14 Edible Fats* and Oils

14.1 Foreword

Most fats and oils consist of triacylglycerides (recently also denoted as triacylglycerols; cf. 3.3.1) which differ in their fatty acid compositions to a certain extent. Other constituents which make up less than 3% of fats and oils are the unsaponifiable fraction (cf. 3.8) and a number of acyl lipids; e. g., traces of free fatty acids, mono- and diacylglycerols.

The term "fat" generally designates a solid at room temperature and "oil" a liquid. The designations are rather imprecise, since the degree of firmness is dependent on climate and, moreover, many fats are neither solid nor liquid, but are semi-solid. Nevertheless, in this chapter, unless specifically emphasized, these terms based on consistency will be retained.

14.2 Data on Production and Consumption

Data on the production of oilseeds and other crops are summarized in Table 14.0. The world production of vegetable fats has multiplied since the time before the Second World War (Table 14.1). There has been a significant rise in production since 1964 of soybean, palm and sunflower oils, as well as rapeseed oil. Soybean oil, butter and edible beef fat and lard are most commonly produced in FR Germany (Table 14.1). The per capita consumption of plant oils in Germany has increased in the past years (Table 14.2).

* Butter is dealt with in Chapter 10.2.3.

14.3 Origin of Individual Fats and Oils

14.3.1 Animal Fats

14.3.1.1 Land Animal Fats

The depot fats and organ fats of domestic animals, such as cattle and hogs, and milk fat, which was covered in Chapter 10, are important animal raw materials for fat production. The role of sheep fat, however, is not significant. The major fatty acids of these three sources are oleic, stearic and palmitic (Table 14.3).

It should be noted that the fatty acid composition of individual fat samples may vary greatly. The fat composition of land animals is affected by the kind and breed of animal and by the feed. The composition of plant fats depends on the cultivar and growth environment, i. e. climate and geographical location of the oilseed or fruit plant (cf. Fig. 3.3.1.5). Therefore only average values are given in the following tables dealing with fatty acid composition.

In contrast to oil from plant tissue, the recovery of animal fat is not restricted by rigid cell walls or sclerenchyma supporting tissue. Only heating is needed to release fat from adipose tissue (dry or wet rendering with hot water or steam). The fat expands when heated, tearing the adipose tissue cell membrane and flowing freely. Further fat separation is simple and does not pose a technical problem (Fig. 14.1).

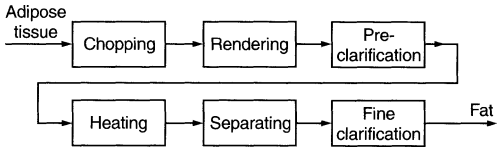


Fig. 14.1. Steps involved in wet rendering

Table 14.0. Production of major oilseeds, 2006 (1,000)[a]

Continent	*(Castorbean)* Castor oil seed	Sunflower seed	Rapeseed	Sesame seed
World	1140	31,332	48,974	3338
Africa	35	868	95	976
America, Central	1	–	–	54
America, North	–	1118	9823	–
America, South and Caribbean	107	4218	228	153
Asia	998	5325	21,421	2207
Europe	1	19,709	16,963	1
Oceania	–	95	444	–

Continent	Linseed	Safflower seed	Cottonseed	Copra
World	2570	583	44,173	5370
Africa	161	11	2887	194
America, Central	–	72	219	208
America, North	1321	89	6666	–
America, South and Caribbean	70	90	2513	263
Asia	764	356	30,665	4714
Europe	245	1	597	–
Oceania	10	36	844	198

Continent	Palm kernel	Palm oil	Olives	Olive oil
World	10,641	37,291	16,926	2710
Africa	1685	2359	2636	340
America, Central	164	503	13	1
America, North	–	–	45	1
America, South and Caribbean	599	1791	193	24
Asia	8256	32,755	2536	285
Europe	–	–	11,493	2060
Oceania	101	386	23	–

Country	*(Castorbean)* Castor oil seed	Country	Sunflower seed	Country	Rapeseed
India	730	Russian Fed.	6753	China	12,649
China	240	Ukraine	5324	Canada	9105
Brazil	92	Argentina	3798	India	8130
Ethiopia	15	China	1820	Germany	5337
Thailand	11	Romania	1526	France	4144
Paraguay	11	France	1440	UK	1870
Vietnam	5	Bulgaria	1197	Poland	1652
South Africa	5	Hungary	1165	Czech. Rep.	880
Philippines	4	India	1120	USA	718
Angola	4	Turkey	1118	Russian Fed.	522
$\sum$ (%)[b]	98	$\sum$ (%)[b]	80	$\sum$ (%)[b]	92

Table 14.0. continued

Country	Sesame seed	Country	Linseed	Country	Safflower seed
China	666	Canada	1041	India	230
India	628	China	480	USA	87
Myanmar	580	USA	280	Kazakhstan	75
Sudan	200	India	210	Mexico	72
Uganda	166	Ethiopia	128	Australia	36
Ethiopia	160	Argentina	54	China	30
Nigeria	100	Bangladesh	50	Argentina	18
Bangladesh	50	UK	49	Kyrgyzstan	14
Paraguay	50	France	43	Ethiopia	6
Tanzania	48	Russian Fed.	36	Tanzania	5
∑ (%)[b]	79	∑ (%)[b]	92	∑ (%)[b]	98

Country	Cottonseed	Country	Copra	Country	Palm kernel
China	13,460	Philippines	2200	Malaysia	4125
India	7128	Indonesia	1310	Indonesia	3860
USA	6666	India	750	Nigeria	1250
Pakistan	4065	Vietnam	243	Thailand	191
Uzbekistan	2376	Mexico	204	Colombia	178
Brazil	1785	Sri Lanka	65	Brazil	122
Turkey	1350	Thailand	65	Ecuador	95
Australia	844	Malaysia	51	Cameroon	75
Syrian Arab Rep.	664	Mozambique	46	Côte d'Ivoire	74
Greece	520	Côte d'Ivoire	45	China	62
∑ (%)[b]	88	∑ (%)[b]	93	∑ (%)[b]	94

Country	Palm oil	Country	Olives	Country	Olive oil
Indonesia	15,900	Spain	5032	Spain	955
Malaysia	15,880	Italy	3424	Italy	627
Nigeria	1287	Greece	2661	Greece	439
Colombia	711	Turkey	1600	Tunisia	205
Thailand	685	Tunisia	1000	Syrian Arab Rep.	130
Côte d'Ivoire	330	Morocco	750	Turkey	90
Ecuador	291	Syrian Arab Rep.	501	Morocco	85
China	230	Algeria	365	Algeria	32
Congo	175	Egypt	310	Jordan	27
Honduras	175	Portugal	276	Portugal	26
∑ (%)[b]	96	∑ (%)[b]	94	∑ (%)[b]	97

[a] Soybean and peanuts are presented in Table 16.1.
[b] World production = 100%.

14.3.1.1.1 Edible Beef Fat

Edible beef fat is obtained from bovine adipose tissue covering the abdominal cavity and surrounding the kidney and heart and from other compact, undamaged fat tissues. The fat is light-yellow due to carotenoids derived from animal feed. It is of a friable, brittle consistency and melts between 45 and 50 °C.

The fatty acid composition of beef fat (Table 14.3) is not influenced greatly by feed intake, but that of hog fat (lard) is. The composition of edible beef fat triacylglycerols is given in 3.3.1.4. The following commercial products are prepared from beef fat: *Prime Beef Fat ("premier jus")* is obtained by melting fresh and selected fat trimmings in water heated to 50–55 °C. The acid value resulting from lipolytic action (cf. 14.5.3.1)

Table 14.1. World production of plant fats (in 10^6 t)

Fat/oil	1935/39	1965	1981	2004
Soya oil	1.23	4.86	12.5	31.9
Sunflower oil	0.56	2.38	4.5	9.5
Cottonseed oil	1.56	2.57	3.25	3.9
Peanut oil	1.51	3.17	2.95	4.8
Rapeseed (Canola) oil	1.21	1.47	3.75	13.1
Palm kernel and palm oil	1.33	1.6	6.16	31.6
Coconut oil	1.93	2.23	2.93	3.3
Olive oil	0.87	1.95[a]	1.33[b]	2.8

[a] Production data for 1964
[b] An estimate for 1982

Table 14.2. Consumption of plant oils and margarine in Germany (kg per capita per year)

Year	Plant oils	Margarine
1993	9.7	7.7
1995	11.4	7.1
1997	13.2	7.3

Table 14.3. Average fatty acid composition of some animal fats (weight-%)

Fatty acid	Beef tallow	Sheep tallow	Lard	Goose fat
12:0	0	0.5	0	0
14:0	3	2	2	0.5
14:1 (9)	0.5	0.5	0.5	0
16:0	26	21	24	21
16:1 (9)	3.5	3	4	2.5
18:0	19.5	28	14	6.5
18:1 (9)	40	37	43	58
18:2 (9, 12)	4.5	4	9	9.5
18:3 (9, 12, 15)	0	0	1	2[a]
20:0	0	0.5	0.5	0
20:1				
20:2	0	0.5	2	
Other	3	3	0	0

[a] It includes fatty acid 20:1.

is not allowed to exceed 1.3 (corresponding to approx. 0.65% free fatty acid).
This beef fat, when heated to 30–34 °C, yields two fractions: oleomargarine (liquid) and oleostearine (solid). Oleomargarine is a soft fat with a consistency similar to that of melted butter. It is used by the margarine and baking industries. Oleostearine (pressed tallow) has a high melting point of 50–56 °C and is used in the production of shortenings (cf. Table 14.18). *Edible Beef Fat (secunda beef fat)* is obtained by melting fat in water at 60−65 °C, followed by a purification step. It has a typical beef fat odor and taste and a free fatty acid content not exceeding 1.5%. Lower quality tallow has only industrial or technical importance, for example, as raw material for the soap and detergent industries.

14.3.1.1.2 Sheep Tallow

The unpleasant odor adhering to sheep tallow is difficult to remove, hence it is not used as an edible fat. Sheep tallow is harder and more brittle or friable than beef tallow. The fatty acid composition of sheep tallow is presented in Table 14.3.

14.3.1.1.3 Hog Fat (Lard)

Hog (swine) fat, called lard, is obtained from fat tissue covering the belly (belly trimmings) and other parts of the body. The back fat is mainly utilized for manufacturing bacon. After tallow and butter, lard is currently the animal fat which is consumed the most (Table 14.1). Its grainy and oily consistency is influenced by the breed and feeding of hogs.
Some commercial products are:
Lard obtained exclusively from belly trimmings (abdominal wall fat). This is the highest quality *neutral lard*. It has a mild flavor, is white in color and its acid value is not more than 0.8.
Lard from other organs and from the back is rendered using steam. The maximum acid value is 1.0.
Lard obtained from all the dispersed fat tissues, including the residues left after the recovery of neutral lard, is rendered in an autoclave with steam (120–130 °C). This type of lard has a maximum acid value of 1.5.
In contrast to the composition of triacylglycerols found in beef fat (Table 3.13), lard contains fewer triacylglycerols of the type SSS and more of the types SUU, USU and UUU (S = saturated; U = unsaturated fatty acid). As a consequence, lard melts at lower temperatures and over a range of temperatures rather than sharply at a single temperature, and its shelf life is not particularly long. In comparison with beef, pig depot fat

contains the saturated fatty acids mainly in the sn-2 position. This difference can be used in the detection of lard, e. g., to control exports to Islamic countries.

14.3.1.1.4 Goose Fat

As the only kind of poultry fat produced, goose fat is a delicacy. Its production is insignificant in quantity. The fatty acid composition of goose fat is given in Table 14.3.

14.3.1.2 Marine Oils

Sea mammals, whales and seals, and fish of the herring family serve as sources of marine oils. These oils typically contain highly unsaturated fatty acids with 4–6 allyl groups, such as (double bond positions are given in brackets): 18:4 (6, 9, 12, 15); 20:5 (5, 8, 11, 14, 17); 22:5 (7, 10, 13, 16, 19); and 22:6 (4, 7, 10, 13, 16, 19) (Table 14.4). Since these acids are readily susceptible to autoxidation, marine oils are not utilized directly as edible oils, but only after hydrogenation of double bonds and refining.
Of analytical interest is the occurrence in marine oils of about 1% branched methylated fatty acids, for example, 12-methyl- and 13-methyltetradecanoic acids or 14-methylhexadecanoic acid. These acids are also readily detectable in hardened marine oils.

Table 14.4. Average fatty acid composition of some marine oils (weight-%)

Fatty acid	Blue whale	Seal	Herrin (*Clupea harengus*)	Pilchard[a]	Menhaden (*Brevoortia tyrannus*)
14:0	5	4	7.5	7.5	8
16:0	8	7	18	16	29
16:1	9	16	8	9	8
18:0	2	1	2	3.5	4
18:1	29	28	17	11	13
18:2	2	1	1.5	1	1
18:3	0.5		0.5	1	1
18:4	0.4		3	2	2
20:1	22	12	9.5	3	1
20:4	0.5		0.5	1.5	1
20:5	2.5	5	9	17	10
22:1	14	7	11	4	2
22:5	1.5	3	1.5	2.5	1.5
22:6	3	6	7.5	13	13

[a] Trade name of grown sardines (*Sardinóps caerulea*).

14.3.1.2.1 Whale Oil

There are two suborders of whales: Baleen whales which have horny plates rather than teeth, and whales which have teeth. The blue and the finback whales, both live on plankton, and belong to the Baleen suborder. The oils from these whales do not differ substantially in their fatty acid compositions.
A blue whale, weighing approx. 130 t, yields 25–28 t of oil, which is usually recovered by a wet rendering process. The ruthless exploitation of the sea has nearly wiped out the whale population, hence their raw oil has become a rare product.

14.3.1.2.2 Seal Oil

The composition of seal oil is similar to that of whale oil (Table 14.4).

14.3.1.2.3 Herring Oil

The following members of the herring fish family are considered to be satisfactory sources of oil: herring, sardines (Californian or Japanese pilchards, etc.), sprat or brisling, anchovies (German Sardellen or Swedish sardell) and the Atlantic menhaden. The fatty acid compositions of the various fish oils differ from each other (Table 14.4).

14.3.2 Oils of Plant Origin

All the edible oils (with the sole exception of oleomargarine-type products) are of plant origin. With regard to the processes used to recover plant oils, it is practical to divide them into fruit and oilseed oils. While only two fruits are of economic importance in oil production, the number of oilseed sources is enormous.

The oils are sold and consumed as pure oil from a single oilseed plant or fruit plant, for example, olive, sunflower or corn oils, or are marketed and used as blended oils, which are generally designated as edible, cooking, frying, table or salad oil.

14.3.2.1 Fruit Pulp Oils

The oils obtained from the fruits of the olive tree and several oil palm species are of great economic importance. The fatty acid compositions of the oils of these fruits are summarized in Table 14.5. Due to the high enzymatic activity in fruit pulp, particularly of lipases, the shelf life of fruit oil is severely limited.

14.3.2.1.1 Olive Oil

Olive oil is obtained from the pulp of the stone fruit of the olive tree (*Olea europaea sativa*).

Table 14.5. Characteristics of olives (fruits/oil) and oil palm

	Olive (*Olea europaea sativa*)	Oil palm (*Elaeis guineensis*)
Fruits		
Length (cm)	2–3	3–5
Width (cm)	2–3	2–4
Fruit pulp (weight-%)	78–84	35–85
Fruit seed (weight-%)	14–16	15–65
Fruit pulp (mesocarp)		
Oil (weight-%)	38–58	30–55
Moisture (weight-%)	to 60	35–45
Fruit pulp oil		
Solidification point (°C)	−5 to −9	27–38
Average fatty acid composition (weight-%)		
	Olive oil	Palm oil
14:0	0	1
16:0	11.5	43.8
16:1	1.5	0.5
18:0	2.5	5
18:1 (9)	75.5	39
18:2 (9,12)	7.5	10
18:3 (9,12,15)	1.0	0.2
20:0	0.5	0.5

More than 90% of the world's olive harvest comes from the Mediterranean region, primarily in Italy and Spain (cf. Table 14.0). Olive tree plantations are found to a smaller extent in Japan, Australia, California and South America.

Oil Production. The disintegrated fruit is kneaded to release the oil droplets from the pulp, occasionally by adding common salt.
The oil is then pressed out or separated by gravity decantation. The initial cold pressing provides virgin oil (provence oil). This is then followed by warm pressing at about 40 °C.
In addition to the conditions used for oil recovery, the quality of olive oil is affected by the ripeness of the fruit (overripe fruit is not preferred) and length of storage. In virgin oils there is a relationship between sensory properties and the content of free fatty acids:

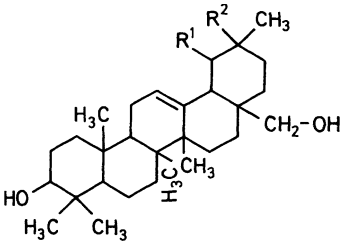
- Virgin olive oil extra (*extra vierge*): Pleasant aromatic taste; up to 0.8% free fatty acids, calculated as oleic acid
- Virgin olive oil (*fine vierge*): Slightly less aromatic in taste; up to 2% free fatty acids
- Lampante oil: Much less taste; more than 2% free fatty acids

For the isolation of refined olive oil, the oil cake is extracted with a solvent. The resulting extraction oil ("sansa" oil) is refined so that it contains at most 0.3% of free fatty acids.
From time to time, the expensive *extra vierge* oils are adulterated with refined "lampante" oils or extraction oils. In particular, the concentrations of waxes, sterol esters, and of the triterpene alcohols erythrodiol (I) and uvaol (II, cf. Formula 14.1) are used for an analytical differentiation (Table 14.6 and 14.5.2.4).
On storage or on thermal treatment, e. g., with steam, 1,2-diacylglycerides (DG) isomerize to 1,3-DG. After separation of the DG fraction on a silica gel column and silylation, 1,2- and 1,3-DG can be determined by gas chromatography. The ratio 1,2-/1,3-DG is calculated from their areas; a value of less than 45% 1,2-DG is regarded as critical and indicates a loss of quality resulting from a longer storage period. Fresh oils contain more than 70% 1,2-DG, the content falling by about 1% per month. If the cold index is also raised, then heat treatment has occurred. The ratio of pyropheophytin A (cf. 17.1.2.9.1) to pheophytin A is known as the cold index.

Table 14.6. Olive oils: concentrations of the minor constituents

Type	Alcohols[a]	Waxes[a,b]	Sitosterol[a]		Erythrodiol[a]	Erythrodiol + Uvaol (%)[c]
			free	esterified		
Extra vierge oil	67	40	914	219	13	1
"*Lampante*" oil, raw	84	292	945	877	10	0.6
"*Lampante*" oil, refined	44	180	692	544	8	0.8
Extraction oil, raw	725	3294	1234	2702	283	13.5
Extraction oil, refined	75	3277	659	2624	116	5.6

[a] Values in mg/kg.
[b] Sum of the wax esters C_{40}–C_{46}.
[c] Percentage of the sum of sterols and triterpene dialcohols.



I : R^1 : H, R^2 : CH_3
II : R^1 : CH_3, R^2 : H (14.1)

The aroma of natural oils is of special interest. The most important aroma substances of two *extra vierge* olive oils with different aromas are shown in Table 14.7. In oil I, green, fruity, and fatty notes are predominant while in oil II, the compounds with a green odor are concealed by an aroma substance with a "blackcurrant" odor, possibly due to a special variety of the olives. The compound involved is the extremely intensive odorant 4-methoxy-2-methyl-2-butanethiol (cf. Table 5.34), which has the highest aroma value of all the volatile compounds in oil II (Table 14.7).

The fatty acid composition of tea seed oil is very similar to that of olive oil. However, these two oils can be differentiated by using the *Fitelson* Test (cf. Table 14.21).

14.3.2.1.2 Palm Oil

This oil is obtained from oil palm, the utilization of which is constantly increasing (cf. Table 14.1). Palm plantations are found primarily in western Malaysia and Indonesia (cf. Table 14.0). The fruits provide two different oils, the first from the pulp and the second from the seeds.

Oil Production. The fruit cluster, which contains about 3000–6000 fruits, is first steam-treated to inactivate the high lipase activity and to separate the pulp from the seed. The oil is recovered by pressing the disintegrated pulp. The crude

Table 14.7. Important aroma substances of two *extra vierge* olive oils[a]

Aroma substance	Aroma quality	Oil I		Oil II	
		C	A_x	C	A_x
Isobutyric acid ethyl ester	Fruity	4.9	7	14	19
2-Methylbutyric acid ethyl ester	Fruity	3.9	5	14	19
Cyclohexanoic acid ethyl ester	Fruity	1.6	4.2	4.3	11
(Z)-3-Hexenal	Green	33	12	53	19
(Z)-2-Nonenal	Green, fatty	9	15	10	17
Acetic acid	Like vinegar	10,490	10	6680	6
4-Methoxy-2-methyl-2-butanethiol	Like blackcurrants	n.d.		1.8	40

[a] Oil I is from Italy, oil II from Spain; concentration C is in µg/kg and the aroma value A_x is calculated on the basis of the odor thresholds (retronasal) in an oil; n.d.: not detectable ($C < 0.05$ µg/kg).

oil is then clarified by centrifugation. Washing with hot water, followed by drying, provides a crude oil product that has a high carotene content (cf. 3.8.4.5) and, hence, the color of the oil is yellow to red. During refining (cf. 14.4.1), the palm oil color is destroyed by bleaching and the free fatty acids are removed. Palm fruit characteristics and oil composition are given in Table 14.5.
Adulteration of palm oil with palm stearin increases the ratio of the triacylglycerides PPP to MOP, which is usually between 3.5 and 4.5.

14.3.2.2 Seed Oils

Some oilseeds have acquired great significance in the large-scale industrial production of edible oils. After a general review of their production, some individual oils, grouped together according to their characteristic fatty acid compositions, will be discussed.

14.3.2.2.1 Production

Conditioning. The ground or flaked seeds are heated with live steam of about 90 °C to facilitate oil recovery. This treatment ruptures all the cells, partly denatures the proteins and inactivates most of the enzymes. The temperature is regulated to avoid formation of undesirable colors and aromas.
After conditioning and moisture adjustment to about 3%, the oil is obtained by pressing and/or solvent extraction. The choice between these two processes depends on the oil content of the seed. Solvent extraction is the only economic choice for seeds with an oil content below 25%.

Pressing. The oil is removed by pressure from an expeller or screw press. The residual oil in the resultant meal flakes is 4–7%. It is, however, more economical to apply lower pressures and to leave 15–20% of the oil in the flakes, and then to remove this oil by a solvent extraction process ("prepress solvent extraction" process).

Extraction. The ground seeds are rolled into thin flakes by passing them between smooth steel rollers. This flaking step provides the enlarged surface area needed for efficient solvent extraction. The extraction is performed using petroleum ether, i. e. technical hexane, as a solvent (boiling point 60–70 °C). In addition to n-hexane, it contains 2- and 3-methylpentane and 2,3-dimethylbutane and is free of aromatic compounds.
Solvent removal from the raw oil-solvent mixture, called miscella, is achieved by distillation. The maximum amount of solvent remaining in the oil is 0.1%. The oil-free flakes are then steamed to remove the solvent ("*desolventizing*") and, after dry heating ("*toasting*"), cooled and sold as protein-rich feed for cattle. The production of oil from soybeans is schematically shown in Fig. 14.2.
The crude oil obtained either by pressing or solvent extraction contains suspended plant debris, protein and mucous substances. These impurities are removed by filtration.

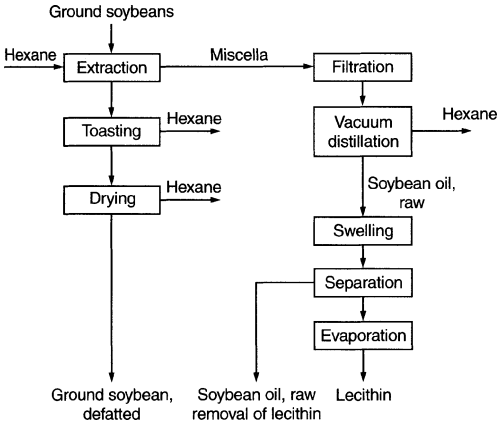


Fig. 14.2. Production of oil and lecithin from soybeans

14.3.2.2.2 Oils Rich in Lauric and Myristic Acids

The most important representatives of this group of oils are coconut, palm seed and babassu oils. The acceptable shelf life stability of these oils is reflected in their fatty acid compositions (Table 14.8). Since linoleic acid is present in negligible amounts, autoxidative changes in these oils do not occur. However, when these oils are used in preparations containing water, microbiological deterioration may occur; this involves release of free C_8–C_{12} fatty acids and their partial degra-

Table 14.8. Characteristics of palm kernel oils

	Oil palm (*Elaeis guineensis*)	Coconut palm (*Cocos nucifera*)	Babassu palm (*Orbignya speciosa*)
Kernel oil content (weight-%)	40–52	63–70	67–69
Fat/oil melting range (°C)	23–30	20–28	22–26
Average fatty acid composition (weight-%)			
8:0	6	8	4.5
10:0	4	6	7
12:0	47	47	45
14:0	16	18	16
16:0	8	9	7
18:0	2.5	2.5	4
18:1 (9)	14	7	14
18:2 (9,12)	2.5	2.5	2.5

dation to methyl ketones ("perfume scent rancidity", cf. 3.7.6).

Coconut and palm seed oils are important ingredients of vegetable margarines which are solid at room temperature. However, they melt in the mouth with a significant heat uptake, producing a cooling effect.

Coconut oil is obtained from the stone fruit of the coconut palm, which grows throughout the tropics. The moisture content of the oil-containing endosperm, when dried, decreases from 50% to about 5–7%. Such crushed and dried coconut endosperm is called "copra" and is sold under this name as a raw material for oil production around the world.

Palm kernel oil is obtained from the kernels of the fruit of the oil palm. The kernels are separated from the fruit pulp, then removed from the stone shells and dried prior to recovery of the oil.

Babassu oil is obtained from seeds of the babassu palm, which is native to Brazil. This oil is rarely found on the world market and is mainly consumed in Brazil.

14.3.2.2.3 Oils Rich in Palmitic and Stearic Acids

Cocoa butter and fats (solid at room temperature) belong to this group, with the latter referred to as cocoa butter substitutes ("cocoa butter interchangeable fats"). They are relatively hard and can crystallize in several polymorphic forms (cf. 3.3.1.2). Their melting points are between 30 and 40 °C. The relatively narrow melting range for cocoa butter, as well as for some other types of butter, is to be expected (Table 14.9). When cocoa butter melts in the mouth, a pleasant, cooling sensation is experienced (cf. 14.3.2.2.2). This is characteristic of only a few types of triacylglycerols present in fats which contain predominantly palmitic, oleic and stearic acids. This fatty acid composition is also reflected by the resistance of these fats to autoxidation and microbiological deterioration (Table 14.9). These fats are utilized preferentially in the manufacturing of chocolates, candy and confections.

Table 14.9. Fatty acid composition of cocoa butter and cocoa butter substitutes

Trade name	Cocoa butter	Illipè butter (Mowrah butter)	Borneo tallow (Tengkawang fat, Illipè butter)	Shea butter (Kerité fat)
Source	Cacao tree (*Theobroma cocao*)	*Madhuca logifolia*	*Shorea stenoptera*	*Butyrospermum parkii*
Fat, melting range (°C)[a]	28–36	24.5–28.5	28–37	23–42
	Average fatty acid composition (weight-%)			
16:0	25	28	20	7
18:0	37	14	42	38
18:1 (9)	34	49	36	50
18:2 (9, 12)	3	9	<1	5

[a] The melting ranges reflect a pronounced fat polymorphism (cf. 3.3.1.2); the highest temperature given represents the melting point of the stable fat modification.

Cocoa butter is the fat from cocoa beans. The seed germ contains up to 50–58% of the fat, which is recovered as a by-product during cocoa manufacturing (cf. 21.3.2.7). It is light yellow and has the pleasant, mild odor of cocoa. Cocoa butter contains 1,3-dipalmito-2-olein, 1-palmito-3-stearo-2-olein, and 1,3-distearo-2-olein in an almost constant ratio of 22:46:31 (% peak area). Since cocoa butter substitutes clearly differ in the content of these TGs, the amount of cocoa butter can be determined by HPLC of the TGs. Bromination of the double bonds (cf. 3.3.1.4) improves the separation of the three TGs. Other indicators of cocoa butter are given in 3.8.2.3.1 and 3.8.2.4. The denotation of the "cocoa butter interchangeable fats" may be confusing since fats from diverse sources are sometimes marketed under a collective name such as Illipè butter. Confusion can be avoided by providing the Latin name of the plant, i. e. the source of the fat.

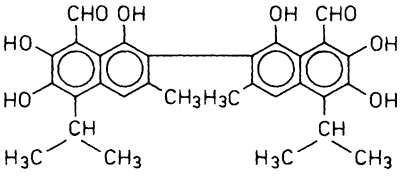
Shea Butter (Kerité Fat) is obtained from seeds of a tree which grows in western Africa and the cultivation of which appears to be uneconomical. The high content of unsaponifiable matter (up to 11%) in this kind of butter is of interest.

Borneo Tallow (Illipè Butter) is obtained from the seeds of a plant native to Java, Borneo, the Philippines and India. It serves as a valuable edible fat in the Tropics. *Mowrah butter* (often marketed as Illipè butter) is derived from a different plant (*Madhuca longifolia*) and is also indigenous to the Asian tropics.

14.3.2.2.4 Oils Rich in Palmitic Acid

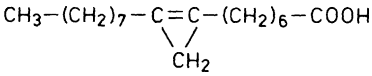
Oils in this group contain more than 10% palmitic acid along with oleic and linoleic acids (cf. Table 14.10).

Cottonseed Oil is obtained from seeds of many cotton plant cultivars. The plant is widely cultivated (cf. Table 14.0). The raw oil is dark, usually dark red, and has a unique odor. It contains a poisonous phenolic, gossypol,



(14.2)

which is removed during refining. Another substance present in this oil is malvalia acid,



(14.3)

which survives refining, but not hydrogenation of the oil. This substance is responsible for detection

Table 14.10. Oils rich in palmitic acid

	Cottonseed (*Gossypium*)	Corn germ (*Zea mays*)	Wheat germ[a] (*Triticum aestivum*)	Pumpkin seed (*Cucurbitapepo*)
Seed oil content (weight-%)	22–24	3.5–5[b]		35
Solidification point (°C)	0 to +4	−10 to −18		−15 to −16
	Average fatty acid composition (weight-%)			
14:0	1.5	0	0	0
16:0	22	10.5	17	16
18:0	5	2.5	1	5
20:0	1	0.5	0	0
16:1 (9)	1.5	0.5	0	0.5
18:1 (9)	16	32.5	20	24
18:2 (9,12)	55	52	52	54
18:3 (9,12,15)	0	1	10	0.5

[a] Oil content in germ amounts to 8–11 weight-%.

[b] Of the seed oil content 80% is located in germ and the rest in seed endosperm.

or identification of the oil by the *Halphen* reaction (cf. Table 14.21).

At temperatures below +8 °C, cottonseed oil becomes turbid due to crystallization of high melting point triacylglycerols. Such undesirable low temperature characteristics are avoided using a "winterization" process (cf. 14.4.4).

Cereal Germ Oils. All cereals contain significant amounts of oil in the germ. It is available after the germ is separated during grain processing. Corn (maize) oil is the most important. Germ separation is achieved during dry or wet processing of the kernels into corn meal and starch (cf. 4.4.4.14.1). The oil is recovered from the germ collected as a by-product by pressing and solvent extraction. After crude oil refining, the corn waxes which originate from the skin-like coating of the epidermis (the cuticle), are removed by a winterization process (cf. 14.4.4).

Corn oil is suitable for manufacture of margarine and mayonnaise (creamy salad dressing), but is used preferentially as salad and cooking oil.

The oil present in wheat and rice is also concentrated in the germ. This oil can be recovered by pressing and/or solvent extraction of the germ. Wheat germ oil has a high content of tocopherol and, therefore, additional nutritive value. Rice germ oil is consumed to a minor extent in Asia. Pumpkin oil is obtained by pressing dehulled pumpkin seeds. In southern Europe it is utilized as an edible oil. It is brown in color and has a nut-like taste.

14.3.2.2.5 Oils Low in Palmitic Acid and Rich in Oleic and Linoleic Acids

A large number of oils from diverse plant families belong to this group (cf. Table 14.11). These oils are important raw materials for manufacturing margarine.

The sunflower is the most cultivated oilseed plant in Europe. Data on the production of the sunflower in regions and countries are given in Table 14.0. Prepressing of dehulled sunflower seeds yields a light yellow oil with a mild flavor. The oil is suitable for consumption once it is clarified mechanically. Refined oils are used in large amounts as salad oil or as frying oil and as a raw material for margarine production. The refining of the oil includes a wax-removal step.

Two legume oils, soybean and peanut (or ground nut), are of great economic significance (cf. Table 14.1). Soybean oil (fatty acid composition in Table 14.11) is currently at the top of the world production of edible oils of plant origin. It is cultivated mostly in the United States, Brazil and China. The refined oil is light yellow and has a mild flavor. It contains in low concentrations (Table 3.9) branched furan fatty acids which are rapidly oxidized on exposure to light. In fact, two of these fatty acids, which differ only in the length of the carboxyl ends (see Formula 3.3), produce the intensive aroma substances 3-methyl-2,4-nonandione (MND) and diacetyl in a side reaction with singlet oxygen. These aroma substances are significantly involved in the "bean-like, buttery, hay-like" aroma defect called *reversion flavor*. In the case of the soybean oils listed in Table 14.12, the two furan fatty acids were almost completely oxidized after 48 hours. However, the amounts of MND formed were very different. This is put down to differences in the stability of the intermediate hydroperoxide (cf. Fig. 3.25).

Other experiments have shown that the hydroperoxides formed from furan fatty acids on exposure to light fragment to the dione, even if the soybean oil is subsequently stored in the dark. In the complete absence of light, soybean oil is relatively stable. The shelf life of the oil is also improved significantly by partial hydrogenation to give a melting point range of 22–28 °C or 36–43 °C. Such oils are utilized as raw materials for the manufacture of margarine and shortening (semi-solid vegetable fats used in baked products, such as pastry, to make them crisp or flaky).

Cultivation using traditional and genetic engineering techniques has made it possible to develop soybean genotypes which have a fatty acid composition which meets the different demands made on edible oils. Table 14.13 shows the extent to which the fatty acid composition of soybean oil has been changed. The genotypes *low linolenic* and *high oleic* are considerably more stable to oxidation than the normal line. In addition, the composition of high oleic corresponds to that of a salad oil, partial hydrogenation is no longer required. Palmitic acid is decreased in the types *low palmitic* and *low saturate*, as it is involved in the increase in cholesterol in LDL (cf. 3.5.1.2)

Table 14.11. Oils low in palmitic acid and rich in oleic and linoleic acids

	Sunflower (*Helianthus annuus*)	Soya (*Glycine max.*)	Peanut[a] (*Arachis hypogaea*)	Rapeseed[b] (*Brassica napus*)	Sesame (*Sesamum indicum*)	Safflower (*Carthamus tinctorius*)	Linseed (*Linum usitatissimum*)	Poppy (*Papaver somniferum*)	Walnut (*Juglans regia*)
Seed oil content (weight-%)	25–30	18–23	42–52	ca. 40	45–55	32–43	32–43	40–51	58–71
Solidification point (°C)	−18 to −20	−8 to −18	−2 to +3	0 to−2	−3 to −6	−13 to −20	−18 to −27	−15 to −20	−15 to −20
Average fatty acid composition (weight-%)									
16:0	6.5	10	10	4	8.5	6	6.5	9.5	8
18:0	5	5	3	1.5	4.5	2.5	3.5	2	2
20:0	0.5	0.5	1.5	0.5	0.5	0.5	0	0	1
22:0	0	0	3	0	0	0	0	0	0
18:1 (9)	23	21	41	63	42	12	18	10.5	16
18:2 (9,12)	63	53	35.5	20	44.5	78	14	76	59
18:3 (9,12,15)	<0.5	8	0	9	0	0.5	58	1	12
20:1 & 20:2	1	3.5	1	1	0	0.5	0	0	0
22:1 (13)	0	0	–	0.5	0	0	0	0	0

[a] African peanut oil. [b] Canola-type oil (practically free of erucic acid).

Table 14.12. Oxidation of furan fatty acids I and II and formation of 3-methyl-2,4-nonandione in three refined soybean oils[a]

Compound[a]	Time[b]	Soybean oil		
		A	B	C
			(mg/kg)	
Furan fatty acid I	0 h	143	148	131
Furan fatty acid I	48 h	5	5	3
Furan fatty acid II	0 h	152	172	148
Furan fatty acid II	48 h	5	5	5
			(μ/kg)	
MND	0 h	<1	<1	<1
MND	48 h	89	3.4	<1
MND	30 d	721	204	43

[a] I: 10,13-Epoxy-11,12-dimethyloctadeca-10,12-dienoic acid;
II: 12,15-Epoxy-13,14-dimethyleicosa-12,14-dienoic acid. MND: 3-Methyl-2,4-nonandione.
[b] The soybean oils were stored at room temperature at a window facing north.

The fatty acid composition of peanut oil is greatly influenced by the region in which the peanuts are grown. In contrast to the peanut oils produced in Africa (Senegal or Nigeria), the peanut oils from South America are enriched in linoleic acid (41% vs 25%, w/w; see fatty acid composition, Table 14.11) at the expense of oleic acid (37% vs 55%, w/w). The contents of arachidic (20:0), eicosenoic (20:1), behenic (22:0), erucic (22:1) and lignoceric (24:0) acids are characteristic of peanut oil. Their glycerols readily crystallize below 8 °C.

Peanut Butter is a spreadable paste made from roasted and ground peanuts by the addition of peanut oil and, occasionally, hydrogenated peanut oil.

Rapeseed Oil. This oil is produced from seeds of two *Brasica* species: *Brassica napus var. napus* and *Brassica rapa var. Silvestris*. The latter plants yield slightly less oil, are shorter (approx. 80 cm), but mature more quickly. They are more tolerant to frost and have improved resistance to pest and diseases. Old rape and turnip rape cultivars contained high levels of erucic acid (45–50 by weight), which is hazardous in human nutrition. "Zero" erucic acid cultivars (22:1 <5% by weight), called *Canola*, have been developed and, recently, "double zero" cultivars, with low levels of erucic in the oil and goitrogenic compounds in the seed meal, have been developed. The major rapeseed-cultivating regions and countries are listed in Table 14.0.

The above-mentioned plants, as *Brassicacea*, contain mustard oil glucosides (glucosinolates, cf. 17.1.2.6.5) which, immediately after seed crushing, are hydrolyzed to esters of isothiocyanic acid. The hydrolysis is dependent on seed moisture and is catalyzed by a thioglucosidase enzyme called myrosinase (EC 3.2.3.1). In the presence of the enzyme, some of the isocyanates are isomerized into thiocyanates (esters of normal thiocyanic acid or rhodanides) and, in part, are decomposed into nitrile compounds which do not contain sulfur. All these compounds are volatile and, when dissolved in oil, are hazardous to health and detrimental to oil flavor. Moreover, they interfere with hydrogenation of the oil by acting as Ni-catalyst poisons (cf. 14.4.2.2). Therefore, in the production of rapeseed oil, a dry conditioning step is used (without live steam) to

Table 14.13. Changes in the composition of soybean oil through cultivation or modification[a] using genetic engineering techniques

	Genotype					
Fatty acid	Normal	Low linolenic	High oleic[b]	Low palmitic	Low saturate[b]	High stearic
16:0	11.2	10.1	6.4	5.9	3.0	9.2
18:0	3.4	5.3	3.3	3.7	1.0	20.5
18:1(9)	21.5	41.1	85.6	40.4	31.0	21.7
18:2 (9,12)	55.8	41.2	1.6	43.4	57.0	43.2
18:3 (9,12,15)	8.0	2.2	2.2	6.6	9.0	2.8

[a] Expressed in weight %.
[b] Developed by genetic engineering techniques.

inactivate the myrosinase enzyme and only then is the seed ground and subjected to prepress and solvent extraction processes.

Despite these precautions, small amounts of volatile sulfur compounds are formed. However, they are removed during the refining process. Irrespective of technical achievements in rapeseed production and processing, the selection and breeding of rapeseed "double zero" cultivars is being continued.

Rapeseed (*Canola*) oil is used as an edible oil. It is susceptible to autoxidation because of its relatively high content of linolenic acid. It is saturated by hyrogenation to a melting point of 32–34 °C and, with its stability and melting properties, resembles coconut oil.

Turnip rape oil has practically the same composition as the *B. napus* oil. It may contain at most 5% of erucic acid, because this can damage the heart muscle in high concentrations.

Sesame Oil is obtained from an ancient oilseed crop (*Sesamum indicum*, L.), which is widely cultivated in India, China, Burma and east Africa (cf. Table 14.0). In its refined form the oil is nearly crystal clear and has a good shelf life. In addition to a considerable amount of tocopherols, it contains another phenolic antioxidant, sesamol, which is derived from hydrolysis of sesamolin (Fig. 14.3).

Sesame oil can be readily identified with great reliability (cf. Table 14.21). Therefore, in some countries, blending this oil into margarine is required by law in order to identify the product as margarine.

Safflower Oil is obtained from a thistle-like plant (*Carthamus tinctorius*) grown in the arid regions of North America and India (cf. Table 14.0). New cultivars have been bred with oil compositions which deviate greatly from those listed in Table 14.11. These new cultivars contain 80% by weight oleic acid (18:1) and 15% by weight linoleic acid (18:2; 9,12).

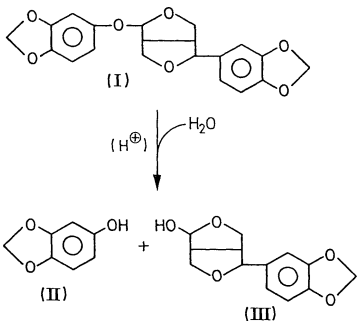


Fig. 14.3. Sesame oil: sesamol (II) and samin (III) formation by sesamolin (I) hydrolysis

Linseed Oil. Flax, used for fiber and seed production and the subsequent processing of the seed into linseed oil, is grown mainly in Canada, China and India (cf. Table 14.0). Due to its high content of linolenic acid (cf. Table 14.11), the oil readily autoxidizes, one of the processes by which some bitter substances are created. Since autoxidation involving polymerization reactions proceeds rapidly, the oil solidifies ("*fast drying oil*"). Therefore, it is used as a base for oil paints, varnishes and linoleum manufacturing, etc. A comparatively negligible amount, particularly of the coldpressed oil, is utilized as an edible oil.

Poppy Oil is very rich in linoleic acid (Table 14.11). The cold-pressed oil from flawless seeds is colorless to light yellow and can be used directly as an edible oil.

Walnut Oil has a pleasant odor and a nut-like taste. It contains relatively high concentrations of linolenic acid (Table 14.11) and, consequently, has a very limited shelf life.

14.4 Processing of Fats and Oils

14.4.1 Refining

Apart from some oils obtained by cold pressing (examples in 14.3.2.1), most of the oils obtained using expeller, screw or hydraulic presses, solvent extraction or by melting at elevated temperatures are not suitable for immediate consumption. Depending on the raw material and the oil recovery process, the oil contains polar lipids, especially phospholipids, free fatty acids, some odor- and taste-imparting substances, waxes, pigments (chlorophyll, carotenoids and their degradation products), sulfur-containing compounds (e. g. thioglucosides in rapeseed oils), phenolic compounds, trace metal ions, contaminants (pesticides or polycyclic hydrocarbons) and autoxidation products.

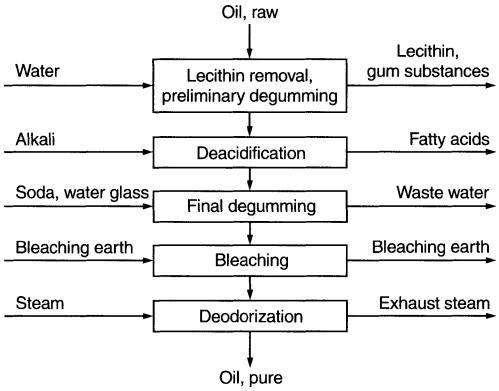


Fig. 14.4. Refining of oils

In a refining process comprising the following steps:

- Lecithin removal
- Degumming
- Free fatty acid removal
- Bleaching
- Deodorization,

all the undesired compounds and contaminants are removed. An overview of the refining process is given in Fig. 14.4. In practice the refining steps used depend on the quality of the crude oil and its special constituents (e. g. carotene in palm oil or gossypol in cottonseed oil). The following precautionary measures are taken during refining in order to avoid undesirable autoxidation and polymerization reactions:

- Absence of oxygen (also required during transport or storage)
- Avoidance of heavy metal contamination
- Maintaining the processing temperatures as low and duration as short as possible.

14.4.1.1 Removal of Lecithin

This processing step is of special importance for rapeseed and soybean oils. Water (2–3%) is added to crude oil, thereby enriching the phospholipids in the oil/water interface. The emulsion thus formed is heated up to 80 °C and then separated or clarified by centrifugation. The "crude lecithin" (cf. 3.4.1.1) is isolated from the aqueous phase and is recovered as crude vegetable lecithin after evaporating the water in a vacuum.

14.4.1.2 Degumming

Finely dispersed protein and carbohydrates are coagulated in oil by addition of phosphoric acid (0.1% of oil weight). A filtering aid is then added and the oil is clarified by filtration. This also removes the residual phospholipids from the previous processing step.

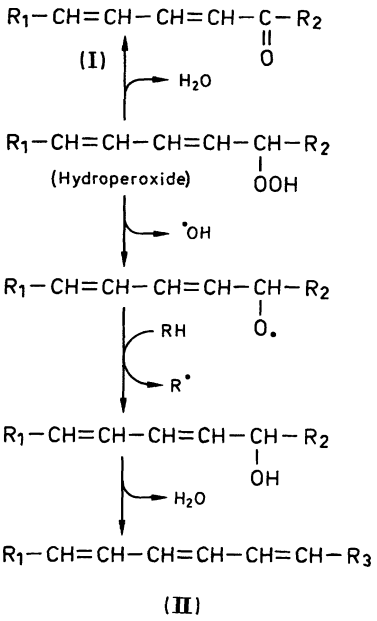
14.4.1.3 Removal of Free Fatty Acids (Deacidification)

Several methods exist for deacidification of fat or oil. The choice depends on the amount of free fatty acidspresent in crude fat or oil. The removal of fatty acids with 15% sodium hydroxide (alkali refining) is the most frequently used method. Technically, this is not very simple since fat hydrolysis has to be avoided and, moreover, the sodium soap (the "soap-stock"), which tends to form stable emulsions, has to be washed out by hot water. After vacuum drying, the fat or oil may contain only about 0.05% free fatty acids and 60 to 70 ppm of sodium soaps. When the fat or oil is treated with diluted phosphoric acid, the content of sodium soaps decreases to 20 ppm and part of the trace heavy-metal ions is removed.
Fats (oils) with a high content of free fatty acids require relatively high amounts of alkali for extraction, resulting in an unavoidably high loss of neutral fats (oils) due to alkaline hydrolysis. Therefore, extraction with alkali is frequently replaced by deacidification by distillation in these cases (14.4.1.5).
In special cases, a selective fluid/fluid extraction is of interest. Ethanol extracts free fatty acids (above a level of 3%) from triacylglycerols in crude oils – this is a suitable way to treat oils with exceptionally high amounts of free acids. At a given temperature, furfural can extract only the polyunsaturated triacylglycerols. On the other hand, propane under pressure preferentially solubilizes the saturated triacylglycerols and leaves behind the unsaturated ones, together with unsaponifiable matter. Pressurized propane is uti-

lized in marine oil fractionation, e. g., in the production of vitamin A concentrates.

14.4.1.4 Bleaching

In order to remove the plant pigments (chlorophyll, carotenoids) and autoxidation products, the fat or oil is stirred for 30 min in the presence of Al-silicates (bleaching or *Fuller's* earth) in a vacuum at 90 °C. The silicate has to be activated prior to use – a suspension in water is treated with hydrochloric acid, followed by thorough washing with water, then drying. The amount of silicate used is 0.5–2% of the fat (oil) weight. It is often used together with 0.1–0.4% activated charcoal.
The bleached oil is removed from the adsorbent by filtration. The oil retained by the absorbent can be recovered by hexane extraction and recycled into the refining process. The residual alkali soaps, gums, part of the unsaponifiable matter and the heavy metal ions are also removed during the bleaching process.
After bleaching, some oils or fats which contain polyunsaturated fatty acids show an increase in absorbance at 270 nm. This is due to decomposition of hydroperoxides, formed by autoxidation, into oxo-dienes (I) and fatty acids with three double bonds (II):



(14.4)

Table 14.14. Removal of chloro pigments in the refining of rapeseed oil (values in mg/kg)

		Amounts after		
	Raw oil	Deacidification	Bleaching	Deodorization
Chlorophyll A	2.62	0.89	0.028	0.007
Chlorophyll B	2.92	0.08	0.059	0.023
Pheophytin A	35.6	31.5	0.235	0.108
Pheophytin B	4.99	6.85	0.071	0.036
Sum	46.1	39.3	0.393	0.174

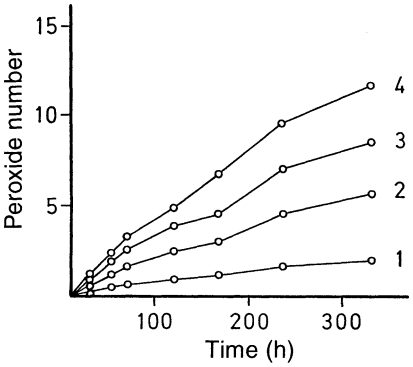


Fig. 14.5. Oxidation of soybean oil on exposure to room light (according to *Usuki* et al., 1984). (1), (2), (3), and (4) contain 39, 233, 425, and 623 µg/kg respectively of the mixture chlorophyll A/chlorophyll B/pheophytin A/pheophytin B (1:3:10:3)

As shown in Table 14.14 with rapeseed oil, most of the chlorophylls and their degradation products are removed during bleaching. However, the rest, which is in the range of 70–1200 µg/kg in refined plant oils, could still accelerate photooxidation (Fig. 14.5). As a result of their high stability on exposure to light, the pheophytins are stronger photooxidants than the chlorophylls. As shown in Table 14.14, the pheophytins are the predominanting pigments.

14.4.1.5 Deodorization

Deodorization is essentially vacuum steam distillation (190–230 °C, 0.5–10 mbar). The volatile compounds, together with undesirable odorants present in the fat or oil, are separated in this re-

fining step. Deodorization takes from 20 min to 6 h, depending on the type of fat or oil and the content of volatile compounds.
The processing loss in this refining step is 0.2%. This is negligible since the fat or oil droplets carried by the steam are caught by baffles or are intercepted by an external trap system.
Deodorization can been combined with deacidification by distillation when the oil has a low content of accompanying substances or if they have been largely removed by degumming and bleaching, e. g., after reduction of the phospholipids to less than 5 mg/kg. Since fatty acids are less steam-volatile than the odorous substances, higher temperatures (up to 270 °C) are used than in deodorization. Carotenoids are decomposed, so that, e. g., palm oil is thermally bleached in this process. The combination of deodorization with distillative deacidification is called physical refining; it is the process of choice in the case of higher acid concentrations (>0.7−1%). The relatively large amounts of waste water which have to be disposed off after alkaline extraction are avoided here. In addition, the fatty acids accumulated as by-products are of higher quality then the "refining fatty acids" obtained by alkali extraction (cf. 14.4.1.3).
In steaming or physical refining, the double bonds of linoleic and linolenic acid isomerize to a small extent. For this reason, an HPLC determination of isomeric linoleic acids is used to distinguish between refined and natural plant oils (cf. 14.5.3.4).

14.4.1.6 Product Quality Control

In addition to sensory evaluation, free fatty acid analysis (the content is usually below 0.05%) and analysis of possible contaminants are carried out. The data given in Table 14.15 illustrate the amounts of pesticides and polycyclic aromatic compounds removed by deodorization. However, this refining step also removes the highly desirable aroma substances which are characteristic of some cold-pressed oils such as olive oil.
The composition of phytosterols and tocopherols does not change appreciably during refining. Therefore, an analysis of these compounds is suitable for the identification of the type of fat. On the other hand, cholesterol can increase during steaming, e. g., due to the cleavage of glycosides. In palm oil, for instance, the percentage of cholesterol in the sterol fraction increased from 2.8% to 8.8%.

Table 14.15. Removal of endrin and polycyclic hydrocarbons during edible oil refining (μg/kg)

Compound	Content in raw oil	Content in oil after deacidification	bleaching	steaming
Endrin	620[a]	590	510	<30
Anthracene	10.1[b]	5.8	4.0	0.4
Phenanthrene	100[b]	68	42	15
1,2-Benzanthracene	14[b]	7.8	5.0	3.1
3,4-Benzpyrene	2.5[b]	1.6	1.0	0.9

[a] Soybean oil.
[b] Rapeseed oil.

14.4.2 Hydrogenation

14.4.2.1 General Remarks

Liquid oils are supplied mostly from natural sources. However, a great demand exists for fats which are solid or semi-solid at room temperature. To satisfy this demand, *W. Normann* developed a process in 1902 to convert liquid oil into solid fat, based on the hydrogenation of unsaturated triacylglycerols using Ni as catalyst; a process designated as "fat hardening". The process rapidly gained great economic importance; even marine oils became suitable for human consumption after the hardening process. Today more than 4 million tons of fat per year are produced worldwide by hydrogenation of oils; most is consumed as food.
The unsaturated triacylglycerols can be fully hydrogenated, providing high-melting cooking, frying and baking fats or partially hydrogenated, providing products such as:

- Oils rich in fatty acids with one double bond. They are stable and resistant to autoxidation and have a shelf life similar to olive oil. They are used as salad oil or as shortening.
- Products in which the linolenic acid is hydrogenated, but most of the essential fatty acid, linoleic acid, is left intact. An example is soy-

bean oil, hydrogenated selectively to increase its stability against oxidation.
- Fats that melt close to 30 °C and have a plastic or spreadable consistency at room temperature.

Fully or partially hydrogenated oils are important raw materials for margarine manufacturing and serve as deep-frying fats (cf. 14.4.8).

Table 14.16. Properties of hydrogenation catalysts

Catalyst	Selectivity S_{32}	Selectivity S_{21}	trans-Fatty acids (weight-%)[a]
Nickel-contact	2–3	40	40
Ni_3S_2-contact	1–2	75	90
Copper-contact	10–12	50	10

[a] trans-Fatty acids as monoenoic acids total content is calculated as elaidic acid.

14.4.2.2 Catalysts

The principle of the heterogeneous catalytic hydrogenation of unsaturated acylglycerols was outlined under 3.2.3.2.4. The most widely used catalyst is carrier-bound nickel. Raney nickel, copper, and noble metals serve special purposes. The choice of catalyst is made according to:

- Reaction specificity.
- Extent of trans-isomer formation
- Duration of activity and cost.

To determine the specificity of a catalyst, the reaction rates for each individual hydrogenation step must be determined. Simplified, there are three reaction rate constants (k) involved (AG = acylglycerol):

$$\begin{array}{ccccc} \text{Triene-AR} & \xrightarrow{k_3} & \text{Diene-AR} & \xrightarrow{k_3} & \text{Monoene-AR} \\ & & & & \downarrow k_1 \\ \text{AR-acylresidue} & & & & \text{Saturated-AR} \end{array} \qquad (14.5)$$

The catalytic reactions considered here require that $k_3 > k_2 > k_1$. The following equations determine the specificity "S":

$$S_{32} = \frac{k_3}{k_2}; \quad S_{21} = \frac{k_2}{k_1}; \quad S_{31} = \frac{k_3}{k_1} \qquad (14.6)$$

That means, the greater the value of "S", the faster the hydrogenation at this step. Therefore, specificity (or selectivity) is proportional to the value of "S". For the three catalysts mentioned, Table 14.16 shows that the hydrogenation of diene → monoene by Ni_3S_2 and the hydrogenation of triene → monoene by copper become accelerated with marked specificity. Copper is particularly suitable for decreasing the linolenic acid content in soybean and rapeseed oils. However, copper catalysts are not sufficiently economical, since they can not be used more than twice. Their complete removal, which is necessary because this is a prooxidatively active metal, is relatively tedious.

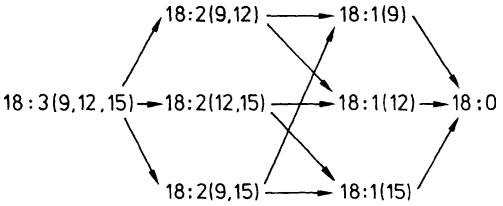
Although noble metals are up to 100 times more effective than nickel catalysts, they are not popular because of their high costs. It is of great advantage that the nickel catalyst can be used repeatedly for up to 50 times under the following conditions: the plant oil must be deacidified, freed of gum ingredients and contain no sulfur compounds (cf. rapeseed oil, 14.3.2.2.5). The favorable ratio of duration of activity to cost places the nickel catalysts ahead with advantages not readily surpassed by any other catalyst. For the production of nickel-carrier catalysts, kieselguhr or zeolite is impregnated with nickel hydroxide, which is precipitated out of a solution of nickel nitrate with sodium hydroxide or carbonate. After drying, nickel hydroxide is reduced to nickel with hydrogen at 350–500 °C.

For the production of carrier-free nickel catalysts, nickel formate is suspended in a fat and then decomposed:

$$Ni(HCOO)_2 \xrightarrow[(200-250\,^\circ C)]{} Ni + 2CO_2 + H_2 \qquad (14.7)$$

The catalysts obtained with a Ni content of 22–25% are pyrophoric. For this reason it is embedded in fat and handled and marketed in this form. To evaluate the catalysts, calculation programs were developed for the determination of the actual selectivity of a catalyst based on the fatty acid composition of the starting material and of the hydrogenated product.

During hydrogenation, linolenic acid yields, among others, isolinoleic and isooleic acids (cf. Reaction 14.8).



(14.8)

The diversity of the reaction products present in partially hydrogenated fat is increased further by the positional- and stereoisomers of the double bonds. Hydrogenation of soybean oil in the presence of a copper catalyst gives, for example, a number of trans-monoene fatty acids (Table 14.17). The extent of isomerization is affected, among other factors, by the type of catalyst used in hydrogenation. Efforts are being made to reduce the formation of trans-fatty acids during hydrogenation because these acids have a detrimental effect on the composition of the blood lipids. Also, the presence of a hydrogenated fat in a mixture is easily detected via the identification of trans-fatty acids, e. g., by IR spectroscopy or gas chromatography (cf. 14.5.2.3).

A further drawback of the partial hydrogenation of an oil is the pattern of linoleic acid isomersformed. The two isomers formed during hydrogenation, linolelaidic acid 18:2 (9 trans, 12 cis) and 18:2 (9 cis, 12 trans) are, unlike linoleic acid, not essential fatty acids (cf. 3.2.1.2).

Table 14.17. Fatty acid composition of a soya oil before and after hydrogenation with a copper catalyst

Fatty acid	Hydrogenation	
	before (weight-%)	after (weight-%)
16:0	10.0	10.0
18:0	4.2	4.2
18:1(9)	26.0	30.4
18:1[a]	0	5.5
18:2(9,12)	52.5	42.5
18:2(conjugated)[b]	0	0.7
18:2[c]	0	5.2
18:3(9,12,15)	7.3	0.7

[a] This fraction contains eight trans fatty acids: 18:1 (7 tr)–18:1 (14 tr); major components are 18:1 (10 tr) and 18:1(11 tr).
[b] It consists of various conjugated fatty acids.
[c] Isolinoleic and isolinolelaidic acids.

14.4.2.3 The Process

The hydrogen required can be obtained by electrolysis of dilute aqueous KOH, through water-to-gas conversion:

$$H_2O + C \rightarrow H_2 + CO$$
$$CO + H_2O \rightarrow H_2 + CO_2 \quad (14.9)$$

or by the decomposition of natural gas with steam:

$$CH_3(CH_2)_\times CH_3 + H_2O \rightarrow H_2 + CO$$
$$CO + H_2O \rightarrow H_2 + CO_2 \quad (14.10)$$

in the latter two processes, the poisonous by products, H_2S and CO, have to be completely removed.

Oil hydrogenation is performed in an autoclave equipped with a stirrer under hydrogen gas pressure of 1–5 bar and a temperature of 150–220 °C. More recent developments aim at a continuous process, e. g., in fixed-bed reactors. A newer hydrogenation process uses a recycling hydrogenation unit equipped with a spraying nozzle, external heat exchanger and recycling pump.

The process conditions have a significant effect on the composition and therefore on the consistency of the end-product. Selective hydrogenation of double bonds is favored by a high concentration of catalyst (which, depending on the Ni activity, is 200–800 g Ni/t fat), a high temperature and low pressure of hydrogen gas. After hydrogenation, the fat is filtered, then deacidified, bleached and deodorized during further refining (cf. 14.4.1.3–14.4.1.5).

Some constituents of the unsaponifiable matter are also affected by the hydrogenation process. Carotenoids, including vitamin A, are hydrogenated extensively. Some of the chlorine-containing pesticide contaminants are hydrogenated. Sterols, under the usual operating conditions, are not affected. The ratios and levels of tocopherols are essentially unchanged.

14.4.3 Interesterification

Natural fats and oils are subjected to extensive interesterification during processing. This in-

volves a rearrangement or randomization of acyl residues in triacylglycerols and thus provides fats or oils with new properties. By choosing the raw material and processing parameters, the interesterification can be controlled to obtain a fat with melting characteristics and consistency which match the intended use ("tailored fats").

The basics of the interesterification process are outlined under 3.3.1.3. Sodium methylate is used almost exclusively as the catalyst. The dried, bleached and deacidified fat (or oil) is stirred at 70–100 °C under a vacuum in the presence of alcoholate (0.1–0.3% of fat weight). When the reaction is completed, the catalyst is destroyed by adding water, then the degraded catalyst together with the resultant soaps are removed from the fat (oil) by repeated washing with water. The interesterified product is then bleached (cf. 14.4.1.4) and deodorized (cf. 14.4.1.5).

Table 14.18 illustrates the changes in triacylglycerols brought about by the process and its influence on fat melting points.

The baking properties of lard (improvement of volume and softness of the baked goods) are improved by interesterification. The uniform distribution of palmitic acid in the triacylglycerols accounts for such an improvement.

Furthermore, interesterification is of importance in the manufacturing of different varieties of margarine with a given composition, for example:

- Vegetable margarine with 30% w/w of 18:2 (9, 12) fatty acid may be produced by interesterification of partially hardened sunflower oil blended with its natural liquid oil.
- Interesterification of palm oil with palm seed or coconut oil (2:1) and the use of 6 parts of this product with 4 parts of sunflower oil provides a margarine which contains 20–25% w/w of linoleic acid and does not contain hydrogenated fat.

Table 14.18. Changes in the pattern of triacylglycerols in a partially hydrogenated palm oil by interesterification

Melting point	Prior to interesterification	Single phase interesterification	Directed interesterification
Melting point (°C)	41	47	52
	Triacylglycerols[a] in mole-%		
S_3	7	13	32
S_2U	49	38	13
SU_2	38	37	31
U_3	6	12	24

[a] S: Saturated, U: unsaturated fatty acids.

14.4.4 Fractionation

The undesirable fat ingredients are removed or the desirable triacylglycerols (TG) are enriched by fractional crystallization. The rising demand of food processors for special fats with standardized properties has led to large-scale isolation of special fractions, particularly from palm oil and the fats and oils listed under 14.3.2.2.2. The following procedures are used for the fractional crystallization of fats: The melted fat is slowly cooled until the high melting TG selectively crystallize, i. e. without forming mixed crystals of low and high melting TG. A sharp separation into two or more fractions is assumed to be satisfactory when the melting points of the fractions differ by at least 10 °C. The separated crystals are either removed by filtration or are washed out with a tenside solution. In the latter case, the fat crystals adsorb a water soluble surface-active agent, such as sodium dodecyl sulfate, and thus acquire hydrophilic properties. The crystals are then transferred to the aqueous phase. The isolated aqueous suspension is then heated and the TG recovered as liquid fat.

An even sharper fractional crystallization procedure may be achieved by solubilization of fat in hexane or some other suitable solvent. However, solvent distillation and recovery are rather time consuming, so the use of this procedure is justified only in very special cases. In the processing step of "winterization" of rapeseed (Canola), cottonseed or sunflower oil, small amounts of higher melting TG or waxes are removed which would otherwise cause turbidity during refrigeration. The basis of winterization is the fractional crystallization by slowly cooling the oil, as outlined above. Other procedures for the production of cold-stable oils are based on the use of crystallization inhibitors. These are mono- and diacylglycerols, esters of succinic acid, etc.

The application of the fractional extraction of fat or oil, instead of crystallization, has been outlined under 14.4.1.3.

14.4.5 Margarine – Manufacturing and Properties

The inventor of margarine, *Mège Mouries*, described in his patent issued in 1869 a process for the production of spreadable fat from beef fat which would substitute for and imitate the scarce and costly dairy butter. Based on the assumption that margaric acid (17:0) is the predominant fatty acid of beef fat, the name "margarine" was suggested for the new product. The assumption was, however, proven to be incorrect (cf. Table 14.3). Nevertheless, the name remained.

Margarine, which is produced worldwide in amounts exceeding 7 million t/a, is a water in oil emulsion. Its stability is achieved by an increase in viscosity of the continuous fat phase due to partial crystallization and through emulsifiers. The fat crystals form a three dimensional network. They should be present in the β′-modification; a conversion $\beta' \rightarrow \beta$ is undesirable because the β-modification causes a "sandy" texture defect. Hydrogenated fats, which are frequently used as raw materials, crystallize in the β′-modification when the lengths of the acyl residues differ. The erucic acid-rich and partially hydrogenated rapeseed fat used in the past crystallizes in the β′-form. The cultivation of rapeseed with a low content of erucic acid at first produced a fat that, after partial hydrogenation, consisted to almost 90% of 18:0 and 18:1 and, as a result of this homogeneity, crystallized in the β-form. By means of cultivation, 16:0 was increased from 5 to 12% at the cost of 18:1, which is sufficient for the stabilization of the β′-form.

14.4.5.1 Composition

The properties of margarine, such as nutritional value, spreadability, plasticity, shelf life and melting properties, resemble those of butter and are influenced essentially by the varieties and properties of the main fat ingredients. Since choice of ingredients is large, numerous varieties of margarine are produced (cf. Table 14.19).

The fat in margarine, which by regulation is 80% by weight (diet margarine is 39–41% fat), contains about 18% of emulsified water. The W/O emulsion is stabilized by a mixture of mono- and diacylglycerols (approx. 0.5%) and

Table 14.19. Examples of margarine types

Type	Comments
A. Household margarine	
Standard product	At least 50% of the fat is vegetable oil, the rest being animal fat.
Vegetable margarine	At least 98% of the fat is vegetable oil; contains at least 15% linoleic acid.
Linoleic acid enriched margarine	At least 30% linoleic acid, otherwise as vegetable margarine.
B. Semi-fat margarine	The fat content is halved. This type is not suitable for baking and frying.
C. Molten or fused margarine	Practically free of water and protein. It is aromatized with diacetyl and butyric acid; soft consistency; with large TG crystals it has a grainy structure; applied in cooking, frying and baking.
D. Special types for industrial processing	
Baking margarine	Strongly aromatized with heat stable compounds that contribute to baked products' aroma; mainly moderately melting TG's.
Margarine for pastry production	This margarine is strongly aromatized; its high melting TG's are embedded in oil phase; suitable for dough extension into thin sheets ("strudel dough") used in flaky pastry production.
Creamy margarine	It is not or only slightly aromatized; has a soft consistency; contains high content of coconut oil and approx. 10 vol-% of air.

crude lecithin (approx. 0.25%). Diet margarines have higher levels of emulsifiers. Skim milk or skim milk powder suspended in water (milk proteins, 1%; 2% in semi-fat margarine) is added in the production of high quality retail brands of margarine. The casein assists the action of the emulsifiers and, together with lactose, provides the desired browning when heated.

The aqueous phase of the margarine acquires a pH of 4.2–4.5 by addition of citric and lactic acids. This not only affects the flavor, but protects against microbial spoilage. In addition, traces of heavy metal ions are complexed. Margarine also contains the aroma substances typical of butter, which can be produced by microbiological souring (cf. 10.2.3.2). Readily available synthetic compounds, such as diacetyl, butyric acid, lactones of C_8–C_{14} hydroxy-fatty acids (cf. 5.3.1.4) and (Z)-4-heptenal, may also be used for aromatization. Common salt (0.1–0.2%) is used to round-off the flavor. Margarine is colored with β-carotene or with gently refined, unbleached palm oil. Attention is also given to maintaining the presence of 1 mg of α-tocopherol per g of linoleic acid. High quality products are vitaminized by the addition of about 25 IU/g vitamin A and 1 IU/g vitamin D_2. The authenticity of margarine is verified in some countries by an indicator substance added to it. This is required by legislation. Gently refined sesame oil (for its detection, see Table 14.22) is one of these substances.

14.4.5.2 Manufacturing

Margarine is manufactured continuously by a process consisting essentially of three steps:

- Emulsification of water within the continuous oil phase.
- Chilling and mechanical handling of the emulsion.
- Crystallization, preserving the type of w/o emulsion by efficient removal of the released heat of crystallization.

The triacylglycerols should preferentially crystallize in their β′-forms (cf. 3.3.1.2). The higher melting β-forms are not desired since they cause a "sandy" texture. The transitioin $\beta' \rightarrow \beta$-form is inhibited by addition of 1% saturated diacylglycerols.

14.4.5.3 Varieties of Margarine

The characteristic features of some varieties of margarine are summarized in Table 14.19.

14.4.6 Mayonnaise

Mayonnaise is an "oil in water" or o/w emulsion (cf. 8.15.1) consisting of 50–85% edible oil, 5–10% egg yolk, vinegar, salt and seasonings (cf. 11.4.2.3). The emulsion is stabilized by egg yolk phospholipids. Products with a lower oil content (<50%) may contain thickening agents such as starch, pectin, traganth, agar-agar, alginate, carboxymethylcellulose, milk proteins or gelatin. Sorbic acid, benzoic acid or the ethyl ester of p-hydroxybenzoic acid are added as preservatives. The stable emulsion is produced in a combinator with a homogenizer and then packed.

14.4.7 Fat Powder

In contrast to fats and oils, fat powders have better stability against autoxidation and, in some food products such as dehydrated soup powders or broths, are easier to handle. They are manufactured from natural or hardened plant fats, sometimes with the addition of emulsifiers and protein carriers. Butter and cream powders are also produced.

Two basic flow diagrams of the production of fat powders are shown in Fig. 14.6.

In a cold-spray process, the melted fat is sprayed under high pressure into a cooled (−35°C) air-blast crystallization chamber, where the fat particles solidify. After being recrystallized, the particles are coated to avoid clumping.

In a spray-drying process, the fat is homogenized with emulsifiers, water and skim milk, spray dried and subsequently crystallized.

14.4.8 Deep-Frying Fats

Traditionally, the fats used for deep frying are those whose stability against autoxidation have

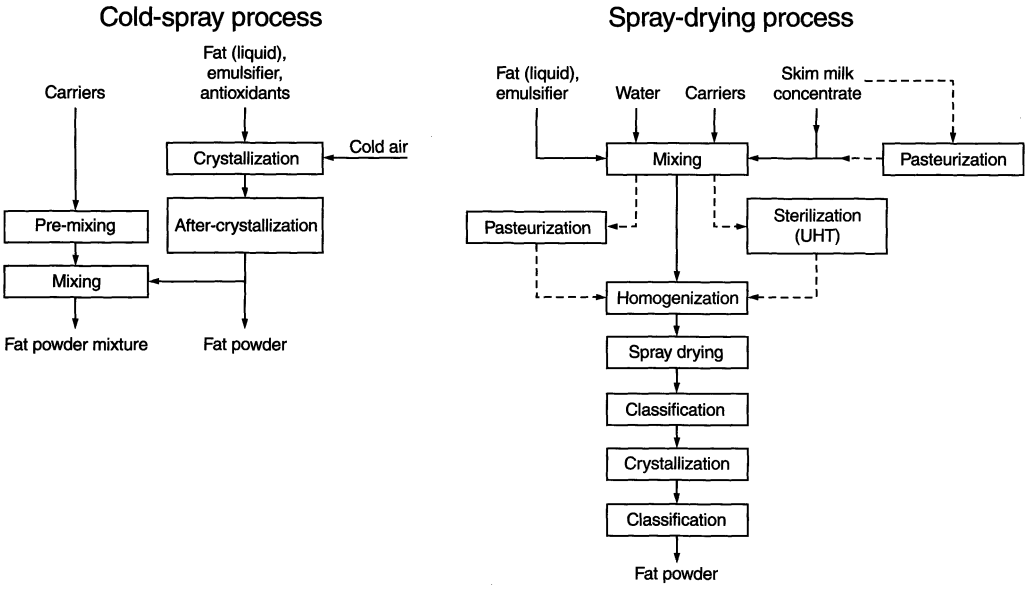


Fig. 14.6. Production of fat powder

been increased by hydrogenation. However, trans-fatty acids are produced in this process (cf. 14.4.2) and these acids are nutritionally and physiologically undesirable. In contrast, fat mixtures containing 70% oleic and 10% linoleic acid offer an improved nutritional value and a pleasant aroma (cf. 3.7.4.1). Small amounts of sesame oil (cf. 14.3.2.2.5) and oil isolated from rice bran are added to provide protection against autoxidation. This oil contains sterol esters of ferulic acid which are called γ-oryzanal. The ferulic acid (cf. 18.1.2.5) is the antioxidatively active component of these esters.

14.5 Analysis

14.5.0 Scope

The problems and scope of fat or oil analysis include identification of the type, determination of the composition of the blend, detection of additives, antioxidants, color pigments, and extraneous contaminants (solvent residues, pesticides, trace metals, mineral oils, plasticizers). In addition, the scope of analysis encompasses determination of other quality parameters, such as the extent of lipolysis, autoxidation or thermal treatments. Also of interest is the extent of refining which the fats and oils have been subjected to as well as detection of hardened fat and products which were interesterified.

14.5.1 Determination of Fat in Food

The methods used for determination of fat or oil in food are often based on extraction with either ethyl ether or petroleum ether and gravimetric determination of the extraction residue. These methods may provide unreliable or incorrect results, particularly with food of animal origin. As shown in Table 14.20, where a corned beef sample was analyzed, the amount and composition of fatty acids in the fat residue were influenced greatly by the analytical methods used. In addition to the accessible free lipids, the emulsifiers present and the changes induced by autoxidation affect the amount of extractable lipids and the lipid-to-nonlipid ratio in the residue. The use of a standard method still does not eliminate the disadvantages shown by analytical methods of fat analysis. Therefore, in questionable cases, quantitative determination of fatty acids and/or glycerol is recommended.

Table 14.20. Determination of the fat content of canned corned beef

Analytical method	Fat content (%)[a]	Fatty acid composition (g/100 g)			
		Saturated acids	18:1 (9)	18:2 (9,12)	18:3 (9,12,15)
1. Dried sample is extracted with ethyl ether	7.9	3.98	2.06	0.05	0.08
2. Sample is homogenized in 95% ethanol and then extracted with ether	15.8	4.0	2.60	0.77	0.32
3. Sample is hydrolyzed with 4 mol/1 HC1 (at 60 °C for 30 min), then extracted with ether	12.3	5.66	3.94	0.95	0.71
4. Sample is hydrolyzed with conc. HC1 (at 100 °C for 1 h), methanol added and then extracted with carbon tetrachloride	13.9	2.45	1.68	0.34	0.21
5. Sample is homogenized in chloroform methanol mixture (2:1 v/v), washed with water and then the chloroform phase recovered	11.2	4.89	3.31	0.85	0.39

[a] The fat is determined gravimetrically after the solvent is evaporated.

A rapid and accurate determination of fats or oils in food is achieved by IR- (cf. 15.3.1) and ^{1}H-NMR spectrometry. The method is based on the fact that hydrogen nuclei in fluids respond to substantially higher magnetic resonance effects than do immobilized hydrogen atoms of solid substances. Thus, the ^{1}H-NMR signal of a fluid, such as an oil, differs from that of a nonoil matrix, such as carbohydrate, protein or firmly-bound water. The intensity of the signal is directly proportional to the oil content. This method is also of great value in oilseed selection or breeding research, since it permits determination of the oil content in a single kernel without damaging it by grinding or drying, i. e. retaining its ability to germinate.

The proportion of solid to fluid triacylglycerols in fat can also be determined using ^{1}H-NMR spectrometry.

14.5.2 Identification of Fat

14.5.2.1 Characteristic Values

For both, the identification and the determination of the quality of a fat or oil, the older lipid chemistry defines a series of characteristic values in which the reagent uptake is used to quantitatively estimate the selected functional groups or calculate the constituents of a fat or oil. The introduction of new analytical methods, such as gas chromatography of fatty acids and the HPLC of triacylglycerols (cf. 3.3.1.4), has made many of these measures obsolete. The values which are still used to differentiate fats or oils are:

Saponification Value (SV). This is the weight of KOH (in mg) needed to hydrolyze 1 g of fat or oil under standardized conditions. The higher the SV, the lower the average molecular weight of the fatty acids in the triacylglycerols (for examples, see Table 14.21).

Acid Value (AV). This value is important for a first quick characterization of the quality of a fat. It is the number of milligrams of KOH needed to neutralize the organic acids present in 1 g of fat.

Iodine Value (IV). This number is the number of grams of halogen, calculated as iodine, which bind to 100 g fat (cf. 3.2.3.2.1). The halogen uptake by fat or oil is affected by the contents of oleic (IV: 89.9), linoleic (IV: 181) and linolenic (IV: 273) acids. Examples of iodine numbers are provided in Table 14.21.

Table 14.21. Iodine (IV) and saponification numbers (SV) of various edible fats and oils

Oil/fat	IV	SV	Oil/fat	IV	SV
Coconut	256	9	Rapeseed		
Palm kernel	250	17	(turnip)	225	30
Cocoa	194	37	Sunflower	190	132
Palm	199	55	Soya	192	134
Olive	190	84	Butter	225	30
Peanut	192	156			

Hydroxyl Value (OHV). This number reflects the content of hydroxy fatty acids, fatty alcohols, mono- and diacylglycerols and free glycerol.

14.5.2.2 Color Reactions

Some oils give specific color reactions caused by particular ingredients. Examples are summarized in Table 14.22. Since many specific nonfat components are removed from oils by refining, these tests are negative when applied to refined oils.

14.5.2.3 Composition of Fatty Acids and Triacylglycerides

The acyl residues of an acylglycerol are released as methyl esters (cf. 3.3.1.3) and are analyzed as such by gas chromatography. However, free fatty acid analysis is also possible by using specially selected stationary solid phases. Capillary-column gas chromatography should be used to differentiate between cis and trans fatty acids, which is required for the detection of partially hydrogenated fats. The fatty acids indicative of the identity or type of fat or oil are summarized in Table 14.23. An enrichment step must precede gas chromatographic separation when fatty acids of analytical significance are present as minor constituents.

Prior to the enrichment step, specific techniques such as "argentation" chromatography (cf. 3.2.3.2.3) or fractionation by urea-adduct formation (cf. 3.2.2.3) are carried out in addition to the usual preparative chromatographic procedure. The methyl branched fatty acids in marine oils are an example. These acids are enriched by the urea-adduct inclusion method since, unlike straight-chain acids, they are unable to form inclusion compounds. These branched-chain fatty acids do not change during hydrogenation, hence they can be used as marine oil indicators, i. e. to reveal the presence of marine oil in hydrogenated vegetable oils such as margarine. Another example is the use of gas chromatography to determine furan fatty acids in soybean oils (cf. Table 3.9), which is possible only after enrichment in an urea filtrate.

In the interpretation of the results of fatty acid analyses, it should be taken into account that the fatty acid composition is subject to considerable variations. It depends on the breed and feed in the case of animal fats, and on the plant variety, geographic location of the area of cultivation, and the climate in the case of plant fats. Therefore, guide values have been set for individual oils and fats (cf. Table 14.24), which can differ from country to country.

The ratio of the content of a fatty acid in position 2 of the triacylglycerides to its total content (E factor, E = *enrichment*) is independent of the origin of the plant oil. After hydrolysis of the fat with pancreatic lipase, separation of the 2-monoglycerides, and their methanolysis, the concentration in position 2 is determined by gas chromatography and the E-factor calculated (examples for linoleic acid are shown in Table 14.25). Adulteration of olive oils with ester oils is shown by an increased E-factor for palmitic acid (cf. 3.3.1.4).

In many cases, the triacylglyceride pattern is more expressive than the fatty acid composition. This pattern can be quickly and easily determined

Table 14.22. Color reactions for fat and oil identification

Reaction according to[a]	Identification of
Baudouin (furfural and hydrochloric acid)	Sesame oil
Halphen (sulfur and carbondisulfide)	Cottonseed oil
Fitelson[b] (sulfuric acid and acetic acid anhydride)	Teaseed oil

[a] Reagents are listed in brackets.
[b] It is a modification of *Liebermann–Burchard* reaction for sterols (cf. 3.8.2.4).

Table 14.23. Fatty acid indicators suitable for determination of fat and oil origin

Fatty acid	Content (%)[a]	Indicator of
4:0	3.7	Milk fat
12:0	45	Coconut-, palm kernel-, and babassu fat
18:1 (9)	65–85[b]	Teaseed-, olive- and hazelnut oil
18:3 (9, 12, 15)	9	Soya-, rapeseed (also erucic acid free) oil
18:2 (9, 12)	50–70	Sunflower-, corn germ-, cottonseed-, wheat germ-, and soya oil
22:0	3	Peanut oil
20:4 (5, 8, 11, 14)	0.1–0.6	Animal fat
18:1 (9, 12-OH)	80	Castor bean oil
Trans-fatty acids		Partially or fully hydrogenated oil/fat[c]
Methyl-branched fatty acids	0.2–1.6	Animal fat[d]

[a] When value range is omitted fatty acid percentage composition is given as an average value.
[b] A high percentage of this acid is a characteristic indicator.
[c] Here precautions are needed: animal fat, e. g. from beef, might contain up to 10% trans fatty acids.
[d] It is relatively high in marine oils (approx. 1%).

Table 14.24. Fatty acid composition of sunflower oil

Fatty acid	Per cent by weight	
	Average	Variation range[a]
16:0	6.2	3.0–10.0
16:1	0.08	<0.1
18:0	4.75	1.0–10.0
18:1 (9)	19.8	14–65
18:2 (9, 12)	67.0	20–75
18:3 (9, 12, 15)	0.08	<0.7
20:0	0.34	<1.5
20:1	0.15	<0.5
22:0	0.89	<1.0

[a] German guide values.

Table 14.25. E-factor of various oils for linoleic acid

Oils/fats	E-factor
Sunflower	1.2
Corn	1.3
Soybean	1.3
Rapeseed	1.7
Peanut	1.7

with the help of HPLC and GC (cf. 3.3.1.4). An example is the detection of foreign fat in milk fat. From extensive data on the triacylglyceride composition (GC differentiation according to the C-number), formulas have been developed which permit the detection of all important plant and animal fats up to a limiting value of 2–5 percent by weight. The older method, which is based on a decrease in the butyric acid concentration due to the foreign fat, does not safely detect an addition of 20 percent by weight because of the biological variation (3.5–4.5 w/w percent 4:0).

14.5.2.4 Minor Constituents

Some fats which can not be unequivocally distinguished by their fatty acid or triacylglyceride composition may be identified by analysis of the unsaponifiable minor constituents. Examples are given in Table 14.26.

Table 14.26. Fat or oil identification by analysis of unsaponifiable constituents

Analysis	Identification
Squalene	Olive or rice oil and fish liver oil
Campesterol/stigmasterol[a] (cf. 3.8.2.3.1)	Cocoa butter substitutes
Carotene (cf. 3.8.4.5)	Raw palm oil
γ-/β-Tocopherol[b] (cf. Table 3.51)	Corn oil
γ-Tocopherol (cf. Table 3.51)	Wheat germ oil
α-/γ-Tocopherol[b] (cf. Table 3.51)	Sunflower oil
γ-/δ-Tocopherol[b] (cf. Table 3.51)	Soybean oil
Cholesterol[c] (cf. 3.8.2.2.1)	Animal fat

[a] Concentration ratios are characteristic.
[b] Concentration of individual compounds and their concentration ratios are characteristic.
[c] Cholesterol concentration must exceed by 5% the total sterol fraction.

The detection of adulteration of oils and fats has been improved further by coupled HPLC and GC of the minor constituents. The saponification of the sample is not required, free and esterified compounds being detected separately.
An example is the differentiation between the olive oil qualities "*extra vierge*" and "*lampante*". After esterification of the free OH-groups with pivalic acid, the free fat alcohols, wax esters, free acids, triterpene alcohols and esters are eluted in a relatively narrow fraction in HPLC and separated from the triacylglycerides. The eluate is transferred to a gas chromatograph and analyzed on an apolar capillary column. As shown in Fig. 14.7, a clear distinction is made between "*lampante*" oils and "*extra vierge*" oils because the former have high contents of wax and sterol esters (sitosterol, 24-methylene cycloartenol) (cf. 14.3.2.1.1).

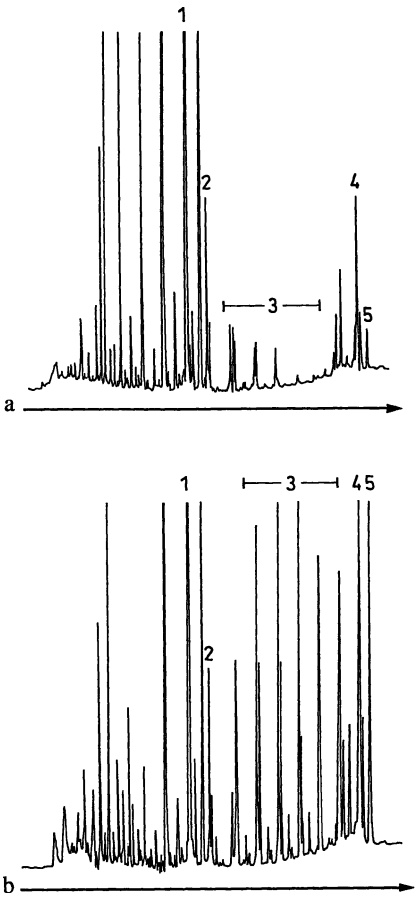


Fig. 14.7. On-line HPLC-GC of sterol and wax fractions of olive oils. **a** "*Extra vierge*" oil, **b** "*lampante*" oil. Peak 1: sitosterol, peak 2: 24-methylene cycloartenol, peak group 3: wax esters, peak 4: sitosterol ester, peak 5: 24-methylene cycloartenolester (according to *Grob* et al., 1991)

14.5.2.5 Melting Points

In addition to specific density, index of refraction, color and viscosity, the melting properties can be used to identify fats and oils.
The composition and the crystalline forms (cf. 3.3.1.2) of triacylglycerols present in fat determine the melting points and the temperature range over which melting occurs. The onset, flow point and end point of melting are of interest. They are determined by standardized procedures. The melting properties of fat are more accurately determined by differential thermal analysis. The temperature difference is measured between the fat sample and a blank, i. e. a thermally inert substance, as a function of the heating temperature (Fig. 14.8). In this way the temperatures at which polymorphic transitions of fat occur are detectable. In addition, the content of solid triacylglycerols can be assessed from the heat absorbed during melting at various temperatures. Thus, the solid triacylglycerol (TG) portion of coconut oil at $-3\,^{\circ}\mathrm{C}$ can be calculated using data from the recorded curve (Fig. 14.8) and the following formula:

$$\%\ \text{Coconut}\,(\text{solid TG}) = \frac{\text{Area (BCDE)}}{\text{Area (AEDA)}} \cdot 100 \qquad (14.11)$$

The solid: liquid ratio of acylglycerols is of importance in fat hydrogenation and interesterification processes (cf. 14.4.3). This ratio can also be assessed using the Solid Fat Index by measuring the expansion of the fat, i. e. the volume increase of a fat during its transition from solid to liquid and by ^{1}H-NMR spectroscopy (cf. 14.5.1).

14.5.2.6 Chemometry

To solve difficult problems in food chemistry, e. g., the detection of the authenticity of olive

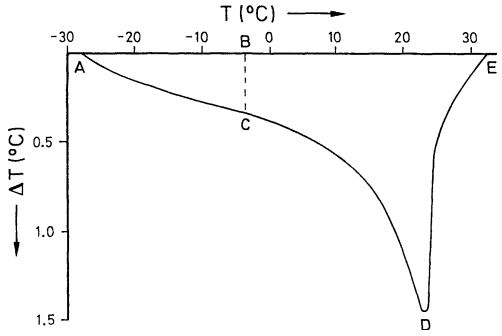


Fig. 14.8. Differential thermal analysis of a coconut fat

oils, the test procedures include chemometry. The measurements are planned and evaluated with the help of mathematical or statistical methods in order to gain the maximum amount of chemical information. An example is the addition of hazelnut oil to olive oil, *Raman* spectra being evaluated for the detection.

14.5.3 Detection of Changes During Processing and Storage

Processes used in recovery and refining and subsequent storage conditions are the main factors affecting the quality of edible fat or oil. A number of analytical methods are available for assessing the quality and deterioration of fat or oil.

14.5.3.1 Lipolysis

The extent of lipolysis (cf. 3.7.1) is determined by the free fatty acid content (FFA or Acid Value). Oils with FFA content exceeding 1% are commonly designated as crude oils, while lard with this level of free acids is considered spoiled. An exception is olive oil, which is still considered suitable for direct consumption even with a 3% FFA content. The FFA content is lowered to less than 0.1% by refining of oil or fat.

There is no relationship between the sensory perception of quality deterioration and the levels of FFA in fats which contain low-molecular acyl residues (e. g., milk, coconut, and palm kernel fats) because among the free fatty acids, the sensory-relevant compounds (C number <14) usually take second place. A better correlation is provided by the analysis of the low-molecular free fatty acids (cf. 3.7.1.1). They are first separated from the fat, e. g., with an ion exchanger, released from the exchanger by esterification with ethyl iodide, and then determined by gas chromatography.

14.5.3.2 Oxidative Deterioration

Fats and oils deteriorate rather rapidly by autoxidation of their unsaturted acyl residues (cf. 3.7.2.1). A number of analytical methods have been developed to determine the extent of such deterioration and to predict the expected shelf life of a fat or oil.

14.5.3.2.1 Oxidation State

Peroxide Value. The method for determination of peroxide concentration is based on the reduction of the hydroperoxide group with HI or Fe^{2+}. The result of the iodometric titration is expressed as the peroxide value. The Fe^{2+} method is more suitable for determining a low hydroperoxide concentration since the amount of the resultant Fe^{3+}, in the form of the ferrithiocyanate (rhodanide) complex, is determined photometrically with high sensitivity (Fe-test in Table 14.27). The peroxide concentration reveals the extent of oxidative deterioration of the fat, nevertheless, no relationship exists between the peroxide value and aroma defects, e. g. rancidity (already existing or anticipated). This is because hydroperoxide degradation into odorants is influenced by so many factors (cf. 3.7.2.1.9) which make its retention by fat or oil or its further conversion into volatiles unpredictable.

Carbonyl Compounds. The analysis of the compounds responsible for the rancid aroma defect of a fat or oil is of great value. Volatile carbonyls (cf. 3.7.2.1.9) are among such compounds.

In a simple test, such as benzidine, anisidine or heptanal values, the volatile aldehydes are not separated from fat or oil, rather the reaction with the group-specific reagents is carried out in the fat or oil. In addition to the odorous aldehydes, the flavorless oxo-acylglycerols and oxo-acids can be

Table 14.27. Analytical aspects related to the determination of the extent of oxidation of unsaturated fatty acids: relative sensitivities of spectrophoto-metric procedures[a]

Method		Autoxidized fatty acid methyl esters	
		18:2 (9,12)[b]	18:3 (9,12,15)[c]
UV-Absorption	234 nm	1.0	1.0
	270 nm	0.1	0.3
Fe^{2+}/Thiocyanate (rhodanide)		9.4	6.3
Thiobarbituric acid test	452 nm	0.1	0.5
	530 nm	0.1	1.0
Kreis-test		0.1	0.1
Anisidine value		0.3	0.75
Heptanal value		0.1	0.1

[a] Related to UV absorption at 234 nm.
[b] Peroxide value: 475.
[c] Peroxide value: 450.

determined. Since the proportion of aroma-active and sensory neutral carbonyls is not known, any correlation found between the carbonyl value and aroma defects is clearly coincidental.

The *thiobarbituric acid test* (TBA) is a preferred method for detecting lipid peroxidation in biological systems. However, the reaction is nonspecific since a number of primary and secondary products of lipid peroxidation form malonaldehyde which in turn reacts in the TBA test. In food containing oleic and linoleic acids, the TBA-test is not as sensitive as the Fe^{2+}-test outlined above.

The *gas chromatographic determination* of individual carbonyl compounds appears to be a method suitable for comparison with findings of sensory panel tests. Analytical methods for the odorants causing aroma defects is still in the early stages of development because only a few fats or fat-containing foods have been examined in such detail that the aroma substances involved are clearly identified.
The well studied warmed-over flavor of cooked meat (cf. 12.6.2.1) is an example. It can be controlled relatively easily because the easy-to-determine hexanal has been identified as the most important off-flavor substance. On the other hand, the easily induced rancid aroma defect of rapeseed oil is primarily caused by the volatile hydroperoxides (1-octen-3-hydroperoxide, (Z)-1,5-octadiene-3-hydroper-oxide) and (Z)-2-nonenal which can be quantitatively detected only by using isotopic dilution analyses (cf. 5.2.6). This limitation also applies to 3-methyl-2,4-nonandione, which appears as the most important off-flavor substance in soybean oil on exposure to light.
To simplify the analytical procedure, individual aldehydes (e. g., hexanal, 2,4-decadienal), which are formed in larger amounts during lipid peroxidation, have been proposed as indicators. In most of the cases, however, it was not tested whether the indicator increases proportionally to the off-flavor substances which cause the aroma defect.

14.5.3.2.2 Shelf Life Prediction Test

To estimate susceptibility to oxidation, the fat or oil is subjected to an accelerated oxidation test under standardized conditions so that the signs of deterioration are revealed within several hours or days. Examples of such tests are the *Schaal test* (fat maintained at 60 °C) and the *Swift stability test* (fat kept at 97.8 °C and aerated continuously). The extent of oxidation is then measured by sensory and chemical tests such as peroxide value (cf. 3.7.2), ultraviolet absorption (suitable for fats and oils containing linoleic or linolenic acids) or oxygen uptake. There are also methods based on the fact that in the process of triglycerol oxidation, when the initiation period is terminated, large amounts of low molecular weight acids are released. They are then determined electro-chemically. During oxidation of a given fat or oil sample, a good correlation exists between the length of the induction period and the shelf-life.

14.5.3.3 Heat Stability

The behavior of a frying oil, when heated, is assessed from the content of oxidized fatty acids which are insoluble in petroleum ether and from the smoke point (cf. 3.7.4) of the fat or oil. The smoke point of a fat or oil is the temperature at which its triacylglycerols start to decompose in the presence of air. Smoke is the sign of decomposition. The smoke point of a fat or oil is normally in the range of 200–230 °C during pro-

Table 14.28. Indicators of refined oils and fats

Refining step	Indicator	Remarks
Bleaching (cf.14.4.1.4)	a. Fatty acids with conjugated triene systems	Determination of "b" is more reliable than the UV measurement of "a"
	b. Disterylether (>0.5 mg/kg)	
Deodorization (cf. 14.4.1.5)	a. Dimeric and oligomeric triacylglycerides	Unlike "a", the indicators "b" appear even on relatively gentle deodorization
	b. Position and substitution isomers of linoleic acids	

longed frying, and it decreases in the presence of decomposition products. When it falls below 170 °C, the fat is considered to be spoiled. At this point, the amount of fatty acids which are insoluble in petroleum ether exceeds 0.7%. However, this petroleum ether method is not reproducible. Fat separation by column chromatography is more reliable. The heated fat or oil is separated into a polar and a nonpolar fraction using silicic acid as an adsorbent. The value of 0.7% oxidized petroleum ether-insoluble fat corresponds, in this chromatographic separation, to 73% nonpolar and 27% polar fractions.

14.5.3.4 Refining

The addition of a refined oil to natural plant oil is detected by the determination of substances which can be formed during bleaching and deodorization (cf. Table 14.28).

14.6 References

Baltes, J.: Gewinnung und Verarbeitung von Nahrungsfetten. Verlag Paul Parey: Berlin. 1975

Bockisch, M.: Nahrungsfette und -öle. Verlag Eugen Ulmer, Stuttgart, 1993

DGF-Einheitsmethoden. Ed. Deutsche Gesellschaft für Fettwissenschaft e.V., Münster/Westf., Wissenschaftliche Verlagsgesellschaft mbH: Stuttgart. 1950–1979

Gertz, C.: Native und nicht raffinierte Speisefette und -öle. Fat Sci. Technol. *93*, 545 (1991)

Gertz, C., Fiebig, H.-J.: Statement on the applicability of methods for the determination of pyropheophytin A and isomeric diacylglycerols in virgin olive oils. German Society for Fat Science (DGF), Division Analysis and Quality Assurance, Münster. 2005

Grob, K., Artho, A., Mariani, C.: Gekoppelte LC-GC für die Analyse von Olivenölen. Fat Sci. Technol. *93*, 494 (1991)

Grosch, W., Tsoukalas, B.: Analysis of fat deterioration – Comparison of some photometric tests. J. Am. Oil Chem. Soc. *54*, 490 (1977)

Guhr, G., Waibel, J.: Untersuchungen an Fritierfetten; Zusammenhänge zwischen dem Gehalt an petrolätherunlöslichen Fettsäuren und dem Gehalt an polaren Substanzen bzw. dem Gehalt an polymeren Triglyceriden. Fette Seifen Anstrichm. *80*, 106 (1978)

Hamilton, R. J., Rossell, J.B. (Eds.): Analysis of oils and fats. Elsevier Applied Science Publ.: London. 1986

Hoffmann, G.: The chemistry and technology of edible oils and fats and their high fat products. Academic Press: London. 1989

Kiritsakis, A., Markakis, P.: Olive oil – a review. Adv. Food Res. *31*, 453 (1987)

Li-Chan, E.: Developments in the detection of adulteration of olive oil. Trends Food Sci. Technol. 5, 3 (1994)

Official methods and recommended practices of the American Oil Chemists' Society, Firestone, D. (Ed.), 4th edn. American Oil Chemists' Society, Champaign, 1989

Reid, L.M., O'Donnell, C.P., Downey, G.: Recent technological advances for the determination of food authenticity. Trends Food Sci. Technol. *17*, 344 (2006)

Schulte, E., Weber, N.: Disterylether in gebleichten Fetten und Ölen – Vergleich mit den konjugierten Trienen. Fat Sci. Technol. *93*, 517 (1991)

Sheppard, A. J., Hubbard, W. D., Prosser, A. R.: Evaluation of eight extraction methods and their effects upon total fat and gas liquid chromatographic fatty acid composition analyses of food products. J. Am. Oil Chem. Soc. *51*, 417 (1974)

Stansby, M. E.: Fish oils. AVI Publ. Co.: Westport, Conn. 1967

Swern, D. (Ed.): Bailey's industrial oil and fat producis. 4th edn., Vol. 1, John Wiley and Sons: New York. 1979

Usuki, R., Suzuki, T., Endo, Y., Kaneda, T.: Residual amounts of chlorophylls and pheophytins in refined edible oils. J. Am. Oil Chem. Soc. *61*, 785 (1984)