

Fatty acids in vegetable oils and their importance in cosmetic industry

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Please cite as: CHEMIK 2014, 68, 2, 103–110

Introduction

Vegetable oils are liquid vegetable fats that remain in the liquid form at room temperature. These lipids are most commonly extracted from various parts of plants such as seeds, fruits, or plant seedlings. Under the chemical terms they are a combination of triglycerides of higher saturated and unsaturated fatty acids. In other words, these compounds are esters of glycerol and higher fatty acids, containing in their structure long (low C I 4:0) aliphatic carbon chains [1]. Vegetable oils, depending upon the individual percentages of fat acids in the molecule, exhibit a variety of properties. Thanks to their beneficial influence, especially on the skin, fatty acids are of great importance in cosmetology, becoming more and more commonly used components of many cosmetic formulations intended for daily care of the face and body. Deficiency in these compounds can cause excessive drying of the skin. Vegetable oils, serving as a cosmetic base, prevent water loss through the skin, mainly by means of making a protective layer on the epidermis. Additionally, they soften the stratum corneum and reduce inflammation of the skin, thereby weakening the sensation of pain. Furthermore, they play a very important role in the proper functioning of the human body. Also medicine recognizes the beneficial effects of vegetable oils, mainly in the biological synthesis of components of cell membranes or eicosanoids (prostaglandins, prostacyclins, thromboxanes, leukotrienes). Oils are also involved in the transport and oxidation of cholesterol. The absence of these oils contained in the fatty acids significantly affects vascular fragility, reduces the immune system workflow, interferes with the clotting process and also increases the likelihood of the development of atherosclerosis [2].

Types of fatty acids

The name of Essential Fatty Acids (EFA) was introduced in 1929 and refers to the fatty compounds important for the proper development and functioning of the human body. Depending on the presence and the number of bonds, fatty acids can be classified into saturated and mono- and polyunsaturated (including the so-called omega-3, omega-6 and omega-9 family) – Fig. 1. This typology is a key parameter determining the usefulness of cosmetic triglycerides [2, 3].

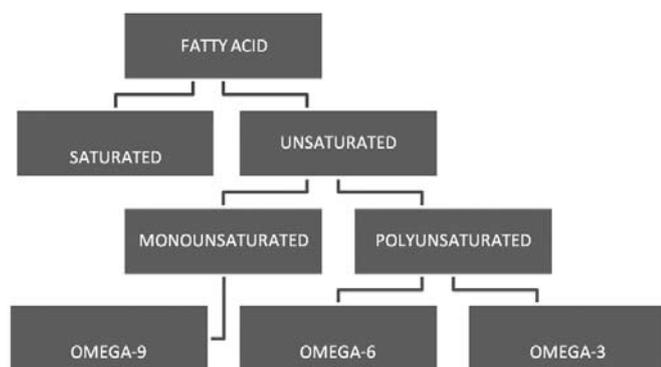


Fig. 1. Fatty acids types

Saturated fatty acids

This group includes fatty acids, which do not contain double bonds in the molecule. Under normal conditions, these compounds are most often white solids. Fatty acids having a chain of more than 10 aliphatic carbon atoms are non-volatile and insoluble in water [4]. Among the saturated fatty acids found in vegetable oils are: myristic acid, palmitic, stearic or arachidic acids (Tab.1). Shorter chain fatty acids (C8–10) occur in nature only in the form of triglycerides.

Table 1
Examples of saturated fatty acids

Systematic name	Common name	Formula	Symbol
Caprylic acid	Octanoic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	C8:0
Capric acid	Decanoic acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$	C10:0
Lauric acid	Dodecanoic acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	C12:0
Myristic acid	Tetradecanoic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	C14:0
-	Pentadecanoic acid	$\text{CH}_3(\text{CH}_2)_{13}\text{COOH}$	C15:0
Palmitic acid	Hexadecanoic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	C16:0
Margaric acid	Heptadecanoic acid	$\text{CH}_3(\text{CH}_2)_{15}\text{COOH}$	C17:0
Stearic acid	Octadecanoic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	C18:0
-	Nonadecanoic acid	$\text{CH}_3(\text{CH}_2)_{17}\text{COOH}$	C19:0
Arachidic acid	Eicosanoic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	C20:0
Behenic acid	Docosanoic acid	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$	C22:0
Lignoceric acid	Tetracosanoic acid	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$	C24:0

Unsaturated fatty acids

The composition of this family includes fatty acids containing double bonds, which are usually colourless liquids. For most of them, all double bonds are in the *cis* position. When determining the position of the double bonds their exact location is pointed out. The most commonly used for this denotation is the symbol: $\Delta^{k,l,m..}$, where k, l, m.. indicate the number of the carbon atom on which there is a double bond, counting from the carboxyl group. For example, linoleic acid can be denoted as $\Delta^{9,12}$, which means that the double bonds are located at the 9 and 12 carbon atoms [4]. Currently, there are two main classes of unsaturated fatty acids, namely the monounsaturated fatty acids, which include omega-9 fatty acids (ω -9 or n-9) and polyunsaturated fatty acids, which include omega-6 (ω -6, n-6) and omega-3 (ω -3, n-3). Polyunsaturated fatty acids have in their structure at least two double bonds, and at least 18 carbon atoms in the alkyl chain. Biological activity of the molecule depends on the configuration and the specified position of the *cis* double bonds. It is worth noting that carbon in $-\text{CH}_3$ group is called the *omega* carbon and also all the double bonds are separated by at least one methylene group. The systematic names of unsaturated fatty acids have to provide the location of a double bond, counting from the carboxyl carbon. For example, linoleic acid is also called 9, 12-octadecadienoic acid [2].

The so-called essential fatty acids (EFAs) include linoleic acid (LA) and α -linolenic acid (ALA), they are not synthesised in the human body

because of the lack of appropriate enzymes. Other polyunsaturated fatty acids can be synthesized only if EFA will be delivered with food and when no enzyme defect would occur in the metabolic pathway. Linoleic acid is considered the most important of all omega-6 fatty acids, because it can be obtained with other acids of this group such as ALA or γ -linolenic acid (GLA) [1 ÷ 4].

The unsaturated fatty acids most important in cosmetology and medicine include [2, 4]:

- monounsaturated fatty acids, containing one double bond, such as palmitoleic acid 16:1 (ω -7), oleic acid 18:1 (ω -9), erucic acid 22:1 (ω -9), nervonic acid 24:1 (ω -9)
- biunsaturated acids (diene) containing two double bonds, such as 18:2 linoleic acid (ω -6, LA)
- triunsaturated acids (triene), containing three double bonds, such as α -linolenic acid 18:3 (ω -3, ALA) acid, γ -linolenic acid 18:3 (ω -6, GLA)
- tetraunsaturated acids (tetraene) containing four double bonds, such as arachidonic acid, 20:4 (ω -6 -related biogenetically prostanoids).

The following are most unsaturated fatty acids present in vegetable oils (Tab. 2).

Table 2
Examples of unsaturated fatty acids [4]

Common name	Systematic name	General formula	Numerical Symbol	Omega family
Palmitoleic acid	(Z)-9-hexadecenoic acid	C ₁₆ H ₃₀ O ₂	16:1	7
Oleic acid	(Z)-9-octadecenoic acid	C ₁₈ H ₃₄ O ₂	18:1	9
Elaidic acid	(E)-9-octadecenoic acid	C ₁₈ H ₃₄ O ₂	18:1	9
Petroselinic acid	(Z)-6-octadecenoic acid	C ₁₈ H ₃₄ O ₂	18:1	12
Vaccenic acid	(E)-11-octadecenoic acid	C ₁₈ H ₃₄ O ₂	18:1	7
Gondoic acid	(Z)-11-eicosenoic acid	C ₂₀ H ₃₈ O ₂	20:1	9
Hydnocarpic acid	11-(2-cyclopenten-1-yl)undecanoic acid	C ₁₆ H ₂₈ O ₂	-	-
Chaulmoogric acid	13-(2-cyclopenten-1-yl)tridecanoic acid	C ₁₈ H ₃₂ O ₂	-	-
Erucic acid	(Z)-13-docosenoic acid	C ₂₂ H ₄₂ O ₂	22:1	9
Nervonic acid	(Z)-15-tetracosenoic acid	C ₂₄ H ₄₆ O ₂	24:1	9
Linoleic acid (LA)	(Z,Z)-9,12-octadecadienoic acid	C ₁₈ H ₃₂ O ₂	18:2	6
α -Linolenic acid (ALA)	(Z,Z,Z)-9,12,15-octadecatrienoic	C ₁₈ H ₃₀ O ₂	18:3	3
γ -linolenic acid (GLA)	(Z,Z,Z)-6,9,12-octadecatrienoic acid	C ₁₈ H ₃₀ O ₂	18:3	6
cis-linolenic acid (CLA)	(E,E,E)-9,12,15-octadecatrienoic acid	C ₁₈ H ₃₀ O ₂	18:3	3
Punicic acid	(Z,E,Z)-9,11,13-octadecatrienoic acid	C ₁₈ H ₃₀ O ₂	18:3	5
Oleostearic acid	(E,E,E)-9,11,13-octadecatrienoic acid	C ₁₈ H ₃₀ O ₂	18:3	5
Arachidonic (AA)	(all-Z)-5,8,11,14-eicosatetraenoic acid	C ₂₀ H ₃₂ O ₂	20:4	6
Eicosapentaenoic acid (EPA), Timnodonic acid	(all-Z)-5,8,11,14,17-icosapentaenoic acid	C ₂₀ H ₃₀ O ₂	20:5	3
Docosapentaenoic acid (DPA), Clupanodonic acid	(all-Z)-4,8,12,15,19-docosapentaenoic acid	C ₂₂ H ₃₄ O ₂	22:5	3
Docosahexaenoic acid (DHA)	(all-Z)-4,7,10,13,16,19-docosahexaenoic acid	C ₂₂ H ₃₂ O ₂	22:6	3
Ricinoleic acid	(R)-12-hydroxy-(Z)-9-octadecenoic acid	C ₁₈ H ₃₄ O ₃	C18:1	9

The effect of lipids and fatty acids on the skin

Table 3 presents concentrations of particular components of human sebum on the skin and excreted by sebaceous glands. The

free fatty acids on the skin are supposed to be generated as a result of decomposition of triglycerides by bacteria. On destruction of the protective barrier or on elevation of the transepidermal loss of water (TEWL), epidermis produces more lipids in the lamellar granules of the stratum granulosum. Unfortunately, with age the reproduction of lamellar granules slows down. It has been shown that the use of lipids containing fatty acids, in particular those belonging to omega-6 series, accelerates the reproduction of lipids in lamellar granules [5]. A lipid barrier forms at the interface between the stratum granulosum and stratum corneum. At this interface the lamellar granules form aggregates, their membranes undergo fusion and the contents of the granules are released in the form of discs and lamellae (Fig. 2). It should be mentioned that the use of a single lipid (e.g. cholesterol) on young skin causes a delay in regeneration of the lipid barrier, but on aged skin it has the opposite effect. The use of a mixture of three lipids (fatty acids with cholesterol and ceramides) on the aged skin brings acceleration of regeneration of the lipid barrier if the dominant component of the cream is cholesterol. On the young skin a similar effect was observed when any of the three components dominated at the ratio 3:1:1 [9].

Table 3
Selected lipid components of human sebum [5, 6]

Lipids group	Content in %	
	On the skin surface	In sebaceous glands
Fatty acid triglycerides	19.5–49.4	24.0–34.0
Free fatty acids	7.9–39.0	-
Waxes and esters of cholesterol	24.1–32.1	17.7–21.5
Squalene	10.1–13.9	25.6–31.6

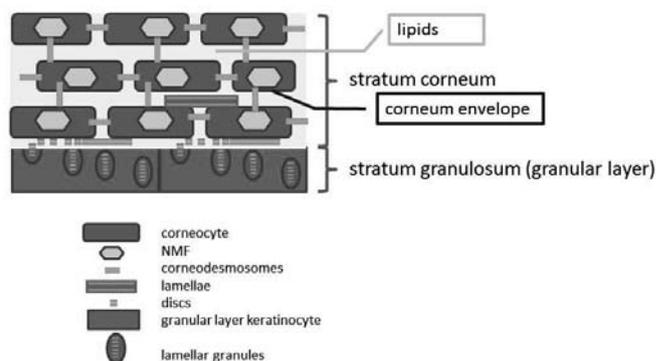


Fig. 2. Structures of the stratum corneum and stratum granulosum and formation of lipids [5 ÷ 8]

The use of selected fatty acids

Linoleic acid occurs most abundantly in sunflower oil, soybean oil, safflower, corn oil, sesame oil, peanut oil, grape seed oil and wheat sprout oil. This compound plays a significant role in the skin. In dry skin it strengthens the lipid barrier of epidermis, protects against transepidermal loss of water and normalises the skin metabolism. Linoleic acid is a natural component of sebum. In persons with acne skin, a decrease in LA content in sebum is observed, which leads to blocked pores and formation of comedos and eczemas. The use of linoleic acid for oily skin and problematic skin care leads to improvement of the work of sebaceous glands, unblocking of pores and decrease in the number of comedos. Moreover, this acid is built in the structure of cell membrane and is also used for production of intercellular cement of the skin. These two processes are possible thanks to the presence of the enzymatic complex in the

stratum corneum of epidermis. It should be noted that Linoleic acid is also a component of ceramide 1 (so far 7 different ceramides have been identified in stratum corneum of human skin) [1, 2].

Another important fatty acid from omega-6 series is γ -linolenic acid formed as a result of delta-6-desaturase enzyme on the pathway of metabolic transformations of linoleic acid. Rich natural sources of GLA are oil from borago officinalis seeds, black currant oil, evening primrose oil and hemp oil [7]. A representative of omega-3 group, α -linolenic acid is found in linseed oil, soybean oil, rapeseed oil, wheat sprout oil, walnut oil, algae and marine phytoplankton. Both α - and γ -linolenic acids are physiological components of cell membranes or mitochondria membranes in human cells. They are involved in inner and outer cell transport, including transmission of signals in the neuronal lattice of the brains [1 ÷ 4, 7]. The other acids such as eicosapentaenoic acid (EPA) or docosahexaenoic acid (DHA) are most often met in fish oil from salmon, cod, herring, mackerel. There are reasons to suppose that deficiency in essential unsaturated fatty acids (wrong diet) is related to the incidence of neoplastic diseases. Omega-3 fatty acids, in particular EPA and DHA, inhibit development of tumours, growth of neoplastic tissue and its spreading [10]. It has been proved that these acids are able to reduce the UV induced post-inflammatory substances. The fatty acids alleviate the effects of sunburn, stimulate healing processes and soothe irritations [1]. Eicosanoids are also engaged in platelet aggregation, chemotaxis and cell growth [11]. The omega series acids ω -9 (oleinic), ω -6 (linolic) and ω -3 (α -linolenic) reduce

the transepidermal water loss so improve the skin moistening, activate regeneration of damaged lipid barrier of the epidermis, heal inflammations and stabilise the skin metabolism [1]. Essential Fatty Acids (EFA) also act as receptors stimulating the synthesis of barrier lipids of the skin and proteins being precursors of the natural moistening factor [12]. Highly beneficial properties of many fatty acids have prompted the interest in vegetable oils and their use as active ingredients of many cosmetic preparations.

Fatty acids in vegetable oils

Unsaturated fatty acids present in vegetable oils are characterised by high absorbability and antiallergic properties. Thanks to their beneficial and diverse effects on the skin they have found wide applications in many branches of industry, in particular in cosmetic industry and cosmetology, pharmacy and medicine. In cosmetic industry, vegetable oils are used mainly as the vehicle for other active ingredients, dissolved or dispersed in oil-water type emulsions. The most often used essential unsaturated fatty acids are those from the omega-3, omega-6 and omega-9 series. The most important among them are 18-carbon acids (C18): monounsaturated (omega-9) – oleic acid, biunsaturated (omega-6) linoleic acid, including *cis*-linoleic acid with conjugated double bonds at positions 3 and 6 (CLA, *conjugated-linoleic acid*), triunsaturated (omega-3), α -linolenic acid (ALA) and (omega-6), γ -linolenic acid (GLA) [1–3]. Table 4 gives a list of most popular vegetable oils and the fatty acids they contain [13 ÷ 16].

Table 4

Composition of selected vegetable oils; estimated percentage content of the main components is given in parentheses [13 ÷ 16]

Name	saturated fatty acids	Unsaturated fatty acids			
		Omega-3	Omega-6	Omega-9	Inne
Argan oil	PA (12,8); SA (5,8)	ALA (0,5)	LA (33)	OA (46,6)	
Chokeberry (seed) oil		ALA (8)	LA (39)	OA (31)	
Avocado oil	PA(4–12); SA (2); ARA		LA (10–20)	OA (60–80)	POA (5–80)
Peach (pits) oil			LA (25)	OA (65)	
Canola oil	PA (6,2)	ALA (6,6)	LA (21,6)	OA (61,3)	
Nigella oil	MA (<1); PA (10–14); SA (1–4)	ALA (<0,5)	LA (50–60); GLA (<0,5)	OA (20–30)	POA (<0,5)
Pumpkin (pumpkin seed) oil	PA (8–15); SA (4–7)		LA(45–60)	OA (22–36)	
Wild rose (seeds)	MA (<0,5); PA (3–5); SA (1,5–2,5)	ALA (28–32)	LA (35–50)	OA (13–18)	POA (<0,5)
Pomegranate seeds oil	PA (5–8); SA (2–6)		LA (9–10)	OA(8–9)	PU (60–65)
Jojoba (liquid wax) oil	PA (<3)			OA (5–15); EA (65–80); EU (10–20)	
Cocoa/cocoa butter				OA (38)	
Wheat sprout oil	PA (14); SA (3)	ALA (8)	LA(57)	OA (28)	
Coconut/coconut butter	LAU (44–55); MA (6–21); PA (7–12); SA (2–5); KYL (4–10); KYN (3–8)		LA (1–2)	OA (4–12)	
Safflower oil	PA (6–7,5); SA (<2,5); ARA (<0,5)	ALA (10)	LA (70–85)	OA(15–25)	
Corn oil	PA (55–65); SA (4)			OA (29)	
Camelina oil	PA (7,8); SA (3)	ALA (31,2)	LA (23)	OA (16,8); EA (12); EU (2,8)	
Flax seed oil	PA (5–7); SA (3–7)	ALA (48–60)	LA (<20)	OA (10–18)	
Macadamia oil	PA (8,5–9); SA (3–3,5)			OA (57–61)	POA (14–20)
Raspberries seeds oil	PA (2,1); SA (0,9)	ALA (23,9)	LA (57,5)	OA (13,3); EA (0,4)	
Meadowfoam seeds oil				EA (63); EU (16); C22:1 (17)	
Passiflora seeds oil	PA (8); SA (2) -	ALA (1)	LA (77)	OA (12)	
Almond oil	PA (3–5); SA	ALA (15–22)	-	OA (70–80)	
Neem oil	PA (19); SA (15); MA (1)		LA (17)	OA (48)	
Moringa oil				OA (85)	
Borago oil	PA (9,5–11,5); SA (2–4,2)		LA (34–40); GLA (18–25)	OA (13,5–18,5)	
Olive oil	PA (11); ARA; BA; MAR	ALA (0,7)		OA (75)	
Peanuts oil	PA (6–16); SA (1–7); ARA (1–3); BA (2–5); LCA 1–3)		LA (13–45)	OA (36–72)	
Hazelnuts oil	PA (4–7); SA (1–6)		LA (7–20)	OA (68–85)	POA (<1)
Walnut oil	PA (5–8); SA (2–6); ARA (<0,5)	ALA (<0,8)	LA (45–65)	OA (14–21); EA (<0,5)	POA (<1)

Palm oil	LAU (51); MA (17); PA (8); SA (2)		LA (5–7)	OA (13)	-
Papaya seeds oil	PA (<16); SA (<5,5)			OA (74)	
Parsley seeds oil	PA; SA	ALA (<1)	LA (16–20)	OA (8–10)	PES (68–72)
Seabuckthorn oil	PA (30–33); SA (<1)	ALA (30)	LA (5–7); GLA (35)	OA (14–18); EA (2)	POA (30–35)
Castor oil	PA (1–2); SA (<1,5); ARA (<0,6)	ALA (<0,5)	LA (5–7)	OA (3–7); RY (80–91)	POA (<0,5)
Rice oil	PA (15); SA (1,9)	ALA (1,1)	LA (39,1); AA (0,5)	OA (42,5)	
Sesame oil	PA (9–10); SA (5–6)	ALA (0,5)	LA (41–45)	OA (41–43)	
Shea butter/ karité butter	SA (30–40)			OA (45–50)	
Sunflower oil	PA (6–7); SA (4–5)	ALA (<0,8)	LA (60–72)	OA (16–25)	
Soybean oil	PA (7–12); SA (2–6); ARA (2)	ALA (4–10)	LA (48–58)	OA (20–30)	
Tamanu oil	PA (13,5); SA (15,6)	ALA (0,2)	LA (33,7)	OA (35,5)	
Evening primrose oil	PA (6,2); SA (1,8)	ALA (<2)	LA (70–75); GLA (10–15)	OA (3,5–5,4)	
Grape seeds oil	PA; SA	ALA (0,5)	LA (72–85)	OA (10)	
Cranberry seeds oil	PA (5,4); SA (1)	ALA (33,8)	LA (34,2)	OA (24,5)	POA (<0,5)

Explanations: PA – palmitic; SA – stearic; ARA – arachidic; BA – behenic; LAU – lauric; MA – myristic; KYL – caprylic; KYN – caprynic; MAR – margaric; LCA – lignoceric; ALA – α -linolenic; LA – linolenic; GLA – γ -linolenic; POA – palmitoleic; OA – oleic; EA – eicosenic; EU – erucic; RY – ricinolenic; PES – petroselinic; AA – arachidonic; PU – punicic

Summary

Vegetable oils are rich source of fatty acids and have been successfully used in cosmetic products. Because of their oiling, softening, smoothing and protective properties they are classified to the group of emollients. They make the skin look smooth and properly moistened. Recently, much attention has been paid to the so-called virgin oils whose composition is the same as that inside the seeds of oleaginous plants. The oil of best quality is obtained by cold pressing. Vegetable oils obtained by this method contain a large number of compounds essential for human organism and many ingredients of high quality cosmetic products for skin and hair care. The strongest cosmetic activity has been established for unsaturated fatty acids contained in triglycerides, in particular omega-6 and omega-3 acids belonging to EFA. For skin care the most important are the oils with high contents of linoleic acid (ω -6) and α -linolenic acid (ω -3), as they are the least comedogenic and restrict the formation of eczemas. Moreover, both these oils are able to incorporate into the lipid components of cell membranes, to regenerate damaged lipid barrier of epidermis and restrict the loss of water. Unsaturated fatty acids show pronounced healing effect on many dermatoses, like e.g. atopic skin inflammation and in skin care [7]. They are used as the base of creams, emulsions, cosmetic milks and creams, ointments, hair conditioners, brilliantine, cosmetic masks, protective lipstick, bath fluids, nail varnish and nail cleaners. In cosmeceutics they are used both as base and active ingredients. Many natural substances of high biological activity such as vitamins A, D, E, provitamin A and phospholipids, hormones, steroids and natural dyes dissolve in fatty acids [1 ÷ 7]. All the above mentioned beneficial effects of vegetable oils and fatty acids they contain illustrate the importance of this group of ingredients for skin and hair care.

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