CONTENTS

CHAPTER 12

Lipids–I

General Structure

Triacylglycerols fuel the long migration flights of the golden plover (*Pluvialis dominica*).

(*Courtesy : Gerard Fuehrer)*

IMPORTANCE

The lipids are important constituents of the diet because of their high energy value and also because of the fat-soluble vitamins and the essential fatty acids found with the fat of the natural foodstuffs. In the body, the fats serve as efficient source of energy which is stored in the adipose tissues. They also serve as an insulating material in the subcutaneous tissues and around certain organs. Fats combined with proteins (lipoproteins) are important constituents of the cell membranes and mitochondria of the cell.

Proteins, polysaccharides, DNA and RNA are macromolecules. *Lipids are not generally classed as macromolecules,* even though they share some of their features: for example, most are synthesized as linear polymers of a smaller molecule (the acetyl group on acetyl-CoA), and they self-assemble into larger structures (membranes). It is noteworthy that water and protein comprise most of the mass of both mammalian and bacterial cells (Table 12–1).

Contents

Table 12–1. **Approximate chemical composition of a typical bacterium and a typical mammalian cell**

Component	*Percent of total cell weight*	
	E. coli bacterium	*Mammalian cell*
H_2O	70	70
Inorganic ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- etc)	1	1
Miscellaneous small metabolites	3	3
Proteins	15	18
RNA	6	1.1
DNA	1	0.25
Phospholipids	2	3
Other lipids	—	2
Polysaccharides	2	2
Total cell volume :	2×10^{-12} cm^3	4×10^{-9} cm^3
Relative cell volume :	1	2,000

DEFINITION

The lipids are a heterogeneous group of compounds related to fatty acids and include fats, oils, waxes and other related substances. These are oily or greasy organic substances, relatively insoluble in water and considerably soluble in organic solvents like ether, chloroform and benzene. They are, thus, **hydrophobic** in nature. These are variously called as *lipins* or *lipoids*. The latter term is, however, sometimes used to refer "fat-like" substances which may not actually be related to the fatty acids. The term 'lipid' was first used by the German biochemist Bloor in 1943 for a major class of tissue components and foodstuffs. The structure of some common fats and fatty acids is presented in Fig.12–1.

Chemical Abstracts and some biochemical journals use the spelling **'lipide'.**

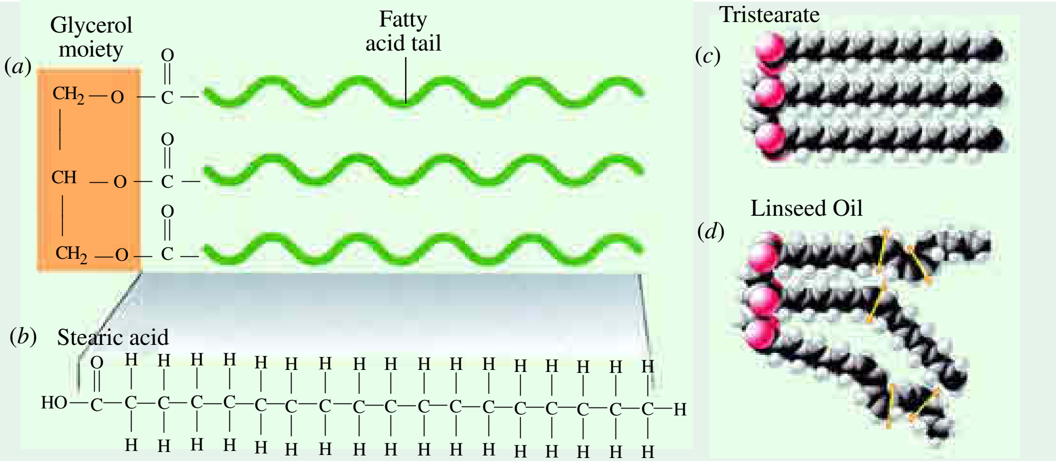
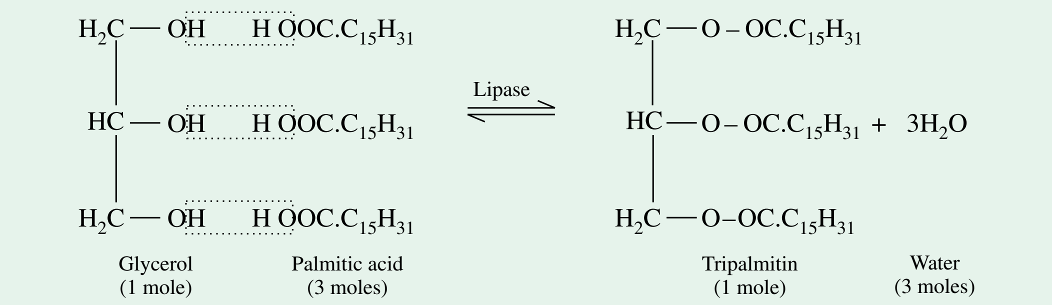


Fig. 12-1. **Fats and fatty acids**

(*a*) **Basic structure of a triacylglycerol (also called a triglyceride or a neutral fat)**. The glycerol moiety, indicated in orange, is linked by three ester bonds to the carboxyl groups of three fatty acids whose tails are indicated in green. (*b*) **Stearic acid.** It is an 18-carbon saturated fatty acid that is common in animals fats. (*c*) **Space-filling model of tristearate.** It is a triacylglycerol containing three identical stearic acid chains. (*d*) **Space-filing model of linseed oil.** It is a triaclglycerol containing two different unsaturated fatty acids, derived from flax seeds. The sites of unsaturation, which produce kinks in the molecule, are indicated by the yellow-orange bars.

Contents

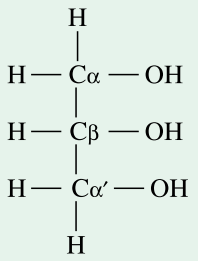
Chemically, the fats are defined as the esters of glycerol and fatty acids or as the triglycerides of fatty acids.



Both these components are described below for a better understanding of the lipids.

ALCOHOLS

Alcohols found in lipid molecules may be **saturated.** These commonly include glycerol, cholesterol and higher alcohols such as cetyl alcohol and myricyl alcohol.



Glycerol

$CH_3(CH_2)_{14}CH_2OH$

Cetyl alcohol

$CH_3(CH_2)_{28}CH_2OH$

Myricyl alcohol

In the structural formula of glycerol, the C atoms are designated by *stereospecific numbers* (*sn*), 1, 2 and 3 from any end. As the C atoms I and 3 are identical, these three carbon atoms are better denoted by an older nomenclature, as α, β and α′.

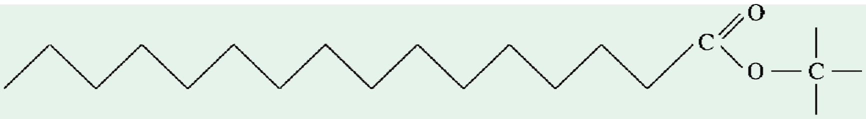
Among the **unsaturated** alcohols found in fats are included a number of pigments like phytol and lycophyll. The former is a constituent of chlorophyll, whereas the latter is found in tomatoes as a purple pigment.

FATTY ACIDS

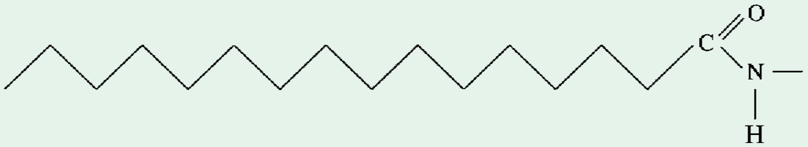
Fatty acids are long-chain organic acids having usually from 4 to 30 carbon atoms; they have a single carboxyl group and a long, nonpolar hydrocarbon 'tail', which gives most lipids their hydrophobic and oily or greasy nature. Fatty acids do not occur in free or uncombined state in cells or tissues but are present in covalently bound form in different classes of lipids. Fatty acids which occur in natural fats are usually monocarboxylic and contain an even number of C atoms as these are synthesized from 2 carbon units. These are usually straight-chain derivatives. The chain may be **saturated** (containing only single bonds) or **unsaturated** (containing one or more double bonds). Some fatty acids may have hydroxyl group(s) in the chain (**hydroxy** or **oxygenated** fatty acids) and still others may possess ring structure (**cyclic** fatty acids). Fatty acids are stored as an energy reserve (fat) through an ester linkage to glycerol to form *triglycerides*. If free, the *carboxyl group* of a fatty acid will be ionized.

But more usually, it is linked to other groups to form either *esters*

Contents

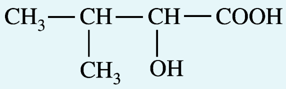


or *amides*.



Nomenclature. The systematic nomenclature of the fatty acids is based on the **Genevan system.** According to this system, the fatty acid is named after the hydrocarbon with the same number of carbon atoms, the suffix -*oic* is written in place of the final letter *e* in the name of the hydrocarbon. The names of saturated fatty acids end with the suffix -*anoic* and those of unsaturated acids with the suffix -*enoic*.

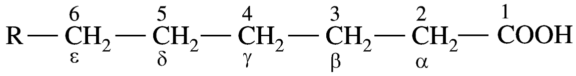
Generally, the numbers are used with the International Union of Pure and Applied Chemistry (IUPAC) **system of nomenclature** and the Greek letters when the common names are employed. For example :



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-COOH$$

2-hydroxy-3-methylbutanoic acid
or
α-hydroxy-*iso*-valeric acid

The position of carbon atoms in the fatty acid chain is indicated either by **numbering** (in which case the carboxyl carbon is numbered as C1, the carbon adjacent to C1 as C2 and so on) or by the **use of Greek letters** (in which case C2 is denoted as α-carbon, C3 as β-carbon and so on). Thus :



$$R-\underset{\varepsilon}{\overset{6}{CH_2}}-\underset{\delta}{\overset{5}{CH_2}}-\underset{\gamma}{\overset{4}{CH_2}}-\underset{\beta}{\overset{3}{CH_2}}-\underset{\alpha}{\overset{2}{CH_2}}-\overset{1}{COOH}$$

A widely-used convention to indicate the number and position of the double bond(s) in the case of unsaturated fatty acids is to write the number of carbon atoms, the number of double bond(s) and the position of the double bonds(s) below the name of the acid. For example, oleic acid having 18 carbon atoms and a double bond between carbon atoms 9 and 10 is written as 18:1; 9. Similarly, linoleic acid (18 carbon atoms and 2 double bonds at C 9 and C 12) is written as 18:2; 9, 12.

The **position of a double bond** is indicated by the lower number of the two carbon atoms involved in double bonding.

An alternative method to write the name of an unsaturated fatty acid is to write first the position of double bond(s) in numerals and then the total number of carbon atoms in Roman followed by the suffix -*enoic* acid. Thus, oleic acid may be written as 9-octadecenoic acid and linoleic acid as 9, 12-octadecadienoic acid.

A description of the various categories of fatty acids involved in lipid formation follows.

1. Saturated fatty acids

The general formula for these acids is $C_nH_{2n+1}COOH$. Table 12.2. lists some even-numbered straight chain saturated fatty acids, found distributed in both plant and animal worlds. In addition, lipids from all sources contain small amounts of saturated fatty acids with an odd number of carbon atoms (C 5 through C 17). Generally, these odd-carbon acids account for less than 1% of the total fatty acids.

In animal fats, palmitic and stearic acids (C_{16} and C_{18}) are the most abundantly found saturated fatty acids, next in order are shorter chain fatty acids (C_{14} and C_{12}) and longer chain fatty acids (C_{20}, C_{22} and C_{24}). Fatty acids of 10 carbon atoms or less are present in limited amounts in animal lipids except the milk fat which contains appreciable amounts of lower molecular weight fatty acids. The preponderance of these acids may, thus, be shown in the descending order as below :

$$C_{16}, C_{18} > C_{14}, C_{12}, C_{20}, C_{22}, C_{24} > C_{10} \text{ and less.}$$

Contents

Table 12–2. Straight chain saturated fatty acids, commonly found in natural fats

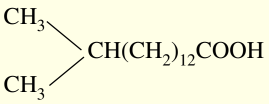
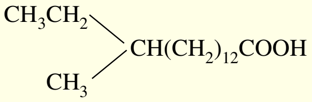
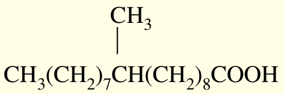
Trivial name	*Systematic name**	*Carbon skeleton*	*Structure†*	*Common source*
Butyric	*n*-Butanoic	4 : 0	$CH_3(CH_2)_2COOH$	Butter
Caproic	*n*-Hexanoic	6 : 0	$CH_3(CH_2)_4COOH$	Coconut and palm oils
Caprylic	*n*-Octanoic	8 : 0	$CH_3(CH_2)_6COOH$	Coconut and palm oils
Capric	*n*-Decanoic	10 : 0	$CH_3(CH_2)_8COOH$	Coconut and palm oils
Lauric (*laurus*^{L} = laurel plant)	n-Dodecanoic	12 : 0	$CH_3(CH_2)_{10}COOH$	Laurel oil, Spermaceti
Myristic (*Myristica*^{L} = nutmeg genus)	*n*-Tetradecanoic	14 : 0	$CH_3(CH_2)_{12}COOH$	Butter and wool fats
Palmitic (*palma*^{G} = palm tree)	*n*-Hexadecanoic	16 : 0	$CH_3(CH_2)_{14}COOH$	Animal and plant fats
Stearic (stear = hard fat)	*n*-Octadecanoic	18 : 0	$CH_3(CH_2)_{16}COOH$	Animal and plant fats
Arachidic (*Arachis*^{L} = legume genus)	*n*-Eicosanoic	20 : 0	$CH_3(CH_2)_{18}COOH$	Groundnut oil
Behenic	*n*-Docosanoic	22 : 0	$CH_3(CH_2)_{20}COOH$	Groundnut oil
Lignoceric (*lignum*^{L}= wood; *cera*^{L} = wax)	*n*-Tetracosanoic	24 : 0	$CH_3(CH_2)_{22}COOH$	Groundnut and Rapeseed oils
Cerotic	*n*-Hexacosanoic	26 : 0	$CH_3(CH_2)_{24}COOH$	Wool fat
Montanic	*n*-Octacosanoic	28 : 0	$CH_3(CH_2)_{26}COOH$	—

* The **prefix *n*-** indicates the "normal" unbranched structure. For instance, "octadecanoic" simply indicates 18 carbon atoms, which could be arranged in a variety of branched forms. Thus, *n*-octadecanoic specifies the linear, unbranched form.

† All **fatty acids** are shown in their unionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that the numbering of carbon atoms begins at the carboxyl group carbon.

In addition to the straight chain fatty acids, a number of branched chain fatty acids having either an even or an odd number of carbon atoms have been identified as minor components of natural fats and oils. Table 12-3 lists a representative sample of these fatty acids.

Table 12–3. Some branched chain saturated fatty acids, identified in natural fats

Trivial	*Systematic atoms*	*No. of C atoms*	*Structure*	*Common source*
Isopalmitic	Isohexa-decanoic	16	 $(CH_3)_2CH(CH_2)_{12}COOH$	Wool fat
Anteiso-palmitic	14-methyl-hexadecanoic	17	 $(CH_3CH_2)(CH_3)CH(CH_2)_{12}COOH$	Wool fat
Tuberculo-stearic	D-(–) 10-methylocta-decanoic	19	 $CH_3(CH_2)_7\overset{CH_3}{\overset{\vert}{C}}H(CH_2)_8COOH$	Bacteria

2. Unsaturated fatty acids

These may be classified, based on the degree of unsaturation.

A. Monoethenoid acids — These contain one double bond and conform to the general formula, $C_nH_{2n-1}COOH$. The common example is oleic acid.

B. Diethenoid acids — Two double bonds;
$C_nH_{2n-3}COOH$; Linoleic acid.

C. Triethenoid acids — Three double bonds;
$C_nH_{2n-5}COOH$; Linolenic acid.

D. Tetraethenoid acids — Four double bonds;
$C_nH_{2n-7}COOH$; Arachidonic acid

Monoethenoid acids are commonly called as *monounsaturated fatty acids (MUFAs)* and the remaining ones as *polyunsaturated fatty acids (PUFAs).* A few important unsaturated acids are listed in Table 12–4. A perusal of the table indicates that in most of the unsaturated fatty acids, there is a double bond (designated Δ^9) between carbon atoms 9 and 10. This is particularly true of the unsaturated fatty acids, commonly found in the plant world. If there are additional bonds, they usually occur between Δ^9 and the methyl-terminal end of the chain. It may, however, be generalized that in mammals, polyunsaturated fatty acids can have up to 22 carbon atoms and 6 double bonds, but in plants these acids do not exceed 18 carbon atoms and 4 double bonds.

Human body can convert stearic acid to oleic acid by inserting a double bond but is incapable of inserting further double bonds so that the oleic acid cannot be converted to either linoleic, linolenic or arachidonic acid. For normal cell functioning esp., of skin tissues any one of these acids is needed. Since they cannot be synthesized by the cells, they must be obtained from diet. On account of the important physiological role, these 3 acids are collectively called as *essential fatty acids (EFA),* a term introduced by Burr and Burr in 1930.

Linoleic acid was once known as **vitamin F**. Its function in this capacity is now discredited. It is a yellow oily liquid with a b.p. 229ºC.

Vegetable oils contain two types of polyunsaturated fatty acids (PUFAs) – linoleic acid (*lin* with 2 double bonds) and α-linolenic acid (*len* with 3 double bonds). In chemical jargon, *lin* and longer chain fatty acids derived from it are referred to as **n-6 fatty acids**, since the first double bond in their molecule occurs on carbon no. 3. *Len* and fatty acids derived from it are referred to as **n-3 fatty acids** since the first double bond in their molecule occurs on carbon no. 3. *Lin* is more abundant in nature and is present in all vegetable oils, whereas *len* is present only in some vegetable oils such as mustard oil, rapeseed and soybean. Fish oils are, however, good sources of both *lin* and *len* fatty acids and hence are considered nutritionally quite rich. *Hydrogenated fat* or *'vanaspati'* is manufactured from vegetable oils by the process of hydrogenation. It is a saturated fat and, though derived from vegetable oils, behaves like other saturated fats of animal origin.

All foods contain small quantities of bound fat or invisible fat. Such bound fat is found in green leafy vegetables and pulses in plenty and is a rich source of *n*-3 fatty acids. About half of the daily human requirement of fat (40 g) can be derived through such bound fat. Thus, the minimum daily requirement of visible fat (oil etc) is only 20 g. For long, the 2 types of PUFAs, *n*-6 and *n*-3, were thought to have similar effects. But recent study shows that *n*-6 and *n*-3 PUFAs have different types of effects on blood lipids and blood clotting and that they should be present in the diet in a certain proportion. Too much of *n*-6 with very little *n*-3 is not desirable. A healthy cooking practice, therefore, would be to blend vegetable oils containing both *lin* and *len*, instead of patronizing any one type of oil, including even the much-publicized unsaturated oils like safflower or rice bran which are very effective in reducing blood cholesterol.

A most unusual unsaturated fatty acid, *nemotinic acid*, is excreted in the growth medium by a

Contents

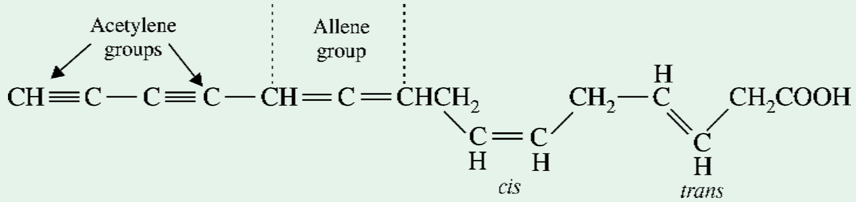
Table 12–4. **Unsaturated fatty acids* commonly found in natural fats**

Trivial name	*Systematic name*	*Carbon skeleton*	*Structure*	*Common source*
Crotonic	2-butenoic	4 : 1 ; 2	$CH_3CH{=}CHCOOH$	Croton oil
Myristoleic	9-tetradecenoic	14 : 1 ; 9	$CH_3(CH_2)_3CH{=}CH(CH_2)_7COOH$	*Pycnanthyus*
Palmitoleic	9-hexadecenoic	16 : 1 ; 9	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	Animal and plant fats
Oleic (*oleum*^{G} = oil)	9-octadecenoic	18 : 1 ; 9	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Animal and plant fats
Vaccenic	11-octadecenoic	18 : 1 : 11	$CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$	Bacterial fat
Linoleic (*linon*^{G} = flax)	9, 12-octadecadienoic	18 : 2 ; 9, 12	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	Linseed and cottonseed oils
Eleostearic	9, 11, 13-octadecatrienoic	18 : 3 ; 9, 11, 13	$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH(CH_2)_7COOH$	Tung oil
Linolenic	9, 12, 15-octadecatrienoic	18 : 3 ; 9, 12, 15	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	Linseed oil
Arachidonic	5, 8, 11, 14-eicosatetraenoic	20 : 4 ; 5, 8, 11, 14	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	Animal fat
Nervonic	15-tetracosenoic	24 : 1 ; 15	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$	–

* All of the unsaturated fatty acids in this table are of the *cis* form with the exception of **eleostearic acid,** which is of the *cis*-9-*trans*-11-*trans*-13 form.

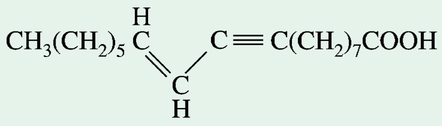
Contents

citrivorium mould. This fatty acid is unique in that it contains the single, double and triple C—C linkages. *Nemotinic acid is one of the few naturally-occurring compounds containing the allene group.*



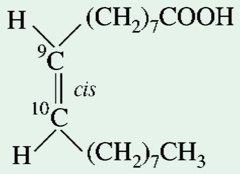
Nemotinic acid

The acetylene group has been detected in a number of unsaturated fatty acids, found in higher plants and microorganisms. For instance, *santalbic acid*, a major component of the seed oil of sandlewood contains 1 acetylene group as against 2 of nemotinic acid.

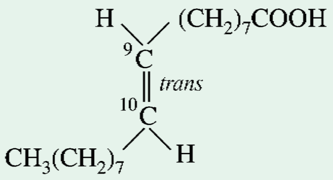


Santalbic acid

Geometric isomerism. On account of the presence of double bond(s), the unsaturated fatty acids exhibit geometric (or *cis-trans*) isomerism. Most unsaturated fatty acids are found as the **unstable *cis* isomer** rather than as the more stable *trans* isomer.



Oleic acid



Elaidic acid

The hydrocarbon chain of saturated fatty acids (stearic acid, for example) has a zigzag configuration with the C—C bond forming a bond angle of 109° (Fig. 12–2).

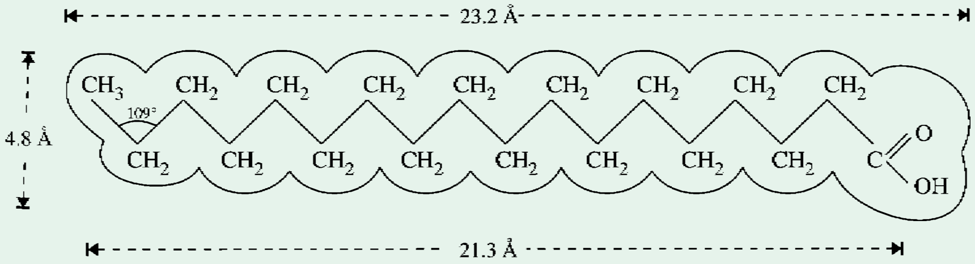


Fig. 12–2. Stearic acid

For the sake of simplicity, the long chains of CH_2 groups are represented by zigzag lines where each corner represents a C atom and the hydrogen atoms are left out. *The zigzag line represents the most stable configuration of such carbon chains.* The free end of this line, if not indicated otherwise, obviously represents the presence of a methyl group. The simplified formula for stearic acid would, thus, be as represented in Fig. 12–3.

Contents

Fig. 12–3. **Stearic acid (simplified formula)**

The double bond in the zigzag line is indicated by drawing an extra line in between the carbon atoms involved in double bond formation.

When a *cis* double bond is inserted (as in oleic acid), the molecule bends assuming the shape, shown in Fig. 12–4. This double bond is *rigid* and creates a *kink* in the chain. The rest of the chain is free to rotate about the other C—C bonds.

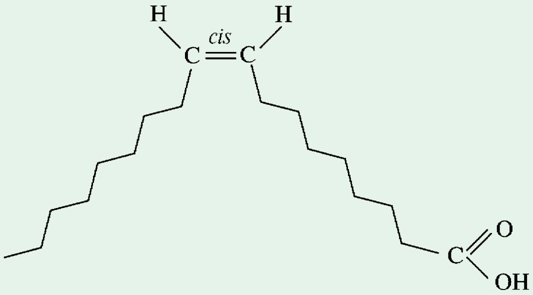


Fig. 12–4. **Oleic acid**

Nonconjugated double-bond system. Another structural peculiarity of naturally occurring polyunsaturated fatty acids is the presence of a **nonconjugated double-bond system.** It has a methylene group (—CH_2—) flanked by double bonds on both the sides as in linoleic, linolenic and arachidonic acids. *The conjugated double-bond system is, however, rarely present.* In it the methylene group is not found in between the double bonds which, henceforth, occur one after the other as in eleostearic acid. This acid has valuable properties as a drying oil since it polymerizes readily. These two double-bond systems (Fig. 12–5) have different chemical reactivities.

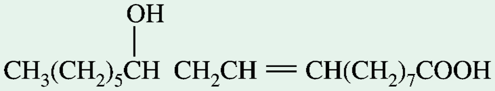
$$—CH{=}CH—CH_2—CH{=}CH—CH_2—CH{=}CH— \quad \text{Nonconjugated system}$$

$$—CH{=}CH—CH{=}CH—CH{=}CH—CH{=}CH— \quad \text{Conjugated system}$$

Fig. 12–5. **Two double-bond systems**

3. Hydroxy or oxygenated fatty acids

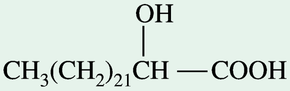
One of these found in castor oil is *ricinoleic acid* (87%). It is a C 18 acid with a double bond at C_9 and an OH group on C_{12}.



$$CH_3(CH_2)_5\overset{\overset{\displaystyle OH}{|}}{C}H\ CH_2CH = CH(CH_2)_7COOH$$

Ricinoleic acid
(12-hydroxyoctadec-9-enoic acid)

Cerebronic acid, a C 24 acid obtained from animal lipid, is another important hydroxy acid with an OH group on C_2.

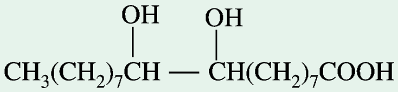


$$CH_3(CH_2)_{21}\overset{\overset{\displaystyle OH}{|}}{C}H—COOH$$

Cerebronic acid
(2-hydroxytetracosanoic acid)

A common oxygenated fatty acid, isolated from plants and bacterial lipids, is *9, 10-dihydroxystearic acid.*

Contents

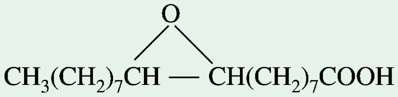


$$CH_3(CH_2)_7\underset{}{\overset{OH}{\overset{|}{C}}}H — \overset{OH}{\overset{|}{C}}H(CH_2)_7COOH$$

9, 10-dihydroxystearic acid

(9, 10-dihydroxyoctadecanoic acid)

Similarly, 9, 10-*epoxystearic acid* is isolated from rust spore lipids (20%).



$$CH_3(CH_2)_7CH \overset{\overset{O}{\diagup\ \diagdown}}{—} CH(CH_2)_7COOH$$

9, 10-epoxystearic acid

(9, 10-epoxyoctadecanoic acid)

4. Cyclic fatty acids

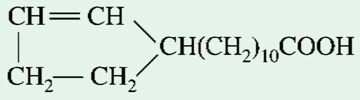
These are of rare occurrence. Chaulmoogra oil, obtained from the plant *Hydnocarpus kurzil* and used in the treatment of leprosy, contains 2 such acids *hydnocarpic* and *chaulmoogric*. Chaulmoogric acid has a cyclopentenyl ring in its 18-carbon structure.

CLINICAL IMPLICATIONS

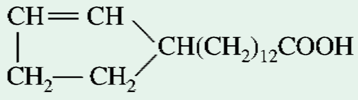
Leprosy, the oldest disease known to mankind, is loathsome, endemic disease. The myth that leprosy was hereditary and a 'Curse of God' was exploded in 1873, when Dr. G. A. Hansen in Norway discovered rod-shaped bacteria in cells from leprosy nodules. *The leprosy bacillus* (*Mycobacterium leprae*), *also called Hansen's bacillus, is the slowest multiplying prokaryote known and takes about 2 weeks to double*. Once infected, it takes a long time for the disease to develop : from less than a year to as long as 30 years, though normally 3-7 years. About 20% of the infected people develop the disease, on an average. In patients with high immune resistance, the disease is relatively mild (*tuberculoid form*); those with low resistance develop highly infectious and more severe conditions (*lepromatous leprosy*), affecting not only nerves and skin but also lymph nodes, eyes, nose, mouth, larynx, spleen etc and the bacilli may appear in tears, nasal mucus, sputum, ulcerating nodules etc. *M. leprae is the only bacterium that can enter and destroy the nerves*. Because of sensory impairment due to nerve damage, the person does not feel pain. However, the primary deformities are pronounced on the face. The infected, untreated individual is the only source of infection. There is no known natural reservoir other than man. Leprosy is only weakly contagious : usually prolonged and close contact is considered necessary. The nose is the main portal of exit of the bacilli. Although leprosy affects individuals of both sexes, *males are more susceptible than females*, often in the ratio of 2 : 1. Although leprosy had assumed epidemic proportions in Europe in 13th and 14th century A.D., at present, Western Europe is virtually free from it. And these days, the leprosy 'hot spots' are India, Indonesia, Myanmar, Brazil, Columbia and few pockets of Central and Eastern Europe. Developed countries are, however, free from leprosy due to their improved socio-economic conditions. Of the estimated disease burden, Asia accounts for about 60%, followed by Africa with 35% and Latin America with 4%; the rest of the world accounting for about 1% of the disease load. India alone accounts for about 1/5th of the total lepers in the world.

Under chemotherapy, the drugs most commonly used against leprosy were *dapsone, rifampicin* and *clofazimine,* the last one being the best alternative as it had the much-desired anti-inflammatory effect and produced least resistance. However, in 1982, the WHO recommended the multi-drug therapy (MDT), combining all the 3 above drugs, as it has a very high potential for control of leprosy. The duration of treatment in most cases is about 3 years or more. A single dose of MDT kills about 95% of bacilli in a patient and there are no significant side effects. However, the overall long duration of the treatment regimen in chemotherapy, has led to the use of immunotherapy, using leprosy vaccines. Under the aegis of WHO, a vaccine was developed combining *M. leprae* (inactivated) derived from armadillo, and the BCG vaccine. Trials of this vaccine have shown that its application can restore cell-mediated immunity in patients and thus it could remarkably suppress the disease in about 18 months only.

Leprosy eradication programme has made spectacular progress worldover. From a long list of 122 endemic countries in 1982, the disease is now endemic only in 24 of them. Ninety per cent of leprosy is now confined to only 12 countries, including India, Brazil, Indonesia, Myanmar, Nepal, Mosambique, Guinea, and Angola.

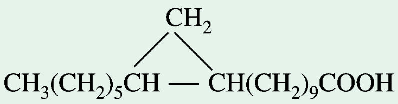


Hydnocarpic acid



Chaulmoogric acid

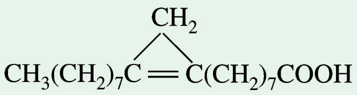
Lipids from the lactobacilli contain a fatty acid, *lactobacillic acid*, with a cyclopropyl group. This fatty acid may result from the addition of a methylene group across the double bond of vaccenic acid (18:1; 11).



$$CH_3(CH_2)_5CH \overset{CH_2}{—} CH(CH_2)_9COOH$$

Lactobacillic acid

Similarly, *sterculic acid* from plant sources has a comparable structure, with a suggested relationship to oleic acid. It may be derived from oleic acid by the addition of a methylene group across the double bond in a manner that the unsaturated nature is not altered, unlike the lactobacillic acid.



$$CH_3(CH_2)_7C \overset{CH_2}{=} C(CH_2)_7COOH$$

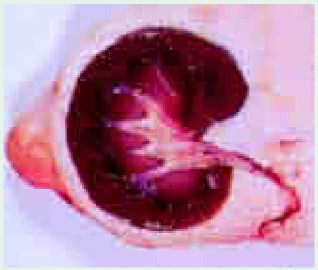
Sterculic acid

The percentage composition of various types of fatty acids in some typical fats and oils is presented in Table 12–5.

BIOLOGICAL ROLES OF LIPIDS

The lipids perform a wide variety of functions (Fig. 12-6). These are briefly listed below:

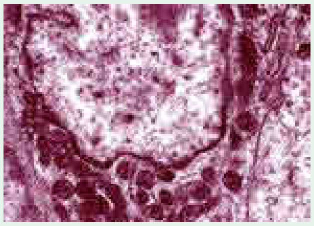
(*a*) The fat under the skin of this elephant seal protects it from the cold



(*c*) Kidneys are embedded in fatty tissue

(*e*) Like water off a duck's back.... Fatty acids on a duck's feathers repel water

(*b*) The wax surface of leaves repels water, but also reduces water loss from the plant



(*d*) Every cell membrane contains lipids

Fig. 12–6. Various functionsperformed by lipids

Contents

Table 12–5. Fatty acid content of some animal and plant fats and oils

Fat/Oil	*Butyric*	*Caproic*	*Caprylic*	*Capric*	*Lauric*	*Myristic*	*Palmitic*	*Stearic*	*Arachidic*	*Palmitoleic*	*Oleic*	*Linoleic*	*Linolenic*	*Others*
Buffer fat	3.6	2.3	0.5	1.0	2.5	11.1	29.0	9.2	2.4	4.6	26.7	3.6	–*	–
Beef tallow	–	–	–	–	–	6.3	27.4	14.1	–	–	49.6	2.5	–	–
Human depot fat	–	–	–	–	–	2.7	24.0	8.4			46.9	10.2		
Pork fat (lard)	–	–	–	–	–	1.3	28.3	11.9	–	2.7	47.5	6.0		
Castor oil	–	–	–	–	Trace	Trace	Trace	–		–	7.4	3.1		88[†]
Corn oil	–	–	–	–	–	1.4	10.2	3.0	–	1.5	49.6	34.3	–	–
Soybean oil	–	–	–	–	0.2	0.1	9.8	2.4	–	0.4	28.9	50.7	6.5	
Linseed oil	–	–	–	–	–	–	6.8	2.5	0.5	–	19.0	24.1	47.4	
Herring oil						7.3	13.0	Trace	–	4.9	–	–	20.7	30.1[a] 23.2[b]
Whale oil					0.2	9.3	15.6	2.8	–	14.4	35.2	–	–	13.6[a] 5.9[b]

* Not detected

† Ricinoleic acid

a C-20 polyunsaturated

b C-22 polyunsaturated

1. Food material. Lipids provide food, highly rich in calorific value. One gram lipid produces 9.3 kilocalories of heat.

2. Food reserve. Lipids provide are insoluble in aqueous solutions and hence can be stored readily in the body as a food reserve.

3. Structural component. Lipids are an important constituent of the cell membrance.

4. Heat insulation. The fats are characterized for their high insulating capacity. Great quantities of fat are deposited in the subcutaneous layers in aquatic mammals such as whale and in animals living in cold climates.

5. Fatty acid absorption. Phospholipids play an important role in the absorption and transportation of fatty acids.

6. Hormone synthesis. The sex hormones, adrenocorticoids, cholic acids and also vitamin D are all synthesized from cholesterol, a steroidal lipid.

7. Vitamin carriers. Lipids act as carriers of natural fat-soluble vitamins such as vitamin A, D and E.

Fig. 12–7. **A cholesterol deposit, (known as atherom) filling almost all the space inside the artery.**

8. Blood cholesterol lowering. Chocolates and beef, especially the latter one, were believed to cause many heart diseases as they are rich in saturated fatty acids, which boost cholesterol levels in blood and clog the arterial passage (Fig. 12–7). But researches conducted at the University of Texas by Scott Grundy and Andrea Bonanome (1988) suggest that at least one saturated fatty acid stearic acid, a major component of cocoa butter and beef fat, does not raise blood cholesterol level at all. The researchers placed 11 men on three cholesterol-poor liquid diets for three weeks each in random order. One formula was rich in palmitic acid, a known cholesterol booster; the second in oleic acid; and the third in stearic acid. When compared with the diet rich in palmitic acid, blood cholesterol levels were 14% lower in subjects put on the stearic acid diet and 10% lower in those on the oleic acid diet.

9. Antibiotic agent. *Squalamine*, a steroid from the blood of sharks, has been shown to be an antibiotic and antifungal agent of intense activity. This seems to explain why sharks rarely contract infections and almost never get cancer.

REFERENCES

See list following Chapter 14.

PROBLEMS

1. Why are the most unsaturated fatty acids found in phospholipids in the *cis* rather than the *trans* conformation ? Draw the structure of a 16-carbon fatty acid as saturated, *trans* monounsaturated, and *cis* monounsaturated.
2. Given these molecular components– glycerol, fatty acid, phosphate, long-chain alcohol, and carbohydrate– answer the following :
   (*a*) Which two are present in both waxes and sphingomyelin ?
   (*b*) Which two are present in both fats and phosphatidylcholine ?
   (*c*) Which are present in a ganglioside but not in a fat ?

3. The melting points of a series of 18-carbon fatty acids are stearic acid, 69.6ºC, oleic acid, 13.4ºC; linoleic acid –5ºC; and linolenic acid, –11ºC. What structural aspect of these 18-carbon fatty acids can be correlated with the melting point ? Provide a molecular explanation for the trend in melting points.
4. How is the definition of "lipid" different from the definitions of other types of biomolecules that we have considered, such as amino acids, nucleic acids, and proteins ?
5. Johann Thudichum, who practiced medicine in London about 100 years ago, also dabbled in lipid chemistry in his spare time. He isolated a variety of lipids from neutral tissue, and characterized and named many of them. His carefully sealed and labeled vials of isolated lipids were rediscovered many years later. How would you confirm, using techniques available to you but not to him, that the vials he labeled "sphingomyelin" and "cerebroside" actually contain these compounds ?
6. How would you distinguish sphingomyelin from phosphatidylcholine by chemical, physical, or enzymatic tests ?
7. Do all kinds of fibre help lower one's cholesterol ?
8. How much fat does one need in his diet ?
9. Is a high-protein diet good for one's health ?
10. Why is tea oil better for frying than olive oil ?