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EVALUATION OF TECHNOLOGICAL QUALITY OF SELECTED RAPESEED OILS*

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A b s t r a c t. This study compares the quality of rapeseed oils produced by different methods and stored under different conditions. The following oxidation parameters were determined in the analysed oils: acid value, peroxide value, anisidine value and Totox value. The evaluated quality parameters were: saponification value, iodine value, colour and fatty acid profile. In the group of the analysed products, Kropla Zdrowia – cold pressed rapeseed oil that was refrigerated in a dark glass bottle – was characterised by high quality (AV = 0, PV = 0.05 meq O_2 kg^{-1}, FFA = 0.4 mg KOH g^{-1}, Totox value = 0). In the cold pressed Organic Virgin oil stored in a clear glass bottle at room temperature, peroxide value, acid value and Totox value were above the norm at PV = 5.6 meq O_2 kg^{-1}, FFA = 4.27 mg KOH g^{-1} and Totox value = 13. The analysed products were characterised by similar fatty acid profiles, and Kropla Zdrowia oil had a higher content of oleic acid (by 10% on average) and a lower total content of linoleic acid and linolenic acid (by 11% on average) in comparison with the remaining products. All oils conformed to standard saponification values. The examined oils differed in colour, and pressed oils were darker. Three of the analysed products – Rapso, Olej Kujawski and Kropla Zdrowia – received high scores in a sensory evaluation. The lower scores noted in the remaining oils probably resulted from lower production standards and inadequate storage.

K e y w o r d s: rapeseed oil, sensory quality, peroxide number, acid number, fatty acid profile

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INTRODUCTION

The range of rapeseed oils available on the retail market has increased significantly in recent years. Consumers can choose from among cold pressed, hot pressed and refined rapeseed oils. Despite the above, not all marketed products conform to the highest quality and nutritional standards. Research results suggest that cold pressed oils have greater nutritional value than refined oils (Koski *et al*. 2002, Obiedzińska and Waszkiewicz-Robak 2012). Cold pressed oils have a shorter shelf life, and their quality is difficult to maintain at a high and stable level. The quality of rapeseed, the conditions during the production process as well as the packaging and storage methods directly influence the final product. Both pressed and refined oils can undergo adverse changes which lead to the formation of harmful compounds such as primary and secondary oxidation products (Wroniak and Łubian 2008, Nair *et al.* 2007). The chemical composition of lipids (fatty acid profile, content of natural antioxidants and prooxidants) is a key determinant of oxidative changes in natural, unrefined oils and their susceptibility to environmental factors (Lamorska and Tys 2011).

The objective of this study was to evaluate the basic quality parameters of Kropla Zdrowia rapeseed oil and of selected rapeseed oils available on the retail market.

MATERIALS AND METHODS

The experimental material comprised six rapeseed oils, including three cold pressed oils: Kropla Zdrowia (Institute of Agrophysics of the Polish Academy of Sciences in Lublin), Organic Virgin oil (J. Brochenin) and Olej rzepakowy (Oleofarm), hot pressed and refined Rapso oil (Vog Polska), and two refined oils: Olej Kujawski and Floriol (ZT Kruszwica). Kropla Zdrowia is obtained from a new variety of rapeseed with high oleic acid content, and its production involves pressing under nitrogen atmosphere.

Kropla Zdrowia oil was stored in a dark glass bottle for 2 weeks at 7°C, whereas the remaining oils, purchased in retail prior to their expiration dates, were analysed immediately after purchase. Organic Virgin and Olej rzepakowy were stored in dark glass bottles. Floriol and Rapso were packaged in clear glass bottles, and Olej Kujawski was purchased in a clear plastic bottle (Tab. 1).

The following parameters were determined in the analysed rapeseed oils in 2 or 3 replications: acid value (free fatty acids, FFA) according to standard PN-EN ISO 660, peroxide value (PV) according to standard PN-EN ISO 3960, anisidine value (AV) according to standard PN-EN ISO 6885, saponification value (SV) according to standard PN-EN ISO 3657, iodine value (IV) according to standard PN-EN ISO 3961, and colour (C) according to standard PN-A-86934. Methyl

esters were obtained from the oils according to standard PN-EN ISO 12966-2, and the fatty acid profile of the analysed products was determined by gas chromatography according to standard PN-EN ISO 5508. The stability of the tested oils was rated based on the COX value (Fatemi and Hammond 1980). The results were processed by one-way ANOVA at significance level of $\alpha = 0.05$.

Table 1. Commercial characteristics of analysed rapeseed oils

Oil	Production method / producer	Packaging / volume (dm^3)	Shelf life (months)
Kropla Zdrowia	Cold pressed / IPAN Lublin	Dark glass / 0.25	12
Organic Virgin	Cold pressed / J. Brochenin	Dark glass / 0.75	15
Olej rzepakowy	Cold pressed / Oleofarm	Dark glass / 0.5	6
Rapso	Hot pressed and refined / Vog Poland	Clear glass / 0.75	11
Kujawski	Refined / ZT Kruszwica	Clear plastic / 0.5	11
Floriol	Refined / ZT Kruszwica	Clear glass / 0.5	7

RESULTS AND DISCUSSION

All analysed oils were characterised by satisfactory sensory attributes typical of rapeseed oils, a pleasant flavour and aroma, clear appearance and absence of sedimentation.

The colour of the evaluated products ranged from light straw in refined oils and the hot pressed and refined oil, through golden yellow in the cold pressed Kropla Zdrowia oil, to green-brown in the remaining cold pressed oils. The ratio of chlorophyll to carotenoid pigments varied across the evaluated products, but all oils contained more carotenoid pigments (Fig. 1).

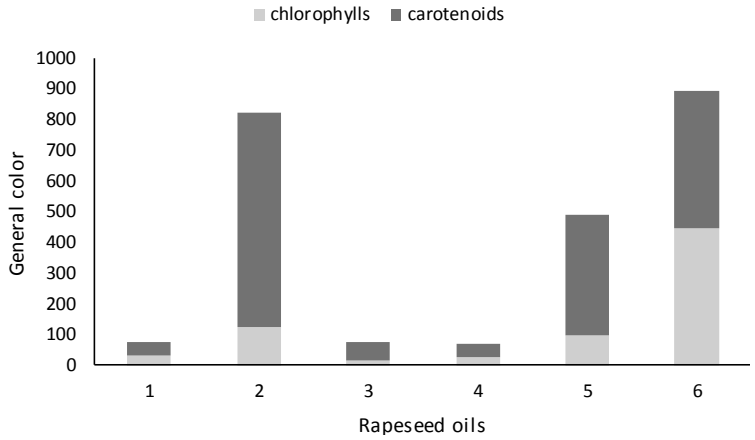

Fig. 1. Content of chlorophylls and carotenoids and total colour value determined in the tested oils: 1 – Floriol, 2 – Olej rzepakowy, 3 – Rapso, 4 – Kujawski, 5 – Organic Virgin, 6 – Kropla Zdrowia

Carotenoids play an important role due to their high nutritional value, chemical properties and prooxidant or antioxidant activity. Cold pressed oils were characterised by high colour saturation which was determined mainly by carotenoid pigments. The pigment ratio was determined at 1:1 only in Kropla Zdrowia oil which had the highest chlorophyll content in the tested product group. Chlorophyll pigments play an important role in oils, in particular in cold pressed oils, because they participate in photochemical reactions. Chlorophylls are photosensibilisers that convert oxygen into singlet oxygen, which initiates the oxidation of unsaturated fatty acids (Rotkiewicz *et al*. 2002). This is a particularly important consideration for oil storage. The analysed refined oils were characterised by significantly lower colour saturation and similar pigment ratios. According to Rotkiewicz *et al*. (2002), the content of carotenoid and chlorophyll pigments in vegetable oils is determined by the species and ripeness of raw materials as well as by the production and refining technology applied. High colour saturation can result from excessively high pressing temperatures (Maniak *et al.* 2012). Oils pressed from pure and healthy seeds are characterised by a higher content of carotenoid pigments, whereas the presence of damaged seeds significantly increases the proportion of chlorophyll pigments. The above can be attributed to the high content of chlorophyll pigments in rapeseed coats and incomplete ripening of pressed seeds (Strobel *et al*. 2005).

The main factors that limit the suitability of vegetable oils (in particular pressed oils) for human consumption are their acid and peroxide values which are indicators of hydrolytic and oxidative changes. Acid value indicates the number of free fatty acids in a lipid. In the group of the analysed cold pressed oils, the most desirable acid value was noted in Kropla Zdrowia (0.4 mg KOH/g), whereas the acid value of Organic Virgin (4.27 mg KOH g^{-1}) slightly exceeded the norm of 4 mg KOH/g (ZN-94/SGO-01) (Fig. 2).

The evaluated refined oils and the hot pressed and refined oil were also characterised by a low degree of hydrolysis (acid value of 0.073 mg KOH g^{-1} to 0.089 mg KOH g^{-1}), where the norm for fresh refined oil is 0.6 mg KOH g^{-1} (Codex Alimentarius 2001).

In cold pressed oils, hydrolytic changes can be induced by water and enzymes (Szukalska 2003). The degree of hydrolysis in such oils is also influenced by the quality of raw materials used in the production process (seed damage, moisture content). A high acid value of oil produced from damaged seeds points to advanced hydrolytic changes in those seeds, and the greater the damage, the higher the activity of lipolytic enzymes and acid value (Krygier *et al.* 2000). The production process, in particularly the method of oil extraction and purification (De Panfilis *et al.* 1998, Giovacchino *et al*. 2002), and storage conditions (Tańska and Rotkiewicz 2003, Tawfik and Huyghebaert 1999), are also important considerations.

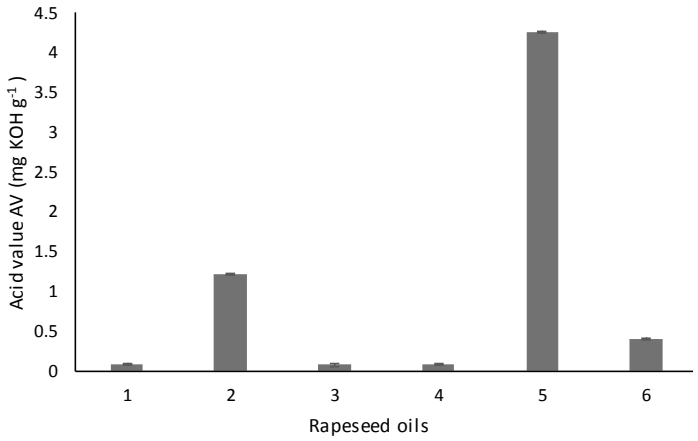

Fig. 2. Acid value FFA in the tested oils (legend as in Fig. 1.)

The peroxide value (PV) describes the number of primary oxidation products, and most of the analysed oils were within the reference ranges in this respect. The peroxide value limit for cold pressed oils is set at 5 meq O_2 kg^{-1} according to the Polish Standards (PN-A-86908) and at 10 meq O_2 kg^{-1} according to industry standards (ZN-94/SGO-01). The lowest PV was noted in Kropla Zdrowia oil (0.05 meq O_2 kg^{-1}) packaged in a dark glass bottle, whereas the PV of Organic Virgin oil stored in a clear glass bottle reached 5.6 meq O_2 kg^{-1} and slightly exceeded the norm (Fig. 3).

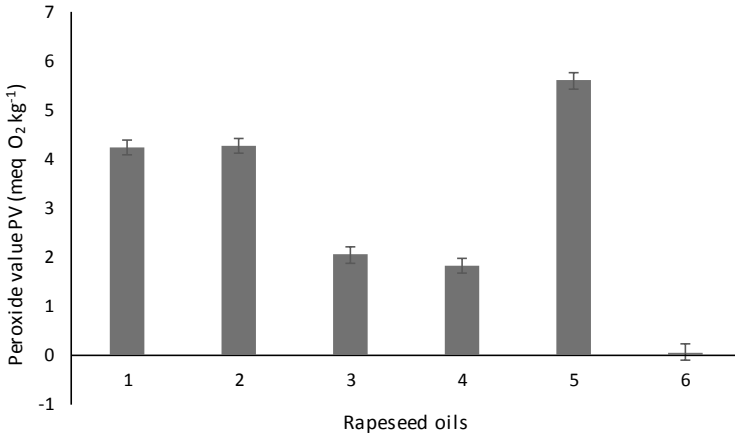

Fig. 3. Peroxide value PV in the tested oils (legend as in Fig. 1)

Adequate packaging significantly limits light and oxygen access and influences the degree of oil oxidation. The PV of products stored in dark glass bottles was several times lower than in oils packaged in clear glass and clear PET bottles (Tawfik and Huyghebaert 1999).

The PV of the remaining products ranged from 1.82 meq O_2 kg^{-1} (Olej Kujawski – clear plastic bottle) to 4.23 meq O_2 kg^{-1} (Floriol – clear glass bottle). The limit for fresh oil is 8 meq O_2 kg^{-1}, and for stored oil before its expiration date – 10 meq O_2 kg^{-1} (ZN-94/SGO-01). The low PV of Olej Kujawski testifies to its freshness. The analysed parameter is also significantly influenced by the product's expiration date. Most Polish cold pressed oils have a shelf life of 6 months, and refined oils – 12 or 24 months (ZN-94/SGO-01).

The stability of oils is also determined their anisidine value (AV) which describes the content of aldehydes, products of peroxide and hydroperoxide decomposition (Jerzewska 1991). The AV of the analysed oils ranged from 0.0 (Kropla Zdrowia) to 2.2 (Rapso) and conformed to the relevant standards (Fig. 4).

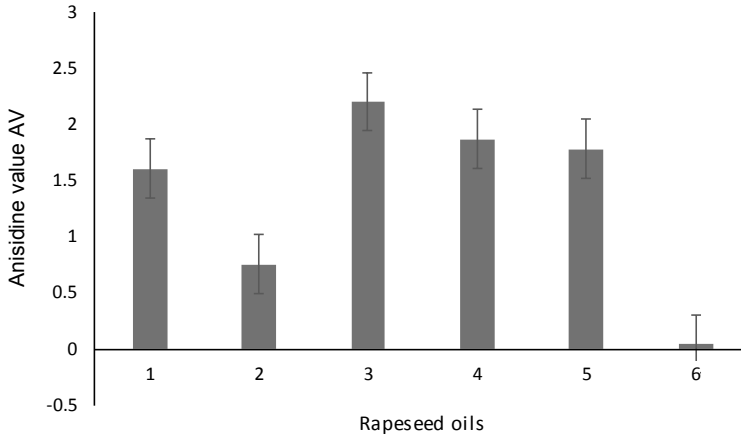

Fig. 4. Anisidine value AV in the tested oils (legend as in Fig. 1)

Anisidine value is not included in European standards for cold pressed oils, whereas in Polish standards, the AV threshold for refined oils is set at 8 (PN-A-86908). In our study, AV was low in fresh cold pressed oils, and Kropla Zdrowia had the lowest content of secondary oxidation products. Unlike refined oils, cold pressed oils are characterised by lower AV because their production process does not involve high temperatures. Refining, in particular dehydration, seems to be responsible for the high content of secondary oxidation products in oils (Makareviciene and Janulis 1999).

Peroxide values and anisidine values were used to calculate the Totox value which is a measure of total oxidation in oils (Jerzewska 1991, Szukalska 2003). In the analysed products, Totox values varied significantly from 0 in Kropla Zdrowia to 13 in Organic Virgin oil (Fig. 5). The threshold Totox value for edible oils of satisfactory quality is 10 (Allen and Hamilton 1998, Jerzewska 1991, Szukalska 2003), and this limit was exceeded by Floriol (10.1) and Organic Virgin oils. Olej rzepakowy also scored high on the Totox scale (9.24). The above products were characterised by high PV and AV, which indicates that their quality was relatively low already before expiry (Wroniak *et al*. 2006).

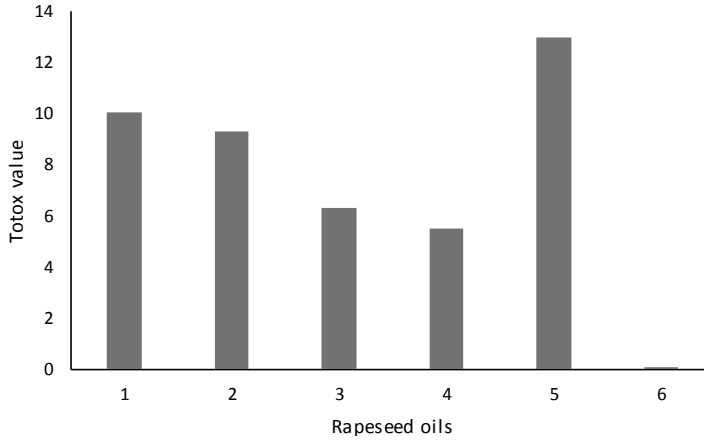

Fig. 5. Value of Totox index in the tested oils (legend as in Fig. 1)

Saponification value is used to calculate the average molecular weight of fatty acids in a given lipid. Lipids with a relatively high content of high-molecular weight fatty acid esters, such as rapeseed oil, have low saponification value. The saponification value of the analysed products ranged from 184 mg KOH g^{-1} (Olej Kujawski) to 206 mg KOH g^{-1} (Floriol), and it remained within the reference ranges of 192-203 mg KOH g^{-1} (PN-EN ISO 3657) in most of the oils (Fig. 6).

Iodine value (IV) describes the content of unsaturated fatty acids in a lipid. The IV of most analysed oils was within the normal range (110-126 g I_2 100 g^{-1}) (ZN-94/SGO-01), except for Kropla Zdrowia where this parameter was considerably lower at 90.65 g I_2 100 g^{-1} (Fig. 7).

The above can be attributed to significant differences in the fatty acid profile. Kropla Zdrowia oil is characterised by a high content of oleic acid (approximately 75%) but a lower content of linoleic acid (12%) and linolenic acids (5%) than normally found in rapeseed oil. Its fatty acid profile is comparable with that of olive oil and, similarly to olive oil, Kropla Zdrowia is also characterised by lower iodine value.

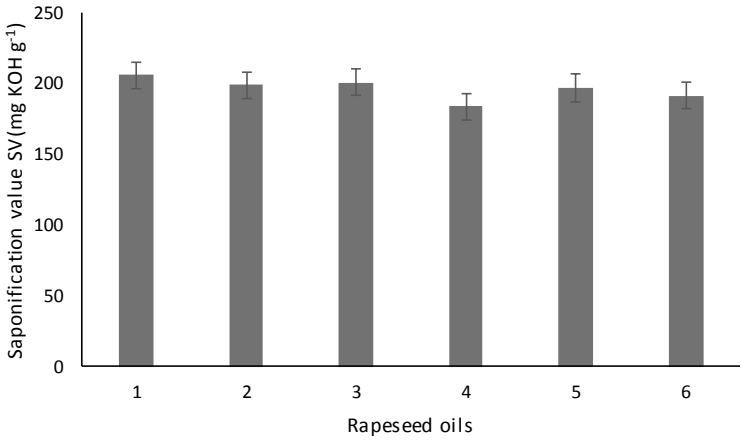

Fig. 6. Saponification value SV in the tested oils (legend as in Fig. 1)

The fatty acid profile of the remaining products was typical of rapeseed oil (Codex Alimentarius 2001). The content of saturated fatty acids was the lowest in Kropla Zdrowia oil (4.46%) and the highest in Organic Virgin oil (7.01%) (Tab. 2).

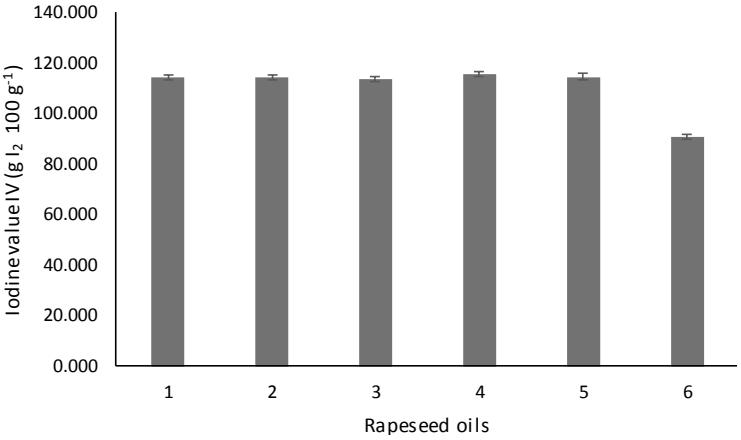

Fig. 7. Iodine value IV in the tested oils (legend as in Fig. 1)

The lowest total content of saturated fatty acids was determined in Kropla Zdrowia oil (4.46%) and the highest – in Organic Virgin oil (7.01%) (Tab. 2). The total concentrations of unsaturated fatty acids were the highest in Kropla Zdrowia oil (95.46%) and the lowest – in Rapso oil (93.03%). The predominant unsaturated fatty acid was oleic acid C18:1 whose content ranged from 63.65% in Olej rzepakowy to 75.59% in Kropla Zdrowia. The second most abundant unsaturated

fatty acid was linoleic acid C18:2 whose content ranged from 12.42% in Kropla Zdrowia to 20.28% in Olej rzepakowy. It was followed by linolenic acid C18:3 in the range of 4.94% (Kropla Zdrowia) to 9.39% (Olej rzepakowy). Kropla Zdrowia was the only oil containing palmitoleic acid C16:1 (0.21%) and gadoleic acid C20:1 (1.18%). All analysed products were characterised by a satisfactory ratio of linoleic acid to linolenic acid. The health benefits of polyunsaturated fatty acids can be attributed to their naturally predominant cis form and a desirable ratio of Ω3 to Ω6 acids which ranges from 1:1 to 1:5 (Achremowicz and Szary-Sworst 2005, Simopoulos 2008). In the evaluated products, this ratio ranged from 1:2.16 in Olej rzepakowy to 1:2.88 in Organic Virgin oil.

Table 2. Percent fatty acid composition

	Oil					
	Kropla zdrowia	Olej rzepakowy	Organic virgin	Rapso	Olej Kujawski	Floriol
C16:0	3.45	4.50	5.20	4.98	4.89	4.90
C16:1	0.21	–	–	–	–	–
C17:0		0.15	0.14	0.16	0.15	0.15
C18:0	0.36	1.85	1.67	1.81	162	0.81
C18:1[1]	75.59	63.65	66.29	64.48	65.00	67.28
C18:2[2](Ω6)	12.41	20.28	19.70	19.54	19.87	19.07
C18:3(Ω3)	4.94	9.39	6.84	8.96	8.47	7.64
C20:0	0.49	–	–	–	–	–
C20:1	1.18	0.06	–	0.05	–	0.05
C22:0	0.16	–	–	–	–	–
C22:1	1.13	–	–	–	–	–
SFA	4.46	6.50	7.01	6.95	6.66	5.86
MUFA	78.11	63.71	66.29	64.53	65.00	67.33
PUFA	17.35	29.67	26.547	28.50	28.34	26.71
Ω3:Ω6	1:2.51	1:2.16	1:2.88	1:2.18	1:2.34	1:2.5

Explanatory note: 1 the sum of oleic acid C18:1n9c and elaidic acid C18:1n9t, 2 the sum of linoleic acid cis C18:2n6c and trans C18:2n6t

Acid profile, in particular the content of oleic, linoleic and linolenic acids, influences the stability of the oil. Susceptibility to oxidation was calculated based on the COX value. Figure 8 shows that Kropla Zdrowia was characterised by the lowest COX value.

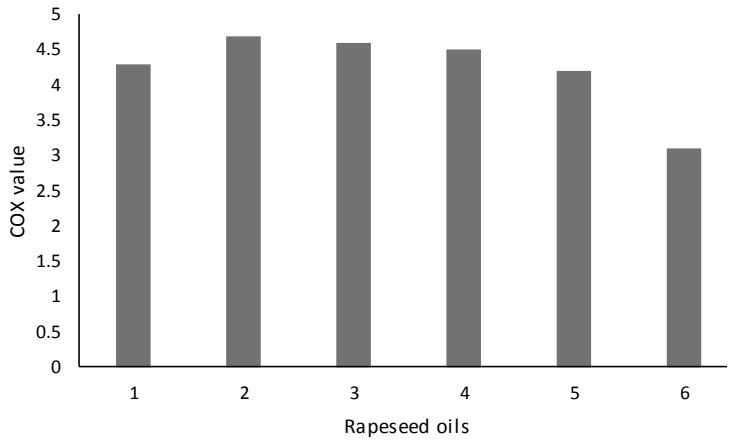

Fig. 8. Value of the index COX in the tested oils (legend as in Fig. 1)

CONCLUSIONS

The highest oxidative stability was determined in Kropla Zdrowia oil which was characterised by a high content of oleic acid and lower concentrations of polyunsaturated fatty acids, compared with the remaining products. A high degree of oxidation in the analysed oils (Floriol, Olej rzepakowy and Organic Virgin) could also be attributed to low quality of raw materials and inadequate production and storage conditions.

SUMMARY

1. The analysed rapeseed oils were characterised by satisfactory sensory attributes and physicochemical properties.

2. Kropla Zdrowia oil was characterised by supreme quality parameters due to the raw material used, the method of pressing, the absence of oxygen, and a short time interval between extrusion and the analysis.

3. Variations were noted in the colour of the evaluated products, and pressed oils were significantly darker than refined oils.

4. The analysed oils were characterised by similar fatty acid profiles (similar iodine values) and a similar content of long-chain fatty acids (similar saponification values) which were typical of rapeseed oil.

5. The anisidine value of the tested products is indicative of their freshness and high stability.

6. The acid value of Organic Virgin oil was slightly above the norm, which could be indicative of hydrolytic changes caused by progressing rancidity.

7. The fatty acid profile of the analysed products was characteristic of rapeseed oil.

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OCENA JAKOŚCI TECHNOLOGICZNEJ WYBRANYCH OLEJÓW RZEPAKOWYCH

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S t r e s z c z e n i e. Celem pracy było porównanie jakości olejów rzepakowych, różniących się sposobem otrzymywania i przechowywania. Oznaczono następujące parametry określające stopień utlenienia oleju: liczbę kwasową, liczbę nadtlenkową, liczbę anizydynową, wskaźnik Totox a także parametry wskazujące na jakość: liczbę zmydlania, liczbę jodową, barwę ogólną oraz profil tłuszczowy. Wśród analizowanych olejów wysoką jakością wyróżniał się olej Kropla Zdrowia, tłoczony na zimno

i przechowywany w ciemnej, szklanej butelce w warunkach chłodniczych (LA = 0, LN = 0,05 meq $O_2 \cdot kg^{-1}$, LK = 0,4 mg $KOH \cdot g^{-1}$, wskaźnik Totox = 0). Z kolei w oleju Organic Virgin, tłoczonym na zimno i przechowywanym w szklanej, bezbarwnej butelce w temperaturze pokojowej, wartości liczby nadtlenkowej, liczby kwasowej oraz wskaźnika Totox przekroczyły dopuszczalne normy i wyniosły odpowiednio: LN = 5,6 meq $O_2 \cdot kg^{-1}$, LK = 4,27 mg $KOH \cdot g^{-1}$, wskaźnik Totox = 13. Oleje charakteryzowały się podobnym składem kwasów tłuszczowych, przy czym olej Kropa Zdrowia odznaczał się wyższą zawartością (średnio o 10%) kwasu oleinowego i niższą zawartością sumy kwasów linolowego i linolenowego (średnio o 11%) w porównaniu do pozostałych olejów. Wszystkie oleje spełniały normy co do wartości liczby zmydlania. Barwa olejów była zróżnicowana, ciemniejszą barwą odznaczały się oleje tłoczone. Spośród badanych olejów trzy z nich: Rapso, Olej Kujawski oraz Kropla Zdrowia wyróżniają się wysoką jakością sensoryczną, w pozostałych niższa jakość wynika prawdopodobnie z braku zachowania odpowiedniego reżimu technologicznego oraz nieprawidłowych warunków przechowywania.

Słowa kluczowe: olej rzepakowy, jakość sensoryczna, liczba nadtlenkowa, liczba kwasowa, profil tłuszczowy