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Original Research Article

INFLUENCE OF DIFFERENT STORAGE CONDITIONS ON RAPESEED OILS QUALITY

ABSTRACT

Aims: The aim was to determine the impact of various storage conditions on the stability of rapeseed oil, which determines the content of free fatty acids, peroxides, aldehydes, conjugated compounds and fatty acid composition

Study design: Storage experiment was performed in 6 months period; Quality of oils was analysed using standard methods. Fatty acid composition of oils was determined using gas chromatography. The data were analysed using Statistica v. 12.5 software.

Place and Duration of Study: Chair of Food Plant Chemistry and Processing, Olsztyn, Poland between December 2014 and July 2015.

Methodology: The material consisted of 24 commercial samples of rapeseed oils. Samples were stored in brown glass bottles for six months in different conditions - in the dark at +20°C, in a refrigerator at +4°C, and in a freezer at -20°C. The quality of rapeseed oil was determined by measuring the acid value, peroxide value and anisidine value. The fatty acid composition and the content of conjugated dienes and trienes were also analyzed.

Results: In control samples cold pressed oils were characterized by the highest acid value and the lowest anisidine and peroxide values. Cold pressed oil samples stored at -20°C had the highest acid value (an increase by 9.21%); however, unlike fresh oils, they also had the highest peroxide value (an increase by 5.17%). The greatest increase in the content of saturated fatty acids during storage was noted for refined hot pressed oils (6.33%). A permanent trend was an increase in the share of monounsaturated fatty acids, and a decrease in the share of polyunsaturated fatty acids. The share of MUFAs increased most following storage at 20°C for refined hot pressed oils (9.38%), and pressed and extracted oils (9.35%). In the same samples, the greatest decrease in the content of PUFAs also occurred by, respectively, 30.78% and 31.22%.

Conclusion: Higher temperatures are more conducive to oxidative changes in oils, which are indicated by higher values of all the analyzed distinguishing quality features of oils. Refined oils are more susceptible to these changes as in the process of purification a number of substances with antioxidant properties are removed.

Keywords: Rapeseed oil, oxidation, storage, quality, fatty acid composition

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1. INTRODUCTION

The oil obtained from rapeseed (*Brassica napus*) has been used in food technology and the catering industry for many years. In terms of global consumption it takes third place, after palm oil and soy oil. Each year an increase in the consumption of vegetable oils (including rapeseed) is observed. In the 2013/14 season global consumption reached 25.63 million tonnes, and for the 2014/15 season it is forecast to increase by 5.35%. The largest producer of rapeseed for oil production is Canada. The size of the rape harvest in this country in 2012 was 15.41 million tonnes. The second largest producer is China (14 million tonnes), and the third is India (6.78 million tonnes) [1,2].

Rapeseed oil is one of the most valuable vegetable fats, due to its nutritional properties. It is a rich source of mono- and polyunsaturated fatty acids, while saturated fatty acids are minor constituents [3]. Rapeseed oil is characterized by high levels of monounsaturated fatty acids (62%) and significant levels of polyunsaturated fatty acids (32%), and it contains very little saturated acids (6%) [4].

Oil from plant materials can by extracted by pressing or with solvents. Extraction with an organic solvent is used for raw materials with a fat content below 20%. Pressing is a method applied to materials with a higher oil amount. This process can be carried out either hot or cold. Cold pressing does not apply heat treatment to raw materials, in contrast to hot pressing, where rape seeds are pre-treated by heating [5]. Disadvantage of pressing is an expeller, that has relatively high fat residue. However, to increase the yield of the oil it can be further extracted with organic solvents. Oils obtained by cold pressing have better preserved natural properties, such as flavor [6].

Crude oils after hot pressing and / or extraction are often subjected to a refining process, which aims to remove undesirable components. It consists of degumming, neutralization, bleaching and deodorization [7]. Cold pressed oils and refined oils differ in their contents of many compounds, such as phenols. Factors affecting their antioxidant properties include the number and position of hydroxyl groups, and polarity, solubility, and stability during processes such as hot pressing or refining [8]. Cold pressed oils are rich in polar phenolic compounds [9]. Siger et al. [10] studied the contents of phenolic compounds in cold pressed and refined oils. All refined oils (rapeseed oil, soybean oil and sunflower oil) have shown lower contents of total phenolic compounds in relation to cold pressed oils, while in the case of phenolic acids, in most refined samples there was not found their presence at all. The differences in these contents are also reflected in variations in antiradical activity - in the case of refined oils this was higher. The participation of compounds which are not triacylglycerols in cold pressed oils is higher than in refined oils [11].

The contents of compounds with antioxidant properties and their activity determines the progress of oxidative changes in oils during storage, and therefore their stability. These changes progress via autoxidation and / or are supported by rays of light. Responsible for this mechanism are various forms of oxygen, respectively, atmospheric triplet oxygen ($^3O_2$) and singlet oxygen ($^1O_2$). Triplet oxygen has two unpaired electrons that react with radical components of food, whereby with the participation of light and atmospheric oxygen singlet oxygen is formed [12]. Autoxidation can be divided into three stages. The first is initiation. This involves removing a hydrogen atom from the fat methylene group, thereby forming the alkyl radical. This is followed by propagation, namely the creation of peroxide radicals, which are capable of reacting with unsaturated fatty acids, resulting in the formation of hydroperoxides. Autoxidation ends with termination that is the formation of non-radical compounds [13]. During the induction time very small changes occur, but in the later stages of oxidation flavor changes are noticeable. In the molecules of unsaturated fatty acids removal refers to the least-bonded hydrogen atom. In polyunsaturated fatty acids it is an atom of a methylene group located between the two

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unsaturated bonds. In molecules of monoene fatty acid hydrogen bonded to a carbon atom adjacent to the double bond is removed [14, 15].

The changes described above cause quality flaws generally known as oxidative rancidity. The second type of rancidity is hydrolytic rancidity, which consist of triglyceride lipolysis, resulting in free fatty acids release. The endogenous lipase catalyzing this reaction is present in rape seeds. Optimal pH for its activity is between 8 and 9 at 37°C [16].

The aim of the study was to determine the impact of various storage conditions on the stability of rapeseed oil, which determines the content of free fatty acids, peroxides, aldehydes, conjugated compounds and fatty acid composition.

2. MATERIAL AND METHODS

The material consisted of 24 commercial samples of rapeseed oils (Table 1.) before the end of shelf life. The oils were made by different manufacturers. The differences between them consist in the process of production, the presence or absence of added antioxidant, and type of package. Control samples were analyzed at the beginning of the study. Samples were stored in brown glass bottles for six months in different conditions - in the dark at + 20°C, in a refrigerator at + 4°C, and in a freezer at -20°C.

Table 1. Samples of rapeseed oils (methods of production and purification).

Method of production and purification	Sample number
Cold-pressed unrefined	1-4
1-step pressed refined oil	5-6; 20-22
pressed and extracted refined oil	7-19; 23-24

The quality of rapeseed oil was determined by measuring the acid value [17], peroxide value [18], and anisidine value [19]. The fatty acid composition [20] and the content of conjugated dienes and trienes [21] were also analyzed. Fatty acid composition was determined by GC chromatography [20]. Methyl esters were prepared according to the method of Zadernowski and Sosulski [22], and their analysis was carried out with a GC 121 8000 FISONS chromatograph equipped with a DB-225 capillary column (30 m × 0.25 mm × 0.25 μm), helium as the carrier gas, and a flame-ionization detector. Fatty acids were identified according to the retention time determined for fatty acid standards (Sigma-Aldrich, Poznań, Poland). In case of determining of content of conjugated dienes and trienes the oil (0.1 g) was placed into 25 ml volumetric flasks and supplemented up to the volume with hexane. This was followed by measuring the absorbance of the solutions using a UNICAM UV / Vis UV2 spectrophotometer at wavelengths of 233, 262, 268 and 274 nm versus hexane [21].

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Oils were divided into groups, taking as a criterion the method of production and method of purification. Statistical analysis of the results was performed using STATISTICA StatSoft version 12.5 (Krakow, Poland). With this program PCA analysis was made.

3. RESULTS AND DISCUSSION

Table 2 presents the average values of particular parameters for the analyzed oils. As compared to control samples, the acid value increased following storage. The highest value thereof was noted for oils stored at 20°C, which is due to the fact that the processes of hydrolysis occur more rapidly at higher temperatures. In control samples a higher content of conjugated dienes was noted, as well as the absence of conjugated trienes, whose presence was demonstrated in the stored samples. The composition of fatty acids also changed during storage. An increase in the share of saturated and monounsaturated fatty acids, and a reduction in the share of unsaturated ones can be observed here. Both control samples and stored samples were characterized by high variation in all analyzed parameters. Fresh oils were most varied in terms of the acid and anisidine values. Variation in those parameters decreased following storage (the variation coefficient decreased the most following storage at 20°C). The situation was opposite for the peroxide value, whose variation was lowest in control samples but increased following storage. The greatest increase in the variation of oils in terms of this parameter was noted following storage at 20°C (cv = 59.3%).

Table 2. The acid, peroxide and anisidine values, the content of dienes, trienes and fatty acid composition in rapeseed oil, depending on the method of storage.

	Fresh		**Storage temperature [ºC]**					
			-20		**4**		**20**	
	x	cv	x	cv	x	cv	x	cv
Acid value [mg KOH/g]	0.29	75.8	0.34	52.9	0.35	60.0	0.44	45.5
Peroxide value [mEq O_2/kg]	1.09	35.8	0.34	50.0	0.53	52.8	0.86	59.3
Anisidine value [-]	1.96	40.8	1.75	34.3	1.86	32.8	2.53	30.4
Dienes [%]	0.22	22.7	0.14	28.6	0.14	21.4	0.17	23.5
Trienes [%]	0.00	0.0	0.03	33.3	0.04	25.0	0.04	50.0
	Fatty acid composition [%]							
SFA	6.92		6.67		6.85		19.46	
MUFA	65.15		71.83		72.83		73.51	
PUFA	27.92		21.56		20.36		19.46	

SFA – Saturated Fatty Acids; MUFA – Monounsaturated Fatty Acids; PUFA – Polyunsaturated Fatty Acids; x – Average value; cv – Variation coefficient;

The acid value in control samples ranged from 0.09 to 0.87 mg KOH/g oil. The lowest value of this parameter was noted for refined oil obtained by single pressing. In turn, the highest acid value was noted for unrefined cold-pressed oil. This is explained by the fact that during the oil refining process a neutralization is applied in order to precipitate free fatty acids in the form of soaps, and separate them from the oil. The highest peroxide value (2.18 mEq O_2/kg) was noted for refined hot pressed oil; the lowest one for unrefined cold-pressed oil. In addition to the undesirable substances, many substances with antioxidant properties are also removed from the oil during the refining process, which could be the reason for this situation. The anisidine value was highest (4.49) for a

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sample of refined oil, hot pressed with no chemical methods applied; the lowest (0.77) value of this parameter was noted for a sample of unrefined cold-pressed oil (Table 3). This situation is due to the application of refining, which removes antioxidants. The anisidine value indicates the presence of secondary products of lipid oxidation, e. g. aldehydes (especially 2-alkenale and 2,4-alkadienale), which are formed by decomposition of hydroperoxides [23]. The principle of this method is the reaction of p-methoxyaniline (p- anisidine) with the aldehyde component. Products of this reaction are yellow and show a maximum absorbance at 350 nm [24].

The values of particular parameters indicative of the stability of oils were averaged for particular oil groups. The method for obtaining oil and its purification was adopted as a criterion (Table 3). In control samples cold pressed oils were characterized by the highest acid value and the lowest anisidine and peroxide values. Similarly to control samples, cold pressed oil samples stored at -20°C had the highest acid value (an increase by 9.21%); however, unlike fresh oils, they also had the highest peroxide value (an increase by 5.17%). The anisidine value remained at the same level as for fresh products.

At a temperature of 4°C a slight increase in the acid value was noted for cold pressed oils (it remained the highest among all the analyzed oils). The peroxide value was about twice higher than for the oils stored at -20°C (Table 3). This indicates that the oxidative changes had progressed in the analyzed fats. The anisidine value remained at a level similar to that for control samples.

For the oils stored at room temperature the greatest changes in the analyzed parameters in relation to fresh oils were noted. The acid value increased by 9.21% for cold pressed oils, by 50% for hot pressed oils, and by 90% for oils obtained by hot pressing combined with extraction (Table 3). Iqbal and Bhanger [25] also analyzed the storage stability of oils. After 24 days of storage they noted an increase in the oils' content of free fatty acids. Similar results were obtained by Kreivaitis et al. [26]. For the rapeseed oils they analyzed, after 70 days of storage at a temperature of 70°C, the acid value increased, as compared to the baseline, by approx. three times, which indicates progressive hydrolysis. The peroxide value decreased for both hot pressed and extracted oils, and those hot pressed only. In turn, the anisidine value for these product groups increased, which could be indicative of the completion of lipid oxidation and the formation of secondary products of this process other than radicals. They can include aldehydes, ketones, or short-chain carboxylic acids [26].

No presence of conjugated trienes of fatty acids was found in control samples. For each oil group, regardless of the storage conditions, the average content of conjugated trienes was the same. The lowest one (0.01%) was noted for unrefined and cold pressed oils, while the highest one (0.05–0.06%) was noted for hot pressed oils or oils pressed, extracted, and purified by refining. Wanasundara al. [27] also studied the content of conjugated dienes and trienes in stored oils (rapeseed and soybean). The amount of these compounds in the samples was tested eight times in a period of thirty days of storage. In both types of oils content of conjugated dienes and trienes increased each measurement. Therefore it can be concluded that during oil storage occur oxidative changes, in which these compounds are formed. The results in the case of the dienes do not coincide with those obtained in this study. In addition, these authors noted a significantly higher content of dienes and trienes, probably due to the use of much higher storage temperatures (65°C).

During the formation of hydroperoxides from unsaturated fatty acids conjugated dienes are typically produced, due to the rearrangement of the double bonds. They can be created from oxydienes or hydroperoxydienes as a result of oxidation, where hydroxydienes are intermediates [23]. Following storage the amount of conjugated dienes decreased for hot pressed oils and refined pressed and extracted oils. The

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greatest decrease (52%) in their content was noted after the storage of hot pressed oil samples at 4°C. For unrefined cold pressed oils the amount of conjugated dienes after storage either remained the same or increased. An increase in the value of this parameter by 27.27% was noted for samples stored at room temperature (Table 3).

Table 3. The average of acid, peroxide and anisidine values and content of dienes and trienes in rapeseed oil, depending on production method.

Storage temperature [ºC]	Production method	Acid value [mg KOH/g]	Peroxide value [mEq O_2/kg]	Anisidine value [-]	Dienes [%]	Trienes [%]
Fresh	Cold pressing	0.76	0.58	1.02	0.11	0.00
	1-step pressing*	0.18	1.24	2.49	0.25	0.00
	Hot pressing + extraction*	0.20	1.18	2.03	0.23	0.00
-20	Cold pressing	0.69	0.61	1.02	0.10	0.01
	1-step pressing*	0.23	0.23	2.02	0.13	0.05
	Hot pressing + extraction *	0.28	0.30	1.85	0.15	0.04
4	Cold pressing	0.79	0.99	1.18	0.11	0.01
	1-step pressing*	0.21	0.42	2.09	0.12	0.05
	Hot pressing + extraction *	0.28	0.45	1.97	0.16	0.04
20	Cold pressing	0.83	1.22	1.74	0.14	0.01
	1-step pressing*	0.27	0.81	2.78	0.15	0.05
	Hot pressing + extraction *	0.38	0.79	2.66	0.19	0.04

**- refined oils*

A number of correlative relationships were demonstrated; they are listed in Table 4. The highest positive value of the correlation coefficient (0.76) was obtained following the storage of oil at 4°C between the acid and peroxide values, as well as between the content of conjugated trienes and the anisidine value. Strongly positive relationships were also demonstrated for fresh oil between the anisidine value and the content of conjugated dienes. In turn, the greatest negative relationship was found between the acid value and the content of conjugated dienes (from -0.75 to -0.78) for all samples following storage. A similar correlation in their study received Shahidi et al. [28], who studied animal oil derived from seals. This may explain the aforementioned fact that the dienes are formed in parallel with the hydroperoxides.

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Table 4. Correlation coefficients calculated for relationships between the parameters defining oils quality.

Parameter	Acid value	Peroxide value	Anisidine value	Dienes	Trienes	Parameter	Acid value	Peroxide value	Anisidine value	Dienes	Trienes
Fresh						**-20°C**					
Acid value		-0.64*	-0.45*	-0.88*	-	Acid value		0.71*	-0.50*	-0.35	-0.78*
Peroxide value			0.08	0.53*	-	Peroxide value			-0.30	-0.20	-0.68*
Anisidine value				0.69*	-	Anisidine value				0.25	0.71*
Dienes					-	Dienes					0.41*
Trienes						Trienes					
4°C						**20°C**					
Acid value		0.76*	-0.48*	-0.31	-0.78*	Acid value		0.44*	-0.42*	-0.26	-0.75*
Peroxide value			-0.29	-0.05	-0.62*	Peroxide value			0.31	-0.13	-0.09
Anisidine value				0.29	0.76*	Anisidine value				0.32	0.72*
Dienes					0.28	Dienes					0.37
Trienes						Trienes					

** - correlation coefficients statistically significant at $P \leq 0.05$*

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The PCA analysis diagrams (Figure 1) show the group with numbers from 1 to 4 isolated from other samples. These are oils produced by cold pressing and not subjected to the refining process. They differ from the other ones both in the control sample (Figure 1A) and following storage under any conditions. In the control sample, in addition to the above-mentioned ones, two oils produced by the hot pressing method (Nos 6 and 20) also differed. Following storage at -20°C (Figure 1B), in addition to the cold-pressed samples, one hot pressed sample (No 22) differed. As regards the samples stored at 4°C (Figure 1C), samples Nos 5 and 22 (cold pressing), as well as 18 and 13 (pressing + extraction) can be distinguished. Following storage at 20°C (Figure 1D), in addition to sample Nos 1 to 4, sample No 6 (hot pressing), as well as Nos 8 and 16 (pressing + extraction) are distinguished. Figures (Figure 1 A-D) show that in the case of quality samples stored in room temperature are much more diversified than fresh samples.

The composition of fatty acids (Table 5) changed in the analyzed oils during storage. One of the apparent trends was an increase in the share of fatty acids in hot pressed oils. On the other hand, the decrease in their content in both cold pressed, and pressed and extracted oils was unexpected. The greatest increase in the content of saturated fatty acids was noted for refined hot pressed oils (6.33%). A permanent trend was an increase in the share of monounsaturated fatty acids, and a decrease in the share of polyunsaturated fatty acids. The share of MUFAs increased most following storage at 20°C for refined hot pressed oils (9.38%), and pressed and extracted oils (9.35%). In the same samples, the greatest decrease in the content of PUFAs also occurred by, respectively, 30.78% and 31.22%. This is due to the fact that acids with a greater number of double bonds in the molecule are more susceptible to oxidation processes [29]. In the refining process a significant proportion of substances with antioxidant properties were removed from oils, which also contributed to the decrease in the share of polyunsaturated acids. This is clearly visible in Table 6, which sums the contents of fatty acids belonging to particular groups. It also presents the ratio of n-6 acids to n-3 acids. After storage at -20°C this ratio did not change. The greatest change was noted for oils stored at room temperature. For these oils this ratio increased the most; however, this change did not significantly reduce the nutritional quality of the oil. Simopoulos [30] reports that the optimum ratio of n-6 acids to n-3 acids for humans ranges from 4/1 to 1/1. This ratio was maintained in most stored oils. Only in refined oils produced by the single pressing method, stored at room temperature, did the average ratio of n-6 acids to n-3 acids exceed 4/1.

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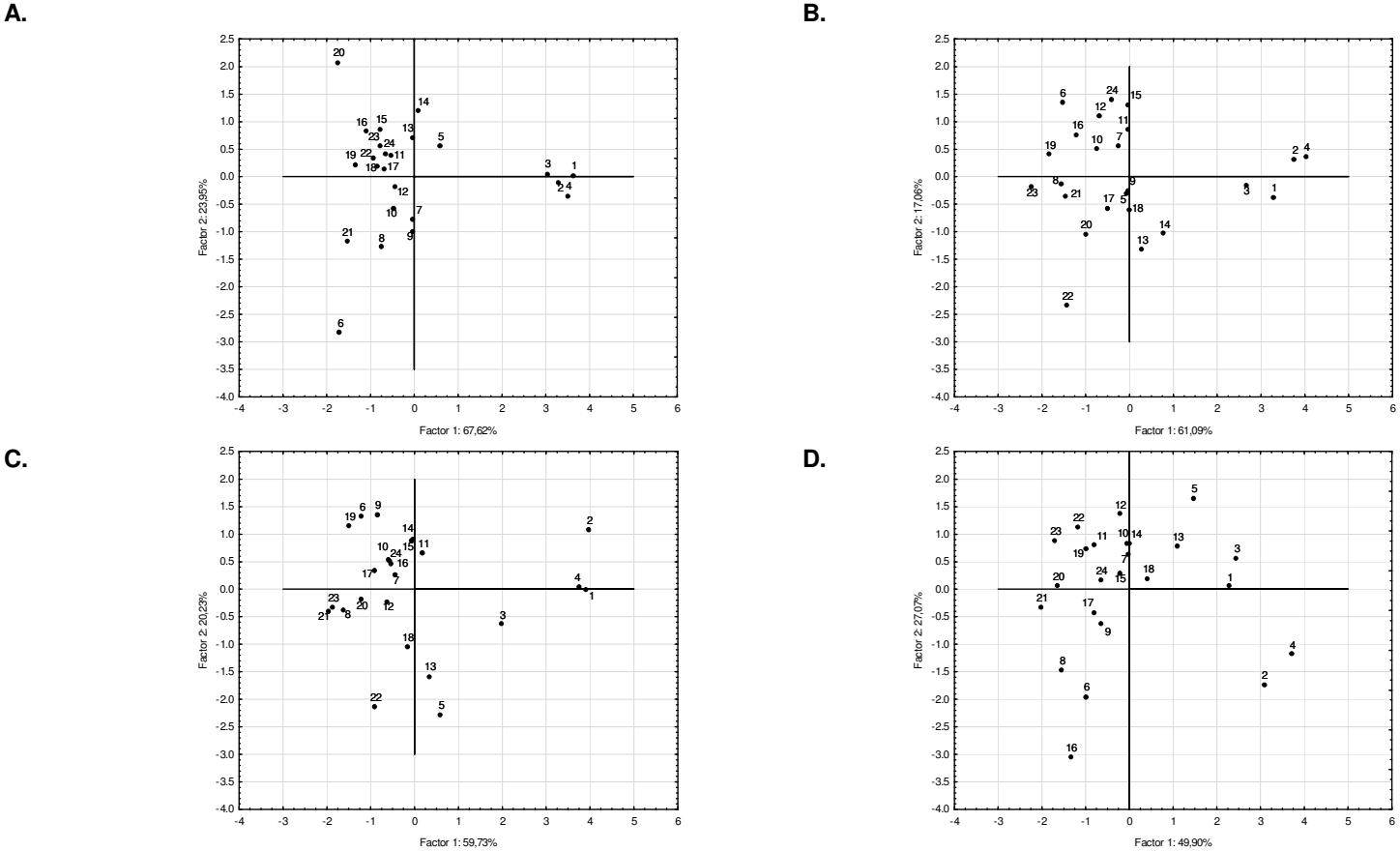

Figure 1. Diagrams of principial component analysis (PCA) of quality features. Numbering corresponds to the samples shown in Table 1. Storage conditions of rapeseed oils – A: fresh; B: -20°C; C: 4°C; D: 20°

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Table 5. The fatty acid composition in rapeseed oils, depending on the method of production.

Storage temperature [°C]	Production method	Fatty acid							
		palmitic	stearic	oleic	linoleic	linolenic	arachidic	eikozenoic	others
Fresh	Cold pressing	4.64	1.67	63.80	18.61	8.20	0.58	1.48	1.04
	1-step pressing*	4.60	1.55	62.95	19.27	8.74	0.55	1.38	0.96
	Hot pressing + extraction*	4.89	1.67	63.10	19.23	8.96	0.45	1.14	0.55
-20	Cold pressing	4.45	1.71	68.44	16.03	4.63	0.54	1.48	2.73
	1-step pressing*	4.57	1.74	67.05	16.67	4.88	0.51	1.35	3.22
	Hot pressing + extraction *	4.50	1.62	67.19	16.75	5.06	0.49	1.15	3.34
4	Cold pressing	4.48	1.77	68.94	15.36	4.38	0.52	1.44	3.13
	1-step pressing*	4.60	1.80	67.76	16.21	4.50	0.51	1.31	3.31
	Hot pressing + extraction *	4.66	1.68	68.26	16.02	4.39	0.51	1.22	3.33
20	Cold pressing	4.50	1.82	68.87	15.54	4.26	0.52	1.41	3.08
	1-step pressing*	4.70	1.72	69.13	15.63	3.76	0.70	1.24	3.12
	Hot pressing + extraction *	4.74	1.73	69.05	15.37	4.02	0.50	1.21	3.31

** - refined oils*

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Table 6. Amount of SFA, MUFA, PUFA and n-6/n-3 ratio of analysed oils.

Storage temperature [°C]	Production method	Fatty acids			
		SFA	MUFA	PUFA	n-6/n-3
Fresh	cold pressing	6.88	66.31	26.80	3.47/1
	1-step pressing*	6.70	65.29	28.01	3.42/1
	pressing + extraction*	7.01	64.80	28.19	3.31/1
-20	cold pressing	6.70	72.65	20.66	3.47/1
	1-step pressing*	6.83	71.62	21.55	3.42/1
	pressing + extraction*	6.61	71.68	21.81	3.31/1
4	cold pressing	6.77	73.50	19.74	3.50/1
	1-step pressing*	6.92	72.38	20.71	3.60/1
	pressing + extraction*	6.84	72.81	20.41	3.64/1
20	cold pressing	6.84	73.36	19.80	3.65/1
	1-step pressing*	7.12	73.49	19.39	4.15/1
	pressing + extraction*	6.98	73.56	19.39	3.82/1

** - refined oils*

4. CONCLUSION

Based on the obtained results it can be concluded that storage has an effect on the stability of rapeseed oil. The extent and severity of the effect depends on the storage conditions, the production method applied, and the purification of the oil. Higher temperatures are more conducive to oxidative changes in oils, which are indicated by higher values of all the analyzed distinguishing quality features of oils. Refined oils are more susceptible to these changes as in the process of purification a number of substances with antioxidant properties are removed. The production method is also important as during hot pressing the applied high temperature is also conducive to fat oxidation and reduces the stability of oils at the very beginning.

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