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PHYSICOCHEMICAL AND HEALTH PROPERTIES OF FATS

Joanna Lamorska, Jerzy Tys

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CONTENTS

List of symbols:

SFA – Saturated Fatty Acids,
MUFA – Monounsaturated Fatty Acids,
PUFA – Polyunsaturated Fatty Acids,
LA – linolenic acid,
EFA – Essential Fatty Acids,
TEAC – Trolox Equivalent Antioxidant Capacity (number of millimoles of Trolox equivalent to the antioxidant activity of 1 millimole of substance analysed),
OLA – oleic acid,
ALA – α-linoleic acid,
TAG – triacylglycerides (triglycerides),
AA – arachidonic acid,
GLA – γ-linolenic acid,
DGLA – dihomogamma-linolenic acid,
EPA – eicosapentaenoic acid,
DHA – docosahexaenoic acid,
CLA – Conjugated Linoleic Acid,
LDL – Low Density Lipoproteins,
HDL – High Density Lipoproteins,
AN – acid number,
PN – peroxide number,
AV – anisidine value,
IV – iodine value,
SV – saponification value,
$^1\sum^+_g O_2$, $^1\Delta_g O_2$ – forms of singlet oxygen,
$^3\sum_g O_2$ – triplet oxygen,
$L^{\bullet}$ – alkyl radical,
$LOO^{\bullet}$ – peroxide radical,
LH – fatty acid,
Sen_0 – sensitiser in ground state,
Sen_1^* – sensitiser in singlet excited state,
Sen_2^* – sensitiser in triplet excited state,
Chl_0 – chlorophyll in ground state,
Chl_1^* – chlorophyll in singlet excited state,

Chl_2^* – chlorophyll in triplet excited state,
$^{\bullet}OH^-$ – hydroxyl radical,
$LO^{\bullet}$ – alkoxide radical,
$Fe{=}O^{2+}$ – ferryl cation radical,
$Fe{=}O^{3+}$ – perferryl cation radical,
LOOH – fatty acid hydroperoxide,
K – β-carotene,
$K^{\bullet-}$ – carotenoid anion radical,
$K^{\bullet}$ – carotenoid radical,
T–OH – tocopherol,
TO^{*+} – tocopheroxyl cation radical,
AsH^- – ascorbic acid,
RFO – reactive forms of oxygen,
ADHD – Attention Deficit Hyperactivity Disorder,
BHA – butylated hydroxyanisole, synthetic antioxidant,
BHT – butylated hydroxytoluene, synthetic antioxidant,
PGE_3, PGI_3, TXA_3, LTB_5 – eicosanoids, derivatives of EPA,
PGE_2, PGI_2, TXA_2, LTB_4 – eicosanoids, derivatives of AA.

1. INTRODUCTION

Fats are a fundamental component of human diet, consumed on a daily basis. Therefore, their quality and dietary value are of fundamental importance for human health. The role of fat in the organism is highly extensive: it is the main source of concentrated energy, it affects the digestive processes, it is a structural material for cell walls, as subcutaneous fat it provides protection against loss of heat, as organ-embedding fat it stabilises the organs within the body, it is a source of many vitamins, including vitamins A, D, E and K. A special role is attributed to plant fats which are a source of essential fatty acids that are not synthesised by the human organism. Those acids are responsible for the correct functioning of, among other things, the nervous system, the heart muscle, or the eye retina. They also have the capacity of preventing clog formation in the blood and of lowering the level of cholesterol and other lipid indicators of the blood.

This indicates that fats play a highly improtant and positive role in the human organism. However, they can also be the cause of many serious disorders, such as obesity or cardiovascular diseases. The diversity of the functions of fats results from the profile of fatty acids included in their composition. The percentage share of the particular fatty acids determines the role of a fat, beneficial or negative, in the human organism. Apart from the fatty acid profile, also other substances included in the composition of fats play important roles. These issues are of particular importance nowadays, due to the high share of processed food products in the diet, as antioxidants included in the oils, such as tocopherols, sterols or carotenoids, perform the function of purifying the organism of dangerous radicals.

The weight of these issues results not only from the research and cognitive point of view, but it also has a key significance in the evaluation of the quality and health properties of such food products as e.g. vegetable oils which more and more frequently substitute fats of other origins.

For these reasons studies on the thermostability, thermo-oxidation, photo-oxidation and auto-oxidation of oils are highly important, both from the research and the practical points of view. Acquisition of knowledge on the antioxidative processes in fats and transfer of the research results into practice (technology of expression of vegetable oils) would have a direct impact on human health, contributing to better control of the increasingly dangerous civilisation diseases, such as cardivascular diseases, tumors, ohpthalmic and dermatological diseases, diabetes, hypertension, as well as Alzheimer and Parkinson diseases, and many other disorders related with the production of free radicals and peroxides in the human

organism. The mechanisms of free radicals effect are not fully studied yet, therefore such research is extremely important. Demonstration of just how important is the role of temperature, oxygen and light in the oxidative processes of oils should be of interest to the process engineers in oil producing companies, as their activity can contribute to the market appearance of oils with enhanced health-promoting values, and not only oils providing a source of energy.

Characterisation of the physicochemical processes taking place in vegetable oils under the effect of external factors is of particular importance now, due to the high share of processed food products in the diet, as antioxidants included in the oils, such as tocopherols, sterols or carotenoids, perform the function of purifying the organism of dangerous radicals.

The physical and physicochemical methods applied in the studies ensure rapid and objective estimation of the quality of oils. They are innovative methods that permit the determination of the mechanisms and the kinetics of the complex processes of photo- and auto-oxidation in the course of the technological processes of acquisition of oils and during their storage. The application of such research in the oil producing industry will permit the production of vegetable oils – nutraceutics with significant health-promoting effects.

However, the levels of those valuable components are dependent on the processing to which particular groups of fats are subjected. Hence the importance of acquiring knowledge on the physicochemical properties of fats, as that will permit the determination of the mechanism of their effect on the human organism.

Triglycerides are the main component of vegetable and animal fats. Comparing the energy released during the oxidation of 1 g of a fatty acid, which is 37.7 kJ, with the energy obtained during the oxidation of 1g of protein or 1 g of a carbohydrate, which amount to only 16.7 kJ, we can see that TAG are a source of concentrated energy. The basis for the utilisation of that energy potential is the reaction of hydrolysis, as a result of which fatty acid is obtained from molecules of fat.

In the human organism fatty acids not only play the function of a source of energy but are also an important element of cell membranes, being included in phospho- and glycolipids. Derivatives of fatty acids also play the role of hormones and carriers of information on the intracellular level (Stryer 1997). At present, a special role is attributed to polyunsaturated fatty acids from the omega-6 group, and especially to the γ-linolenic acid (GLA, 18:3) which has anti-carcinogenic effects, and to acids from the omega-3 group: α-linoleic acid (ALA, 18:3) and the long-chain EPA (20:5) and DHA (22:6), with proven health-promoting properties. Similar properties are displayed by the isomer 9-*cis*, 11-*trans* of the linoleic acid CLA. Those fatty

acids are classified as functional food components, i.e. components of food that, apart from the basic nutrients and required sensory features, have also health-promoting components with prophylactic effects, as well as those that have a positive effect on the human sense of well-being.

The composition of vegetable fats and of certain animal fats includes also numerous non-nutrient substances with prophylactic and therapeutical properties, such as carotenoids, tocopherols and, occurring only in vegetable fats, phytosterols and polyphenols. Those components are referred to as nutraceutics. They play an especially important role in the prophylaxis of an increasingly large number of diseases called civilisation diseases, such as atherosclerosis, hypertension, obesity and cancers. The prophylaxis of those diseases requires a change in food habits and strict control of the quality of food products. Properly selected diet may have an effect on the following:

- lowering of the level of LDL cholesterol in the blood serum,
- reduction of free oxygen radicals,
- limitation of the synthesis of eicosanoids derived from LA, with a strong pro-inflammatory action.

Therefore, food should contain small amounts of saturated fatty acids (SFA), abound in monounsaturated fatty acids (MUFA), and also have a content of omega-3 and omega-6 fatty acids in suitable proportions. The presence of anti-oxidants and phytosterols in the diet is also necessary.

The above recommendations can be fulfilled not only by the meditteranean diet, the main components of which are olive oil, fish and frutti di mare, as well as vegetables and fruits. Countires where natural occurrence of those components is limited should also promote a diet that makes use of valuable compounds contained in the seeds of rapeseed which is sometimes called “the olive of the North”.

The present work is a monograph devoted to the characterisation of vegetable and animal fats and their components, and of the effect of the consumpotion of fats on human health. The information contained herein should contribute to an increase in the consumption of vegetable oils with unique and universal traits, that can supplement our diet while imparting excellent technological and sensory properties fo the food products.

2. DEFINITION OF LIPIDS AND THEIR CLASSIFICATION

Lipids are naturally occurring organic molecules with diverse structure, the common trait of which is absence of water solubility. Due to the non-polar character of the molecules, they can be extracted from tissues or from cells with non-polar organic solvents such as acetone, benzene, chloroform, ethyl ether, petroleum ether, carbon tetrachloride and alcohols. Lipids also include compounds that do not comply with the definition, e.g. butyric acid.

Lipids are classified in three categories (Tab. 1), relative to similarities in their molecular structure, as follows:

- ***simple lipids*** which are esters of glycerol and fatty acids or esters of fatty acids and alcohols other than glycerol,
- ***compound lipids*** whose molecules contain fatty acids, alcohols and additional compounds, e.g. phosphoric acid, sugar, sphingoid,
- ***secondary or derivative lipids*** which are formed through hydrolysis of simple and compound lipids, having the properies of their component substances.

Table 1. Classification of lipids (Drozdowski 2007)

Lipids		
simple lipids	compound lipids	derivative lipids
proper lipids (acylglycerols)	phospholipids (lipids containing phosphoric acid)	fatty acids
waxes (esters of higher fatty acids and alcohols other than glycerol)	-glycerophospholipids -sphingophospholipids	
	glycerolipids (lipids containing one sugar residue attached to the lipid part by a glycosidic linkage)	alcohols (other than glycerol)
	-glycoglycerolipids -glycosphingolipids -other, e.g. sulpholipids	hydrocarbons

Lipids perform a variety of functions in the organism:

- structural, being the main structural component of celluar membranes,
- signalling, as hormones and cellular messengers,
- energy storage – triacylglycerols, as strongly reduced and anhydrous compounds, constitute the main form of energy storage in the organism (Stryer 1997).

2.1. Physicochemical properties of vegetable and animals fats

In terms of their chemistry, animal and vegetable fats are mixtures of various lipids. A greater part of those mixtures are triacylglycerols (TAG), i.e. triesters of glycerol and three molecules of higher carboxyl acids (Fig.1) , therefore TAG are classified as simple, proper lipids.

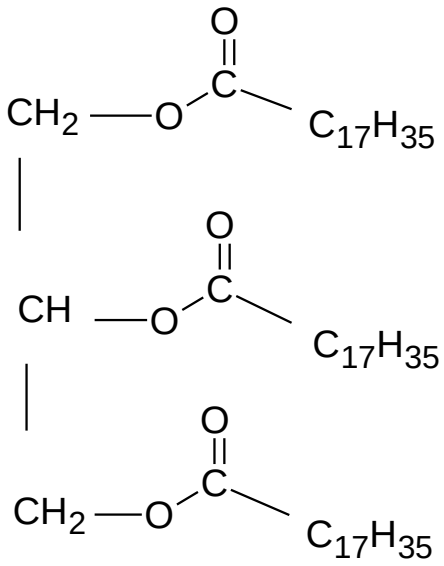
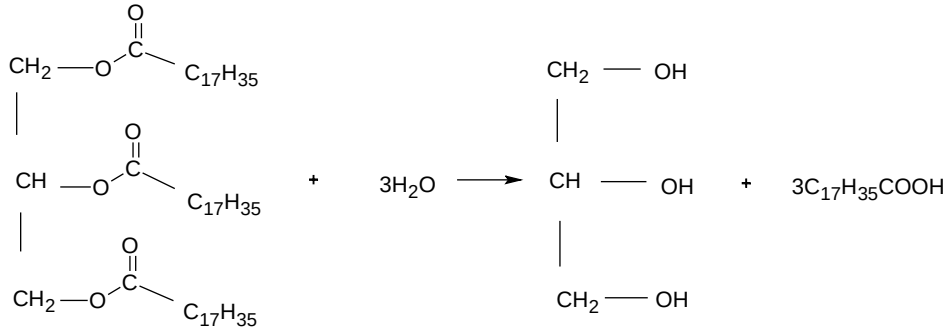


Fig. 1. Structural formula of a molecule of fat

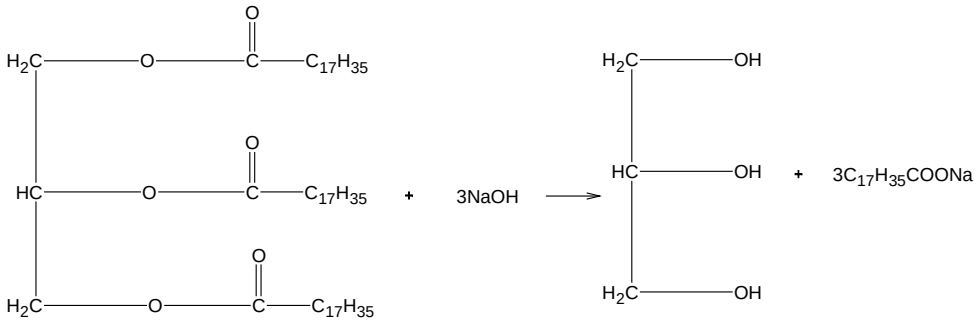
The remaining components of fats constitute the so-called phase that does not undergo saponification, and include pigments, tocopherol, sterols, polyphenols, squalene.

2.1.1. Chemical reactions characteristic for fats

In animal organisms fats undergo the reaction of hydrolysis under the effect of lipases – hormonally regulated enzymes present in lipocytes or fat cells.



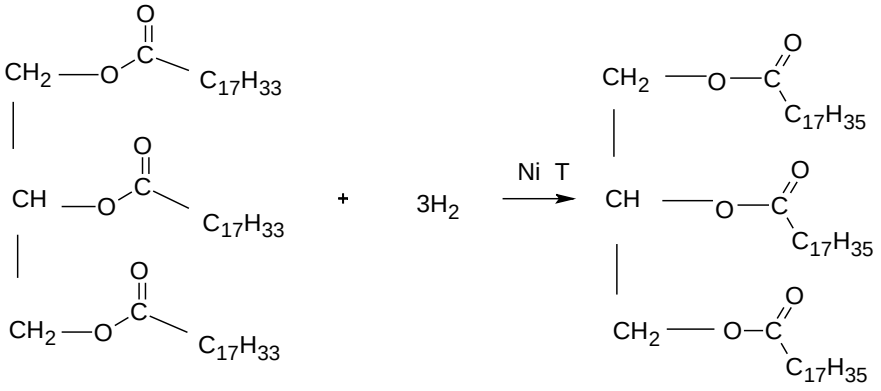
Frequently used in industry for the production of soap is the reaction of alkaline hydrolysis, so-called saponification reaction.



In the reaction of hydrolysis fatty acid is evolved from a fat molecule.

Triacylglycerols in solid state undergo polymorphic transformations under the effect of temperature, which means that they can occur in several crystalline forms. The presence of unsaturated linkages in mono- and polyunsaturated acids determines their capacity for the reaction of hydrogenation, i.e. addition, consisting in the breaking of a double bond and atachment of hydrogen to fatty acid

molecule. That reaction involves a change in the physical state, from liquid to solid, and is used in industry for the hardening of fats (production of margarine).



2.1.2. Classification of fatty acids

Fatty acids are derivatives of saturated or unsaturated hydrocarbons, with simple chains, most frequently containing an even number of carbon atoms, from C_2 to C_{24}.

- **Saturated fatty acids (SFA)** are characterised by the presence of only single linkages in the molecule. The occurrence of the major saturated fatty acids is presented in the Table 2 below.

Table 2. Occurrence of saturated fatty acids (Drozdowski 2007)

Nuber of C atoms	Common name	Occurrence
4	butyric acid	milk fat
6	caproic acid	
8	caprylic acid	
10	capric acid	coconut oil, palm seed oil
12	lauric acid	
14	myristic acid	
16	palmitic acid	palm oil, cotton oil, animal fats, fish oils
18	stearic acid	animal fat, cocoa butter

- **Monounsaturated fatty acids (MUFA)** contain a single unsaturated linkage in the molecule and most often occur in configuration *cis*. A naturally occurring monounsaturated fatty acid in configuration *trans* is the vaccenic acid formed in the rumen of cows. Most of the monounsaturated fatty acids belong to the family ω-9. The most important fatty acid in that family is the oleic acid (OLA), consituting ca. 40% of all fatty acids occurring in nature, and the erucic acid which dominates in traditional rapeseed cultivars. Most commonly occurring monounsaturated fatty acids are summarized in Table 3.

Table 3. Occurrence of monounsaturated fatty acids (Drozdowski 2007)

Number of C atoms	Common name	Occurrence
16	palmitoleic acid	animal fats
18	oleic acid	animal and vegetable fats
18	vaccenic acid	milk fat
20	gadoleic acid	fats of sea animals
22	brasidic acid	
22	erucic acid	traditional rapeseed cultivars

- **Polyunsaturated faty acids (PUFA)** have at least two unsaturated likages in the molecule, primarily in configuration *cis*. *Trans* isomers of polyunsaturated fatty acids are formed in the process of hardening of vegetable oils. PUFA comprise two important families of acids: ω-6 and ω-3, which occurrence in nature is presented in Table 4.

Table 4. Occurrence of polyunsaturated fatty acids

Fatty acids		Occurrence
ω-6 family	linoleic acid	vegetable oils, meat, and fish oils
	γ-linolenic acid	
	arachidonic acid	
ω-3 family	α-linolenic acid	
	EPA	
	DHA	

Representatives of ω-6 acids include linoleic acid (LA) (C18:2 n-9), γ-linolenic acid (GLA) (C 18:3 n-6) and arachidonic acid (AA) (C 20:4 n-6). The precursor of acids from the ω-3 family is α-linolenic acid (ALA) (C 18:3 n-3). Other ω-3 acids are EPA (C 20:5 n-3) and DHA (C 22:6 n-3).

2.1.3. Fatty acids melting point

Fatty acids occur in solid or in liquid state. Most saturated fatty acids are solids, but fatty acids with from 4 to 10 carbon atoms in a molecule are in liquid state at room temperature (Tab. 5).

Table 5. Melting points of major saturated, monounsaturated and polyunsaturated fatty acids

Number of carbon atoms	Systematic name of fatty acid	Common name of fatty acid	Melting point (ºC)
$C_{4:0}$	butanoic acid	butyric acid	–5.3
$C_{6:0}$	hexanoic acid	caproic acid	–3.2
$C_{8:0}$	octanoic acid	caprylic acid	16.5
$C_{10:0}$	decanoic acid	capric acid	31.6
$C_{12:0}$	dodecanoic acid	lauric acid	44.8
$C_{14:0}$	tetradecanoic acid	myristic acid	54.4
$C_{16:0}$	hexadecanoic acid	palmitic acid	62.9
$C_{18:0}$	octadecanoic acid	stearic acid	70.1
$C_{20:0}$	eicosanoic acid	arachidic acid	76.1
$C_{22:0}$	docosanoic acid	behenic acid	80.0
$C_{24:0}$	tetracosanoic acid	lignoceric acid	84.2
$C_{14:1}$	*cis*-9-tetradecenoic acid	myristoleic acid	–4.5
$C_{16:1}$	*cis*-9-hexadecenoic acid	palmitoleic acid	–0.5
$C_{18:1}$	*cis*-9-octadecenoic acid	oleic acid	16.3
$C_{18:1}$	*trans*-9-octadecenoic acid	elaidic acid	46.5

Table 5. **Cont.** Melting points of major saturated, monounsaturated and polyunsaturated fatty acids

Number of carbon atoms	Systematic name of fatty acid	Common name of fatty acid	Melting point (ºC)
$C_{18:1}$	*trans*-11-octadecenoic acid	vaccenic acid	39.5
$C_{20:1}$	*cis*-9-icosenoic acid	gadoleic acid	23.5
$C_{22:1}$	*cis*-13-docosenoic acid	erucic acid	33.5
$C_{22:1}$	*trans*-13-docosenoic acid	brassidic acid	61.9
$C_{18:2}$	*cis,cis*-9,12-octadecadienoic acid	linoleic acid	–6.2
$C_{18:3}$	all *cis*-9,12,15-octadecatrienoic acid	linolenic acid	–12.6
$C_{20:4}$	all *cis*-5,8,11,14-icosatetraenoic acid	arachidonic acid	–49.5

The melting point of faty acids increases with increasing molecular mass. Oils have the form of a liquid because the melting point decreases with the apearance of unsaturated linkages in the carbon chain. The melting point of fatty acids is affected by the following factors: number of double linkages, their configuration and position in the triacyloglycerol molecule.

2.1.4. Water solubility of fatty acids

Another physical trait characterising fats is their water solubility. The saturated faty acid $C_{4:0}$ (butyric acid) dissolves in water without any limitations, acids from $C_{6:0}$ to $C_{12:0}$ have limited water solubility, while for acids with more than 12 carbons in molecule the phenomenon of water solubility is virtually nonexistent.

The Table 6 below presents the values of water solubility of selected fatty acids, based on data freely available in the literature.

Apart from the composition of fatty acids, the properties of fats are also affected by their TAG composition and structure. This is of importance for the processing of fats, as well as for the processes of digestion and absorption.

Table 6. Water solubility of selected fatty acids

Number of carbon atoms	Systematic name of fatty acid	Common name of fatty acid	Water solubility (10^{-2} g cm^{-3}) at temperature of 20ºC
$C_{4:0}$	butanoic acid	butyric acid	no limitation
$C_{6:0}$	hexanoic acid	caproic acid	1
$C_{8:0}$	octanoic acid	caprylic acid	0.68
$C_{10:0}$	decanoic acid	capric acid	0.15
$C_{18:0}$	octadecanoic acid	stearic acid	0.0003

2.1.5. Fatty acid profile of animal fats

Animal fats originating from the tissues and milk of terrestial animals and from the tissues of marine animals are primarily a source of saturated faty acids (Tab. 7). Terrestial animal fats, primarily butter, lard and backfat, as well as meat, contain 35% of fatty acids $C_{16:0}$ and $C_{16:1}$, and 65% of fatty acids $C_{18:1}$, $C_{18:0}$, $C_{18:2}$, $C_{18:3}$. Notably more varied in terms of fatty acid composition are the storage fats of marine animals. They contain fatty acids $C_{18:1}$, $C_{16:0}$ and also, absent from other animal fats, fatty acids $C_{20:5}$ and $C_{22:6}$, which makes the marine animal fats an important component of the diet.

Milk fat contains over 400 different fatty acids, including short- and medium-chain fatty acids from $C_{4:0}$ to $C_{12:0}$ constituting 10-14%, more than a half of the number being accounted for by acids $C_{16:0}$ and $C_{18:1}$ (Drozdowski 2007). Milk is also the main source of conjugated diens of linoleic acid CLA (Conjugated Linoleic Acid). The name CLA refers to a group of compounds which are positional and geometric isomers of *cis*-9, *cis*-12 octadecadienic acid, i.e. linoleic acid, containing a system of conjugated linkages. The most frequent isomer of CLA is the rumenic acid presented in Figure 2. (Białek and Tokarz 2009).

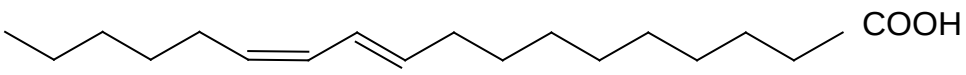


Fig. 2. Structural formula of rumenic acid molecule

Table 7. Percentage content of fatty acids in animal fats (Drozdowski 2007)

Fatty acid	Fish oil	Lard	Beef tallow	Milk fat
$C_{4:0}$	–	–	–	3.5
$C_{6:0}$	–	–	–	2.0
$C_{8:0}$	–	–	–	1.1
$C_{10:0}$	–	0.1	–	2.5
$C_{12:0}$	–	0.1	0.1	3.0
$C_{14:0}$	9.5	0.5	3.0	11.0
$C_{14:1}$	0.5	–	0.1	1.0
$C_{15:0}$	1.0	0.1	0.5	2.0
$C_{16:0}$	19.5	26.0	24.5	27.0
$C_{16:1}$	12.0	3.3	4.0	2.0
$C_{16:2}$	1.5	–	–	–
$C_{16:3}$	1.5	–	–	–
$C_{16:4}$	1.0	–	–	–
$C_{17:0}$	1.2	0.4	1.5	0.5
$C_{17:1}$	–	0.2	0.8	–
$C_{18:0}$	3.5	13.5	18.5	12.0
$C_{18:1}$	11.5	44.0	42.4	28.5
$C_{18:2}$	1.5	9.5	2.5	3.0
$C_{18:3}$	1.5	0.4	0.7	0.5
$C_{18:4}$	3.5	–	–	–
$C_{20:0}$	0.3	0.2	0.2	–
$C_{20:1}$	2.0	0.6	0.3	0.4
$C_{20:2}$	–	0.1	–	–
$C_{20:4}$	2.0	–	–	–
$C_{20:5}$	14.4	–	–	–
$C_{22:0}$	0.1	–	–	–
$C_{22:1}$	0.5	–	–	–
$C_{22:5}$	2.5	–	–	–
$C_{22:6}$	9.0	–	–	–

The fatty acid profile of animal fats may undergo changes under the effect of the season of the year and the method of animal feeding (Tab. 8).

Table 8. Percentage content of fatty acids in milk fat (Talpur *et al.* 2008)

Fatty acid	Percentage content of fatty acids in milk fat vs. season of the year			
	Winter	Spring	Summer	Autumn
$C_{4:0}$	3.74	4.02	4.18	3.66
$C_{6:0}$	2.78	2.22	1.67	2.63
$C_{8:0}$	2.98	2.05	1.82	2.80
$C_{10:0}$	3.21	2.12	1.80	2.45
$C_{12:0}$	3.92	3.14	2.39	2.91
$C_{14:0}$	10.88	10.74	9.96	10.97
$C_{16:0}$	26.49	28.45	30.17	26.97
$C_{18:0}$	13.79	12.08	10.78	13.69
$C_{14:1\ cis}$	0.64	0.66	0.76	0.61
$C_{16:1\ cis}$	1.24	1.49	2.02	1.49
$C_{18:1\ cis}$	23.33	24.26	25.17	23.63
$C_{14:1\ trans}$	0.27	0.29	0.41	0.51
$C_{18:1\ trans}$	1.72	1.92	2.44	1.92
$C_{18:2\ trans}$	0.47	0.52	0.36	0.60
CLA c9, t11	0.32	0.35	0.55	0.32
$C_{18:3}$ n-3	0.57	0.55	0.90	0.70
$C_{20:4}$ n-6	0.27	0.38	0.39	0.34
$C_{20:5}$ n-3	0.18	0.08	0.15	0.29
$C_{22:6}$ n-6	0.08	0.11	0.13	0.15

The fatty acid composition of the storage fat of animals is characteristic for the species and for the race, an example of which is the difference in the fatty acid

profiles of backfat from two genetic groups of fattening pigs (Fig.3). The differences relate to the content of unsaturated fatty acids (primarily oleic acid) and saturated fatty acids (palmitic and stearic acids). Apart from the race of the animal, the fatty acid profile is also affected by such factors as the age, diet, sex, and hormones (Krasnowska and Salejda 2008).

The level of unsaturated fatty acids in the tissue fat can be increased through suitable feeding of fattening pigs (Migdał *et al.* 2002). The addition of seeds of oil bearing plants or of vegetable oil to the feed causes an increase in the level of linoleic and linolenic acids with a simultaneous decrease in the content of stearic and palmitic acids (Busboom *et al*. 1991, Barowicz *et al.* 1997, Migdał *et al*. 2002).

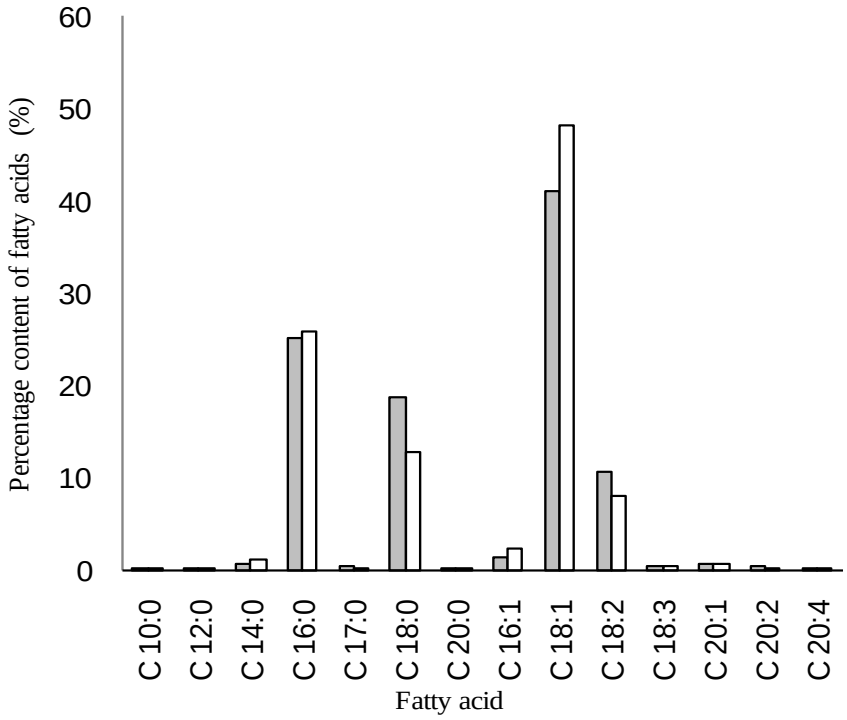


Fig. 3. Comparison of fatty acid profiles in backfat from fattening pigs of two genetic groups (Krasnowska and Salejda 2008)

Fish oil and meat contain unique, not encoutered in other products of animal origin, long-chain polyunsaturated fatty acids from the family ω-3: $C_{20:5}$ and $C_{22:6}$. A rich source of those fatty acids is oil from the Menhaden fish. Fish from the species Menhaden, feeding on phyto- and zooplankton, constitute food for many other species of

fish and birds. Man utilises those fish in the form of fishbone meal used as an additive for fodders and as the main product for te obtainment of ω-3 acids.

The fatty acid profile of fish oils varies with relation to the species (Tab. 9).

Table 9. Fatty acid profile of oils from selected species of fish (Perez-Valazquez *et al*. 2008)

Fatty acids	Content of fatty acids (mg g^{-1})				
	golden cownose (*Rhinoptera steinachneri*)	spotted (*Aetobatus narinari*)	cownose (*Rhinoptera bonasus*)	stingray (*Disambiguation*)	Menha-den
$C_{16:0}$	104.00	166.16	106.98	84.76	93.33
$C_{18:0}$	17.44	12.15	30.46	19.39	14.94
$C_{18:1}$	58.38	47.70	64.72	77.57	59.76
$C_{18:2}$ n-3	127.41	147.95	121.16	104.60	90.63
$C_{18:3}$ n-6	8.01	21.39	7.06	8.63	13.92
$C_{20:4}$ n-6	25.57	52.16	21.74	19.28	8.33
$C_{20:5}$ n-3	62.87	16.82	64.67	61.53	99.64
$C_{22:6}$ n-3	81.01	9.45	101.64	64.91	108.09
SFA	136.18	197.86	177.95	115.56	151.17
MUFA	94.88	109.28	114.29	132.87	174.47
∑ n-3	176.24	68.40	194.03	152.47	240.89
∑ n-6	155.25	201.21	144.93	125.55	100.77

SFA – $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{18:0}$, $C_{20:0}$, $C_{22:0,}$
MUFA – $C_{16:1}$, $C_{18:1}$, $C_{20:1}$, $C_{22:1,}$
∑ n-3 – $C_{18:3}$, $C_{20:3}$, $C_{20:5}$, $C_{22:5}$ $C_{22:6,}$
∑ n-6 – $C_{18:2}$, $C_{20:3}$, $C_{20:4}$.

2.1.6. Fatty acid profile of vegetable oils

Vegetable oils are a rich source of unsaturated fatty acids. Due to their chemical composition and common use, vegetable oils play a very important role in human diet, providing monounsaturated fatty acids, mainly oleic acid, as well as

polyunsaturated fatty acids: linoleic and α-linolenic. The fatty acid composition and the percentage content of fatty acids in vegetable oils depend on the type of raw material used for their production. The Table 10 and Table 11 below presents the fatty acid composition of selected vegetable oils.

Exceptionally valuable are such vegetable oils as evening primrose oil and borage seed oil, oil from the seeds of blackcurrant and from seeds of Echium (Echium oil). Compared to other vegetable oils, they are characterised by farmacological properties that can be used in medicine, and are the only vegetable oils to contain γ-linolenic acid (GLA), Additionally, the blackcurrant oil and Echium oil are a source of stearidonic acid SDA. The fatty acid profiles of those oils are presented in the Table 12 and Table 13 below.

Table 10. Fatty acid profile of selected vegetable oils and olive oil (Czechowska-Liszka 2006, Sambanthamurthi *et al*. 2000, Gutiérrez *et al*. 2002, Stefanoudaki *et al*. 1999)

Fatty acid	Fatty acid profile of selected vegetable oils and olive oil				
	rapeseed oil	sunflower oil	soybean oil	olive oil	palm oil
$C_{8:0}$	0.00-0.01	0.00-0.01	–	–	–
$C_{10:0}$	0.00-0.02	0.00-0.01	0.00-0.03	–	–
$C_{12:0}$	0.00-0.05	0.03-0.16	0.00-0.11	–	0.00-1.00
$C_{14:0}$	0.07-0.23	0.08-0.15	0.01-0.09	0.00-0.01	0.90-1.50
$C_{16:0}$	4.75-9.47	6.13-7.08	9.30-12.01	8.88-14.04	39.2-45.8
$C_{18:0}$	1.90-2.79	3.39-4.00	3.64-4.47	1.79-3.39	3.70-5.10
$C_{16:1}$	0.19-0.32	0.10-0.31	0.01-0.32	0.46-1.27	0.00-0.40
$C_{18:1}$	53.00-80.00	28.75-37.82	25.51-31.80	71.27-80.41	37.4-44.1
$C_{18:2}$	7.00-23.00	47.24-56.02	43.20-50.44	3.06-9.39	8.70-12.5
$C_{18:3}$	2.00-8.00	0.34-0.86	6.58-7.45	0.45-0.81	0.00-0.60
$C_{20:0}$	0.59-0.60	0.31-0.39	0.34-0.46	0.34-0.52	0.00-0.40
$C_{20:1}$	1.43-1.98	0.20-0.62	0.29-0.59	0.26-0.32	–
$C_{22:0}$	0.32-0.44	0.32-0.73	0.33-0.40	0.12-0.18	–

Table 11. Content of total fatty acids in selected vegetable oils (Krzymański *et al.* 2009)

Oil	Percentage content of total fatty acids			
	SFA	OLA	LA	ALA
linseed oil	10	23	16	51
rapeseed oil 00	7	62	20	10
high-oleic rapeseed oil	7	77	7	7
soybean oil	14	21	56	9
olive oil	15	75	9	1
maize oil	13	27	59	1
sunflower oil	14	18	68	trace amounts
safflower oil	13	7	80	trace amounts
sesame oil	13	45	42	trace amounts
arachis oil	19	51	30	–
palm oil	50	40	10	0.3

Table 12. Fatty acid profiles of evening primrose oil and borage seed oil (Pieńkowska 2003)

Fatty acid	Evening primrose oil	Borage seed oil
$C_{16:0}$	5.73-5.89	10.94-11.14
$C_{16:1}$	trace amounts	0.45-0.49
$C_{18:0}$	1.59-1.83	4.75-4.91
$C_{18:1}$	5.35-5.51	18.92-19.02
$C_{18:2}$	67.77-68.87	36.62-36.98
$C_{18:3}$	0.14-0.16	trace amounts
γ- $C_{18:3}$	9.38-9.64	21.06-21.3
$C_{20:0}$	0.29-0.31	0.30-0.32
$C_{20:1}$	0.08-0.10	4.09-4.25

$C_{20:2}$	trace amounts	trace amounts
$C_{22:0}$	0.15-0.17	0.18-0.20
$C_{22:1}$	-	2.10-2.52
∑ SFA	7.98	16.37
∑ MUFA	5.52	25.92
∑ PUFA	77.98	56.98

Table 13. Fatty acid profile of blackcurrant seed oil and Echium oil (Mińkowski 2008)

Fatty acid	Blackcurrant seed oil	Echium oil
$C_{16:0}$	6.2 ± 0.2	6.9 ± 0.4
$C_{16:1}$	0.1	0.3 ± 0.1
$C_{17:0}$	–	0.2
$C_{17:1}$	–	0.1
$C_{18:0}$	1.5 ± 0.1	3.0 ± 0.1
$C_{18:1}$	12.9 ± 0.3	15.8 ± 0.5
$C_{18:2\ n-6}$	49.1 ± 1.5	17.6 ± 0.7
$C_{18:3\ n-6}$	12.7 ± 0.3	10.6 ± 0.5
$C_{18:3\ n-3}$	13.0 ± 0.4	31.3 ± 1.2
$C_{18:4\ n-3}$	2.4 ± 0.2	12.4 ± 0.6
$C_{20:0}$	0.1	0.1
$C_{20:1}$	0.9 ± 0.1	0.1
$C_{20:2}$	0.2	0.1
$C_{22:0}$	0.1	0.1
$C_{22:1}$	–	0.2
$C_{24:0}$	–	0.1
$C_{24:1}$	-	0.2

Bio-oils with considerable importance in the cosmetics industry are oils from hazel nuts, walnuts, and also from almonds. The fatty acid profiles of those oils are given in Table 14 below.

Table 14. Fatty acid profiles of hazel nut, walnut and almond oils (Jasińska-Stępniak 2009)

Fatty acid	Walnut oil	Hazel nut oil	Almond oil
$C_{14:0}$	0.04	0.04	0.05
$C_{16:0}$	7.38	5.10	6.62
$C_{16:1}$	0.09	0.20	0.49
$C_{17:0}$	0.05	0.05	0.12
$C_{18:0}$	2.59	2.41	1.43
$C_{18:1}$	17.10	77.17	61.28
$C_{18:1\ n-9}$	0.91	1.06	1.42
$C_{18:2\ n-6}$	60.25	13.39	26.31
$C_{18:3\ n-3}$	11.22	0.24	0.30
$C_{20:0}$	0.12	0.13	0.11
$C_{20:1}$	0.24	0.20	1.87

The fatty acid profiles are strongly affected by the weather and by the cultivar. In the case of rapeseed, atmospheric conditions have the greatest effect on the content of oleic, linoleic, linolenic and palmitic acids. Whereas, significant differences between cultivars are observed in the contents of such fatty acids as palmitic, palmitoleic, stearic, oleic, linoleic, linolenic and behenic acids (Kotecki *et al*. 2001). Similar differences, with the exception of palmitoleic acid, were observed by Jędrzejak *et al*. (2005).

The time and technology of seed harvest play an important role in shaping the fatty acid profile of vegetable oils (Jackowska and Tys 2006; Pisulewska *et al*. 1998, Rybacki 2003). Differences in the content of saturated fatty acids in rapeseed oil when the single-stage harvest technology is employed at very early and delayed times of harvest may even reach 300% (Rybacki 2003). Early single-stage harvest has an unfavourable effect on the fatty acid profile, an increase be-

ing observed in the content of saturated fatty acids with a decrease in that of unsaturated fatty acids (Fig. 4-11).

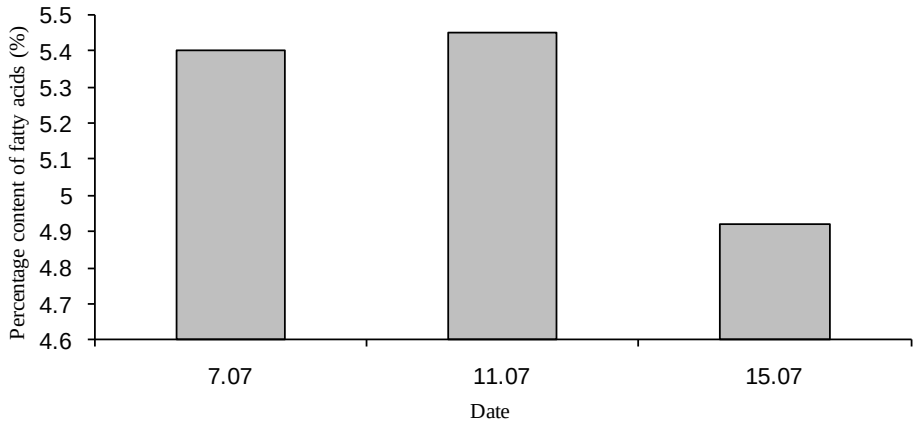


Fig. 4. Percentage content of palmitic acid in rape seed seeds cv. Rasmus in two-stage harvest technology in relation to the date of harvesting in 2001 (Rybacki 2003)

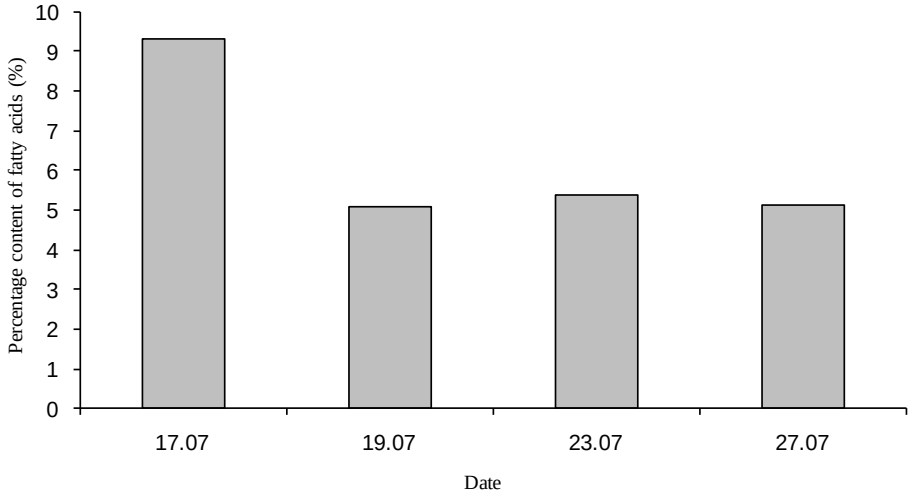


Fig. 5. Percentage content of palmitic acid in rape seeds cv. Rasmus in single-stage harvest technology in relation to the date of harvesting in 2001 (Rybacki 2003)

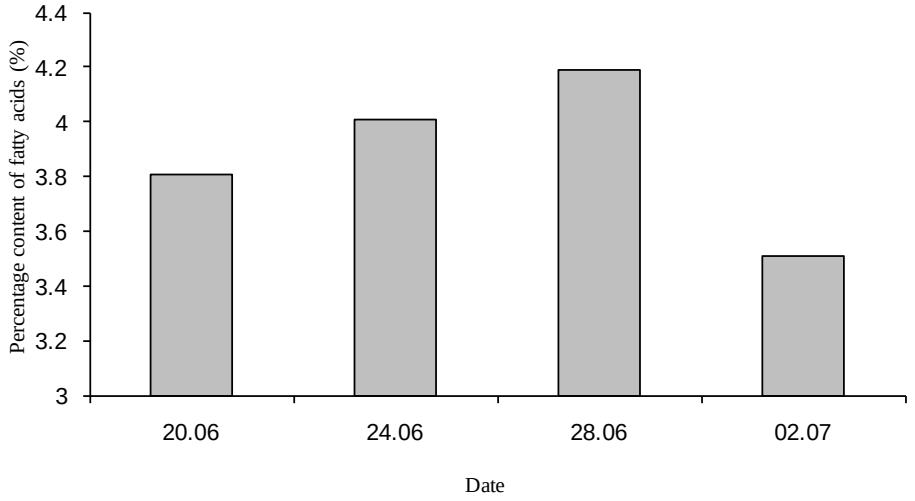


Fig. 6. Percentage content of palmitic acid in rape seeds cv. Rasmus in two-stage harvest technology in relation to the date of harvesting in 2002 (Rybacki 2003)

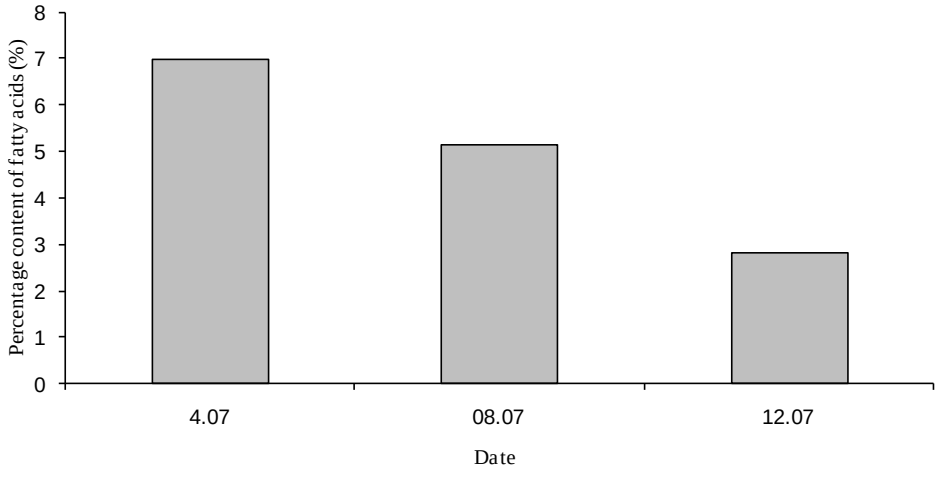


Fig. 7. Percentage content of palmitic acid in rape seeds cv. Rasmus in single-stage harvest technology in relation to the date of harvesting in 2002 (Rybacki 2003)

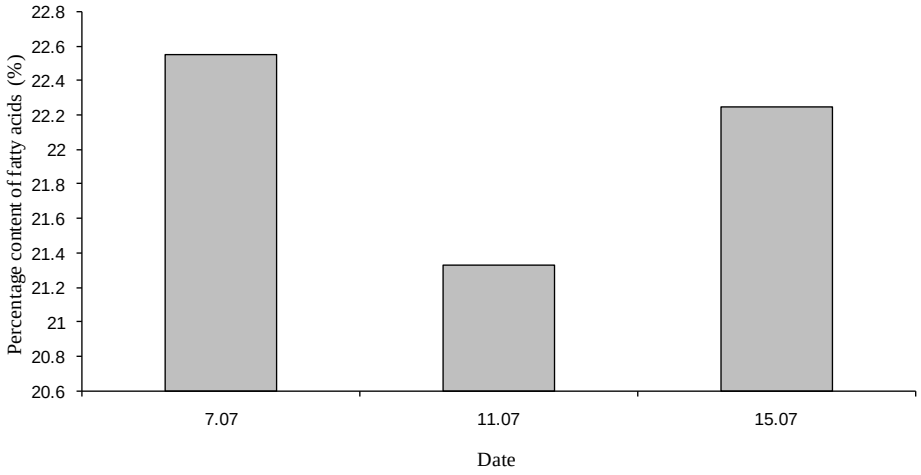


Fig. 8. Percentage content of linoleic acid in rape seeds cv. Rasmus in two-stage harvest technology in relation to the date of harvesting in 2001(Rybacki 2003)

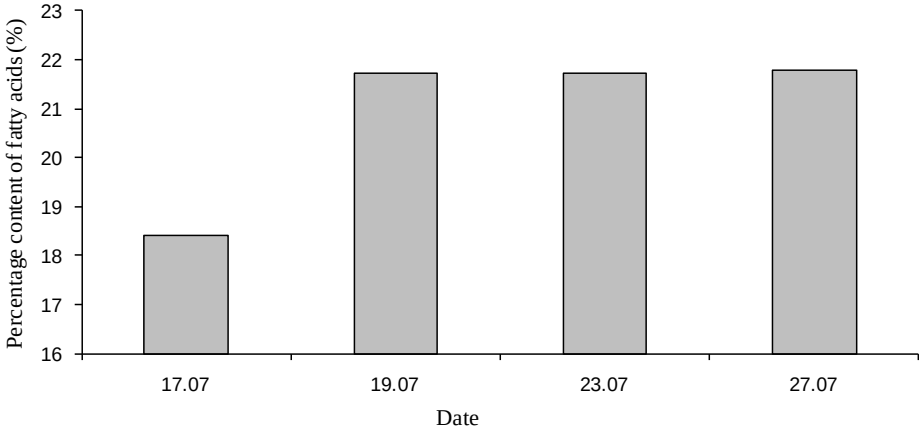


Fig. 9. Percentage content of linoleic acid in rape seeds cv. Rasmus in single-stage harvest technology in relation to the date of harvestng in 2001 (Rybacki 2003)

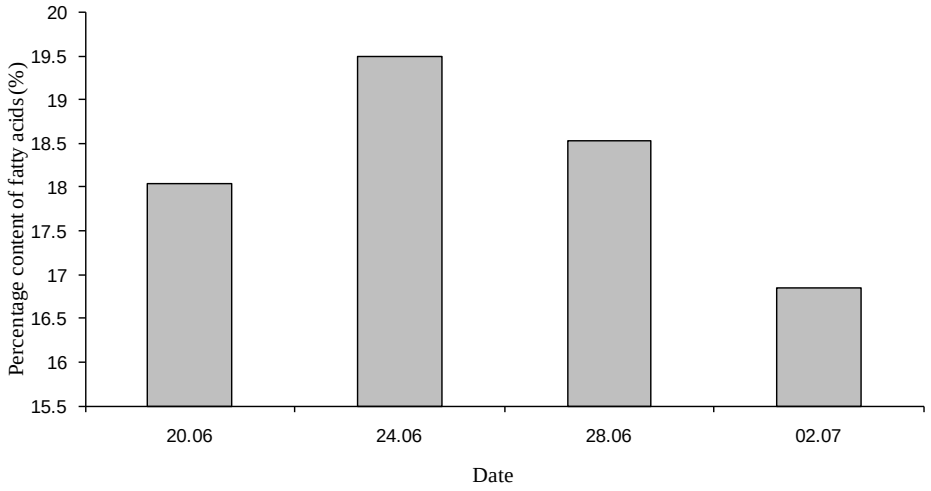


Fig. 10. Percentage content of linoleic acid in rape seeds cv. Rasmus in two-stage harvest technology in relation to the date of harvesting in 2002 (Rybacki 2003)

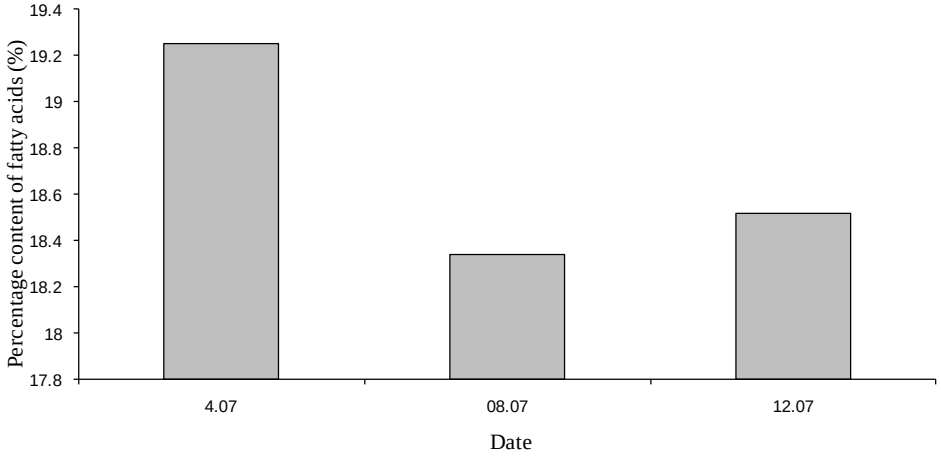


Fig. 11. Percentage content of linoleic acid in rape seeds cv. Rasmus in single-stage harvest technology in relation to the date of harvesting in 2002 (Rybacki 2003)

Nitrogen fertilisation up to the dose of 120 kg N ha^{-1} increases markedly the level of palmitic acid in the oil, while lowering the level of vaccenic acid. Increase of nitrogen dose to 150 kg N ha^{-1} causes a reduction of the contents of oleic and erucic acids, and an increase in the levels of stearic, linoleic and linolenic acids (Jędrzejak *et al*. 2005).

Seed drying and storage conditions are other factors that affect the content of faty acids. Studies on the effect of drying temperature on the content of faty acids in seeds of various rapeseed cultivars revealed an increase in the level of linoleic acid and a decrease in the content of oleic acid at drying temperatures above 120^{o}C (Krasucki *et al*. 2002, Rybacki 2003, Gawrysiak-Witulska and Rudzińska 2007).

The fatty acid profile can by modified by means of the genetic-breeding method. An example of this is rapeseed oil. In the nineteen-seventies, in Canada, double-improved (00) canola-type rapeseed was created. That rapeseed was bred from the Polish rapessed Bronowski and, through blocking the enzyme elongase (Rakowska 1988), contains less than 2% of the saturated erucic acid. Canola-type rapeseed is also characterised by a low content of glucosinolates (below 30 μM g^{-1} of fat-less dry mater of seeds) (Krzymański *et al.* 2009).

The content of fatty acids is also affected by environmental factors: lower level of OLA and high of the PUFA acids in rapeseed grown at Northern lattitudes (Krzymański *et al*. 2009).

3. QUALITY FACTORS OF FATS

In quality control of vegetable and animal fats sensory methods, physico-chemical measurements and analytical assays are employed (Ratusz *et al*. 2005). The first of those methods is a sensitive one, but it is based on subjective taste, visual and flavour assessments, therefore it can only be used for a preliminary evaluation of fat quality (Tab.15). Its application is also problematic due to the fact that it is time-consuming and requires a properly trained team. The remaining two methods of estimation of the extent of fat oxidation are more reliable as they consist in the measurement of changes in the concentration of the primary and secondary products of peroxidation.

The degree of reduction of the quality of fats can be determined by studying the values of the following parameters: acid number (AN), peroxide number (PN), anisidine value (AV), iodine value, saponification value, index Toto (total oxidation). Apart from the existing ones, there is a continued search for newer and more accurate methods for the estimation of the quality of oils. We should mention here such methods as measurement of chemiluminescence kinetics, static photoacoustics, measurement of the concentration of free radicals in magnetic field, and also time-domain photoacoustics (Pieńkowska 2003).

Table 15. Scale of sensory assessment of refined oil (Czechowska-Liszka 2006)

Quality factor	5 pts	4 pts	3 pts	2 pts	1 pt
Colour	golden-yellow with less or more light hue	golden-yellow with slightly darker hue	golden-yellow with darker hue	golden-yellow with distinct dark hue or light yellow, pale	golden-yellow with brown hue or distinctly discoloured
Clarity	highly clear	clear	slightly opal-escent	turbid	strongly turbid, with sediment
Flavour	fresh, very clean, lightly detectable	fresh, clean, lightly detect-able	somewhat less clean, more strongly detectable	unclean, with detectable rancid, fishy or other foreign note	strongly changed, very rancid, stale, mouldy or other foreign note
Taste	fresh, highly clean, almost undetectable	fresh, clean, lightly detect-able, typical for given type of oil	somewhat less clean, with detect-able oily note	unclean, with detectable distinct oily, acid, bitter or rancid note	strongly changed, with very rancid, bitter, acid or other foreign note

3.1. Acid number

The acid number AN represents the amount of free fatty acids, so it is a measure of the degree of hydrolysis of a fat. It is defined as the amount (mg) of potassium hydroxide necessary for the neutralisation of free fatty acids present in 1 g of the fat studied.

The principle of AN determination is based on titration, an analytical method in which the titrant is a potassium hydroxide solution of a known concentration, while the analyte is a fat dissolved in a mixture of ethanol and ethyl ether (1:1). The titration is conducted in the presence of colour indicators: phenolphthalein for

light-coloured fats, or thymolphthalein for dark-coloured fats. Acid number can be calculated from the fomula (1):

$$AN = 56.1\ (V\text{-}V_0)\ C\ m^{-1} \qquad (1)$$

where: V – volume of potassium hydroxide used to titrate a sample of fat (cm^3),
V_0 – volume of potassium hydroxide used to titrate a blind sample (cm^3),
C – concentration of the titrant (mol dm^{-3}),
m – weight of fat sample (g),
56.1 – molar mass of potassium hydroxide (g).

The highest permissible values of acid number for selected fats are presented in Table 16 (PN-A-86908, BN-91/8052-01, PN-90/A-85802).

Table 16. Highest permissible values of AN of selected fats

Kind of fat	Max AN
sunflower oil	
rapeseed oil	
soybean oil	0.3
coconut oil	
palm oil	
olive oil, refined	0.6
lard	1.1

3.2. Peroxide number

The peroxide number PN is a measure of the degree of rancidity of a fat, as it provides information on the level of peroxides, i.e. the products of oxidation of fats. A sample of a fat is dissolved in a solution composed of glacial acetic acid, chloroform and potassium iodide. The peroxide number is expressed in milli-equivalents of active oxygen per kilogram of fat (mEq O_2 kg^{-1}) and it is defined as the amount of standard (0.002 M) solution of sodium thiosulphate (cm^3) required to titrate iodine evolved from potassium iodide solution through the action of peroxides. At the same time a blind sample is made. The peroxide number is calculated from the following formula (2):

$$PN = [(V-V_0)\ C/m]\ 1000 \quad (2)$$

where: V – volume of sodium thiosulphate used to titrate a sample of fat (cm^3),
V_0 – volume of sodium thiosulphate used to titrate the blind sample (cm^3),
C – concentration of sodium thiosulphate slution (mol dm^{-3}).
m – weight of fat sample (g)

Table 17 contains maximal values PN of selected fats.

Table 17. Highest permissible values of PN of selected fats (PN-A-86908, BN-91/8052-01, PN-90/A-85802)

Kind of fat	Max PN
sunflower oil	
rapeseed oil	
soybean oil	5.0
coconut oil	
palm oil	
olive oil	20.0
lards	6.0

3.3. Anisidine value

The anisidine value AV is defined as one hundred-fold value of absorbance of a solution of a sample of fat containing aldehydes which have reacted with p-anisidine. The absorbance is measured spectrophotometrically at wavelength of 350 nm, in a 10 mm cuvette, for three solutions:

- reacted: p-anisidine and sample of fat – A_1,
- non-reacted: acetic acid and sample of fat – A_0,
- blind sample: p-anisidine and isooctane – A_2.

The anisidine value is used for the assessment of poorer quality oils, with low values of peroxide number.

The anisidine value can be calculated from the formula (3):

$$AV = 100\ Q\ V\ [1.2(A_1-A_2)-A_0]\ m^{-1} \quad (3)$$

where: Q – content of sample in the solution based on which the anisidine value is expressed (g cm^{-3}),

V – volume in which the fat sample is dissolved (V = 25cm^3),
m – weight of fat sample (g).

The highest permissible value of AV for edible oils is 8.

3.4. Iodine value

The iodine value IV is a measure of the unsaturation of fatty acids. It is characteristic for a given fat and can be used for its identification. A sample of fat is dissolved in a mixture of glacial acetic acid and carbon tetrachloride. Then iodine bromide is added to the solution. There takes place the reaction of the attachment of halogens to the unsaturated bonds of the fatty acids contained in the fat studied. Next, to determine the non-reacted halogen element, potassium iodide is introduced to the solution with the analysed sample. The iodide anion oxidises to free iodine which is then titrated with a standard solution of sodium thiosulphate. Ten iodine value can be calculated from the following formula (4):

$$IV = 12.69\ C\ (V_0\text{-}V_1)\ m^{-1} \qquad (4)$$

where: C – concentration of sodium thiosulphate solution (mol dm^{-3}),
V_0 – volume of sodium thiosulphate solution used for the blind sample (cm^3),
V_1 – volume of sodium thiosulphate solution used to titrate a sample of fat (cm^3),
m – weight of fat sample (g).

Table 18 below presents the ranges of iodine values for selected kinds of fats as given by the relevant standards (PN-A-86908, BN-91/8052-01, PN-90/A-85802).

Table 18. Range of IV for selected fats

Kind of fat	Range of IV
sunflower oil	136-148
rapeseed oil	110-126
soybean oil	124-139
palm oil	50-55
coconut oil	6-11
olive oil	75-94
lard	45-70

3.5. Saponification value

The saponification value SV is the amount of potassium hydroxide necessary to hydrolyse 1g of fat and to neutralise in it the fatty acids formed. High values of SV are characteristic for fats containing a large number of short-chain fatty acids. The level of SV is also afected by substances contained in fats and not undergoing the reaction of saponification (sterols, pigments – reduce its value). A sample of fat is dissolved in an excessive amount of potassium hydroxide solution. The ecxess of potassium hydroxide is then titrated with a standard slution of hydrochloric acid. The saponification value is calculated from the following formula (5):

$$SV = 56.11 (n_1 V_1 - n_2 V_2) m^{-1} \quad (5)$$

where: n_1, V_1 – number of moles and volume of potassium hydroxide,
n_2, V_2 – number of moles and volume of hydrochloric acid,
m – weight of fat sample (g).

4. PROCESSES AFFECTING THE OXIDATIVE STABILITY OF FATS

The phenomenon of oxidation of fats is a factor determining their quality. The oxidation of vegetable and animal fats causes a deterioration of their taste values and primarily of their health qualities. The rate at which the process proceeds depends on the levels of anti- and pro-oxidation substances, and also on the fatty acid profile. Under the effect of a variety of factors, such as temperature, time of storage, exposure to light and to atmospheric oxygen (Tańska and Rotkiewicz 2003), as well as enzymes produced by microorganisms, there take place transformations, the products of which are peroxides and hydroperoxides of lipids. Subsequent reactions of the products of peroxidation lead to the breakage of the carbon chain and to the formation of so-called secondary products of oxidation: aldehydes, ketones, hydrocarbons, esters, lactones, alcohols and ethers (Drozdowski 2007). Those compounds reduce the nutritive value of fats, and impart to them an unpleasant taste and rancid smell (Ziemlański and Budzyńska-Topolowska 1991).

Changes of parameters characterising the stability of vegetable oils have been the subject of numerous studies (Zadernowski *et al*. 2002, Rotkiewicz and Konopka 1998, Krygier et al. 2000, Osek 2000, Wroniak and Łukasik 2007, Ratusz *et al*. 2005, Tys and Szwed 1998, Gawrysiak-Witulska *et al*. 2007, Maszewska and Krygier 2005, Górecka *et al*. 2003, Rotkiewicz *et al*. 2002, Wroniak *et al*.

2006, Ratusz and Krygier 1997, Grabska *et al*. 1994, Rotkiewicz *et al*. 1995, Krygier *et al*. 1995, Krygier *et al*. 1995).

- **effect of moisture, seed damage, time of seed storage and heating**

The AN of rapeseed oil from seeds with moisture of 14% increases rapidly after a week in storage and depends on the extent of damage to the seeds. Oil from seeds with moisture levels of 6% and 10% is characterised by AN increase from the fourth week of storage, dependent on the extent of seed damage, while the PN increases from the third week of storage and does not depend on seed damage (Grabska. 1994). The effect of damaged seeds on the values of AN and PN for cold-expressed rapeseed oils is one of the aspects in a study by Krygier *et al*., 2000, the results of which are presented in the Table 19 below.

Table 19. Mean values of AN and PN of cold-expressed rapeseed oil with a share of damaged seeds (Krygier *et al*. 2000)

Parameter	Cold-expressed rapeseed oils with an admixture of damaged seeds					Norm
	0%	10%	20%	30%	100%	
AN	0.75	2.30	3.70	5.74	20.40	4.0
PN	2.05	2.78	2.94	3.48	7.89	10

Rotkiewicz and Konopka (1998) studied the shelf-life of rapeseed oils cold-expressed from seeds of varied ripeness, species homogeneity and degree of cleanliness. The stability of the oils was examined in a storage test and determined on the basis of measurements of AN, PN and AV. Changes in the values of those parameters for selected oil samples are presented in the Figures 12-14 below.

The acid number of the sample of oil obtained from clean seeds of the same cultivar with the initial value of 0.49 increased three-fold during the storage, while the acid number of the sample of oil from industrial grade winter rapeseed increased from 1.69 to 6.28, i.e. as much as four-fold, and exceeded the permissible norm.

Similar relations can be observed in the case of changes in the values of the peroxide number PN and the anisidine value AV.

The size of rape seeds also has an effect on the values of PN, AV and AN of oils. Those relations were studied by Rotkiewicz *et al*. (2002) for three size groups of rape seeds: > 0.2 mm, 0.2 mm-1.6 mm, <1.6 mm (Tab.20).

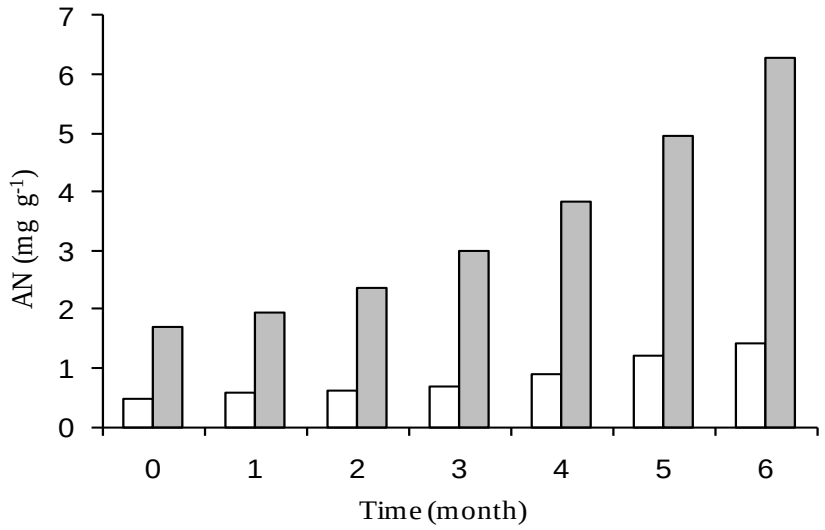


Fig. 12. Changes of AN of two samples of cold-expressed rapeseed oil with different initial AN values, over a period of 6 months

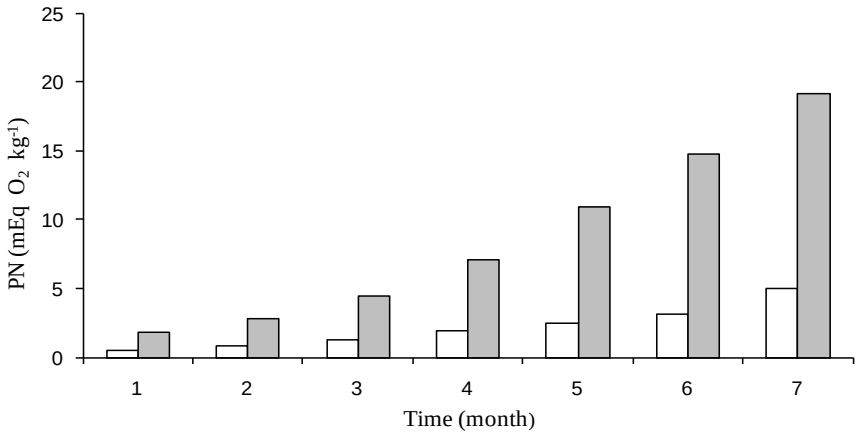


Fig. 13. Changes of PN of two samples of cold-expressed rapeseed oil with significantly different initial PN values, over a period of 6 months

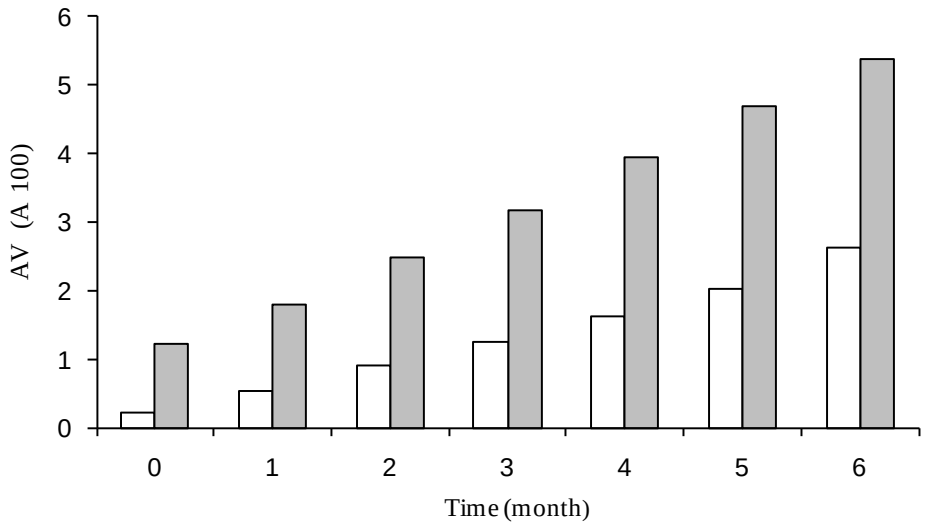


Fig. 14. Changes of AV of two samples of cold-expressed rapeseed oil with significantly different initial AV values, over a period of 6 months

Heat treatment of seeds causes an increase in the AN of oil produced from them, but this relates only to fragmented seeds. This relation does not apply to whole seeds. Thermal treatment of seeds causes also an increase of PN; the mean PN value for seeds treated at temperature of 180°C is higher by 61% than the PN value for unheated seeds, while temperatures up to 100°C have no increasing effect on the value of AV (Górecka *et al*. 2003).

Table 20. Mean values of the parameters AN, AV and PN of rapeseed oil pressed from seeds with different sizes (Rotkiewicz *et al*. 2002)

Parameter	Oil from seeds of sizes (mm)		
	> 0.2	0.2-1.6	<1.6
AN	1.19	2.85	4.69
AV	1.05	1.55	2.12
PN	1.92	2.79	2.83

The time of seed storage is significant for the values characterising the stability of oils. Seeds with moisture of 30%, stored at temperature of 30°C for 100 days are characterised by a notable increase of PN, while the values of AN display, in this case, cultivar-related differences. The AN value for cv. Bolko varied, after 180 days in storage, from 0.5 to 4.5, and for cv. Leo – after the same storage period – from 0.5 to 1.9 (Tys and Szwed 1998). Low temperature of storage and low seed moisture have the strongest inhibiting effect on oxidation transformations (Tys and Szwed 1998). Osek (2000) studied, among other things, the effect of storage time and conditions on changes on AN and PN in rape seeds. She found that the duration of storage, irrespective of the storage conditions, had no effect on AN, while notable changes were observed in the case of PN, whose value increased from the initial level of 3.57 to 10 after four months of storage.

- **conditions and time of storage of oils and methods of their obtainment**

Storage time of oils has an increasing effect on the values of AN and PN, the changes being less pronounced for samples of oils stored under refrigerated conditions (Osek 2000, Krygier *et al.* 1995). Osek (2000) measured the values of AN and PN for rapeseed oil stored under various conditions for a period of 8 months (Tab. 21-22).

Exposure to oxygen increases the rate of oxidation transformations of oils: oils kept in open bottles at room temperature with access to oxygen oxidise faster than oils in closed bottles (Wroniak and Łukasik 2007).

The methods used to obtain oils have a decisive effect on the oxidative stability of vegetable oils: oils obtained through cold expression and hot expression are characterised by lower oxidative stability compared to refined oils (Krygier *et al*. 1995, Zadernowski *et al*. 2002, Ratusz and Krygier 1997) (Tab.23).

Table 21. AN values of rapeseed oil during storage under various conditions (Osek 2000)

Storage conditions	Duration of storage (months)				
	0	2	4	6	8
Laboratory Room	2.19	2.28	2.33	2.38	2.51
Sheetmetal Shed	2.19	2.28	2.37	2.42	2.58
Refrigerator	2.19	2.27	2.23	2.24	2.42

Table 22. PN values of rapeseed oil during storage under various conditions (Osek 2000)

Storage conditions	Duration of storage (months)				
	0	2	4	6	8
laboratory room	3.43	7.54	1502	21.47	28.02
sheetmetal shed	3.43	8.80	14.80	21.37	18.32
refrigerator	3.43	7.09	12.42	14.76	15.03

Table 23. Changes of PN in thermostatic test of rapeseed oils and olive oil obtained with different methods (Krygier *et al*. 1995)

Days of test	Rapeseed oil			Olive oil
	cold-expressed	hot-expressed	rafined	
0	2.6	4.6	0.1	5.0
1	2.8	4.9	0.2	5.0
2	12.2	12.6	1.2	5.8
3	18.0	19.6	1.8	6.4
4	23.6	25.8	2.2	6.8
5	31.2	33.6	4.0	8.6
6	36.2	38.8	7.0	9.0
7	41.4	46.8	10.8	11.4
8	52.8	56.4	18.6	14.6
9	62.2	67.6	33.2	18.2
10	69.6	74.8	49.6	24.8

Oils obtained through expression and extracted from seeds of borage and evening primrose have similar values of parameters characterising their oxidative stability (Zadernowski *et al*. 2002) (Tab. 24).

- **kind of oil, content of antioxidants**

Wroniak and Łukasik (2007) studied the oxidative stability of various kinds of cold-expressed oils. They found that in the Rancimat test the highest stability

was demonstrated for maize and rapeseed oils, and the lowest for sunflower and soybean oils (Tab. 25).

Table 24. Values of parameters AN, PN, IV and SV of evening primrose and borage oils in relation to the method of their obtainment (Zadernowski *et al*. 2002)

Parameter	Method of obtainment of oil					
	hydraulic press		expeller		extraction	
	ev. primrose	borage oil	ev. primrose	borage oil	ev. primsore	borage oil
AN	1.0	1.2	1.5	2.0	7.1	3.9
PN	1.3	1.0	1.5	2.0	2.9	5.1
IV	159	155	159	155	158	157
SV	206	209	206	209	210	210

Table 25. Values of AN, PN, IV and AV for various kinds of oils (Wroniak and Łukasik 2007)

Kind of oil	AN	PN	IV	AV
Rapeseed oil	1.3	5.1	102.7	1.4
Sunflower oil	2.6	7.4	142.3	1.8
Soybean oil	1.8	4.0	123.6	2.1
Arachis oil	2.5	7.0	85.6	1.2
Sesame oil	2.9	6.2	92.8	1.2
Linseed oil	0.9	1.5	127.6	0.5
Maize oil	4.0	2.0	68.5	1.1

Certain factors causing the process of oxidation of fatty acids can be eliminated through the use of suitable conditions for the production of oils and for storage of the ready products. It has been demonstrated that the use of dark glass bottles or metal cans for the packaging of oils results in a lower degree of oxidation of the oils stored in them, while the use of plastic bottles notably reduces the

Table 26. Values of AN and PN of olive oil in relation to temperature, time of storage and kind of packaging (Tawfik *et al*. 1999)

Parameter	Temperature (°C)	Time of storage (days)	Kind of packaging				
			glass	PET	PVC	PP	PS
AN	24	0	0.16	0.16	0.16	0.16	0.16
		20	0.16	0.22	0.17	0.29	0.29
		60	0.18	0.23	0.23	0.35	0.45
	37	20	0.17	0.24	0.23	0.34	0.29
		60	0.19	0.28	0.27	0.44	0.49
PN	24	0	5.81	5.81	5.81	5.81	
		20	6.97	8.00	7.43	15.36	14.50
		60	7.29	10.7	9.36	22.00	23.36
	37	20	7.16	9.28	8.81	15.69	14.86
		60	8.64	12.57	11.69	23.78	25.02

Table 27. Values of AN and PN of sunflower oil in relation to temperature, time of storage and kind of packaging (Tawfik *et al.* 1999)

Parameter	Temperature (°C)	Time of storage (days)	Kind of packaging				
			glass	PET	PVC	PP	PS
AN	24	0	1.78	1.78	1.78	1.78	1.78
		20	1.80	2.05	20.01	2.33	0.38
		60	1.89	2.19	2.14	2.59	2.66
	37	20	1.83	2.10	2.10	2.49	2.46
		60	1.92	2.21	0.25	2.79	2.80
PN	24	0	14.88	14.88	14.88	14.88	14.88
		20	15.80	16.00	15.35	35.00	30.24
		60	17.51	25.95	22.62	60.95	61.34
	37	20	17.05	17.57	18.35	37.13	32.13
		60	18.75	27.28	24.06	75.84	75.84

PET – polyethylene, PVC – polyvinyl chloride, PP – polypropylene, PS – polystyrene.

oxidative stability of oils irrespective of the kind of oil stored and of the storage temperature (Tawfik *et al*. 1999) (Tab. 26-27).

Oxidation of fatty acids may take place in the reactions of photo-oxidation and auto-oxidation.

4.1 Photo-oxidation

To discuss the photochemical reactions we need to introduce the concept of singlet and triplet states of oxygen molecule, these being related with the electron structure of the molecule. As opposed to most molecules, the ground state of oxygen is the triplet state, as a non-excited molecule of oxygen has two electrons on mutually perpendicular orbitals p. The spins of those electrons are parallel, so the resultant spin of the molecule is 1, which corresponds to three different energy levels at which an oxygen molecule can be (Bartosz 2008). The state of excitation of oxygen is the singlet state; due to the energy suplied the pairing of electrons takes place and the resultant spin of the molecule is 0. The transition from the triplet state to the singlet state can be caused by absorption of a quantum of high-energy radiation, or by the occurrence of specific chemical transformations (Bartosz 2008). The result of that process is the formation of two forms of singlet oxygen:

$$^3\sum_g O_2 + 94\ kJ\ mol^{-1} \rightarrow {}^1\Delta_g O_2$$

$$^3\sum_g O_2 + 157\ kJ\ mol^{-1} \rightarrow {}^1\sum^+_g O_2$$

The half-life (in water slution) of $^1\sum^+_g O_2$ is very short ($< 10^{-11}$) compared to the half-life of $^1\Delta_g O_2$ ($2 \cdot 10^{-6}$) (Bartosz 2008), and therefore form Δ plays a decisive role in the process of oxidation.

The mechanism of photo-oxidation is based on two types of reactions:

- type I of photoreaction occurs when oxygen in triplet state ($^3\sum_g O_2$) reacts with a fatty acid molecule with participation of a sensitiser in excited state, which leads first to the formation of the alkyl radical $L^{\bullet}$ and next – of the peroxide radical $LOO^{\bullet}$

$$Sen_0 + h\nu \rightarrow Sen_1^* \rightarrow Sen_2^*$$

$$Sen_2^* + LH \rightarrow H\text{-}Sen^{\bullet} + L^{\bullet}$$

$$L^{\bullet} + {}^3\sum_g O_2 \rightarrow LOO^{\bullet}$$

This type of photoreaction does not play any significant role in the process of oxidation of lipids, as the constant of the rate of reaction of triplet oxygen with an unsaturated fatty acid is ca. 1450-fold lower than the constant of the rate of reaction of an unsaturated fatty acid with singlet oxygen in form Δ (Rawls and Van Santen 1970).

- type II of photoreaction takes place when molecules of a fatty acid react with snglet oxygen; the first stage of the photoreaction consists in the excitation of a molecule of triplet oxygen by an excited sensitiser which, in oils, is most frequently chlorophyll.

$$Chl_0 + h\nu \rightarrow \ Chl_1^* \rightarrow Chl_2^*$$
$$Chl_2^* + {}^3\textstyle\sum_g O_2 \ \rightarrow \ Chl_0 + {}^1\textstyle\sum^+_g O_2 \qquad \text{or}$$
$$Chl_2^* + {}^3\textstyle\sum_g O_2 \ \rightarrow \ Chl_0 + {}^1\Delta_g O_2$$
$${}^1\textstyle\sum^+_g O_2 + LH \rightarrow LOOH \qquad \text{or}$$
$${}^1\Delta_g O_2 \ + LH \rightarrow LOOH$$

In the reaction of addition, singet oxygen is attached to the unsaturated bonds of fatty acids; in such a case radical reactions do not take place (Frankel 1984, Bartosz 2009), and the products of the reaction are hydroperoxides with no conjugated linkages (Gardner 1998, cit. after Pieńkowska 2003).

4.2. Auto-oxidation

As in the case of photo-oxidation the products of the process of auto-oxidation are hydroperoxides (Fig. 15). However, the mechanism of the process is based on free radical reactions composed of three phases:

- **initiation phase:**

in this phase an atom of hydrogen is detached from the carbon atom situated directly at the double bond of the molecule of an unsaturated fatty acid. Due to the loss of the hydrogen, at the carbon atom there is an unpaired electron, which leads to a regrouping of the double bonds and to the formation of a stable configuration of conjugated linkages. The occurrence of peroxidation is evidenced in the spectra of electromagnetic radiation absorption in th UV band, generated by the system of conjugated linkages that do not appear in natural fatty acids (Pieńkowska 2003, Bartosz 2008). The process can be caused by the action of such radicals as the hydroxyl radical $^{\bullet}OH$, alkyl radical $L^{\bullet}$, alkoxide radical $LO^{\bullet}$, peroxide radical $LOO^{\bullet}$, ferryl cation radical $Fe{=}O^{2+}$ and perferryl cation radical $Fe{=}O^{3+}$ (Qian et al. 2000, Ohyashiki 2002), as well as of ozone O_3, nitrigen dioxide $NO^{\bullet}_2$, nitrogen oxide $NO^{\bullet}$ (Hiramoto et al. 2003), sulphur dixoide $SO^{\bullet}_2$ and hypochlorite ClO^- (Panasenko 1995). The reaction of initiation can be written as:

$$LH + O_2 \rightarrow L^{\bullet} + HOO^{\bullet}$$

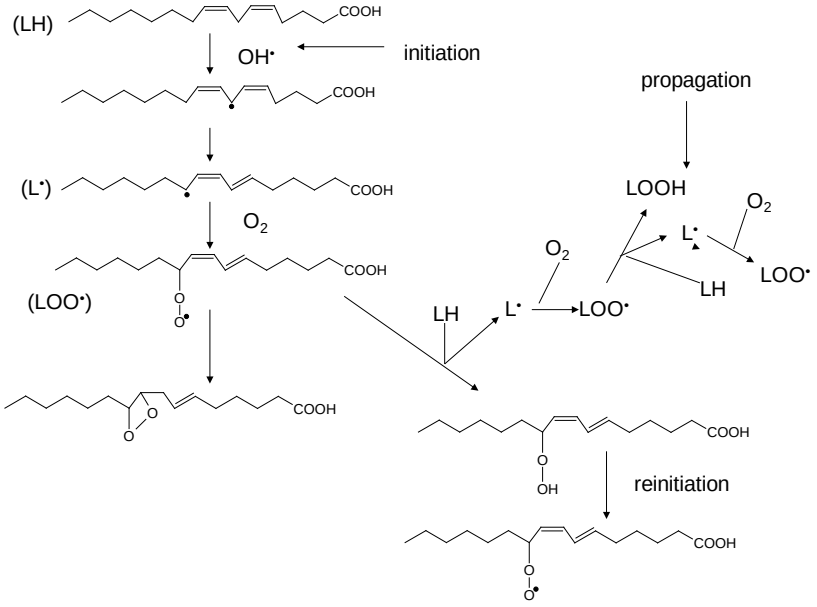


Fig. 15. Scheme of peroxidation of polyunsaturated faty acids

- **prolongation phase:**

at this stage of oxidation the alkyl radicals $L^{\bullet}$ enter into reaction with oxygen, and the result of that reaction are free peroxide radicals $LOO^{\bullet}$ which, in turn, can detach an atom of hydrogen from molecules of fatty acids, leading to the formation of fatty acid peroxide LOOH (Frankel 1991, Bartosz 2008, Qian *et al*. 2000).

$$L^{\bullet} + O_2 \rightarrow LOO^{\bullet}$$

$$LOO^{\bullet} + LH \rightarrow LOOH + L^{\bullet}$$

Also possible is a reaction in which oxygen, undergoing the reaction of addition to a double bond of an unsaturated fatty acid, leads to the formation of hydroperoxides.

- **termination phase:**

in this phase recombination of radicals takes place, and quenching of the radical reaction. The product of reaction of two free radicals are non-radical dimers of fatty acids, as well as oxo- and hydroxyacids (Pieńkowska 2003).

$$L^{\bullet} + L^{\bullet} \rightarrow L{-}L$$

$$LOO^{\bullet} + LOO^{\bullet} \rightarrow LOOL + O_2$$

$$LOO^{\bullet} + L^{\bullet} \rightarrow LOOL$$

In the discussion of peroxidation we should also mention re-initiation, i.e. a phenomenon which consists in the decomposition of fatty acid peroxides, leading to the reappearance of free radicals; in such a case peroxidation depends on the concentration of LOOH. This process is initiated by iron and copper cations (Frankel 1990, Qian 2000) :

$$LOOH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + LO^{\bullet}$$

$$LOOH + Fe^{3+} \rightarrow Fe^{2+} + H^{+} + LOO^{\bullet}$$

Secondary products of peroxidation of polyenic fatty acids are compounds formed through the decomposition of hydroperoxides of fatty acids. Due to the breaking of the carbon chain there appear short-chain saturated and unsaturated hydrocarbons, aldehydes, ketones, esters, lactones, alcohols andi ethers (Drozdowski 2007).

The rate of auto-oxidation depends on the degree of unsaturation of fatty acids; the larger the number of double bonds in a fatty acid the faster the process of peroxidation (Puzanowska-Tarasiewicz *et al*. 2008). Linoleic acid containing two double bonds oxidises 10-40-fold faster than oleic acid which has one unsaturated linkage (Drozdowski 2007).

4.2.1. Thermo-oxidation

Thermooxidation consists in the oxidation of fats under the effect of temperatures above 100^{o}C with or without access to oxygen. The process takes place during thermal treatment of fats: frying, roasting. At temperatures of 170-200^{o}C (frying temperature) hydroperoxides of lipids formed as a result of photo- or auto-oxidation undergo secondary oxidation, the producs of which are toxic hydroxyacids, epoxide and carbonyl compounds, including malonic aldehyde and 4-hydroxynonenal. Water present in the process of frying causes the hydrolysis of TAG to free fatty acids and glycerol. Next, glycerol undergoes transformations to acrolein, and free fatty acids to cyclic monomers; in both cases compounds noxious to human health are produced. At high temperatures and in the presence of amino acids acrolein can undergo further transformations to the toxic acrylamide which can damage genes and initiate the neoplastic proces. If animal fats are used

for the process of frying, there appear the noxious oxidised derivatives of cholesterol: 25- and 26-hydroxycholesterols (Tynek and Hazuka 2004). Limitation of thermo-oxidative transformations is aimed at reducing the level of toxic products of secondary oxidation in frying fats and can be achieved through the application of three options:

- use of oils with reduced content of PUFA (below 15%) and linolenic acid (below 1.5%) as frying fats,
- use of additives with antioxidative properties, so-called antioxidants,
- lowering of frying temperature to below 180^{o}C.

Antioxidants are compounds which, even at low concentrations of 0.001–0.1%, cause retardation of the reaction of oxidation of lipids. The substances, added to oil, must not affect its sensory qualities and have to be resistant to thermo-oxidation. The efectiveness of an antioxidant depends on its concentration in oil and must be determined experimentally, e.g. in the Rancimat test or the thermostat test.

Natural antioxidants, the effect of which is based on the properties of polyphenolic compounds, sterols and phenolic acids, include extracts of rosmarinus, sage and tea (Mińkowski 2008), oregano (Wroniak and Łubian 2008), marjoram and thyme. Also used as antioxidants are fractions of tocopherols obtained from oils with high tocopherol contents: rapeseed oil (Nogala-Kałucka *et al.* 1998), wheat germ oil, sunflower oil, maize oil, soybean oil, cotton oil. Other natural antioxidants include orisanol obtained from rice and rice bran, sesamol and sesaminol originating from sesame oil, Δ-5 and Δ-7 avenosterol and brassicasterol, components of oils from oat, rapeseed oil and olive oil, and – primarily obtained from olive oil - squalene.

For the stabilisation of frying fats synthetic antioxidants are used: BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), and also esters of gallic acid: propyl gallate, octyl gallate and dodecyl gallate (Mińkowski 2008).

The enumerated substances are secondary antioxidants, i.e. such whose antioxidative properties consist in the interruption of the radical chain reaction.

Secondary antioxidants display their properties through the bonding of metal ions, oxygen atoms, absorption of radiation or regeneration of primary antioxidants (Tynek and Hazuka 2004). Secondary antioxidants include also acids: ascorbic acid, citrinic acid and phosphoric acid. Apart from the primary and secondary antioxidants there are also “other” compounds which act as inhibitors of thermo-oxidative transformations of oils (Tab. 28).

Oxidative stability is determined by the induction time, defined as the period between the moment an oil sample has reached the measurement temperature and

the point of suddent increase in the level of peroxides (Coppin and Pike 2001). The number of methods describing oxidative stability is constantly changing and evolving. Oil subjected to the effect of increasing temperature in the presence of too much air oxygen undergoes accelerated thermo-oxidation. This process forms the basis of one of the methods for the estimation of oxidative stability – the Rancimat test, and it can be determined automatically with the use of two commonly available types of apparatus: Rancimat and OSI (Oxidative Stability Instrument) (Tan *et al*. 2002, Velasco *et al*. 2004). In the Rancimat test the measured products of oxidation are mainly dicarboxylic acids which differ from hydroperoxides, hence the inaccuracy of the method, yet on the other hand the high temperature applied in the test causes that the test can be used for the determination of changes in fats used for deep frying (Hęś *et al*. 2001). The application of the heat treatment method for the determination of oxidative stability of oil was the subject of study by numerous researchers. Cross (1970) and Hassel (1976) used DSC (Differential Scanning Calorimetry) in an isothermal model with pure oxygen for the determination of oxidative stability (Tan *et al*. 2002). A method equivalent to the DSC in the determination of stability of oils is ESR (Electron Spin Resenance spectroscopy) (Giuffrida *et al*. 2007).

Table 28. Additives used with frying fats (Tynek and Hazuka 2004)

Name of additive	Mechanism od action or purpose of additive	Optimum amount
PDMS E900 PSE	limitation of air access to the surface of soil by covering it with a molecular layer	1-3 ppm
citrus oil	elimination of unpleasant smell in frying	100-1000ppm

Oxidative stability of vegetable oils depends primarily on their fatty acid composition - the higher the level of unsaturated fatty acids the shorter the induction time in the Rancimat test, and also on their content of natural antioxidants (Wroniak *et al*. 2006, Wroniak and Łukasik 2007) (Fig. 16).

Thermo-oxidative stability of fats subjected to the effect of very high temperatures during frying can be determined through the measurement of TAG polymers which are formed at that time. This is done with the help of the index OSET (oxidative stability at elevated temperature), defined with the relation OSET = 100% of polymers (Tynek and Hazuka 2004) (Tab. 29).

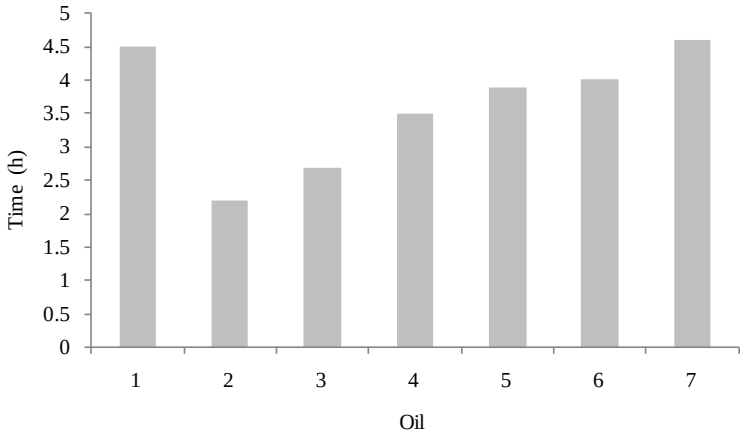


Fig. 16. Induction time of selected cold-expressed oild (Wroniak and Łukasik 2007). 1 – rapeseed oil, 2 – sunflower oil, 3 – soybean oil, 4 – arachis oil, 5 – sesame oil, 6 – linseed oil, 7 – maize oil.

Table 29. Values of OSET index for selected oils with the addition of vgarious antioxidants (Berger 2005)

Kind of antioxidant added, 0.25%	OSET index	
	rapeseed oil	high-oleic sunflower oil
None	44	21
Squalene from olive oil	48	23
Phytosterols from rapeseed oil	60	29
Phytosterols from sunflower oil	85	36
Orisanol	65	31
BHA	52	22
BHT	54	24

5. CHEMICAL COMPONENTS OF VEGETABLE OILS AND ANIMAL FATS WITH PRO- AND ANTIOXIDATIVE PROPERTIES

Apart from fatty acids, vegetable oils and animal fats contain also chemical compounds with nutritional and health-promoting values that at the same time perform pro- or antioxidative functions. In vegetable oils they constitute 1% of the oil obtained (Krzymański *et al.* 2009) and in milk fat 1.5% of its composition (Stołyhwo and Rutkowska 2007), and belong to so-called unsaponifiable fractions. They include aliphatic and isoprenoid hydrocarbons naturally occurring in fats and oils: carotenoid pigments, chlorophyll, squalene, tocopherols, polyphenols, sterols.

5.1. Squalene

The main representative of isoprenoid hydrocarbons is the colourless squalene (Fig. 17), commonly occurring in vegetable oils and animal fats (olive oil 0.1-0.7%, rapeseed oil 0.03%, milk fat 3.7%) (Sikorski 2007). Notable amounts of squalene can be found in rice bran and wheat germs (Reddy and Couvreur 2009), and it also appears in palm oil (0.04-0.09%) (Kohr and Chieng 1997). Particularly large amounts of squalene are contained in oil obtained from shark liver (40%-82%) (Reddy and Couvreur 2009, Bakes and Nichols 1995). Squalene is a polyunsaturated triterpene (C-30) with antioxidative and fungicidal properties, containing 6 units of isopropene; it is an intermediate of cholesterol, has an adjunctive effect in the elimination of toxins by the liver, and also displays some anticarcinogenic effects (Reddy and Couvreur 2009). Squalene in included in the lipid coat of the human skin (Tab. 30).

Table 30. Composition of sebum in humans (Zih-Rou Huang *et al.* 2009)

Substance	Composition (%)
Wax esters	25
Squalene	13
Cholesterol	2
Triglycerides, free fatty acids, diglycerides	57
Other	3

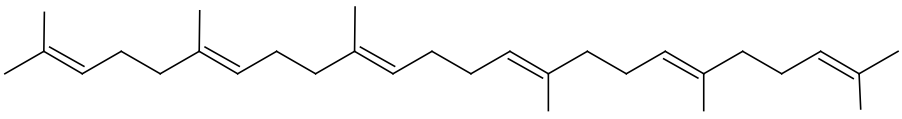


Fig. 17. Structural formula of squalene molecule

5.2. Pigments

Pigments occurring in vegetable oils and animal fats are classified as compounds containing nitrogen, including derivatives of pyrrole, e.g. chlorophyll present in vegetable oils, and substances that do not contain nitrogen in their molecules, such as carotenoids that appear both in vegetable oils and in milk fat (Blaim 1967).

One of the parameters determining the quality of crude, bleached and refined vegetable oils is the general colour which is assayed spectrophotometrically for oil samples diluted in CCl_4, at two wavelengths:

- λ = 460 nm for carotenoid pigments,
- λ = 666 nm for chlorophyll piments.

Absorbance values obtained for carotenoid and chlorophyll pigments are summed up, multiplied by 1000, and given in the form of an integer or as general colour value (BN-86/8050-30)

$$B = (A_{460} + A_{666})\ 1000.$$

When measurement of absorbance is made with another method, e.g. acc. to PN-A-86934:95, oil samples are dissolved in hexane and the measurement is made at wavelengths of:

- λ = 442 nm for carotenoid pigments,
- λ = 668 nm for chlorophyll pigments.

The value of general colour is calculaed in a manner analogous to the case above

$$B = (A_{442} + A_{668})\ 1000.$$

The general colour of oils depends on a number of factors, such as the conditions of seed harvest and storage, drying temperature, seed damage degree. The general colour of oil is also affected by the method of its obtainment.

The maximum level of carotenoids in rape seeds is observed in the case of very early harvest, and it does not decrease much in relation to the harvest date. The level of chlorophylls assayed for the same seeds is ca. six-fold lower and decreases with delay of harvest date. Thus, with optimum harvest time, we can almost completely eliminate the chlorophyll pigments while preserving the level of carotenoid pigments. Similar relations can also be observed for oil, but the level of the pigments is about ten-fold lower (Strobel *et al*. 2005).

Drying temperature of rape seeds has a significant effect on the content of chlorophylls and carotenoids, and thus also on the general colour. The most unfavourable changes take place at above 120^{o}C. The graphs below illustrate that relation (data from Tys *et al*. 2002) (Fig. 18-19).

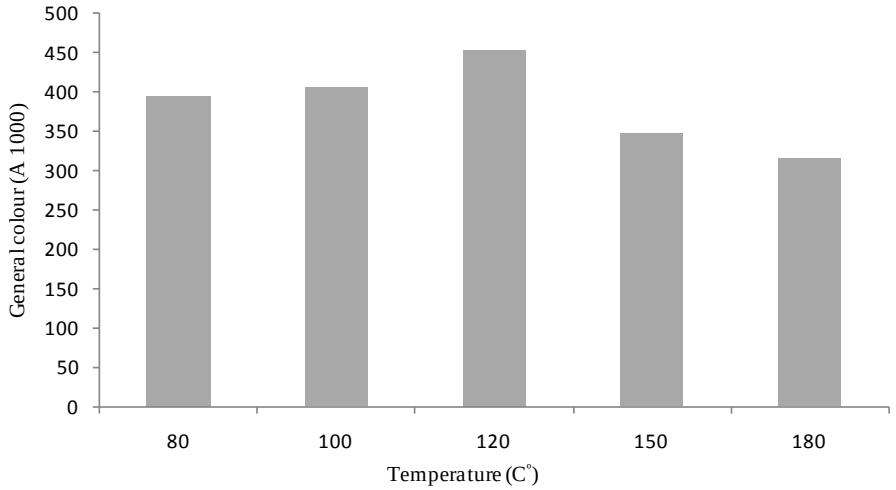


Fig. 18. General colour of rape seeds cv. Kana as related to drying temperature

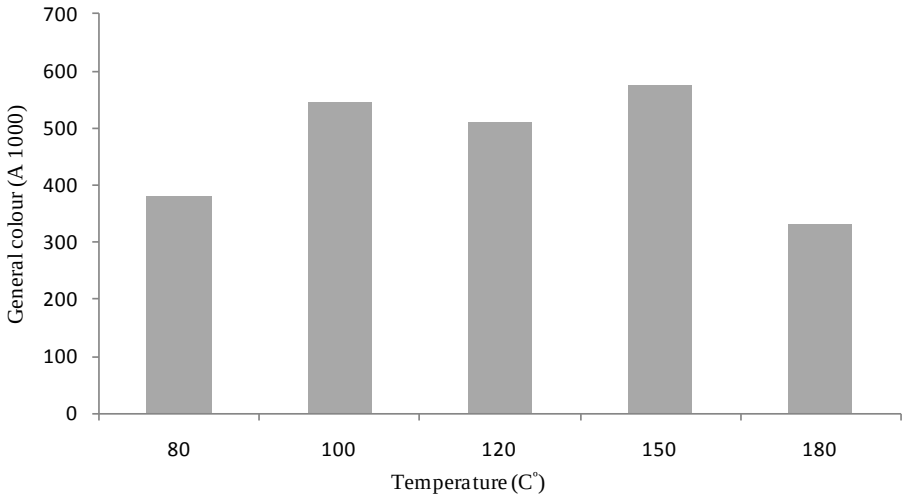


Fig. 19. General colour of rape seeds cv. Lisek as related to drying temperature

The general colour changes also in relation to the kind of oil and to the method of its obtainment (Tab. 31).

Changes in the general colour (A_{442} + A_{668}) 1000 in relation to the method of oil obtainment were one of the issues addressed by Zadernowski *et al*. (2002).

They measured the general colour of evening primrose seed and borage seed oil obtained with a hydraulic press and an expeller and with the solvent extraction method. The lowest values of general colour were those of solvent-extracted oils, and the lowest were obtained for oils pressed with an expeller (Tab. 32).

Table 31. General colour values of selected oils in relation to the method of their obtainment (Rotkiewicz *et al.* 1995, Pieńkowska *et al*. 1999, Pieńkowska 2003)

Kind of oil	Method of obtainment	General colour $(A_{460} + A_{666})$ 1000
Rapeseed oil	cold-pressed from whole raw seeds	730
	cold-pressed from oiled raw seeds	620
	refined	11
	hot-pressed from whole heated seeds	870
	extracted from whole raw seeds	730
	extracted from oil cake of whole oiled seeds	940
	bleached	86
Evening primrose seed oil	pressed	336
	bleached	90
Borage seed soil	pressed	590
	extracted	500

Table 32. General colour values of evening primrose seed and borage seed oils in relation to the method of their obtainment (Zadernowski *et al*. 2002)

Kind of oil	Value of general colour $(A_{442} + A_{668})$ 1000		
	hydraulic press	expeller	extraction
Evening primrose oil	310	350	238
Borage seed oil	598	600	511

Rapeseed oils obtained from heat-treated fragmented seeds are characterised by lower values of general colour than oils obtained from heat-treated whole seeds (Górecka *et al*. 2003) (Tab. 33).

Table 33. General colour values in relation to the form of rape seeds (Górecka *et al*. 2003)

Temperature °C	General colour (A_{442} + A_{668}) 1000	
	fragmented seeds	whole seeds
80	1263	1178
100	1382	1324

Rapeseed oil pressed from clean and undamaged seeds is characterised by three-fold lower general colour value than oil pressed from damaged seeds (Krygier *et al*. 2000), which results from its greater content of seed coat (Zadernowski *et al*. 1993). In oil pressed from whole seeds the level of carotenoids is 40% higher than that of chlorophylls, while in oil obtained from undamaged seeds the concentration of chlorophyll pigments is greater than that of carotenoid pigments (Krygier *et al*. 2000) (Fig. 20-21).

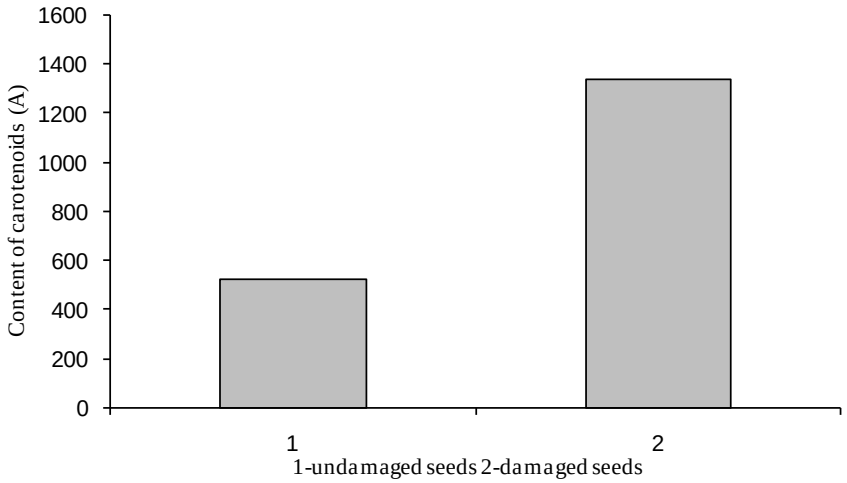


Fig. 20. Content of carotenoids in rapeseed oil pressed from undamaged (1) and damaged (2) seeds

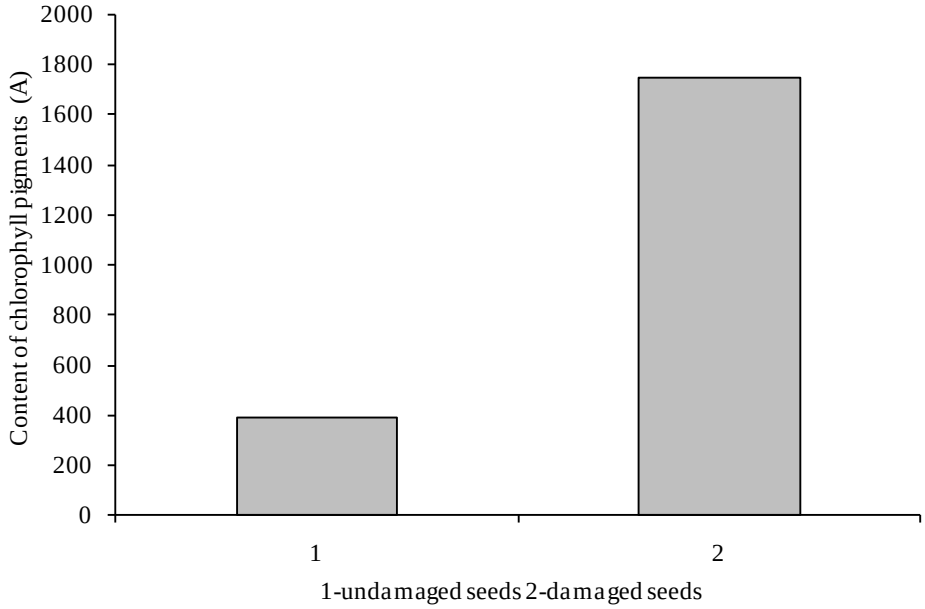


Fig. 21. Content of chlorophyll pigments in rapeseed oil pressed from undamaged (1) and damaged (2) seeds

5.2.1. Carotenoid compounds

For the first time carotene was isolated from carrot, in the form of ruby-red crystals, by Wackenroder in 1831. Since then more than 600 carotenoids have been identified (Beutner *et al*. 2001).

Caretonoids are classified among isoprenoid hydrocarbons usually built of eight isoprene units, with conjugated double linkages in the *trans* configuration. The presence of the linkages determines the occurrence of colours from yellow to red, and with increasing numbers of the linkages there takes place a bathochromic shift of absorption bands (Pieńkowska 2003).

Carotenoids most frequently occur as acyclic, monocyclic and bicyclic forms.

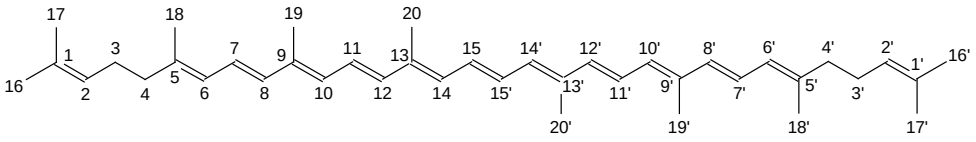


Fig. 22. Structural formula of lycopene molecule (ψ,ψ carotene)

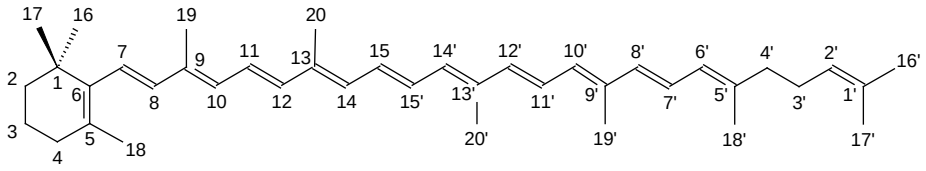


Fig. 23. Structural formula of γ-carotene molecule (β,ψ carotene)

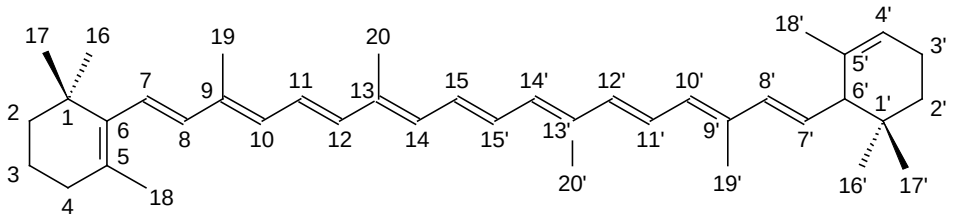


Fig. 24. Structural formula of α-carotene molecule (β,ε carotene)

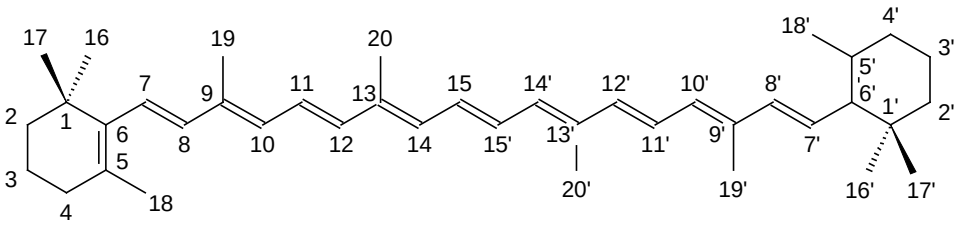


Fig. 25. Structural formula of β-carotene molecule (β,β carotene)

The lycopene derivatives presented (Fig. 23-25) above are not water-soluble, but they can dissolve in fats.

A mixture of α and β-carotenes, in which β-carotene accounts for ca. 90-95%, is known as carotene (Blaim 1967). The most important health-promoting function is that of β-carotene which plays the role of provitamin A (Tab. 34). Deficit of vitamin A causes the so-called nocturnal amblyopia, which in consequence may lead to the keratosis of the epithelium of the cornea. Vitamin A plays also a role in the process of growth and affects the reproductory functions of the organism (Drozdowski 2007). Moreover, this vitamin plays an adjunctive role for the immune system, protecting the organism against infectious and invasive diseases (Karłowicz-Bodalska and Bodalski 2007).

Table 34. Selected carotenoids with the activity of vitamin A. (acc. to Goodwin 1965, cit. after Blaim 1967)

Carotenoid	Biological activity (β-carotene = 100%)
α-carotene	53
γ-carotene	43
β-zeacarotene	40
cryptoxanthin	57
5,8-epoxy- β-carotene	50
4-oxo- β-carotene	44

Among carotenoids we include also xantophylls (oxycarotenoids) (Fig. 26-30), easily soluble in alcohols products of oxidation of carotene isomers, containing oxygen in the form of hydroxyl, ketone, aldehyde or carboxyl groups.

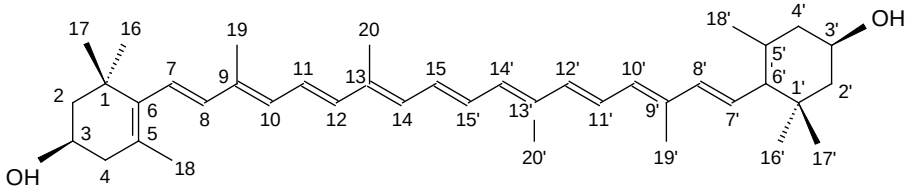


Fig. 26. Structural formula of zeaxanthin- 3,3' – dihydroxy – β-carotene

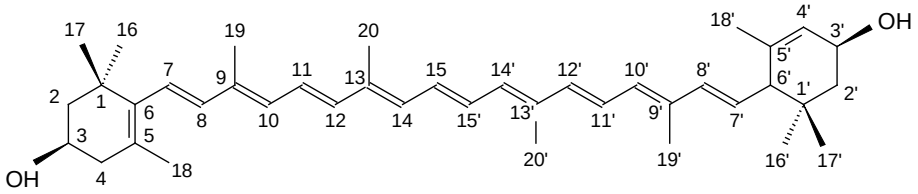


Fig. 27. Structural formula of lutein- 3,3'- dihydroxy- α-carotene

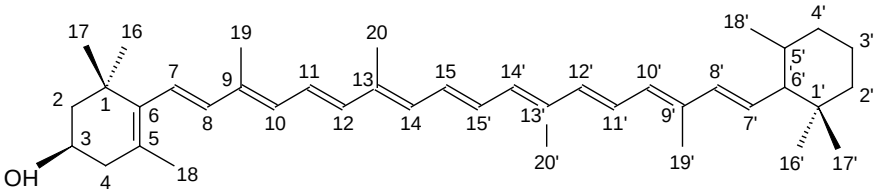


Fig. 28. Structural formula of cryptoxanthin- 3-hydroxy- β-carotene

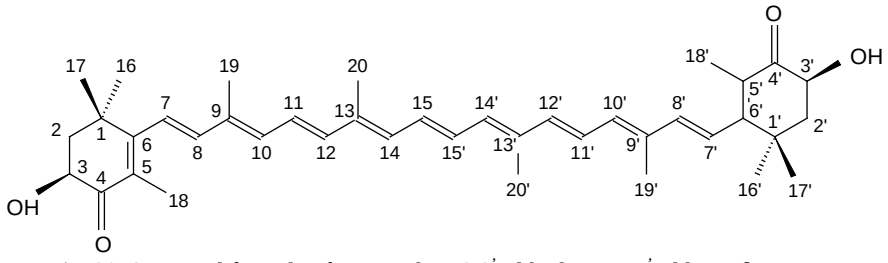


Fig. 29. Structural formula of astaxanthin- 3,3'- dihydroxy-4,4'- diketo- β-carotene

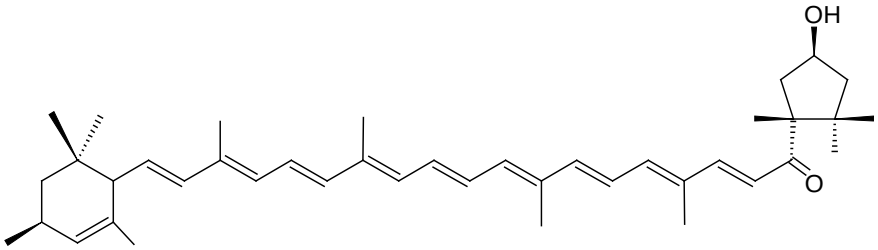


Fig. 30. Structural formula of capsanthin

These compounds are widespread in the plant world: they can be found in leaves, fruits, seeds, flowers and roots. The most frequent carotenoid in leaves is β- and α-carotene. Bixin and norbixin (xantophylls), components of the red-yellow pigment annatto, were isolated from the seeds of the tropical bush *Bixa orellana* (Drozdowski 2007), lycopene can be found in tomatoes (Stryer 1997), capsorubin and capsanthin were isolated from chilli peppers *Cayenne* (Pieńkowska 2003), γ-carotene was obtained for the first time from the fruits of lily of the valley (*Convallaria majalis*). Zeaxanthin was first isolated from leaves in 1932 by Khun and Brockmann (Blaim 1967). Lutein and zeaxanthin are two polar carotenoids, belonging to xantophylls, that were discovered in the lipid membranes of the yellow spot in the retina of the eye of mammals. So far there have been no studies that would provide an explanation of the physiological role of

these two pigments, but probably they play an important role in the process of vision, providing protection against UV radiation (Tys *et al*. 2002).

The highest content of carotenoids is characteristic of palm oil (Tab. 35).

Table 35. Content of carotenoids in selected oils (Chih Chiu *et al.* 2009, Pieńkowska 2003, Toro-Vazqez 1991 cit. after Rotkiewicz *et al.* 2002, Mińkowski 2008)

Kind of oil	Content of carotenoids (mg kg^{-1})
Palm oil	500-700
Rapeseed oil	47.3
Evening primrose seed oil	34.2
Borage seed oil	24.3-41.7
Linseed oil	147.5
Camelina seed oil	160.1
Blackcurrant seed oil	7.2
Echium oil	42.1
soybean oil maize oil cotton seed oil pumpkin seed oil	16-128

Carotenoid compounds have antioxidative properties, which results from their capacity to react with singlet oxygen and also with free radicals formed as a result of auto-oxidation of lipids (Bartosz 2008) (Tab. 36).

Table 36. Reaction of selected carotenoids with radicals (Krinsky, Yeum 2003)

Carotenoid	Radicals with which it can react
lycopene, β-carotene	$O_2^{-\bullet}$
β-carotene	$SCN_2^{\bullet}$, $Br_2^{-\bullet}$, $LOO^{\bullet}$, $LO^{\bullet}$, $NO_2^{\bullet}$, $AscH^{\bullet}$
lycopene	$NO_2^{\bullet}$

The ability of carotenoids to quench excited oxygen results from the fact that the energy of the triplet state of the compounds is lower than the energy required to excite triplet oxygen to the singlet form Δ (94 kJ mol^{-1}) (Wilkinson *et al*. 1995, cit. after Rotkiewicz 2002) at, e.g., for all-trans β-carotenue 88 kJ mol^{-1} (Beutner *et al.* 2001). Carotenoids can quench singlet oxygen in two ways: physically and chemically. In the first case, the structure of carotenoid molecule is not degraded; it absorbs the energy of singlet oxygen excitation and then passes, in the non-radiant manner, to the ground state and the energy is transmitted to the environment in the form of heat (Forte and Denny 1968, cit. after Rotkiewicz 2002). Such carotenoids have been classified as "unusual" antioxidants, and include, among others, astaxanthin, canthaxanthin and zeaxanthin (Beutner *et al*. 2001).

$$^{3}Sen^{\bullet} + {}^{1}K \rightarrow {}^{1}Sen + {}^{3}K^{\bullet}$$
$$^{1}O^{\bullet}_{2} + {}^{1}K \rightarrow {}^{3}O_{2} + {}^{3}K^{\bullet}$$
$$^{3}K^{\bullet} \rightarrow {}^{1}K + \text{heat}$$

The chemical quenching of singlet oxygen by a carotenoid molecule involves its degradation. Beutner *et al*. classify such carotenoids as class II antioxidants, and include among them lycopene and β-carotene. The products of degradation of carotenoid molecule depend on the degree of the degradation and also on the kind of pigment (Rotkiewicz 2002). The products of degradation of *trans*- β-carotene include, among other things, epoxides, carotenals, carotenons (Henry *et al*. cit. after Rotkiewicz 2002).

The lipid peroxide radical undergoes the reaction of attachment to β-carotene, and the product of that transformation is a radical with an unpaired electron on carbon atom:

$$LOO^{\bullet} + K \rightarrow LOO{-}K^{\bullet}$$

The reaction can continue and multiple adducts are formed as a result (Van den Berg *et al*. 2000, Rotkiewicz *et al.* 2002, Bartosz 2008):

$$LOO{-}K^{\bullet} + LOO^{\bullet} \rightarrow LOO{-}K{-}OOL$$
$$LOO{-}K{-}OOL + LOO^{\bullet} \rightarrow (LOO)_2{-}K{-}OOL^{\bullet}$$
$$(LOO)_2{-}K{-}OOL^{\bullet} + LOO^{\bullet} \rightarrow (LOO)_2{-}K{-}(LOO)_2$$

The mechanism of scavenging of free radicals by carotenoids is based not only on addition. The reaction where a carotenoid molecule is the donor of an

electron for the radical NO_2^* or the tocopheroxyl cation radical TO^{*+} (Böhm *et al*. 1998) can be written as follows:

$$LOO^{\bullet} + K \rightarrow LOO^{-} + K^{\bullet+}$$

As a result of the reaction of reduction, the carotenoid molecule attaches an electron, the effect of which is the formation of a carotenoid anion radical:

$$K + e^{-} \rightarrow K^{\bullet-}$$

In the case of breaking of C−H linkage and removal of hydrogen atom from saturated carbon atom of an acyclic polyenic chain in a carotenoid we obtain carotenoid radicals (Britton 1995):

$$LOO^{\bullet} + K{-}H \rightarrow LOOH + K^{\bullet}$$

Carotenoids may display both pro- and antioxidative activity, which is related to a number of factors.

Compounds formed as a result of the reaction of addition can initiate the formation of new radicals, undergoing such reactions as:

- degradation of the bis-adduct LOO−K−OOL to carbonyl compounds and radicals $LO^{\bullet}$,
- degradation to epoxides

$$LOO{-}K^{\bullet} \rightarrow K{-}\text{ epoxide} + LO^{\bullet},$$

- reaction with $^3O_2$ (Rotkiewicz 2002, Ali Ey-Agamey *et al.* 2004)

$$LOO{-}K^{\bullet} + {}^3O_2 \rightarrow LOO{-}K{-}OO^{\bullet}$$

With increase in the partial presssure of oxygen and at high concentrations of carotenoids their pro-oxidative character is revealed (Burton and Inglod 1984 cit. after Edge, Truscott 1997). The effectiveness of carotenoids in quenching singlet oxygen depends on their colour, being the highest for compounds with purple, crimson and blue colours (Beutner *et al.* 2000). Apart from the colour, factors that determine the antioxidative power of carotenoids include the number of conjugated linkages in the molecule (Edge *et al.* 1997) and the presence of functional groups (Beutner *et al*. 2000).

Carotenoids are eliminated from oils in the rafinement processes of bleaching and deodorisation (Rotkiewicz *et al*. 2002) (Fig. 31).

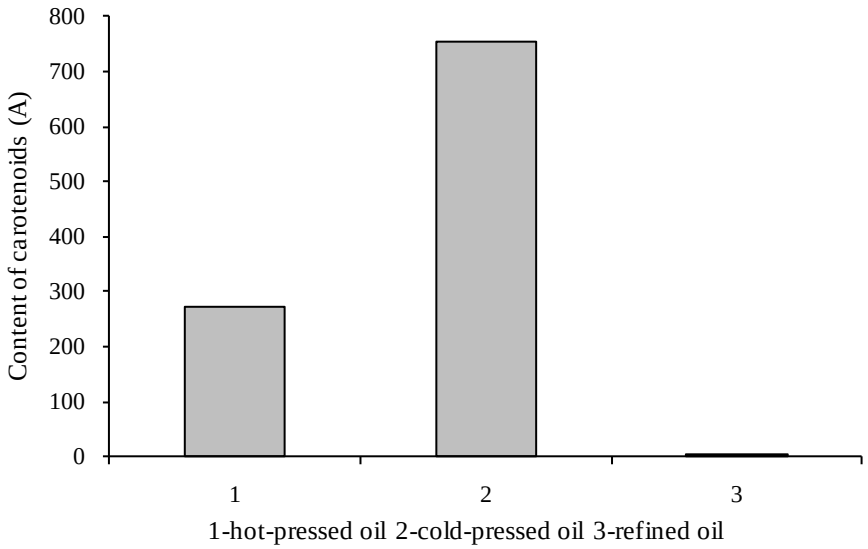


Fig. 31. Content of carotenoids in rapeseed oils obtained wirth various methods (Krygier *et al.* 1995)

5.2.2. Chlorophyll

Chlorophyll is a lipid pigment characteristic for plant organisms. The chlorophyll molecule is built of four pyrrole rings distributed around an atom of Mg^{2+}; at the extreme carbon atoms of the pyrrole rings there is the remainder of prioprionic acid, esterified with phytol, and the remainder of acetic acid, esterified with methanol (Blaim 1967) .

In plants there occur two kinds of chlorophyll - *a* and *b*. The blue-green chlorophyll *a* has a CH_3 group at the 7^{th} atom of carbon in the pyrrole ring, while the green-yellow chlorophyll *b* has, at the same carbon atom, a CHO group (Fig. 32-33).

Chlorophylls have double conjugated linkages, due to which they are extremely effective photoreceptors. They are classified among so-called polyenes, i.e. compounds with strong absorption bands within the range of visible light – values of the coefficient of absorbance ε for chlorophyll *a* and *b* are greater than 10^5 cm^{-1} M^{-1} (Stryer 1997) (Fig. 34). The first band, so-called Soret band, is within the range of 400-500 nm, and the coefficients of absorbance ε for that wavelength range are 10^5-10^6 cm^{-1} M^{-1}. The second band, Q, is approximately 10-fold weaker and located within the range of 500-700 nm.

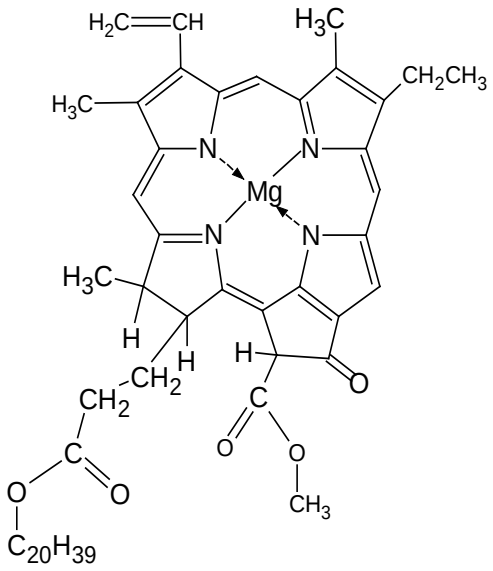


Fig. 32. Structural formula of molecule of chlorophyll *a*

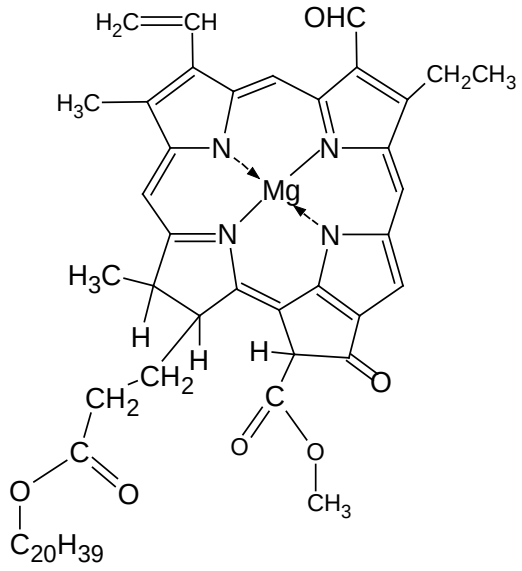


Fig. 33. Structural formula of molecule of chlorophyll *b*

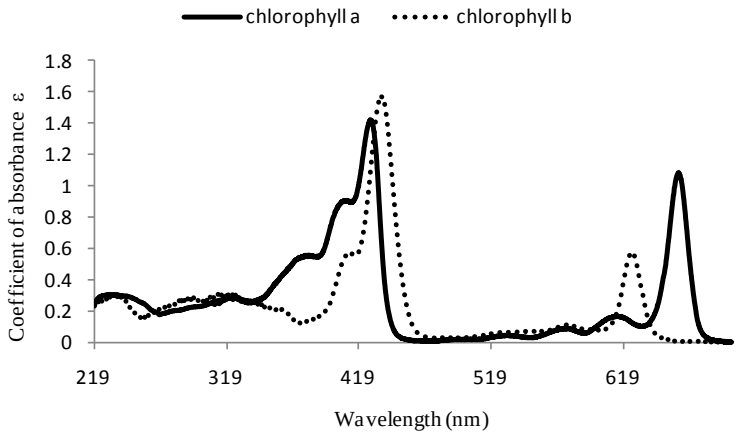


Fig. 34. The coefficient of absorbance of chlorophyll *a* and chlorophyll *b* dissolved in diethyl ether in relation to wavelength

Chlorophylls are unstable compounds and undergo transformations, changing their colour under the effect of a number of factors, such as high temperature, exposure to light and oxygen, the reaction of the environment, and enzymatic activity (Fig. 35). Under the effect of an acid, cation Mg^{2+} is substituted by hydrogen cations H^{+} and, depending on the reaction, either pheophytin, with olive-green colouring (pH< 7), or brown pheophorbide (pH<< 7) are formed (Gossauer and Engel 1996). Acting with alkali on chlorophylls we can abstract phytol and methanol; the effect is the formation of a compound with the initial colouring, containing a magnesium ion and free carboxyl groups – chlorophyllin (Blaim 1967). The enzyme chlorophyllase, naturally occurring in plants, causes catalytic breakdown of chlorophyll, the effect of which is the appearance of chlorophyllides, green-coloured compounds free of phytol (Ward *et al.* 1994c).

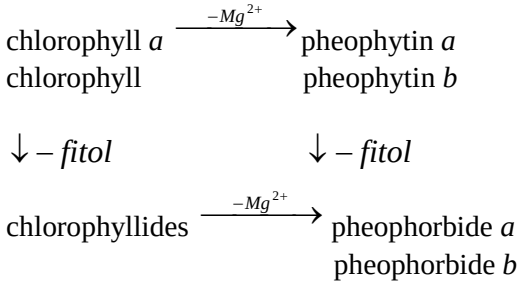


Fig. 35. Pathway of transformation of chlorophyll *a* and chlorophyll *b*

Pyropheophytins are derivatives of pheophytins formed through the abstraction of the group $–COOCH_3$ under the effect of high temperatures and acids, e.g. phosphoric acoid or citric acid (Endo *et al*. 1992).

Chlorophyll and its derivatives give oils undesirable colouring, may have a pro-oxidative effect, and also retard the process of hydrogenation (Endo *et al*. 1992) (Fig. 36) (Tab. 37). Chlorophyll derivatives occurring in rapeseed oil, as well as their content in rape seeds and rapeseed oil and in both black and green olive oil are given in the Tables 38-39 below. The data are given after the followign authors: Endo *et al*. (1992), Ward *et al*. (1994 a,b,c), Rahmani and Csallany (1991).

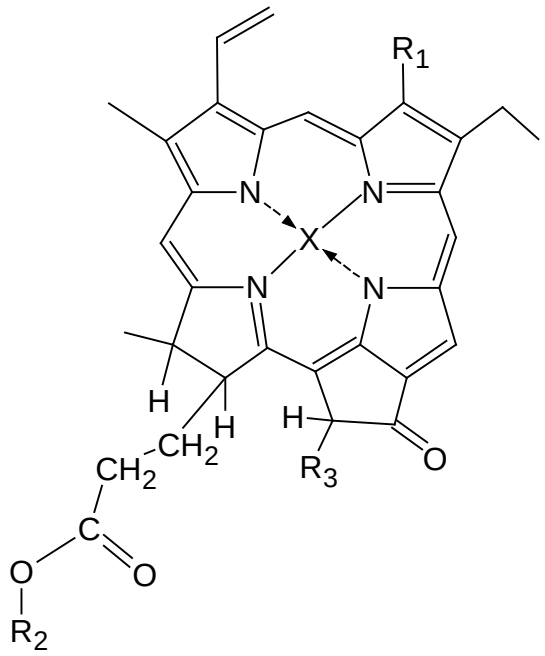


Fig. 36. Chemical structure of chlorophyll molecule

Unripe rape seeds contain from 962 to 1166 mg kg^{-1} of chlorophylls and derivatives, and seeds from late harvest only from 1 to 2 mg kg^{-1} (Ward *et al*. 1994c). Therefore the time of harvest and suitable ripeness of seeds play an important role in ensuring high quality of oils. Accelerated harvest of seeds causes an increase in the level of chlorophylls (Szot and Tys 2003). In their study, Szot and Tys (2003)

assayed different stages of rapeseed canopy ripeness based on their own experiments and on the method developed by Muśnicki and Horodyski (1989) (Fig. 37).

With progressing ripening of seeds there is a change in the ratio of chlorophyll *a* to chlorophyll *b* from 1:1 to 3:1 (Endo *et al*. 1992, Ward *et al.* 1994a).

Table 37. Derivatives of chlorophyll (Endo *et al.* 1992)

Compound	X	R_1	R_2	R_3
Chlorophyll a	Mg	CH_3	$C_{20}H_{39}$	CO_2CH_3
Chlorophyll b	Mg	CHO	$C_{20}H_{39}$	CO_2CH_3
Pheophorbide a	H_2	CH_3	H	CO_2CH_3
Pheophorbidw b	H_2	CHO	H	CO_2CH_3
Methylpheophorbide a	H_2	CH_3	CH_3	–
Pheophytin a	H_2	CH_3	$C_{20}H_{39}$	CO_2CH_3
Pheophytin b	H_2	CHO	$C_{20}H_{39}$	CO_2CH_3
Pyropheophytin a	H_2	CH_3	$C_{20}H_{39}$	H
Pyropheophytin b	H_2	CHO	$C_{20}H_{39}$	H

Table 38. Content of chlorophylls *a* and *b* and their derivatives in rape seeds and in rapeseed oil. (Endo *et al*. 1992)

Chlorophyll or its derivative	Content of chlorophyll or its derivative (mg kg^{-1}) in rape seeds and in rapeseed oil		
	seeds	extraction oil	slimefree oil
Chlorophyll a	9.0-23.7	–	–
Chlorophyll b	2.5-8.3	–	–
Pheophytin a	0.1-1.0	13.4-35.2	6.8-9.0
Pheophytin b	–	2.0-5.8	0.2-3.0
Pheophorbide a	0.0-0.1	0.3-1.0	–
Methylpheophorbide a	0.0-0.1	0.4-2.0	0.3-0.5
Pyropheophytin	–	1.2-6.7	6.1-30.9
Total	11.6-33.2	17.3-50.7	14.4-43.4

Table 39. Content of chlorophylls *a* and *b* and their derivatives in oil from green and black olives (Rachmani, Csallany 1991)

Chlorophyll or its derivative	Content of chlorophyll or its derivative (mg kg^{-1})	
	black oilve oil	green olive oil
Chlorophyll a	0.00	0.00-2.86
Chlorophyll b	0.00	0.00
Pheophytin a	6.66	35.73
Pheophytin b	0.00	0.00-3.16

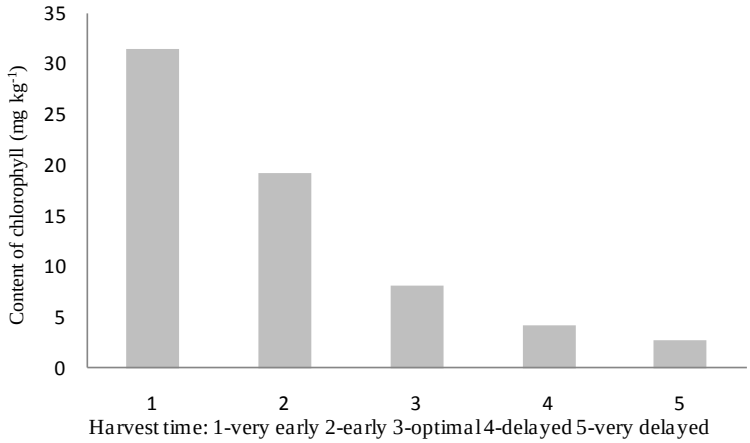


Fig. 37. Chlorophyll content in rape seeds in relation to harvest time

Content of chlorophylls in vegetable oils depends on kind of plant (Tab.40).

Table 40. Content of chlorophylls in selected oils (Mińkowski 2008)

Kind of oil	Chlorophyll content (mg kg^{-1})
Linseed oil	0.4 ± 0.1
Camelina oil	0.9 ± 0.1
Borage seed oil	2.8 ± 0.2
Blackcurrant seed oil	0.2
Echium oil	6.5 ± 0.3

5.3.Tocopherols and tocotrienols

We distinguish four kinds of tocopherol - α, β, γ and δ, that together with four kinds of tocotrienols – α, β, γ and δ are included in the composition of vitamin E.

The basic structure of tocopherols and tocotrienols is the same; they are built of a ring benzopyrene system (two condensed rings – a benzene ring and a tetrahydropyran ring) and a 16-carbon phytin chain attached at position 2, the phytin chains of tocopherols having an unsaturated character, while tocotrienols have double bonds at carbon atoms 3,7 and 11 (Fig.38-39).

The biological activity of tocopherols (methyltocols) and tocotrienols (methyltocotrienols) is dependent on the substituents in the benzopyrene ring (positions 5, 7, 8) which can be a hydrogen radical or a methylene radical (Tab.41).

Tocopherols are fat-soluble compounds with a high antioxidative and biological importance. They are synthesised only by plant organisms and can be stored by animal organisms in the liver.

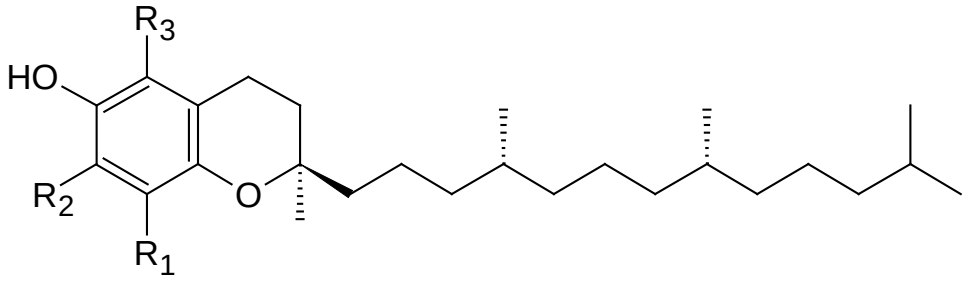


Fig. 38. Chemical structure of tocopherol molecule

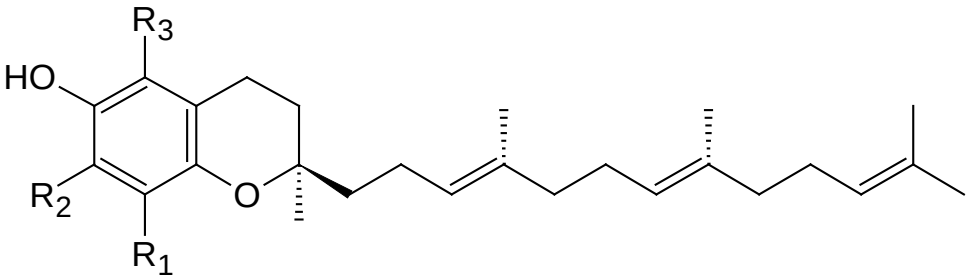


Fig. 39. Chemical structure of tocotrienol molecule

Table 41. Substituents of tocopherol and tocotrienol derivatives

Compound	R_1	R_2	R_3
α-tocopherol α-tocotrienol	CH_3	CH_3	CH_3
β-tocopherol β-tocotrienol	CH_3	H	CH_3
γ-tocopherol γ-tocotrienol	CH_3	CH_3	H
δ-tocopherol δ-tocotrienol	H	H	H

The biological activity of tocopherol forms is inversely proportional to their antioxidative properties. The highest biological activity is diplayed by variants α which at the same time are the least effective antioxidants (Fig. 40).

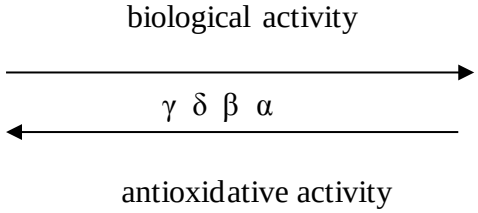


Fig. 40. Biological and antioxidative activity of tocopherol forms

Tocotrienols α, β, δ and γ are compounds with the *trans* configuration, and the biological activity of α-tocotrienol constitutes approximately 20-30% of that of α-tocopherol (Drozdowski 2007). The antioxidative activity of tocopherols consists both in quenching singlet oxygen and in participation in reactions with secondary organic radicals of the peroxidation of lipids. The mechanism of the reaction of tocopherols with lipid peroxides can be presented as follows:

$$LOO^{\bullet} + T{-}OH \rightarrow LOOH + T{-}O^{\bullet}$$

The rate constants of the reaction of tocopherol with various kinds of peroxide radicals are from 10^4 to 10^9 mol dm^{-3} s^{-1} (Sies, Stahl 1995).

The created tocopheryl radical can participate in the process of termination of the free-radical reaction through (Bartosz 2008, Ouchi et al. 2009):

- reaction with a peroxide radical

$$T{-}O^{\bullet} + LOO^{\bullet} + H^{+} \rightarrow LOOH + T{=}O$$

- recombination with another tocopheryl radical

$$T{-}O^{\bullet} + T{-}O^{\bullet} \rightarrow TO{-}OT$$

- addition to a peroxide radical

$$T{-}O^{\bullet} + LOO^{\bullet} \rightarrow LOO{-}OT$$

A tocopheryl radical, entering into reaction with another antioxidants, e.g. ascorbic acid, leads to the recreation of a tocopherol molecule (Ouchi 2009)

$$T{-}O^{\bullet} + AsH^{-} \rightarrow T{-}OH + As^{\cdot -}$$

In an aquatic medium, with tocopherol concentration of 0.05 mole per 1 mole of linoleic acid, α-tocopherol displays peroxidative properties, whereas γ- and δ-tocopherols behave as antioxidants (Cillard and Cillard 1980).

In such a case, the α-tocopheryl radical can also participate in the process of propagation of fatty acid oxidation (Cillard and Cillard 1980, Ouchi 2009) through reactions with:

- a fatty acid hydroperoxide

$$\alpha T{-}O^{\bullet} + LOOH \rightarrow T{-}OH + LOO^{\bullet}$$

- a fatty acid molecule

$$\alpha T{-}O^{\bullet} + LH \rightarrow \alpha T{-}OH + L^{\bullet}$$

Tocopherols can also play the role of antioxidants through reactions with singlet oxygen, but only when thay have a free non-esterified OH group at position 6 of the chroman ring (Sies and Stahl 1995).

The rate constants of the reaction of singlet oxygen scavenging for tocopherol homologues fall within the range of 10^{6}-10^{8} mol dm^{-3} s^{-1} and their values decrease in the order of α- > β- > γ- > δ-tocopherol (Sies and Stahl 1995).

Apart from their antioxidant activiy, tocopherols also play physiological functions in the organism. Vitamin E is responsible for the regulation of functioning of the reproductory organs: in pregnant females its deficit causes resorption of the foetus, while in male organisms it results in artophy of the testicles and muscular atrophy. In the case of anaemia in children, vitamin A stimulates the production of erythrocytes (Drozdowski 2007).

Vegetable oils contain considerable amounts of α-, β-, γ-, δ-tocopherols. The content of tocopherols in selected oils is presented in the Table 42 below.

Table 42. Content of tocopherols in selected oils (Warner and Mounts 1990, Ong 1992, Drozdowski 2007, Krzymański *et al.* 2009, Mińkowski 2008, Jasińska-Stępniak 2009)

Content of tocopherols (mg kg^{-1})	Kind of oil
300-2680	rapeseed oil
1800-4500	oil from wheat germs
600-3380	soybean oil
713.6	camelina seed oil
800-1100	cotton-seed oil
440-1520	sunflower oil
1410.2	borage seed oil
257.7	echium oil
540	maize oil
90-185	olive oil
505.9	linseed oil
294	sesame seed oil
1231.6	blackcurrant seed oil
597.7	walnut oil
479.1	hazelnut oil
835.7	almond oil

The percentage share of the particular homologues of tocopherols depends on the kind of oil. The graphs below have been compiled based on data from works by Warner and Mount 1990 and Krzymański *et al*. 2009 (Fig. 41-44).

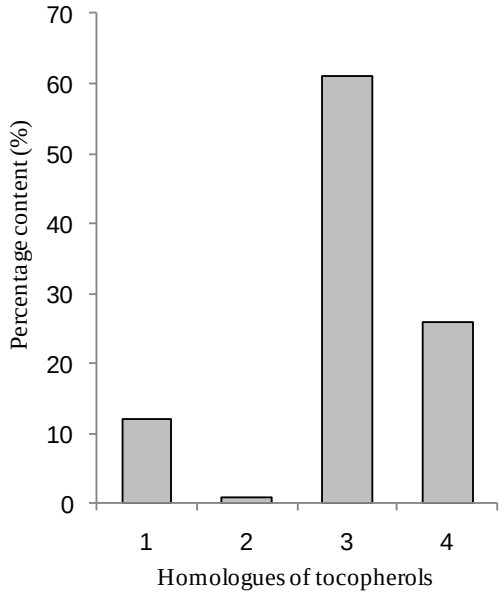


Fig. 41. Percentage content of α-, β-, γ- δ-tocopherols in soybean oil. 1-α-tocopherol, 2-β-tocopherol, 3-γ-tocopherol, 4-δ-tocopherol

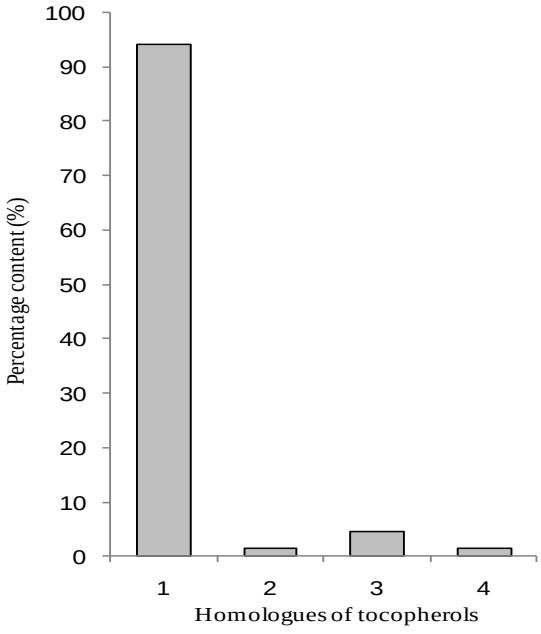


Fig. 42. Percentage content of α-, β-, γ- δ-tocopherols in sunflower oil. Explanations as in Figure 41.

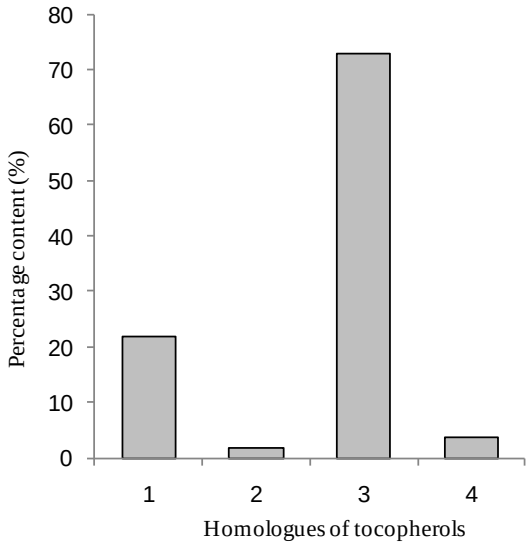


Fig. 43. Percentage content of α-, β-, γ- δ-tocopherols in maize oil. Explanations as in Figure 41

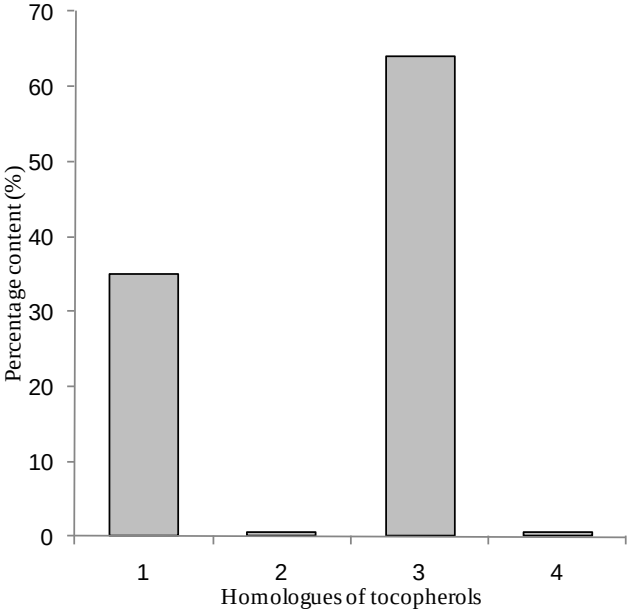


Fig. 44. Percentage content of α-, β-, γ- δ-tocopherols in rapeseed oil. Explanations as in Figure 41

Rich sources of tocotrienols include palm oil, rice bran oil and also latex (sap-like extract from the rubber tree *Hevea brasilensis*); apart from that they can be found in rapeseed oil, soybean oil and in oil from wheat germs (Tab. 43).

Table 43. Content of tocotrienols in selected oils (Ong 1993, Sheppard *et al.*1993, Gogolewski 1995)

Content of tocotrienols (mg kg^{-1})	Kind of oil
386[a]-494[b]	palm oil
379[b]	palm oil, refined
585[b]	rice bran oil
308[b]	rice bran oil, refined
207[*]	oil from wheat germs
3.3[c]	soybean oil

*contains α-, β-tocotrienol, [a]contains α-, β-, γ-, δ-tocotrienol, [b]contains α-, γ-, δ-tocotrienol, [c]contaions α-, β-, γ-tocotrienol.

Tocopherols and tocotrienols occur also in animal fats, about 95% of the tocopherols being accounted for by α-tocopherol (Tab. 44).

Table 44. Content of derivatives of tocopherols and tocotrienols in selected animal fats (Sheppard *et al.* 1993, Drozdowski 2007)

Kind of fat	α-tocopherol (mg kg^{-1})	β-tocopherol (mg kg^{-1})	γ-tocopherol (mg kg^{-1})	δ-tocopherol (mg kg^{-1})	α-tocotrienol (mg kg^{-1})	β-tocotrienol (mg kg^{-1})
cod liver	220	–	–	–	–	–
herring meat	92	–	–	–	–	–
back fat	12	–	7	–	7	–
tallow	27	–	–	–	–	–
butter	10-50	–	–	–	–	–

During the refining of oils there takes place a considerable loss of tocopherols, and their degradation is also affected by such factors as oil deterioration, initial level and kind of tocopherol homologues in the oil, presence of pigments, and also contamination with bivalent cations of metals (Nogala-Kałucka 2005) (Fig. 45-47).

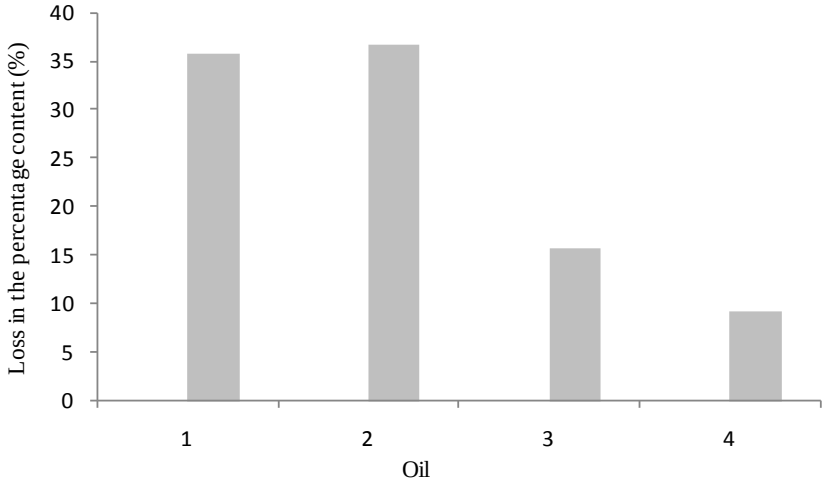


Fig. 45. Loss in the percentage content of α-tocopherol in rapeseed oil at the successive stages of refining (Zadernowski *et al.* 1995). 1 – crude oil, 2 – hydrogenated oil, 3 – neutralised oil, 4 – bleached oil

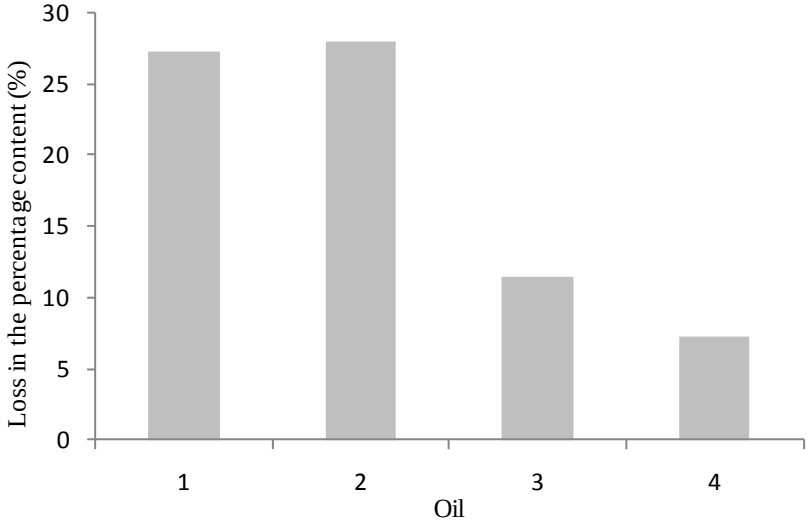


Fig. 46. Loss in the percentage content of γ–tocopherol in rapeseed oil at the sucessive stages of refining (Zadernowski *et al*. 1995). Explanations as in Figure 45.

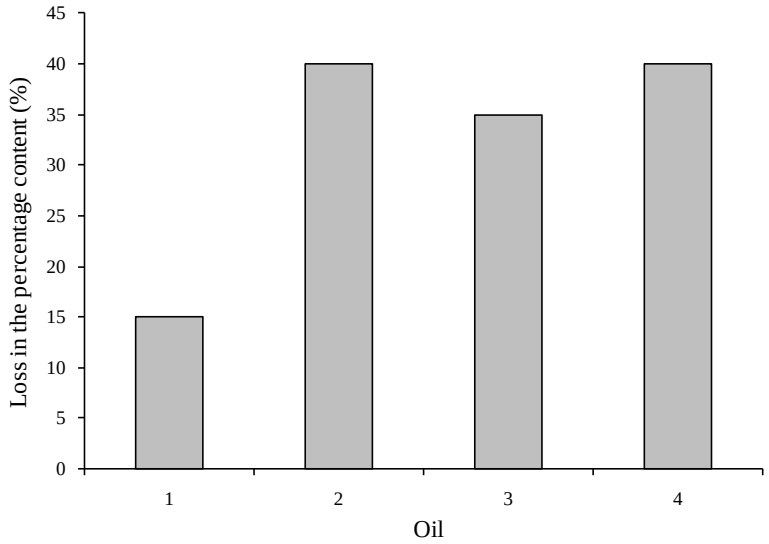


Fig. 47. Percentage losses of the content of tocopherols of selected oils during the process of refining (Nogala-Kałucka 2005). 1 – olive oil, 2 – sunflower oil, 3 – soybean oil, 4 – rapeseed oil

5.4. Polyphenols

Polyphenols comprise a broad range of compounds classified as secondary metabolites formed through metabolic transformations of the primary metabolites: L-phenylalanine or L-tyrosine. Simple phenols and quinones are synthesised through transformations of acetic acid, while hydroxycinnamic acids and coumarins are formed on the shikimic acid pathway. The effect of the combination of both transformations is the formation of flavonoids (Mitek and Gasik 2007). In terms of their chemical structure, the term polyphenols is applied to compounds that contain in their molecule a benzene ring with hydroxyl groups, though there are substances that do not have that characteristic structural element and yet are classified among polyphenols, e.g. cinammic acid, quinic acid (Mitek and Gasik 2007). Those compounds have been classified on the basis of the number of carbon atoms building the skeleton of the molecule (Tab. 45).

Table 45. Classification of polyphenols (Robards *et al.* 1999, Miller and Ruiz-Larrea 2002 cit. after Mitek and Gasik 2007, Prescha and Biernat 2008)

Number of carbon atoms	Class	Example of compound	Occurrence
C_6	simple phenols benzoquinones	catechol, resorcinol, hydroquinone	
C_6-C_1	phenolic acid hydroxybenzoic acids	salicylic acid	aniseed, marjoram
		vanillic acid	vanilla,
		gallic acid	olive oil
		protocatechuic acid	blackcurrant
		p-hydroxybenzoic acid	raspberry, gooseberry
C_6-C_2	phenylacetic acids	*p*-hydroxyphenylacetic acid	
C_6-C_3	hydroxycinnamic acids	*o*-coumaric acid	cherry, plum
		p-coumaric acid	apple, cranberry, sugar beet, olives, cereal grain
		ferulic acid	citrus fruits, nuts, cereal grain, coffee
		sinapinic acid	rape seeds
		caffeic acid	coffee, apples, grapes, tomato, cabbage, potato
		chlorogenic acid	apple, pear, coffee
	phenylpropenes	eugenol, myristicin	
	coumarins	umbelliferone, scopoletin	
	chromones	eugenin	
C_6-C_4	naphthoquinones	juglone	wallnuts
C_6-C_1-C_6	xanthones	mangostins, mangiferin	mango
C_6-C_2-C_6	stilbenes	resveratrol	grapes
	anthraquinones	emodin	

Number of carbon	Class	Example of compound	Occurrence
C_6-C_3-C_6	flavonoids flavones	sinensetin, rutin nobiletin, luteolin diosmin, chrysin	citrus fruits, olives, celery, parsley
	flavonols and their glycosides	quercetin, kaempferol	inions, blueberries, tea
	flavanonols	dihydroquercetin, dihydrokaempferol and their glycosides	grapes
	flavanones	hesperetin, naringenin	citrus fruits, grapes
	flavanone glycosides	hesperidin, neohesperidin, narirutin, naringin	citrus fruits, strawberry
	anthocyanins	cyanidin, delphinidin, malvidin, pelargonidin, peonidin, petunidin and their glycosides and ary-lated derivatives	grapes, raspberry, pear, cranberry, strawberry, currants, cherries, plums, peaches, oranges, apples,
	flavanols – flavan-3-ols (catechins)	catechin,(-) epigallocatechin, (-)epicatechin, and their derivatives, e.g. epicatechin gallate, epigallocatechin gallate	red wine
	chalcones	phloretin, glycosides, e.g. -phloretin-2-O-glucoside (phlorizin)	apples, tomatoes, pears
$(C_6$-$C_3)_2$	lignins lignans	pinoresinol secoisolarciresinol matairesinol sesamin	linseed, sesame seeds, sunflower seeds, olive, nuts
$(C_6$-C_3-$C_6)_2$	biflavonoids	agatisflavone amentoflavone	

Phenolic acids are derivatives of the benzoic acid and cinnamic acid, whose structure is presented on Figues 48 and 49. Dependent on kind of substituent one can get various phenolic acids (Tab. 46-47). Phenolic acids occur in nature mainly in bound forms, being included in the composition of lignins and tannins, or as esters and glycosides (Wilska-Jeszka 2007).

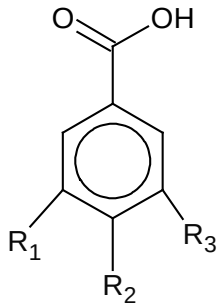


Fig. 48. Chemical structure of benzoic acid molecule

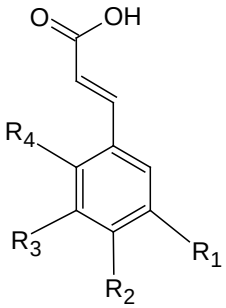


Fig. 49. Chemical structure of cinnamic acid molecule

Table 46. Benzoic acid derivatives (Robards *et al*. 1999)

Benzoic acid derivatives	R_1	R_2	R_3
p-hydroxybenzoic acid	–H	–OH	–H
Protocatechuic acid	–H	–OH	–OH
Gallic acid	–OH	–OH	–OH
Vanillic acid	–H	–OH	$–OCH_3$

Table 47. Cinnamic acid derivatives (Robards *at al*. 1999)

Cinnamic acid derivatives	R_1	R_2	R_3	R_4
Hydroxycinnamic acid	–	–	–OH	–
Ferulic acid	–H	–H	–OH	$–OCH_3$
Caffeic acid	–H	–H	–OH	–OH
Sinapinic acid	–H	$–OCH_3$	–OH	$–OCH_3$
o-coumaric acid	–OH	–H	–H	–H
p-coumaric acid	–H	–H	–OH	–H

Another highly important group of polyhenolic compounds are flavonoids, most frequently occurring in forms bound with saccharides as glycosides (Fig. 50).

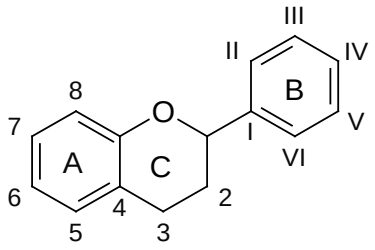


Fig. 50. Chemical structure of flavonoid molecule. A – benzene ring, B – phenyl ring, C – pyran ring

The division of flavonoids into specific classes depends on the degree of unsaturation and oxidation of the particular rings composing the molecule (Robards *et al*. 1999), and of C-ring in particular (Wilska-Jeszka 2007). Figures 51-56 present general structure of chosen flavonoids.

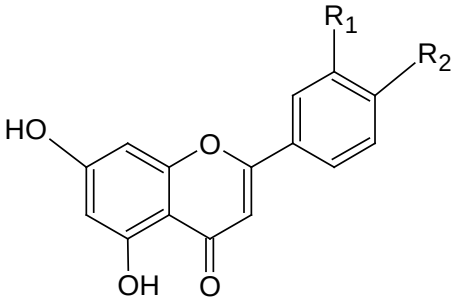


Fig. 51. Chemical structure of flavonone molecule

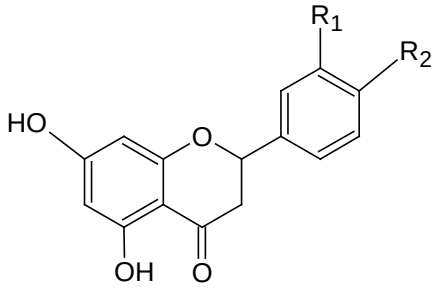


Fig. 52. Chemical structure of flavanone molecule

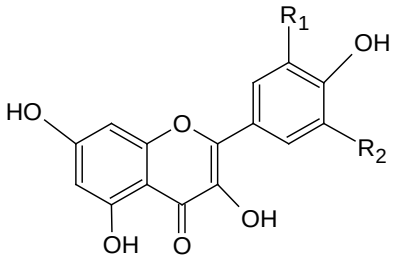


Fig. 53. Chemical structure of flavonol molecule

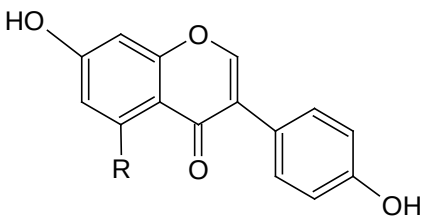


Fig. 54. Chemical structure of isoflavone molecule

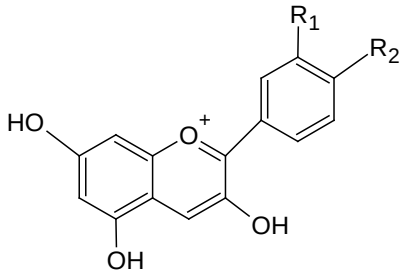


Fig. 55. Chemical structure of anthocyan molecule

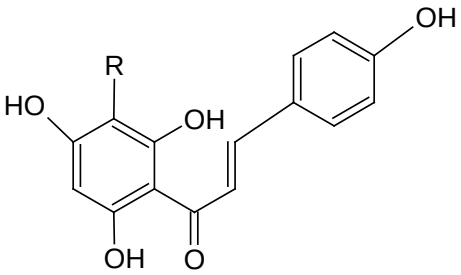
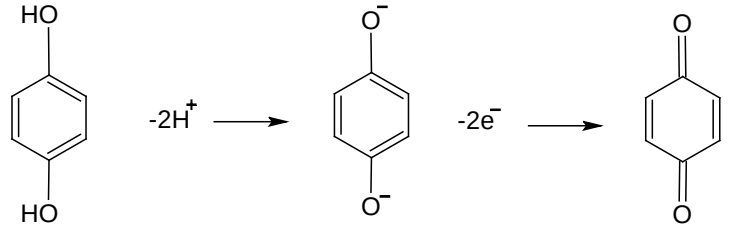


Fig. 56. Chemical structure of chalcone molecule

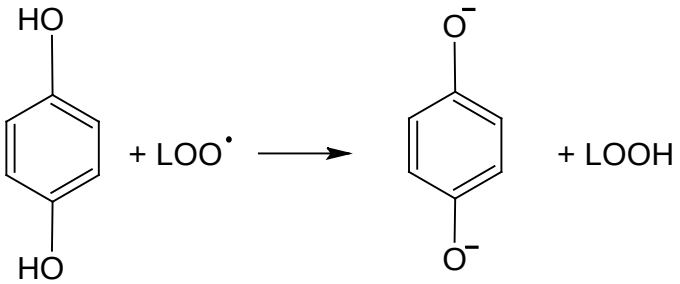
Due to the presence of hydroxyl groups, polyphenols can be proton donors. They oxidise forming a stable phenoxyl radical. That radical can undergo the process of further oxidation, producing quinone.

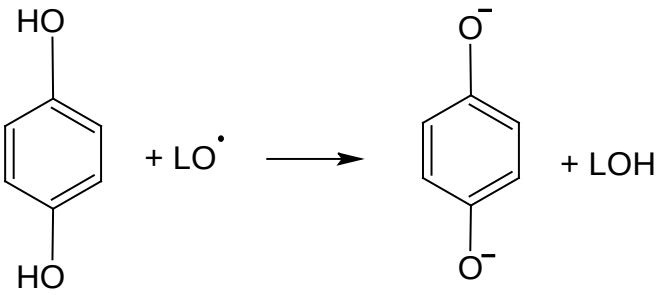


The oxidation of phenols is catalysed by cations of heavy metals (Cu^{2+}) and by enzymes from the group of oxidases (catecholase, laccase). That process leads to the formation of brown polymeric compounds, which can be easily observed e.g. on damaged fruits. The enzymatic oxidation of polyphenols can be inhibited by lowering the pH of the environment (Wilska-Jeszka 2007).

Polyphenols are compounds with a strong antioxidant activity as they:

- can interrupt the chain reactions of oxidation of lipids by reacting with lipid oxides or peroxides, stopping the phase of prolongation,





- are active quenchers of singlet oxygen: constant rates of reaction of polyphenols with $^1O_2$ are 10^6-10^8 M^{-1} s^{-1} (Beutner *et al*. 2001),
- dihydroxypolyphenols having hydroxyl groups at position ortho have the capacity of chelating copper ions Cu^{2+} (Rice-Evans *et al.* 1996),
- can act as inhibitors of oxidases, enzymes reducing oxygen to the peroxide anion radical or to hydrogen peroxide:

$$O_2 + e^- \rightarrow O_2^{\bullet -}$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$

- react with oxidants: nitrogen peroxide $ONOO^-$, hydroxyl radical $^{\bullet}OH$ (Gawlik-Dziki 2004), H_2O_2,
- regenerate, through reduction, the α-tocopheroxyl radical to α-tocopherol (Rice-Evans *et al.* 1995).

The antioxidative abilities of polyphenols are related with their molecular structure. The antioxidant properties of monohydroxyl polyphenols increase with the appearance of additional methoxyl groups in the ring:

coumaric acid < ferulic acid < sinapinic acid.

The antioxidant power and stability of phenolic acids is higher when at the ortho position there are substituents that are electron donors (methoxyl, alkyl) (Tab. 48).

The antioxidant activity of hydroxybenzoic and hydroxycinnamic acids (TEAC- Trolox Equivalent Antioxidant Capacity) is presented in the Table 49 below. (TEAC value is the number of millimoles of Trolox equivalent to the antioxidant activity of 1 millimole of the substance studied).

The dominant polyphenols in rapeseed oil are the following compounds: phenolic acids, coumarins, flavonoids, tannins and lignins (Sosulski 1979). Deriva-

tives of hydroxybenzoic and hydroxycinnamic acids occur in the form of free phenolic acids or as insoluble esters. The basic phenols in rapeseed are sinapinic acid, at the level of 0.5-1%, and a choline ester of sinapinic acid – sinapine, at the level of 1.35%-4% (Shahidi and Naczk 1992).

Table 48. Antioxidant activity of phenolic acids in selected oxidative processes (Gawlik-Dziki 2004)

Kind of oxidative process	Antioxidative activity of phenolic acids
Action of $ONOO^-$ on cells	caffeic≈chlorogenic≈ferulic>p-coumaric>o-coumaric acid
Auto-oxidation of lipids	caffeic>ferulic>p-coumaric acid

Table 49. TEAC values of hydroxybenzoic and hydroxycinnamic acids (Mitek and Gasik 2007)

Acid	TEAC value (mmol)
p-hydroxybenzoic acid	0.84
Vanillic acid	1.43
Protocatechuic acid	1.19
Gallic acid	3
Caffeic acid	1.26
Chlorogenic acid	1.24
p-coumaric acid	2.22
Ferulic acid	1.90
Sinapinic acid	1.62

The content of free phenolic acids of the seeds of rapeseed depends on a number of factors:

- rapeseed cultivar,
- climate and soil conditions,
- soil fertilisation.

The graphs below illustrate the content of selected phenolic acids in the seeds of selected rapeseed cultivars (Siger *et al*. 2004) (Figs. 57-62).

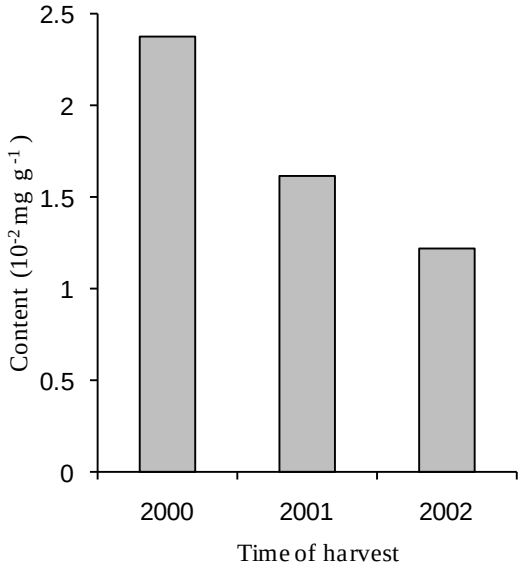


Fig. 57. Content of protocatechuic acid in rape seeds cv. Lisek in relation to time of harvest

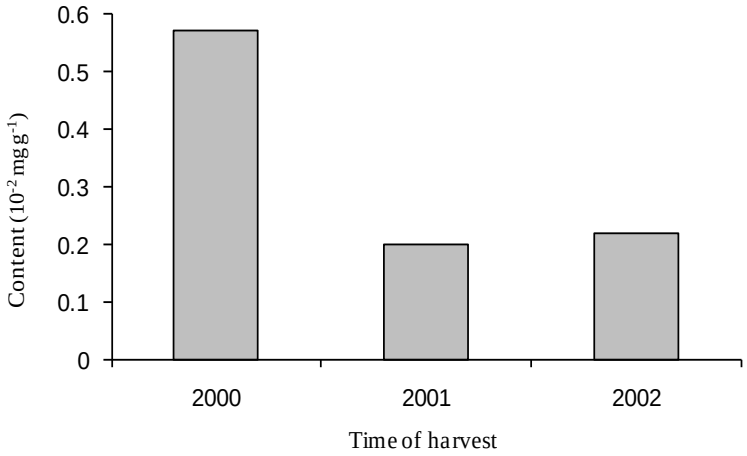


Fig. 58. Content of p-hydroxybenzoic acid in rape seeds cv. Lisek in relation to time of harvest

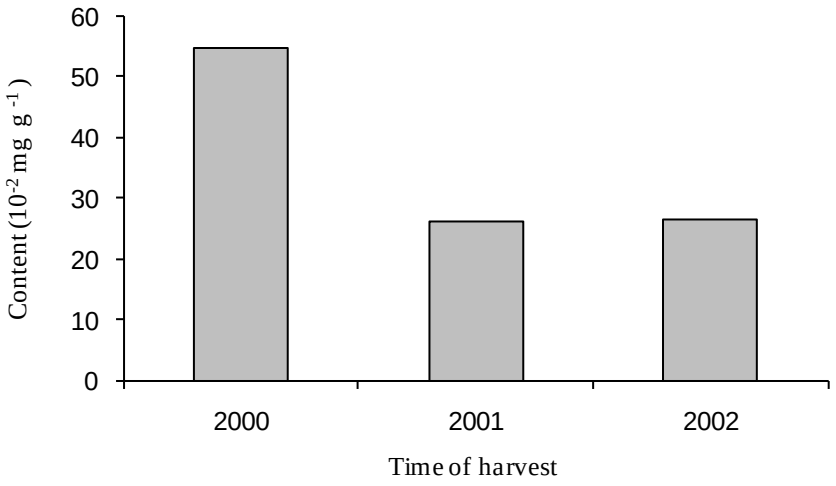


Fig. 59. Content of sinapinic acid in rape seeds cv. Lisek in relation to time of harvest

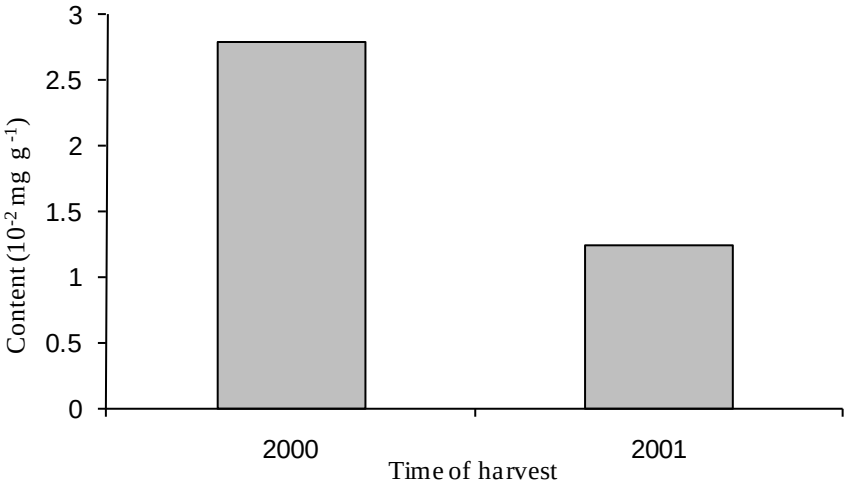


Fig. 60. Content of protocatechuic acid in rape seeds cv. Silvia in relation to time of harvest

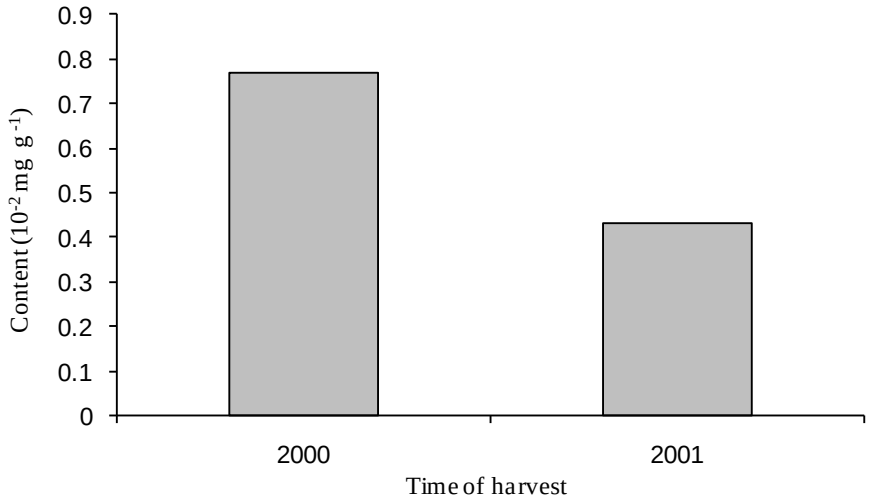


Fig. 61. Content of p-hydroxybenzoic acid in rape seeds cv. Silvia in relation to time of harvest

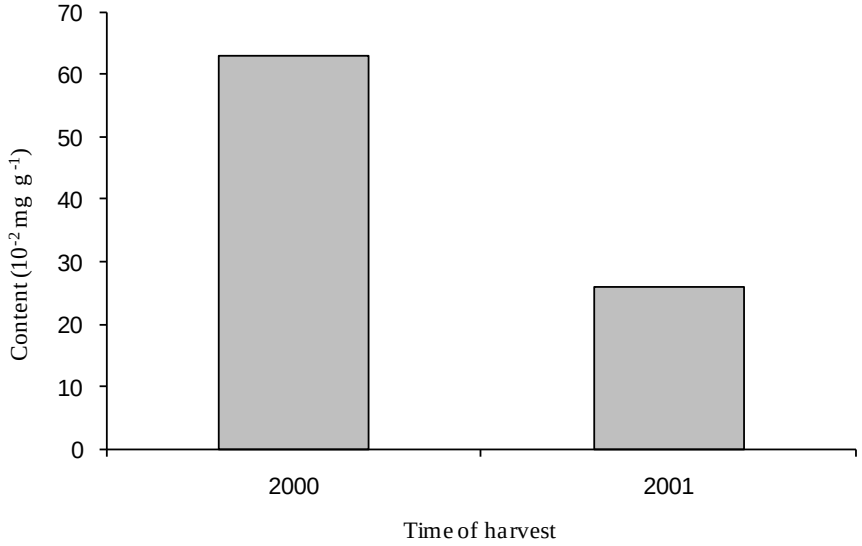


Fig. 62. Content of sinapinic acid in rape seeds cv. Silvia in relation to time of harvest

Polyphenols have a strong effect on the stability of olive oil. A high correlation has been found between the concentration of polyphenols and the stability of oilve oil: r = 0.98 (Baldioli *et al*. 1996). The content of polyphenols in olive oil

depends on such factors as e.g. olive cultivar, soil-climate conditions and the stage of ripeness. Table 50 presents selected polyphenol compounds contained in the olive oil.

Table 50. Content of selected polyphenols in oilve oil (own data and Brenes et al. 2000)

Polypyhenol compound	Content in mg kg^{-1}
Vanillic acid	0.1-0.2
p-coumaric acid	0.1-0.3
Pinoresinol	19-34
Ferulic acid	0.0-2.4
Caffeic acid	0.0-0.1

Linseed oli, sesame seed oil and sunflower seed seed oil contain notable amounts of lignans. Those polyphenols, next to stilbens and isoflavones, are classified as phytoestrogens, compounds with high health-promoting values.

5.5. Sterols

Sterols are alicyclic alcohols from the group of steroids. Steroids comprise a broad range of substances which are derivatives of a system of condensed perhydrocyclopentanophenanthrene rings (Fig. 63).

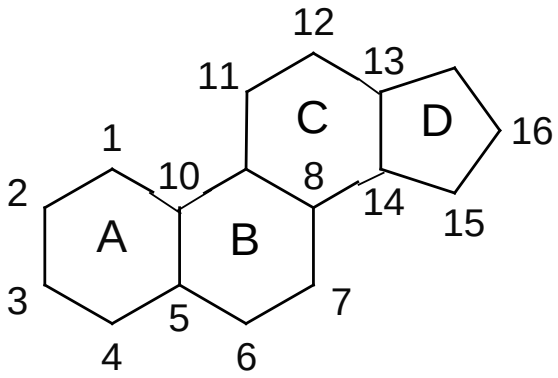


Fig. 63. Chemical structure of steroid molecule

Sterols are highly common in nature. They can be found in all animal and plant organisms. They are hydrophobic compounds, easily fat-soluble, with a high melting point. In nature they occur in free form or as compounds with four types of linkages, where the hydroxyl group at C-3 can be esterified by fatty acids or by phenilic acid. The hydroxyl group can also be attached to glucose or to acyloglucose, forming glycoside sterol or acyloglycoside sterol (Piironen et al. 2000)
In the form of glycosides sterols appear mainly in the seeds of cereals. All sterols are characterised by the presence of the following functional groups:

- hydroxyl group –OH at C-3 in position β,
- side-chain at C-17,
- methyl groups – CH_3 at C-10 and C-13 in configuration β.

Though there are exceptions to the rule, the positioning of rings B and C as well as C and D relative to each other occurs in configuration *trans* while rings A and B can be conjugated in confiduration *cis* or *trans*. The number of carbons in the molecule varies from 27 to 29. The molecular structure of a sterol determines its properties, and differences among sterols concern mainly:

- the degree of B-chain saturation,
- the presence of double bonds in the side-chain,
- the presence of additional bifurcations in the side-chain at C-24 (Lagarda *et al*. 2006, Drozdowski 2007).

5.5.1. Cholesterol

The most important animal sterol (also occurring in small amounts in plant organisms), and the best described so far, is cholesterol (Fig. 64).

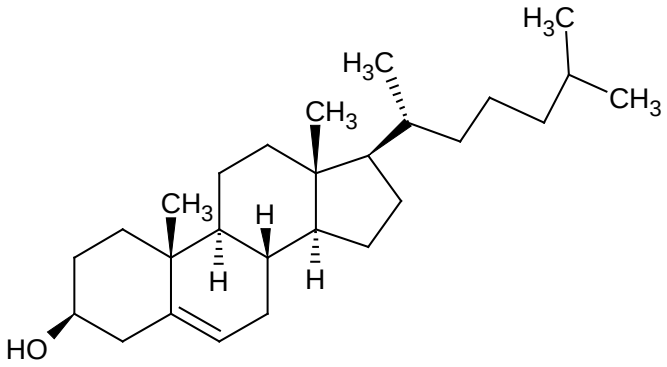


Fig. 64. Chemical structure of cholesterol molecule

The oxygen atom in the hydroxyl group of cholesterol comes from atmospheric oxygen. The largest amounts of cholesterol are found in cell membranes. Cholesterol is the isitial compound for the synthesis of steroid hormones, including progesterone and testosterone, and is also important for the permeability of cell membranes (Russel 1992, Stryer 1997). Other sterols occurring in animal organisms are dihydrocholesterol, coprosterol, and 7-dehydrocholesterol which is the provitamin for vitamin D (Fig. 65).

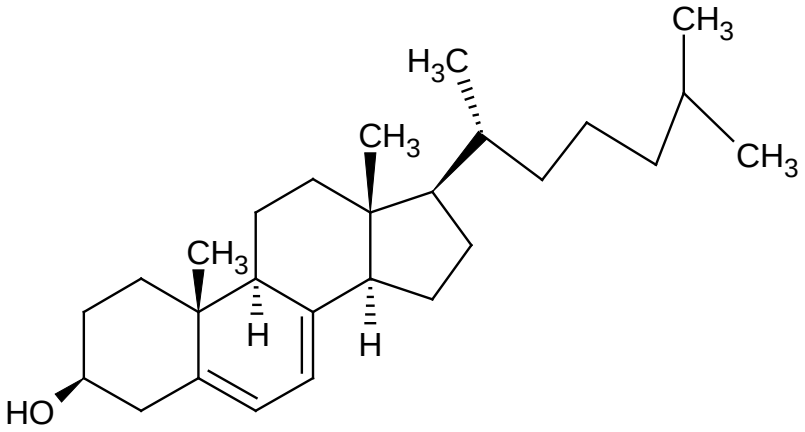


Fig. 65. Chemical structure of 7-dehydrocholesterol molecule

Vitamin D is characterised by antirachitic effect, regulates the calcium-phosphate metabolism, and participates in the formation of the bones. Deficit of that vitamin causes rickets in children and in adults it is manifested by osteomalacia and osteoporosis and also by weakening of the bone structure (Drozdowski 2007).

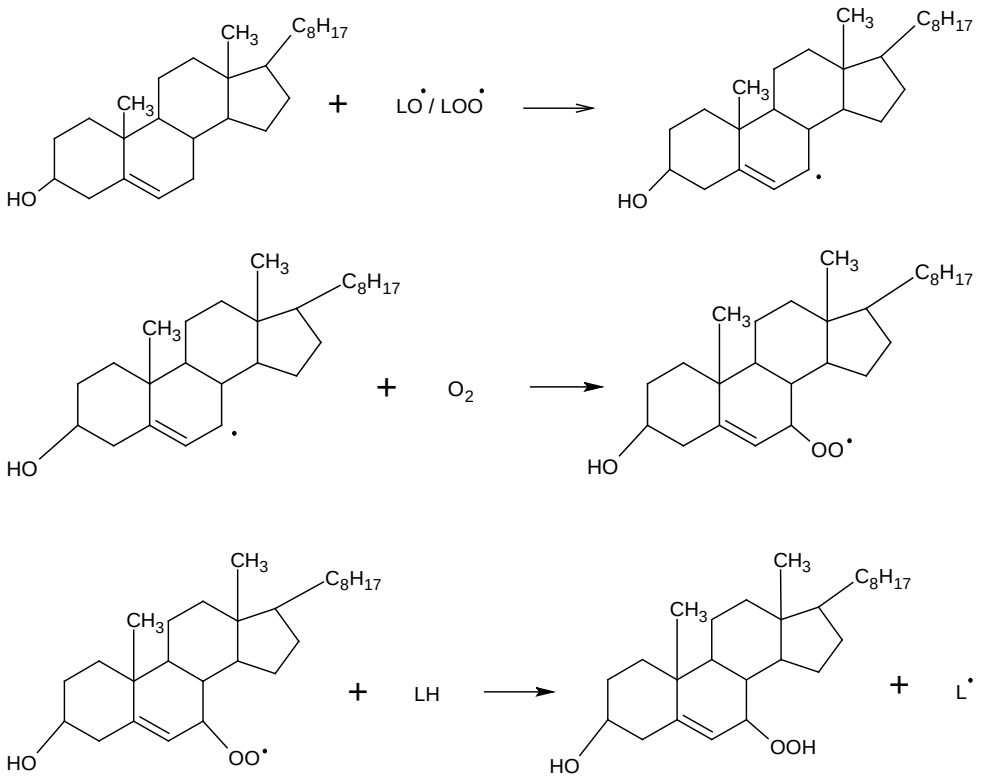
Cholesterol is synthesised in the liver and in the bowel, and can also be supplied with food (Tab.51) In the blood serum cholesterol is transported in the form of lipoproteins: LDL (Low Density Lipoproteins) and HDL (High Density Lipoproteins). Thanks to LDL cholesterol is transported to peripheral tissues where it participates in the synthesis of cell membranes and suitable hormones. Elevated levels of LDL cholesterol in the blood leads to the formation of cholesterol deposits in the arteries and, in consequence, to the development of atherosclerosis. HDL, on the other hand, have the ability to absorb excess cholesterol and to transport it back to the liver. Ultimately, cholesterol is excreted in the form of bile

acids (Stryer 1997, Cuchel and Rader 2006, Krzymański *et al*. 2009). The concentration of the LDL fraction of cholesterol in the blood serum should not exceed 3 mmol dm^{-3} and that of cholesterol of the HDL fraction should be at least about 1.2 mmol dm^{-3}, and the concentration of total cholesterol should not exceed the level of 5 mmol dm^{-3} (Krzymański *et al*. 2009).

Cholesterol undergoes oxidative transformations of radical character under the effect of atmospheric oxygen, free radicals, and also under the effect of high temperature and metals (Chang *et al*. 1996). More than 100 different oxysterols have been identifed, being oxidised derivatives of cholesterol (Rudzińska *et al*. 2001). Oxysterols, occurring in meat, eggs, milk, and their products, have a negative effect on human health as they display mutagenic, carcinogenic and cystotoxic effects (Baggio and Bragagnolo 2006, Sikorski 2007). The primary products of cholesterol oxidation are cholesterol 7α- and 7β-hydroperoxides (Chang *et al*. 1996, Drozdowski 2007).

Table 51. Cholesterol content in selected food products (Drozdowski 2007, Krzymański *et al*. 2009)

Food product	Cholesterol content (10^{-2} mg g^{-1})
Poultry meat	50-70
Smoked meats, cheese	60-90
Backfat, lard	90-100
Butter	220
Egg yolk	1790
Calve's brains	2500
Yoghurt	6
Milk, 2%	8
Tuna fish	55
Pork meat	89
Milk, 3.2%	13
Cream, 12%	39
Vegetable oils	0



In food products eight oxidised cholesterol derivatives are most frequently identified (Larkeson *et al.* 2000) (Fig. 66-71):

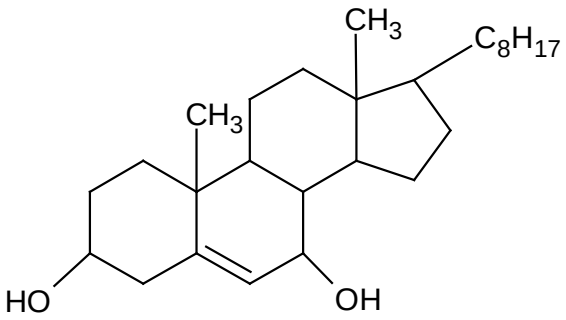


Fig. 66. Chemical structure of 7β-hydroxycholesterol molecule

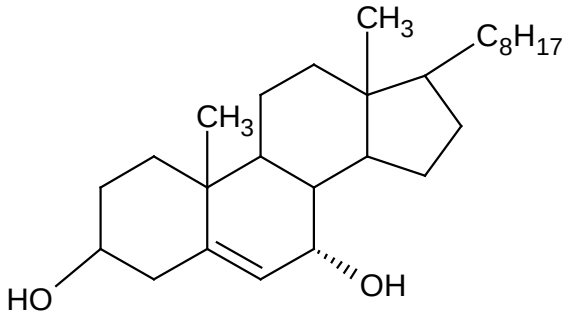


Fig. 67. Chemical structure of 7α-hydroxycholesterol molecule

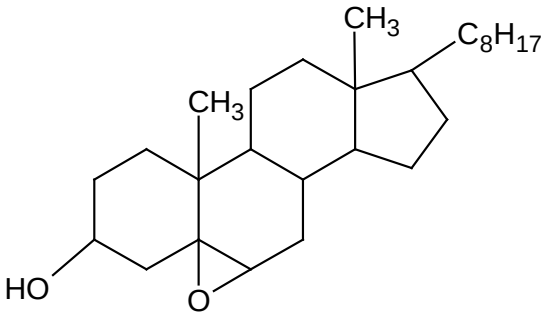


Fig. 68. Chemical structure of β-epoxycholesterol molecule

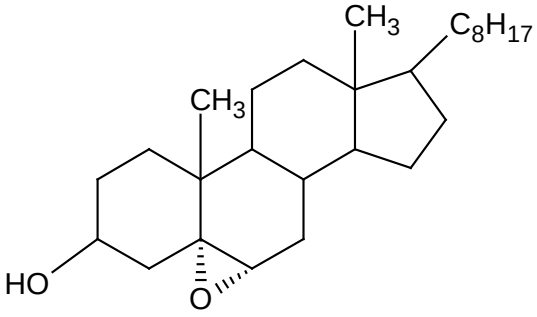


Fig. 69. Chemical structure of α-epoxycholesterol molecule

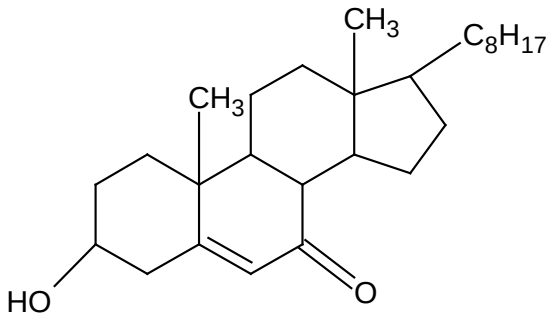


Fig. 70. Chemical structure of 7-ketocholesterol molecule

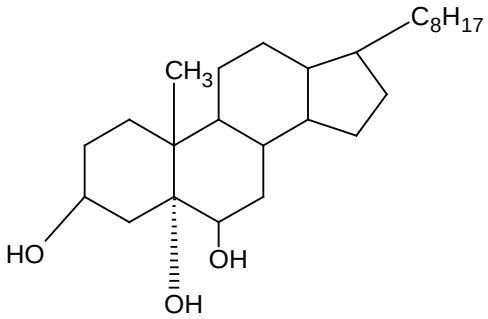


Fig. 71. Chemical structure of 3β, 5α, 6β trihydroxycholesterol mlecule

The remaining two oxysterols: 25-hydroxycholesterol and 20α-hydroxycholesterol are formed through transformations in the side-chain of cholesterol.

5.5.2. Phytosterols

Plant sterols, otherwise referred to as phytosterols, constitute an important element of plant tissues. They play an important role in the structure and functioning of cells, regululating the permeability of phospholipid membranes, just as cholesterol does in cells of animal tissues (Moreau *et al*. 2002). The sterols are also substrates for a large group of secondary metabolites, e.g. cardenolides. Phytosterols include such cmpounds as β-sitosterol, stigmasterol, campesterol, avenasterol and, characteristic for rapeseed oil – brassicasterol. Not all sterols are equally effective in enhancing the permeability of plant cell membranes. Sitosterol and campesterol are more effective, as opposed to stigmasterol which dis-

plays a reducing effect. Phytosterols participate also in the differentiation of cells (Piironen *et al*. 2000).

Plant sterols consumed with food lower the level of total cholesterol by 0.5-26%, and of the LDL fraction of cholesterol by 2-33% (Jones *et al*. 2000). The structure of a phytosterol molecule is analogous to that of cholesterol structure, with phytosterols containing a methyl group $–CH_3$ (campesterol, brassicasterol) or an ethyl group $–C_2H_5$ (stigmasterol, phytosterol) at C-24 in the side- chain (Piironen *et al*. 2000) (Fig.72) (Tab. 52).

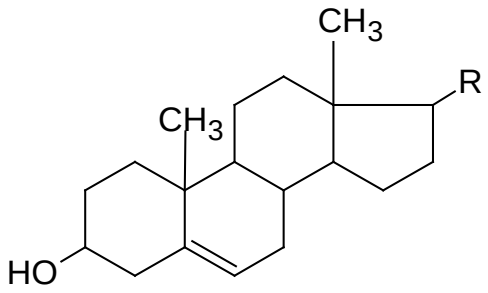


Fig. 72. Chemical structure of phytosterol molecule

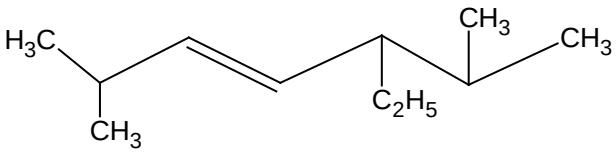
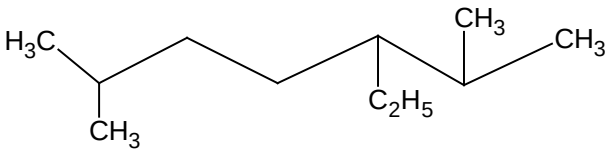
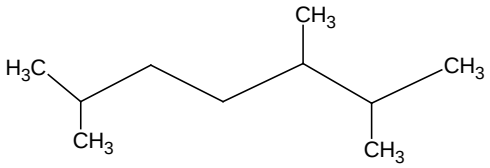
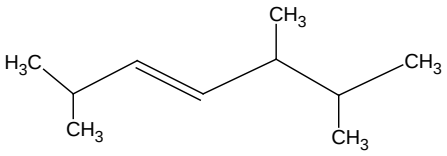
Oxidised derivatives of phytosterol display similarities in their structure and properties to the oxidised derivatives of cholesterol (Johnsson, Dutta 2003). Oxidised derivatives of phytosterols identified in vegetable oils include 7α-, 7β-hydroxy-, α and β-epoxy- and triols. The analogy in the structure of oxysterols and oxyphytosterols suggests toxic properties of the latter (Grandgirard *et al*. 1999).

Phytosterols are found in seeds of cereal plants, oil-bearing plants, in vegetable oils and in nuts. Richest in those compounds are seeds of rapeseed, maize and cotton, 100 g of those seeds containing 824 mg, 924 mg and 459 mg of phytosterols, respectively (Verleyen *et al*. 2002).

The content of phytosterols is characteristic for particular cultivars and their concentration depends on the stage of oil production, but always the dominant plant sterol is sitosterol.

The content of the particular phytosterols in selected food products is presented in the Table 53 below on the basis of data given in the works of several authors (Rudzińska *et al*. 2001, Verleyen *et al*. 2002, Rudzińska *et al*. 2003, Rudzińska *et al*. 2005, Mińkowski 2008)

Table 52. Structure of side chains of phytosterols

Phytosterol	Structure of side-chain R
stigmasterol	
sitosterol	
campesterol	
brassicasterol	

There is a scarcity of studies on the content of oxidised derivatives of phytosterols, which is related with the lack of suitable standards of oxyphytosterols, diversity of those compounds, and their low levels in food products, e.g. 7α-OH-stigmasterol is the only derivative of stigmasterol in refined rapeseed oil, one gram of the oil containing 0.33 µg of 7α-OH-stigmasterol (Rudzińska *et al*. 2001). The graphs below have been prepared based on data from the work by Rudzińska *et al*., 2001 (Fig.73-74).

Table 53. Content of phytosterols in selected food products (Rudzińska *et al*. 2001, Verleyen *et al.* 2002, Rudzińska *et al.* 2003, Rudzińska *et al*. 2005, Mińkowski 2008)

Food product	Content of phytosterols (10^{-2}mg g^{-1})				
	brassica-sterol	campe-sterol	stigma-sterol	β-sito-sterol	aveno-sterol
linseed oil*	–	75	15	169	52
rapeseed oll*	104	252	6	382	25
sunflower oil *	–	44	24	237	20
rapeseed oilr	98	245	–	352	30
olive oilr	–	7	3	144	31
rape seeds cv. Lisek	72	161	4	300	15
rape seeds cv. Kaszub	71	209	5	286	17
margarines	66	218	19	359	14
pea nuts	–	84	39	281	63
soybean oilr	–	60,4	47	164	12
cotton seed oilr	–	32	4	357	15
camelina seed oil	27	114.1	0.0	311.2	54.7
linseed oil	4.1	132.4	27.3	238	69.5
borage seed oil	0.3	83.2	7.5	131	75.1
blackcurrant seed oil	0.0	48.9	5.6	463.4	13.1
echium seed oil	0.0	155.1	11.0	161.7	82.8

*cold-expressed, r – rafined.

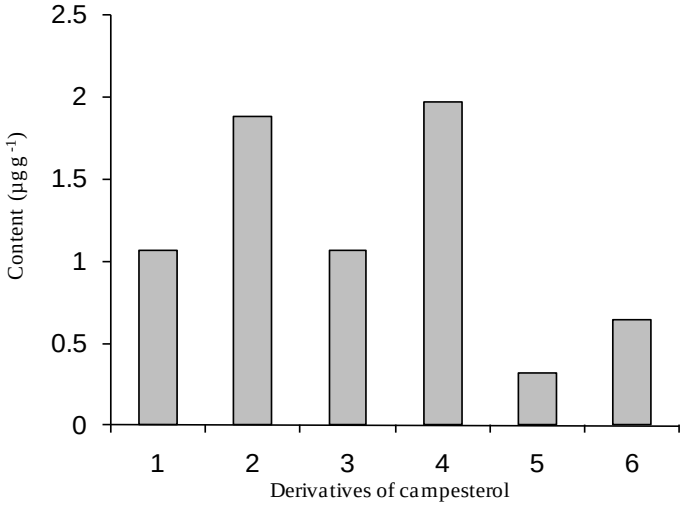


Fig. 73. Content of derivatives of campesterol in refined rapeseed oil. 1-7-keto-campesterol, 2-triol-campesterol, 3-α-epoxy-campesterol, 4-β-epoxy-campesterol, 5-7β-OH-campesterol, 6-7α-OH-campesterol

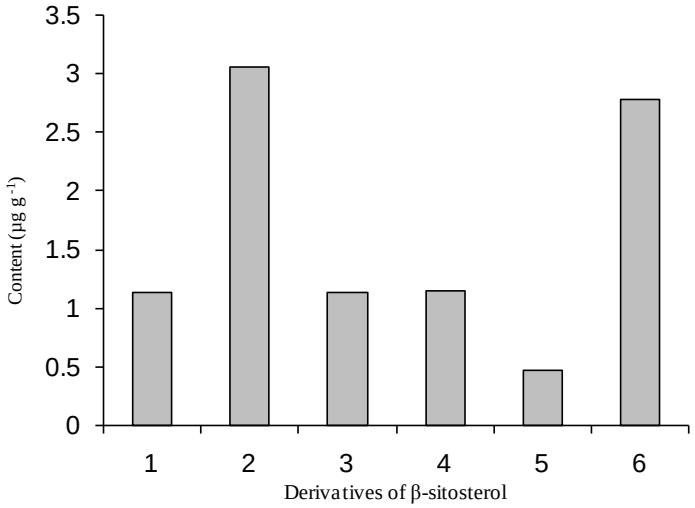


Fig. 74. Content of derivatives of β-sitosterol in refined rapeseed oil. 1-7-keto- β-sitosterol, 2-triol-β-sitosterol, 3-α-epoxy- β-sitosterol, 4-β-epoxy- β-sitosterol, 5-7β-OH-z, 6-7α-OH- β-sitosterol

6. VARIATION IN COMPOSITION AND PROPERTIES OF VEGETABLE OILS IN RELATION TO THE METHODS OF THEIR OBTAINMENT AND STORAGE

Oil from seeds of oil-bearing plants can be obtained in three ways: through hot expression, so-called first-pressing oil, with the press-extraction method, or through cold expression. Each of the methods permits the production of oils that differ from one another in terms of their properties and oxidative stability.

Refined oil is now the dominant product, as the method permits maximum extraction of oil from seeds and is characterised by the highest efficiency. On the industrial scale oil is producted with the method of hot expression and then subjected to extraction and refinement. The process of oil expression takes place in expellers, and the resultant oil – "first pressing oil" – is characterised by a low content of contaminants and therefore the next stage, refinement, can be a less violent process (Krzymański *et al*. 2009). The oil cake produced in the course of preliminary expression, containing ca. 15-20% of fat, is subjected to extraction with solvents: extraction naphtha (class I or II) or technical hexane (Rotkiewicz *et al.* 1999). When the solvent has been distilled out we obtain so-called crude oil which requires two-stage purification:

- lecitin removal (hydration), consisting in the elimination of hydrated lecitin
- refinement.

The process of refinement comprises four stages of purification and is aimed at the elimination of all noxious compounds that might have a negative effect on the stability and on the sensory traits of oil (Tab. 54).

Cold-expressed oil has a number of advantages thanks to which it is gaining a growing number of consumers. The technology of oil extraction from seeds with this method is characterised with low energy inputs, it is ecological and inexpensive. At the same time, the elimination of the stages of solvent extraction and refining causes that the oil is free of chemical additives and contributes to environmental protection – no wastes produced. However, the method of cold expression of oil has also certain drawbacks. First of all it has a low level of efficiency – the oil cake still contains a residue of 6-15% of oil, and the quality of the oil produced depends on a number of parameters in the process of expression.

The expression of oil is conducted by means of expellers or hydraulic presses at temperature not exceeding 40-50^{o}C, which contributes to the obtainment of oil with high sensory quality. The oil obtained is subjected to purification through filtering and decanting. An extremely important element of production is the maintenance of

cleanliness of the presses or expellers, filters and vats, as residues of old oil can have a negative effect on the quality of the product (Wroniak and Krygier 2006).

Table 54. Stages of the process of oil refining (Krzymański *et al*. 2009)

Process of oil refining			
de-gumming	alkali refining	bleaching	deodorising
removal of phspholipids with the acid method using phosphoric or citric acid; permissible content of phosphorus is 10 mg·kg^{-1}	elimination of free fatty acids through reaction with soda lye RCOOH + NaOH → RCOONa + H_2O	elimination of chlorophyll pigments that cause oil oxidation and also such contaminsnts as phospholipids, products of oxidation, metals (Fe, Cu, Ca, Mg), soaps, heavy metals (Pb, Cd, Hg, As), polycyclic aromatic hydrocarbons. In the method strong adsorbents are used – bleaching earth and activated carbon	elimination of free fatty acids, products of oxidation, sulphur compounds and products of pigment transformations

The differences between refined and cold-expressed oils are related to such physicochemical properties as the peroxide number, acid number, anisidine value, iodine value, general colouring, flavour and taste, and also the content of carotenes and chlorophylls and of natural antioxidants: tocopherols, phytosterols and polyphenols (Tab. 55). Cold-expressed oils are also characterised by lower oxidative stability.

Cold-expressed oils are characterised by higher values of acid number and peroxide number, which results from the absence of the stage of refining. The colouring of the oils is darker than that of refined oils due to the presence of chlorophyll and carotene pigments, high level of chlorophylls being correlated with the use of damaged and unripe seeds for processing (Krygier *et al*. 2000, Strobel *et al*. 2005). The ratio of chlorophyll to carotenoid pigments in cold-expressed oils varies, though usually carotenoid pigments predominate (Wroniak *et al*. 2006).

Table 55. Values of AN, PN, AV, IV for refined and cold-expressed rapeseed and sunflower seed oils (Ratusz *et al*. 2005, Wroniak and Łukasik 2007, Rudzińska *et al*. 2001)

Kind of oil	Acid number (mg KOH g^{-1})	Peroxide number (mEq O_2 kg^{-1})	Anisideine value (absorbance 100)	Iodine value (10^{-2} g I_2 g^{-1})
Rapeseed oil, cold- expressed	1.3	5.1	1.4	102.7
Rapeseed oil, refined	0.44	0.4	1.57	136.5
Sunflower oil, cold-expressed	2.6	7.4	1.8	142.3
Sunflower oil, re-fined	0.51	0.35	4.31	143.4

In refined oils the pigments are eliminated in the process of de-colourising and deodorising. The taste and flavour of cold-expressed oil have characteristic vegetable traces that may vary in relation to the species of oil-bearing plant from which the oil is produced. Refined oils of good quality have no taste or smell.
The content of tocopherols in refined oils is lower than the concentration of those compounds in cold-expressed oils (Prior *et al.* 1991) (Fig. 75-77).

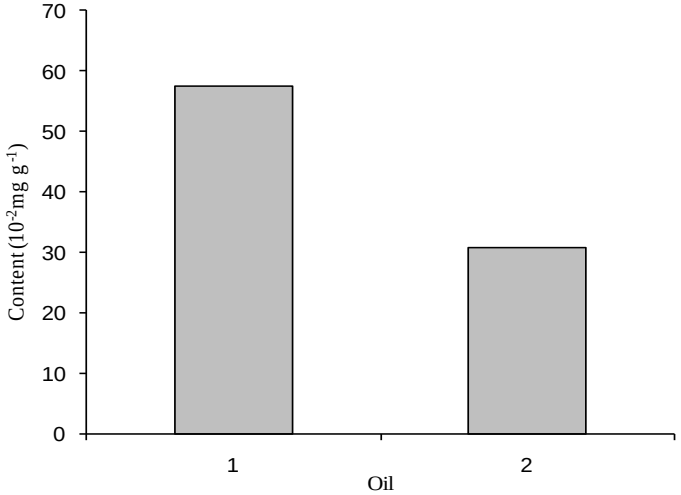


Fig. 75. Total tocopherol content in rapeseed oils produced with different methods. 1 – cold-expressed oil, 2 – refined oil

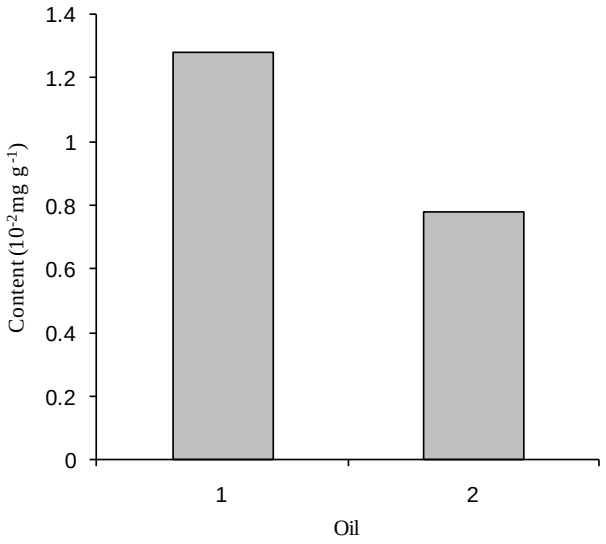


Fig. 76. Content of phenolic compounds in rapeseed oils produced with different methods
Explanations as in Figure 74

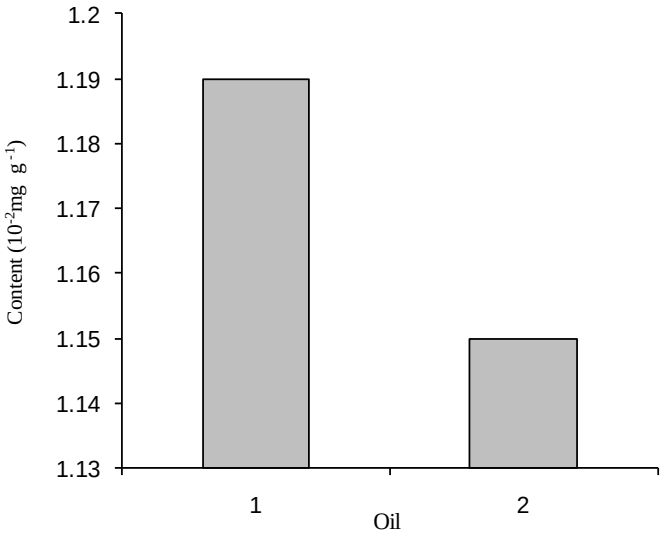


Fig. 77. Content of phenolic compounds in sunflower seed oils producted with different methods
Explanations as in Figure 74

As opposed to refined oils, cold-expressed oils have a notable content of phenolic acids and other polyphenolic compounds; refined sunflower seed and rapeseed oils have no polyphenolic acids in their composition (Singer *et al*. 2005) (Tab. 56).

Table 56. Content of phenolic acids in rapeseed oil (Singer *et al*. 2005)

Phenolic acid (10^{-2} μg g^{-1})	Rapeseed oil	
	refined	cold-expressed
p-hydroxybenzoic acid	–	1.62
vanillic acid	–	–
caffeic acid	–	0.3
p-coumaric acid	0.28	13.15
ferulic acid	–	5.61
sinapinic acid	5.60	236.1

The content of phytosterols in refined oils and cold-expressed oils is comparable. Total sterols content in refined rapeseed oil is 7.69 (mg g^{-1}) and in cold-expressed oil 7.25 (mg g^{-1}) (Rudzińska *et al*. 2001).
Whereas, notable differences are observed in the content of oxidised derivatives of phytosterols that in refined oils is about 2.5-fold higher than in cold-expressed oils (Rudzińska *et al*. 2001) (Tab. 57-59).

The properties of cold-expressed oils and refined oils are the result of the technology of their production. Refined oils are more stable than cold-expressed oils due to the elimination, in the process of refining, of pigments and the products of peroxidation of lipids that may augment the oxidation of the oil. Cold-expressed oils, however, have a higher nutritional value as they contain valuable antioxidants and provitamins: carotenoids, tocopherols, polyphenols. Oils produced exclusively with the method of expression are characterised by low levels of oxyphytosterols, carcinogenic and mutagenic compounds, and also by a lack of trans isomers of fatty acids.

Table 57. Content of campesterol derivatives in selected oils (Rudzińska *et al.* 2001)

Kind of oil	Sum of campesterol derivatives (μg g^{-1})	
	refined oil	cold-expressed oil
Maize oil	8.76	2.31
Rapeseed oil	6.96	1.75
Sunflower seed oil	22.09	5.65
Soybean oil	5.55	5.27

Table 58. Content of stigmasterol derivatives in selected oils (Rudzińska *et al*. 2001)

Kind of oil	Sum of stigmasterol derivatives (μg g^{-1})	
	refined oil	cold-expressed oil
Maize oil	6.06	1.38
Eapeseed oil	6.96	-
Sunflower seed oil	9.16	4.70
Soybean oil	2.66	2.48

Table 59. Content of β-sitosterol derivatives in selected oils (Rudzińska et al. 2001)

Kind of oil	Sum of β-sitosterol derivatives (μg g^{-1})	
	refined oil	cold-expressed oil
Maize oil	23.12	4.84
Rapeseed oil	9.74	6.07
Sunflower seed oil	17.51	12.83
Soybean oil	29.36	13.31

7. HEALTH PROPERTIES OF ANIMAL FATS

Animal fats are the primary source of saturated fatty acids (SFA) (Tab. 60). The highest levels of those acids are found in pork fat: backfat and lard, and also in meat and in milk products. In turn, the fat and meat of fish abound in polyunsaturated fatty acids (PUFA)

Table 60. Percentage content of fat in selected products (Kołżyn-Krajewska and Sikora 2007, Ziemlański and Socha 1999)

Product	Percentage content of fat (%)
Meat, depending on kind	3-55
Fish meat, depending on kind	0.1-13
Whole milk	3.2
Cottage cheese	1-9
Ripening cheese	17-30
Backfat	83-95.5
Lard	99.3-99.6
Premium butter	82

Apart from saturated faty acids, milk fat contains also certain health-promoting components which cause that milk and its products are an important component of human diet. Moreover, cow's milk has a sterospecific structure, i.e. distribution of fatty acids in triacylglycerols, that is very similar to that of human milk, due to which it is well assimilable by the child organism and permits the maintenance of proper levels of calcium (Cichon and Stołyhwo 1999) (Tab.61).

CLA is synthesised in the gastrointestinal tract of ruminants and it is found, apart from milk and its products, in beef, lamb and veal meat. CLA displays multidirectional beneficial effects in the organism: thanks to its antioxidative properties it prevents atherosclerotic and carcinogenic processes (Stachowska *et al.* 2002) and also lowers the content of fat in the body mass (Bartnikowska *et al.* 1999). Congjugated linoleic acid lowers the level of triglycerides in the blood serum, the level of total cholesterol and of the LDL fraction (Pariza *et al*. 2000). Research conducted on animals demonstrated the effectiveness of CLA in inhibition of the development of cancers of the skin, the large intestine, mammary can-

cers and gastric carcinoma. The tumors that do appear are characterised by smaller dimensions and their metastasis is limited or completely stopped. The anticarcinogenic effect of CLA is optimum at its content in the diet at the level of ca. 1% (Jelińska 2005). CLA administered to animals enhances their resistance to toxins, including *E. coli* (Migdał et al. 2002).

Table 61. Effect of selected components of milk fat on the human health (Stołyhywo and Rutkowska 2007, Russo *et al.* 1999, Ip *et al.* 1996, Ip *et al*. 2003)

Milk fat component	Effect on human health
butyric acid $C_{4:0}$	anticarcinogenic, through inhibition of the synthesis of DNA neoplastic cell nuclei
rumenic acid, CLA $C_{18:2}$ (9c, 11t) and its isomers	antiatherosclerotic, bacteriostatic, and anticarcinogenic
short- and medium-chain fatty acids $C_{6:0} – C_{14:0}$	antomycotic and antibacterial, source of energy used in metabolism and to maintain constant body temperature
α-tocopherol	vitamin E, antioxidant
squalene	precursor of cholesterol
caretonoids	vitamin A
cholesterol	regulates the permeabiliy of lipid membranes of cells, precursor of hormones, e.g. progesterone, oestrone, testosterone, cortisol

Fish meat and oil are also sources of valuable fat whose composition includes the following fatty acids:

- arachidic acid (AA) (C 20:4 n-6),
- eicosapentaenoic acid (EPA) (C 20:5 n-3),
- docosahexaenoic acid (DHA) (C 22:6 n-3).

EPA and DHA are found in algae and phytoplankton, and indirectly in the meat and oil of such sea fish as mackerel, herring or cod (Bartach *et al.* 1999). Acids AA, EPA and DHA are in the group of eicosanoic acids. They play an im-

portant role in the organism: they are the structural material of cell membranes, lower the level of triglycerides in the blood, are present at high concentrations in the nerve tissue and in the retina (Karłowicz-Bodalska and Bodalski 2007), and also they are the initial substances in the process of synthesis of eicosanoids, i.e. tissue hormones. The substances, among which we include prostaglandins, prostacyclins, thromboxanes, leukotrienes and lipoxins, belong to the group of lipid mediators.

Eicosanoids derived from AA are characterised by high biological activity compared to eicosanoids derived from EPA, and at low concentrations display anti-inflammatory and anti-atherosclerotic effects, and cause relaxation of smooth muscles of blood vessels (vasodilation) (Karłowicz-Bodalska and Bodalski 2007). However, at high concentrations eicosanoids derived from AA amplify anaphylactic reactions, intensify atherosclerotic changes, and have pro-inflamatory and thrombotic effects. They also have a positive effect on the development of neoplastic cells and tissues.

Eicosanoids derived from EPA have similar, though notably weaker, effects on the human organism (James *et al*. 2000) (Tab.62).

An example of fish oil with a broad range of applications in pharmacology is cod liver oil, obtained from the liver of Atlantic cod (*Gadus morhua*) and of other fish from the family Gadidae. Cod liver oil, apart from long-chain polyunsaturated fatty acids, contains also vitamins A and D. The oil displays anti-inflammatory, anti-atherosclerotic and immunotropic effects. Administered to patients with strong and moderate muscular pains it causes a lowering of the intensity of the pain. The anti-inflammatory effect of cod liver oil has been tested in the treatment of nonspecific intestinal inflammations and its high effectiveness has been demonstrated in the treatment of the Leśniowski-Crohn disease (Karłowicz-Bodalska and Bodalski 2007). Acids from the family ω-3 contained in cod liver oil also cause the lowering of the level of triglycerides in the blood: daily consumption of over 4 mg of ω-3 acids can reduce the level of triglycerides by 25-40% (Dudzisz-Śledź *et al*. 2006). Fish oil supplementation for infants born on time revealed the leading role of DHA in the development of the organ of vision, while deficit of AA in premature infants has a retarding effect on their growth and psychomotor development (Karłowicz-Bodalska and Bodalski 2007). Human milk contains EPH and DHA in amounts from 0.05% to 1.9%, and therefore scientists recommend that artificial preparations for infant feeding should also contain acids from the ω-3 family (Dudzisz-Śledź *et al*. 2006).

Table 62. Biological functions of selected eicosanoids (James *et al.* 2000, Jelińska 2005)

Biological functions of selected eicosanoids	
derivatives of EPA	derivatives of AA
PGE_3 – pro-inflammatory effect, synthesised at very low efficiency	PGE_2 – pro-inflamatory, pro-carcinogenic effects
PGI_3 – vasodilation and anti-aggregation effects	PGI_2 – vasodilation and anti-aggregation effects
TXA_3 – weak pro-aggregation and contractile effects	TXA_2 – very strong pro-aggregation and contractile effects
LTB_5 – slight pro-inflammatory effect	LTB_4 – strong pro-inflammatory and pro-alergic effects

Numerous studies demonstrated negative effects of diet rich in saturated fatty acids on human health (Willet *et al*. 1990). Palmitic acid, myristic acid and stearic aid dislpay hyperlipaemising properties and cause the development of atherosclerosis and ischaemic heart disease.

However, certain authors report (Sundram *et al*. 1994) that in the case of normolipaemic patients palmitic acid can reduce the level of total cholesterol. In turn, stearic acid – by blocking the absorption of cholesterol from food – causes a reduction of its concentration in the blood serum and in the liver (German and Gillard 2004). High-fat diet in developed coutries is one of the primary causes of the occurrence of prostatectomy, cancer of the colon and mammary cancer (Bartsch *et al*. 1999, Rose 1997, Willett 1995). However, the content of fat in the diet is but one of many factors causing neoplastic diseases. Another important factor is the kind of fatty acids consumed. Numerous sudies demonstrated that a high level of saturated fatty acids from lard and beef tallow or from palm oil and coconut oil inhibits the process of carcinogenesis compared to the same amounts of PUFA from vegetable oils (Imrhan and Hsueh 1998, Hopkins *et al.* 1981, Carroll and Hopkins 1979, cit. after Jelińska 2005). The use of lard and butter as frying fats with simultaneous excessive consumption of pork and beef leads to overweight and obesity, and also to the ischaemic heart disease (Pawelec 2005, Ziemlański and Socha 1999). Excessive levels of saturated fatty acids cause an elevation of the concentration of total cholesterol in the blood serum, and of

the level of the LDL fraction responsible for the appearance of atherosclerotic changes and causing increased coagulability of blood (Cuchel *et al*. 2006, Krzymański *et al*. 2009).

Atherosclerosis is the primary cause of cardiovascular diseases, and it is promoted by hypertension and high levels of cholesterol resulting from bad dietary habits and from the smoking of tobacco. The risk factors include also obesity and diabetes that most frequently appear as a result of high consumption of saturated fatty acids.

Atherosclerosis develops already in the second decade of human life: cholesterol begins to accumulate under the endothelium lining the walls of arteries. For the next three decades the artery wall thickens, which in consequence leads to the formation of atheromatous deposits that reduce the lumen of the arteries and cause their serious weakening. The narrowing of the arterial lumen causes ischaemia of the heart and lower limbs, causing pain. In the sixth decade artery rupture may occur and a clog can be formed, blocking the arteries. The result of such changes is cardiac infarction or cerebral stroke. In the case of atherosclerotic changes in the cerebral arteries arteriosclerosis may occur (Krzymański *et al*. 2009).

The prophylaxis of atherosclerosis consists in observing a suitable diet, rich in mono- and polyunsaturated fatty acids, vegetables and fruits, stopping smoking, and limiting the consumption of alcohol.

The recommended daily dose of fats in human diet should not exceed 30% of the energy requirement, with saturated fatty acids accounting for a maximum of 10% of the dose and isomers of saturated fatty acids for less than 2% of the dose (Ziemlański and Socha 1999).

8. HEALTH PROPERTIES OF VEGETABLE OILS

Due to their content of primarily unsaturated fatty acids, vegetable oils are an important component of food. Numerous studies demonstrated a positive effect of diet rich in non-processed vegetable oils on human health, such oils being also characterised by the presence of other health-promoting components: antioxidants, polyphenols and sterols which play an important role in the neutralisation of free radicals and products of metabolism.

The dominant monounsaturated fatty acid in food is oleic acid. It constitutes the main component of all vegetable oils, and particularly high levels of that acid are found in olive oil and rapeseed oil. Monounsaturated faty acids lower the level

of the LDL fraction of cholesterol without affecting the level of the HDL cholesterol (Krzymański *et al*. 2009). They also reduce the risk of peroxidation of lipids in the HDL and LDL fraction, and thus prevent the deposition of the atheromatous plaque, which means that they have an anti-atherosclerosis effect. It is also suggested that diet rich in monounsaturated fats is effective in the treatment of obesity, diabetes and the metabolic syndrome (Krzymański *et al*. 2009).

Polyunsaturated fatty acids, as opposed to saturated and monounsaturated fatty acds, are not produced by the organism as it does not have the enzymes which are responsible for the introduction of double bonds into the carbon chain of the acids at positions n-3 and n-6. For this reason those acids have been named the Essential Fatty Acids (EFA). EFA comprise acids from the families ω-6 and ω-3. Acidsy ω-6 are found in large amounts in maize oil, rapeseed oil, soybean oil and sunflower seed oil, while linseed oil, rapeseed oil and fish oils are a source of acids ω-3. Nutrition standards concerning the daily consumption of EFA recommend that the daily intake of omega-6 acids should provide from 2 to 8% of energy, and the diet should contain 2 g of ALA and 200 mg of long-chain omega-3 acids (Achremowicz and Szary-Sworst 2005).

The metabolic pathways of omega-3 and omega-6 acids include the participation of the same enzymatic systems, therefore an excessive level of LA in the diet causes a limitation of the synthesis of EPA and DHA from ALA, and thus also of eicosanoids derived from EPA and DHA. At the same time there is an intensification of the cascade of AA and its derivatives - tissue hormones which have carcinogenic and pro-inflammatory effects (Rose 1997, Larrson *et al.* 2004, Jelińska 2005) (Fig. 78). For this reason it is important to observe proper proportions between the levels of omega-3 and omega-6 acids in the diet (Simonsen *et al.* 1998). The correct ratio should be 1:3 (Krzymański *et al.* 2009) or 1:5 (Marciniak-Łukasiak and Krygier 2004). At present that ratio is disturbed and oscillates between 1:20 and 1:30 (Simopoulos 1999). This is the effect of diet rich in oils containing large amounts of linoleic acid, with simultaneous limitation of the consumption of fish. Oils abounding in polyunsaturated fatty acids omega-6 can reduce the level of LDL cholesterol with simultaneous increase in the concentration of HDL cholesterol (Krzymański *et al*. 2009).

Trans isomers of unsaturated faty acids are formed as a result of processes of hydrogenation. They can be found in confectionery products and in hydrogenated margarines (Krzymański *et al*. 2009). PUFA with the trans configuration are more noxious than the saturated fatty acids, as they increase the concentration of the LDL fraction of cholesterol and at the same time cause a lowering of the level of

HDL cholesterol in the blood serum (Hunter 2006, Krzymański *et al.* 2009). A relationship has also been observed between low body mass at birth and smaller head circumference of newborn babies and the presence of trans isomers of unsaturated fatty acids with concurrent reduced levels of PUFA in the mothers' diet (Hornstra 2000, Ziemlański and Socha 1999). Elaidic acid, trans isomer of acid C 18:1, is a component of atheromatous plaque and can affect the processes of oxidation of atheromatous deposits (Stachowska *et al*. 2002). It has been demonstrated that trans isomers of polyunsaturated fatty acids also have an unfavourable effect on, among ther things, the level of testosterone and on the efficiency of LA transformation to AA (Ziemlański and Socha 1999).

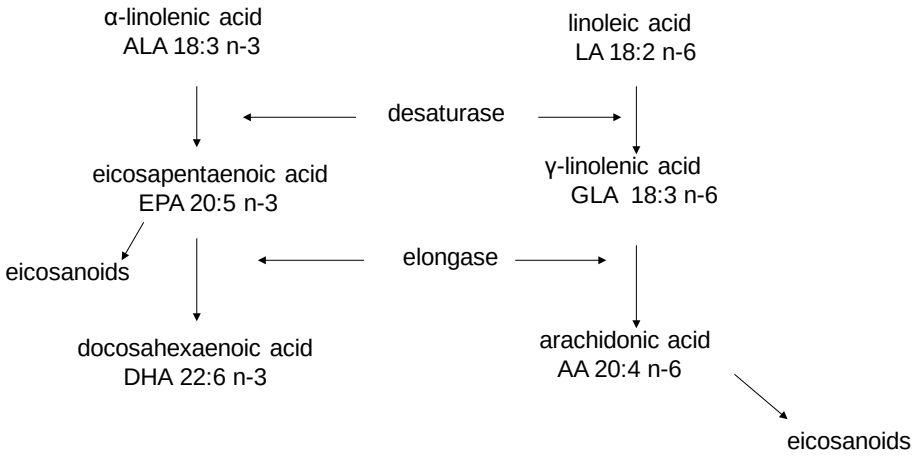


Fig. 78. Schematic diagram of metabolism of polyunsaturated fatty acids

Vegetable oils containing high levels of EFA should be consumed cold as under the effect of high temperature they undergo oxidation and become a source of noxious products of lipid peroxidation. More stable are those vegetable oils which are based on monounsaturated fatty acids.

8.1. Brief characterisation of selected oils with particular health-promoting effects

Rapeseed oil

The oil that is the most frequently consumed in Poland is rapeseed oil 00, called also the "olive of the North" due to its similarly high content of oleic acid. Apart from this, rapeseed oil is characterised by correct ratio of ω-3 to ω-6 acids (1:2), low content of saturated fatty acids, and the presence of extremely valuable additional substances: tocopherols, phytosterols and carotenoid pigments (Krzymański *et al*. 2009). Due to the dominance of monounsaturated fatty acids, resistant to thermoxidation, rapeseed oil – like olive oil – can be used as a frying fat (Krzymański *et al.* 2009).

Rapeseed oil reduces the concentration of LDL cholesterol without causing a reduction of the level of HDL cholesterol, and also has a reducing effect on arterial hypertension (Tab. 63).

Table 63. Effect of selected oils on blood pressure in rats with autopathic arterial hypertension (Aguila *et al*. 2005, cit. after Krzymański *et al*. 2009)

Kind of oil	Rate of blood pressure reduction
Fish oil	–35%
Rapeseed oil	–15%
Olive oil	–6%
Soybean oil	–6%

The anti-atherosclerosis properties of rapeseed oil result also from its high content of antioxidants, tocopherols and phytosterols, limiting the absorption of cholesterol (Tab. 64).

The consumption of organic rapeseed oil reduces the probability of damage to cell membranes by RFO (reactive forms of oxygen). RFO can be the cause of many diseases such as tumors, diseases of the circulatory system, diabetes, hypertension, cataract, Alzheimer disease, Parkinson disease, multiple sclerosis (MS), rheumatoid arthritis (Addis and Warner 1991).

Phenolic compounds present in rapeseed oil have anti-mutagenic and anti-carcinogenic effects and its consumption involves a reduction of the risk of de-

velopment of such neoplastic disorders as the breast cancer, cancers of the bladder and of the gastrointestinal tract (Gutierrez *et al*. 2002).

Table 64. Mean contents (mg kg^{-1}) of tocopherols and phytosterols in rapeseed oil and olive oil (Krzymański *et al*. 2009)

Component	Rapeseed oil	Olive oil
α-tocopherol	13.9	7.6
γ-tocopherol	34.1	0.4
δ-tocopherol	3.3	3.0
∑ of tocopherols	51.2	11.1
Brassicasterol	55.7	0
Campesterol	159.4	15.4
Betasitosterol	225.9	134.0
Avenasterol	22	10.8
Stigmasterol	0	50.2
∑ of phytosterols	463.0	210

The oil has an adjunctive effect in the process of treatment of insulin-dependent type II diabetes through a reduction of insulin-resistance and stabilisation of correct level of glucose. Moreover, it improves the assimilability of vitamins A, D and K, and – used externally – protects the skin against irritations, improves its elasticity, and also alleviates virus-induced changes: herpes and eczemas (Addis and Warner 1991, Grzymisławski 2000, Stark and Madar 2002).

Carotenoids, including lutein and zeaxanthin, due to their their valuable antioxidant and provitamin properties, are valuable components of rapeseed oil.

Rapeseed oil is a source of ω-3 and ω-6 acids whose beneficial effects have been partially described in chapter 7. The Table 65 below presents the available data on the effect of ω-3 and ω-6 acids on human health.

Table 65. Effect of ω-3 and ω-6 acids on human health (Karłowicz-Bodalska and Bodalski 2007, Dudzisz-Śledź *et al.* 2006, Jelińska 2005, Connor 2000, Woutersen *et al*. 1999)

Acids	
ω-3	ω-6
play a role in reducing the risk of the ischaemic heart disease through anti-anti-arrythmia and antithrombotic effects, reduce the risk of sudden death after cardiac infarct, minimise death rate related with circulkatory system dieseases by even 30%	have a beneficial effect on the level of cholesterol
reduce the risk of impairment of congnitive functions and of occurrence of dementia as a result of their anti-inflammatory properties and beneficial effect on nerve tissue	in *in vitro* studies, γ-linolenic acid (GLA) is characterisaed by the highest cytotoxicity with relation to noeplastic cells among all EFA
prevent depression and other psychic disorders	GLA displays beneficial effects when administered to patients with bone, liver and cerebral cancers, directly to the neoplastic tissue
display anti-carcinogenic effects	have a beneficial effect on defatting of the liver
have a protective effect on skin against harmful radiation	proper ratio between ω-3 and ω-6 acids – in mothers' diet prevents premature birth and low birth body mass of babies, and in babies' diet has a beneficial effect on the development of central nervous system and learning ability -reduces the rist of appearance of alergies and atopic changes
have beneficial effects in asthma, psoriasis, eczema, schizophrenia, systemic lupus, nephrotic syndrome, menstrual pains, mucoviscidosis, diabetes	excessive level of ω-6 acids in relation to ω-3 acids is conducive to the development of tumors
increase the rate of success of immunosuppressive treatment in patients after kidney transplant	

Camelina oil

Camelina oil is obtained from seeds of camelina (*Camelina sativa*). Its health-promoting properties result from its unique fatty acid composition and also from its high concentration of tocopherols which have a significant effect on its stability. The oil was known as far back as the Bronze Era, and until recently has been an important component of the diet of European populations (Zubr 1997). The fatty acid profile of camelina oil is given in Table 66.

Table 66. Percentage content of fatty acids in *Camelina sativa* oil, a – (Abramovič and Abram 2005), b – (Budin *et al.* 1995), c (Eidhin *et al.* 2003), d – (Zubr and Matthäus 2002)

Fatty acid	Content of fatty acid (%)			
	a	b	c	d
16:0	6.43	5.7-8.4	5.5	5.3-5.6
18:0	2.57	1.4-3.5	2.3	2.3-2.7
18:1	17.40	14.2-19.4	14.9	14.0-16.9
18:2	16.90	19.0-24.0	15.8	13.5-16.5
18:3	35.20	27.1-34.7	38.9	34.9-39.7
20:0	1.24	2.0-8.1	0.4	1.2-1.5
20:1	14.90	12.3-14.7	16.2	15.1-15.8
20:2	2.12	2.0-8.1	2.1	1.7-2.0
20:3	1.61	2.0-8.1	1.3	1.3-1.7
22:1	1.62	0.0-4.0	2.4	2.6-3.0

Polyunsaturated fatty acids constitute about 50-60% of all fatty acids, the content of linoleic acid accounting for 15-20% and of linolenic acid for 35-40%. The ratio of ω-6 to ω-3 acids is approximately 1:2 and it is extremely favourable.

The content of tocopherols in camelina oil depends on the type of cultivation, on the climate and soil conditions Zubr and Matthäus 2002), and also on the conditions of storage of the oil (Abramovič *et al.* 2007). The concentration of the particular varieties of tocopherol in camelina oil is presented in Table 67.

Table 67. Content of α-, γ- δ-tocopherols in *Camelina sativa* oil (Zubr and Matthäus 2002)

Oil	Content of α-, γ- δ-tocopherols (mg kg^{-1})			
	α-tocopherol	γ- tocopherol	δ-tocopherol	total
Camelina sativa oil	15.2-33.4	679-824	17.0-24.1	723-897

The consumption of camelina oil notably reduces the level of triglycerides and cholesterol in the blood (Eidhin *et al*. 2003), and its high content of polyunsaturated fatty acids causes that it can also be used as a cosmetic oil or as a component for creams (Zubr 1997).

Valuable vegetable oils with medicinal importance are oils obtained from alternative plants: evening primrose, borage, blackcurant and viper's bugloss (*Echium vulgare*). Those oils are a source of EFA and also of many substances with biological activity: tocopherols, carotenoids, phytosterols and polyphenols. The main drawback of the "virgin" oils is their low oxidative stability and susceptibility to a number of oxidising factors. An improvement of the oxidative stability of the oils can be achieved through an addition of natural antioxidants.

The fatty acid profiles of evening primrose oil, borage seed oil, echium oil and blackcurrant seed oil have been presented in Chapter 2.

Evening primrose seed oil

This oil is characterised by a content of γ-linolenic acid (GLA) – 10%, linoleic acid – 71%, and the absence of α-linolenic acid (biologically inactive). All EFA contained in evening primrose oil are in the form of *cis* isomers. In the process of biochemical transformation, GLA is transformed into the dihomogammalinolenic acid (DGLA). Both of those acids are highly biologically active and their further metabolic transformations lead to the formation of arachidonic acid (AA – Fig. 74). Under the effect of the enzyme Δ-6-desaturase, prostacycline, a derivative of AA is formed which – produced in the lungs and released to the blood stream – is a very strong anti-atherosclerosis agent inhibiting the most effectively the aggregation of thrombocytes and causing vasodilation of coronary vessels. The enzyme Δ-6-desaturase is destroyed, *i.a.*, by peroxides of EFA, and its activity can be reduced by improper diet, advanced age, alcohol, diabetes. Therefore, evening primrose seed oil can be administered as a prophylactic meas-

ure to supplement the level of GLA, but it has to be enriched with additives with antioxidant properties, e.g. vitamin E (Pieńkowska 1992).

The health properties of evening primrose oil are presented below (Karłowicz-Bodalska and Bodalski 2007, Pieńkowska 1992).

The consumption of evening primrose seed oil:

- has a favourable effect on behavioural changes and is used e.g. in the ADHD syndrome;
- alleviates diseases with inflammatory basis, such as diabetes, multiple sclerosis, schizophrenia;
- treats states of elevated levels of cholesterol in the blood, arterial hypertension, alergies, diseases of the skin, the nervous system and of the caridovascular system;
- has an adjunctive role in the treatment of bronchial asthma and chronic ulcerations of various origins.

Borage seed oil

Borage seed oil is the richest source of GLA, its content varying from 20% to 25%. That oil is characterised by high activity in lowering the level of HDL in the blood (Tab. 68).

Table 68. Activity of selected oils in lowering the level of HDL (%) (Mińkowski 2008)

Activity (%)	Kind of oil				
	Echium oil	Borage seed oil	Blackcurrant seed oil	Linseed oil	Camelina oil
	56	100	84	50	72

The main tocopherol of borage seed oil is δ-tokoferol; the content of the particular varieties of tocopherol in borage seed oil is presented in Table 69.

Table 69. Content of α-, δ-, γ-tocopherols in Borage seed oil (Mińkowski 2008)

Oil	Tocopherol content (mg kg $^{-1}$)			Total tocopherols (mg kg $^{-1}$)
	α-T	γ-T	δ-T	
Borage	16.1	246.6	1147.5	1410.2

Comparing the content of phytosterols in borage seed oil to the levels of those compounds in blackcurrant seed oil or echium oil one can note that their level in borage seed oil is low (Tab.70a,b).

Tab 70b. Content of phytosterols in Borage seed oil (Mińkowski 2008)

Oil	Phytostrol content (mg g^{-1})			Total phytos-terols (mg g^{-1})
	Δ 5 Avenasterol	Δ 7 Stigmasterol	Δ 7 Avenasterol	
Borage	75.1	21.0	1.4	319.5

Table 70a. Content of phytosterols in Borage seed oil (Mińkowski 2008)

Oil	Phytostrol content (mg g^{-1})			
	Brassicasterol	Campesterol	Stigmastrol	β-Sitosterol
Borage	0.3	83.2	7.5	131.0

Applied externally, the oil restores the physiological equilibrium of the skin, protects its lipid barrier, and also alleviates inflammations and protects against infections. Consumed, borage seed oil regulates the metabolism, improves the structure of hair and fingernails, and also plays an adjunctive role for the organism in prolonged or chronic stress.

Blackcurrant seed oil

Blackcurrant seed oil, like evening primrose seed oil and borage seed oil, is a source of GLA, the content of which varies from 15% to 20%. Apart from that, it is an alternative source of stearidonic acid SDA (2%), the highest amounts of which are found in the oil of Atlantic fish species. The ratio of ω-3 to ω-6 acids in blackcurant seed oil conforms to the nutrition recommendations and amounts to 1:5. Blackcurrant seed oil displays greater activity in lowering total cholesterol and the LDL fraction compared to echium oil, linseed oil, camelina oil and borage seed oil (Mińkowski 2008). Blackcurrant seed oil is a rich source of α-tocopherol (453.3 mg kg^{-1}) and contains twice as much vitamin E (525.1 mg kg^{-1}) as rapeseed oil (Mińkowski 2008) (Tab.71).

The dominant phytosterol in blackcurrant seed oil is β-sitosterol, accounting for 82.4% of all polysterols in the oil in question (Mińkowski 2008) (Tab.72).

Table 71. Content of α-, δ-, γ-tocopherols in Blackcurrant seed refined oil (Mińkowski 2008)

Oil	Tocopherol content (mg kg $^{-1}$)			Total tocopherols (mg kg $^{-1}$)
	α-T	γ-T	δ-T	
Blackcurrant	453.3	711.1	67.2	1231.6

Table 72. Content of phytosterols in Blackcurrant seed refined oil (Mińkowski 2008)

Oil	Phytostrol content (mg g^{-1})						Total phytos-terols (mg g^{-1})
	Campes-terol	Stig-mas-trol	β-Sitos-terol	Δ 5 Avenas-terol	Δ 7 Stigmas-terol	Δ 7 Avenas nas-terol	
Blackcurrant	48.9	5.6	463.4	13.1	23.0	8.1	562.1

The oil is used in the treatment of atopic inflammation of skin, eczems, psoriasis, leproma. It has an adjunctive effect in brittleness of fingernails and in hair loss.

Echium oil

Echium oil is the richest vegetable oil in terms of the content of stearidonic acid SDA – 12.4%, and for this reason it has a high health-promoting value – it is recommended in deficiency of the enzyme Δ-6-desaturase (Mińkowski 2008).

Compared to other oils, echium oil is not particularly outstanding in terms of the content of phytosterols (Tab.73a,b) and tocopherols (Tab.74), and additionally its high levels of SDA cause that echium oil is an unstable oil.

Table 73a. Content of phytosterols in *Echium vulgare* oil (Nogala-Kałucka *et al.* 2010)

Oil	Phytostrol content (mg g^{-1})				
	Brasicasterol	Campesterol	Stigmasterol	Sitosterol	Avenasterol
Echium vulgare	0.07	2.63	0.18	1.37	2.18

Table 73b. Content of phytosterols in *Echium vulgare* oil (Nogala-Kałucka *et al.* 2010)

Oil	Phytostrol content (mg g^{-1})				Total phytosterols (mg g^{-1})
	Δ7-stigmasterol	Cycloartenol	Citrostadienol	24methylene-cycloartenol	
Echium vulgare	0.44	0.26	0.15	0.15	7.44

Table 74. Content of α-, δ-, γ-tocopherols in *Echium vulgare* oil (Mińkowski 2008)

Oil	Tocopherol content (mg kg $^{-1}$)			Total tocopherols (mg kg $^{-1}$)
	α-T	γ-T	δ-T	
Echium vulgare	39.2	199.3	19.2	257.7

Amaranth seed oil

The seeds of Amaranthus, commonly known as amaranth, are the source of amaranth seed oil. Amaranth was known as far back as 5000 years ago and was the basic element of the diet of the Aztecs, Mayas and Incas. The dominant fatty acids in the oil include palmitic acid (21.4-23.8%), oleic acid (22.8-31.5%) and linoleic acid (39.4-49.1%) (Jahaniaval *et al.* 2000). Apart from UFA, amaranth seed oil contains large amounts of squalene which is an important component of cosmetics and pharmaceutical products. The content of squalene in crude amaranth seed oil is 65.61 10^3 g kg^{-1} (in olive oil it is 4.23 10^3 g kg^{-1}) (León-Camacho *et al.* 2001). The content of squalene in amaranth seed oil varies only slightly among the various amaranth varieties (Tab.75).

Table 75. Percentage content of squalene in amaranth seed soil depending on the variety (Becker *et al.* 1981, Bertoni *et al.* 1989, cit. after Berganza *et al.*2003)

Content of squalene (%)	Amaranth variety			
	A.cruentus	*A.edulis*	*A.mantegazzianus*	*A.caudatus*
	4.6-7.65	6.7	5.21	5.84

The fatty acid profile of amaranth seed oil is presented in Table 76.

Table 76. Percentage content of fatty acids in *Amaranthus cruentus* oil (%) (Jahaniaval *et al.* 2000)

Fatty acid	Fatty acid composition in *Amaranthus cruentus* oil (%)
14:0	0.27
16:0	22.2
16:1	0.11
18:0	3.57
18:1	30.1
18:2	42.2
18:3	0.69
20:0	0.68
22:0	0.24

Due to its high content of phytosterols, amaranth seed oil finds an application in pharmacological products (Tab.77a,b). Clerosterol, the main sterol of amaranth seed oil, displays antibacterial effects, while sitosterol and stigmasterol are used in the pharmaceutical industry as semi-products for steroids (León-Camacho *et al.* 2001).

Table 77a. Precentage content of phytosterols in *Amaranthus cruentus* oil (%) (León-Camacho *et al.* 2001)

Oil	Percentage content of phytosterol (%)			
	24-methylen-cholesterol	Campesterol	Stigmasterol	Δ-7 Campesterol
Amaranthus cruentus	0.3	1.6	0.9	24.8

Table 77b. Precentage content of phytosterols in *Amaranthus* cruentus oil (%) (León-Camacho et al. 2001)

Oil	Percentage content of phytosterol (%)				
	Clerosterol	β-sitosterol	Δ-5 Avena-sterol	Δ-7 Stigma-stenol	Δ-7 Avena-sterol
Amaranthus cruentus	42.0	1.3	2.0	15.2	11.9

Amaranth seed oil does not have a high content of tocopherols (Tab. 78), the main tocopherol being β-tocopherol. The consumption of amaranth seed oil lowers the LDL fraction of chlesterol in the blood, and when applied externally, it has an alleviating effect on atopic and acne-type changes.

Table 78. Content of α-, β-, δ-tocopherols in *Amaranthus cruentus* oil (León-Camacho *et al.* 2001)

Oil	Tocopherol content (mg kg^{-1})		
	α-T	β-T	δ-T
Amaranthus cruentus	248	546	8

Common sea-buckthorn oil

Common sea-buckthorn oil is obtained from both the seeds and the fruits that can contain from 1.4 to 13.7% of fat, depending on the cultivar and the type of cultivation, and also on the size and colour of the fruits (Yang and Kallio 2002).

Oil from the seeds differs in terms of its fatty acid profile and content of additional compounds from the oil obtained from fruit pulp, the latter having better health-promoting properties (Tab. 79, 80).

Table 79. Percentage content of fatty acids in Sea buckthorn seed oil, (Yang and Kallio 2002), (Yang *et al.* 2000)

Oil	Fatty acids (%)						
	16:0	16:1 n-7	18:0	18:1 n-7	18:1 n-9	18:2 n-6	18:3 n-3
Sea buckthorn seed oil	11.3-20	4.4	2-5	2-4	13-30	30-40	20-35

Table 80. Percentage content of fatty acids in Sea buckthorn pulp oil, (Yang and Kallio 2002), (Yang *et al.* 2000), (Ranjith *et al.* 2006)

Oil	Fatty acids (%)							
	14:0	16:0	16:1 n-7	18:0	18:1 n-9	18:1 n-7	18:2 n-6	18:3 n-3
Sea buckthorn pulp oil	0.1-1.1	17-47	16-54	0.1-35	9.7-26.2	7.3	5.1-16.1	0.6-5.6

Both Common sea-buckthorn oil s are characterised by high concentration of carotenoid compounds, especially β-carotene, tocopherols and tocotrienols as well as phytosterols, but the oil from the fruits is richer in those compounds (Tab.81).

Table 81. Content of carotenoids, phytosterols, tocopherols and tocotrienols in *Sea buckthorn* pulp oil and seed oil (Erkkola and Yang 2003)

Oil	Carotenoids (mg 100 g^{-1})	Phytosterols (%)	Tocopherols and tocotrienols (mg 100 g^{-1})
Seed oil	10-50	1-2	100-200
Pulp oil	100-400	2-3	100-400

The content of carotenoids, tocopherols and tocotrienols is dependent on the cultivar, geographic situation and type of cultivation (Tab. 82, Fig. 79).

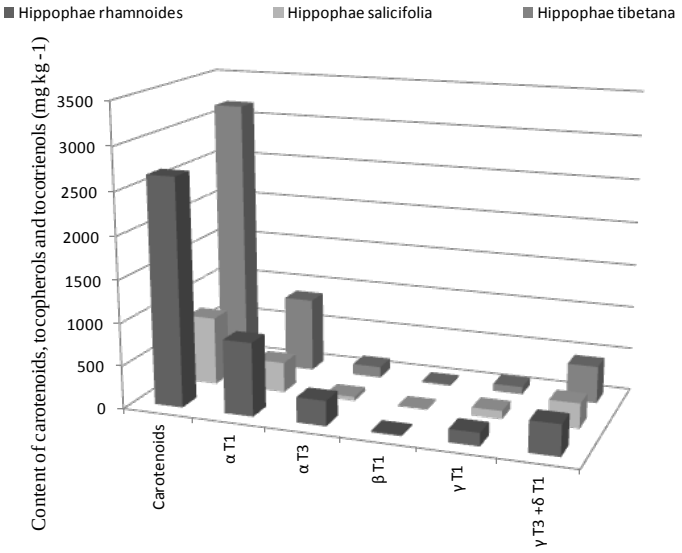


Fig.79. Content of carotenoids, tocopherols and tocotrienols in oils from three different varieties of sea-buckthorn

Table 82. Content of carotenoids, tocopherols and tocotrienols in Sea buckthorn *Hippophaë rhamnoides* pulp oil from different region (Ranjith *et al.* 2006)

Region	Carotenoids (mg kg^{-1})	Tocopherols and tocotrienols (mg kg^{-1})					
		α T1	α T3	β T1	γ T1	γ T3 + δ T1	δ T1
Lahaul	2660	859	293	16	152	362	12
Spiti	2576	1006	183	18	170	228	17
Ladakh	2400	954	95	27	126	187	14

α T1 α-tocopherol, α T3 α-tocotrienol, β T1 β-tocopherol, γ T1 γ-tocopherol, γ T3 + δ T1 γ-tocotrienol + δ-tocopherol, δ T1 δ-tocopherol.

Zadernowski *et al.* (2003) studied the content of tocopherols in oil from the fruits of various cultivars of sea buckthorn, as well as the relation of the concentration of tocopherol varieties and vitamin E with the date of harvest, and with the colour and size of the fruits (Tab. 83).

Phytosterols are another group of compounds occurring in large amounts in sea-buckthorn oil. Li *et al.* (2007) identified phytosterols in common sea-buckthorn oil obtained with three different methods of extraction. The highest levels of phy-

tosterols were determined in oil extracted with the SFE method, but irrespective of the extraction method the dominant phytosterol in sea-buckthorn oil is sitosterol (Tab. 84).

Table 83. Content of tocopherols, vitamin E in Sea buckthorn pulp oil cv.Nadbaltycka in relation on the harvesting time, diameter of berry and color of berry (Zadernowski *et al.* 2003)

Harvesting time	Tocopherols (mg 100 g $^{-1}$oil)					Diameter of berry (mm)	Color of berry
	α T	γ T	δ T	Total	Vitamin E		
10.07.2000	30.1	10.1	10.2	40.4	31.4	4	Green
28.07.2000	39.3	11.0	30.6	80.9	41.4	4.5	Green
16.08 2000	31.7	6.0	31.0	68.7	33.2	5	Olive
13.09.2000	74.9	Traces	34.9	109.8	75.9	5.5	Olive-yellow
03.10.2000	67.9	Traces	35.7	103.6	69.0	6	Light-orange
14.10.2000	65.4	Traces	36.1	101.5	66.5	7	Orange
15.11.2000	74.0	Traces	36.3	110.3	75.1	10	Orange
01.12.2000	71.4	Traces	36.6	108.0	72.5	10	Orange
29.12.2000	71.7	Traces	38.6	109.7	72.3	10	Orange

Table 84. Content of phytosterols (mg 100 g $^{-1}$oil) in Sea buckthorn seed oil from different extractions (Le *et al.* 2006)

Phytosterols component	Content of phyosterols (mg 100 g $^{-1}$oil) from extractions method		
	SFE	HE	CPE
Campesterol	24.0	20.6	13.9
Clerosterol	14.3	11.9	8.4
Sitosterol	787.4	673.0	462.2
Δ5 Avenasterol	218.5	165.9	97.3
Δ7 Avenasterol	17.7	14.2	9.2
24-methylenecycloartanol	105.8	76.1	37.7

SFE – supercricital fluid extraction, HE – hexane extraction, CPE – cold press extraction.

The effect of common sea-buckthorn oil on human health has been the object of numerous studies (Zhao 1994, Erkkola and Yang 2003, Yang *et al*. 2000, Yang *et al.* 1999, Larmo 2011) in which the authors describe the positive effect of the oil on skin with atopic changes, on the mucous membrane, and on skin with burns. Antioxidant properties of the oil *in vivo* and *in vitro* have been presented, among others, in the publication by Hung-Chih Ting *et al*. 2010 (Tab. 85); common sea-buckthorn oil displays a high activity in quenching free radicals.

Table 85. The effective concentration in sample of Sea buckthorn seed oil (mg ml^{-1}) that can decrease the RFO concentration by 50% (Hung-Chih *et al.* 2010)

Kind of radicals	Sea buckthorn seed oil (mg ml^{-1})
H_2O_2	2.63
Superoxide anion	2.16
Hydroxyl radicals	0.77

Some of the major applications of sea-buckthorn oil in medicine have been addressed in their studies by Zeb (2004) and Larmo (2011) (Tab. 86).

Table 86. Some important medicinal properties of Sea buckthorn oil (Zeb 2004)

Medicinal property
Cardiovascular diseases
Reducing fat and antioxidant
Atherosclerosis
Treatment of liver fibrosis
Protective effect of liver injury
Treatment of chronic hepatitis
Skin burning
Atopic dermatitis
Other skin diseases

Fish oil

An especially valuable animal fat is the oil obtained from shark liver (Szostak and Szostak-Węgierek 2006). That oil is characterised by a high concen-

tration of squalene and of alkylglycerols which have bacterio-static and fungi-static properties (Baskaran *et al.* 1996, Bordier *et al.* 1996).

The fatty acid composition of shark liver oil varies with relation to the species of the fish and to the area of its habitation (Tab. 87).

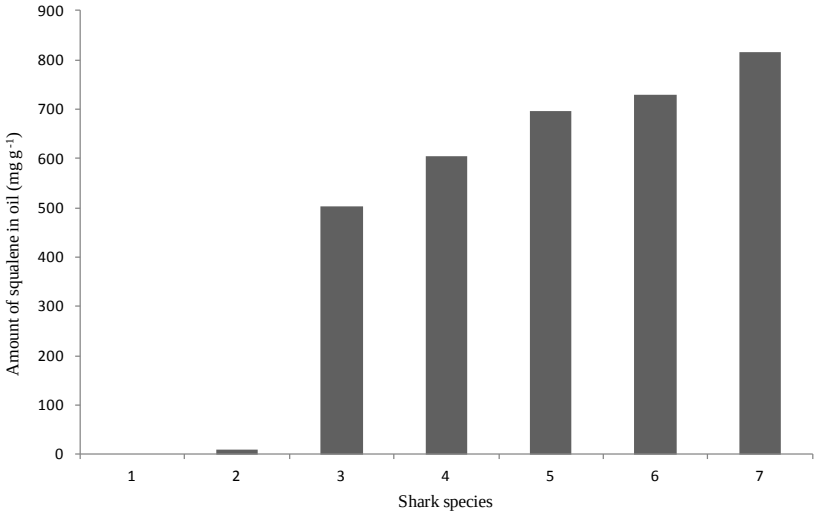
Table 87. Percentage composition fatty acid of liver oils from deep-sea sharks (Bakes and Nichols 1995) and pelagic sharks species (Navarro-Garcia *et al.* 2000)

Fatty acid	Depp-sea shark species			Pelagic sharks species	
	Deania calcea	*Centroscymnus plunketi*	*Centrophorus scalpratus*	*Carcharhinus falciformis*	*Galeocerdo cuvier*
14:0	0.9	0.4	1.5	3.03	3.61
16:0	21.3	9.1	19.8	22.79	22.48
16:1	3.2	2.8	3.9	3.48	7.32
17:0	0.3	0.1	0.3	1.44	0.95
17:1	0.6	0.5	0.5	0.66	0.80
18:0	2.5	1.3	3.1	8.42	6.70
18:1 n-9	30.3	36.8	37.6	10.98	28.44
18:1 n-7	2.3	1.9	3.0	2.85	5.50
18:2	0.8	0.8	1.0	1.33	1.53
18:3	–	–	0.5	3.16	6.22
20:2	0.3	0.3	0.2	0.66	–
20:4	0.4	–	0.5	2.29	5.22
20:5	0.8	–	1.0	5.14	1.09
24:1	0.6	1.1	0.4	0.52	0.90
22:6	4.2	1.2	5.9	25.05	0.32

The dominant fatty acids in oil from deep sea shark liver are monounsaturated fatty acids that constitute from 62 to 84% of total fatty acids. The levels of saturated fatty acids is within the range of 11-26%, while polyunsaturated fatty acids account for only 1-13% of the total content of fatty acids (the most important polyunsaturated fatty acid, DHA, amounts to even 7% of the fatty acid content) (Bakes and Nichols 1995). Fatty acids in the oil from pelagic shark liver have a different composition: the dominant fatty acids are saturated fatty acids (43-

44%), monounsaturated fatty acids constitute about 20% of the total fatty acid content, while polyunsaturated fatty acids are present at the level of 15-37%, with DHA accounting for up to 25% of all fatty acids (Navarro-Garcia *et al*. 2000).

The content of squalene, which is the main component of shark liver oil, depends primarily on the species of the fish and may constitute over 82% of the content of lipids (Fig. 80).



1 – *Somniosus pacificus*, 2 – *Centroscymnus plunketi*, 3 – *Etmopterus granulosus* I*, 4 – *Etmopterus granulosus* II*, 5 – *Deania calcea*, 6 – *Centroscymnus crepidater*, 7 – *Centrophorus scalpratus* I*, II* – two different samples

Fig. 80. Content of squalene in oil from different species of deep-sea sharks (Bakes and Nichols 1995)

Due to its strong antioxidant properties, squalene found an application in the pharmaceutical and cosmetics industries as a component of preparations protecting against UV radiation, delaying the ageing of skin and also augmenting the treatment of dry and atopic skin (Nowicki and Barańska-Rybak 2007, Zih-Rou Huang *et al*. 2009). By affecting the cells of organs responsible for the resistance of the human organism, such as the liver, squalene indirectly augments the immune system of the organism and also shortens the time of healing of wounds (Nowicki and Barańska-Rybak 2007).

Alkylglycerols are other important components of shark liver oil that determine its health-promoting properties. Studies revealed their cytotoxic effect on

neoplastic cells and also protective properties in radiotherapy in the process of cancer treatment (Andreesen *et al*. 1978, Lewkowicz *et al*. 2006).

Examples of the application of preparations based on shark liver oil are presented in Table 88.

Table 88. Examples of applications of preparations based on shark liver oil

Effect on human health	References
Treatment of bacterial infections	Lewkowicz *et al.* 2002 Lewkowicz *et al.* 2006
Support in treatment of psoriasis	Nowicki and Barańska-Rybak 2007
Reduced risk of allergy, asthma and cancers	Norrish *et al.* 1999 Gonzales *et al.* 1993
Improvement of the state of skin in atopic dermatitis	Dunstan *et al.* 2003 Nowicki and Barańska-Rybak 2007
Accelerated healing of recurring aphthous ulcer	Gurańska *et al.* 2001
Improvement of natural resistance in healthy humans	Tchórzewski *et al.* 2002

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10. SUMMARY

The work gives a description of the physicochemical properties of vegetable and animal fats, taking into acount also their effect on human health. It is a review-type work, presenting a descritpion of values characterising the quality of fats and thair suitability for consumption: acid number AN, saponification value SV, peroxide number PN, anisidine value AV, and iodine value IV. Numerous examples fatty acid profiles of vegetable and animals fats are given, as well as a discussion of factors affecting their composition. A detailed presentation is provided concerning the components of the non-saponifiable phase: squalene, carotenoid and chlorophyll pigments, tocopherols, polyphenolic compounds and sterols, their antioxidant properties, contents in various kinds of fats, as well as the parameters that determine those contents. The work presents also the effect of consuming fats on human health, the positive and the negative.

The presented literature review, concerning both vegetable oils and animal fats, permits the readers to form their own views and opinions on the very important food components that we all consume daily. The advantages and disadvantages of fats have been the object of great interest, especially in recent years. However, the information given within the scope of that discussion is frequently fragmentary, and often burdened with the basic flaw of being part of advertising campaigns. There is, therefore, a shortage of information that would not be based on research results presented in a selective manner, but which would represent comprehensive data based on the latest achievements of science. For this reason the primary objective of the authors of this work was to accumulate the most important knowledge on the problem as a whole.

The problem of quality of animal and vegetable fats, and the latter in particular, consists in the great instability of most of the biologically active compounds included in their composition. Yet it is the role of those compounds that is of special importance in terms of the quality and health properties of the food that we consume.

The authors tried to emphasise not only the energy-source role of fats, that being equally health-promoting and noxious (especially in recent years, when our food contains increasing levels of industry-processed products).

Numerous studies, especially those describing correct diet, focus on the role of faty acid profiles of various fats. Therefore, the authors made an effort to emphasise that role of unsaturated faty acids and to make the presentation objective.

That role is important, because those acids play an unquestionable prophylactic role in the prevention of many of the civilisation diseases of the last century.
Keywords: vegetable and animal fats, physical properties, chemical properties, quality of fat, health

11. STRESZCZENIE

FIZYKO-CHEMICZNE I ZDROWOTNE WŁAŚCIWOŚCI TŁUSZCZÓW

W pracy opisano właściwości fizyko-chemiczne tłuszczów roślinnych i zwierzęcych z uwzględnieniem ich wpływu na zdrowie człowieka. Jest to praca przegladowa zawierająca opis wielkości charakteryzujących jakość tłuszczów i ich przydatnośc do spożycia: liczbę kwasową LK, liczbę zmydlania LZ, liczbę nadtlenkową LN, liczbę anizydynową LA oraz liczbę jodową LI. Przytoczono liczne przykłady profili kwasów tłuszczowych tłuszczów roślinnych i zwierzęcych oraz omówiono czynniki wpływające na ich skład. Szczegółowo omówiono także składniki fazy niezmydlającej się: skwalen, barwniki karotenoidowe i chlorofilowe, tokoferole, związki polifenolowe oraz sterole, ich właściwości antyoksydacyjne, zawartość w różnych rodzajach tłuszczów a także parametry decydujące o ich zawartości. W pracy przedstawiono wpływ spożycia tłuszczów na zdrowie człowieka zarówno pozytywny jak i negatywny.

Przedstawiony przegląd literatury dotyczący zarówno olejów roślinnych jak i tłyszczów zwierzęcych pozwala wyrobić sobie pogląd na bardzo ważny składnik żywności jaki jest przez nas spożywany codziennie. Zalety i wady tłuszczów są szczególnie w ostatnich latach bardzo upowszechniane. Są to jednak informacje wycinkowe, które bardzo często obciążone są wadą jaką niesie reklama. Brakuje więc informacji opartych nie na wynikach badań wybiórczo przedstawianych lecz całościowych opartych na najnowszych osiągnięciach nauki. Dlatego celem zasadniczym jaki stawiają sobie autorzy tej pracy było zgromadzenie najważniejszej wiedzy dotyczącej całości tego zagadnienia.

Problem jakości tłuszczów zarówno zwierzęcych jak i roślinnych, ale szczególnie tych ostatnich polega na wielkiej niestabilności większości związków aktywnych biologicznie, które są w nich zawarte. Jednak to właśnie ich rola jest szczególnie ważna, gdy mówimy o jakości czy walorach zdrowotnych spożywanej przez nas żywności.

W pracy starano się więc uwypuklić nie tylko energetyczną rolę tłuszczów, która to rola jest w takim samym stopniu ważna dla zdrowia , jak i szkodliwa

(szczególnie w ostatnich latach gdy spożywamy znaczną ilość produktów przemysłowo przetworzonych).

W wielu pracach, szczególnie tych opisujących prawidłową dietę zwraca się uwagę na szczególną rolę profilu kwasów tłuszczowych wchodzących w skład tłuszczów. Więc tę rolę kwasów nienasyconych w pracy starano się uwypuklić i obiektywnie przedstawić. Jest to rola bardzo ważna , ponieważ wykazuja one niewątpliwie profilaktyczna rolę w zapobieganiu bardzo wielu chorobom cywilizacyjnym ostatniego stulecia.

Słowa kluczowe: tłuszcze roślinne i zwierzęce, właściwości fizyczne i chemiczne, jakość tłuszczu, zdrowie

Address of Authors:

Jerzy Tys
Departament of Physical and Technological Properties of Agricultural Materials
Institute of Agrophysics, Polish Academy of Sciences
ul. Doświadczalna 4, 20-290 Lublin
e-mail: j.tys@ipan.lublin.pl

Joanna Lamorska
The Istitute of Agricultural Sciences,
The State School of Higher Education in Chełm
ul.Pocztowa 54, 22-100 Chełm

Adresy autorów:

Jerzy Tys
Zakład Fizycznych Właściwości Materiałów Roślinnych,
Instytut Agrofizyki im. Bohdana Dobrzańskiego PAN
ul. Doświadczalna 4, 20-290 Lublin
e-mail: j.tys@ipan.lublin.pl

Joanna Lamorska
Instytut Nauk Rolniczych, Państwowa Wyższa Szkoła Zawodowa w Chełmie
ul. Pocztowa 54, 22-100 Chełm