

The Chemical Nature of Lipids

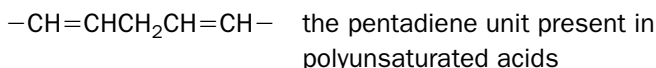
The word 'lipid' is the scientific name given to a wide range of natural compounds based on fatty acids (or closely related molecules such as fatty alcohols or sphingosine bases). Oils and fats are an important subsection of lipids differing from one another in whether they are liquid or solid at ambient temperature. This physical property depends mainly on the fatty acids that they contain. Most animal fats are solids and most vegetable fats are liquid but there are some solid tropical vegetable fats often described as 'butters' (e.g. cocoa butter). This chapter is a review of the nature of fatty acids, triacylglycerols, and the lipid-soluble compounds that are present as minor but significant components of natural oils and fats.

1.1 Fatty acids

Well over 1000 natural fatty acids have been identified but most food scientists need to be familiar with only around 20 of these. Although there are exceptions, the most common fatty acids have a straight chain of 8–22 carbon atoms (even numbers only) and frequently have one or more unsaturated centres (almost entirely double bonds of *cis* configuration) occurring at preferred positions in the carbon chain.

The position of a double bond may be indicated by its relationship to the carboxyl group (delta or Δ nomenclature) or to the end methyl group (omega or ω nomenclature). The most common monounsaturated acid – oleic acid – is both $\Delta 9$ and $\omega 9$ (Figure 1.1). Acids are described as saturated, monounsaturated, or polyunsaturated (PUFA) depending on the number of unsaturated centres they contain. Double bonds in polyunsaturated acids are usually separated by one methylene group (CH_2). Consequently these acids contain

structures such as the pentadiene unit shown below which have characteristic and important properties based on the presence of a doubly activated methylene group (see Chapter 6).



Melting points (Chapter 5) increase with chain length and decrease with the number of (*cis*) double bonds. *Trans* compounds are higher melting than their *cis* isomers. These claims are illustrated in Table 1.1.

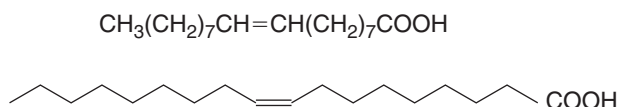


Figure 1.1 Oleic acid [9*c*-18:1 or ω 9-18:1]. The shorthand symbol indicates a C_{18} acid with one *cis* unsaturated centre starting on C-9 with respect to both the COOH and CH_3 groups.

Table 1.1 Names, structure, and melting points of the more common fatty acids. All the unsaturated acids listed here occur in the all-*cis* form

Trivial name	Systematic name	Short-hand	Double bonds*		MP (°C)	Molecular weight
			Δ	ω		
Butyric	Butanoic	4:0			-5.3	78.1
Caproic	Hexanoic	6:0			-3.2	116.2
Caprylic	Octanoic	8:0			16.5	144.2
Capric	Decanoic	10:0			31.6	172.3
Lauric	Dodecanoic	12:0			44.8	200.3
Myristic	Tetradecanoic	14:0			54.4	228.4
Palmitic	Hexadecanoic	16:0			62.9	256.4
Stearic	Octadecanoic	18:0			70.1	284.5
Oleic	Octadecenoic	18:1		9	16.2	282.5
Vaccenic	Octadecenoic	18:1	11	7	44.1	282.5
Linoleic	Octadecadienoic	18:2	9,12	6	-5	280.4
Linolenic	Octadecatrienoic	18:3	9,12,15	3	-11	278.4
Arachidonic	Eicosatetraenoic	20:4	5,8,11,14	6	-49	304.5
EPA	Eicosapentaenoic	20:5	5,8,11,14,17	3		302.5
DHA	Docosahexaenoic	22:6	4,7,10,13,16,19	3		328.5

*When using ω nomenclature only one number is cited. This gives the position of the first double bond with respect to the end methyl group. It is assumed that additional double bonds display the usual methylene-interrupted pattern of unsaturation. For example, this term is commonly employed for the class of omega-3 acids. The term omega acids (without a number) has no meaning.

1.2 Triacylglycerols

Fatty acids occur mainly as glycerol esters. Glycerol contains three carbon atoms each of which carries a hydroxyl group [$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$]. It can form several different types of esters. The outer hydroxyl groups on C-1 and C-3 differ from one another only in a subtle way (which will be largely ignored throughout this book) but the two primary hydroxyl groups differ more obviously from the secondary hydroxyl group attached to C-2. Depending on the number of hydroxyl groups that are acylated (*i.e.* esterified with a fatty acid or acyl group) the glycerol esters are termed monoacylglycerols (MAG), diacylglycerols (DAG), and triacylglycerols (TAG). These terms are preferred to the older names monoglycerides, diglycerides, and triglycerides though these latter are still frequently used in industry and in medical/nutritional texts.

There are two types of monoacylglycerol designated with numbers or Greek letters as for example 1-(or α -)monostearin and 2-(or β -)monostearin. The first of these forms the more stable crystals and an equilibrium mixture of the two will be 90% 1-monostearin. There are also two isomers of distearin designated as 1,2-distearin and 1,3-distearin. These are sometimes described as the symmetrical (1,3-) and unsymmetrical (1,2-) isomers. More frequently there will be two different acyl groups and this will increase the number of isomeric forms (Figure 1.2).

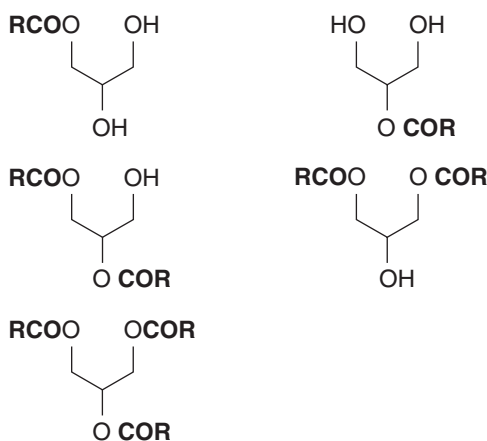


Figure 1.2 Glycerol esters (1- and 2-MAG, 1,2- and 1,3-DAG and TAG). **RCO** represents the acyl group from the fatty acid **RCOOH**. All other letters relate to atoms derived from the glycerol molecule.

When a triacylglycerol contains only one kind of fatty acid then there is only one form of this (e.g. triplamitin, PPP). With two different acids there will be a symmetrical and an unsymmetrical isomer such as POP and PPO where P and O represent palmitic and oleic acid in the 1, 2, and 3 positions. If a fat contains three different fatty acids then it can theoretically be a mixture of 18 different TAG containing one or more of these acids though in practice some of these will be present only at low levels. These are detailed in Table 1.2. Three-letter codes such as POP represent palmitic acid at positions 1 and 3 and oleic acid at position 2. Isomeric TAG containing P, O, and St exist as POST, PStO, and OPSt (ignoring the subtle difference between POST and StOP). However a fat containing these three acids may also contain other TAG as indicated in Table 1.2. Since most fats contain at least four or five different fatty acids the number of potential TAG is even larger, and a natural fat is usually a mixture of all possible structures. However the distribution of acyl groups between the glycerol hydroxyl groups is not generally random because of the regioselectively controlled reactions by which these molecules are assembled under the influence of enzymes. In vegetable fats particularly, the *sn*-2 position of glycerol tends to be acylated with unsaturated rather than with saturated acids so, for example, the proportion of POP (the symmetrical isomer) will greatly exceed that of PPO (the unsymmetrical isomer). Because of this non-random distribution the triacylglycerol composition of natural fats (and hence their physical and biological properties) can

Table 1.2 Eighteen TAG can be present in a fat containing only palmitic (P), oleic (O), and stearic (St) acids

Number of different fatty acids	TAG
One	PPP, OOO, StStSt
Two	PPO, POP, PPSt, PStP, OOP, OPO, OOST, OStO, StStP, StPSt, StOSt, StStO
Three	POST, OPSt, PStO

These three-letter structures are to be read as indicating the fatty acids present in the *sn*-1, 2, and 3 positions of glycerol, respectively. There are subtle differences between the *sn*-1 and 3 positions so that PPO differs only in special ways from its enantiomer OPP but this has been ignored in this table. Symbols such as POST are used here to represent a single triacylglycerol molecule (actually a mixture of two enantiomers – POST and StOP). Sometimes these three-letter symbols are used to represent all the different TAG that contain these three acids. The reader must be alert to decide which on the basis of the context.

be changed through randomisation of the acyl groups (interesterification). In the past lard was frequently interesterified because the randomised product (with modified triacylglycerol composition) was a better shortening than the non-randomised product.

1.3 Ester waxes

The term wax is used to describe materials with certain physical appearance and properties. They are generally mixtures of several types of medium- and long-chain compounds including hydrocarbons (RCH_3), alcohols (RCH_2OH), aldehydes (RCHO), acids (RCOOH), and esters (RCOOR'). The last of these are better classified as ester waxes with around 40 carbon atoms in each molecule formed mainly from saturated or monounsaturated long-chain fatty acids and fatty alcohols. Thus $\text{RCO}-\text{OR}'$ represents the ester from the acid $\text{RCO}-\text{OH}$ and the alcohol $\text{R}'\text{O}-\text{H}$. Waxes are of both vegetable (carnauba, jojoba) and animal (beeswax, woolwax) origin. Some solvent-extracted oils contain low levels of wax from the seed coatings (hulls) and may need to be dewaxed (Section 3.5).

1.4 Phospholipids

The phospholipids (often referred to as phosphatides, Figure 1.3) are molecules of the highest biological importance. Every cell in living plants or animals is a sac within which essential life-supporting processes take place. This sac is surrounded by a permeable membrane made up of phospholipids and other lipid components. The membrane permits the controlled movement of molecules into and out of the cell. These movements are dependant on the quality and integrity of the cell membranes. Phospholipids also have significant properties based on their amphiphilic nature that make them important in foods, cosmetics, and pharmaceuticals. They are largely removed during the refining of vegetable oils at the degumming stage but can be recovered as lecithin. This is a crude mixture of different phospholipids (see Figure 1.3 for typical structures) along with TAG and glycolipids. Lecithin can be used in this crude form but more usually it is refined and is supplied as a phospholipid concentrate virtually free of TAG

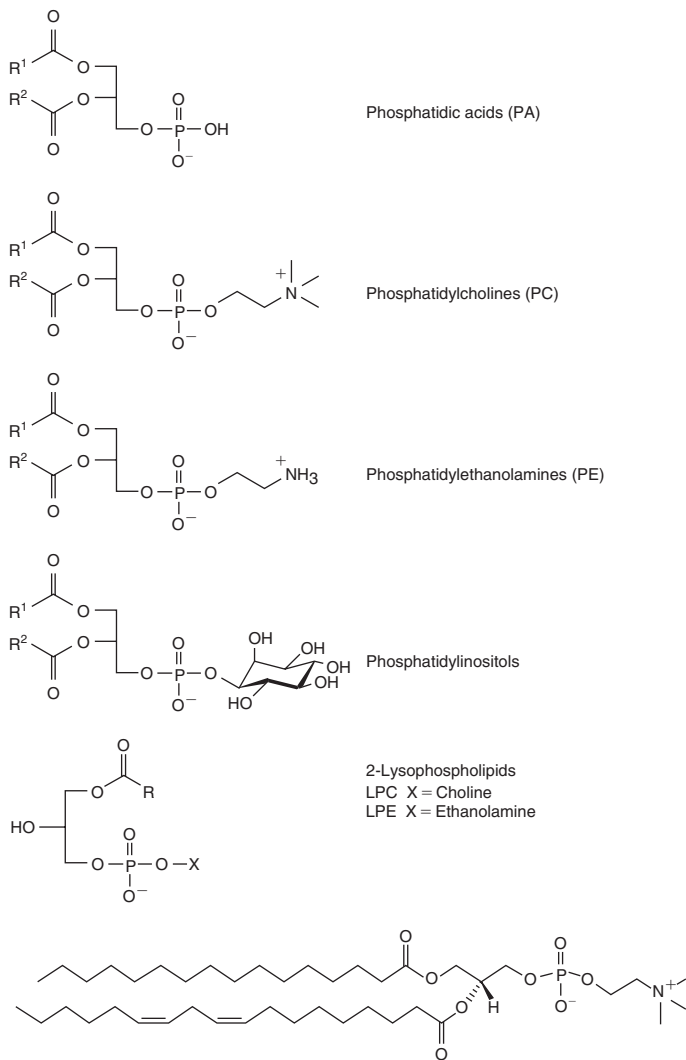


Figure 1.3 Structures of selected phospholipids (PA, PC, PE, PI, lysoPL). These are correctly named in the plural because natural products are mixtures of compounds varying in the nature of the acyl groups R¹CO and R²CO. Also an alternative representation of a PC containing palmitic acid and linoleic acid is shown. These molecules (apart from phosphatidic acid) contain four ester bonds. On complete hydrolysis they furnish fatty acids, glycerol, phosphoric acid, and a hydroxy compound (choline, etc). A series of phospholipases exist which catalyse selective hydrolysis (lipolysis) of these ester groups. Most of these structures have been taken from 'Lipid Glossary 2' (The Oily Press, 2000) which can be downloaded free via The Oily Press website by permission of the authors and the publisher.

or as individual phospholipid classes (such as phosphatidylcholines). The phospholipids can be further modified by chemical or enzymatic processes to make them more suitable for a particular purpose.

Crude soya bean oil (~3%), rapeseed oil (~3%), sunflower oil (~1%), and palm oil (negligible) contain phospholipids at the levels indicated and the first three (particularly soya bean) are the major source of commercial lecithin. A typical crude soya bean lecithin contains phosphatidylcholines (PC, 10–15%), phosphatidylethanolamines (PE, 9–12%), and phosphatidylinositols (PI, 8–10%) along with other lipids.

When hydrolysed, glycerophospholipid molecules give glycerol, fatty acids (2 mols), and low molecular weight alcohols frequently containing nitrogen as in choline ($\text{HOCH}_2\text{CH}_2\text{NMe}_3$) and ethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$). Individual classes of phospholipids are still mixtures because of variation in the fatty acids present. Some typical structures are given in Figure 1.3.

1.5 Sterols and sterol esters

Though not strictly lipids, sterols occur in many oils and fats, share some of their physical properties, and are closely related to oils and fats in any discussion on food and health. Cholesterol has long been associated with coronary heart disease (CHD) and many recommendations concerning lipid intake are related to its influence on the cardiovascular system (Section 7.13) (Figure 1.4).

Most crude vegetable oils contain 1000–5000 mg/kg (0.1–0.5%) of phytosterols, partly as free sterols and partly as sterols esterified with fatty acids. The ratio of esterified to free sterol varies with free sterols (40–80%) generally predominating. Palm oil and the two lauric oils have very low levels of phytosterols (40–50 mg/kg). Above average levels are present in rapeseed oil (5–11 g/kg, mean ~7.5) and in corn oil (8–22 g/kg, mean 14). Sitosterol is generally the major phytosterol (50–80% of total sterols) with campesterol, stigmasterol, and Δ^5 -avenasterol frequently attaining significant levels. These are present at lower levels in refined oils with some, but not all, having being partially removed in the deodorisation process. Sterols can be recovered from deodoriser distillate (along with other compounds) and these provide a valuable source of precursors of many pharmaceutical steroids. Phytosterols are now added to spreads and other foods to reduce cholesterol absorption (Sections 7.7 and 7.13).

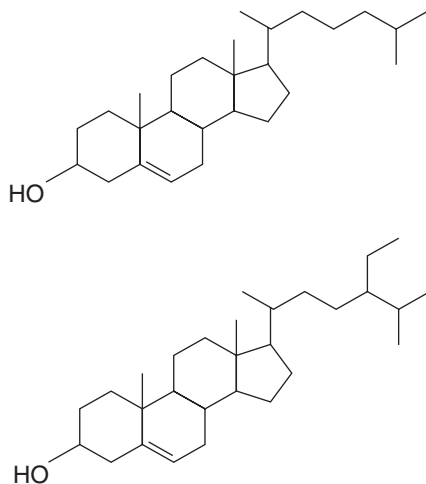


Figure 1.4 Cholesterol (upper) and sitosterol (lower).

Cholesterol is a zoosterol almost entirely of animal origin and is not present in plant systems at any significant level. The normal value of 20–50 ppm in vegetable oils compares with the much higher levels reported for depot animal fats (up to 1000 ppm), fish oils (up to 7000 ppm), dairy fats (2000–3000 ppm), and egg yolks (12,500 ppm). To advertise a vegetable oil as cholesterol-free is true but slightly misleading since such oils would not be expected to contain cholesterol.

1.6 Tocols

There are eight tocots (tocopherols and tocotrienols) with the structures shown in Figure 1.5. They are phenolic heterocyclic compounds with a C_{16} lipid-soluble isoprenoid side chain. The tocots have two valuable but not identical properties: they show vitamin E activity and they are powerful, natural lipid-soluble antioxidants. The total tocol content of crude vegetable oils can range from 10 ppm (equivalent to mg/kg) in coconut oil to 1370 ppm in soya bean oil. Levels of the tocopherols in selected samples of crude vegetable oils are listed in Table 1.3. The tocotrienols are insignificant in

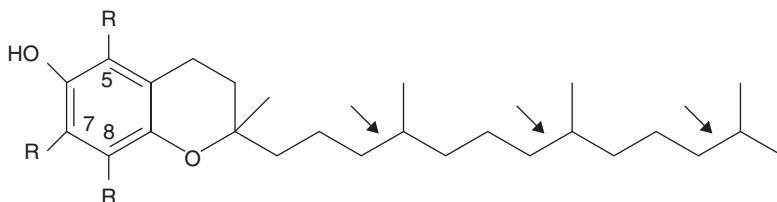


Figure 1.5 Tocopherols and tocotrienols. Tocopherols have a saturated C_{16} side chain, tocotrienols have double bonds at the three positions indicated by the arrows. R = H or CH_3 ; α = 5,7,8-trimethyltolcol; β = 5,8-dimethyltolcol; γ = 7,8-dimethyltolcol; δ = 8-methyltolcol.

Table 1.3 Levels (ppm) of the four tocopherols in crude rapeseed, palm, soya bean, and sunflower oils

	α	β	γ	δ
Rapeseed	179	0	415	10
Palm	190	0	0	0
Soya bean	120	10	610	190
Sunflower	610	10	30	10

Adapted from Warner (2007) *Lipid Technol.*, **19**, 231.

most oils other than palm oil and rice bran oil. Some tocopherols appear in the deodoriser distillate after refining and soya bean deodoriser distillate is the major source of mixed natural tocopherols, apart from the oils themselves. Tocols rich in tocotrienols can be recovered from palm oil. α -Tocopherol can also be made synthetically and this represents 80–90% of total available tocopherol.

Natural tocopherol mixtures are used as antioxidants at levels up to 500 ppm, frequently along with ascorbyl palmitate which extends the tocol antioxidant activity. At higher levels (>1000 ppm) α -tocopherol is considered to act as a pro-oxidant (Section 6.2). Since vegetable oils contain tocols at 200–800 ppm further additions show only a limited effect. The tocols themselves are very sensitive to oxidation and are more stable in esterified form where the all-important hydroxyl group is not free. However such esterified compounds do not show antioxidant activity until they have been hydrolysed *in vivo* to the free phenolic form.

