# 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

*Edible Oil Processing*, Second Edition. Edited by Wolf Hamm, Richard J. Hamilton and Gijs Calliauw.

**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) |
|---|---|---|
| | | *Seven oilseeds* |
| 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 |
| | | *Nine vegetable oils*[b] |
| 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) |

[a] Copra is the source of coconut oil.
[b] Vegetable 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, tocols (tocopherols and tocotrienols, including vitamin E) and hydrocarbons. Phospholipids are recovered during degumming and sterols and tocols 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] |
|---|---|---|
| *Saturated* | | |
| Lauric | Dodecanoic | 12 : 0 |
| Myristic | Tetradecanoic | 14 : 0 |
| Palmitic | Hexadecanoic | 16 : 0 |
| Stearic | Octadecanoic | 18 : 0 |
| *Monounsaturated* | | |
| Oleic | 9-octadecenoic | 18 : 1 |
| Erucic | 13-dodecenoic | 22 : 1 |
| *Polyunsaturated (n-6)* | | |
| Linoleic | 9,12-octadecadienoic | 18 : 2 |
| γ-linolenic | 6,9,12-octadecatrienoic | 18 : 3 |
| Arachidonic | 5,8,11,14-eicosatetraenoic | 20 : 4 |
| *Polyunsaturated (n-3)* | | |
| 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 |

[a]The unsaturated centres in these acids have *cis* configuration.
[b]The 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 (—CH=CHCH$_2$CH=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,

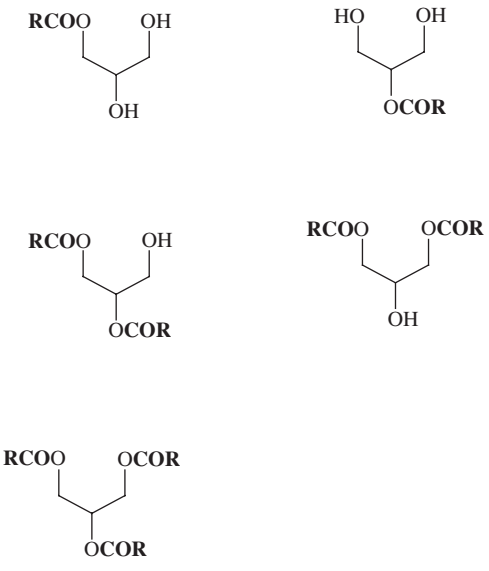



**Figure 1.1** Glycerol esters (1- and 2-monoacylglycerols, 1,2- and 1,3-diacylglycerols and triacylglycerols). **RCO** represents the acyl group from the fatty acid **RCOOH**. All other letters relate to atoms derived from the glycerol molecule.

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).

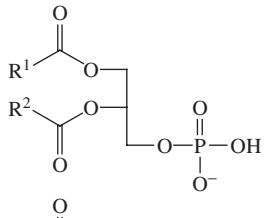
### 1.2.2 Phospholipids

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.

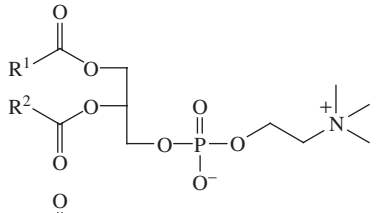
### 1.2.3 Sterols

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 $\sim$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 $\Delta^5$-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).

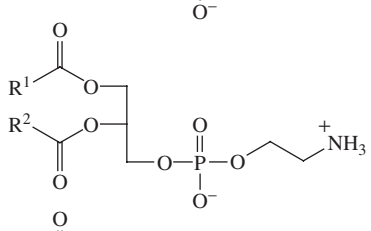
Phytosterol (plant sterol) esters are now being added to spreads at significant levels up to 10% because they are considered to reduce cholesterol levels (Sato *et al.*, 2003). These phytosterols are recovered during wood



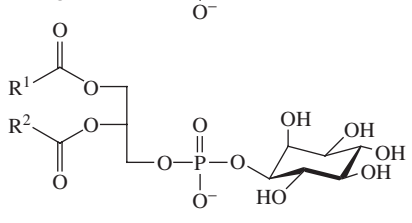
phosphatidic acids (PAs)



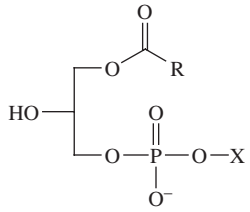
phosphatidylcholines (PCs)



phosphatidylethanolamines (PEs)



phosphatidylinosititols



2-lysophospholipids:
LPC, X = choline;
LPE, X = ethanolamine

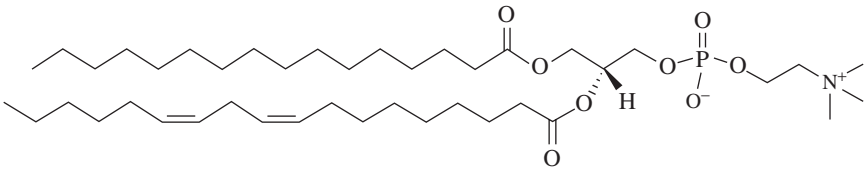


**Figure 1.2** Structures of selected phospholipids (PAs, PCs, PEs, PIs, lysoPLs). These are correctly named in the plural because natural products are mixtures of compounds which vary in the nature of the acyl groups $R^1CO$ and $R^2CO$. The final structure is an alternative representation of a PC containing 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.

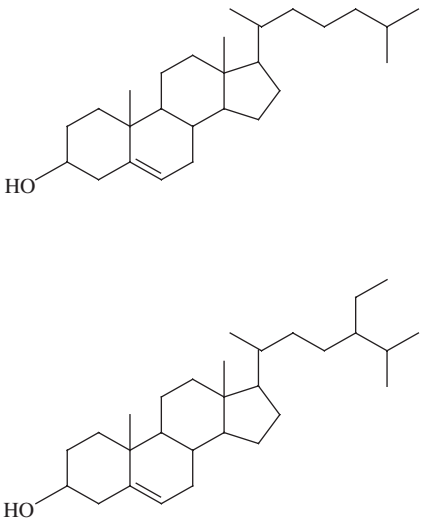



**Figure 1.3** Cholesterol (top) and sitosterol (bottom).

**Table 1.5** Major sterols (campesterol, stigmasterol and β-sitosterol) in vegetable oils as percentage of total sterols.

| | Total sterols (mg/kg) | Camp | Stig | β-sito |
|---|---|---|---|---|
| Palm | 300–700 | 19–27 | 8–14 | 50–62 |
| Rape[a] | 4500–11300 | 25–39 | 0–1 | 45–58 |
| Soybean | 1800–4500 | 16–24 | 15–19 | 47–60 |
| Sunflower | 2400–5000 | 6–13 | 6–13 | 50–70 |

[a]Rape also contains brassicasterol 5–13% (see Table 1.6).
Source: Codex Standard for Named Vegetable Oils, Codex-Stan 210–1999 (adopted 1999, revised 2001, amendments 2003, 2005), Table 3 (available from www.codexalimentarius.org).

processing or are obtained from soybean deodoriser distillate. During high-temperature deodorisation (see Chapter 5), the following are removed in the distillate: aldehydes, ketones and other short-chain compounds resulting from oxidation, tocopherols (vitamin E), sterols, carotene degradation products, nitrosamines, residual extraction solvent, organochlorine pesticides and volatile sulfur compounds (Kao *et al.*, 1998; Torres *et al.*, 2009).

## 1.2.4 Tocols and other phenolic compounds

Tocol extracts are mixtures of up to eight compounds. There are four tocopherols with a saturated, branched, polyisoprenoid $C_{16}$ side chain and

**Table 1.6** Content (mg/100 g) of major esterified and free sterols in crude and refined vegetable oils.

| | Esterified sterols | | | | | Free sterols | | | | | Total sterols | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | sum | Cp | Sg | Si | Av | sum | Cp | Sg | Si | Av | sum | Cp | Sg | Si | Av |
| *Crude oils* | | | | | | | | | | | | | | | |
| Palm | 25 | 5 | 2 | 17 | – | 51 | 10 | 5 | 36 | – | 79 | 20 | 7 | 52 | – |
| Soya | 59 | 6 | 5 | 40 | 9 | 255 | 63 | 55 | 137 | – | 327 | 71 | 61 | 184 | 10 |
| Rape | 475 | 193 | – | 257 | 26[a] | 336 | 97 | – | 171 | 68[a] | 824 | 293 | – | 420 | 111[a] |
| Sun | | | | | | | | | | | | | | | |
| *Refined oils* | | | | | | | | | | | | | | | |
| Palm | 28 | 6 | 3 | 17 | 2 | 29 | 6 | 4 | 18 | – | 60 | 14 | 7 | 36 | 3 |
| Soya | 88 | 11 | 9 | 58 | 10 | 193 | 39 | 40 | 113 | – | 267 | 47 | 48 | 159 | 12 |
| Rape | 485 | 191 | – | 255 | 39[a] | 278 | 93 | – | 158 | 26[a] | 767 | 300 | – | 390 | 77[a] |
| Sun | 124 | 13 | 4 | 81 | 26 | 192 | 19 | 22 | 138 | 12 | 330 | 36 | 27 | 225 | 42 |

[a]These numbers in rapeseed oil relate to the content of brassicasterol.
Cp, campesterol; Sg, stigmasterol; Si, β-sitosterol; Av, $\Delta^5$-avenasterol.
Source: Adapted from Verleyen 2002a and 2002b.

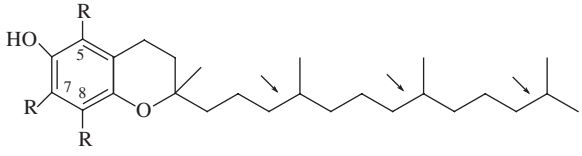



**Figure 1.4** Tocopherols and tocotrienols. Tocopherols have a saturated $C_{16}$ side chain, tocotrienols have double bonds at the three positions indicated by the arrows. R=H or $CH_3$. α = 5,7,8-trimethyltocol, β = 5,8-dimethyltocol, γ = 7,8-dimethyltocol, δ = 8-methyltocol.

four tocotrienols with three double bonds in the side chain (Figure 1.4). The tocotrienols, though significant in palm oil and in rice bran oil, are less common than the tocopherols, and less is known about their biological properties. The four tocopherols differ in the number of methyl groups attached to the heterocyclic moiety (chroman). They are designated α (5,7,8-trimethyl), β (5,7-dimethyl), γ (7,8-dimethyl) and δ (8-methyl). These compounds are sometimes incorrectly described as isomers, but this is true only for the β and γ compounds.

The tocols have two valuable properties: they show vitamin E activity and they are powerful antioxidants (Elmadfa & Wagner, 1997). These two properties are not identical. For vitamin E activity, the order is α (1.0), β (0.5), γ (0.1), δ (0.03), with total activity expressed in α-tocopherol units. For antioxidants, this order is reversed. Some typical levels are presented in Table 1.7. Among the readily available oils, palm and sunflower (as well as walnut and wheatgerm) are good sources of vitamin E because of the

**Table 1.7** Tocols in the major vegetable oils (mg/kg equivalent ppm).

| Vegetable oil | Total (mg/kg) | Tocopherols | | | | Tocotrienols | | |
|---|---|---|---|---|---|---|---|---|
| | | α | β | γ | δ | α | γ | δ |
| Palm | 150–1500 | 4–193 | 0–234 | 0–526 | 0–123 | 4–336 | 14–710 | 0–377 |
| Rape | 430–2680 | 100–386 | 0–140 | 189–753 | 0–22 | ND | ND | ND |
| Soybean | 600–3370 | 9–352 | 0–36 | 89–2307 | 154–932 | 0-69 | 0-103 | ND |
| Sunflower | 440–1520 | 409–935 | 0–45 | 0–34 | 0–7 | ND | ND | ND |
| Wheatgerm | 2540 | 1210 | 650 | 240 | 250 | 20 | 170 | |
| PFAD | 744–8192 | (21%) | – | – | – | (16%) | (39%) | (24%) |

Deodoriser distillates are enriched in tocols but have variable composition. SBDD is reported to contain 19 and 11% tocopherols (mainly gamma and delta) in two reports, and PFAD typically has the composition shown in the table.

Further information on the four major oils is available in appropriate chapters of Gunstone (2011) and in Yang (2003).

Source: Codex Standard for Named Vegetable Oils, Codex-Stan 210–1999 (adopted 1999, revised 2001, amendments 2003, 2005), Table 4 (available from www.codexalimentarius.org, last accessed 8 January 2013).

**Table 1.8** Levels (ppm, equivalent to mg/kg) of the four tocopherols in crude rapeseed, palm, soybean and sunflower oils.

| Oil | α | β | γ | δ |
|---|---|---|---|---|
| Rapeseed | 175 | 0 | 415 | 10 |
| Palm | 190 | 0 | 0 | 0 |
| Soybean | 120 | 10 | 610 | 190 |
| Sunflower | 610 | 10 | 30 | 10 |

Source: Adapted from Warner (2007).

high levels of the α compound, whereas soybean tocopherols are effective antioxidants due to their high levels of γ and δ compounds (Evans *et al.*, 2002; Wagner & Isnardy, 2006; Warner, 2007; Warner *et al.*, 2008). The tocopherols are recovered from refinery byproducts such as palm fatty acid distillate (PFAD) and soybean deodoriser distillate (SBDD) (Table 1.8). The compositions of PFAD and SBDD are somewhat variable depending on the refining conditions employed.

Netscher reported in 1999 that production of vitamin E was about 20 000 tonnes. This included synthetic vitamin E (90%) – a mixture of eight racemic forms – made from trimethylhydroquinone and (all-*rac*-)-phytol and natural vitamin E (10%) principally from soybean. The latter product is an excellent antioxidant but its vitamin E activity is limited because of the low proportion of the α compound. This can be raised by a per-methylation reaction, which

converts the mono- and dimethyl compounds to the trimethyl derivative. These products, whether natural or synthetic, are used in the animal feed, food and pharmaceutical industries.

Crude palm oil contains up to 800 ppm of tocols, of which α-tocopherol represents 22% and β-, γ- and δ-tocotrienol represent 20, 46 and 12%, respectively. About 70% of this mixture remains in the oil after refining, with the remainder present in PFAD at a level 5–10 times higher than in the original oil. This is used as a source of Palm Vitee$^{TM}$, which is 95% tocols rich in tocotrienol (>60%) (Basiron, 2005). Tocols in other oils have been discussed by Clark (1996), Ghosh & Bhattacharyya (1996) and Walsh *et al.* (1998).

Natural tocopherol mixtures are usually used as antioxidants at levels up to 500 ppm (along with ascorbyl palmitate, which extends antioxidant activity). At higher levels (>1000 ppm), α-tocopherol acts as a prooxidant. Since vegetable oils generally contain tocols at 200–800 ppm, further additions show only a limited effect. Evans *et al.* (2002) have discussed the optimal tocopherol blend for inhibiting soybean oil oxidation. The tocols are themselves very sensitive to oxidation and are more stable in an esterified form when the all-important hydroxyl (phenolic) group is not free. However, such compounds do not show antioxidant activity until they have been hydrolysed *in vivo* to the free phenolic form.

Many plant sources of lipids contain phenolic compounds other than the tocols. Some of these are water-soluble and are not extracted with the nonpolar lipids. However, they may be present in oils that are obtained by pressing rather than by hexane extraction. This holds for olive oil, which contains a wide range of phenolic compounds (Boskou, 2011), and for the growing range of cold-pressed oils. Sesame and rice bran oils are known for their high oxidative stability. They contain phenolic compounds which act as powerful antioxidants, including the sesamin lignans in sesame oil and the oryzanols (esters of ferulic acid – 3-methoxy 4-hydroxy cinnamic acid – $MeO(HO)C_6H_3CH{=}CHCOOH$) in ricebran oil (Kochhar, 2011).

### 1.2.5 Chlorophyll

Chlorophyll and its magnesium-free derivative (phaeophytin) are not wanted in refined oils because they produce an undesirable green hue and act as sensitisers for photooxidation (Section 1.5.2). No general listing of chlorophyll/phaeophytin levels has been discovered, but the following information has been gleaned from a range of sources (the levels cited for chlorophyll include phaeophytin):

- *Olive oil*: chlorophyll pigment levels vary with the maturity of the olive and the method of extraction. Unrefined oil contains 10–30 ppm chlorophyll.

- *Canola oil*: levels of chlorophyll in crude oil (5–35 ppm) are much reduced (<50 ppb) by alkali refining and bleaching (Przybylski, 2011).
- *Soybean oil*: low levels of chlorophyll in crude oil (1.0–1.5 ppm) are reduced to about 15 ppb after refining.
- *Sunflower oil*: crude oil contains 200–500 ppb chlorophyll, but in refined oil this is reduced to <30 ppb.
- *Palm oil*: crude palm oil contains 250–1800 ppb chlorophyll (mean 900 ppb, SD 100). The level falls with increasing maturity of the palm fruit.

## 1.2.6 Hydrocarbons

Though hydrocarbons are minor components of oils and fats, they are of dietary and legislative interest. They include alkanes, alkenes (such as squalene and carotenes) and polycyclic aromatic hydrocarbons (PAHs).

### 1.2.6.1 Alkanes

Many studies of alkanes ignore the more volatile compounds (up to $C_{12}$ and including $C_6$, used as an extraction solvent) because of analytical difficulties arising from their volatility. They are not likely to be significant in refined oils that have been submitted to high-temperature deodorisation. Levels of $C_{13}$–$C_{33}$ alkanes in crude oils are usually between 40 and 100 mg/kg (ppm), with lower levels for refined oils. Typical values, in ppb, reported by McGill *et al.* (1993) are 30–100 for olive, 100–170 for sunflower, 25–35 for corn and 25–35 for groundnut oil in samples purchased from retail outlets. There is a preference for odd-chain molecules, as illustrated in Table 1.9. The variation between different oils can be used to fingerprint them, and the consistency in the proportion of different alkanes – if not of the total levels present – suggests that they may be endogenous and not exogenous artefacts. Kao *et al.* (1998) have described some $C_8$–$C_{18}$ unsaturated hydrocarbons present in deodoriser distillate, but these are probably thermal-decomposition products of glycerol esters.

### 1.2.6.2 Squalene

Squalene ($C_{30}H_{50}$, Figure 1.5) is a highly unsaturated open-chain triterpene used in the cosmetics industry after hydrogenation to squalane ($C_{30}H_{62}$). The most abundant source of squalene is the liver oil of the deep-sea dogfish (*Squalus acanthus*, hence the name 'squalene') and of some other marine species. Vegetable sources of potential interest include olive oil and amaranthus oil. Squalene levels of 100–1200 mg/100 ml of oil have been reported in olive oil, with most samples containing 200–500 g/100 ml (de Leonardis *et al.*, 1998). This rises to 200–500 mg/100 ml in the deodoriser distillate (Bondioli *et al.*, 1993). Amaranthus contains 6–8% squalene and this

**Table 1.9** Odd-chain alkanes in selected seed oils (mg/kg, ppm).

| Alkane (carbon atoms) | Sunflower | Olive (extra virgin) | Sesame |
|---|---|---|---|
| 23 | <1 | 19 | <1 |
| 25 | 2 | 18 | 1 |
| 27 | 11 | 16 | 6 |
| 29 | 50 | 12 | 18 |
| 31 | 48 | 9 | 14 |
| 33 | 4 | 6 | 7 |
| 23–33 | 115 | 80 | 46 |
| Total alkanes[a] | 105–166 (5) | 28–99 (6) | 22–82 (4) |

[a]Number in brackets = number of samples examined.

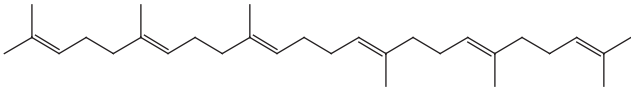


**Figure 1.5** Squalene ($C_{30}H_{50}$).

concentration can be raised 10-fold after short-path high-vacuum distillation (Sun *et al.*, 1997).

#### 1.2.6.3 Carotenes

Carotenes are minor components of most vegetable oils but occur to a greater degree in palm oil. These molecules contain a long chain of conjugated unsaturation and are yellow/orange in colour (Figure 1.6). Crude palm oil normally contains 500–700 ppm carotenes. These are mainly α-carotene (24–42% of total carotenes) and β-carotene (50–60%), with low levels of several other carotenes. Carotenes are also present in palm leaves and in the pressed fibre that remains when oil has been expressed from palm fruits. This fibre still contains 5–6% of oil that is very rich in carotenes (4000–6000 ppm). When palm oil is refined, bleached and deodorised in the normal way, the carotenes are completely destroyed. Carotenes are a biological source of vitamin A, act as powerful antioxidants against both autoxidation and photooxygenation (Section 1.5.2) and show anticancer activity. Attempts have therefore been made to retain these valuable materials in refined palm oil or to recover them in concentrated form.

Products such as red palm oil and Nutrolein™ are palm oils or palm oleins that retain most of the original carotene obtained by carrying out deodorisation at temperatures below 150 °C. Carotenes can be recovered from palm methyl esters, prepared by methanolysis of palm oil and produced in large quantities for biodiesel and other purposes. This is achieved by

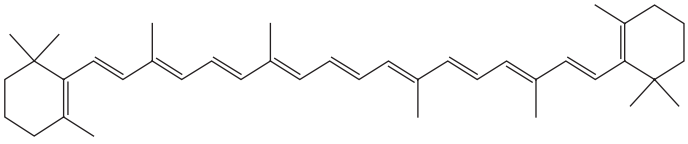


**Figure 1.6** β-carotene ($C_{40}H_{56}$). Other carotenes vary in the nature of the cyclic end groups.

chromatography in an open column or by molecular distillation. The latter option gives a carotene concentrate (8%) that can be further purified (>90%) by chromatography (Baharin *et al.*, 1998; Ooi *et al.*, 1994; Yanishlieva *et al.*, 1998). The various methods for obtaining carotene from palm oil have been reviewed by Thyrion (1999).

Muller (1995) has reported the daily intake of individual carotenes and Yanishlieva and coworkers (1998) have reviewed the role of β-carotene as an antioxidant. Stanley (1999) has described some of the conflicting results concerning the biopotency of carotene supplied as a concentrate rather than as part of a food.

#### 1.2.6.4 Polycyclic aromatic hydrocarbons

PAHs are present at levels up to about 150 μg/kg (ppb) in a number of crude vegetable oils, but less after refining (<80 ppb). They are removed to a small extent during bleaching and somewhat more during deodorisation. This is particularly the case for the more volatile tri- and tetracyclic compounds. The pentacyclic and other less volatile compounds are best removed with activated charcoal, which can be added to earth during bleaching. These values do not hold for crude coconut oil when the copra is dried with combustion gases, where values around 3000 ppb are normally recorded. Normal values are obtained after charcoal treatment (Larsson *et al.*, 1987). In Finland, Hopia and coworkers (1986) examined margarines, butters and vegetable oils for their levels of 38 different PAHs. Apart from a sample of crude coconut oil (4600 ppb), they gave values between 1 and 90 ppb. These compounds probably result from PAHs present in the atmosphere as a result of human-induced combustion of gas, coal or oil. Gertz & Kogelheide (1994) reported on PAHs in 40 native and refined vegetable oils. Extracted oils may contain pesticides resulting from agricultural processes, but these are usually removed during deodorisation.

Gossypol is a toxic hexaphenolic $C_{40}$ compound present in cotton boll cavities. When the seed is extracted, the gossypol adheres to the protein meal and only a small proportion remains in the crude oil. Residual gossypol gives a red-brown colour to crude cottonseed oil but is largely removed during chemical refining and is present only at safe levels of 1–5 ppm in the final

product. Kenar (2006) has reviewed the reaction chemistry of gossypol and its derivatives.

#### 1.2.6.5 Contaminants and specifications

A typical specification includes the following impurities and limits for refined oils based on customer requirements, industry standards and EU legislation: taste and colour (bland), moisture (max. 0.05%), phosphorus (max. 5 ppm), insolubles (not visible), free fatty acids (max. 0.1%), peroxides (max. 1 meq/kg), iron (max. 0.5 ppm), copper (0.05 ppm), lead (max. 0.01 ppm), hexane (max. 5 ppm), benz(a)pyrene (max. 2 ppb), pesticides (maximum residue level in seeds, limit of detection in oils), dioxins (0.75 pg), aflatoxins (2 ppb aflatoxin B1, 4 ppb aflatoxin B1, B2, G1, G2), mineral oil (LOD) and residues of previous cargoes (complete removal).

## 1.3 Fatty acid composition

The food uses of lipids depend on their physical, chemical and nutritional properties, which are linked to their fatty acid and triacylglycerol composition. The latter is important but can be quite complex and for most practical purposes lipids are discussed in terms of their fatty acid composition. Typical values for the fatty acid composition of a range of oils and fats are presented in Table 1.10. These will not be considered in detail, but a few general points will be made. Figures cited in these tables must be considered merely as typical values. Debruyne (2007), Wilkes (2008) and Watkins (2009) have described some of the new varieties being investigated.

Coconut and palm kernel oils (Table 1.11) are typical lauric oils and differ from most of the other vegetable oils. They are important in both the food and the oleochemical industries and are characterised by high levels of lauric acid (12 : 0), significant levels of myristic acid (14 : 0) and useful levels of octanoic (8 : 0) and decanoic acids (10 : 0). The lauric oils are rich in saturated acids (80–90%) and contain very little unsaturated acid. Palm kernel oil is one of two products from the oil palm and must not be confused with the very different palm oil, which is the major product from this tree.

Most vegetable oils contain palmitic, oleic and linoleic (Table 1.10). The writer has calculated that the world's commodity oils in 2004/05 – both vegetable and animal fats – contained 83% of these three acids (Gunstone, 2005). Calculations were based on the fatty acid composition of each oil and on the level of production in that year. Palmitic as the major saturated acid reaches significant levels in palm oil (46%) and in cottonseed oil (27%). Some oils are rich in oleic acid (olive, canola), some in linoleic acid (corn, cottonseed, linola, soybean and sunflower) and some in both acids (groundnut). Seed breeders have produced oleic-rich varieties of many of

**Table 1.10** Typical fatty acid compositions (%wt) of selected oils and fats.

| | 14:0 | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 |
|---|---|---|---|---|---|---|---|
| **Cocoa butter** | – | 26 | – | 34 | 35 | – | – |
| **Corn** | – | 13 | – | 3 | 31 | 52 | 1 |
| **Cottonseed** | – | 27 | – | 2 | 18 | 51 | tr |
| **Groundnut** | – | 13 | – | 3 | 38 | 41 | tr |
| **Linola** | – | 6 | – | 3 | 16 | 72 | 2 |
| **Linseed** | – | 6 | – | 3 | 17 | 14 | 60 |
| **Olive** | – | 10 | – | 2 | 78 | 7 | 1 |
| **Palm** | – | 46 | – | 4 | 40 | 10 | tr |
| **Palm olein** | – | 40 | – | 4 | 43 | 11 | tr |
| **Rape**[a] | – | 3 | – | 1 | 16 | 14 | 10 |
| **Rape**[b] | – | 4 | – | 2 | 56 | 26 | 10 |
| **Soybean** | – | 11 | – | 4 | 22 | 53 | 8 |
| **Sunflower** | – | 6 | – | 5 | 20 | 60 | tr |
| **Sunola**[c] | – | 4 | – | 5 | 81 | 8 | tr |
| **Nusun** | – | 4 | – | 5 | 65 | 26 | – |
| **Butter**[d] | 12 | 26 | 3 | 11 | 28 | 2 | 1 |
| **Lard** | 2 | 27 | 4 | 11 | 44 | 11 | – |
| **Beef tallow** | 3 | 27 | 11 | 7 | 48 | 2 | – |
| **Mutton tallow** | 6 | 27 | 2 | 32 | 31 | 2 | – |

[a]High erucic (also 20:1 6% and 22:1 55%).
[b]Low erucic.
[c]High oleic sunflower.
[d]Also 4:0 (3%), 6:0 (2%), 8:0 (1%), 10:0 (3%) and 12:0 (4%).
tr, trace (<1%).

**Table 1.11** Typical fatty acid compositions (%wt) of lauric oils.

| | 8:0 | 10:0 | 12:0 | 14:0 | 16:0 | 18:0 | 18:1 | 18:2 |
|---|---|---|---|---|---|---|---|---|
| **Coconut** | 8 | 7 | 48 | 16 | 9 | 2 | 7 | 2 |
| **Palm kernel** | 3 | 4 | 45 | 18 | 9 | 2 | 15 | 3 |

these oils. For example, commodity sunflower oil normally contains about 20% oleic acid and 60% linoleic, but two other varieties are now commercially available with higher levels of oleic acid and lower levels of linoleic acid. NuSun contains about 65% oleic acid and high-oleic sunflower is at least 80% oleic acid. These have been produced by conventional seed breeding procedures and are not genetically modified products (Anon, 1998; Watkins, 2009; Wilkes, 2008).

Linolenic acid (18:3) is the major acid in linseed oil (60%) and is the basis for most of the industrial uses of this oil. 'Linola' is the name given to a chemically induced mutant with low levels of linolenic acid and high

levels of linoleic acid (Table 1.10). Linolenic acid is also present in soybean oil (8%) and in rapeseed oil (10%). There is some ambivalence about this acid. Its presence promotes undesirable oxidation and foods containing it have reduced shelf life. This problem has been overcome traditionally by a very light hydrogenation (brush hydrogenation), which halves the level of linolenic acid. More recently, new varieties of these oils have been developed with lower levels of linolenic acid – some of them by genetic modification.

Cocoa butter, the lipid component in chocolate, is an unusual vegetable fat with saturated (~60%) and monoene (~35%) acids in such proportions that its triacylglycerols are mainly of the SOS type (S = saturated, O = oleic). These are responsible for the characteristic melting behaviour of this fat, which is so important in chocolate (Timms, 2003). Other vegetable fats with similar compositions and similar melting characteristics are designated cocoa butter equivalents (CBEs).

These comments hold for the major vegetable oils and fats and also for most of the minor seed oils, but some other oilseeds illustrate the rich diversity of plants in their ability to generate unusual fatty acids, sometimes at very high levels. Examples include castor oil (90% ricinoleic acid – 12-hydroxyoleic acid), coriander oil (80% petroselinic acid – 6-octadecenoic acid), *Vernonia galamensis* seed oil (75% vernolic acid – *cis*-12,13-epoxyoleic acid) and the seed oil of *Picramnia sow* (95% tariric acid – 6-octadecynoic acid).

The major animal fats are more saturated than vegetable oils and contain only low levels of PUFAs. They generally consist of 40–60% saturated acids and 30–60% monounsaturated acids. Butter has acids with a wide range of chain lengths (4–18 carbon atoms) but, like the animal depot fats, it is rich in saturated and monoene acids and low in polyunsaturates. Because of the large number of fatty acids in milk fat, differing in chain length and unsaturation, the triacylglycerol composition is much more complex than that of most vegetable oils. This makes fractionation of anhydrous milk fat (AMF), based on only slightly different properties among the many triacylglycerols, very difficult. Some indication of triacylglycerol complexity was given in a paper by Robinson & MacGibbon (1998). Using silver ion thin-layer chromatography (TLC) and reversed-phase high-performance liquid chromatography (RP-HPLC) they isolated 61 fractions, each of which contained one to four major triacylglycerol components. Some of the difficulties of fractionation were discussed by Bhaskar and coworkers (1998) in a paper comparing the physical and chemical properties of milk fat fractions obtained by commercial melt crystallisation and supercritical carbon dioxide extraction.

Fish oils are characterised by the wide range of acids present and, particularly, by the highly unsaturated members. Saturated (14 : 0 and 16 : 0), monoenoic (16 : 1, 18 : 1, 20 : 1 and 22 : 1) and omega-3 polyenoic acids (eicosapentaenoic acid, 20 : 5 and docosahexaenoic acid, 22 : 6) are frequently major components, and fish oils are valued for the latter.

# 1.4 Physical properties

## 1.4.1 Polymorphism, crystal structure and melting point

Important physical properties relevant to this book are polymorphism, crystal structure and melting point, which combine in the melting behaviour of lipid mixtures.

In the solid state, long-chain compounds frequently exist in more than one crystalline form and may consequently have more than one melting point. This property of polymorphism is of both scientific and technical interest. Understanding this phenomenon is essential for the satisfactory blending and tempering of fat-containing materials, such as baking and confectionery fats, which must attain a particular physical appearance during preparation and maintain it during storage. Problems of graininess in spreads and of bloom in chocolate, for example, are both related to polymorphic changes. The experimental methods used most extensively to examine melting and crystallisation involve dilatometry, low-resolution pulsed $^{1}$H NMR spectroscopy, differential scanning calorimetry (DSC), infrared spectroscopy and X-ray diffraction (Larsson *et al*., 2006; Timms, 2003).

Alkanoic acids exist in three polymorphic forms, designated A, B and C for acids with an even number of carbon atoms. Form C has the highest melting point and is physically the most stable. It is obtained by crystallisation from the melt or from polar solvents. Crystallisation from nonpolar solvents gives form A or forms B and C.

For the purpose of this book, the melting point of triacylglycerols is more important. It has long been known that fats show multiple melting points. As far back as 1853, glycerol tristearate was known to have three melting points (52, 64 and 70 °C). When the melt of a simple triacylglycerol is cooled quickly, it solidifies in the form with lowest melting point (α) with perpendicular alkyl chains in its unit cell (angle of tilt is 90°). When heated slowly, this melts, and held just above the melting point, it will resolidify in the β′ crystalline form. In the same way, a more stable β form can be obtained from the β′ form. The β form has the highest melting point and is obtained directly from solvent by crystallisation. The β′ and β forms have tilted alkyl chains, which permit more efficient packing of the triacylglycerol molecule in the crystal lattice. Glycerol esters with only one type of acyl chain have been thoroughly studied. The results have provided useful guidance, but such molecules are not generally significant components of natural fats (except perhaps after complete hydrogenation). With mixed saturated triacylglycerols such as PStP (P = palmitic, St = stearic), the β form is only obtained with difficulty, and such compounds usually exist in their β′ form. Among unsaturated triacylglycerols, symmetrical compounds (SUS and USU, where S = saturated and U = unsaturated acyl chains) have higher

melting β forms (more stable) but the unsymmetrical compounds (USS and UUS) have stable β′ forms.

Crystallisation occurs in two stages: nucleation and growth. A crystal nucleus is the smallest crystal that can exist in solution and is dependent on concentration and temperature. Spontaneous (homogeneous) nucleation rarely occurs in fats. Instead, heterogeneous nucleation occurs on solid particles (dust etc.) or on the walls of the container. Once crystals are formed, fragments may drop off and either redissolve or form nuclei for further crystals. The latter is not desirable in fat crystallisation, so agitation during fractionation should be kept to the minimum required to facilitate heat transfer (see Chapter 6).

Nucleation rates for the different polymorphs are in the order $\alpha > \beta' > \beta$ so that α and β′ are more readily formed in the first instance, even though the β polymorph is the most stable and favoured thermodynamically. Crystal nuclei grow by incorporation of other molecules from the adjacent liquid layer, at a rate depending on the amount of supercooling and the viscosity of the melt (Gibon, 2006; Lawler & Dimock, 2002; Mori, 1988; Timms, 2005).

In the production of spreads and shortenings, the β′ crystalline form is preferred over the β form. β′ crystals are relatively small and can incorporate a large amount of liquid. This gives the product a glossy surface and a smooth texture. β crystals, on the other hand, though initially small, grow into needle-like agglomerates. These are less able to incorporate liquid and produce a grainy texture. Spreads and shortenings made from rape/canola, sunflower or partially hydrogenated soybean oil generally develop crystals. This can be inhibited or prevented by incorporation of some palm oil or palm olein, which stabilises the crystals in the β′ form. These changes in crystallisation pattern are linked with the larger amount of palmitic acid in the palm products. Glycerol esters with $C_{16}$ and $C_{18}$ acyl chains are more likely to be stable in the β′ form than glycerol esters with three $C_{18}$ chains.

Cocoa butter is particularly rich in three 2-oleo-1,3-disaturated glycerol esters, namely POP, POSt and StOSt. The solid fat has been identified in six crystalline forms, designated I–VI (the melting points and the nature of the double/triple chain lengths are indicated in Table 1.12). Of these, form V ($\beta_2$) is preferred for chocolate. This crystalline form gives good demoulding characteristics and has a stable gloss and a favourable snap at room temperature. Two procedures have been employed to promote the formation of this particular crystalline form. The most widely used is tempering; that is, putting molten chocolate through a series of cooling and heating processes. This optimises the production of the appropriate polymorph. An alternative procedure requires seeding of the molten chocolate with cocoa butter already prepared in form V ($\beta_2$) or VI ($\beta_1$), but this method is restricted by the difficulty of obtaining adequate supplies of these crystalline forms. The synthetic glycerol ester, 2-oleo-1.3-dibehenin (BOB, O = 18 : 1, B = 22 : 0), may

**Table 1.12** Polymorphism in cocoa butter.

| | I | II | III | IV | V | VI |
|---|---|---|---|---|---|---|
| **MP (°C)** | 17.3 | 23.3 | 25.5 | 27.3 | 33.8 | 36.3 |
| **Chain length** | D | D | D | D | T | T |

D, double chain length; T, triple chain length; MP, melting point.

be added to cocoa butter to prevent bloom formation by keeping it in its form V at temperatures above 30 °C (Longchampt & Hartel, 2004; Norberg, 2006; Timms, 2003; other relevant references are Gibon, 2006; Martini *et al*., 2006; and Smith, 2009).

Oils rich in saturated acids may contain high-melting triacylglycerols that crystallise from the oil when stored. When this is considered to be undesirable, the oil is subjected to winterisation (see Chapter 6). This process is applied to cottonseed oil and to partially hydrogenated soybean oil.

## 1.4.2 Density

Density is very important in the oil trade since fatty oil shipments are sold on a weight basis but measured on a volume basis. Since these two values are related by density, it is important to have correct and agreed values for this unit. Density is not the same for all oils but depends on fatty acid composition and on minor components, as well as on temperature. An equation taking these variables into account is based on iodine value (IV), saponification value (SV) and temperature (Pantzaris, 1985):

$$d = 0.8543 + 0.000308\,(SV) + 0.000157\,(IV) - 0.000681t \qquad (1.1)$$

where d is apparent density (g/ml or kg/l) and t is temperature.

Density can be defined in various ways and the correct form must be used when relating volume to weight:

- Density (absolute density or density in vacuum) is the 'mass in vacuum of a volume of oil at t °C ÷ volume of the oil at the same temperature', expressed in g/ml or kg/l.
- Apparent density (density in air, weight-by-volume or litre-mass) is the 'mass in air of a volume of oil at t °C ÷ volume of the oil at the same temperature', expressed in g/ml or kg/l.
- Relative density (specific gravity, density in relation to water) is the 'mass in air of a given volume of oil at $t_1$ °C ÷ mass in air of same volume of water at $t_2$ °C'. This is a ratio without units. It is important to note that two temperatures are involved and the value is meaningless unless both

figures are cited. Relative density is the value most commonly employed and equations exist to connect these three expressions.

Halvorsen and coworkers (1993) have described a method for estimating the density of fatty acids and vegetable oils based on critical volume, critical temperature, critical pressure and a modified Racket equation. Some data have been published by Coupland & McClements (1997), and Topallar and coworkers (1995) have reported the effect of hydrogenation on the density and viscosity of sunflower seed oil.

### 1.4.3 Viscosity

Viscosity can be reported as kinematic viscosity or dynamic viscosity, with the two values related through density. The viscosity of a vegetable oil depends on its chemical composition (summarised in its IV and SV) and the temperature of measurement. Equations have been derived which permit the calculation of viscosity from a knowledge of these three parameters. They have been developed empirically from observation of a range of oils at different temperatures and have been reported by Duff & Prasad (1989), Toro-Vazquez & Infante-Guerrero (1993), Rabelo *et al.* (2000), Azian *et al.* (2001) and Fasina *et al.* (2006). Coupland & McClements (1997) and Fisher (1998) have related viscosity with density, refraction, surface tension and other physical properties. The relation between temperature and viscosity has been described for coconut oil, palm kernel oil, palm oil and mixtures (Timms, 1985), and for several vegetable oils (Noureddini *et al.*, 1992). Changes in viscosity have been used to monitor interesterification (De Filippis *et al.*, 1995) and hydrogenation (Topallar *et al.*, 1995).

### 1.4.4 Refractive index

The refractive index is easily measured using small amounts of material. The refractive index increases with chain length (though not in a linear fashion) and with increasing unsaturation. Geometric isomers differ from one another and methylene-interrupted polyenes differ from those with conjugated unsaturation. Triacylglycerols have higher values than free acids. Values for commercial oils are given in Table 1.13.

### 1.4.5 Solubility of gases in oils

A recent discussion (Hilder, 1997) of the solubility of gases in vegetable oils included the data for oxygen, nitrogen and air presented in Tables 1.14 and 1.15. When an oil is in contact with air, the dissolved gases will depend on

**Table 1.13** Physicochemical properties of selected commodity oils and fats.

| | Specific gravity (temperature °C) | Refractive index (40 °C) | Refractive index (25 °C) | Iodine value | Saponification value | Titre (°C) | Unsaponifiable (%) | Mp (°C) |
|---|---|---|---|---|---|---|---|---|
| Cocoa butter | 0.973–0.980 (25/25) | 1.456–1.458 | – | 32–40 | 192–200 | 45–50 | 0.2–1.0 | 31–35 |
| Coconut | 0.908–0.921 (40/20) | 1.448–1.450 | – | 6–11 | 248–265 | – | <1.5 | 23–26 |
| Corn | 0.917–0.925 (20/20) | 1.465–1.468 | 1.470–1.473 | 107–128 | 187–195 | – | 1–3 | – |
| Cottonseed | 0.918–0.926 (20/20) | 1.458–1.466 | – | 100–115 | 189–198 | – | <2 | – |
| Linseed | 0.930–0.936 (15.5/15.5)[a] | 1.472–1.475 | 1.477–1.482 | 170–203 | 188–196 | 19–21 | 0.1–2.0 | – |
| Olive | 0.910–0.916 (20/20) | – | 1.468–1.471 | 75–94 | 184–196 | – | 1.5 | −3–0 |
| Palm kernel | 0.899–0.914 (40/20) | 1.452–1.488 | – | 14–21 | 230–254 | – | <1.1 | 24–26 |
| Palm | 0.891–0.899 (50/20) | 1.449–1.455[b] | – | 50–55 | 190–209 | – | <1.4 | 33–40 |
| Palm olein | 0.899–0.920 (40/20) | 1.459–1.459 | – | >55 | 194–202 | – | <1.4 | – |
| Palm stearin | 0.881–0.891 (60/20) | 1.447–1.451 | – | <49 | 193–205 | – | <1.0 | – |
| Peanut | 0.914–0.917 (20/20) | 1.460–1.465 | – | 86–107 | 187–196 | – | <1.1 | – |
| Rape[c] | 0.910–0.920 (20/20) | 1.465–1.469 | – | 94–120 | 168–181 | – | <0.21[d] | – |
| Rape[e] | 0.914–0.920 (20/20) | 1.465–1.467 | – | 110–126 | 182–193 | – | <0.21[d] | – |
| Sesame | 0.915–0.923 (20/20) | 1.465–1.469 | – | 104–120 | 187–195 | – | <2.1 | – |
| Soybean | 0.919–0.925 (20/20) | 1.466–1.470 | – | 124–139 | 189–195 | – | <1.6 | – |
| Sunflower | 0.918–0.923 (20/20) | 1.467–1.469 | 1.472–1.476 | 118–145 | 188–194 | – | <1.6 (max. 2.0) | – |
| Sunflower[f] | 0.915–0.920 (20/20) | – | 1.467–1.469 | 75–90 | | | 0.8–1.0 (max. 2.0) | – |

[a] Also 0.924–0.930 (25/25).
[b] 50 °C.
[c] High-erucic rapeseed oil.
[d] These values are correctly copied from the source but they are in error. Better values are 0.5–1.2%.
[e] Low-erucic rapeseed oil.
[f] High-oleic sunflower seed oil.
Source: Adapted from Firestone (1999).

**Table 1.14** Solubility of gases in oils.

| Temp. (°C) | Oxygen (ppm, 1 bar) | Nitrogen (ppm, 1 bar) |
|---|---|---|
| 0 | 170 | 80 |
| 25 | 180 | 85 |
| 50 | 165 | 90 |
| 75 | 190 | 95 |
| 100 | 200 | 105 |
| 125 | [a] | 110 |
| 150 | [a] | 115 |

[a]Oxygen solubilities at higher temperatures are not reliable because oxidation occurs.
Source: Adapted from Hilder (1997).

**Table 1.15** Gas content of oil saturated with air.

| | Solubility (ppm) | Air dissolved in oil (ppm) |
|---|---|---|
| **Oxygen** | 180 | 38 |
| **Nitrogen** | 85 | 66 |
| **Argon** | 270 | S |

Source: Adapted from Hilder (1997).

their individual solubility as well as on their concentration in air. The high solubility of monatomic argon enhances its concentration, so that 1% in air becomes 3% in oil.

Koetsier (1997) has summarised data on the solubility of hydrogen in vegetable oil. This information is important for hydrogenation. He cites solubility values (maximum concentration in oil at a given temperature and pressure) from two sources at 1 bar and 100–200 °C of 2.60–3.36 and 2.76–3.40 mol/m$^3$. The concentration of hydrogen is therefore much lower than the concentration of unsaturated centres; for a fish oil hydrogenated at 5 bar and 180 °C, Koetsier gives concentrations of ~7000 and 16 mol/m$^3$ for the olefinic groups and the hydrogen, respectively.

## 1.4.6 Other physical properties

Gross heats of combustion (HGs) for saturated and unsaturated triacylglycerols can be related to the number of valence electrons (ENs). Freedman & Bagby (1989) have given equations for saturated (Equation 1.2) and unsaturated (Equation 1.3) triacylglycerols, while Krisnangkura (1991) has

expressed this relationship in terms of SV and IV (Equation 1.4).

$$HG = -109.20 + 26.38\ EN \tag{1.2}$$

$$HG = 115.87 + 25.88\ EN \tag{1.3}$$

$$HG = 1\,896\,000/SV - 0.6\ IV - 1600 \tag{1.4}$$

In a useful paper, Coupland & McClements (1997) reported several physical properties (density, viscosity, adiabatic expansion coefficient, thermal conductivity, specific heat, ultrasonic velocity and ultrasonic attenuation coefficient) for a number of liquid oils (coconut, corn, cottonseed, crambe, grapeseed, groundnut, olive, palm, palm-olein, palm kernel, rape, rice bran, safflower, sesame, soybean and sunflower). Timms (1978) reviewed and significantly extended information on the heats of fusion of glycerol esters. He derived an equation for the heat of fusion of mono-acid triacylglycerols in the β polymorph form and showed how this could be adapted to calculate the heat of fusion of most glycerol esters of commercial interest. Chumpitaz *et al*. (1999) have recently reported the surface tensions of four fatty acids (lauric, myristic, palmitic and oleic) and two triacylglycerols (tricaprylin and tripalmitin) over a range of temperatures. These data are important for processes involving gas–liquid contact, such as distillation and stripping columns, deodorisers, reactors and equipment for physical refining. Fisher (2000) has presented equations correlating several properties of *n*-fatty acids and derivatives with chain length.

Some useful data in this section (Table 1.13) have been taken from the AOCS publication *Physical and Chemical Characteristics of Oils, Fats, and Waxes* (Firestone, 1999).

## 1.5 Chemical properties

### 1.5.1 Hydrogenation

Hydrogenation and, more importantly, partial hydrogenation of some of the unsaturated centres in a liquid oil to convert it into a solid or semisolid fat is an important procedure in making them usable as spreads. However, with current concern about *trans* acids, this process has become less useful. The topic is discussed in Chapter 6 and will not be pursued further in this chapter.

### 1.5.2 Oxidation

Part of the refining process (see Chapter 5) involves removal of oxidation products, with their undesirable flavour and aroma, after which further oxidation must be inhibited as efficiently as possible during processing of oils

and fats, food processing and storage up to the moment of consumption. The word 'inhibited' is used because it is virtually impossible to prevent oxidation. It is therefore important to understand this reaction in order that the lipid is always handled under appropriate conditions. It is only possible to give a brief account of this topic in the present volume. The best, fullest and most relevant accounts are to be found in two recent books by Frankel (2005, 2007); the topic is also fully reviewed in *Food Lipids*, edited by Akoh & Min (2008).

Non-enzymatic oxidation occurs by two routes, and it is necessary to protect against both. Lipid oxidation is accelerated by metals, light, heat and several initiators (prooxidants) and can be inhibited by avoiding prooxidants and including antioxidants. The primary products are allylic hydroperoxides. Double bonds remain, though they may have changed configurations and position in the fatty acid chain. These compounds are not directly responsible for the undesirable flavour and aroma associated with rancid fat, but they are unstable molecules which readily undergo a series of secondary reactions, including the formation of short-chain aldehydes:

$$RCH=CHCH_2CHR' \rightarrow RCH(OOH)CH=CHR' \rightarrow RCHO \qquad (1.5)$$

and other compounds.

### 1.5.3 Autoxidation

This is a radical chain reaction; that is, the intermediates are radicals (odd electron species) and the reaction involves an initiation step, a propagation sequence and one or more termination steps:

| | |
|---|---|
| Initiation | $RH \rightarrow R\bullet$ resonance-stabilised alkyl radical |
| Propagation | $R\bullet + O_2 \rightarrow RO_2\bullet$ fast reaction to give a peroxy radical |
| | $RO_2\bullet + RH \rightarrow RO_2H + R\bullet$ rate-determining step |
| Termination | $RO_2\bullet + RO_2\bullet \rightarrow$ stable products |
| | $RO_2\bullet + R\bullet \rightarrow$ stable products |
| | $R\bullet + R\bullet \rightarrow$ stable products |

where RH represents an olefinic compound in which H is attached to an allylic carbon atom and $RO_2H$ is a hydroperoxide.

There is usually an induction period, during which oxidation occurs only slowly, followed by a more rapid reaction. It is desirable to extend the induction period (and hence the shelf life of the product) as long as possible.

The detailed nature of the initiation step is not fully understood, but any or all of three reactions may be involved: (1) metal-catalysed decomposition of existing hydroperoxides produces initiating radicals (it is very difficult to obtain olefinic compounds entirely free of oxidation products); (2) photooxygenation (a very rapid reaction – see below) may be responsible for the first-formed hydroperoxides; and (3) thermal initiation is possible in a heated sample. In the propagation sequence, given an adequate supply of oxygen, the reaction between alkyl radical (R•) and molecular oxygen is fast, and the subsequent reaction of peroxy radical (ROO•) with another olefinic molecule is rate-determining. Autoxidation can be inhibited by minimising the initiation step and/or promoting a termination step so that the propagation cycle goes through as few cycles as possible. The methods of achieving these ends are discussed later.

There is some evidence that PUFAs are more stable to oxidation when located in the *sn*-2 position of triacylglycerols than when in the *sn*-1(3) (Wijesundera *et al*., 2008).

### 1.5.4 Photooxidation

Photooxidation mainly involves interaction between a double bond and a highly activated singlet oxygen molecule produced from ordinary triplet oxygen. Energy from light is transferred to oxygen via a sensitiser such as chlorophyll, erythrosine, rose bengal or methylene blue. This reactive oxygen species (ROS) reacts with olefins to give allylic hydroperoxides. Photooxidation differs from autoxidation in several important respects:

- It involves reaction with singlet oxygen produced from triplet oxygen by light and a sensitiser.
- It is an ene reaction and not a radical chain process.
- It displays no induction period.
- It is unaffected by many of the antioxidants used to inhibit autoxidation but is inhibited by singlet oxygen quenchers such as carotene.
- Oxygen addition is confined to olefinic carbon atoms but the double bond moves and changes configuration from *cis* to *trans*.
- It gives allylic hydroperoxides that are similar in type but not identical in composition to those obtained by autoxidation.
- It is a quicker reaction than autoxidation, especially for monounsaturated acids. The rate is related to the number of olefinic centres and not to the number of doubly allylic allylic groups (photooxidation of oleate is ~30 000 times quicker than autoxidation).

## 1.5.5 Decomposition of hydroperoxides to short-chain compounds

Hydroperoxides are unstable compounds which readily undergo further change, giving, among other products, a range of short-chain compounds. The volatile compounds include aldehydes, ketones, alcohols, hydrocarbons, acids, esters, lactones and ethers, of which the aldehydes are of most concern for odour and flavour. They are produced from the hydroperoxides mainly by homolytic fission and also, in a minor way, by heterolytic breakdown. Each hydroperoxide (there are many) can produce two aldehydes, of which the short-chain volatile member is the more significant. In a glycerol ester, the other aldehyde remains as a glycerol derivative – sometimes called the core aldehyde – and may not be removed during refining.

Most of the short-chain aldehydes have a very low threshold value, so they need only be present at minute levels in order to exert their olfactory effect. For example, the 9-hydroperoxide from linoleate gives 2,4-decadienal with a deep-fried flavour at a concentration equivalent to 0.5 ppb.

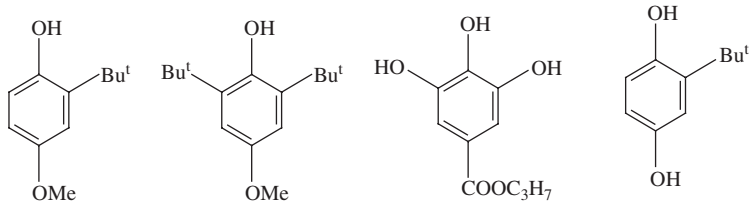
## 1.5.6 Antioxidants

The antioxidants which can be added to fats and to fat-containing foods are rigorously controlled. Only permitted substances can be used, and then only below agreed maximum levels. The matter is further complicated by the fact that not all of these substances are universally accepted. For example, tertiary-butyl hydroquinone is allowed in the USA but not in the EU. Antioxidants permitted in Europe have E numbers (the European Community designation for permitted food additives) assigned to them. Antioxidants can be classified according to their mode of action and, in addition, can be described as natural or synthetic. There is an increasing demand for the former, even though the latter are cheaper and there are not enough natural antioxidants to meet total demand (Section 1.2.4). Much of the large processed-food industry would be impossible to run without antioxidants of some kind. They are essential to inhibiting the development of rancidity and thereby extending shelf life.

Important synthetic antioxidants include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and tertiarybutyl hydroquinone (TBHQ) (Figure 1.7). Natural antioxidants include vitamin E (tocopherols), ascorbyl palmitate, β-carotene and compounds present in a range of spices and herbs.

### 1.5.6.1 Primary antioxidants

Primary antioxidants promote the termination process (Figure 1.7) and thereby shorten the propagation sequence. They are mainly phenols or




BHA (E320) BHT (E321) PG (E310) TBHQ (no E number)

**Figure 1.7** The structures and E numbers of synthetic antioxidants. TBHQ has no E number because it is not a permitted antioxidant in the EU.

amines, though the latter are not accepted as food antioxidants. Some are compounds with extensive conjugated unsaturation, such as carotene. The intermediate radicals (A• or ROOB•) are stabilised by extensive delocalisation of the odd electron and do not support the propagation sequence. They are usually converted to dimers or to substitution products and it is important that, in addition to the antioxidants themselves, their oxidation products are also acceptable in food products.

$$\mathrm{ROO\bullet} + \mathrm{AH} \rightarrow \mathrm{ROOH} + \mathrm{A\bullet} - - - \rightarrow \text{products} \qquad (1.6)$$

$$\mathrm{ROO} + \mathrm{B} \rightarrow \mathrm{ROOB\bullet} - - - \rightarrow \text{products} \qquad (1.7)$$

where AH = amines or phenols and B = β-carotene and so on.

β-carotene and similar substances containing extensive conjugated unsaturation inhibit photooxygenation due to their ability to quench singlet oxygen, but they also inhibit autoxidation through their ability to react with and remove peroxy radicals. When this happens, the odd electron is delocalised over the conjugated polyene system. Under other conditions, β-carotene can act as a prooxidant.

Antioxidants act in a sacrificial manner and the induction period ends when they have been expended. However, some compounds (Section 1.5.6.2) are able to regenerate spent antioxidants and to extend their useful life. Moreover, some antioxidants react twice with peroxy radicals, and sometimes the oxidised antioxidants themselves have further antioxidant activity.

Natural phenolic antioxidants are present in a wide range of plant sources, such as rosemary, thyme, sage, myrtle, tea and oats. Sesame and rice bran oils are very rich in antioxidants and may be added to other oils to stabilise them.

### 1.5.6.2 Secondary antioxidants

Secondary antioxidants operate by inhibiting the initiation process, acting mainly through chelation of the metal ions that promote initiation, particularly

copper and iron. The concentration of metals required to reduce the keeping time of lard at 98 °C is 0.05 ppm for copper and 0.6 ppm for iron. In addition to avoiding these metals in equipment used to handle oils and fats, it is common to add a metal chelator such as ethylenediamine tetra-acetic acid (EDTA), citric acid, phosphoric acid or certain amino acids. These are often added along with chain-breaking primary antioxidants. Some phospholipids are also able to chelate metals.

Citric acid can be used in refining processes in various ways: to assist degumming, in the bleaching step, to convert soaps to the more easily removed free acids and, of greatest importance, to act as a metal chelating agent. It may also be added during storage of crude oils to inhibit oxidation. Citric acid decomposes rapidly above 150 °C and so should be added after deodorisation, even if it has been used earlier in the refining process. It is usually added at the rate of 50–100 ppm in the form of a 30–50% aqueous solution (Law & Berger, 1984).

Other compounds can also be used to enhance antioxidant activity. Vitamin C, for example, is useful because it reacts with spent tocopherols (vitamin E), causing regeneration. However, vitamin C is a water-soluble compound with low lipid solubility and is more commonly employed as ascorbyl palmitate, which is more lipophilic. Ascorbyl palmitate is also reported to act as an oxygen scavenger. Phospholipids promote antioxidant activity through chelation of metal ions and/or by acting as an emulsifying agent, bringing antioxidant and fat together.

These materials are concerned with the inhibition of autoxidation and have no effect on photooxygenation, which proceeds along a different reaction pathway. This process is inhibited by singlet oxygen quenchers, of which the best known are the carotenes. These may be present in natural fats, and if not can be added at levels of 5–10 ppm.

It is important to recognise that antioxidants do not prevent oxidation. They serve only to extend the induction period during which oxidation is very slow and of no great consequence. It follows that appropriate antioxidants should be added before oxidation has started. No amount of antioxidant can regenerate a fat that is already oxidised. The best antioxidant mixtures combine primary and secondary antioxidants and an emulsifying agent. Conditions which promote oxidation must be scrupulously avoided during all handling and storage. This involves avoiding unnecessarily elevated temperatures, unnecessary contact with air (by nitrogen-blanketing when possible, avoiding splashing, which increases access to air, and avoiding half-full containers) and exposure to light. Storage should always be under the best possible conditions and exposure to iron and copper in storage vessels and pipelines should be avoided (see Chapter 9). Changes which can occur during storage have been discussed by Patterson (1989).

### 1.5.7 Stereomutation

Natural unsaturated acids are almost entirely *cis* isomers. These acids can also exist in the *trans* form, which is thermodynamically more stable and is therefore the dominant form in an equilibrium mixture of the two. For example, oleic (*cis*) and elaidic (*trans*) acids form a 1 : 4 equilibrium mixture. The *trans* isomers are usually higher-melting and have different nutritional properties to the *cis* compounds. The change of configuration from *cis* to *trans* is described as stereomutation. It can be promoted by chemical reagents (not discussed here) or by exposure to high temperatures during processing (see Section 1.6.2).

### 1.5.8 Double-bond migration and cyclisation

Double-bond migration (accompanied by stereomutation, particularly in polyene acids) is promoted by acidic and basic reagents, but the conditions required are generally vigorous and migration does not present a serious problem during processing. Double-bond migration occurs during partial hydrogenation (see Chapter 5). At higher temperatures, the migration process may continue to give cyclised products. Monocyclic derivatives may contain a five- or six-membered carbocyclic ring. Such compounds have been recognised in overheated frying oils (Dobson, 1998; Le Querre & Sebedio, 1996).

### 1.5.9 Hydrolysis

Fats can be hydrolysed to free acids by water, in what is probably a homogeneous reaction between fat and water dissolved in the fat phase. Loncin (1952), in a study covering the hydrolysis of various vegetable oils, suggested that the reaction is autocatalytic, accelerating once a certain level of free fatty acid has been reached. His report indicates the risk of hydrolysis occurring when oils are stored for extensive periods at temperatures above ambient. Crespo (1973) studied the hydrolysis of beef tallow and showed that an increase in partial glyceride content accompanies the formation of free acid during this process.

As a result of lipolysis, crude oils frequently contain some free fatty acid, which is removed at appropriate stages during refining (see Chapter 5). The presence, at low levels, of hydrolysis during deodorisation or physical refining has sometimes been given as the reason for the difficulty experienced in removing free fatty acids completely in this part of the refining process, but this has proved difficult to confirm.

Complete hydrolysis of fats is applied on a large scale for the production of fatty acids for the soap and oleochemical industries, using high pressures (20–60 bar) and a temperature of approximately 250 °C. This hydrolytic

reaction can be carried out under milder conditions using biocatalysts (lipases), but such reactions have not yet achieved industrial status.

## 1.5.10 Ester formation

The formation of esters is important in lipid science and technology. Esters can be made by the catalysed reaction of fatty acids with an appropriate alcohol. They can also be produced from existing triacylglycerols (or other esters) by reaction with an alcohol, leading to an exchange of alcohol moieties (alcoholysis), with an acid, leading to an exchange of acyl functions (acidolysis), or with another ester, leading to randomisation of all the possible esters (interesterification). All these processes require a catalyst, which may be acidic, basic or an enzyme (lipase). The latter provides opportunities for specificity that are not possible with wholly chemical operations. Examples of all of these are significant as industrial procedures.

## 1.5.11 Methanolysis

Fatty acid methyl esters are important in gas chromatographic analysis (mg or less) and also on an industrial scale. The methyl esters rank among the basic oleochemicals and are used as solvents, as biodiesel and as intermediates in the preparation of fatty alcohols. Large-scale methanolysis involves appropriate oils and fats, an excess of methanol and preferably a basic catalyst. Many recipes have been reported. One paper suggests that at a molar ratio of 27 : 1 at 23 °C, methanol converts soybean and other oils into methyl esters in a yield >99% in only 7 minutes. This molar ratio represents about equal weights of the two substrates (Boocock *et al.*, 1998). Glycerol is also formed in this reaction, and it can be recovered as a secondary product and then employed as a 'platform chemical' to produce other valuable molecules, such as 1,2-propanediol, 1,3-propanediol, epichlorohydrin (2,3-epoxypropylchloride), acrolein (propenal), glycerol carbonate, polyglycerols and others (Kenar, 2007).

## 1.5.12 Glycerolysis

When a triacylglycerol is heated with glycerol and a basic catalyst such as sodium hydroxide or sodium methoxide, the following equilibrium is established:

$$\text{triacylglycerol} + \text{glycerol} \rightleftharpoons \text{monoacylglycerol} + \text{diacylglycerol} \qquad (1.8)$$

The composition of the equilibrium mixture depends on the amount of glycerol dissolved in the lipid phase. This is an important route to mixtures of monoacylglycerols and diacylglycerols, and 90–95% concentrates of the

former are obtained by molecular distillation. Monoacylglycerols and some derivatives of these are important food emulsifiers (Krog, 1997).

### 1.5.13 Interesterification

The redistribution of acyl chains among glycerol molecules in an oil or mixture of oils is an important way of modifying physical properties and is of greater importance now that partial hydrogenation is less commonly employed for this purpose. This process is known as interesterification and requires either an alkaline or an enzymatic catalyst. Details can be found in Chapters 6 and 7.

## 1.6 Effect of processing on food oil components

Some changes take place in oils and fats during bleaching in the presence of an earth at 80–160 °C, but more extensive alterations are associated with the deodorisation process conducted at 200–260 °C. Ferrari and coworkers (1996) have charted the decline of sterols and tocols and the rise of *trans* acids and polymers during processing. In an early study of cottonseed oil (Gumuskesen & Cakaloz, 1992), it was reported that in order to keep changes to a minimum deodorisation should be carried out at temperatures not exceeding 220 °C for 3 hours at most. Changes in the levels of tocopherols and carotenes were discussed in Sections 1.2.4 and 1.2.5. There have been additional reports by Willner and coworkers (1997) and Schone and coworkers (1998).

In a study of 70 fat samples (vegetable fats, olive oils, animal fats and margarines), sterol dienes were observed at levels between 1 and 200 mg/kg. These are formed by dehydration of 3-hydroxy sterols (Figure 1.8). Since these compounds are probably absent from the native oils, their presence provides some evidence of the history of the oil. The detection of these compounds is indicative that certain refining processes have been carried out, and Grob and coworkers (Grob *et al*., 1992; Grob & Bronz, 1994) showed that claims that many oils were cold-pressed and therefore nonrefined were false. Similar changes have been reported by Kochhar (1983), Schulte (1994) and Amelia and coworkers (1998).

Vegetable oils, particularly soybean, rape/canola and olive, are significant dietary sources of vitamin $K_1$. However, this compound is converted to

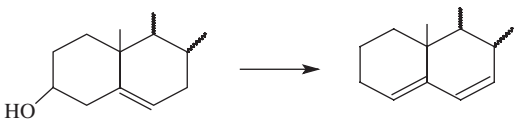



**Figure 1.8** Formation of steradienes by thermal dehydration.

its 2′3′-dihydro derivative during partial hydrogenation of an oil and it is estimated that ~30% of total vitamin $K_1$ intake is in this dihydro form in the US diet. Further investigation of the biological activity of this artefact is clearly desirable (Booth *et al*., 1996a, 1996b).

Heat-induced stereomutation of linolenic acid and its esters is very slow at 190 °C but quicker under the normal conditions for semicontinuous or continuous deodorisation at 210–270 °C. At these temperatures, about 35% of natural (all-*cis*) linolenic acid is converted to four of the seven possible *trans* isomers (9*c*12*c*15*t*, 48–50% of total *trans* isomers; 9*t*12*c*15*c*, 41%; 9*c*12*t*15*c*, 6–7%; and 9*t*12*c*15*t*, 4–5%). The similar reaction with linoleate esters is 12–15 times slower (Wolff, 1992).

Recently there has been some concern about the presence of traces of glycidol (epoxypropanol) in vegetable oils and of 3-chloropropane-1,2-diol (monochloropropanediol, MCPD, $ClCH_2CH(OH)CH_2OH$) in prepared foods. There is some evidence that glycidol may be carcinogenic. Both compounds may be present as acyl esters. Appropriate methods of analysis are being devised. It is believed that glycidol is a product of high-temperature deodorisation. MCPD is produced from the epoxide in a reaction involving a chloride ion, probably from salt (MCPD Web site: http://www.aocs.org/tech/3-mcpd.cfm, last accessed 8 January 2013).

When exposed to high temperatures (especially under frying conditions), PUFAs undergo cyclisation to give monocyclic compounds with five- or six-membered rings (Dobson, 1998; Le Querre & Sebedio, 1996). The formation of polycyclic compound is less well understood (Gertz, 2006).

A study of fish oil deodorisation indicates that these oils should not be heated at temperatures above 180 °C, in order to avoid stereomutation of eicosapentaenoic acid and docosahexaenoic acid. At higher temperatures, polymers, cyclic monomers and geometrical isomers are formed (Fournier *et al*., 2006).

Cottonseed oil is unusual in that it contains malvalic acid ($C_{18}$) and sterculic acid ($C_{19}$) at combined levels up to 1%. These acids contain a cyclopropene unit and are toxic, but they are removed or modified to less toxic materials during processing – especially deodorisation and hydrogenation – and the product is entirely safe.

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