



Edible Oil Processing

SECOND EDITION

Edited by Wolf Hamm, Richard J. Hamilton and Gijs Calliauw



 WILEY-BLACKWELL

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Second Edition

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List of Abbreviations

ADI	Acceptable Daily Intake
ARfD	Acute Reference Dose
AMF	Anhydrous Milk Fat
ALARA	As Low As Reasonably Achievable
ATEX	Atmospheres Explosive
AES	Atomic Emission Spectroscopy
Barg	Bar gauge
CBE	Cocoa Butter Equivalents
CBI	Cocoa Butter Improvers
CBS	Cocoa Butter Substitutes
DSC	Differential Scanning Calorimetry
DHA	4,7,10,13,16,19-Docosahexaenoic acid
DACC	Donor Accepted Column Chromatographic
DOBI	Deterioration of Bleachability Index
EPA	5,8,11,14,17-Eicosapentaenoic Acid
ECD	Electron Capture Detection
EDTA	Ethylene Diamine Tetra-acetic Acid
EU-27	European Union – 27
FOSFA	Federation of Oils, Seeds and Fats Associations
FID	Flame Ionisation Detection
FFA	Free Fatty Acids
GCFID	Gas Chromatography–Flame Ionisation Detection
GC-MS	Gas Chromatography–Mass Spectrometry
GPC	Gel Permeation Chromatography
HACCP	Hazard Analysis and Critical Control Points
HAZOP	Hazard and Operational Study
HPLC	High-Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
IMO	International Maritime Organization

MARPOL	International Convention for the Prevention of Pollution from Ships
ISO	International Organization for Standardization
LOD	Limit of Determination
LDL	Low-Density Lipoprotein
MRL	Maximum Residue Limits (s)
3-MCPD	3-Monochloropropane-diol
NIOP	National Institute of Oilseeds Products
NORES	Neutral Oil Recovery System
NPD	Nitrogen Phosphorus Detection
BOB	2-Oleo-1.3-dibehenin
EO	Operational Efficiency
PFAD	Palm Fatty Acid Distillate
PFR	Plug-Flow Reactor
PAHs	Polycyclic Aromatic Hydrocarbons
PG	Propyl allate
POP	Oleo-dipalmitin
POS	Oleo-palmitin – stearin
POSt	Oleo-palmitin – stearin
PStP	Stearo-dipalmitin
SSHEs	Scraped-Surface Heat Exchangers
Silver-ion HPLC	Silver ion High Performance Liquid Chromatography
SFC	Solid Fat Content
SBDD	Soybean Deodoriser Distillate
SOS	Oleo-distearin
SUS	Saturated Unsaturated Saturated triglyceride
StOSt	Oleo-distearin
UUS	Unsaturated Unsaturated Saturated triglyceride
USU	Unsaturated Saturated Unsaturated triglyceride
USS	Unsaturated Saturated Saturated triglyceride
TBHQ	Tertiary Butyl hydroquinone

Introduction

In the years since the first edition of *Edible Oil Processing* was published (in 2000), there have been many changes in the processing of oils. Two major factors have been involved: first, the need to reduce the hydrogenated fats in food products, and second, the move to use enzymes. These two issues both originate from an overall increased awareness of the possible impact of processing on consumers' health and on the environment. This edition tries to bring this awareness, and the way in which it has altered the nature of edible oil processing, to the forefront of the discussion.

In Chapter 1, Gunstone outlines the makeup of fats and oils, from the major components such as triacylglycerols (TAGs) to minor constituents such as squalene. He illustrates the changes in oils that have been obtained by seed breeding procedures, such as Nu Sun oil. He also deals with the physical properties on which much of the processing of oils is based.

In Chapter 2, Hamm explains how multi-compartmented parcel tankers play a major role in the transport of oils and fats. He highlights the systems and regulations pertaining to oil shipments, and he deals with the role of FOSFA and NIOP in greater detail than in the first edition.

In Chapter 3, van Doosselaere describes how important seed handling and storage are to the overall production of good-quality oils. In sampling incoming seeds, moisture, foreign material, damaged or broken seeds, protein content and oil content must all be controlled. He explains the methods of storing seeds used to maintain their high quality. Preparation and extraction of seeds are covered in a general way before the special care that must be taken for soybean, rapeseed, cottonseed, corn germ, copra, peanut, rice bran, olive and of course palm oils is discussed.

In Chapter 4, Kemper describes how hexane became the industry's solvent of choice for the extraction of oils, and considers the effects of various plant and processing parameters on solvent extraction plant performance. He also records how important solvent recovery and heat recovery are to the overall

economy of the process. The chapter provides a comprehensive overview of solvent extraction as used in edible oil production.

In Chapter 5, De Greyt deals with the refining of food oils in a sustainable manner. He explains how new technologies have become available and how some have been employed commercially, such as hydrodynamic Nano Reactors and enzymatic degumming. Some processes are still at the pilot plant stage, such as the use of chlorophyllases. He finishes with a look at the future for short-path distillation and supercritical processing, and what this might bring to this field of oil processing.

In Chapter 6, Kellens and Calliauw describe how hydrogenation, inter-esterification and fractional crystallisation are still used to modify oils and fats. Health concerns have led to a large reduction (6–30 million tonnes) in the amount of oil being hydrogenated, and the authors touch on the proposed newer methods of cutting down on *trans* fatty acid composition. They elaborate on the discussion of fractional crystallisation given in the first edition, examining everything from intersolubility to industrial practice, and noting that multistage processing and continuous operation hold the most promise for oil modification technology.

In Chapter 7, Cowan shows the considerable change that has occurred in the use of enzymes since the first edition of this book. By using gene transfer between microorganisms and low-cost immobilisation techniques, it has been possible to move the technology from one restricted to high-value products to one with much wider applications. He covers the use of cellulases, proteolytic enzymes, phospholipases, esterase and lipases, and considers their environmental impacts.

Chapter 8 deals with the applications of edible oils and the considerable reformulation resulting from the reduction of the use of hydrogenated oils. Bot and Flöter also explain fat crystal networks, the polymorphic changes in spreads, the lower-fat versions of mayonnaises and the use of tropical fats in nondairy creams.

Verhoeff and van Duijn concisely describe in Chapter 9 the methods used to measure the natural components of edible oils, including free fatty acids (FFA), peroxides, phosphorus, moisture, dirt, colour, metals and tocopherols, as well as contaminants such as polycyclic aromatic hydrocarbons, pesticides, hydrocarbons and mycotoxins. The authors go on to describe the crude oil risk matrix and finish with a consideration of hazard analysis and critical control points (HACCP).

In Chapter 10, van Duijn and den Dekker explain the steps needed to decide whether the building of a new refinery can be justified. They outline the process routes to a fully refined oil based on lowest costs. Batch and continuous processes and chemical and physical refining are contrasted, and the design parameters for storage tanks and piping are fully covered. The authors provide estimates based on best-practice data, which can be used

for first-design purposes. They then explain that occupational safety hazards must be considered from an early stage in the planning.

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1

Composition and Properties of Edible Oils

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1.1 Introduction

According to US Department of Agriculture (USDA) statistics, the production of nine vegetable oils from seven seeds and from palm fruit and olive was 153 million tonnes worldwide in 2010/11 (Table 1.1). In addition, production of four animal fats (butter, lard, tallow and fish oil) amounted to about 25 million tonnes. Over time, animal fats have fallen in market share, and they now make up only 15% of total annual production. Among vegetable oils, palm, soya, rape and sun oils have become increasingly important, with palm and soya dominant (Table 1.1). It is interesting that these four vegetable oils are produced in different parts of the world (Table 1.2). It should also be noted that crops grown in the southern and northern hemispheres are harvested at different times of the year, with the exception that palm oil is produced in all months of the year. This is particularly significant for soybeans, grown predominately in North and South America. Palm oil and olive oil are obtained by pressing the fruits in the countries where they grow, and trade is confined to the oil or to downstream products. Exports/imports of vegetable oils represent 41% of total production, but there is also considerable trade in unprocessed seeds (24%), especially in soybeans, with extraction occurring in the importing country.

Oils and fats are used mainly for food purposes, but both oilseeds and extracted oil are also used in some part as animal feed. Oils also have industrial uses. Traditionally, these have been mainly in the production of soap and other surface-active molecules, but increasingly they are for energy-producing purposes, such as transport use by automobiles, trains, aeroplanes

Table 1.1 Annual production of major vegetable oils (million tonnes) between 2007/08 and 2010/11, 2011/12 (estimate) and 2012/13 (forecast).

	07/08	08/09	09/10	10/11	11/12 (e)	12/13 (f)
Palm	41.08	44.02	45.87	47.95	50.67	52.77
Soya bean	37.83	35.90	38.88	41.24	41.85	43.62
Rapeseed	18.43	20.56	22.44	23.58	23.76	23.52
Sunflower	10.03	11.95	12.11	12.21	14.14	14.52
Cottonseed	5.21	4.78	4.62	4.99	5.32	5.24
Groundnut	4.86	5.08	4.74	5.10	5.24	5.37
Palm kernel	4.88	5.17	5.50	5.56	5.84	6.09
Coconut	3.53	3.54	3.63	3.83	3.56	3.52
Olive	2.78	2.78	3.05	3.04	3.10	3.09
Total	128.62	133.78	140.84	147.50	153.48	157.74

Source: USDA figures (June 2012).

Table 1.2 Major geographical regions for the production of oilseeds and vegetable oils in 2011/12.

Product	Weight (million tonnes)	Major producing countries/regions (percentage of total)
<i>Seven oilseeds</i>		
Total	437.0	
Soya	236.4	USA (35), Brazil (28), Argentina (18), China (6), India (5)
Rape	60.7	EU-27 (31), Canada (23), China (21), India (11)
Sunflower	39.1	Russia (25), Ukraine (24), EU-27 (21), Argentina (9)
Cottonseed	46.6	China, India, USA, Pakistan
Groundnut	35.5	China, India
Palm kernel	13.3	Indonesia, Malaysia
Copra ^a	5.5	Philippines, Indonesia, India
<i>Nine vegetable oils^b</i>		
Total	153.48	
Palm	50.67	Indonesia (50), Malaysia (37), Thailand (3)
Soya	41.85	China (25), USA (21), Argentina (17), Brazil (17), EU-27 (5), India (4)
Rape	23.76	EU-27 (37), China (23), Canada (12), India (10), Japan (4)
Sunflower	14.14	Ukraine (26), Russia (23), EU-27 (21), Argentina (10)
Cottonseed	5.32	China (28), India (23), USA (6)
Groundnut	5.24	China (48), India (26)
Palm kernel	5.84	Indonesia, Malaysia
Coconut	3.56	Philippines, Indonesia, India
Olive	3.10	EU-27 (77)

^aCopra is the source of coconut oil.

^bVegetable oils may be extracted from indigenous and/or imported seeds.

Source: USDA figures (June 2012).

Table 1.3 Consumption of vegetable oils in 2011/12 in China, EU-27, India and the USA.

	Population (millions)	Million tonnes	Percentage of world total	kg/person/year
China	1345	29.05	19.2	21.6
EU-27	502	23.99	15.9	47.8
India	1198	16.93	11.2	14.1
USA	315	12.94	8.6	41.1
World total	7022	151.16	–	21.5

Source: USDA figures (June 2012).

or boats, or the direct production of energy. These new uses underlie the food versus fuel debate (Gunstone, 2011).

Total consumption covers all these differing uses and is not to be equated with food consumption. It should also be remembered that dietary intake of fat goes beyond these commodity oils and includes sources such as nuts, meat products and dairy products other than butter (milk and cheese). The major consuming countries/regions of vegetable oils are China, EU-27, USA and India, as shown in Table 1.3. It is sometimes convenient to express consumption (for all purposes) on a *per capita* basis by dividing it by population. In 2011/12, the world average was 21.5 kg for vegetable oils, but the figure shows great variation for individual countries/regions. The world figure has grown steadily over the last 60 years and production of vegetable oils has grown more quickly than population. The figure for China has increased recently and is now close to the world average. The Indian figure has changed less and remains well below average. Higher figures are apparent for the USA and Europe, with the European figure inflated by the significant production of biodiesel, made mainly from rapeseed oil. The very large kg/person figure of 159 for Malaysia reflects the presence of a large oleochemical industry in a country with modest population (27.5 million).

The lower section of Table 1.2 shows the major producing countries/regions for nine vegetable oils. Since these oils can be produced, in some part, from imported seeds, the upper part of the table is a better indication of their geographical origin.

1.2 Components of natural fats

The oils and fats of commerce are mixtures of organic molecules. They are mainly triacylglycerols (commonly referred to as triglycerides), accompanied by lower levels of diacylglycerols (diglycerides), monoacylglycerols (monoglycerides) and free fatty acids, and by other minor components, some of which are important materials in their own right. Materials (1–3%) that are

not soluble in aqueous alkali after hydrolysis are sometimes referred to as nonsaponifiable or unsaponifiable material. Although oils and fats are the source of dietary lipids, they are also an important source of other essential dietary requirements. These minor components include phospholipids, phytosterols, tocopherols (tocopherols and tocotrienols, including vitamin E) and hydrocarbons. Phospholipids are recovered during degumming and sterols and tocopherols are enriched in deodoriser distillate. Thus soybeans are not only the source of soybean oil and soybean meal (protein) but are also the major source of lecithin (a crude mixture containing phospholipids), sterols and sterol esters, and of natural vitamin E (Clark, 1996; Ghosh and Bhattacharyya, 1996; Gunstone, 2011; Walsh *et al.*, 1998).

1.2.1 Fatty acids and glycerol esters

Over 1000 natural fatty acids have been identified. These vary in chain length (commonly C_{12} – C_{22}), degree of unsaturation (usually in the range 0–6 *cis* olefinic centres) and the presence or absence of other functional groups such as hydroxy or epoxy. However, only a limited number – perhaps 25–50 – are likely to be important to most lipid scientists and technologists. The most common members of this group are detailed in Table 1.4. They are divided into four categories: saturated acids, monounsaturated acids

Table 1.4 Structures of the most common fatty acids.

Common name	Systematic name ^a	Shorthand ^b
<i>Saturated</i>		
Lauric	Dodecanoic	12:0
Myristic	Tetradecanoic	14:0
Palmitic	Hexadecanoic	16:0
Stearic	Octadecanoic	18:0
<i>Monounsaturated</i>		
Oleic	9-octadecenoic	18:1
Erucic	13-dodecenoic	22:1
<i>Polyunsaturated (n-6)</i>		
Linoleic	9,12-octadecadienoic	18:2
γ -linolenic	6,9,12-octadecatrienoic	18:3
Arachidonic	5,8,11,14-eicosatetraenoic	20:4
<i>Polyunsaturated (n-3)</i>		
α -linolenic	9,12,15-octadecatrienoic	18:3
EPA	5,8,11,14,17-eicosapentaenoic acid	20:5
DHA	4,7,10,13,16,19-docosahexaenoic acid	22:6

^aThe unsaturated centres in these acids have *cis* configuration.

^bThe shorthand designation indicates the number of carbon atoms and of *cis* unsaturated centres in the molecule. It is not necessary to prefix the numbers with the letter 'C'.

and polyunsaturated acids of the n-6 and n-3 families (also referred to as omega-6 and omega-3 acids). The terms 'n-6' and 'n-3' refer to the positions of the first double bond with respect to the end methyl group. For the most part, unsaturation is confined to olefinic systems with *cis* configuration, and the polyunsaturated fatty acids (PUFAs) have methylene-interrupted patterns of unsaturation. They will thus contain one or more pentadiene group ($-\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}-$) with a doubly activated CH_2 function, which has an important influence on their properties. The (largely unnatural) *trans* acids differ from their *cis* isomers in their physical properties (especially higher melting points) and in their nutritional properties. There has been wide recognition of the undesirable nutritional properties of most *trans* acids in the past 10 years, which has had important consequences for food processors. In some countries, the content of *trans* acids above a certain level has to be reported on the packaging; even where this is not required by law, processors have sought to keep levels to a minimum. This has had important consequences for the blends of fats used in spreads and in the production of baking fats, as processors have struggled to maintain desirable physical properties while achieving higher nutritional status. Another nutritional factor that has become more significant in the last 10 years is the recognition of the importance of omega-3 (n-3) acids, particularly those with more than 18 carbon atoms.

These common fatty acids are easily recognised and separated by gas chromatography of their methyl esters, and this technique is a standard analytical procedure in quality-control laboratories (see Chapter 9). Other analytical procedures used in research laboratories, including mass spectrometry (MS) and nuclear magnetic resonance (NMR), are also starting to be used in some quality-control centres.

An oil or fat will usually contain at least 95% triacylglycerols before refining. After refining, this number will generally be in the range 97–99%, depending on the level of unsaponifiable material the oil or fat still contains. Triacylglycerols are fatty acid esters of the trihydric alcohol glycerol (1,2,3-trihydroxypropane) and contain three acyl chains in each molecule, usually from two or three different fatty acids (Figure 1.1). In the biosynthesis of a vegetable oil, acylation of a glycerol phosphate is enzyme-promoted, and the fatty acids are not distributed in a random manner. If the natural mixture is randomised, the resulting material has the same total amount of fatty acids but different triacylglycerols and, consequently, different melting behaviour (see Chapter 6). In vegetable oils, the *sn*-2 position is esterified almost entirely by unsaturated fatty acids, while saturated acids and the remaining unsaturated acids are in the *sn*-1(3) positions.

An oil with n different fatty acids could contain $(n^3 + 3n^2 + 2n) \div 6$ triacylglycerols if all possibilities of isomerism were included. This corresponds to values of 10, 20 and 35 for 3, 4 and 5 fatty acids, respectively. In reality,

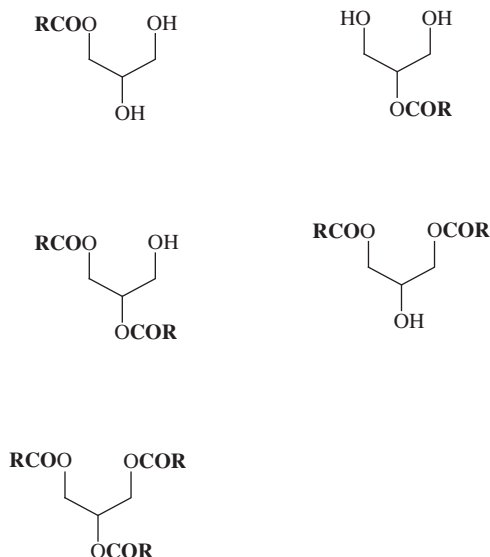


Figure 1.1 Glycerol esters (1- and 2-monoacylglycerols, 1,2- and 1,3-diacylglycerols and triacylglycerols). **RCO** represents the acyl group from the fatty acid **RCOOH**. All other letters relate to atoms derived from the glycerol molecule.

these values are too low, since all the minor acids have been ignored. The number becomes very much greater in fats, such as dairy fats, fish oils and partially hydrogenated oils, with very complex fatty acid compositions. There are methods of triacylglycerol analysis, but these are not trivial, and the results can be complex. This level of analysis is therefore not routine. There are, however, standardised procedures for distinguishing fatty acids in the *sn*-2 position from those in the *sn*-1(3) positions.

Accompanying the triacylglycerols are low levels of diacylglycerols, monoacylglycerols and free acids. These can result from incomplete biosynthesis in immature seeds or from post-harvest lipolysis. Almost all of the free acids and most of the monoacylglycerols will be removed by refining, but diacylglycerols tend to remain in the product. These are usually in the range 0–2%, but refined palm oil contains 3–8% diacylglycerols (Wai-Lin & Wee-Lam, 1995).

After conventional refining, some oils, such as rape/canola, corn, rice bran and sunflower, contain high-melting material that slowly crystallises during storage at ambient temperature. This causes a haze, which – though harmless from a nutritional standpoint – does not find favour with users of salad oil and frying oil. This haze is caused mainly by wax esters and can be removed by holding the oil at ~5 °C for several hours and then filtering (at a slightly higher temperature, to reduce viscosity) with the assistance of a filter aid. Undesirable solids present in some biodiesel samples have been identified as monoacylglycerols and sterol glucosides (Tang *et al.*, 2008).

1.2.2 Phospholipids

Crude oils generally contain phospholipids, which are removed during refining at the degumming stage (Chapter 4). The valuable crude product containing phospholipids and other lipid molecules is termed 'lecithin'. It is the basis of the phospholipid industry, and phospholipids are used extensively in food products, animal feed and industrial products; their uses are based mainly on their amphiphilic properties (i.e. different parts of the molecule show lipophilic and hydrophilic properties). The major components (phosphatidylcholines, phosphatidylethanolamines and phosphatidylinositols) are accompanied by smaller proportions of other phospholipids (Figure 1.2). Soybean oil, rapeseed oil and sunflower seed oil contain 1.5–2.5%, $\leq 2.5\%$ and $\sim 1\%$ phospholipids, respectively. Soybean oil is the major source of commercial lecithin, and this raises a problem in that most soybean oil now comes from genetically modified sources. Those who want to avoid GM products must either find identity-preserved soybean lecithin or use sunflower lecithin from non-GM seeds. The typical composition of a commercial deoiled soybean lecithin is 81% phospholipids (mainly PCs, PEs and PIs), 10% glycolipids and 6% carbohydrates (Gunstone, 2008). Palm oil contains little or no phospholipid.

1.2.3 Sterols

Most vegetable oils contain 1000–5000 ppm (1–5 g/kg) of sterols, partly as free sterols and partly as esterified sterols. Higher levels are present in rapeseed oil (5–11 g/kg, mean ~ 7.5 g/kg) and in corn oil (8–22 g/kg, mean 14 g/kg). β -sitosterol (Figure 1.3) is generally the major phytosterol (50–80% of total sterol), with campesterol, stigmasterol and Δ^5 -avenasterol frequently attaining significant levels (Tables 1.5 and 1.6). Brassicasterol is virtually absent from the major seed oils, apart from rapeseed oil, in which it makes up 10% of total sterol. Kochhar (1983) reviewed sterol composition and sterol content in edible vegetable oils and the changes that take place in these as a result of processing (Section 1.6). Verleyen *et al.* (2002a, 2002b) have described an analytical procedure by which to measure free sterols and sterol esters and have examined the changes that occur during refining. Cholesterol (Figure 1.3) is considered to be a zoosterol and is not present in plant systems at a significant level. The normal value of 20–50 ppm in vegetable oils is much lower than the levels reported for animal fats (up to 1000 ppm), fish oils (up to 7000 ppm), dairy fats (2000–3000 ppm) and egg yolk (12 500 ppm).

Phytosterol (plant sterol) esters are now being added to spreads at significant levels up to 10% because they are considered to reduce cholesterol levels (Sato *et al.*, 2003). These phytosterols are recovered during wood

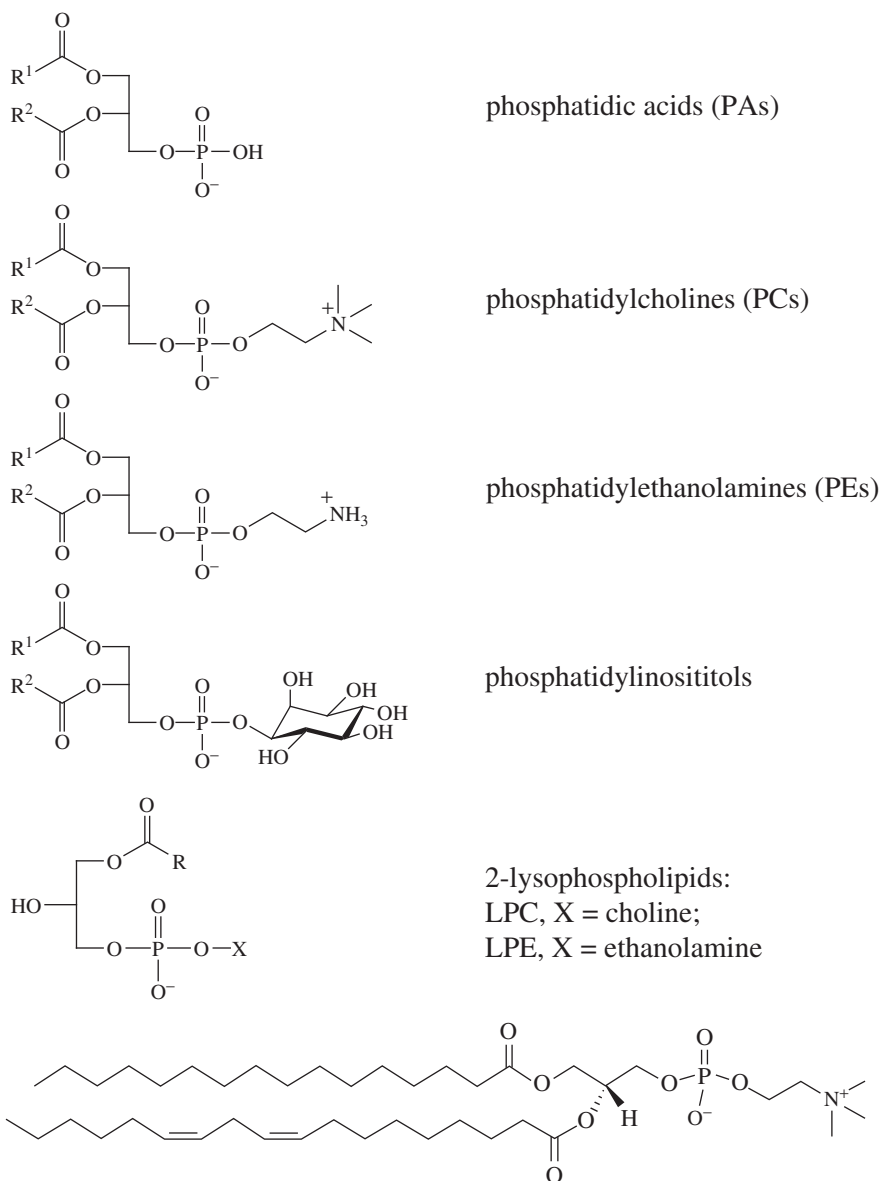


Figure 1.2 Structures of selected phospholipids (PAs, PCs, PEs, PIs, lysoPLs). These are correctly named in the plural because natural products are mixtures of compounds which vary in the nature of the acyl groups R¹CO and R²CO. The final structure is an alternative representation of a PC containing palmitic acid and linoleic acid. 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 which catalyse selective hydrolysis (lipolysis) of these ester groups exists.

Source: 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.