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ANALYSIS OF OXIDATIVE CHANGES OCCURRING IN OLIVE OIL DURING STORAGE

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Key words: olive oil, oxidation, peroxide value, fatty acids, kinetic analysis

The objective of the studies was to determine oxidative changes in the stored olive oils. The analysis was based on the changes in peroxide values and the changes in fatty acid composition. Kinetic analysis methods were used to work out the results.

After 5 weeks storage at 21°C in the dark a significant increase in the value of peroxide value (11.6–15.3 $mEqO_2$/kg) occurred in the case of raw olive oils. All these olive oils are unsuitable for consumption. For other samples with refined olive oil added, the peroxide values are 3.6 – 7.6 $mEqO_2$/kg. The calculated values of the time of attaining the critical value of PV are very differentiated (5.3-9.5 week).

All the studied fat oxidation processes were of aw type, of the rate rising in time. They are characterised by various dynamics. It is confirmed by diverse process orders varying from 1.6 aw to 6.6 aw. It was found that the initial peroxide value does not decidedly affected the auto-oxidation process course nor on the time of reaching of critical value. Pressed olive oils proved to be more stable (n=1.6 aw and n=2.4 aw). After 5 weeks storage a minor decrease in the UFA content and a small increase in the SFA content occurred. Olive oil did not contain trans fatty acids.

INTRODUCTION

The Mediterranean diet, popular in Poland at present, ensures a daily consumption of polyunsaturated fatty acids of n-3 family at the level of about 1.50 g (calculated as alpha-linolenic acid C 18:3 (n-3)) [Marciniak-Łukasik & Krygier, 2004]. Olive oil is a nutritionally valuable vegetable fat because of its high fatty acid content MUFA (mainly oleic acid). It controls blood pressure, increases the assimilability of vitamins, exhibits anticancer properties [Daniewski *et al*., 2000]. Pressed and refined olive oil and their mixtures occur in commodity circulation on the Polish market. The olive oil comes from producers in Italy, Greece and Spain, and less often from France.

Fat is sensitive to many factors that can significantly lower its quality. One of the adverse processes that occur is auto-oxidation, which is a spontaneous reaction of oxygen with fat molecules that proceeds by the formation of corresponding radicals. The types and amounts of particular oxidation products depend on the fat type, comprised in them antioxidants and storage, including light, oxygen and temperature conditions [Ching Man Cheung, 2007; Siger, 2005; Flaczyk *et al.*, 2005; Tańska & Rotkiewicz, 2003; Wąsowicz, 2004].

It is purposeful to verify the quality of fat products, including olive oil, with respect to the fatty acid profile and hydroperoxide content. The determination of the peroxide value indicating the hydroperoxide content and fatty acid composition is recommended for fat quality assessment [Jerzewska, 1998; Marquez-Ruiz & Dobarganes, 1997; Płatek, 2004; Szukalska, 2003; Thurnhofer *et al.,* 2006].

The so-called normal test is best suitable for the assessment of changes in fat quality. The tested product is stored in household or warehouse conditions. Samples are analysed at appropriate time intervals. The occurring changes result in an increase in peroxide values and changes in fatty acid composition [Kondratowicz-Pietruszka, 2006; Kalua *et al.,* 2006; Luna *et al.,* 2006; Ratusz *et al*., 2005; Wąsowicz, 2004].

Compared with the accelerated test the normal test is more advantageous in the determination of ageing dynamics under consumer use conditions [Kondratowicz-Pietruszka *et al.,* 2001; Macebo-Campos *et al.*, 2007; Ostasz *et al.,* 2004].

Many works provide data on the variation of quality parameters including *e.g.* peroxide values during storage however the presented tabular summaries or graphical presentations are not sufficient for determining the dynamics of occurring processes [Hęś *et al.,* 2007; Florek *et al.,* 2007]. The method presented here allows for a better interpretation of the findings than general discussions found in many publications.

The methods of kinetic analysis allow process dynamics to be determined, the rates (of the same order, *n*) to be compared and the critical values to be calculated [Kondratowicz-Pietruszka *et al.,* 2001; Kondratowicz-Pietruszka, 2006, 1995].

The objective of the studies was to determine oxidative changes in the stored olive oils available on the Polish market. The analysis was based on the changes in peroxide values and the changes in fatty acid composition. Kinetic analysis methods were used to work out the results.

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MATERIAL AND METHODS

Olive oils purchased in retail shops in Cracow were the subject of the studies. The oils were denoted by the following symbols:

A – Olio Extra Vergine – first cold pressed olive oil produced by Costa d'Oro (Italy),
B – Goccia d'oro – first cold pressed olive oil produced by F.LLI RUATA (Italy),
C – Olivital – first cold pressed olive oil produced by Fraz. Baroli (Italy),
D – Olio di Sansa, Salvadori – a mixture of refined pomace olive oil and extra olive oil of first pressing produced by Salvadori (Italy),
E – Olio di Sansa di Oliva, Olive Pomace Oil – a mixture of refined pomace olive oil and extra olive oil of first pressing produced by Basso Fedele e Figli (Italy),
F – elisa – Pomace Olive Oil – a mixture of refined pomace olive oil and extra olive oil of first pressing. Only the distributor's address (Atlanta A.M. Sp.z o.o.) was given but not the oil producer (Spain).

The olive oils were characterised by the following initial parameters: peroxide value PV, acid value AcV and iodine value IV [Polish Standard PN-ISO 3960:2001; 3961:1998; 660:1999]. Table 1 presents the values of these parameters and demands Commission Regulation (EC) No 1989/2003.

All the olive oil samples were stored at 21°C in sealed bottles protected from light for 5 weeks. Samples of the olive oils were taken to be tested every week. Peroxide value determined by the iodometric method and the composition of higher fatty acids was used to assess oxidative changes in the olive oil. The fatty acids were analysed by GLC in the form of methyl esters in samples prepared with BF_3 according to the standard. The analysis was carried out on an SRI 9610C Gas Chromatograph fitted with a Restek RTX-2330 column of 105 m length and 0.25 mm in diameter and FID using hydrogen as the carrier gas. AOCS Standard #3 by Restek (Catalogue No. 35024) was applied as the quantitative standard [Polish Standard PN-ISO 5508:1996; PN-EN ISO 5509:2000; Riemersma, 2002].

The obtained experimental data was subjected to kinetic analysis [Brimberg & Kamal-Eldin, 2003; Kondratowicz-Pietruszka, 1995]. The aim of this analysis was to determine the dynamics of fat oxidation processes. By dynamics, we mean the variation in the rates V(PV) of peroxide value PV_t changes and accelerations A(PV) on the strictly defined path of the process. The order of the functions used for the description of the process is used as its index. This parameter is treated as the index of the elementary mechanism of the oxidation process event. The amount of these events increasing in time creates the process course path. The experimental curve and PV_t function that describes it makes the path of the process.

Equations of aw type describe the curves in Figure 1 [Kondratowicz-Pietruszka, 1995; Kondratowicz-Pietruszka *et al.,* 2001, 2002]. This type of curve is characterised by the rates rising in time.

Kinetic functions were applied to determine peroxide value variation dynamics in time. Rate constants w_n and the process order n were described using the following formula:

$$w_n = \frac{(PV_0^{1-n} - PV_t^{1-n})}{(n-1)\cdot t}$$

The variation of peroxide value in time was described by a function of the following form:

$$\hat{P}V_t = [PV_0^{1-n} - w_n \cdot (n-1)]^{\frac{1}{1-n}}$$

The accuracy of the description was defined by mean per cent deviation of empirical values from the calculated ones e_m.

Rate equations $\hat{V}$ (PV) and acceleration equations $\hat{A}$ (PV) were incorporated into the description:

$$\hat{V}(\mathrm{PV}) = \mathrm{wn}\cdot \mathrm{PV_t^n} = \mathrm{dPV_t/dt},\ (\mathrm{mEqO_2/kg})\cdot \mathrm{week^{-1}}),$$

$$, \mathrm{w_n} > 0, \mathrm{n} > 0,$$

$$\hat{A}(\mathrm{PV}) = \mathrm{w_n}\cdot \mathrm{n}\cdot \mathrm{PV_t^{n-1}} = \mathrm{a_n}\cdot \mathrm{PV_t^{n-1}} = \mathrm{d^2PV_t/dt^2},$$

$$(\mathrm{mEqO_2/kg})\cdot \mathrm{week^2},$$

where: w_n – rate constant of dimension $(mEqO_2/kg)^{1-n}\cdot week^{-1}$; n – dimensionless function order; and a_n – acceleration constant of dimension $(mEqO_2/kg)^{2-n}\cdot week^{-2}$.

The acceleration was identified with the aggressiveness of factors producing changes in PV_t and simultaneously with the susceptibility of the products to oxidation.

The time in which the individual olive oils studied attain the peroxide value accepted as critical [Commission Regula-

TABLE 1. Initial parameters of olive oil samples.

Olive	PV_0 (mEq O_2/kg)	PV /EC (mEq O_2/kg)	AcV_0 (mg KOH/g)	AcV/EC (mg KOH/g)	IV_0 (g I_2/100g)
A	9.3	≤20	1.68	≤0.8	128
B	9.1	≤20	1.73	≤2.0	134
C	7.0	≤20	1.52	≤2.0	130
D	2.4	≤15	1.05	≤1.0	118
E	4.6	≤15	1.56	≤1.0	116
F	2.6	≤15	1.60	≤1.0	118

tion (EC) No 1989/2003] was calculated from the equation (Table 1):

$$t_{crit.} = \frac{PV_0^{1-n} - PV_k^{1-n}}{w_n \cdot (n-1)}$$

RESULTS AND DISCUSSION

Figure 1 presents the changes in peroxide value. The per cent increase in the value of this parameter was diverse depending on the sample type. The final value of the peroxide value indicates a significant ageing of all samples. In the case of raw olive oils a considerable increase in the value of peroxide value occurred (11.6–15.3 $mEqO_2$/kg). Olive oils obtained by mixing raw oil with the refined contained less hydroperoxides. This was reflected in lower peroxide values (3.6–7.6 $mEqO_2$/kg).

Tables 2 and 3 present calculated values of the rate and acceleration of the changes in peroxide values for each process.

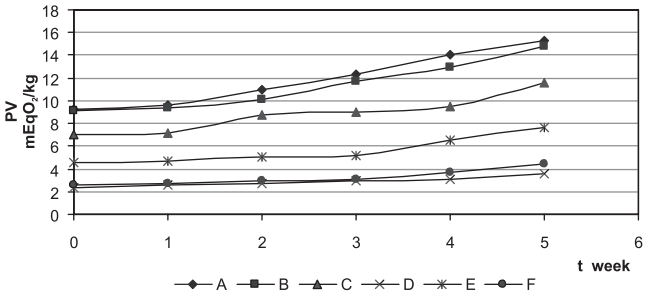

FIGURE 1. Changes peroxide value during storage.

TABLE 2. Values of rates in the changes in peroxide value for the stored samples.

t (week) \ Olive	$\hat{V}$ (PV) ($mEqO_2$/kg·week^{-1})					
	A	B	C	D	E	F
0	0.843	0.389	0.407	0.123	0.154	0.106
1	0.887	0.457	0.435	0.163	0.177	0.130
2	1.103	0.655	0.686	0.186	0.267	0.192
3	1.318	1.366	0.744	0.239	0.345	0.278
4	1.622	2.226	0.847	0.301	1.507	0.735
5	1.869	4.425	1.368	0.560	4.228	2.157

TABLE 3. Values of acceleration in the changes in peroxide value for the stored samples.

t (week) \ Olive	$\hat{A}$ (PV) ($mEqO_2$/kg·week^{-2})					
	A	B	C	D	E	F
0	0.145	0.214	0.727	0.178	0.221	0.221
1	0.148	0.243	0.756	0.218	0.249	0.262
2	0.160	0.324	0.985	0.240	0.352	0.361
3	0.171	0.584	1.033	0.286	0.439	0.488
4	0.185	0.863	1.115	0.338	1.530	1.082
5	0.195	1.495	1.474	0.527	3.673	2.610

Using the methods of qualimetric kinetics, the process order and the rate constant were calculated for each set of experimental data. Table 4 summarises:

– final values of peroxide values PV_k,

– the per cent rate and acceleration increase S_V, S_A:

$$S_V = \frac{V(PV_k)}{V(PV_0)} \cdot 100\,, \qquad S_A = \frac{A(PV_k)}{A(PV_0)} \cdot 100$$

– the order of the describing function and the rate constant.

The calculated values of the mean per cent deviation of the empirical data from the calculated ones indicate good fitting of the describing function. These values range from 1.1 to 2.8%. The sequence of setting the processes in Table 5 corresponds with decreasing dynamics of the occurring oxidation processes. The highest dynamics was shown by the process E of the highest order n=6.6 aw.

Based on the parameters from Table 4, functions describing the oxidative changes occurring in the studied fats are shown. Models are also given for the calculation of the process rates and the aggressiveness of factors that affect the changes in peroxide value (Table 5).

The calculated values of t_{crit} define the time after which a given olive oil attains the critical value of PV and should not be destined for consumption because of a too hydroperoxide content.

The composition of fatty acids is typical of the olive oil [Dubois *et al*., 2007, Olivier, 2003, Vichi, 2007]. Tables 6 and 7 present the results of the determination of individual fatty acids in samples of fresh olive oil and after storage period. Based on chromatographic analyses carried out it was found that the unsaturated acid UFA content ranges from 84.73% to 86.83%, in it 74.12–78.23% are monoenic MUFA and 6.70–11.49% are polyenic acids PUFA. The oleic acid content in the studied samples of olive oil from various producers varied between 73.15 and 77.42%.

The saturated fatty acid SFA content is higher than for example in rapeseed oil and ranged from 13.18% to 15.27% [Daniewski *et al.* 2000, Jerzewska.1998]. The calculated ratios of unsaturated UFA to saturated acid SFA contents varied for individual olive oils studied. They assume values from 5.55 to 6.59.

Comparing the ΣUFA/ΣSFA ratios in fresh olive oils and after 5 weeks storage it can be noticed that for the A, B and

TABLE 4. Values of parameters characterising the oxidative changes in olive oils.

Olive	PV_k	S_V (%)	S_A (%)	n	w_n ($(mEqO_2/kg)^{1-n}$·week^{-1})	e_m (%)
E	15.78	2749.0	1663.8	6.6 aw	$6.498 \cdot 10^{-6}$	2.4
F	4.50	2043.2	1180.5	5.5 aw	$5.510 \cdot 10^{-4}$	1.4
B	14.74	1137.9	699.7	5.0 aw	$6.232 \cdot 10^{-6}$	2.5
D	3.60	455.0	295.1	3.5 aw	$5.744 \cdot 10^{-3}$	1.4
C	11.60	336.1	202.8	2.4 aw	$3.814\ 10^{-3}$	2.9
A	15.30	221.8	134.8	1.6 aw	$2.378 \cdot 10^{-2}$	2.3

TABLE 5. Functions describing the rate of the changes in peroxide value and critical value $t_{crit.}$

Olive	$\hat{PV}_t$ (mEqO$_2$/kg)	$\hat{V}(PV)$ ((mEqO$_2$/kg)·week^{-1})	$\hat{A}(PV)$ ((mEqO$_2$/kg)·week^{-2})	$t_{crit.}$ (week)
A	$[9.3^{-0.6} - 2.378 \cdot 10^{-2} \cdot 0.6 \cdot t]^{-1.667}$	$2.378 \cdot 10^{-2} \cdot \hat{PV}_t^{1.6}$	$0.038 \cdot \hat{PV}_t^{0.6}$	6.8
B	$[9.1^{-4} - 6.232 \cdot 10^{-6} \cdot 4 \cdot t]^{-0.25}$	$6.232 \cdot 10^{-6} \cdot \hat{PV}_t^{5}$	$3.116 \cdot 10^{-5} \cdot \hat{PV}_t^{4}$	5.6
C	$[7.0^{-1.5} - 3.814 \cdot 10^{-3} \cdot 1.5 \cdot t]^{-0.667}$	$3.814 \cdot 10^{-3} \cdot \hat{PV}_t^{2.4}$	$9.535 \cdot 10^{-3} \cdot \hat{PV}_t^{1.4}$	9.5
D	$[2.4^{-2.5} - 5.744 \cdot 10^{-3} \cdot 2.5 \cdot t]^{-0.4}$	$5.744 \cdot 10^{-3} \cdot \hat{PV}_t^{3.5}$	$0.02 \cdot \hat{PV}_t^{2.5}$	7.7
E	$[4.6^{-5.6} - 6.498 \cdot 10^{-6} \cdot 5.6 \cdot t]^{-0.1786}$	$6.498 \cdot 10^{-6} \cdot \hat{PV}_t^{6.6}$	$4.29 \cdot 10^{-5} \cdot \hat{PV}_t^{5.6}$	5.3
F	$[2.6^{-4.5} - 5.510 \cdot 10^{-4} \cdot 4.5 \cdot t]^{-0.222}$	$5.510 \cdot 10^{-4} \cdot \hat{PV}_t^{5.5}$	$0.003 \cdot \hat{PV}_t^{4.5}$	5.5

TABLE 6. Fatty acids composition in fresh olive oils (%).

Fatty acids \ Olive	A	B	C	D	E	F
C 16:1 (cis-9)	1.02	0.81	0.81	0.96	0.71	0.86
C 18:1 (cis-9)	73.15	76.43	77.42	74.94	73.41	75.10
C 18:2 (cis-9.12)	9.86	7.69	6.08	10.37	10.74	9.14
C 18:3 (cis-9.12.15)	0.70	0.67	0.62	0.56	0.75	0.68
Σ UFA	84.73	85.60	84.93	86.83	85.61	85.78
Σ MUFA	74.17	77.24	78.23	75.90	74.12	75.96
Σ PUFA	10.56	8.36	6.70	10.93	11.49	9.82
C 16:0	12.13	11.13	11.34	9.96	10.99	10.65
C 18:0	2.67	2.80	3.30	2.72	2.86	3.09
C 20:0	0.47	0.47	0.41	0.50	0.51	0.48
Σ SFA	15.27	14.40	15.05	13.18	14.36	14.22
Σ UFA/Σ SFA	5.55	5.94	5.64	6.59	5.96	6.03

TABLE 7. Fatty acids composition after 5 weeks of storage (%).

Fatty acids \ Olive	A	B	C	D	E	F
C 16:1 (cis-9)	1.05	0.85	0.94	0.97	0.94	0.94
C 18:1 (cis-9)	73.31	76.09	77.45	73.72	72.92	74.48
C 18:2 (cis-9.12)	9.86	7.83	6.22	10.14	10.27	8.78
C 18:3 (cis-9.12.15)	0.69	0.72	0.68	0.64	0.69	0.76
Σ UFA	84.91	85.49	85.29	85.47	84.82	84.96
Σ MUFA	74.36	76.94	78.39	74.69	73.86	75.42
Σ PUFA	10.55	8.55	6.90	10.78	10.96	9.54
C 16:0	11.95	11.03	10.88	11.27	11.75	11.45
C 18:0	2.61	2.98	3.36	2.67	2.82	3.11
C 20:0	0.52	0.50	0.46	0.59	0.60	0.48
Σ SFA	15.08	14.51	14.70	14.53	15.17	15.04
Σ UFA/Σ SFA	5.63	5.89	5.80	5.88	5.59	5.65

C samples these ratios varied significantly in time. For the remaining olive oil samples the ΣUFA/ΣSFA ratios decreased by 0.71% for D, 0.37% for E and 0.38% for sample F. The results are evidence that adverse changes in UFA occurred. UFA content slightly decreased and SFA content increased to a small degree. No trans fatty acids were formed upon storage.

CONCLUSIONS

After 5 weeks storage at 21°C in the dark a significant increase in the value of peroxide value (11.6–15.3 mEqO$_2$/kg) occurred in the case of raw olive oils. For other samples with refined olive oil added, the peroxide values are 3.6–7.6 mEqO$_2$/kg. For individual olive oils the calculated t_{crit} values are very diversified. No relationship between time and olive oil type or its initial peroxide value can be shown.

All the studied fat oxidation processes were of aw type, of the rate rising in time. They are characterised by various dynamics. It is confirmed by diverse process orders varying from 1.6 aw (olive A) to 6.6 aw (olive E). The per cent rate and acceleration increase S_V, S_A are diversified for all olive oil samples.

It was found that the initial peroxide value does not decidedly affected the auto-oxidation process course. It was found that the initial peroxide value does not crucially affect the course of autoxidation process or the time of attaining the critical value of peroxide value. Pressed olive oils proved to be more stable: A (n=1.6 aw) and C (n=2.4 aw).

The fatty acid composition was typical of olive oil. The saturated fatty SFA acid profile is little diversified and on average is equal to 14.99%. The fatty acid MUFA content amounts on average to 75.69%, in it 75.08% is the average oleic acid content, the most characteristic of this type fat. After 5 weeks storage a minor decrease in the UFA content and a small increase in the SFA content occurred. Olive oil did not contain trans fatty acids.

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ANALIZA ZMIAN OKSYDACYJNYCH ZACHODZĄCYCH W OLIWIE Z OLIWEK W CZASIE PRZECHOWYWANIA

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Badano zmiany oksydacyjne w przechowywanych 5 tygodni oliwach z oliwek, w temperaturze 21°C, bez dostępu światła. W badaniach wykorzystano liczbę nadtlenkową oraz skład kwasów tłuszczowych. W opracowaniu wyników zastosowano metody analizy kinetycznej. Obliczono rzędy procesów, stałe szybkości oraz czasy osiągania wartości krytycznej liczby nadtlenkowej. Badane procesy oksydacji tłuszczów były typu aw, o narastającej szybkości w czasie. Charakteryzowały się one różną dynamiką, rzędy procesów wynosiły od n=1,6 aw do n=6,6 aw. Bardziej stabilne okazały oliwy tłoczone: A (n=1,6 aw), C (n=2,4 aw). W przypadku oliw surowych nastąpił znaczny wzrost wartości liczby nadtlenkowej (11,6–15,3 $mEqO_2$/kg). Dla pozostałych prób, z dodatkiem oliwy rafinowanej, wartości te wynosiły 3,6 – 7,6 $mEqO_2$/kg. Czasy osiągnięcia wartości krytycznej dla liczby nadtlenkowej w badanych oliwach wynosiły od 5,3 do 9,5 tygodni.

Po okresie przechowywania nastąpiło nieznaczne zmniejszenie się zawartości kwasów UFA oraz nieznaczny wzrost zawartości kwasów SFA. Porównując stosunki ΣUFA/ΣSFA w oliwach świeżych i po 5 tygodniach przechowywania stwierdzono, że dla prób A, B, C wartości te nie zmieniły się istotnie w czasie. Dla pozostałych prób oliwy stosunki te zmniejszyły się odpowiednio o wartość: 0,71% (D), 0,37% (E), 0,38% (F). Świadczy to o niekorzystnych zmianach w grupie kwasów UFA. Oliwy nie zawierały kwasów trans.