FOOD LIPIDS

Jan Pokorný and Jana Dostálová

Department of Food Chemistry and Analysis, Institute of Chemical Technology, Prague, Czech Republic

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Contents

Summary

Lipids are compounds of fatty acids with glycerol, sometimes also with other substances. They are present in animal or plant tissues, and obtained in the industry by heating in case of animal fats, or by expeller pressing and solvent extraction in case of plant raw materials. Natural lipids are solid fats or liquid oils, consisting mostly of triacylglycerols, and accompanied by polar lipids and lipophilic minor substances. Lipids may be modified by different procedures, such as refining, fractionation, emulsification, hydrogenation, and are deteriorated by oxidation reactions. Lipids belong to main nutrients, are indispensable in the nutrition. They are the most important source of energy; they contain essential fatty acids, sterols, and lipophilic vitamins. Lipids are raw materials for many edible lipid products, such as table or frying oils, margarines, mayonnaise, and shortenings. The intake of lipids and their fatty acid composition have great impact on human health.

1. Introduction

Proteins, lipids, and saccharides belong to the main nutrients. Lipids are defined as naturally occurring derivatives of fatty acids. Fats (solid lipids) and oils (liquid lipids) consist mostly of triacylglycerols. They are reserves of energy for plants or animals. More polar lipids, such as phospholipids, glycolipids and lipoproteins, have important biological functions. Lipids, being hydrophobic, are usually accompanied in natural fats and oils by non-lipidic hydrophobic substances, such as sterols, lipophilic vitamins, hydrocarbons, terpenes, liposoluble phenolic derivatives, and chlorophyll and carotenoid pigments.

Lipids were known in prehistoric times, but the chemical structure of lipids was first discovered nearly 200 years ago by M.-E. Chevreul, who found that fats and oils consisted of esters of fatty acids and glycerol, and determined the chemical structure of several fatty acids. The industrial lipid processing started in the middle of 19th century. The production of margarine was developed, in the beginning of the 20th century, solid fats were produced by hydrogenation of liquid oils, and vegetable oils began being refined for edible use. The hydrolysis of triacylglycerols to free fatty acids was developed, a basis for the modern soap making. Chemical analysis of fats and oils is done using procedures 100-150 years old, but the modern lipid analysis started by introduction of gas-liquid chromatography, and 20 years later of high-performance liquid chromtography. Environment-safe fat and oil industry, and the nutritional importance of lipids are in the center of interest now.

2. Chemical Composition

2.1. Fatty Acids

A – saturated fatty acids
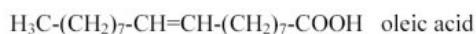
H_3C-$(CH_2)_{14}$-COOH   palmitic acid

B – monoenoic fatty acids

H_3C-$(CH_2)_7$-CH=CH-$(CH_2)_7$-COOH   oleic acid

C – dienoic fatty acids (n-6)

H_3C-$(CH_2)_4$-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH   linoleic acid

D – trienoic fatty acids (n-3)

H_3C-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_7$-COOH   linolenic acid

E – trienoic fatty acids (n-6)

H_3C-$(CH_2)_4$-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_4$-COOH   γ-linolenic acid
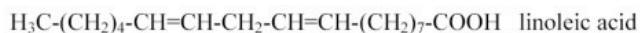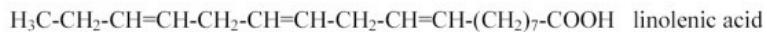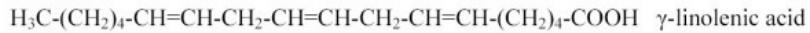
Figure 1: Chemical formulae of fatty acid classes

Fats and oils consist of about 95 % fatty acids. Fatty acids found in edible lipids have long straight hydrocarbon chains of 4-26 carbon atoms in the molecule, and a carboxyl group at the carbon atom 1 (Figure 1). The carboxyl group is dissociated only in small degree so that higher fatty acids belong to very week acids. Fatty acids have 18 carbon atoms in most lipids. Even carbon number fatty acids prevail, and the content of odd carbon number fatty acids only rarely exceeds 1 %, almost exclusively in milk and depot fats of ruminants. Branched chain fatty acids are only trace components in some animal fats. Cyclic fatty acids are only an exception, being present as a trace component in rare edible lipids. Fatty acids with a very long hydrocarbon chain are present in most waxes, but their importance in the human diet is very low.

The hydrocarbon chain of natural fatty acids may be either saturated (Figure 1A), or unsaturated, containing 1-6 double (ethene) bonds in the molecule. Fatty acids

containing triple (ethine) bonds are not present in edible lipids. The most important saturated fatty acids are listed in Table 1. Saturated fatty acids with the carbon number up to 10 are liquids; higher saturated fatty acids are solids, forming crystals of two metastable and a stable modification. The melting point increases with the increasing number of carbon atoms. The melting point depends on the crystalline modification of the acid. Boiling points of saturated fatty acids are very high so that they are usually distilled at reduced pressure. Higher fatty acids are almost insoluble in water, but their alkaline soaps are water soluble. Saturated fatty acids are very stable on storage and moderate heating up to about 100 °C.

Systematic name	Trivial name	Chemical formula
Butanoic	Butyric	$C_4H_8O_2$
Hexanoic	Capronic	$C_6H_{12}O_2$
Octanoic	Caprylic	$C_8H_{16}O_2$
Decanoic	Capric	$C_{10}H_{20}O_2$
Dodecanoic	Lauric	$C_{12}H_{24}O_2$
Tetradecanoic	Myristic	$C_{14}H_{28}O_2$
Hexadecanoic	Palmitic	$C_{16}H_{32}O_2$
Octadecanoic	Stearic	$C_{18}H_{36}O_2$
Eicosanoic	Arachic	$C_{20}H_{40}O_2$
Docosanoic	Behenic	$C_{22}H_{44}O_2$

Table 1: Saturated fatty acids

Monounsaturated fatty acids contain a double bond, mainly the *cis*-stereomer. Numerous monounsaturated fatty acids are possible. The position of the double bond is, however, regulated by enzymic pathways so that only a few monounsaturated fatty acids are found in edible fats. The most common monounsaturated acid is oleic acid (Figure 1B), with its double bond located between the 9th and 10th carbon atoms (counted from the carboxyl end). In studies concerning lipid physiology, the double bond position is often counted from the methyl end (the nth carbon atom; the last carbon atom is also called ω carbon atom, as ω is the last letter of the Greek alphabet) of the hydrocarbon chain. In case of oleic acid, it is again the 9th carbon atom, but the way of expressing the double bond position should be defined by indicating, it is an n-9 or ω-9 monounsaturated acid. The enzymic synthesis is not completely selective so that oleic acid is usually accompanied by small amount of the 11-octadecenoic acid. Another group of monoenoic acids has the double bond closer to the carboxyl group (6-monoenoic acids) and still another group belongs to n-9 homologues of oleic acid (Table 2). Unsaturated fatty acids have lower melting points than the corresponding saturated fatty acids, but the boiling points are nearly the same as those of saturated fatty acids. On storage, the monounsaturated fatty acids are slowly oxidized so that they should be protected against the access of oxygen.

Contrary to *cis*-unsaturated fatty acids, the isomeric *trans*-unsaturated fatty acids are only rare in edible fats, excepting milk and depot fats of ruminants, but their content rarely exceeds 2-3 %. Vaccenic acid (Table 2) is a typical representative. The *cis,trans*-isomerization is possible in course of various processes involving free radicals, such as heating to temperatures above 220 °C, autoxidation or hydrogenation. Hydrogenated

fats are very rich in *trans*-monoenoic fatty acids. The sterical structure of *trans*-monoenoic fatty acids is closer to that of saturated fatty acids. Their melting points are higher than those of the respective *cis*-fatty acid, but lower than those of saturated fatty acids with the same number of carbon atoms. Their reactivity is lower than that of *cis*-monounsaturated fatty acids.

Systematic name	Trivial name	Chemical formula
9-*cis*-Hexadecenoic	Palmitoleic	$C_{16}H_{30}O_2$
9-*cis*-Octadecenoic	Oleic	$C_{18}H_{34}O_2$
9-*trans*-Octadecenoic	Elaidic	$C_{18}H_{34}O_2$
6-*cis*-Octadecenoic	Petroselinic	$C_{18}H_{34}O_2$
11-*trans*-Octadecenoic	Vaccenic	$C_{18}H_{34}O_2$
13-*cis*-Docosenoic	Erucic	$C_{22}H_{42}O_2$
9,12-*cis,cis*-Octadecadienoic	Linoleic	$C_{18}H_{32}O_2$
9,12,15-*cis,cis,cis*-Octadecatrienoic	Linolenic	$C_{18}H_{30}O_2$
5,8,12,14-*all-cis*-Eicosatetraenoic	Arachidonic	$C_{20}H_{32}O_2$
5,8,11,14,17-*all-cis*-Eicosapentaenoic	EPA	$C_{20}H_{30}O_2$
4,7,10,13,16,19-*all-cis*-Docosahexaenoic	DHA	$C_{22}H_{30}O_2$

Table 2: Unsaturated fatty acids

All unsaturated fatty acids with 2-6 double bonds are included in the group of polyenoic fatty acids. They are viscous liquids, very easily oxidized, and isomerized on heating.

Dienoic fatty acids have two double bonds in the hydrocarbon chain (Table 2). Similarly as in case of monoenoic fatty acids, many isomers are possible, but the enzymic synthesis leads to only a few alternatives.

The two double bonds are usually separated by a methylene group, forming a pentadienoic system (-CH=CH-CH$_2$-CH=CH-). Linoleic acid is the most important dienoic acid in edible lipids (Figure 1C). The first double bond from the carboxyl is on the 9th carbon atom, similarly as in oleic acid.

From the final methyl group, the first double bond is located on the 6th carbon atom; therefore, linoleic acid belongs to the n-6 series of unsaturated fatty acids. The *cis, cis*-double bond system of linoleic acid is readily isomerized into a mixture of *cis,trans*- and *trans,cis*-isomers in course of heating to more than 220 °C.

Isomers with conjugated double bonds in the 9, 11- and 10, 12-positions are formed during free radical reactions, and are present in natural lipids, too, e. g. in ruminant lipids.

Trienoic acids, with three double bonds in the molecule, are less common than dienoic fatty acids in edible lipids. The number of isomers is also restricted in course of the *in vivo* synthesis. Only linolenic acid (Figure 1D) is important in the diet. The first double bond is located again at the 9th carbon atom as in case of oleic or linoleic acid.

The next double bond is separated by a methylene group, and the third double bond is again separated by a methylene group from the second double bond. Counted from the carboxyl group, linolenic acid is the 9, 12, 15-octadecatrienoic acid, and when counted from the final methyl group, the first double bond is at the n-3 position. Linolenic acid thus belongs to the n-3 series of polyenoic fatty acids. Physiologists call linolenic acid as alpha-linolenic acid. Another isomer is present in some seed oils (e. g. evening primrose oil), where the position of double bond is shifted by three carbon atoms to the carboxyl, so that the first double bond, when counted from the final methyl group, is located on the 6th carbon atom. The n-6 isomer is called γ-linolenic acid (Figure 1E). Both isomers have different physiological functions as they are precursors of different essential fatty acids. Still more unsaturated fatty acids are found in animal lipids. The most important tetraenoic fatty acid is arachidonic acid (Figure 1E and Table 2), which belongs to the n-6 group. The eicosapentaenoic fatty acid (EPA) and docosahexaenoic acid (DHA) belong to the n-3 group (Table 2). All double bonds are of *cis*-configuration, always separated by a methylene group from each other. The application of modern sophisticated chromatographic techniques revealed great number of minor fatty acids of different structures, present in very small amounts. Up to about 60 different fatty acids were detected in some lipids. Because of their low intake, they are of little importance in the human nutrition.

2.2. Triacylglycerols, Phospholipids, Glycolipids, Lipoproteins
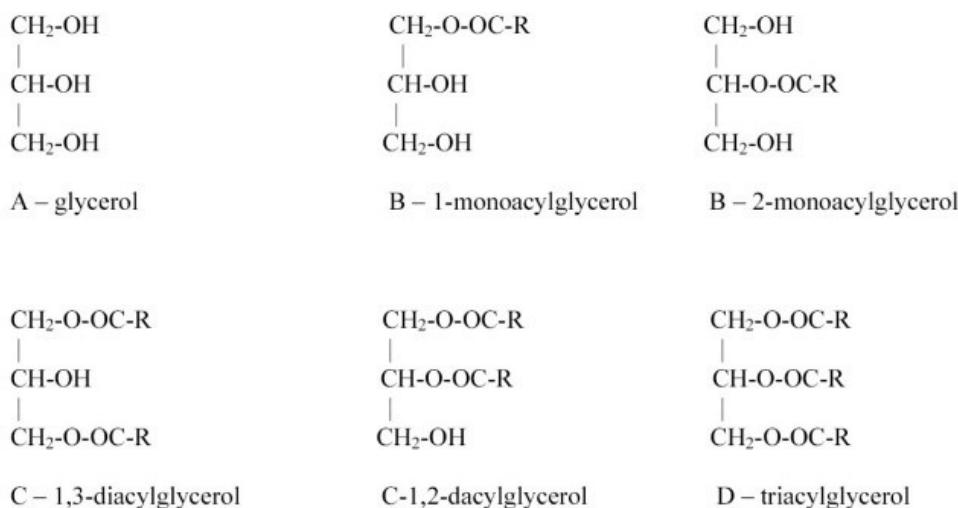
Figure 2: Esters of fatty acids with glycerol

Free fatty acids are present in fats and oils only in small amounts. They are mostly bound to glycerol in the form of esters. As glycerol has three hydroxyl groups (Figure 2A), the formation of various esters is possible. Monoacylglycerols (former monoglycerides) are esters of glycerol with one molecule of a fatty acid (Figure 2B); two isomers are possible: 1-monoacylglycerol and less stable 2-monoacylglycerol. A monoacylglycerol molecule can react with another molecule of a free fatty acid, forming a diacylglycerol molecule (earlier diglyceride). Two isomers are possible

(Figure 2C), and 1,3-diacylglycerol is more stable than 1,2-diacylglycerol. Diacylglycerols react with the third molecule of a fatty acid with formation of triacylglycerols (earlier called triglycerides). Most fatty acids are present as triacylglycerols (Figure 2D) in edible lipids. Fatty acids bound in a triacylglycerol molecule may be the same or two or three different acids, therefore, positional isomers are possible.

The ester groups on the 1st or 3rd carbon atom of the glycerol molecule and the ester group on the 2nd carbon atom are not equivalent, and their esterification is catalyzed by different enzymes. Therefore, the distribution of fatty acids in a triacylglycerol molecule is not random. Saturated fatty acids in vegetable oils are preferentially bound at the carbon atoms 1 and 3, while polyunsaturated fatty acids are bound in higher degree to the carbon atom 2. The stereospecificity of lipases regulating the esterification in the position 2 may be different in animal lipids, e. g. palmitic acid is bound almost exclusively in the positions 1 and 2 in palm oil or in cocoa butter, but in lard, palmitic acid is bound in the position 2 at high degree. In the past decades, new cultivars of oilseed plants were bred with modified fatty acid composition. If the fatty acids bound on the 1st and 3rd carbon atoms of the glycerol molecule are different, or a hydroxyl is not esterified, the 2nd carbon atom of glycerol in the triacylglycerol molecule becomes asymmetric, increasing the possibility of isomer formation. As differences between two acyl residues are very small, differences between the optical properties of enantiomers are only negligible. A specific enzyme catalyzes only the esterification of 1- or 3- positions of the glycerol moiety, while another enzyme catalyzes only the esterification in the position 2. The respective sites of glycerol are then esterified with fatty acids of different composition. The stereospecificity of a triacylglycerol is expressed by putting a prefix *sn* (sterically numbered) in front of the systematic name.

$$CH_2-O-OC-R \qquad CH_2-O-OC-R \qquad CH_2-O-OC-R$$
$$|\qquad\qquad |\qquad\qquad |$$
$$CHO-O-OC-R \qquad CH-O-OC-R \qquad CH-O-OC-R$$
$$|\qquad\qquad |\qquad\qquad |$$
$$CH_2-O-P=O \qquad CH_2-O-P=O \qquad CH_2-O-P=O$$
$$/\backslash \qquad\qquad /\backslash \qquad\qquad /\backslash$$
$$HO\ O^- \qquad O^-\ O-O-CH_2-CH_2-N^+(CH_3)_3 \qquad O^-\ O-CH_2-CH_2-N^+H_3$$
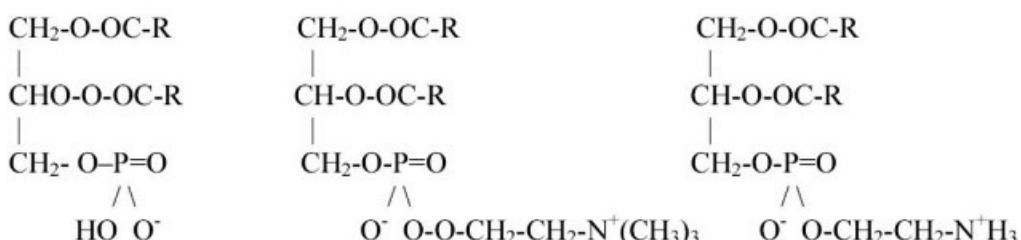
A – phosphatidic acid   B – phosphatidylcholine   C – phosphatidylethanolamine

Figure 3: Chemical structure of phospholipids

Monoacylglycerols and diacylglycerols are present only in negligible amounts in edible lipids, but they are produced in the industry by transesterification of triacylglycerols. They are used as emulsifying agents in the production of emulsified fats. If oil raw materials, such as corn germ or rice bran, are stored for a longer time, lipases present in the material can catalyze the hydrolysis of the triacylglycerol fraction, producing larger amounts of diacylglycerols. Phospholipids contain fatty acids, an alcoholic moiety and bound phosphoric acid. The most important phospholipid classes are the classes of glycerophospholipids. Phosphatidic acids (Figure 3A) are 1,2-diacylgycerols, where the

third hydroxyl group of glycerol is esterified with phosphoric acid. Bound phosphoric acid can be esterified with another molecule of glycerol (phosphatidylglycerol) or with another diacylglycerol (cardiolipin), but most often with choline (phosphatidylcholine, Figure 3B) or ethanolamine (phosphatidylethanolamine,

Figure 3C). Phosphatidylcholine is often called lecithin, but it is better to use the term lecithin only for natural phospholipid concentrates. Phosphatidylserine and phosphatidylinositol are also common representatives of phospholipids. The inositol residue can be esterified with another phosphoric acid. In most phospholipids, the fatty acid bound at the position 1 of the glycerol residue is mainly palmitic acid, while fatty acid bound at the position 2 of the glycerol residue is linoleic acid or another unsaturated fatty acid. The position 3 is mostly occupied by phosphoric acid.

In the case that the fatty acids bound in a molecule are different, the carbon atom 2 in the glycerol residue becomes asymmetric so that most phospholipids are optically active. If the position 2 is free, a more polar derivative is formed, called lysophospholipid, e. g. lysophosphatidylcholine or lysophosphatidylethanolamine.

All phosholipids are ionic compounds; acidic phospholipids have a negative charge, e. g phosphatidic acids, while phospholipids containing a nitrogen group, such as phosphatidylcholine, can form positive or negative ions, and form amphoteric salts. The ionic character of phospholipids increases the hydrophilic character of the molecule. Phospholipids are crystalline hydroscopic substances of high melting points, insoluble in acetone. They are soluble in hexane, and form stable emulsions with the aqueous phase.

Sphingolipids are another class of phospholipids. They do not contain glycerol, but fatty acids are bound as amides to long-chain bases, such as sphingosin and related compounds. The most important group of sphingolipids is that of sphingomyelins. Lipids containing bound sugars are glycolipids.

They often contain phosphorus, too. Saccharides bound most frequently in glycolipids are galactose and glucose; one or several sugar molecules are bound in different glycolipids. Some polar lipids contain bound sialic or neuraminic acids; their structure is often rather complicated, and they are sometimes called mucolipids.

Most polar lipids are bound in lipoproteins. They may have either a globular structure or may form membranes. In globular lipoproteins, hydrophobic chains of fatty acids are oriented to the center, while the polar moiety of lipids is oriented outside, being bound to proteins by multiple hydrogen bonds. Therefore, globular lipoproteins are polar and are easily dispersed in the aqueous phase.

They are important in milk and dairy products, but they are also present in meat and other foodstuffs. Membranes usually consist of a lipid bilayer, where the hydrophobic moieties are oriented outside, and the hydrophilic groups inside so that the membrane is hydrophobic, being able to separate cells or cell organelles.

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Biographical Sketches

Jan Pokorný, D.Sc., Professor of the Department of Food Chemistry and Analysis, Faculty of Food and Biochemical Technology, at Prague Institute of Chemical Technology, was born in 1928 in Southern Bohemia, Czech Republic. He received his M.Sc. Degree in Chemical and Food Engineering in 1951, his Ph.D. in 1956, his Dr. hab. Degree in 1955, and his D.Sc. degree in 1963. He acted as the Dean of the Faculty, and Chairman of the Food Section of the Czech Academy of Agricultural Sciences. He is

member of the Polish Academy of Sciences. He is the president of the Czech Society of Nutrition; he has been a member of the governing board of the Czech Chemical Society, and Secretary of the Section of Fat and Oil Sciences. He acted as a member of the IUPAC Committee on Fats, Oils and Oleochemicals, and of the IUPAC Food Science Board. He is a member of editorial boards of several Czech and international journals, such as European Journal of Food Science and Technology or Journal of Food Lipids. Among other awards, he received the prestigious Chevreul Medal, and Fachini Medal, and was nominated as the pioneer of Lipid Science by the AOCS. He received the State Prize of Science and Technology (the highest degree). His main reasearch topics are lipid science, particularly lipid oxidation and antioxidants, lipid hydrogenation, sensory evaluation of lipid foods, and role of lipids in human nutrition. He has published more than 700 original papers in local and international journals. He is a co-author of more than 20 books, and the editor of 4 books, and several textbooks.

Jana Dostálová MSc., PhD., Associate Professor of the Department of Food Chemistry and Analysis at Prague Institute of Chemical Technology was born in 1943 in Prague, Czech Republic. Prof. Dostálová received her MSc. degree in Chemistry in 1966 and her PhD. degree in Technical Sciences (Food chemistry and technology) in 1975.
She is a member of presidium of the Czech Nutrition Society, member of the Forum Healthy Nutrition, secretary of the Division of Nutrition and Food Quality of the Czech Academy of Agricultural Sciences, secretary of the Division of Food and Agricultural Chemistry and treasurer of the Division for Fats and Oils of the Czech Chemical Society, president of the Division for Nutrition and Food of the National Board for Obesity, member of the committee of the Czech Union Scientific and Technical Societies, member of the Committee for quality of plant raw materials and products and a member of the European Federation for the Science and Technology of Lipids. She is a member of the editorial boards of several Czech professional journals.
Prof. Dostálová´s main research activities are in food chemistry and analysis (oxidation changes of lipids, carbohydrates of legumes, fatty acids composition of fats in various foods) and applied nutrition. She has published more than 300 articles in Czech and international journals and she is author or coauthor more than 40 books and textbooks.