Consortium for
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Module on

LIPIDS

By

Dr. Hilal A Lone

Asstt. Professor (Botany)

Amar Singh College,

Srinagar

helallone@gmail.com

The term lipid is used to describe a variable assortment of compounds. It is derived from the Greek word *lipos*, meaning fat. The term lipid was first used by Bloor in 1943. They form about 3.5 percent of the cell contents. The lipids are naturally occurring molecules from plants or animals.

The lipids are a heterogenous group of compounds related more by their physical rather than by their chemical properties. They have the common properties of being relatively insoluble in water and soluble in non-polar solvents such as acetone, benzene, chloroform and ether. The lipids are basically made up of carbon, hydrogen and sometimes oxygen in which the content of oxygen is always small as compared to hydrogen and carbon. Many lipids contain small amounts of additional elements like phosphorus, nitrogen and sulphur. Common examples of lipids include butter, ghee, cooking oil, natural rubber, cholesterol, carotene, lycopene, eucalyptus oil, menthol, vitamins A, E and K.

The lipids are a chemically diverse group of hydrocarbons. Lipid molecules contain large hydrocarbon portion and not many polar functional groups, which accounts for their solubility behavior. The property they all share is insolubility in water, which is due to the presence of many nonpolar covalent bonds. Nonpolar hydrocarbon molecules are hydrophobic and preferentially aggregate among themselves, away from water, which is polar. When these nonpolar molecules are sufficiently close together, weak but additive van der Waals forces hold them together. These huge macromolecular aggregations are not polymers in a strict chemical sense, since their units (lipid molecules) are not held together by covalent bonds, as are, for example, the amino acids in proteins. But they can be considered polymers of individual lipid units.

Lipids are important dietary constituents not only because of their high energy value but also because of the fat-soluble vitamins and the essential fatty-acids contained in the fat of natural foods.

Classification of lipids

Lipids are distinguishable in to three types: Simple, Compound and Derives lipids.

(a) Simple Lipids

The simple lipids are formed from fatty acids and alcohol or esters of fatty acids with various alcohols. They do not have any additional groups. The simple lipids are further of two sub-types:

(i) Neutral or true fats: These are esters of fatty acids with glycerol.

(ii) Waxes: These represent the esters of fatty acids with alcohol other than glycerol.

Fats and Oils

Chemically, fats and oils are triglycerides, also known as simple lipids. Triglycerides that are solid at room temperature (20°C) are called fats; those that are liquid at room temperature are called oils. Triglycerides are composed of two types of building blocks- fatty acids and glycerol. Glycerol is a small molecule with three hydroxyl (-OH) groups (an alcohol). A fatty acid is made up of a long nonpolar hydrocarbon chain and a polar carboxyl group (-COOH). A triglyceride contains three fatty acid molecules and one molecule of glycerol. The carboxyl group of a fatty acid can form a covalent bond with the hydroxyl group of glycerol, resulting a functional group called an ester and water.

The three fatty acids in a triglyceride molecule need not all have the same hydrocarbon chain length or structure, e.g. in saturated fatty acids, all the bonds between the carbon atoms in the hydrocarbon chain are single bonds, and there are no double bonds. That is, all the bonds are saturated with hydrogen atoms. These fatty acid molecules are relatively rigid and straight, and they pack together tightly, like pencils in a box. In unsaturated fatty acids, the hydrocarbon chain contains one or more double bonds. Oleic acid, for example, is a monounsaturated fatty acid that has one double bond near the middle of the hydrocarbon chain, which causes a kink in the molecule. Some fatty acids have more than one double bond, and are called polyunsaturated. Polyunsaturated fatty acids are further classified in to two families according to the position of the first double bonds. These are (i) Omega-6 (or □-6) fatty acids which have the first double bond at the 6th carbon atom along the fatty acid chain, e.g. linoleic acid and (ii) Omega-3 (or □-3) fatty acids which have the first double bond at the third carbon atom along the fatty acid chain, e.g. linolenic acid. Among the polyunsaturated fatty acids, linoleic and linolenic acid are essential to human health.

The polyunsaturated fatty acids have multiple kinks. These kinks prevent the molecules from packing together tightly. The kinks in fatty acid molecules are important in determining the fluidity and melting point of a lipid. The triglycerides of animal fats tend to have many long-chain saturated fatty acids, packed tightly together; these fats are usually solids at room temperature and have a high melting point. The triglycerides of plants, such as corn oil, tend to have short or unsaturated fatty acids. Because of their kinks, these fatty acids pack together poorly and have a low melting point, and these triglycerides are usually liquids at room temperature.

Waxes

Waxes are esters of long chain fatty acids with long chain alcohols. Waxes are responsible for making the plant and animal tissues water proof and reduces the rate of transpiration in plants. The waxes are complicated mixtures of long chain alkanes with an odd number of carbon atoms ranging from C25 to C35 and oxygenated derivatives such as secondary alcohols and ketones. In other words, chemically, they are esters of higher fatty acids with higher monohydroxy alcohols. They are chemically inert. They bear no double bond in their hydrocarbon chain and are insoluble in water. Some of the important types of waxes are plant waxes, bee's wax, lanolin or wool fat, spermaceti, paraffin wax, etc.

(b) Compound Lipids

Compound lipids are the esters of fatty acids containing groups in addition to an alcohol and a fatty acid. The additional group may contain phosphorus, nitrogen, sulphur or it may be a protein.

(i) Phospholipids: These are major structural components of cell membranes. They are, therefore, called membrane lipids. The phospholipids are esters of fatty acids with glycerol where one fatty acid is replaced by a phosphoric acid residue (phosphatidic acid) often linked to additional nitrogenous groups like choline (in lecithin) and ethanolamine (in cephalin). The phosphate functional group has a negative electric charge, so this portion of the molecule is hydrophilic, attracting polar water molecules. But the two fatty acids are hydrophobic, so they tend to aggregate away from water. A substance having both polar and non-polar groups is called amphipathic.

In an aqueous environment, phospholipids line up in such a way that the nonpolar, hydrophobic "tails" pack tightly together and the phosphate-containing "heads" face outward, where they interact with water. The phospholipids thus form a bilayer, a sheet two molecules thick, with water excluded from the core. Biological membranes have this kind of phospholipid bilayer structure.

Some of the types of phospholipids are lecithins, cephalins, plasmalogens, and sphingomyelins.

(ii) Glycolipids: Lipids containing a fatty acid, sphingosine, and carbohydrate are called glycolipids. They differ from sphingomyelins by having a carbohydrate group at C1 instead of a phosphate bonded to a choline. The glycolipids are components of cell membranes, particularly in myelin sheath of nerve fibers and on outer surface of nerve cells; and of chloroplast membranes. It includes two major groups-cerebrosides and gangliosides. The cerebrosides are abundant in the myelin sheath of nerves and the white matter of the brain. They are based on sphingosine, and contain in addition a fatty acid and a monosaccharide sugar, but no phosphoric acid or glycerol. In Gaucher's disease they accumulate in large amounts in the liver and spleen. The gangliosides are based on ceramide (an amide of sphingosine and a fatty acid), possess sugar residues glucose, galactose, sialic acid and acetyl glucosamine. They influence ion transport through the membrane as well as function as receptor of viral particles. Gangliosides occur in grey matter. The excessive accumulation of gangliosides produces disorders like Tay-Sachs disease.

(iii) Lipoproteins: Lipoproteins contain lipids (mainly phospholipids) and proteins in their molecules. Membranes are composed of lipoproteins. Lipids are transported in the blood plasma and lymph as lipoproteins. Lipoproteins occur in the milk and egg yolk.

(iv) Other complex lipids: Sulpholipids, aminolipids and lipopolysaccharides are among the other complex lipids.

(c) Derived Lipids

The group, derived lipids, includes hydrolytic products of lipids and in addition other lipid like compounds such as sterols, carotenoids, essential oils, prostaglandins etc.

Sterols are groups of molecules that include cholesterol, ergosterol, bile acids, sex hormones like estrogen and progesterone etc. All steroids are composed of four rings of carbon fused together, with various functional groups protruding from them. These are derivatives of a complex ring system called 'cyclopentano per hydrophenanthrene' ring system.

The sterols are widely distributed in plants, animals and micro-organisms. They are found in cell membranes and other cellular components containing lipids. Unlike other lipids, sterols cannot be saponified and by this process they can be separated from other lipids. The best known animal sterol is cholesterol. Cholesterol is a steroid, a member of the class of lipids that all contain the same four ring system. Cholesterol serves two important purposes: as a component of cell membranes and as starting materials for the synthesis of all other steroids.

Carotenoids (carotene and xanthophyll) are also included in the lipids because of their solubility in fat solvents. The carotenes consist of carbon and hydrogen only, whereas xanthophylls contain oxygen in addition to carbon and hydrogen.

Essential oils are also grouped under lipids because of their solubility and natural occurrence. Most of the essential oils are either terpenes related to isoprene or isopentene or benzene derivatives. Some are straight chain carbon compounds without any side branches. The essential oils are usually obtained from plants such as pine, peppermint, rose, lemon, eucalyptus etc.

Prostaglandins are a group of about 20 lipids that are modified fatty acids, with two nonpolar "tails" attached to a five-carbon ring. They are found in human seminal fluid, testis, kidney, placenta, uterus, stomach, lung, brain and heart. There are sixteen or more different hormones such as estrogen, progesterone, testosterone and corticosterone, affecting cellular activities by influencing gene expression. Prostaglandins act as local chemical messengers in many vertebrate tissues.

Other derived lipids such as fatty acids, glycerols, aldehydes etc. occur only in very small amounts as intermediates of metabolic conversion.

(d) Cis- and trans-fatty acids: Unsaturated fatty acids can also be classified as 'Cis' (Latin on this side) and trans (Latin across) indicating whether the alkyl groups are on the same or opposite sides of the molecule.

The cis configuration is the naturally occurring form, however in the meat and milk of ruminants such as cattle and sheep and in products containing industrially modified oils that have undergone a hardening process known as partial hydrogenation, a proportion of the unsaturated fatty acids exist in the transfer form. Trans fatty acids are risk factors in the development of (H1) and cancer. Transfer fatty acids not only raise LDL-Cholesterol, but they also lower the level of the good HDL-Cholesterol.

Foods rich in the various types of fatty acids

(i) **Saturated:** Butter, cheese, meat and meat products, full fat milk, lard, hard margarines, baking fats, coconut and palm oil.

(ii) **Monounsaturated**: Olives, rapeseed, nuts (almonds, cashew), avocados, peanuts and their oils.

(iii) **Polyunsaturated:**

(a) **Omega-3 polyunsaturated:** Fish species such as mackerel, salmon, herring, trout, rich in eicosapentaenoic acid (EPA) and docosahexanoic acid (DPA), walnuts, rapeseed, soybean and their oils.

(b) **Omega-6 polyunsaturated:** Sunflower seeds, sesame, wheat germ, walnuts, corn oil etc.

(iv) **Trans fatty acids:** Some frying and baking fats (e.g. hydrogenated vegetable oils), dairy products, fatty meat and meat products.

Functions of Lipids

1. Reserve Food: The lipids act as storage compounds in animals, in the fruits and seeds of plants and in other organisms. In oilseeds like groundnut, mustard, coconut, fat is stored in cotyledon or endosperm to provide food to the developing embryo. Animals contain fat droplets in the form of adipocytes. In plants, they are deposited during the development of seed and are mobilized and reutilized as a source of energy during the germination and growth of the seedling.

In some animals, fats stored under the skin serve not only as energy stores but as insulation against low temperatures. Seals, walruses, penguins, and other warm-blooded polar animals are amply padded with fats. In hibernating animals (bears, for example), the huge fat reserves accumulated before hibernation serve the dual purposes of insulation and energy storage. The low density of fats is the basis for another remarkable function of these compounds. In sperm whales, a store of fats and waxes allows the animals to match the buoyancy of their bodies to that of their surroundings during deep dives in cold water.

2. Fuel: The main function of fats is that they serve as a source of energy. Complete combustion of one gram of fat releases 9.3 kcal of energy. There are two significant advantages to using fats as stored fuels, rather than polysaccharides such as glycogen and starch. First, because the carbon atoms of fatty acids are more reduced than those of sugars, oxidation of fats yields more than twice as much energy, gram for gram, as the oxidation of carbohydrates. Second, because fats are hydrophobic and therefore unhydrated, the organism that carries fat as fuel does not have to carry the extra weight of water of hydration that is associated with stored polysaccharides (2 g per gram of polysaccharide).

3. Structural Component: They act as structural cellular components particularly in cell membranes. They are found in the form of phospholipids, glycolipids and sterols (cholesterol). The central architectural feature of biological membranes is a double layer of lipids, which acts as a barrier to the passage of polar molecules and ions. Membrane lipids are amphipathic: one end of the molecule is hydrophobic, the other hydrophilic. Their hydrophobic interactions with each other and their hydrophilic interactions with water direct their packing into sheets called membrane bilayers.

4. Synthesis: They take part in the synthesis of steroids, hormones, vitamin D, A, E and K. Steroid hormones, derived from sterols, serve as powerful biological signals, such as the sex hormones. Vitamins D, A, E, and K are fat-soluble compounds made up of isoprene units. All play essential roles in the metabolism or physiology of animals. Vitamin D is precursor to a hormone that regulates calcium metabolism. Vitamin A furnishes the visual pigment of the vertebrate eye and is a regulator of gene expression during epithelial cell growth. Vitamin E functions in the protection of membrane lipids from oxidative damage, and vitamin K is essential in the blood-clotting process.

5. Trap light energy: The carotenoids help plants capture light energy. The carotenoids are a family of light-absorbing pigments found in plants and animals. Beta-carotene (β-carotene) is one of the pigments that traps light energy in leaves during photosynthesis. In humans, a molecule of β-carotene can be broken down into two vitamin A molecules, from which we make the pigment rhodopsin, which is required for vision. Carotenoids are responsible for the colors of carrots, tomatoes, pumpkins, egg yolks, and butter.

6. Wax coating repel water and store energy: Biological waxes are esters of long-chain saturated and unsaturated fatty acids with long-chain alcohols. Their melting points are generally higher than those of triacylglycerols. In plankton, the free-floating microorganisms at the bottom of the food chain for marine animals, waxes are the chief storage form of metabolic fuel. Waxes also serve a diversity of other functions related to their water-repellent properties and their firm consistency. Certain skin glands of vertebrates secrete waxes to protect hair and skin and keep it pliable, lubricated, and waterproof. Birds, particularly waterfowl, secrete waxes from their preen glands to keep their feathers water-repellent.

The shiny leaves of holly, rhododendrons, poison ivy, and many tropical plants are coated with a thick layer of waxes, which prevents excessive evaporation of water and protects against parasites.

7. Pharmaceutical importance: Biological waxes find a variety of applications in the pharmaceutical, cosmetic, and other industries. Lanolin (from lamb's wool), beeswax, carnauba wax (from a palm tree), and wax extracted from spermaceti oil (from whales) are widely used in the manufacture of lotions, ointments, and polishes.

8. Functions of fatty acids in Foods:

(i) Emulsions: Fats and oils especially phospholipids (lecithins) are an important component in most emulsions such as margarines, salad dressings, gravies and cheese sauces. Emulsions are the dispersion of a fat or oil in to water or vice versa. Emulsifying fats in to a liquid produces unique flavor and texture qualities.

(ii) Appearance: Fats and oils can alter a foods appearance by creating a glossy or moist visual texture. The ability of fat to reflect light is also responsible for the opaque appearance of milk.

(iii) Flavour: Fats has the unique ability to absorb and preserve flavours. Fats also contain compounds that lend specific flavours to their own. The way fat coats the tongue and allows flavours to linger can also alter a flavor experience.

(iv) Heat transfer: Fats provide one of the most efficient modes of heat transfer during deep fat frying. Hot oil is able to transfer high levels of heat to the surface of food without overheating the interior portions.

(v) Nutrition: Fats are the most calorie dense compounds in food, weighing twice the calories per gram of protein or carbohydrates. Fats are also an effective method of delivering calories when needed. Fats are also important for delivering soluble vitamins such as vitamin A, D, E and K.

(vi) Shortening: Fats play an important role in the texture of bakery products. When fat is added to dough like in biscuits, the fat gets in the way of the gluten formation, therefore the final product tender and flakey.

(vii) Texture: Fats provide a very specific, lubricating mouth feel, which is why most dry crackers or chips are served with high fat content chips or spreads. Emulsions made with fats are responsible for the creamy texture of many items like cream, mayonnaise and other sauces. Fats are also responsible for the texture and smooth body of ice cream and other dairy products.