Core Course 12:Unit 3

FOOD CHEMISTRY – Lipids

Part A: Classification & Structure of lipids

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Introduction

Lipids are a broad group of chemically diverse compounds that are soluble in organic solvents. Food lipids are generally referred to as fats or oils. Fats are solid at room temperature and oils are liquids at room temperature. The total lipid content and the lipid composition of foods can vary tremendously. Food lipids play an important role in food quality. They contribute to attributes such as texture, flavor, nutrition and caloric density. Some fats are essential, such as linolenic and linoleic fatty acids. They cannot be synthesized by body. Therefore, they have to be met through diet. Fats and oils are insoluble in water and have a greasy feel that one may feel or can notice on a napkin or dinner plate. As a group, fats and oils should be used sparingly in the diet. Fats and oils are triglycerides, the major constituent of lipids. Overall, lipid is the umbrella term that includes the triglycerides, phospholipids and sterols.

Thorough study of this unit will be able to understand:

- ✓ Structure of fat
- ✓ Classification of lipids
- ✓ Minor Components of Fats and Oils
- ✓ Nomenclature of Fatty Acids

1. Structure of fat

The building blocks of fats are fatty acids and glycerol. A fatty acid is made up of a chain of carbon atoms, with a methyl group at one end and an acid group at the other (**Figure 1**). Fatty acids occur primarily as unbranched hydrocarbon chains with an even number of carbons.

1.1. Glycerides

Glycerides include *monoglycerides, diglycerides* and *triglycerides*. The most abundant fatty substance in food is the triglycerides (>95%). Triglycerides are insoluble in water and may be either liquid or solid at room temperature.

Structurally, glycerides contain a glycerol molecule backbone joined to one or more fatty acid molecules. A *monoglyceride* contains glycerol esterified to *one* fatty acid molecule (**Figure 2).** If *two* fatty acids are esterified to glycerol, a *diglyceride* is formed. If *three* fatty acids undergoing the same reaction make a *triglyceride*. If a triglyceride contains three *identical* fatty acids, it is called a *simple triglyceride*. If it contains two/ three *different* fatty acids it is called a *mixed triglyceride*.

2. Classification of Lipids

Among the many compounds classified as lipids, only a small number are important as dietary energy sources. Based on the structure, the classification of lipids are

i. Simple lipids
ii. Compound lipids
iii. Derived lipids

2.1. Simple lipids:

Simple lipids are esters of fatty acids with various alcohols. They are classified according to the nature of the alcohols.

a) **Fats and Oils:**

Fats and oils are forms of lipids present in foods. They are esters of fatty acids and glycerol. At room temperature, oils are liquids and fats are solids.

b) **Waxes:**

The chemical definition of a wax is an ester of a long- chain acid and a long-chain alcohol. Food waxes are a combination of chemical classes including wax esters, sterol esters, ketones, aldehydes, alcohols, hydrocarbons and sterols. Waxes can be classified according to their origin as animal (beeswax), plant (carnauba wax), and mineral (petroleum waxes). Waxes are found on the surface of plant and animal tissues.

2.2. Compound Lipids:

The compound lipids are esters of fatty acids, containing groups of phosphorous, carbohydrate or protein. They are present in addition to an alcohol and fatty acid.

a) **Phospholipids:**

Phospholipids are similar to triglycerides but contain only *two* fatty acids esterified to glycerol. In place of the third fatty acid, there is phosphoric acid and a nitrogen-containing group. The most common phospholipid is known as ***lecithin*** (**Figure 3**). Lecithin is found in nearly every living cell. The word is derived from the Greek *lekithos*, which means "yolk of an egg," and lecithin is in egg yolk.

b) Glycolipids: contain a fatty acid, carbohydrate and a nitrogenous base. They have a carbohydrate component within their structure like phospholipids. They are generally not major components of food lipids.

c) **Aminolipids, sulpholipids:** The sulpholipids yield sulphuric acid on hydrolysis. Similar to cerebrosides except that sulphuric acid is present as cerebronic acid ester. They are generally not major components of food lipids.

d) **Lipoproteins**: are macromolecular complex of lipids with proteins **(Figure 4)**. These compounds are found in mammalian plasma bound with proteins. The lipid mostly consists of cholesterol esters and phospholipids. They contain stearic, palmitic, oleic, palmitoleic, linoleic and arachidonic acids.

2.3. Derived Lipids:

Derived lipids are substances liberated during hydrolysis of simple and compound lipids. They retain the properties of lipids.

Sterols, fatty acids and alcohol are the important members of derived lipids.

a) ***Sterols***: Sterols are derivatives of steroids. They contain a common steroid nucleus, an 8–10 carbon side chain and an alcohol group. Based on their origin sterols are classified as cholesterol (animal origin) and phytosterol (in plants).

Cholesterol is the primary *animal sterol* (**Figure 5**). It is regularly synthesized by and stored in the liver. Cholesterol plays an important role in membrane function. Cholesterol is also important because it is the precursor for the synthesis of bile acids and 7-dehydrocholesterol.

The most common *Plant sterols*, or stanols, are sitosterol and stigmasterol. Other plant sterols are found in "margarine"-type products.

b) ***Fatty acids:***

Fatty acids are long hydrocarbon chains with a methyl group (CH_3) at one end of the chain and a carboxylic acid group (COOH) at the other. Most natural fatty acids contain from 2 to 21 carbon atoms and most contain an even number of carbon atoms in the chain.

Fatty acids can be saturated or unsaturated, depending on the degree of unsaturation; they are (a) saturated fatty acids (SFA), (b) unsaturated–i. monounsaturated fatty acids (MUFA) and ii. polyunsaturated fatty acids (PUFA)

(a). Saturated Fatty Acids: If the Fatty acid has all the hydrogen atoms it can hold is said to be saturated. They have a linear shape and there are no double bonds between carbons. They contain only single carbon-to-carbon bonds and have the general formula $CH_3\ (CH_2)_n\ COOH$ **(Figure 6d, Table 1)**

(b). Unsaturated Fatty Acids: If some of the hydrogen atoms are missing and have been replaced by a double bond between carbon atoms, then the fatty acid is said to be unsaturated. Generally, unsaturated fats are liquid at room temperature (**Table 1)**

(i). Monounsaturated Fatty Acids: If there is one double bond, the fatty acid is known as a monounsaturated fatty acid **(Figure 6).** .

(ii). Polyunsaturated fatty acid (PUFA): If there is more than one double bond, then the fatty acid is known as a PUFA. In PUFAs, the hydrogen atoms can be arranged in one of two ways. One arrangement is called is cis, the other is called trans. They represent the different isomeric structures of fatty acids.

- In the ***cis*** form, the hydrogen atoms are attached to the carbon atoms of the double bond. Hydrogen atoms are located on the same side of the double bond **(Figure 7)**.
- In the **trans** configuration of the isomer, the hydrogen atoms are located on opposite sides of the double bond, across from one another **(Figure 7)**..

The configuration of the double bonds affects shape of a fatty acid molecule. Trans configurations do not significantly change the linear shape of the molecule. However, a cis double bond causes a bend in the chain.

All naturally occurring fats and oils that are used in food exist in the cis configuration. Hydrogenation of oils causes conversion of double bonds to the trans configuration. With this property some trans fats may be used in food.

Essential Fatty Acids:

The body cannot make all the fatty acids it needs except for two, known as alpha linolenic acid (n-3) and linoleic (n-6) fatty acids. These are called the Essential Fatty Acids (EFAs) and must be supplied in the diet. From these fatty acids we can make others which are important for health. From linoleic acid we can make arachidonic acid and from α –linolenic acid we make Eicosapentaenoic acid (EPA) and docosahaexanoic acid (DHA). The latter two can also be from oily fish and fish oil supplements. The n-3 (or omega 3) fatty acids, particularly alpha-linolenic acid, are also present in the meat or eggs of animals fed n-3 enriched diets. Foods produced in this way could be considered alternative sources of oily fish. Although the amounts of the long chain n-3 fatty acids (EPA and DHA) present may be considerably less.

3. Minor Components of Fats and Oils

Tocopherols are important minor constituents of most vegetable oils. Animal fats contain little or no tocopherols. Tocopherols are antioxidants, helping to prevent oxidative rancidity. They are good sources of vitamin E. They are partially removed by the heat of processing. They may be added after processing to improve oxidative stability of oils. If vitamin E is added to oil, the oil frequently is marketed as a source of vitamin E or as an antioxidant-containing oil.

Fats are not good sources of vitamins, apart from vitamin E. In order to increase the nutritive value, fat-soluble vitamins-A and D may be added to foods such as margarine and milk.

Pigments such as carotenoids and chlorophylls may be present in fats, and these may impart a distinct color to a fat (milk).

Isomerism

Fatty acids may have geometric or positional isomers, which are similar in number of C, H, and O, but form different arrangements. Therefore, they offer different chemical and physical properties. Oleic and elaidic acids are examples of geometric isomers, existing in the cis and trans forms, respectively.

4. Nomenclature of Fatty Acids

Fatty acids are named in three ways,

i. **Common or trivial name**: which has been used for many years
ii. **Systematic or Geneva name**: which is more recent and has the advantage of describing the structure of the fatty acid to which it belongs
iii. **The omega system:** classifies fatty acids according to the position of the first double bond, counting from the methyl end of the molecule

Fatty acids also are denoted by two numbers. The first signifies the number of carbon atoms in the chain and the second indicates the number of double bonds present. For example, oleic acid, which contains 18 carbon atoms and 1 double bond, could be written as 18:1.

4.1.Geneva or Systematic Nomenclature

The Geneva naming system is a systematic method of naming the fatty acids. Each name completely describes the structure of the fatty acid to which it belongs. Each unsaturated fatty acid is named according to the number of carbon atoms in the chain **(Table 1)**. For example, stearic acid, which has 18 carbon atoms in its chain, has the name octadecanoic acid; octadec means 18. The -oic ending signifies that there is an acid group (COOH) present. Anoic signifies that there are no double bonds in the chain. Palmitic acid, which contains 16 carbon atoms, is named hexadecanoic acid. Hexadec means 16 and the anoic ending again shows that there are no double bonds in this fatty acid chain.

Fatty acids containing double bonds are named according to the number of carbon atoms they contain. Therefore, oleic acid (18:1), linoleic acid (18:2), and linolenic acid (18:3) all have octadec as part of their name, signifying that they each contain 18 carbon atoms. The rest of the name differs, because they contain one, two, or three double bonds. The number of double bonds and their position in the fatty acid chain are both specified in the name. It is important to note that the position of each double bond is specified counting from the functional group or acid end of the molecule, not from the methyl end.

- Oleic acid has the name 9-octadecenoic acid. The number 9 refers to the position of the double bond between carbon-9 and carbon-10, counting from the acid end. The name ends with enoic acid, the en signifies that there is a double bond present.

- Linoleic acid is named 9,12-octadecadienoic acid. The position of double bonds is counted from the acid end. Octadeca means that there are 18 carbon atoms in the chain and dien signifies that there are two double bonds in the chain **(Figure 8)**.

- Linolenic acid, which contains three double bonds, is named 9,12,15-octadecatrienoic acid. The letters trien indicate that there are three double bonds in the chain.

The configuration of the double bonds also may be specified in the name. For example, oleic acid and elaidic acid are geometric isomers. The double bond in oleic acid exists in the cis configuration. Elaidic acid contains a double bond in the trans configuration. The complete name for oleic acid is cis, 9-octadecenoic acid and elaidic acid is named trans, 9-octadecenoic acid.

By looking at a systematic name for a fatty acid, it is possible to tell how many carbon atoms it contains and how many double bonds and where they are located. Each name gives important information about the fatty acid that is not available just by looking at the trivial or omega name of the acid.

4.2. The Omega Naming System

The omega naming system is used for unsaturated fatty acids. It denotes the position of the first double bond in the molecule, counting from the methyl (CH_3) end, not the acid (as in the Geneva system). This is because the body lengthens fatty acid chains by adding carbons at the acid end of the chain. Using the omega system, a family of fatty acids can be developed that can be made from each other in the body. For example, an omega-6 fatty acid contains its first double bond between carbon-6 and carbon-7, counting from the methyl end **(Figure 8)**. Linoleic acid is an example of an omega-6 fatty acid and it is the primary member of the omega-6 family. Given linoleic acid, the body can add two carbon atoms to make arachidonic acid (20:4), which also is an omega-6 fatty acid. The primary omega-3 fatty acid is linolenic acid, which contains three double bonds. The first double bond is located on carbon-3, counting from the methyl end. The body can synthesize both eicosapentaenoic acid (EPA: 20:5) and docosahexaenoic acid (DHA: 22:6) from linolenic acid. Both EPA and DHA are omega-3 fatty acids, because their first double bond is located at carbon-3 (again, counting from the methyl end of the molecule).

5. Conclusion:

Food lipids play an important role in food quality. They contribute to attributes such as texture, flavor, nutrition and caloric density. A fatty acid is made up of a chain of carbon atoms, with a methyl group at one end and an acid group at the other. Lipids are classified as simple, compound and derived lipids. Based on degree of saturation, fatty acids are classified into Saturated Fatty Acids & Unsaturated Fatty Acids. Essential Fatty Acids viz, alpha linolenic acid and linoleic acid cannot be synthesized in the body; therefore, they must be supplied through the diet. Minor components of fats and oils include tocopherols and pigments. Fatty acid chains of even number may exist as geometric or positional isomers. Nomenclature may be according to a common name, systemic or Geneva name, or omega system.

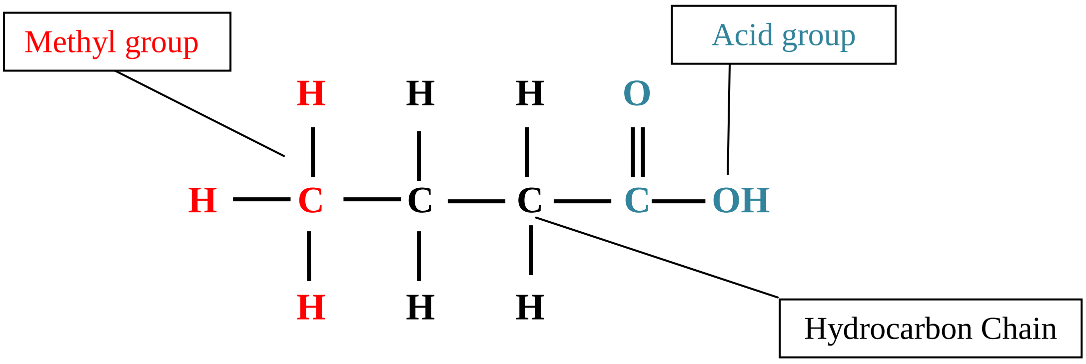

Figure 1: Structure of fatty acid

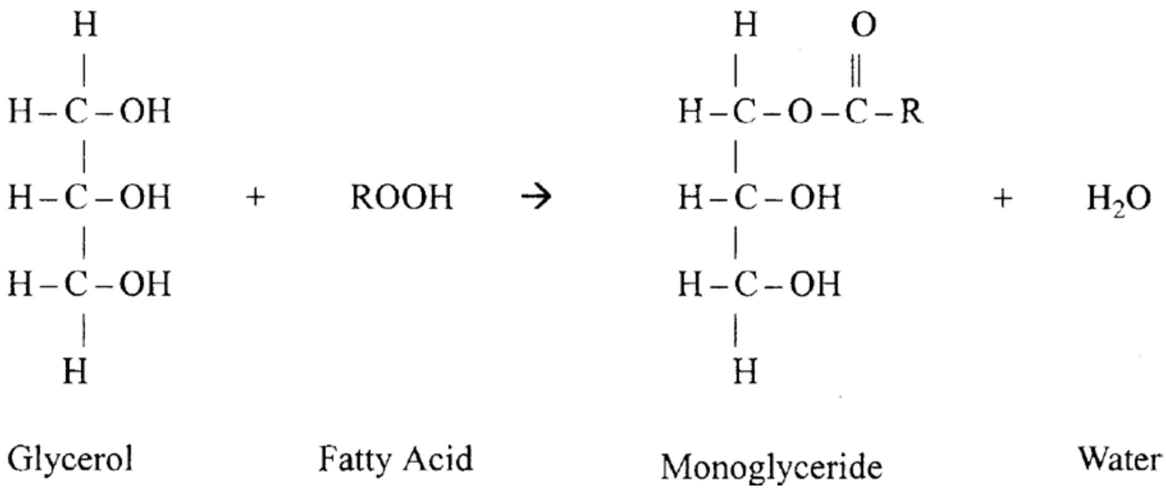

Figure 2: Formation of a monoglyceride

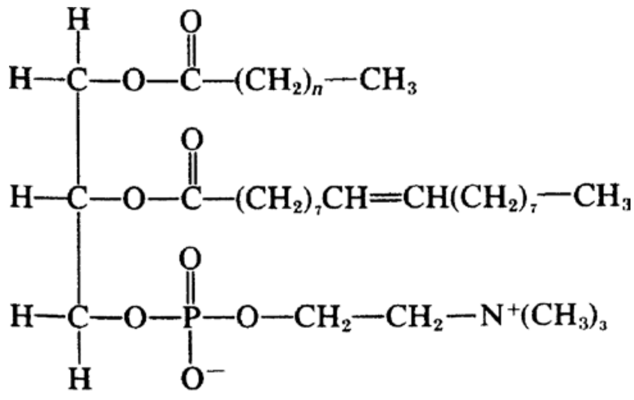

Figure 3: Lecithin (phosphatidyl choline)

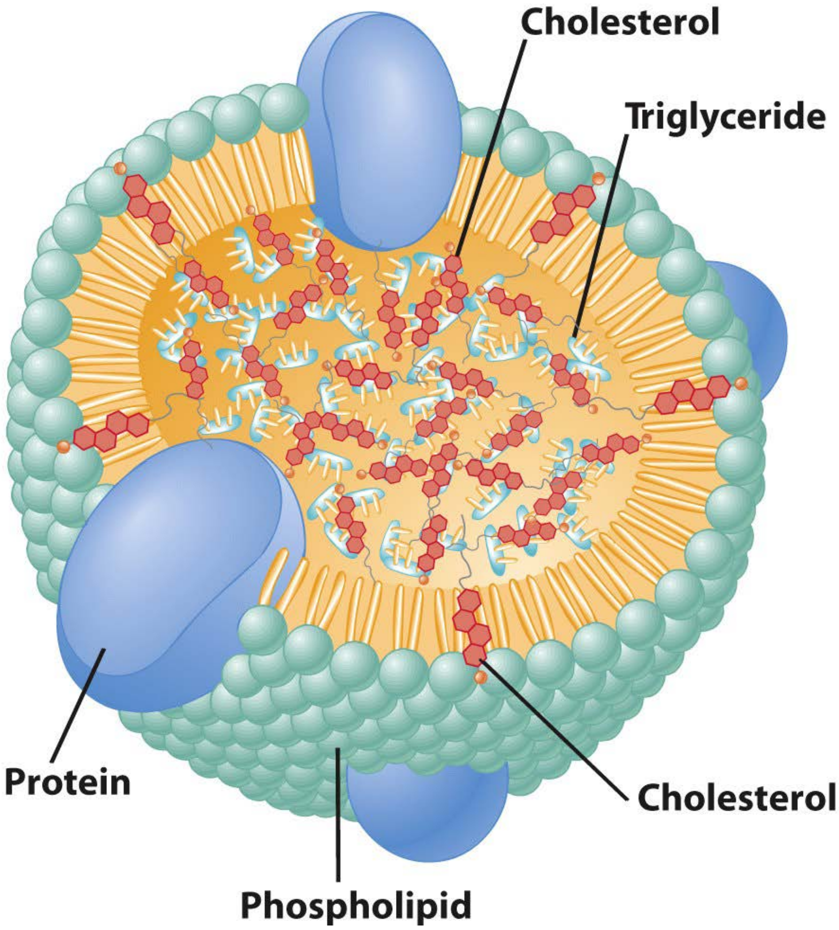

Figure 4: Lipoproteins

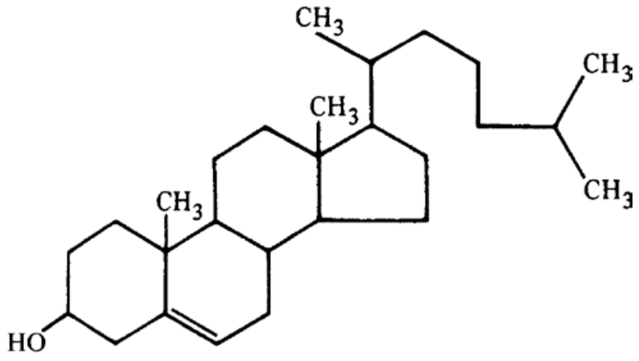

Figure 5: Cholesterol, phytosterols.

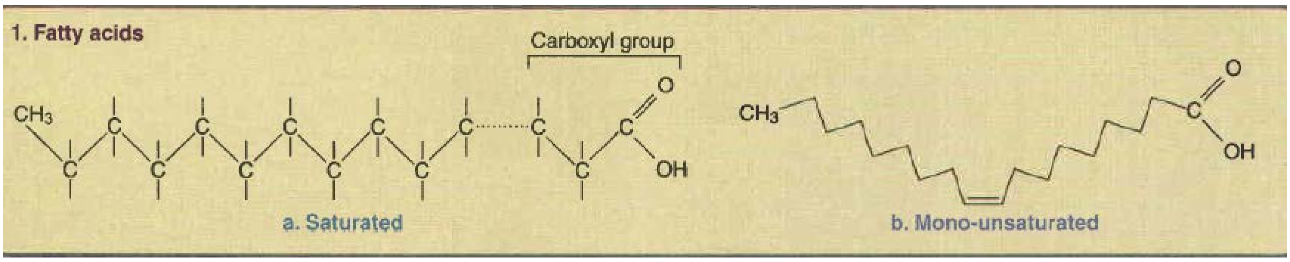

Figure 6: Different types of fatty acids

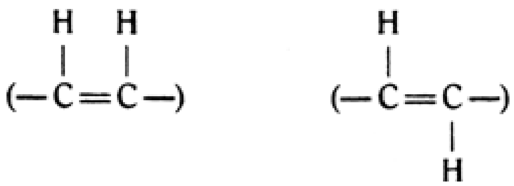

Figure 7: Cis (left) and trans (right) configurations representing isomeric structures of fatty acids

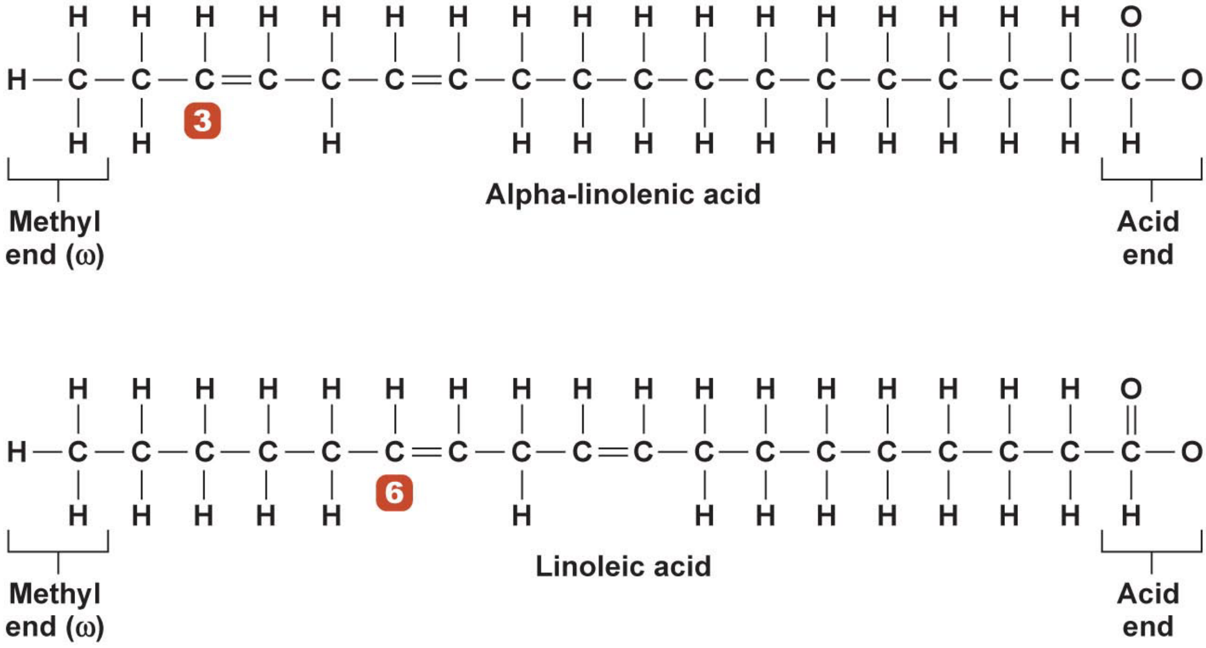

Figure 8: The Omega Fatty Acids

Source: Vickie and Elizabeth, In Essentials of Food Science, 2008.

Table 1: Common Fatty Acids

Common Name	Systematic Name	Number of Carbon Atoms*	Number of Double Bonds	Typical Fat Source
Saturated Fatty Acids				
Butyric	Butanoic	4	0	Butterfat
Caproic	Hexanoic	6	0	Butterfat
Caprylic	Octanoic	8	0	Coconut oil
Capric	Decanoic	10	0	Coconut oil
Lauric	Dodecanoic	12	0	Coconut oil, Palm kernel oil
Myristic	Tetradecanoic	14	0	Butterfat, Coconut oil
Palmitic	Hexadecanoic	16	0	Cocoa butter, animalfat
Stearic	Octadecanoic	18	0	Cocoa butter, animal fat
Arachidic	Eicosanoic	20	0	Peanut oil
Behenic	Docosanoic	22	0	Peanut oil
Unsaturated Fatty Acids				
Caproleic	9-Decenoic	10	1	Butterfat
Lauroleic	9-Dodecenoic	12	1	Butterfat
Myristoleic	9-Tetradecenoic	14	1	Butterfat
Palmitoleic	9-Hexadecenoic	16	1	Some fish oils, beef fat
Oleic	9-Octadecenoic	18	1	Olive oil, canola oil
Elaidic	9-Octadecenoic*	18	1	Partially hydrogenated oils
Vaccenic	11-Octadecenoic*	18	1	Butterfat
Linoleic	9,12-Octadecadienoic	18	2	Most vegetable oils, especially safflower, corn, soybean, cottonseed
Linolenic	9,12,15-Octadecatrienoic	18	3	Soybean oil, canola oil, walnuts, wheat germ oil, flaxseed oil
Gadoleic	9-Eicosenoic	20	1	Some fish oils
Arachidonic	5,8,11,14-Eicosatetraenoic	20	4	Lard, meats

Common Name	Systematic Name	Number of Carbon Atoms*	Number of Double Bonds	Typical Fat Source
	5,8,11,14,17-Eicosapentaenoic	20	5	Some fish oils
Erucic	13-Docosenoic	22	1	Rapeseed oil
	4,7,10,13,16,19-Docosahexaenoic	22	6	Some fish oils, shell fish

*All double bonds are in the cis configuration except for elaidic acid and vaccenic acid which are trans

Source: Mahan and Stump. In Krause's Food and Nutrition Therapy, 2008.