1. Chemistry of lipids

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Abstract. This chapter introduces the definition, classification and chemistry of lipids. Due to complexity of lipids different definitions and classification ways exist. Chemical diversity of lipid compounds is presented along with different nomenclature systems. The occurrence and importance of each group of lipids both in living organisms and in food is also briefly described. Moreover, chapter presents the traditional lipid classification and specification of the following groups of lipid constituents: fatty acids, waxes, acylglycerols, phospholipids, sphingolipids, sterols, tocopherols and tocotrienols, carotenoids, and other compounds.

Introduction

The denomination “lipids” presents the most differentiated group of natural, chemical compounds. Almost all chemical classes of molecules containing carbon, hydrogen and oxygen atoms are included in lipids. Namely hydrocarbons, alcohols, ethers, ketones, acids, esters. Different carbon skeletons are presented in lipids, i.e., unbranched aliphatic chains, prenyl chains, aliphatic and aromatic rings, heterocycles. Beside carbon,
hydrogen and oxygen, also phosphorus and nitrogen are the building atoms in phospho- and sphingolipids.

There are a few, various lipid classification systems commonly used. The most logical seems to be the one that is based on lipid chemical structures. Fortunately, this classification agrees to some extent with the biological function of lipid classes. Other classification systems will be briefly presented, too. In this chapter lipid compounds will be divided and described according to the traditional chemical classification into the following groups: fatty acids, acylglycerols, phospholipids, sphingolipids, sterols, tocopherols and tocotrienols, carotenoids, and others.

Two main naming or nomenclature systems used in organic chemistry include systematic (standard) and common (trivial). The first system uses names created accordingly to the strict rules, and the second uses traditional names. Due to complexity of many lipid compounds, trivial names are commonly accepted in lipid nomenclature. However, nomenclature of some highly heterogenic lipid groups is still confusing. For example, for sterols different names are used. Different naming systems in lipid groups will be presented and illustrated.

Many of simple lipids such as sterols, tocols or carotenoids, have long and complicated systematic chemical names, therefore their trivial names have been included in systematic nomenclature and accepted to commonly use. The same refers to complex lipids.

**Definition and classification of lipids**

Lipids are organic molecules occurring in almost all living organisms. They can be isolated from plant and animal tissues using different methods. In plants, lipids are most abundant in seeds, however, fleshy mesocarp of some fruits also can contain pronounced amount of lipids. The main lipid features are their complexity and heterogenicity. Due to these features different definitions and classification systems of lipids exist based on divers criteria.

From the chemical point of view lipids are multicomponent mixtures of constituents with extremely variable chemical structures. The most essential are acylglycerols, i.e., glycerol esters with fatty acids. Among them triacylglycerols are the most abundant. However, mono- and diacylglycerols are also presented. Other important groups of lipid constituents are: phospholipids, sterols, tocopherols, carotenoids. Some lipids contain moderate or small amounts of long chain hydrocarbons, alcohols, and free fatty acids. Saturated and unsaturated fatty acids of different carbon chain
length constitute the main substructure of acylglycerols, phospholipids, waxes, and they are also present in sterols.

Food chemists and biochemists define lipids as substances derived from living organisms that are insoluble in water and soluble in non-polar organic solvents such as hydrocarbons, chloroform or diethyl ether. However, this definition is unprecise because it does not include synthetic and structured lipids, i.e., modified natural products as well as trans fatty acids that are not derived directly from living organisms. O’Keefe [1] stated that no exact definition of lipids exists and therefore discussed different of them.

Due to great diversity of lipid features different classification systems are used basing on their:

1. origin: plant and animal
2. consistency at room temperature: solid and liquid
3. fatty acid composition: saturated and unsaturated
4. polarity: neutral and polar
5. physiological role: functional and storage
6. structure: simple, complex and derived.

Fatty acids that are the main building blocks of lipids are additionally classified based on their importance for humans as essential and nonessential and divided according to the length of chain to short and long chain ones or short, medium and long chain ones.

The three first classifications are to some extent coincident because the origin of lipid partly dictates its chemical composition and physical properties. Plant lipids that are mostly liquid in room temperature are named oils and consist mainly unsaturated fatty acids in acylglycerol moieties. In solid animal lipids called fats saturated fatty acids predominate. There are of course some exceptions to these rules. The most spectacular is cocoa butter.

Lipids are generally hydrophobic. Polar lipids include mostly phospholipids and majority of other lipid constituents are neutral with acylglycerols and sterols as the most common.

Functional lipids are involved in vital and metabolic processes in living organism and typically comprise less than 1% of weight of the plant tissue. They include mainly phospholipids and isoprenyl-derived compounds (e.g., sterols and carotenoids). Storage lipids are deposited as oil bodies in seeds or fruit and serve as carbon source during germination of seeds. Their content in plant tissue can reach up to 66% by weight in oil-bearing plants [2].

Classification of lipids based on their chemical structure is a little unclear due to their structural complexity. Simple lipids yield at most two types of hydrolysis products, usually an alcohol and an acid. This group of
lipids is represented by e.g., triacylglycerols, waxes. On the contrary, complex lipids yield three or more hydrolysis products. Phospholipids are the most important group of complex lipids. Derived lipids are building blocks of simple and complex lipids. These three definitions are commonly accepted. However, different authors diversely classified some lipids, e.g., sterols and tocopherols are included either to simple lipids [1] or to derived lipids [3].

It is noteworthy that Fahy et al. [4] to facilitate international communication proposed a comprehensive classification of lipid molecules, and divided lipids into eight categories: fatty acyls, glycerolipids, glycerophospholipids, sphingolipids, sterol lipids, prenol lipids, saccharolipids, and polyketides. It is also proposed to revise of naming and structure drawing of lipid molecules, and the shorthand notation for some lipid categories.

**Fatty acids**

Fatty acids constitute the essential part in lipid structures. The term fatty acid (FA) designates aliphatic monocarboxylic acids liberated by hydrolysis from natural fats and oils. Fatty acids vary in chain length and in the number, position, and configuration of double bonds. They are generally unbranched and contain an even number of carbon atoms mostly between 12 and 22 carbon atoms, however, acids containing 4 to 10 or more than 22 carbon atoms also occur in lipids. The first real acid occurring in lipids is butyric or butanoic acid which is important in dairy fats. Recently, the very short chain acids C1-C3 may be constituents of synthetic acaloric lipids [1]. Fatty acid moiety consists of carbon chain with methyl group on one end and carboxyl group on the other end. Fatty acids may contain one or more double bonds and are called monounsaturated (MUFA) or polyunsaturated (PUFA) fatty acids, respectively. Some of them have other substituents such as hydroxyl, epoxy, and keto groups, of which hydroxy fatty acids are most common.

There are two main nomenclature systems for fatty acids. The International Union of Pure and Applied Chemistry (IUPAC) and International Union of Biochemistry (IUB) Commission on Biochemical Nomenclature recommended comprehensive nomenclature standards for fatty acids and lipids based on IUPAC organic nomenclature called systematic nomenclature [5]. Systematic names allow unequivocally to draw the structure. Trivial or common acid names derive from their source names and are not connected with their structure. However, traditional acid nomenclature is more commonly used than systematic one, especially for the common acids. Excellent contemporary reference for fatty acids
Chemistry of lipids

classification and nomenclature include Lobb and Chow [6] and O’Keefe [1]. Both systems of acid nomenclature systematic and common are illustrated in Tables 1 and 2 for the important saturated and unsaturated fatty acids, respectively, giving systematic names, trivial names and abbreviations.

According to systematic nomenclature rules the name of saturated carboxylic acid is formed from aliphatic hydrocarbon name with the same carbon atoms by replacing the final -e from the hydrocarbon with the -oic and adding acid; for example, alkane becomes alkanoic acid. The unsaturated fatty acids are named in a similar way: alkene becomes alkenoic acid, alkadiene – alkadienoic acid, etc. The names of acyl groups derived from acids are formed according to the example: alkanoic acid – alkanoyl. The position of desaturation and of other substituents that occur in fatty acids, should be pointed by locants. Additionally, the configuration of all double bonds should be described.

### Table 1. Important saturated fatty acids.

<table>
<thead>
<tr>
<th>Systematic name</th>
<th>Common name</th>
<th>Formula</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanoic</td>
<td>Formic</td>
<td>CH₃–COOH</td>
<td>1:0</td>
</tr>
<tr>
<td>Ethanoic</td>
<td>Acetic</td>
<td>CH₃(C₂H₄)–COOH</td>
<td>2:0</td>
</tr>
<tr>
<td>Propanoic</td>
<td>Propionic</td>
<td>CH₃(CH₂)–COOH</td>
<td>3:0</td>
</tr>
<tr>
<td>Butanoic</td>
<td>Butyric</td>
<td>CH₃(CH₂)₂–COOH</td>
<td>4:0</td>
</tr>
<tr>
<td>Pentanoic</td>
<td>Valeric</td>
<td>CH₃(CH₂)₃–COOH</td>
<td>5:0</td>
</tr>
<tr>
<td>Hexanoic</td>
<td>Caproic</td>
<td>CH₃(CH₂)₄–COOH</td>
<td>6:0</td>
</tr>
<tr>
<td>Hepatanoic</td>
<td>Enanthic</td>
<td>CH₃(CH₂)₅–COOH</td>
<td>7:0</td>
</tr>
<tr>
<td>Octanoic</td>
<td>Caprylic</td>
<td>CH₃(CH₂)₆–COOH</td>
<td>8:0</td>
</tr>
<tr>
<td>Nonanoic</td>
<td>Pelargonic</td>
<td>CH₃(CH₂)₇–COOH</td>
<td>9:0</td>
</tr>
<tr>
<td>Decanoic</td>
<td>Capric</td>
<td>CH₃(CH₂)₈–COOH</td>
<td>10:0</td>
</tr>
<tr>
<td>Undecanoic</td>
<td>CH₃(CH₂)₉–COOH</td>
<td>11:0</td>
<td></td>
</tr>
<tr>
<td>Dodecanoic</td>
<td>Lauric</td>
<td>CH₃(CH₂)₁₀–COOH</td>
<td>12:0</td>
</tr>
<tr>
<td>Tridecanoic</td>
<td>CH₃(CH₂)₁₁–COOH</td>
<td>13:0</td>
<td></td>
</tr>
<tr>
<td>Tetradecanoic</td>
<td>Myristic</td>
<td>CH₃(CH₂)₁₂–COOH</td>
<td>14:0</td>
</tr>
<tr>
<td>Pentadecanoic</td>
<td>CH₃(CH₂)₁₃–COOH</td>
<td>15:0</td>
<td></td>
</tr>
<tr>
<td>Hexadecanoic</td>
<td>Palmitic</td>
<td>CH₃(CH₂)₁₄–COOH</td>
<td>16:0</td>
</tr>
<tr>
<td>Heptadecanoic</td>
<td>Margaric or daturic</td>
<td>CH₃(CH₂)₁₅–COOH</td>
<td>17:0</td>
</tr>
<tr>
<td>Octadecanoic</td>
<td>Stearic</td>
<td>CH₃(CH₂)₁₆–COOH</td>
<td>18:0</td>
</tr>
<tr>
<td>Nonadecanoic</td>
<td>CH₃(CH₂)₁₇–COOH</td>
<td>19:0</td>
<td></td>
</tr>
<tr>
<td>Eicosanoic</td>
<td>Arachidic</td>
<td>CH₃(CH₂)₁₈–COOH</td>
<td>20:0</td>
</tr>
<tr>
<td>Docosanoic</td>
<td>Behenic</td>
<td>CH₃(CH₂)₁₉–COOH</td>
<td>22:0</td>
</tr>
<tr>
<td>Tetracosanoic</td>
<td>Lignoceric</td>
<td>CH₃(CH₂)₂₂–COOH</td>
<td>24:0</td>
</tr>
<tr>
<td>Hexacosanoic</td>
<td>Cerotic</td>
<td>CH₃(CH₂)₂₄–COOH</td>
<td>26:0</td>
</tr>
</tbody>
</table>
Systematic nomenclature describes a double bond position giving the number of the first of two doubly bonded carbon atoms in relation to the carbon atom in carboxyl group numbered as first one. Designation “Δ” is sometimes used for double bond, however usually it is omitted. For example, the 16-carbon fatty acid with a double bond between the 9\textsuperscript{th} and 10\textsuperscript{th} carbon atom is named Δ9-hexadecenoic acid or simply 9-hexadecenoic acid, and according to the up to date recommendation hexadec-9-enoic acid. However, the latter style of fatty acid nomenclature is rather discouraged. In this system all double bonds are shown.

The other system for double bond position in unsaturated fatty acids is widely used by biochemists and food chemists. In this system the alternative terms “ω” or “n” (more up-to-date) refer to the position of the first double bond counting from the methyl group to end of the fatty acid molecule and only this double bond is shown. For example, 9-hexadecenoic acid is ω-7 or n-7 acid. Both these rules are illustrated in Figure 1 for linoleic acid (\textit{cis, cis-}octadeca-9,12-dienoic acid).

![Diagram showing Δ and ω numbering systems for linoleic acid.](attachment:linoleic_acid_diagram.png)

**Figure 1.** Example of Δ and ω (n) numbering systems for linoleic acid.

In both mentioned systems abbreviations in which carbon number and double bond number separated by colon and followed by appropriate description are preferably used. For example, for 9-hexadecenoic acid the abbreviations are: 16:1Δ9 or 16:1ω-7 equal to 16:1n-7. In ω style for polyunsaturated FA only first double bond is pointed and it is assumed that successive double bonds are separated by one methylene group (-CH\textsubscript{2}-). This assumption is true only for most common polyunsaturated fatty acids, e.g., linoleic acid, linolenic acid. However, in some plant oils conjugated acids (–C=C-C=C–) or allenic acids (–C=C=C–) rarely occur. It is also assumed that all double bonds have \textit{cis} (Z) configuration. It should be mentioned that in natural mono- and polysaturated FA sometimes double bonds of \textit{trans} (E) configuration occur. These acids form during the processing of oils and can be found in partly hydrogenated or deodorized oils.
Two systems are used for description of double bond configuration: *cis/trans* and *Z/E* (Figure 2). In both systems the relative positions of pointed atoms or groups attached to both doubly bonded carbon atoms is described. In *cis/trans* system the mass of atoms/groups and in *Z/E* system the priority according to strict priority rules [1] is taken into consideration. Although these systems differ in details, in the case of common fatty acid *cis*-acids are (*Z*)-acids and *trans*-acids are (*E*)-acids. Naturally occurring FA have mostly configuration *cis* (*Z*) what means that alkyl groups lie on the same side of double bond plane in the molecule. Recently, prefixes *cis* or *trans* are often abbreviated to *c* and *t*, respectively. Abbreviations in ω/n system are used only for all- *cis* configuration and are reported in Table 2.

![Figure 2. Example of cis/trans and Z/E nomenclature of double bond.](image_url)

<table>
<thead>
<tr>
<th>Systematic name</th>
<th>Common name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-9-Dodecenoic</td>
<td>Lauroleic</td>
<td>12:1ω3</td>
</tr>
<tr>
<td>c-9-Tetradecenoic</td>
<td>Myristoleic</td>
<td>14:1ω5</td>
</tr>
<tr>
<td>c-9-Hexadecenoic</td>
<td>Palmitoleic</td>
<td>16:1ω7</td>
</tr>
<tr>
<td>c-6- Octadecenoic</td>
<td>Petroselinc</td>
<td>18:1ω12</td>
</tr>
<tr>
<td>c-9-Octadecenoic</td>
<td>Oleic</td>
<td>18:1ω9</td>
</tr>
<tr>
<td>t-9-Octadecenoic</td>
<td>Elaidic</td>
<td>a</td>
</tr>
<tr>
<td>c-11-Octadecenoic</td>
<td>Asclepic (<em>cis</em>-Vaccenic)</td>
<td>18:1ω7</td>
</tr>
<tr>
<td>t-11-Octadecenoic</td>
<td>Vaccenic</td>
<td>a</td>
</tr>
<tr>
<td>c-9, c-12-Octadecadienoic</td>
<td>Linoleic (LA)</td>
<td>18:2ω6</td>
</tr>
<tr>
<td>c-9, c-12, c-15-Octadecatrienoic</td>
<td>α-Linolenic (ALA)</td>
<td>18:3ω3</td>
</tr>
<tr>
<td>c-6, c-9, c-12-Octadecatrienoic</td>
<td>γ-Linolenic (GLA)</td>
<td>18:3ω6</td>
</tr>
<tr>
<td>c-6, c-9, c-12, c-15-Octadecatetraenoic</td>
<td>Stearidonic</td>
<td>18:4ω3</td>
</tr>
<tr>
<td>c-8, c-11, c-14-Eicosatrienoic</td>
<td>Dihomo-γ-linolenic</td>
<td>20:3ω6</td>
</tr>
<tr>
<td>c-5, c-8, c-11, c-14-Eicosatetraenoic</td>
<td>Arachidonic</td>
<td>20:4ω6</td>
</tr>
<tr>
<td>c-5, c-8, c-11, c-14, c-17-Eicosapentaenoic</td>
<td>Eicosapentaenoic (EPA)</td>
<td>20:5ω3</td>
</tr>
<tr>
<td>c-13-Docosenoic</td>
<td>Erucic</td>
<td>22:1ω9</td>
</tr>
<tr>
<td>c-7, c-10, c-13, c-16, c-19-Docosapentaenoic</td>
<td>Docosapentaenoic (DPA)</td>
<td>22:5ω3</td>
</tr>
<tr>
<td>c-4, c-7, c-10, c-13, c-16, c-19-Docosahexaenoic</td>
<td>Docosahexaenoic (DHA)</td>
<td>22:6ω3</td>
</tr>
</tbody>
</table>

*Abbreviation nomenclature cannot be used to name *trans* fatty acids
Other groups of unusual rare fatty acids constitute: branched chain saturated, acetylenic (triple bond), hydroxy- (ricinoleic acid), epoxy- (vernolic acid) and keto- (licanic acid) acids, and cyclic acids including acids with cyclopropane, cyclopropene, cyclopentene, and furane rings [1].

Fatty acid profile is quite different in functional and storage lipids. Functional lipid FA are essentially restricted to palmitic, palmitoleic, trans-hexadec-3-enoic, hexadeca-7,10,13-trienoic, stearic, oleic, linoleic, and linolenic acids [2]. On the contrary, in storage lipids a great diversity of FA is observed and each fat and oil has its characteristic composition of fatty acids.

The most common and important saturated fatty acids contain between 12 and 22 carbon atoms and are present in many different plant and animal fats. Lauric acid and myristic acid are major components of palm kernel and coconut oils. Palmitic and stearic acids are minor components in most vegetable oils although in some plant fats they occur in significant amounts (>30% of total FA), namely palmitic acid in palm fruit oil and stearic acid in cocoa butter.

More than 100 natural monounsaturated fatty acids (MUFA) have been identified so far but majority of them are very rare. The most abundant is oleic acid (18:1ω9 and Δ9). Olive oil is a particularly rich dietary source of oleic acid, other plant sources rich in it are nuts. The double bond position Δ9 is the most common in MUFA and is present, for example, in erucic acid (22:1ω9) that is the undesired acid in rapeseed oil. Two acids of ω7 family palmitoleic (16:1ω7) and asclepic acid (18:1ω7) are minor components of many vegetable oils. Some plants accumulate in significant amounts other acids, e.g., petroselinic acid (18:1ω12) in seeds of Apiaceae family (carrot, parsley, coriander). It is noteworthy mention that trans isomers of some MUFA have their own names, e.g., elaidic acid is trans isomer of oleic acid.

Among polyunsaturated fatty acids (PUFA), the most important are the ω-3 and ω-6 fatty acids. α-Linolenic acid (ALA, 18:3ω3) and linoleic (LA, 18:2ω6) are the main essential FA, that are synthesized by plants but not by human or animal organism. These acids can serve as precursors for biosynthesis of longer chain ω3 and ω6 PUFA (20 and 22 carbon atoms) in human body. Eicosapentaenoic acid (EPA, 20:5ω3) is subsequently converted to metabolically active compounds called eicosanoids, prostaglandins and leukotrienes. Linoleic and α-linolenic acids are significant constituents of many important vegetable oils including four major oil crops: soybean, rapeseed (or rapeseed with low erucic acid content called canola oil), palm oils, as well as olive, corn and sunflower oils. In sunflower oil either linoleic or α-linolenic acid predominate depending on cultivar. α-Linolenic acid predominates in linseed oil. γ-Linolenic acid (GLA, 18:3ω6) is the other
important natural PUFA produced by few plants. Evening primrose, borage and black currant seed oils are good sources of this fatty acid [2, 7].

**Waxes**

Waxes are mixtures of esters derived from fatty acids and long chain aliphatic alcohols. They are named by replacing the -ol from the alcohol with -yl and the -ic from the acid with -ate. Both systematic or trivial names can be used for wax molecules. For example, the ester of C16 alcohol and C16 acid is named hexadecyl hexadecanoate or by trivial name cetyl palmitate. Simple waxes are esters of long chain fatty acids (C16, C18) and medium or long chain aliphatic alcohols (C8 to C18). Complex waxes are formed from diols or from hydroxyacids. Waxes are found on the surface of leaves, fruits, and flowers. Their role is to prevent uncontrolled water losses. Natural plant waxes that are most important for food and cosmetic industry are jojoba oil and carnauba wax. They have pleasant smell, therefore they are commonly used, e.g., in candies and gum production.

**Acylglycerols**

Acylglycerols are the predominant components of all lipids. They constitute up to 98% of fats and oils. Acylglycerols are mono-, di-, and triesters of glycerol (propane-1,2,3-triol) with fatty acids. They are called monoacylglycerol, diacylglycerol, and triacylglycerol, respectively. The designation acylglycerols includes mixture of any or all of these. Plant oils consist almost entirely of triacylglycerols (TAG). Acylglycerols have been previously called glycerides, however, these older names are recently discouraged. Systematic nomenclature rules allow different names for acylglycerols. A typical plant lipid, which is the most abundant in olive oil can be named in the same way as other esters: glycerol trioleate or glyceryl trioleate, and in the other way: trioleoylglycerol or tri-O-oleoylglycerol [5]. For mono-, diacylglycerols and for triacylglycerols esterified with different acids the position of each acyl group is pointed.

Due to different substitution patterns and a great number of fatty acids huge diversity of acylglycerols is observed in lipids. There are some plant oils in which a single acylglycerol dominates, e.g., trioleoylglycerol in olive oil and 1-palmitoyl-2-oleoyl-3-stearoyl-sn-glycerol in cocoa butter. However, such oils are rather exceptions than rules. A large number of plants has unusual fatty acid composition. Some of them like sea buckthorn and palm plants can provide two distinctly different fats, one from seed kernel and the other from fleshy mesocarp.
It is interesting that although glycerol is not chiral, its derivatives can be chiral due to the fact that both primary OH groups are enantiotopic. Esterification of at least one of them gives a chiral molecule. Glycerol 1-phosphate is optically active (Figure 3). In order to designate the configuration of acylglycerols, the carbon atoms are numbered stereospecifically and the prefix *sn* is used in the name. Carbon atoms in glycerol molecule are numbered starting from the top in Fischer projection in which hydroxyl group at C2 lies to the left (Figure 3), e.g., 1,2-dioleoyl-3-palmitoyl-*sn*-glycerol or *sn*-1,2-dioleoyl-3-palmitoylglycerol. Nomenclature of acylglycerols is shown in Figure 4.
The chemical nature as well as biological and functional properties of lipids depend on both fatty acid structure and their distribution on the glycerol backbone. The three positions are not equivalent when it comes to bioavailability. In natural acylglycerols the fatty acid distribution is nonrandom. For instance in vegetable oils saturated FA are located almost exclusively at the sn-1- and sn-3-positions and unsaturated FA are mainly esterified on sn-2 position.

**Phospholipids**

Phospholipids are along with acylglycerols the most abundant and important group of lipids. Together with proteins they are major components of biological membranes in bacteria, plant and animal organisms.

Phospholipids are heterogeneous group of complex lipids that are diesters of orthophosphoric acid $\text{H}_3\text{PO}_4$. Phospholipids are divided into two main groups. Phosphoacylglycerols called also phosphoglycerides or glycerophospholipids contain a glycerol backbone. Phosphosphingolipids are a subclass of sphingolipids compounds with sphingosyl backbone. The detailed classification of phospholipids is presented by Parkin [2]. Phosphoacylglycerols are composed of glycerol, fatty acids, phosphate and usually an organic base or polyol. The acyl groups are typically substituted

\[
\begin{align*}
R_1 & = \text{OH} & \text{phosphatidic acid} \\
R_2 & = \text{O-CH}_2\text{-CH}_2\text{-NH}_2 & \text{3-}\text{sn-phosphatidylethanolamine} \\
R_2 & = \text{O-CH}_2\text{-CH}_2\text{-C(NH}_2)_3 \text{ } & \text{3-}\text{sn-phosphatidylcholine} \\
R_2 & = \text{O-CH}_2\text{-CH(NH}_2)_3\text{-COOH} & \text{3-}\text{sn-phosphatidyl-L-serine} \\
R_3 & = \text{OH} & \text{3-}\text{sn-phosphatidyl-L-myoinositol}
\end{align*}
\]

**Figure 5.** Structures and nomenclature of phosphoacylglycerols.
at sn-1,2 positions and the phosphoric acid moiety at sn-3 position in the glycerol backbone. The second hydroxyl group of phosphoric acid is esterified by ethanolamine, choline, L-serine, or inositol. Although diacyl forms of the phosphoacylglycerols predominate, small amounts of ether derivatives with vinyl alcohols called plasmogens, also appeared.

Phosphoacylglycerols are commonly named as derivatives of phosphatidic acid (sn-1,2-diacyl-glycerol-3-phosphate), e.g., sn-1-stearoyl-2-oleoyl-3-phosphatidylethanolamine, or by standard names, e.g., 1-stearoyl-2-oleoyl-sn-glycerol-3-phosphoethanolamine. Some common phosphoacylglycerols are presented in Figure 5.

Phosphoglycerols are amphiphilic molecules that have a hydrophilic group with a high affinity for water and lipophilic fatty acid chain with a high affinity for oil and therefore phosphoglycerols are emulsifiers.

**Sphingolipids**

Sphingolipids are diverse class of lipid compounds that contain a long chain base containing 12-22 carbon atoms, typically sphingosine (2S,3R,4E)-2-aminoctadec-4-ene-1,3-diol, also called D-erythro-sphingosine), fatty acids, and other various moieties, such as monosaccharides, other organic bases or phosphoric acid. Sphingolipids are derivatives of ceramides, that are sphingosine amides of fatty acids. Cerebrosides are derivatives of ceramides in which carbohydrate molecule, mostly galactopyranose, is attached to primary hydroxyl group.

Phosphosphingolipids are compounds with head groups that are attached to the primary hydroxyl group via phosphodiester linkages. The most common compound is sphingomyelin, a ceramide with a phosphocholine moiety. Sphingomyelin is a major lipid in certain membranes of animals, it plays minor role in plants. Structures and nomenclature of some sphingolipids and their parent compounds are shown in Figure 6.

![Figure 6: Structures and nomenclature of sphingolipids.](image_url)
Sterols

Sterols are abundant in nature. Sterol family comprises over 200 compounds where plant sterols include over 100. They are classified according to their source into three groups: animal-derived called zoosterols, fungi-derived mycosterols, and plant-derived phytosterols. The most important animal sterol is cholesterol and ergosterol is a common mycosterol. Phytosterols play an important role as structural components of plant membranes. All these sterols are components of human diet. Oils, fruits, vegetables, and cereals are their major sources. Their main role is connected with the absorption of cholesterol and reducing its level.

Sterols are triterpene compounds. The main sterol skeleton consists of four joined rings built of 17 carbon atoms to which two to four methyl groups (at C10, C13, and optionally at C4 – one, two or none), a branched chain of at least seven carbon atoms at C17, and a hydroxyl group at C3 in β-configuration are attached. One double bond in the ring system and the second one in the side chain may occur. Saturated phytosterols called phytostanols are also present in nature. However, they are less abundant and occur usually in trace levels with the exception of a few cereal species where they are present in higher amounts.

Systematic sterol nomenclature is complicated and confusing, and therefore simple trivial names of sterols are commonly accepted. The numbering of carbon atoms in sterols according to the recent IUPAC-IUB rules is presented in Figure 7 for cholesterol, cholest-5-en-3β-ol [8]. Other sterols beside their common names, can be alternatively named as cholestane (saturated cholesterol carbon skeleton) derivatives.

Depending on the number of methyl groups at C4, sterols are divided into three groups: 4,4-dimethylsterols, 4-monomethylsterols and 4-demethylsterols. Sterols of two first groups are intermediates in
biosynthesis of the third group, and are usually present in very low amounts in plants. 4-Demethyl sterols include 27 carbon sterol, cholesterol, and the most important 28 and 29 carbon phytosterols. These sterols have usually double bond between C5 and C6 and are called Δ5 sterols or between C7 and C8 (Δ7 sterols). Both may have the second double bond in the side chain. The most common phytosterols in higher plants are: C28 sterol, campesterol (24α-methylcholest-5-en-3β-ol), and two C29 sterols, sitosterol (24α-ethylcholest-5-en-3β-ol, called also β-sitosterol), and stigmasterol (24α-ethylcholesta-5, 22E-dien-3β-ol) (Figure 8). Cholesterol which is predominant in animals, often accounts for 1-2% of total plant sterols. In seed oils from Solanum species it accounts >5% [8].

![Figure 8. Structures of some sterols.](image)

In plant tissues sterols occur as free compounds in which the 3β hydroxyl group is underivatised and as conjugates. Two groups of derivatives include esters with fatty acids or hydroxycinnamic acids, and glycosides or acylated glycosides. Fatty acid esters are particularly significant in total sterols of maize and wheat germ oils.

The content of sterols in plant oils varies significantly. Rapeseed oil contain 700-800 mg/100 g of total sterols, mainly sitosterol and campesterol. Olive oil contain ca. 270 mg/100 g of sterols. Both oils contain about 6 mg/100 g of stanols [9]. Amaranth oil contain 1249 mg/100 g sterols [10]. The good source of both sterols (4240 mg/100 g) and stanols (>100 mg/100g) is wheat germ oil [9].

**Tocopherols and tocotrienols**

Tocopherols and tocotrienols are two subgroups of tocols, lipid soluble compounds that have a number of functions in plants. The primary feature of tocols is their antioxidant activity that protects plants from oxygen activity. Due to antioxidant activity tocols play important role in human diet and health. Tocopherols and tocotrienols are vitamin E compounds. Plants are
the main source of them. Tocopherols together with vitamin C are the most important commercial natural antioxidants. They are natural antioxidant constituents of vegetable oils.

Molecules of tocopherols and tocotrienols consist of two moieties, the polar 6-chromanol head and the 16 carbon atom hydrophobic prenyl side chain linked to it. Two subgroups of tocols differ in the degree of saturation in a prenyl chain: tocopherols have saturated chain, and in tocotrienols three double bonds occur, two have $trans$ configuration. In both subgroups four homologues occur depending on the number and position of methyl substituents in aromatic ring of chromane moiety: $\alpha$, $\beta$, $\gamma$, and $\delta$ (Figure 9).

![Tocopherol](image1)

**Tocopherol**

![Tocotrienol](image2)

**Tocotrienol**

<table>
<thead>
<tr>
<th>Tocopherol or Tocotrienol</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$- 5,7,8-trimethyl</td>
<td>$\text{CH}_3$</td>
<td>$\text{CH}_3$</td>
<td>$\text{CH}_3$</td>
</tr>
<tr>
<td>$\beta$- 5,8-dimethyl</td>
<td>$\text{CH}_3$</td>
<td>H</td>
<td>$\text{CH}_3$</td>
</tr>
<tr>
<td>$\gamma$- 7,8-dimethyl</td>
<td>H</td>
<td>$\text{CH}_3$</td>
<td>$\text{CH}_3$</td>
</tr>
<tr>
<td>$\delta$- 8-methyl</td>
<td>H</td>
<td>H</td>
<td>$\text{CH}_3$</td>
</tr>
</tbody>
</table>

**Figure 9.** Structures of tocopherols and tocotrienols.

Tocopherols have been found in almost all the photosynthetic organisms as well as fungi and animals. In higher plants they are present in all botanical parts. Tocopherols content in plants varies in broad range from $<1 \mu\text{g/g dry weight}$ in potato tuber to $>1 \text{mg/g dry weight}$ in seeds and leaves. $\alpha$-Tocopherol predominates in all plant parts with the exception of seeds,
which contain as the main compound either α or γ form, and small amounts of other tocopherols. Tocotrienols are found in high amounts only in seeds of higher plants. However, in insignificant amounts they are present in leaves of some species [11]. The content and profile of tocols in plant oils is diverse, too. Rapeseed oil contain 60-70 mg/100 g of tocopherols mainly γ and α, and no tocotrienols. Olive oil contain ca. 20 mg/100 g of tocopherols, especially α, and traces of tocotrienols. The good source of both tocopherols (257 mg/100 g) and tocotrienols (11 mg/100g) is wheat germ oil [9].

It is generally agreed that the antioxidant activities of tocopherols against lipid oxidation measured \textit{in vivo} in fats and oils decrease as follows $\alpha>\beta>\gamma>\delta$. On the contrary, this dependency is reversed ($\delta>\beta>\gamma>\alpha$) when tested \textit{in vitro} in liposomes. $\alpha$-Tocopherol has the highest vitamin E activity and it has the greatest importance for human health [11].

\section*{Carotenoids}

Carotenoids are very abundant plant pigments of yellow, orange, and red colour. They are synthesized by plants and microorganisms but not animals.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Structures of some carotenoids.}
\end{figure}
Carotenoids are ubiquitously present in fruits and vegetables that constitute the main sources of carotenoids in human diet. Because of their solubility in lipids, carotenoids occur also in plant oils giving them colour.

Carotenoids are tetraterpenes, i.e. 40-carbon isoprenoids. They have a long chain with conjugated double bonds and methyl groups as substituents. Some of carotenoids have a chain structure (e.g., lycopene) and majority of them has a C6 ring with three methyl groups (β-ionone ring) on both ends of the chain (e.g., β-carotene). The terminal rings can be the same or different and they may contain oxygen atoms commonly in the form of hydroxyl group (luteolin and cryptoxanthins), but also as keto group (canthaxanthin) or both hydroxyl and keto (astaxanthin). Other oxygen-containing groups in carotenoids are: methoxyl, ethoxyl, and carboxyl. Structures of some common carotenoids are shown in Figure 10. Carotenoids are a diverse group, over 600 compounds have been identified to date.

According to absence or presence of oxygen in molecule carotenoids are divided into two classes: carotenes and xanthophylls, respectively. Carotenes (e.g., β-carotene and lycopene) are hydrocarbons that vary in degree or position of unsaturation. Xanthophylls (e.g., lutein, astaxanthin) are synthesized from carotenes by hydroxylation and epoxidation and therefore contain oxygen groups.

Only about 40 carotenoids are present in a typical human diet. Close to 90% of the dietary carotenoids is represented by β-carotene, α-carotene, lycopene, lutein and cryptoxanthin. The main sources of carotenoids in human diet are deeply pigmented fruit and vegetables. Yellow-orange vegetables and fruits, e.g., carrot, apricot, provide most of the β-carotene and α-carotene, orange fruit provide cryptoxanthin, dark green vegetables, e.g., spinach, broccoli, provide lutein and tomatoes provide lycopene [12]. The content of carotenoids in plants varies greatly.

The main roles of carotenes in human diet are connected with their biological activity of vitamin A (retinol) and antioxidant activity. About 10% carotenoids are referred to as provitamin A compounds and almost all reveal antioxidant activity. In both respects, β-carotene is the most important not only because of its abundance but also of the highest vitamin A activity [12]. β-Carotene has an intense orange red colour and is used as food pigment, primarily for oils and fats. β-Carotene and other carotenoids can act as primary antioxidants by trapping free radicals or as secondary antioxidants by quenching singlet oxygen.

Carotenoids are unstable and their stability is affected by oxygen, heat, pH, light, and the presence of metals. They have trans configurated double bonds that may undergo isomerisation to cis isomers as well as oxidation.
Other constituents

Along with the compounds presented above, plant oils comprise other components possessing biological activity. Long chain hydrocarbons, aliphatic alcohols, (fatty alcohols) and free fatty acids are the most common. The most important hydrocarbons in oils are isoprenoids from which triterpene squalene is a precursor of sterols.

Some lipid constituents are present in the form of glycosides where carbohydrate is usually mono- or disaccharide. Glycerolipids or glycolipids are 1,2-diacyl-sn-acylglycerols with a carbohydrate moiety at the sn-3 position, galactose is the most common one. Some glycosides are additionally esterified by FA in carbohydrate molecule.

Vitamin K1 (phylloquinone) is found in some vegetable oils, green vegetables (spinach) and tomatoes. Some plant oils are a source of coenzyme Q, known as ubiquinone, an efficient antioxidant. Chlorophyll a and b, the green plant pigments, are found in crude olive and grape seed oils, and in other oils obtained from unripe seeds [13].

References