Novel Technologies for Food Processing and Shelf Life Extension
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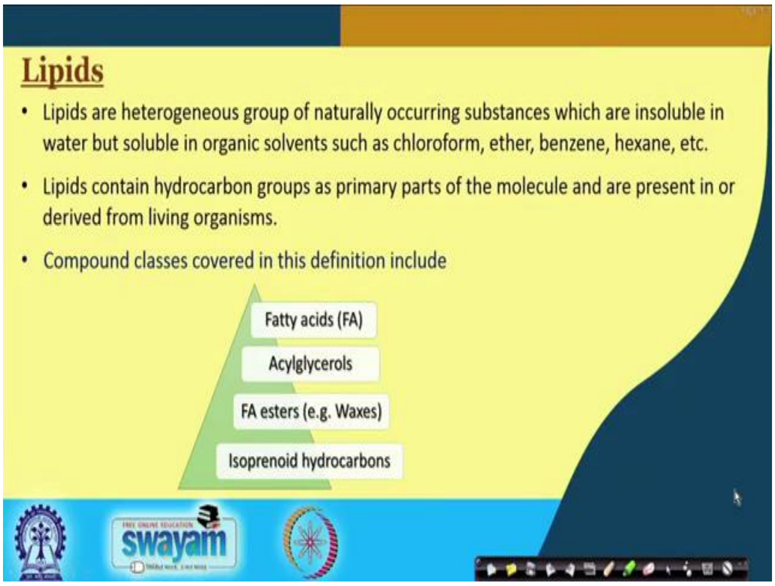
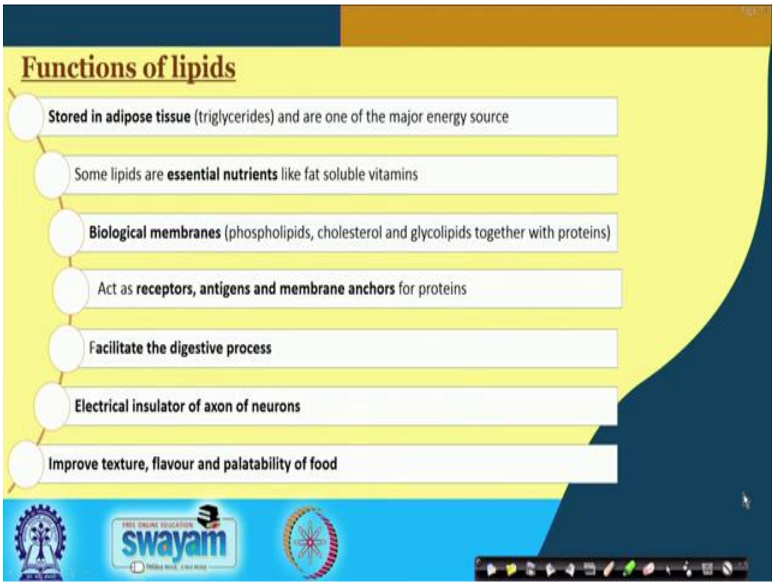
Lecture - 29
Food Lipids (Nature & Occurrence)

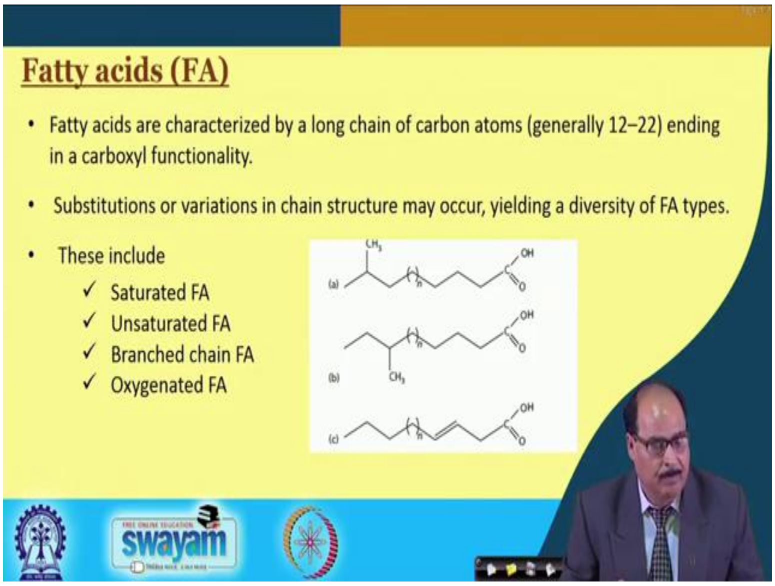
This part of the lecture on food lipids will mainly focus on the nature and occurrence of lipids in various biological materials.



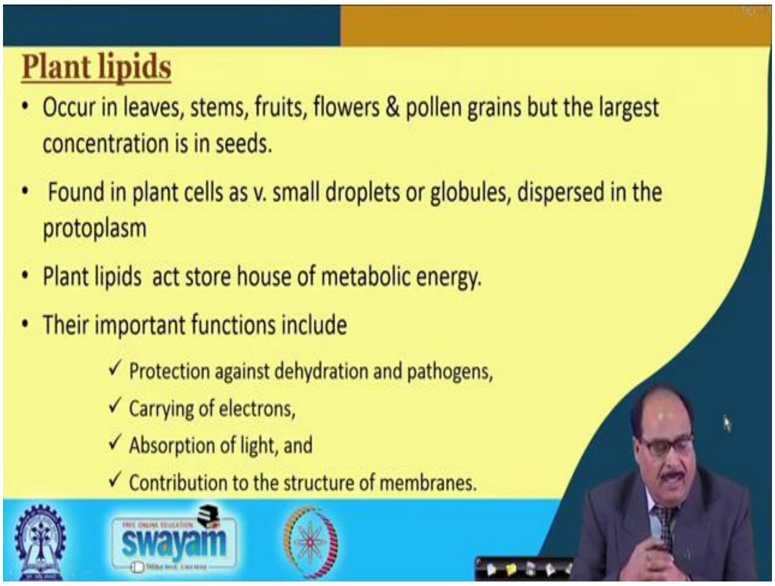
Lipids are heterogeneous group of naturally occurring substances which are insoluble in water, but soluble in organic solvents such as chloroform, ether, benzene, hexane, etc. They contain hydrocarbon groups as primary parts of the molecule and are present in or derived from living organisms, may be either from plant source or from animal source. The compound classes of lipids which are covered in this definition include fatty acids, acylglycerols, fatty acid esters and isoprenoid hydrocarbons.



Functions of lipids: These lipids are stored in adipose tissues in the form of triglycerides. They are one of the major sources of energy to the cell. Some lipids are essential nutrients like fat soluble vitamins. They also are the constituents of biological membrane and are very important to their structure and function. They act as receptors, antigens and membrane anchors for proteins. They facilitate the digestive process, they act as electrical insulator of action of neurons and, more importantly they improve texture, flavour and palatability of foods.

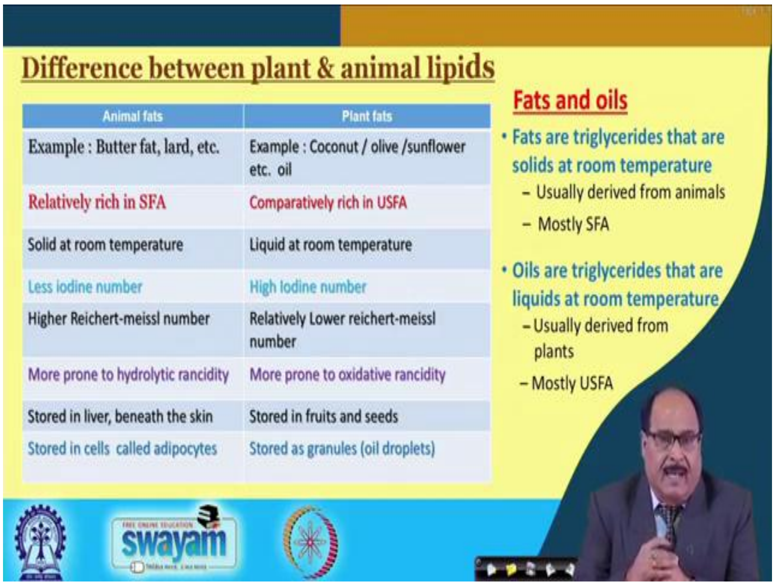


The lipids constitute of fatty acids. So, the fatty acids are characterized by a long chain of carbon atoms generally 12 to 22 carbons, ending in a carboxyl functionality. There might be different substitutions or variations in the chain structure and which may result into different types of fatty acids, including saturated, unsaturated, branched chain, or oxygenated fatty acids.



Plant lipids occur in leaves, stems, flowers, fruits, pollen grains and but the largest concentration of the lipid in plants is found in seeds. They are found in plant cells as very small droplet or globules dispersed in the protoplasm. Plant lipids act as store house of metabolic energy. Their important functions in the plant include protection against dehydration and pathogens, carrying of electrons, absorption of light and contribution to the structure of membrane.

The commonly found lipids in plant systems include saturated fatty acids (SFA) like palmitic acids, monounsaturated fatty acids (MUFA) like oleic acid and polyunsaturated fatty acid (PUFA) such as linoleic and linolenic acids. Plants contain comparatively less saturated fatty acids like lauric and myristic acids. Plant oils are mixture of mixed triglycerides.

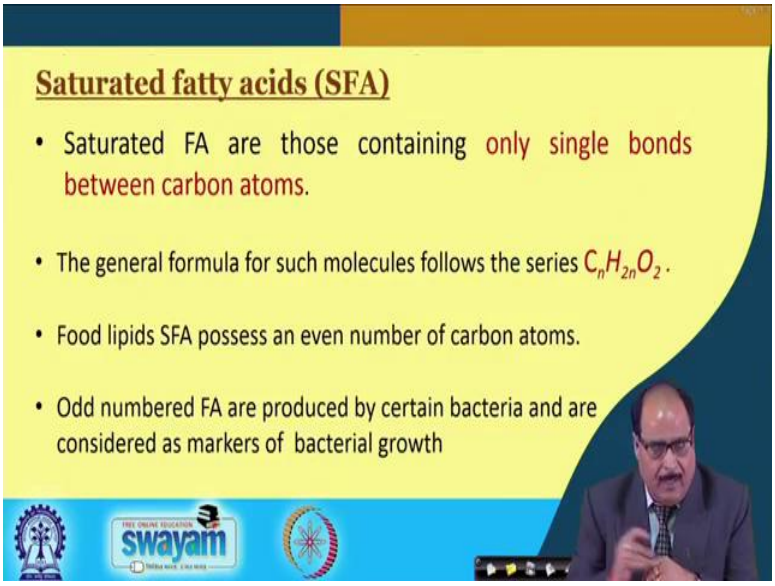


Difference between the plant lipids and animal lipids:

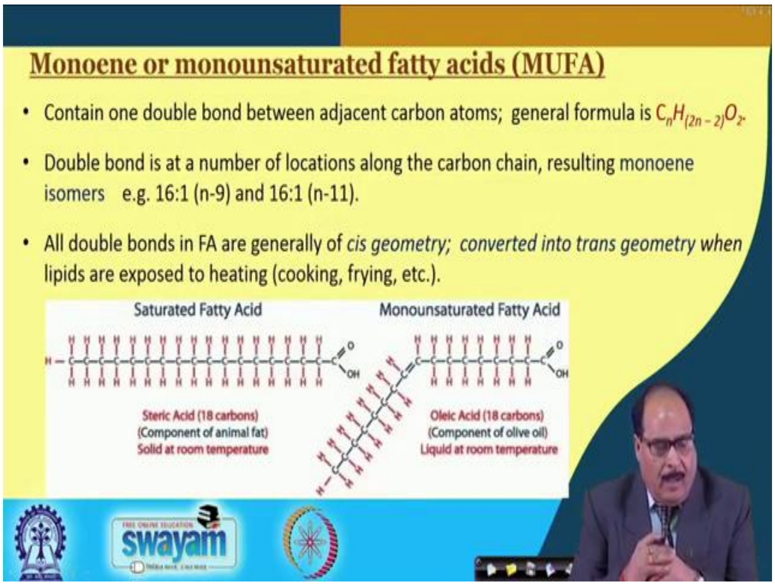
Animal fats	Plant fats
Example : Butter fat, lard, etc.	Example : Coconut / olive /sunflower etc. oil
Relatively rich in SFA	Comparatively rich in USFA
Solid at room temperature	Liquid at room temperature
Less iodine number	High Iodine number
Higher Reichert-meissl number	Relatively Lower reichert-meissl number
More prone to hydrolytic rancidity	More prone to oxidative rancidity
Stored in liver, beneath the skin	Stored in fruits and seeds
Stored in cells called adipocytes	Stored as granules (oil droplets)

In fact, fats and oils basically are in form of lipids. They are triglycerides that are solid or may be liquid at room temperature.

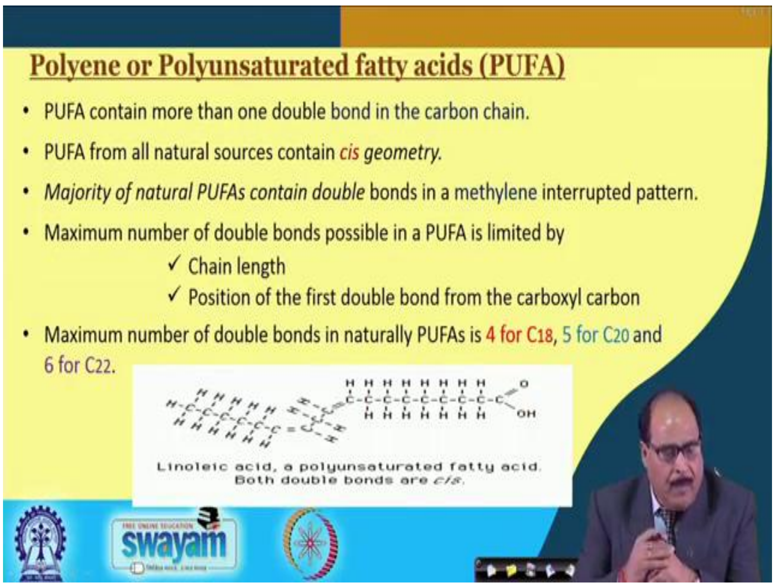
So, the triglycerides which are solid at room temperature are generally termed as fat. They are usually derived from animals and they contain mostly saturated fatty acids. Whereas, the oils are the triglycerides that are mostly liquid at room temperature, they are usually derived from plants and they have more amount of unsaturated fatty acids. So, chemically both of them are triglycerides. And, it is the basic difference of the fatty acids which are present in them like nature of the fatty acid, chain of the fatty acid lengths or degree of saturation of the fatty acids, which makes them solid or liquid.



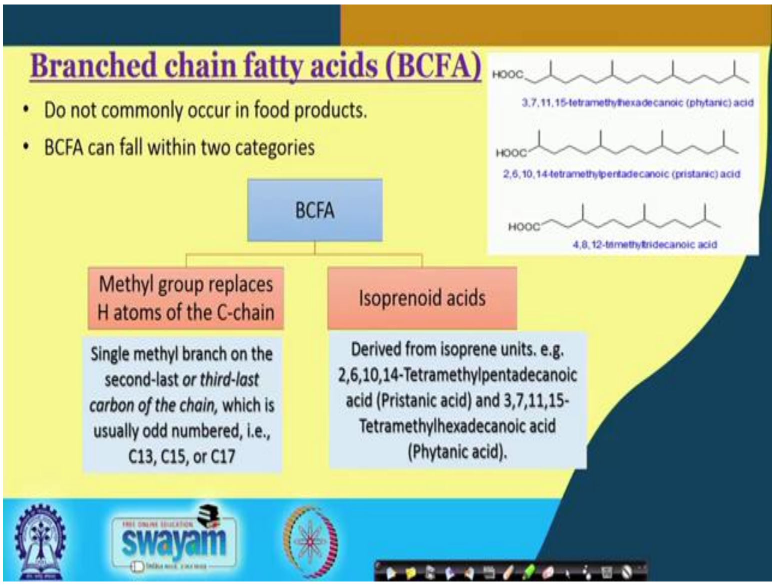
Saturated fatty acids are those that contain only single bond between carbon atoms. They fit to the general formula $C_nH_{2n}O_2$. Food lipids saturated fatty acids possess in general an even number of carbon atoms; odd numbered fatty acids are produced by certain bacteria and are considered as markers of the bacterial growth.



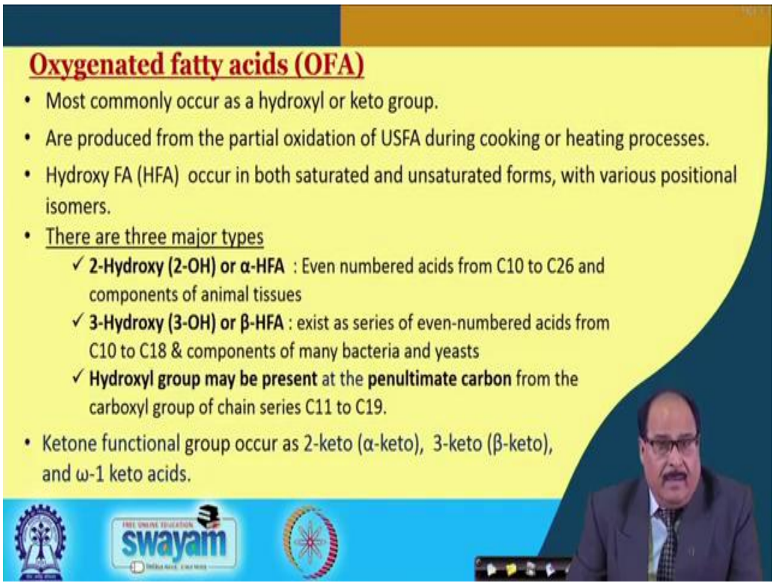
Unsaturation means all the carbon balances are not saturated; there is some double bond. So, the monounsaturated means 1 double bond; this is a fatty acids that contain 1 double bond between adjacent carbon atoms and they fit to the general formula of $C_nH_{2n}O_2$. The double bonds in monounsaturated fatty acids is generally at a number of locations along the carbon chain, resulting monoene isomers for example, 16:1 (n-9) and 16:1 (n-11). All double bonds in fatty acids are generally of cis geometry. However, when these fats are exposed to heat treatment like cooking, frying etc., then cis is converted into trans geometry. In cis geometry, in a double bond OH groups are on the same side of the chain whereas, in the trans geometry they are located on the opposite side of the chain. So, the composition of cis and trans fats is of nutritional significance and importance in food science.



Polyunsaturated fatty acids contain more than 1 double bond; poly i.e. 2, 3, 4, 5 or more double bond in the carbon chain. Polyunsaturated fatty acids are commonly called as PUFA. They contain double bonding in cis geometry; majority of natural PUFA contain double bond in a methylene interrupted pattern. The maximum number of double bond possible in a PUFA is limited by the chain length and position of the first double bond form the carboxyl atom. Maximum number of double bonds in naturally occurring polyunsaturated fatty acids are 4 for C18 carbon, 5 for C20 carbon and 6 for C22 carbon containing fatty acids. So, most of the food fats or oils contain double bonds ranging from 1 to 6. So, polyunsaturated fatty acids are those that contain higher number of double bonds like 4, 5, 6 in their structure.



Another important fatty acids is the branched chain fatty acid (BCFA); however, they are normally not found in food materials. They are of 2 types; methyl group replaces hydrogen atom of the carbon chain in one group of the branched chain fatty acids. In another group, it is the isoprenoid acids (normally derived from isoprene units).

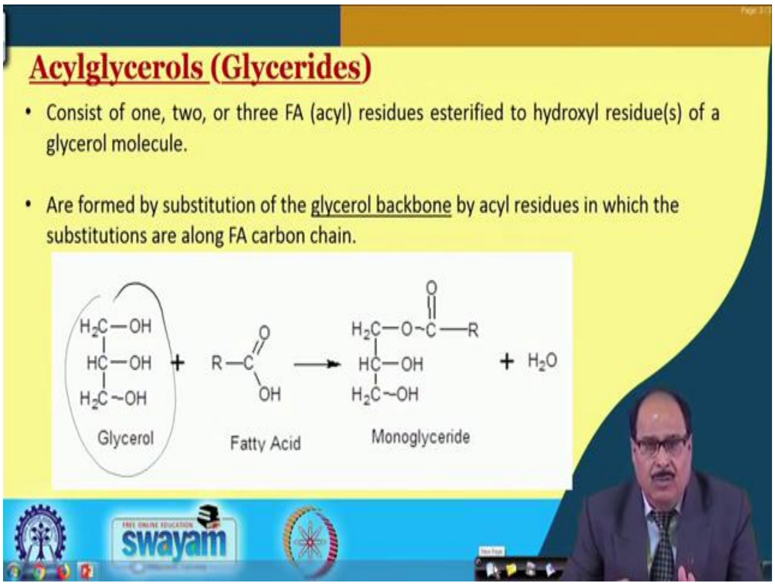


Oxygenated fatty acids (OFA):

They most commonly occur as a hydroxyl or keto group. They are produced from the partial oxidation of unsaturated fatty acids, during cooking or heating processes. And therefore, they become of nutritional significance that is of concern in food science and processing. Hydroxy fatty acids (HFA) occur in both saturated and unsaturated forms with various positional isomers. There are 3 major types of OFA or HFA:

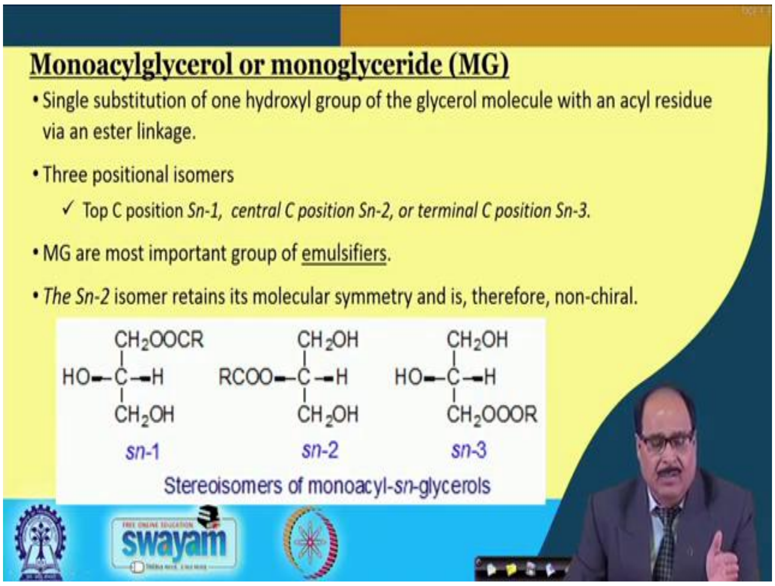
- ✓ 2-Hydroxy (2-OH) or α-HFA : Even numbered acids from C10 to C26 and components of animal tissues
- ✓ 3-Hydroxy (3-OH) or β-HFA : exist as series of even-numbered acids from C10 to C18 & components of many bacteria and yeasts
- ✓ Hydroxyl group may be present at the penultimate carbon from the carboxyl group of chain series C11 to C19.

Ketone functional group occur as 2-keto, 3-keto or omega 1-keto acids.

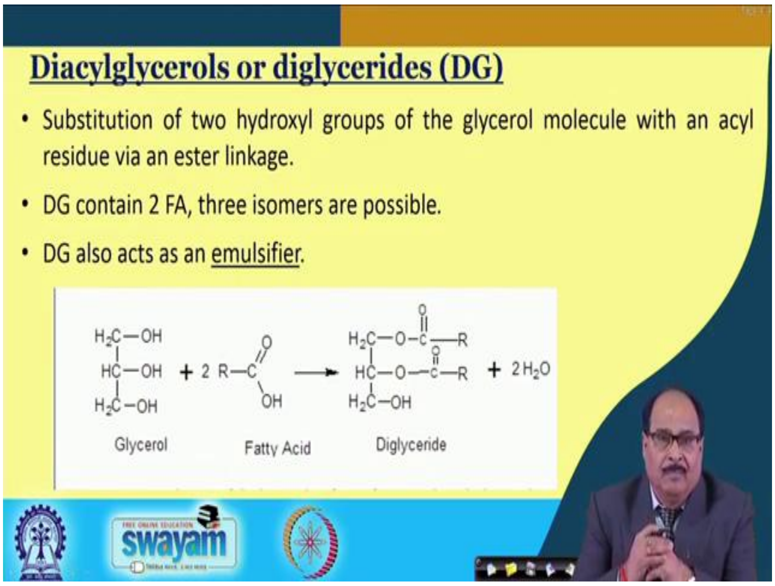


Acylglycerols or glycerides consist of 1, 2 or 3 fatty acid residues esterified to hydroxyl residue of a glycerol molecule. A glycerol molecule having 3 hydroxyl groups reacts with fatty acids fatty acids (RCOOH). So, ester linkage is formed between the hydroxyl group, as well as carboxyl group of the glycerol and fatty acids. The resulting compounds like glyceride, monoglyceride, diglycerides, or triglycerides are formed. In this case, it is one fatty acid esterified with alcohol linkage of the glycerol molecule. So, monoglycerides are formed by substitution of glycerol backbone by acyl residues in which substitutions are along with the fatty acids carbon chain.

So, if it is 1 substitution, it is monoglyceride; 2 substitutions diglycerides and if all the 3 hydroxyl groups are substituted by fatty acids or esterified with fatty acids, then it becomes triglycerides.



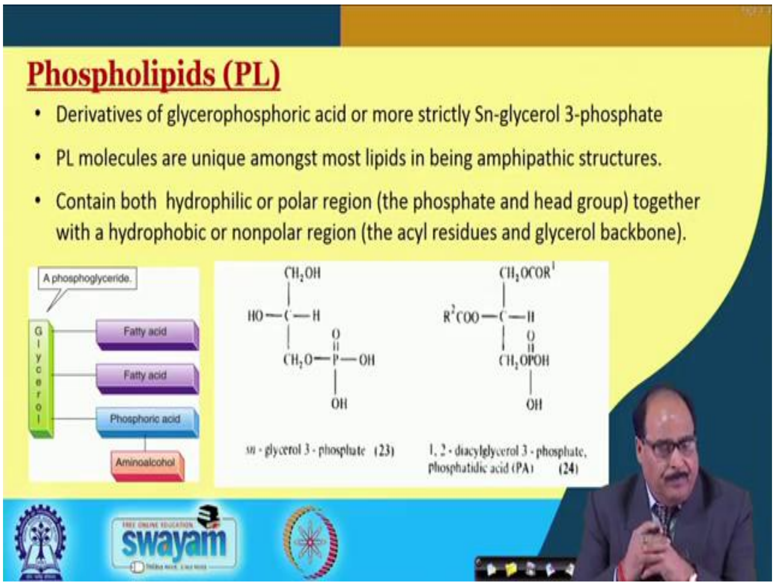
Monoglycerol or monoglyceride (MG): The fatty acids may join at the Sn-1 position, at Sn-2 position, or at Sn-3 positions. And, depending upon their position there may be 3 isomers, or 3 positional isomers like, like Sn-1 isomer Sn-2 isomer or Sn-3 isomers; Sn-2 isomer retains its molecular symmetry and is therefore, non-chiral. These are very important group of lipids, which are generally used as emulsifier in food processing in preparation of different types of product.



Diacylglycerols or diglycerides (DG): There are 2 hydroxyl group of the glycerol molecule esterified with 2 fatty acids. Again 3 isomers might be possible i.e. Sn-1 Sn-2, Sn-3, etc. Diglycerides also act as emulsifiers.

In case of triglycerides or triacylglycerols (TG), there is full substitution i.e. all the 3 hydroxyl groups of the glycerol molecule are esterified. It may so happen that all the 3 hydroxyl groups are esterified with the same fatty acid i.e. 3 molecules of same fatty acid like stearic acid. Stearic acid is attached in all the 3 positions Sn-1, Sn-2, Sn-3, or 2 fatty acids Sn-1, Sn-2, may be stearic acid and Sn-3 may be formic acid or in all the 3 positions, Sn-1, Sn-2, Sn-3; there may be 3 different fatty acids. So, if at all the 3 positions there are same fatty acids attached, it is called simple triglyceride and if the 3 fatty acids are different, the resulting triglyceride is known as mixed triglyceride and most of the food fats and oils are mixtures of mixed triglycerides.

Triglycerides from the plants like palm, coconut, etc., contain comparatively high proportion of saturated fatty acids and are solid at room temperature. And, on the other hand, the triglycerides from plant materials like corn, peanuts, soyabean, sunflower oil etc. or even olive oil contain high proportion of unsaturated fatty acids, or polyunsaturated fatty acids, and they are liquid at room temperature.

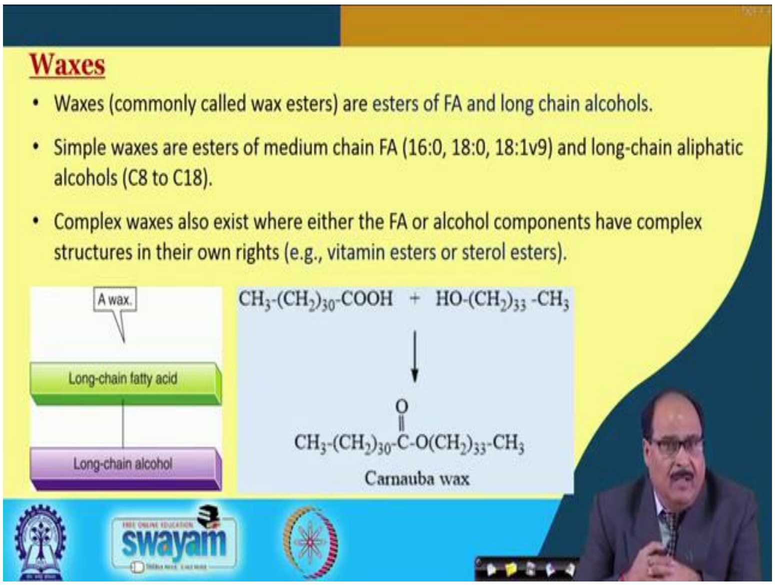


Phospholipids are another important category of lipids. They are the derivatives of glycerophosphoric acid or more strictly Sn-glycerol 3-phosphate.

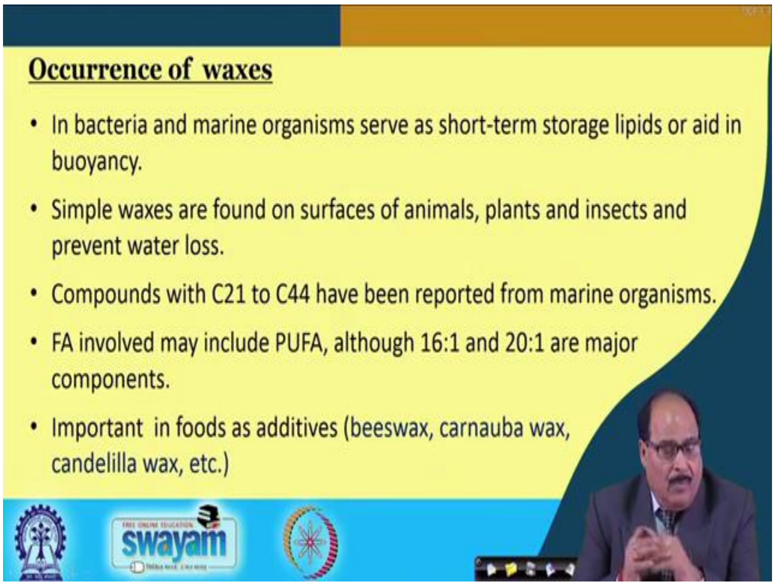
The fatty acid at Sn-3 position (see Fig.) is replaced with a phosphoric acid. And, the phosphoric acid in turn may be joined with another molecule. Like in the case of lecithin, phosphatidylcholine, phosphatidylethanolamine, phosphatidylserine, phosphatidyl helin etc. are attached.

These phospholipids are very important groups of lipids commonly found in the food materials. They contain hydrophilic or polar region (the phosphate and head group) together with a hydrophobic or non-polar region (the acyl residues and glycerol backbone).

And accordingly from the structure and function wise they are very important in the food processing or food chemistry.

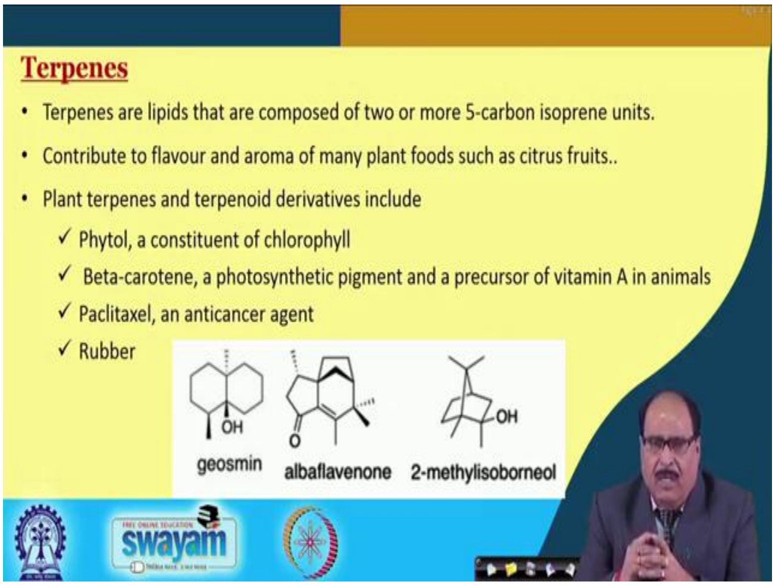


The other group of lipids is the waxes commonly called wax esters. These are the esters of fatty acids and long chain alcohol generally monohydric alcohol. Simple waxes are esters of medium chain fatty acid (16:0, 18:0, 18:1v9) and long-chain aliphatic alcohols (C8 to C18). Complex waxes also exist where either the fatty acid or alcohol components have complex structures in their own rights; for example, vitamins esters or sterol esters etc.



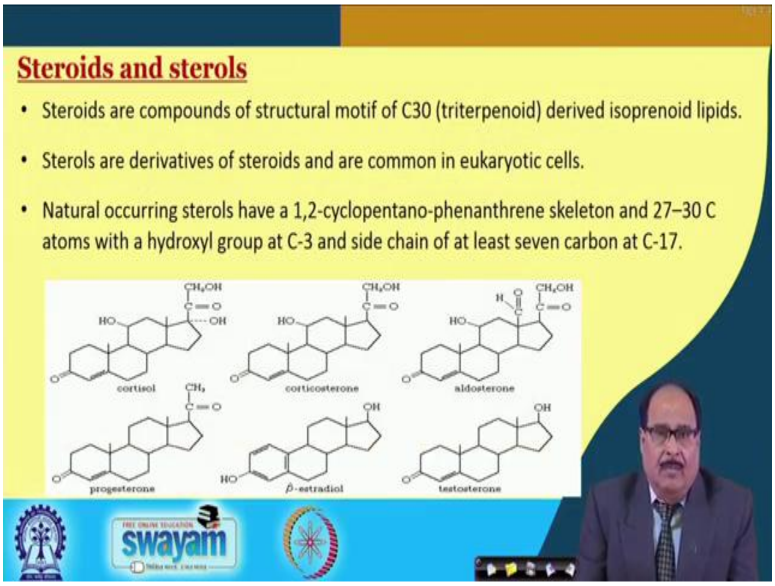
Waxes generally occur in bacteria and marine organisms and they serve as short term storage lipids or aid in their buoyancy. Simple waxes are found on surfaces of animals, plants and insects and they prevent water loss. Compounds with C21 to C44 have been reported from marine organisms. Fatty acid involved in the waxes may include polyunsaturated fatty acids (PUFA), although 16:1 and 20:1 are major components.

Important waxes in food as additives are beeswax, carnauba wax, candelilla wax, etc. They are used for several processes like edible coating application etc. and in food processing for different functions to perform different operations.

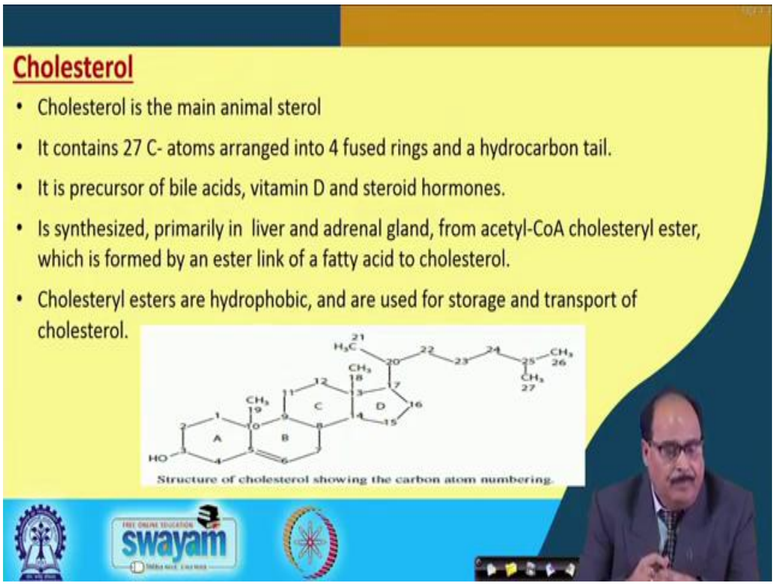


Another important category is Terpenes. They are lipids that are composed of 2 or more 5-carbon isoprene units. They contribute to the flavour and aroma of many plant foods such as citrus foods. Plant terpenes and terpenoid derivatives include phytol (a constituent of chlorophyll), beta carotene (a photosynthetic pigment and precursor of vitamin A in animals). They are also found in rubbers etc. Geosmin, albaflavenone, 2-methylsoborneol borneol all these are the examples of terpenes.

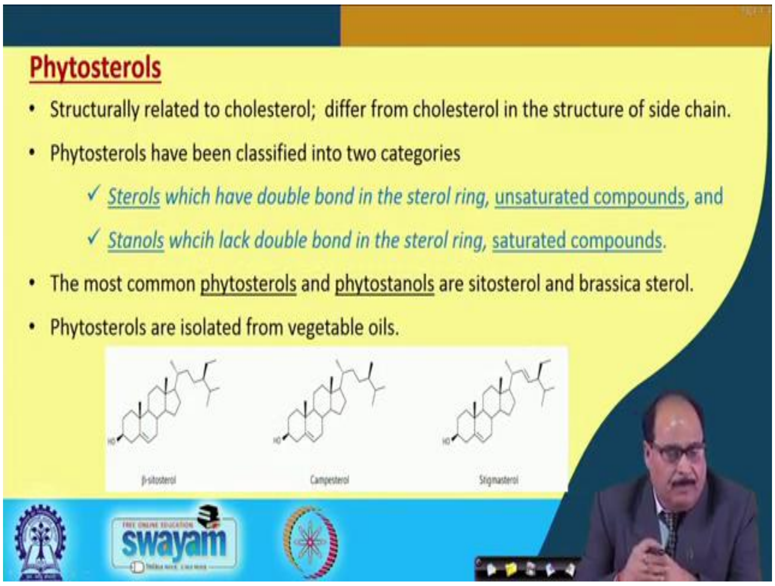
Isoprenoid lipids are the major classes of compound such as terpenoids, steroids, carotenoids, etc. The backbone structure from multiple, repeating, branched chain unsaturated C-5 units called isoprene or isopentile units. And, lipid can be easily identified by the ability to divide the compound structure neatly into its original isoprene synthetic units. Their subsequent cyclization and addition of functional groups may take place at sites of unsaturation. Large diversity of complex nomenclature of isoprenoid is available there.



Another important group of the lipids include steroids and sterols. Steroids are compounds of structural motif of C30 (triterpenoid) derived isoprenoid lipids. They are derivatives of steroids and are common in eukaryotic cells. Natural occurring sterols have a have a 1,2-cyclopentano-phenanthrene skeleton and 27–30 C atoms with a hydroxyl group at C-3 and side chain of at least seven carbon at C-17.

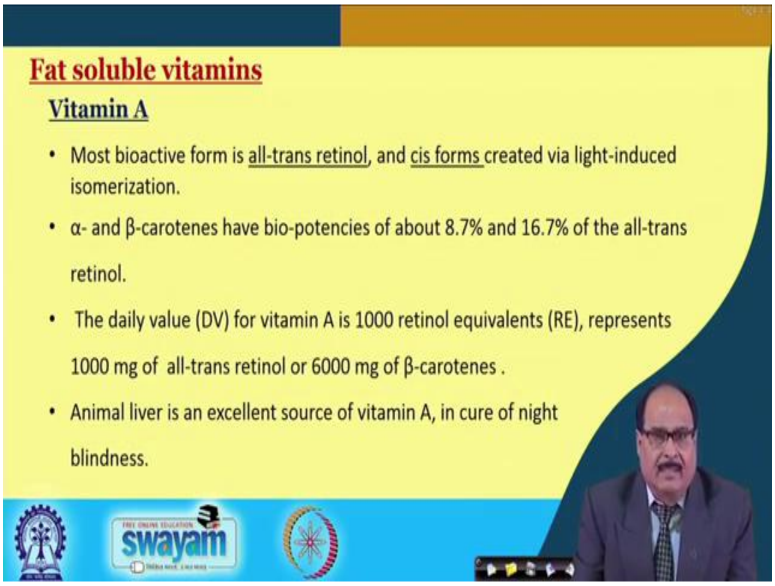


Cholesterol is another important group; the main animal sterol. Although it is a sterol, but it is found associated with the phospholipids in food materials. It contains 27-C atoms arranged into 4 fused rings and a hydrocarbon tail. It is the precursor of bile acids vitamin D and steroid hormones. It is synthesized primarily in liver and adrenal gland. Cholesteryl esters are hydrophobic, and are used for storage and transport of cholesterol. And, this cholesterol has important functions to perform in our diet. It is also synthesized in our body, but many times it needs to be regulated, because excess of cholesterol gets deposited in the body and may create some problems.



Phytosterols constitute another group of lipids having structure related to cholesterol. Only difference which they have with the cholesterol is in the structure of side chain. Phytosterol are of two types; one is the sterol in which double bond is present in the sterol ring, generally unsaturated compound; other is the stanols which do not have any double bond; so they are saturated compound.

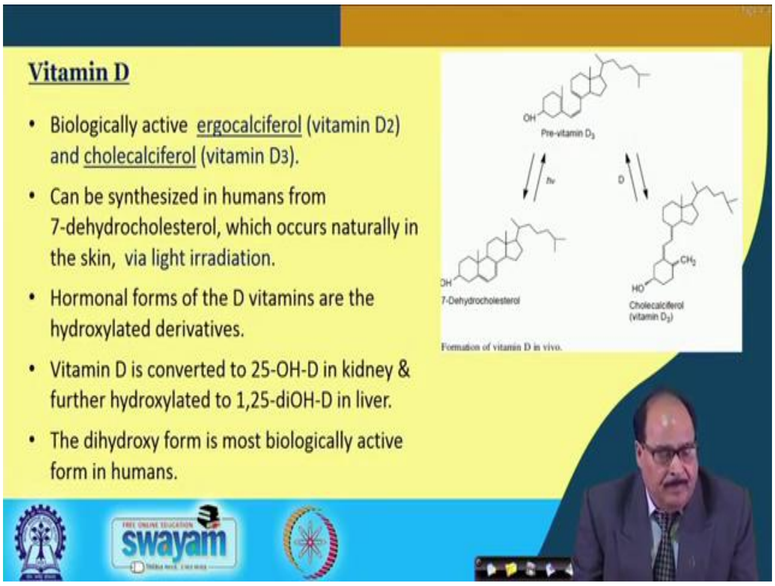
The most common phytosterol and phytostanols are sitosterol and brassica sterol. Phytosterols are isolated from vegetable oils.



Another important components of lipids which are of nutritional importance are fat soluble vitamins.

Vitamin A

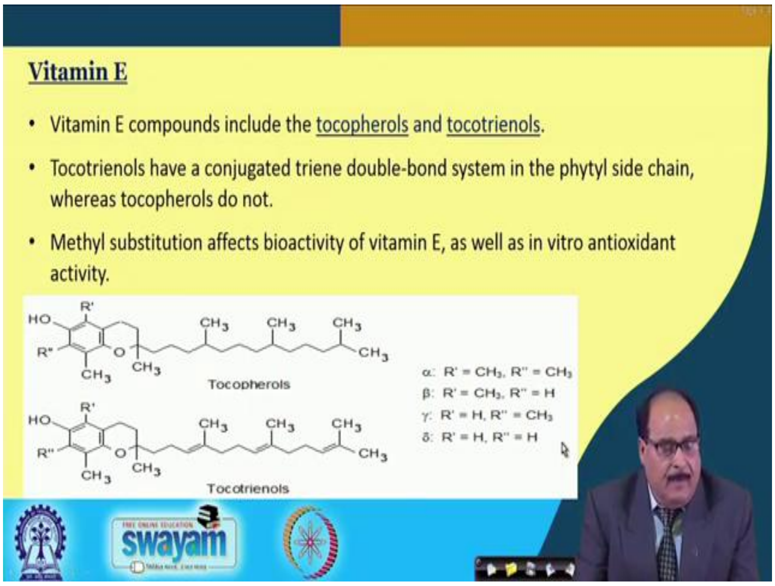
- Most bioactive form is all-trans retinol, and cis forms created via light-induced isomerization.
- α- and β-carotenes have bio-potencies of about 8.7% and 16.7% of the all-trans retinol.
- The daily value (DV) for vitamin A is 1000 retinol equivalents (RE), represents 1000 mg of all-trans retinol or 6000 mg of β-carotenes .
- Animal liver is an excellent source of vitamin A, it helps in cure of night blindness.



Vitamin D

- Biologically active ergocalciferol (vitamin D2) and cholecalciferol (vitamin D3).
- Can be synthesized in humans from 7-dehydrocholesterol, which occurs naturally in the skin, via light irradiation.
- Hormonal forms of the D vitamins are the hydroxylated derivatives.
- Vitamin D is converted to 25-OH-D in kidney & further hydroxylated to 1,25-diOH-D in liver.
- The dihydroxy form is most biologically active form in humans.

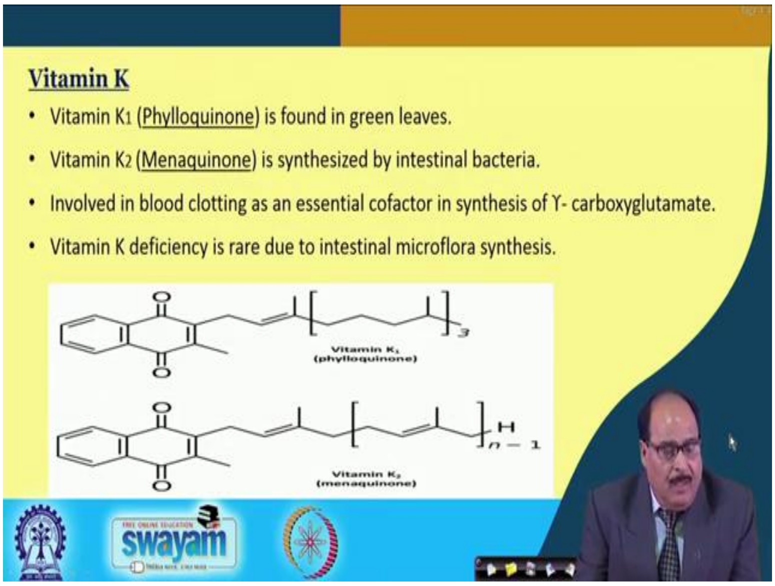
The structure of 7-dehydro cholesterol gets converted into pro vitamin D3 and vitamin D3 cholecalciferol.



Vitamin E

- Vitamin E compounds include the tocopherols and tocotrienols.
- Important group of antioxidants.
- Tocotrienols have a conjugated triene double-bond system in the phytyl side chain, whereas tocopherols do not.
- Methyl substitution affects bioactivity of vitamin E, as well as in vitro antioxidant activity.

The structure depending upon the side chain, i.e. whether CH_3 or R-H-R, alpha, beta, gamma and delta tocotrienols and tocopherols are found, and their antioxidant properties vary significantly.



Vitamin K

- Vitamin K1 (Phylloquinone) is found in green leaves.
- Vitamin K2 (Menaquinone) is synthesized by intestinal bacteria.
- Involved in blood clotting as an essential cofactor in synthesis of ϒ-carboxyglutamate.
- Vitamin K deficiency is rare due to intestinal microflora synthesis.

So, lipids are very important in food processing, food science, food engineering and food products manufacturing or in human nutrition.