  
**Indian Institute of Technology Kharagpur**  
**Week – 02**  
**Lecture - 10**



**NPTEL ONLINE CERTIFICATION COURSES**

**Food Oils and Fats: Chemistry & Technology**

**Professor H N Mishra**

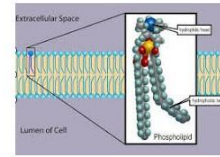
Agricultural and Food Engineering Department  
Indian Institute of Technology Kharagpur

**Module 02 : Food Lipids – Nature & Occurrences**

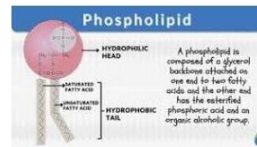
**Lecture 10 : Phospholipids and Sterols**

Hello everyone. Namaste. Now, we are in the 10th lecture.

## Concepts Covered



- Phospholipids
  - ✓Types, properties & functions
- Lecithin
- Sterols
- Plant sterols

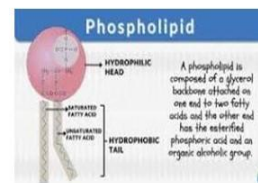
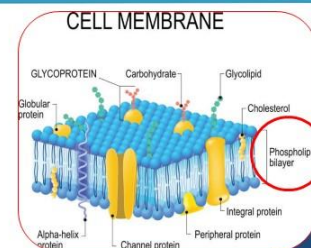


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In this half-hour time, we will discuss phospholipids and sterols that we will discuss the types, properties, and functions of phospholipids, and also specific phospholipids like lecithin. We will discuss its characteristics and its importance in food processing and then sterols, particularly the plant sterols we will discuss in little detail.

### □ Phospholipids

- Phospholipids are lipids containing a phosphoric acid residue.
- They are nature's principal surface-active agents.
- They are found in all living cells, whether of animal or plant origin.
- In humans and in animals, the phospholipids are concentrated in the vital organs, such as the brain, liver, and kidney.
- In vegetables, they are highest in the seeds, nuts, and grains.
- As constituents of cell membranes, and active participants in metabolic processes, they are essential to life.

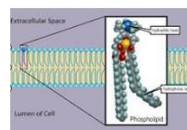
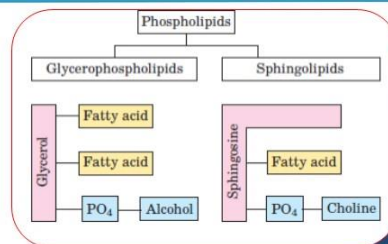


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Now, earlier also we briefly told that phospholipids are lipids containing a phosphoric acid residue. You can see here that there is a hydrophilic head and a hydrophobic tail. In the hydrophilic head, it has a phosphoric group that is in the third carbon atom SN3 normally. So, they are found in all living cells whether they are of animal or plant origin. In humans and animals, phospholipids are concentrated in vital organs such as the brain,

liver, and kidney. In vegetables, they are the highest in the seeds, nuts, and grains. As constituents of the cell membranes and active participants in the metabolic process, phospholipids are essential to our life.

- Three distinct polymeric alcohols provide the basic constituents for the various phospholipids.
- The first of these is **glycerol**, and the phospholipids containing it are referred to as **glycerophospholipids**.
- Included herein, in addition to **PC, PE, and PS**, are the **acetalphospholipids** or **plasmalogens** (in **body fluids, muscles, and egg**), the **lysophospholipids**, and the **phosphatidic acids**.
- The second polyhydric alcohol is the **amino-dihydroxy compound sphingosine**, which is the basis for not only **sphingomyelin** (in the **brain and spinal cord**), but also for other **glycolipids**.
- All of these compounds based on sphingosine are also referred to as **sphingolipids**.
- The third polyhydric alcohol is **inositol**, which is included in **PI**.



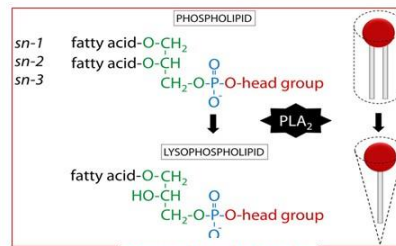
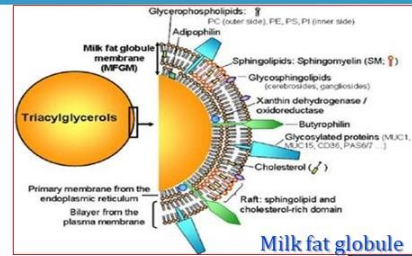
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There are three distinct polymeric alcohol that provides the basic constituent of various phospholipids. The first of these is the glycerol and then the phospholipids containing it are referred to as glycerophospholipids. As you see that is the phospholipids that are glycerophospholipids or sphingolipids. So, glycerol and phospholipids that is which are the fatty acids, two fatty acids, and then phosphor and it is connected with another moiety.

So, included here in addition to PC, PE, and PS that is phosphatidylcholine, phosphatidylethanolamine, and phosphatidylserine are the acetylphospholipids or plasmogens that are in the body fluids, muscles, and egg, and the lysophospholipids and the phosphatidic acids these are the important phospholipids which are present. The second polyhydric alcohol is the amino-dihydroxy compound sphingosine, which is the basis of not only the sphingomyelin that is seen here sphingomyelin that is in the brain and spinal cord but also for the other glycolipids. All of these compounds based on sphingosine are also referred to as sphingolipids ok. The third polyhydric alcohol is inositol which is also included in phosphatidyl inositol.

## Lysophospholipids

- ✓ Phospholipids also form complexes with proteins (e.g. vitelline in egg yolk, animal and plant tissues, lipoproteins in blood serum, and milk), carbohydrates, glycosides, alkaloids, minerals, enzymes, cholesterol, and other substances.
- ✓ Lysophospholipids represent a special class of compounds resulting from the chemical or enzymatic hydrolysis of phospholipids.
- ✓ The role of phospholipases in normal and pathological conditions as well as in cell metabolism is of great biological significance.



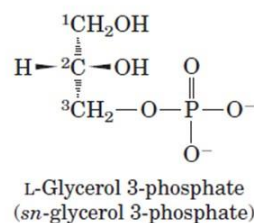
Lysophospholipids

So, lysophospholipids that is the phospholipids also form complexes with proteins like vitelline in egg, oak, animal and plant tissues, and lipoprotein in blood serum and milk. So, the phospholipids form complexes with these proteins. They can form complexes also with carbohydrates like glycolipids, alkaloids, minerals, enzymes, cholesterol, and other substances. So, lysophospholipids represent a special class of compounds resulting from the chemical or enzymatic hydrolysis of the phospholipids. The role of phospholipids in normal and pathological conditions as well as in cell metabolism is of great biological significance. You can see here that is the phospholipids where S1 and SN2 are the fatty acids and in SN3 it is a phosphoric acid group and that is the oxygen head group that is PLA2. So, then this phospholipid is converted into lysophospholipids times that is in the lysophospholipids. You can see the difference between that there are only SN1 fatty acids, SN2 is alcohol and then SN3 is the phosphatidyl group. So, that is how phospholipids and what is the difference between phospholipids and lysophospholipids.



## Glycerophospholipids

- Glycerophospholipids, also called phosphoglycerides, are membrane lipids in which two fatty acids are attached in ester linkage to the first and second carbons of glycerol, and a highly polar or charged group is attached through a phosphodiester linkage to the third carbon.
- Glycerol is prochiral; it has no asymmetric carbons, but attachment of phosphate at one end converts it into a chiral compound, which can be correctly named either L-glycerol 3-phosphate, D-glycerol 1-phosphate, or sn-glycerol-3-phosphate.
- Glycerophospholipids are named as derivatives of the parent compound, phosphatidic, according to the polar alcohol in the head group. Phosphatidylcholine & phosphatidylethanolamine have choline and ethanolamine in their polar head groups.

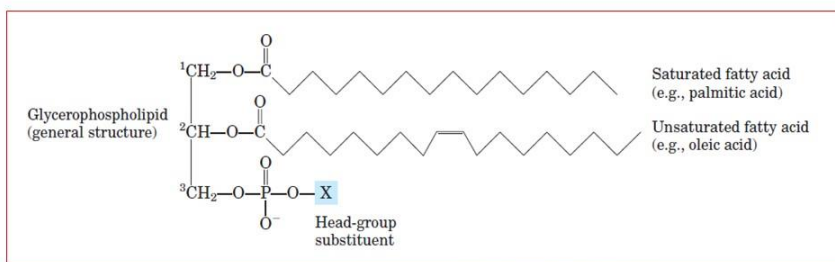


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Glycerophosphoglycerides, they are also called phosphoglycerides, are membrane lipids in which two fatty acids are attached in ester linkage to the first and second carbon of the glycerol, and a highly polar or charged group is attached through a phosphodiester linkage to the third carbon atom SN3 carbon atom ok. Glycerol is a prochiral, it has no asymmetric carbon, but attachment of phosphate at one end converts it into a chiral compound which can be correctly named either L-glycerol 3-phosphate, D-glycerol 1-phosphate or SN-glycerol 3-phosphate as the case may be.

Glycerophospholipids are named as derivatives of the parent compound phosphatidic according to the polar alcohol in the head group like phosphatidylcholine and phosphatidylethanolamines, they have choline and ethanolamine in their polar head groups.

- ✓ The common glycerophospholipids are diacylglycerols linked to head-group alcohols through a phosphodiester bond.
- ✓ **Phosphatidic acid, a phosphomonoester, is the parent compound.**
- ✓ Each derivative is named for the head-group alcohol (X), with the prefix "phosphatidyl-." In cardiolipin, two phosphatidic acids share a single glycerol.



The common glycerophospholipids are diacylglycerides or diacylglycerols linked to a head group through a phosphatidyl bond. See, phosphatidic acid which is a phosphomonoester is the parent compound. Each derivative is named for the head group alcohol X, that is it is X which is present there, and at X what is the X compound based on that it is a name the phospholipidic name the two phosphatidic acids here a single glycerol. So, this is the glycerophospholipid general structure, and then here as I told you it is the X group which is there in the SN3 attached to the phosphoric acid group.

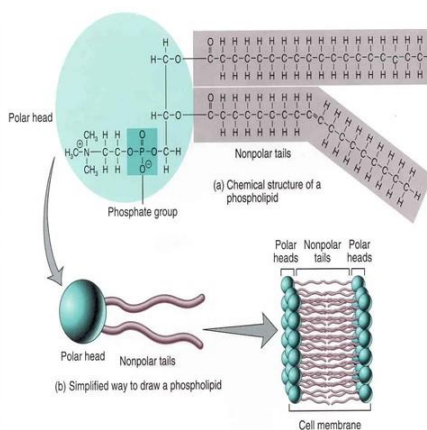
Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	—H	-1
Phosphatidylethanolamine	Ethanolamine	—CH <sub>2</sub> —CH <sub>2</sub> —N̄H <sub>2</sub>	0
Phosphatidylcholine	Choline	—CH <sub>2</sub> —CH <sub>2</sub> —N̄(CH <sub>2</sub> ) <sub>3</sub>	0
Phosphatidylserine	Serine	—CH <sub>2</sub> —CH(NH <sub>2</sub> )—COO <sup>-</sup>	-1
Phosphatidylglycerol	Glycerol	—CH <sub>2</sub> —CH(OH)—CH <sub>2</sub> —OH	-1
Phosphatidylinositol 4,5-bisphosphate	<i>myo</i> -Inositol 4,5-bisphosphate		-4
Cardiolipin	Phosphatidyl-glycerol		-2

This X, and what is that X based on that the phosphoryl is named that. For example, if the X is H then the resulting phospholipids become phosphatidic acid, ok. If it is

ethanolamine, then phosphatidyl ethanolamine, has a net charge at pH 7 is 0, whereas, phosphatidic acid is negatively charged. Then if the X is choline, it becomes phosphatidylcholine and this is also normally called lecithin. Then if X is serine the phospholipid becomes phosphatidylserine, Phosphatidylserine also is negatively charged it has one negative charge.

Then if the glycerol X may be glycerol it becomes phosphatidyl glycerol ok and here it again has a one negative charge. X may be monoenoitol 4, 5 bio phosphate then it becomes phosphatidyl enoitol 4, 5 bio phosphate. It has 4 negative charges at pH 7, of course. Then phosphatidyl glycerol is known as cardiolipin the phosphatidin name has two negative charges. So, it is the X moiety which is attached to the phosphoric acid group of the SN31 in the phospholipid that decides the name of the phospholipids.

### ☐ Glycerophospholipids: Structure-property relations



- The head group is joined to glycerol through a phosphodiester bond, in which the phosphate group bears a negative charge at neutral pH.
- The polar alcohol may be negatively charged (as in phosphatidylinositol 4,5-bisphosphate), neutral (phosphatidylserine), or positively charged (phosphatidylcholine, phosphatidylethanolamine).
- These charges contribute greatly to the surface properties of membranes.

Then let us see the structure property relationships of the glycerophospholipids. The head group is joined to glycerol through a phosphatizer bond in which phosphate groups bear a negative charge at total pH. The polar alcohol may be negatively charged as in phosphatidyl inositol 4, 5 bio phosphate, neutral or phosphatidylserine, or positively charged like it is in the case of phosphatidylcholine or phosphatidyl ethanolamine. These charges contribute greatly to the surface properties of the membrane, which you can see here in this figure. Also, it has been shown that, yes that is the cell membrane is there. It has non-polar heads as well as non-polar heads as well as polar heads. The polar heads this is the simple way to dry phospholipids out. Both have a polar and non-polar head.

- The **fatty acids in glycerophospholipids** can be any of a **wide variety**, so a given **phospholipid** (phosphatidylcholine, for example) may consist of a **number of molecular species**, each with its **unique complement of fatty acids**.
- The **distribution of molecular species** is **specific for different organisms, different tissues of the same organism, and different glycerophospholipids in the same cell or tissue**.
- In **general, glycerophospholipids** contain
  - a **C16 or C18 saturated fatty acid at C-1** and
  - a **C18 to C20 unsaturated fatty acid at C-2**.
- With **few exceptions, the biological significance of the variation in fatty acids and head groups is not yet understood**.



The fatty acid in glycerol phospholipids can be any of a wider variety. So, a given phospholipid that is phosphatidylcholine for example, may consist of several molecular spectra each with its unique complement or fatty acids. Spectra each with its unique complement or fatty acids. The distribution of molecular species is specific for different organisms, different tissues of the same organism, and different glycerophospholipids in the same cell or tissue. In general, glycerophospholipids contain 16 carbon or 18 carbon saturated fatty acids at SN1 position at its carbon 1 and contain 18 carbon or 20 carbon unsaturated fatty acids at second carbon, carbon 2, SN2 position. So, that is in the phospholipids normally glycerophospholipids' first carbon, carbon 1 is a saturated fatty acid and in the second position, it contains generally unsaturated fatty acid. Within few exceptions or with few exceptions, the biological significance of the variation in fatty acids and head groups is not yet very clearly understood, but there are some variations.



## □ Lecithin

- The commercial term “lecithin” is very general, and it describes a composition of lipid constituents and surface-active compounds present in the product rather than in the chemical entity: phosphatidylcholine (PC).
- Thus, in general usage, lecithin refers to a complex, naturally occurring mixture of polar lipids obtained by water-degumming crude vegetable oils and separating and drying the hydrated gums.
- It is, however, the phospholipid portion of lecithin that is mainly responsible for giving form and function to commercial lecithin.
- Commercial lecithin is an important coproduct of edible oil processing because of its dietary significance and multifaceted functionality in food systems and industrial applications.



So, now the phosphatidylcholine that is known commercially for its commercial name is lecithin. It is very general and it describes a composition of the lipid constituents and surface active compounds that are present in the product rather than the chemical entity. That is although we say that it is chemically it is phosphatidylcholine, commercially when it is these gums or in general uses in these gums are taken from the refining process during degumming steps, then these gums natural gums contain a mixture of polar lipids which are obtained that by during degumming process from the crude vegetable oils. And there formally the degumming operation, details of degumming operation we will discuss maybe in a week when we discuss talk about refining process.

Here, these gums are taken, they are sprayed, and dried, and then these gums dehydrated gums or dried gums are used in terms of lecithin and they are used as emulsifiers in food processing operations in many operations. So, chemically it may be phosphatidylcholine however along with that some other compounds also may be present. This phospholipid fraction portion of the lecithin is mainly responsible for giving the functional properties or functions to the commercial lecithin. Commercial lecithin is an important co-product of the edible oil processing industry because of its dietary significance and multi-fathered functionality in the food system and industrial application it is widely used as an emulsifier in many foods.

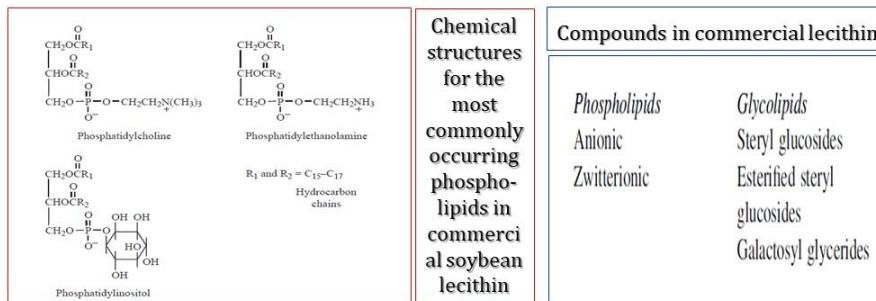
- Lecithin has a long history of use in foods, dating back more than 60 years.
- The 1930s brought widespread use of commercial solvent extraction techniques for vegetable oil production, and because “degumming” of crude vegetable oil became necessary for shipping stability, a large supply of crude lecithin “gums” was produced.
- Lecithin ingredients are now recognized as valuable products that have both nutritional value and commercial, i.e., food/feed/industrial utility.
- Two of the earliest edible applications of lecithin and are still popular and widely used
  - Viscosity reduction in chocolate and confectionery products, and
  - Emulsification/Anti-spatter properties in margarine.
- In addition, other early uses such as in bakery goods, pasta, textiles, insecticides, and paints, among others, are still active today.



Lecithin has a long history of use in foods dating back more than 60 years. In 1930 that is the year 1930, widespread use of commercial solvent extraction techniques for vegetable oil production and because regumming of crude oil became necessary for shipping stability. A large supply of crude lecithin gums was produced. Lecithin ingredients are now recognized as valuable products that have both nutritional value and commercial value like they can be used they are used in food feed as well as for industrial applications. Two of the edible applications of lecithin are the which are now still popular the one is the viscosity reduction in chocolate and the confectionary product that is lecithin has been found very useful in this purpose for this purpose. And the second is that lecithin is used for emulsification or anti-spatter properties in margarine. So, in addition to other early uses such as in bakery goods, pasta, textiles, insecticides, paints, etc. among others they are still active today the lecithin is being used for these products' purposes.

## ☐ Compounds in Commercial Lecithin

- **PC** and **PE** are **cationic** and **anionic** at the **same time**; that is, they are **zwitterions**, and thus they can have some **buffering action** for **both bases and acids**.
- **PI**, however, is a **relatively strong acid** and, therefore, **is anionic**.



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So, the compounds that are present in the commercial lecithin you can see here that is phosphatidylcholine and phosphatidylethanolamine are cationic and anionic, and at the same time that is they are zwitter ions, and thus they can have some buffering action with both bases and acids. The PI that is phosphatidylinositol, however, is a relatively strong acid and therefore, is anionic. So, the phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol, and in this both  $R_1$  and  $R_2$  will be 350 into 17 hydrocarbon chains. So, this is the chemical structure for most of the commonly occurring phospholipids in commercial. So, have been less than the compounds that are generally found in commercials.

So, have been less than include phospholipids, anionic and zwitter ionic that is phospholipids have glycolipids anionic, hystereglycoside, and zeternionic are esterified hystereglycosidic and galactoside glycerides etc.

## □ Properties & food uses of Lecithin

- Lecithin's **multifunctional properties** and its "**natural**" status make it an **ideal food ingredient**.
- The **main functional properties** are emulsification, antispatter, instantizing/wetting/dispersing, release/ parting, viscosity modification, and baking applications.
- These functional characteristics are primarily derived from **chemical structures of lecithin's** major phospholipids.
- Phospholipid molecules contain **two long-chain fatty acids esterified to glycerol**, as well as a **phosphodiester bonding a choline, inositol, or ethanolamine group**.
- A **phospholipid's fatty acid end** is **nonpolar** and thereby **lipophilic (or fat loving)**.
- Conversely, the **phosphodiester**, with its constituents, is **zwitterionic (or dipolar)**, explaining the **hydrophilic (or water loving)** properties of this portion of the molecule.

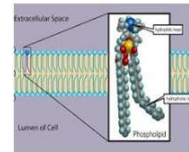


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As far as the properties and food uses of lecithin as concerned I already explained a little bit, but let us say lecithin mouth multifunctional properties of lecithin and its natural status make it an ideal food ingredient. The main functional properties of lecithin are emulsification, antispatter, instantizing, wetting, dispersing, releasing, parting, viscosity modification, and many more even including baking applications. These functional characteristics are primarily derived from the chemical structure of the lecithins, which are the major phospholipids. This phospholipid molecule in the lecithin contains two long-chain fatty acids esterified to glycerol as well as a phosphodiester bonding to a choline inositol or ethanolamine group.

So, the phospholipids fatty acid end is nonpolar and thereby it has a lipophobic or fat-loving property. The phosphodiester group with its constituents that is zwitterionic or dipolar explains the hydrophilic or water-loving properties of this portion of the molecule. Therefore, they have both water-loving which is hydrophilic as well as fat-loving lipophilic properties and that is why this has this keeps both these polar and nonpolar compounds together it acts as a bridge.

Ingredient in	Function(s)
<b>Commercial bakery items</b> <ul style="list-style-type: none"> <li>- Breads, Rolls, Donuts</li> <li>- Cookies, Cakes, Pies</li> <li>- Pasta products</li> </ul>	Crystallization control, emulsifier, wetting agent, release agent (internal and external)
<b>Cheese products</b> <ul style="list-style-type: none"> <li>- Pasteurized processed</li> <li>- Cheese and cheese food</li> <li>- Imitation cheese</li> </ul>	Emulsifier, release agent
<b>Meat and poultry processing</b> <ul style="list-style-type: none"> <li>- Meat and poultry glazes and basting compounds</li> <li>- Pet foods</li> <li>- Bacon</li> </ul>	Browning agent, phosphate dispersant Dietary supplement, release agent, emulsifier

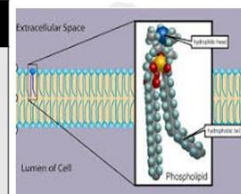


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So, uses of lecithin in commercial products there are in commercial bakery items like bread, rolls, donuts, cookies, cakes, pies, and pasta products it is used for crystallization control, emulsification, wetting agent, it is used as a release agent like internal and internal both. Then in the case of cheese products like pasteurized processed cheese and cheese food or imitation cheeses, this is used as an emulsifier or as a releasing agent.

In meat and meat poultry processing it is meat and poultry glazes and basting compounds, fat foods, vacuums etcetera it is used as a browning agent, phosphate dispersion, dietary supplement, release agent, emulsifier, and so on.

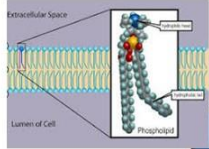
Ingredient in	Function(s)
<b>Dairy and imitation dairy products</b> <ul style="list-style-type: none"> <li>- Infant, milk formulas</li> <li>- Milk and cream replacers</li> <li>- Egg replacers</li> <li>- Imitation eggs</li> <li>- Whipped toppings</li> <li>- Ice cream</li> <li>- Flavored milks</li> <li>- Flavored butters (garlic, etc.)</li> <li>- Basting butters</li> </ul>	Emulsifier, wetting and dispersing agent, anti-spattering agent, release agent
<b>Miscellaneous products</b> <ul style="list-style-type: none"> <li>- Peanut spreads</li> <li>- Salad products</li> <li>- Flavor and color solubilization</li> </ul>	Crystallization control, emulsifier



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In the dairy and imitation dairy products like infant milk, formulas, milk and cream replacers, egg replacers, imitation eggs, whipped toppings in ice cream, flavored milk, flavored butter like garlic flavored butter or basting butter, etc. This lecithin is used as an emulsifier, wetting and dispersing agent, anti-spattering agent or release agent, and miscellaneous applications even peanut spread as margarine peanut butter, it has both crystallization control as well as an emulsifier in peanut butter as I had to 10 percent of the less thing is used sometimes. In the salad products, in the flavor and color stabilization, this is used to control the crystallization process as well as an emulsifier it is used.

Ingredient in	Function(s)
<b>Packaging aid</b> <ul style="list-style-type: none"> <li>- Polymer package, interior coating</li> <li>- Can interior coating</li> <li>- Sausage casing coating</li> <li>- Stocking net</li> </ul>	Release agent, sealant
<b>Processing equipment</b> <ul style="list-style-type: none"> <li>- Frying surfaces</li> <li>- Extruders</li> <li>- Conveyors</li> <li>- Broilers</li> <li>- Dryers</li> <li>- Blenders</li> <li>- Evaporators</li> </ul>	Internal (in product) and/or external release agent, lubricant

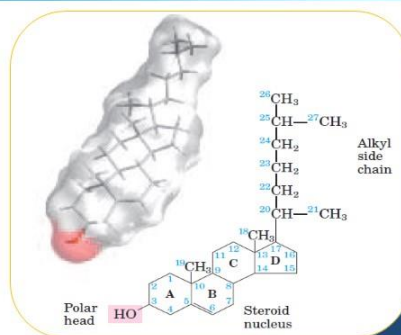


In the packaging aids like polymer package, interior coating, sausage casing, or coating that the coating of cane interior or the sausage casing coating or stocking net and all things release agent or sealant as a sealant helps the property.

Then in the processing equipment like frying surfaces, extruders, conveyors, broilers, dryers, blender evaporators, and all these things that it is internal or in product and or external release agent or is also used as a lubricant in the equipment. So, you can see that lecithin has a large scale void industrial application.

## □ Sterols

- Structures of **sterols** are based on a **steroidal alcohol framework** comparable with that of cholesterol.
- The **molecules** are **planar** and are based on a **tetracyclic cyclopentaphenanthrene system with four fused rings (A, B, C, and D)**.
- The **hydroxyl group at C-3, side chain at C-17, and two methyl groups at C-18 and C-19** are all **angular to the ring structure and have  $\beta$ -stereochemistry (i.e., above plane configuration)**.
- Cholesteryl esters are hydrophobic, and are used for storage and transport of cholesterol.



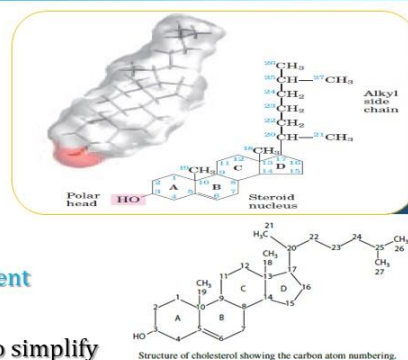
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Then another important group which are present in the oils these are the sterols. The structures of sterols are based on a steroid alcohol framework comparable with that of the cholesterol. You can see the structure of cholesterol here.

Here the molecules are planar and they are based on a tetracyclic cyclopentane and threonine system with 4 fused rings like A, B, C, and D. These are the 4 fused rings. The hydroxyl group at the third carbon atom you see here the third carbonation the hydroxyl group, side chain at the 17 carbon atom has a side chain. And 2 methyl groups are at C18 and C like the methyl group is at 18 and 19 C18 and C19 are the methyl groups. They are all angular to the ring structure and have beta stereochemistry that is above plane configuration. Cholesterol esters are hydrophobic and are used for the storage and transport of cholesterol.

## ❑ Cholesterol

- Cholesterol is the main animal sterol. It contains 27 C- atoms arranged into 4 fused rings and a hydrocarbon tail.
- **It is precursor of bile acids, vitamin D and steroid hormones.**
- Is synthesized, primarily in liver and adrenal gland, from acetyl-CoA cholesteryl ester, which is formed by an ester link of a fatty acid to cholesterol.
- **The stick structure of cholesterol is visible through a transparent surface contour model of the molecule.**
- In the chemical structure, the rings are labelled A through D to simplify reference to derivatives of the steroid nucleus, and the carbon atoms are numbered in blue.
- **The C-3 hydroxyl group (pink in both representations) is the polar head group. For storage and transport of the sterol, this hydroxyl group condenses with a fatty acid to form a sterol ester.**



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And so, the cholesterol is the main animal sterol. It contains about 27 carbon atoms arranged into 4 fused rings and a hydrocarbon chain as I told you earlier in the last slide. It is the precursor of bile acids, vitamin D, and steroid hormones. It is synthesized primarily in the liver and adrenal gland from acetyl CoA or CoA style esters which is formed by an ester linked of a fatty acid to cholesterol. The structure of cholesterol is visible through a transparent surface color module of the molecule. In the chemical structure the rings are labeled A through D to simply reference to derivatives of a steroid nucleus and the carbon atoms are numbered in blue.

You can see here that these carbon atoms are numbered in blue. The C3 hydroxyl group is pink in both representations and is a polar head for the storage and transport of the cholesterol.



## □ Plant sterols

- The sterols are generally the major components of the unsaponifiable fractions of vegetable oils.
- Plant sterols, or phytosterols, are generally the predominant compounds in the unsaponifiable fractions of vegetable oils that generally account for about 1% of the oils.
- The main sterols belong to the 4-desmethylsterols family, but 4-methylsterols and 4,4-dimethylsterols (also called triterpene alcohols) are present as minor components in most oils.
- Apart from some exceptions, the desmethylsterol,  $\beta$ -sitosterol, is generally the most abundant and is usually accompanied by variable levels of campesterol, stigmasterol, 5-avenasterol, and other sterols.



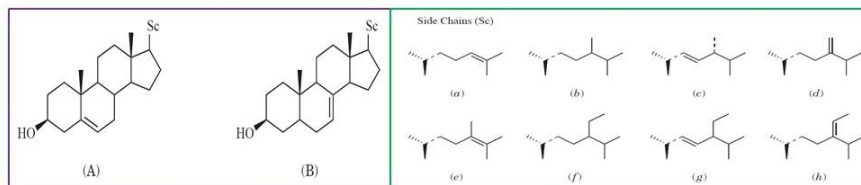
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This hydroxyl group condenses into a fatty acid to form a sterol esters. Then plant sterols which are generally the major components of the unsaponifiable fractions of the vegetable oils. Plant sterols or phytosterols are generally the predominant compounds in the unsaponifiable fraction of vegetable oil that generally account for about 1 percent of the oil.

The main sterols belong to the 4-desmethyl sterol family, but 4-methyl sterols and 4,4-dimethyl sterols that is also called triterpene alcohol are present as minor component in most of the oils. Apart from some exceptions the desmethyl sterols that are beta-cytosterol the generally the most abundant and are usually accompanied by variable levels of campesterol, stigmasterol, 5-avenasterol, and other sterols.

## Desmethyl sterols

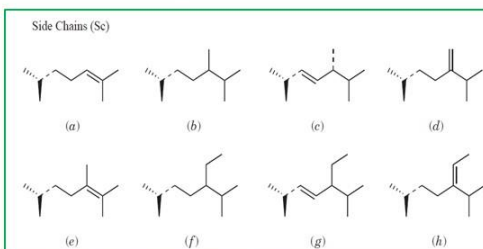
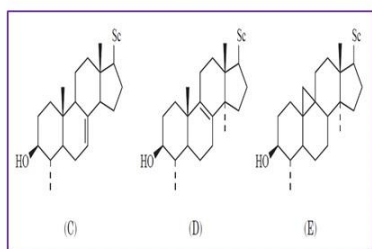
Sterol Skeleton	Side Chain	Trivial Name	IUPAC Name
A	c	Brassicasterol	24 $\beta$ -methyl cholest-5,22E-dien-3 $\beta$ -ol
A	b	Campesterol	24 $\alpha$ -methyl cholest-5-en-3 $\beta$ -ol
A	g	Stigmasterol	24 $\alpha$ -ethyl cholest-5,22E-dien-3 $\beta$ -ol
A	f	Sitosterol	24 $\alpha$ -ethyl cholest-5-en-3 $\beta$ -ol
A	h	$\Delta$ 5-Avenasterol	24E-ethylidene cholest-5-en-3 $\beta$ -ol
B	f	Stigmastenol	24 $\alpha$ -ethyl cholest-7-en-3 $\beta$ -ol
B	h	$\Delta$ 7-Avenasterol	24E-ethylidene cholest-7-en-3 $\beta$ -ol



So, desmethyl sterol you can see here there is the sterol skeleton. You see that it may be either A or this B ring which is shown here is mostly the same. The simple difference is that here the double bond position you can see in the B ring. Otherwise other is the same. So, this might be either A or B then the side chain that A, B, C, and D side chain is a then. So, if the I discussed then is A and this side chain becomes A like there is a C, A, and C it is brachycholesterol. A and B will become campesterol, A and G stigmasterol that is A and F is the side chain. This F becomes Sitosterol. Then A and H, H is here you see it is a saturated that is at 5 saturation saturated ring is there it is 5-Avenasterol. And when the side chain is B and H you can say B and H again it becomes 7-Avenasterol. So, these are the trivial names and accordingly, the IUPAC names are also given here. So, these are some of the desmethyl sterols that are found in plant oils.

## 4-Methyl sterols

Sterol Skeleton	Side Chain	Trivial Name	IUPAC Name
C	f	24-ethyl lophenol	4 $\alpha$ -methyl-24 $\alpha$ -ethyl cholest-7-en-3 $\beta$ -ol
C	d	Gramisterol	4 $\alpha$ -methyl-24-methylene cholest-7-en-3 $\beta$ -ol
C	h	Citrostadienol	4 $\alpha$ -methyl-24E-ethylidene cholest-7-en-3 $\beta$ -ol
D	d	Obtusifoliol	4 $\alpha$ ,14 $\alpha$ -dimethyl-24-methylene-cholest-8-en-3 $\beta$ -ol
E	d	Cycloeucaenol	9,19-cyclo-4 $\alpha$ ,14 $\alpha$ -dimethyl-24-methylene-cholest-8-en-3 $\beta$ -ol

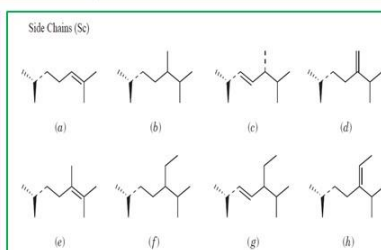
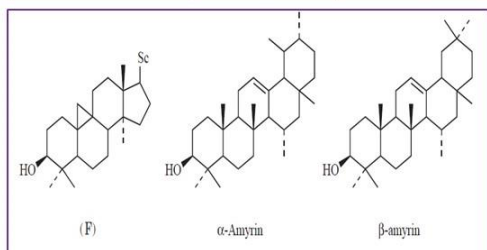


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4-methylsterol similarly that its structure main structure may be either C or D or E that is A, B, C, D, the structure which is the C or D or E, ok. So, if again this skeleton is the C and side chain if it is F then it becomes 24-ethyllopanol, ok. So, this here the IUPAC name if the structure is D like this where you see the here chain in this double bond positioning. So, if the side is the main chain is D and the side chain is also D then D and D the side chain is D. Here it becomes obtusifoliol and its IUPAC name is also there. So, these are the different types of 4-methylsterols.

## 4,4-Dimethyl sterols & triterpene alcohols

Sterol Skeleton	Side Chain	Trivial Name	IUPAC Name
F	a	Cycloartenol	9,19-cyclo-4,4,14a-trimethyl-cholest-24-en-3 $\beta$ -ol
F	d	24-Methylenecycloartenol	9,19-cyclo-4,4,14a-trimethyl-24-methylene-cholestan-3 $\beta$ -ol
F	e	Cyclobranol	9,19-cyclo-4,4,14a,24-tetramethyl-cholest-24-en-3 $\beta$ -ol
-	-	$\alpha$ -Amyrin	5 $\alpha$ -urs-12-en-3 $\beta$ -ol
-	-	$\beta$ -Amyrin	5 $\alpha$ -olean-12-en-3 $\beta$ -ol



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4,4-dimethyl sterols and triterpene alcohols are similar like this structure may be here F or alpha and beta this in F it is the difference in you can see here just this group and this

bonds that main difference in alpha and beta other things are same almost. So, alpha-amyirin or beta-amyirin that is skeleton is F. So, if F is there a side chain is A then it becomes Cycloartenol or alpha-amyirin, beta-amyirin, cyclobranol, 24-methylene cycloartenol, and so on. So, these are the different 4-4-dimethylsterols and triterpene alcohols found.

## Plant sterols (Contd...)

- Some sterols are characteristic for certain oils and can be used to detect the presence of this oil in foods.
- Sterols occur in vegetable oils in free & esterified forms in relative levels that are dependent on type of oil.
- In the sterol esters of vegetable oils, the hydrogen of the hydroxyl group at C-3 is substituted with a fatty acyl or with ferulic acid as in  $\gamma$ -oryzanols.
- Due to their unique sterol profile, vegetable oils can be authenticated by using their sterol profile.



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Plant sterols there is sterols are characteristics of certain oils and can be used to detect the presence of this in oil in the foods. Sterols occur in vegetable oils in free as well as in esterified form in relative levels that are dependent on the type of the oil. In the sterol esters of vegetable oils, the hydrogen of the hydroxyl group at carbon 3 is substituted with a fatty acyl or with ferulic acid, and in the case of gamma-oryzanols. Due to their unique sterol profile vegetable oils can be authenticated by using their sterol profile.

That is gamma-oryzanol is a common constituent present in the rice bran oil it is a plant sterol. So, the rice bran oil you can see that this from the paddy is when it is milled then you get husk and the bran, then bran is used for oil. The oil see that is the husk portion is the rice germ the bran, and starchy endosperm. So, the bran just covers the starchy endosperm, and this bran oil it is highly unsaturated fatty acids present it is vitamin E as well as gamma-oryzanol, these are the gamma-oryzanol is the antioxidant present in the rice bran oil.

## Major sterols present in common vegetable oils

Class of Sterol	Coconut	Cottonseed	Olive	Wheat germ	Rice bran
<b>Desmethyl Sterols (mg/100 g)</b>	<b>102</b>	<b>510</b>	<b>150</b>	<b>1425</b>	<b>105.5</b>
- Campesterol	8%	7%		19%	24%
- Stigmasterol	13%				11%
- Sitosterol	47%	86%	82%	60%	52%
- $\Delta^5$ -avenasterol	26%			7%	8%
<b>4-Methyl Sterols (mg/100 g)</b>	<b>7</b>	<b>12</b>	<b>68</b>	<b>59</b>	<b>3 main unknown compounds in addition to obtusifoliol and gramisterol</b>
- Obtusifoliol	9%	8%		14%	
- Gramisterol		11%		25%	
- Cycloeucaenol	36%	5%	14%	6%	
- Citrostadienol	33%	42%	22%	30%	
<b>4,4-Dimethyl Sterols (mg/100 g)</b>	<b>20</b>	<b>17</b>	<b>292</b>	<b>59</b>	
- $\alpha$ -amyrin	7%	7%		7%	
- $\beta$ -amyrin	5%			12%	
- Cycloartenol	55%	12%	18%	25%	<b>Present as <math>\gamma</math>-oryzanol</b>
- 24-methylene- cycloartanol	22%	21%	31%	33%	<b>Present</b>
- Cyclobranol			10%		

So, these are the major sterols present in common vegetable oils that are just coconut, cottonseed, olive, wheat germ, and rice bran oil. So, you see desmethyl sterols that are campesterol it is present in coconut oil at around 8 percent, cotton seed at 7 percent, wheat germ at 19 percent, and rice bran at about 24 percent.

Similarly, cytosterol, stigmasterols, or the 5-avenasterols, etc. are all present in this. Then 4 methyl sterols are present in the coconut it is present in the account of 7 milligrams per 100 grams, in cottonseed 12 milligrams per 100 grams, and in olive oil, it has more amount than 68 milligrams per 100 grams. In wheat germ also it contains 59 milligram per 100 gram and the different function that is the specific compound, obtusifoliol, gramisterol, cycloeucaenol, then citrostadienol, all these are proportionate. So, these are the 3 main compounds in addition to the obtusifoliol and gramisterol.

Then, similarly, 4 methyl sterol they are present in 20 mg per 100 gram in coconut, and 17 mg per 100 gram in cotton seed, but in olive oil their content is very high 292 milligrams per 100 gram and in wheat germ oil also it has got around 50. So, the cycloartenol is 55 percent in coconut, the cotton seed 12 percent, olive 18 percent, and wheat germ oil 25 percent. And these are present as gamma-oryzanol this 24-methylene-cycloartenol is also present in the rice bran oil. So, this rice bran oil contains around 105.

5 milligrams per 100 grams, this methyl stanol. There are other compounds present that 3 main compounds and gamma-oryzanols and this 24 methylene cycloartanol present.



## □ Food applications of plant sterols

- **Phytosterols** are industrially isolated from the distillates, resulting from the **deodorization of vegetable oils**.
- **Phytosterols** are sometimes **hydrogenated** to produce **phytostanols**.
- As the **solubility of sterols and stanols is very low (<1% at 25 °C)**, it **limits their application in food products**.
- **Esterification of sterol and stanols** is, therefore, performed to make them **fat-soluble** and **easy to incorporate in food products**.
- **Two margarines containing 8–9% sterols (Becel Proactiv of Unilever) or stanols (Benecol of Raisio)**, in the form of esters, are now available in the **markets in Europe and the United States**.



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So, the food applications of plant sterols like this phytosterol are industrially isolated from the distillates which results from the deodorization of the vegetable oil. Phytosterols are sometimes hydrogenated to produce phytostanols as the solubility of the sterols and stanols is very low which is less than 1 percent at 25 degree Celsius. It limits their application in food products. Sterification of the sterols and stanols is, therefore, performed to make them fat-soluble and easy to incorporate in food products. Two margarines containing 8 to 9 percent sterols like Becel Proactiv of Unilever or stanol like Benecol of Raisio or in the form of esters are now available in the markets in Europe and the United States.

## Summary

- The minor components of lipids are an important class of lipids.
- **Phospholipids are important for their role as emulsifiers.**
- Lecithin is an important phospholipid that is used as an emulsifier in chocolate products.
- **Sterols are important for their role in providing characteristic feature to oils useful for their authentication.**
- Sterol-based food products represent an interesting opportunity for new product development.



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So, now I summarize this lecture by saying that the minor components of lipids are an important class of lipid and their sterols. Phospholipids are important for their role as emulsifiers. Lecithin is an important phospholipid that is used as an emulsifier purpose in chocolate products and many other confectionery and bakery products. Sterols are important for their role in providing characteristic features to oils which are useful for their authentication. Sterol-based food products present an interesting opportunity for new product development. So, both phospholipids and sterols including animal sterols and plant sterols are very very important classes of compounds that are present in food fats and oils, and they must be looked at carefully many commercial they are produced from the by-products of oil refining industry like either gums or even distillates of their deodorization processes. They have also as you have seen earlier that is they had many applications in many non-food industry operations in pharmaceuticals etc. they are used widely.

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So, these are the references which are used in this lecture.



Thank you very much for your patience here.