POLISH JOURNAL OF NATURAL SCIENCES
Abbrev.: Pol. J. Natur. Sc., Vol 27(2): 229–241, Y. 2012

COMPARISON OF THE QUALITY OF TWO CLASSES OF OLIVE OIL: EXTRA VIRGIN AND REFINED OIL

Marta Ambrosewicz, Małgorzata Tańska, Daniela Rotkiewicz

Chair of Plant Raw Materials Processing and Chemistry
University of Warmia and Mazury in Olsztyn

K e y w o r d s: olive oils, phenolic compounds, tocopherols, squalene, degree of hydrolysis, degree of oxidation, fatty acid composition.

A b s t r a c t

The aim of the study was to perform comparative characterisation of different olive oils with respect to important quality features. Two groups of olive oils, 4 samples of extra virgin oil and 4 samples of refined oils (2 *olive oil* and 2 *pomace*) were used as the study material. The quality features under analysis included: the content of phenolic compounds, tocopherols, squalene, products of hydrolysis and oxidation as well as the fatty acid composition.

The content of phenolic compounds, α-tocopherol and squalene in the oils used in the study varied significantly at the level of significance of 0.05. The *extra virgin* oils contained more phenolic compounds and squalene than the refined oils. On the other hand, the highest amount of α-tocopherol was found in refined *pomace* oils. The degree of hydrolysis and the degree of oxidation of *extra virgin* samples was higher than those of refined oils, which was indicated by a higher acid value and anisidine number for those products. The fatty acid composition in all the oil samples was typical of olive oils; however, the percentage of individual acids varied between the groups of oils under study and within each of them.

PORÓWNANIE JAKOŚCI DWÓCH KLAS OLEJÓW OLIWKOWYCH – EXTRA VIRGIN Z RAFINOWANYMI

Marta Ambrosewicz, Małgorzata Tańska, Daniela Rotkiewicz

Katedra Przetwórstwa i Chemii Surowców Roślinnych
Uniwersytet Warmińsko-Mazurski w Olsztynie

S ł o w a k l u c z o w e: oleje oliwkowe, związki fenolowe, tokoferole, skwalen, stopień hydrolizy, stopień utlenienia, skład kwasów tłuszczowych.

Address: Marta Ambrosewicz, University of Warmia and Mazury, pl. Cieszyński 1, 10-957 Olsztyn, Poland, phone: +48 (089) 523 33 99, e-mail: marta.ambrosewicz@uwm.edu.pl

Abstrakt

Celem badań była charakterystyka porównawcza różnych olejów oliwkowych pod względem ważnych wyróżników jakościowych. Materiał badawczy stanowiły 2 grupy olejów oliwkowych, 4 próbki *extra virgin* oraz 4 próbki olejów rafinowanych (2 *olive oil* oraz 2 *pomace*). Analizowanymi wyróżnikami jakościowymi były: zawartość związków fenolowych, tokoferoli, skwalenu, produktów hydrolizy i utleniania oraz skład kwasów tłuszczowych.

Wykazano, iż zawartość związków fenolowych, α-tokoferolu i skwalenu w badanych oliwach była istotne zróżnicowana na poziomie istotności 0.05. Oliwy *extra virgin* cechowały się wyższą zawartością związków fenolowych oraz skwalenu niż oleje rafinowane. Z kolei najwyższą zawartość α-tokoferolu stwierdzono w rafinowanych oliwach *pomace*. Stopień hydrolizy oraz utlenienia próbek oliwy *extra virgin* był wyższy niż olejów rafinowanych, o czym świadczyły wyższe wartości liczby kwasowej i anizydynowej tych produktów. Skład kwasów tłuszczowych wszystkich próbek olejów był charakterystyczny dla olejów oliwkowych, jednakże między badanymi grupami olejów oliwkowych, jak również w obrębie każdej z nich, stwierdzono zróżnicowanie udziału poszczególnych kwasów tłuszczowych.

Introduction

The European Union is the largest producer of olive oil, with Spain, Italy and Greece being the leading producers, together accounting for 75% of the world's olive oil (*IOOC* 2011). Other important producers include Turkey, Syria, Morocco and Tunisia. According to estimates by the *IOOC* (2011), the global production output and consumption in 2010/2011 amounted to about 3 million tonnes.

Oil quality depends on many factors, including olive variety, maturity of fruit and the harvesting method, the time between harvest and processing, processing technology (method of extraction, clarification, refinement), type of packaging and storage conditions (exposure to oxygen and light, change of the material and oil temperature). Agriclimatic factors, associated with the cultivation area, are also important (JELNICKA et al. 2008, KWIATKOWSKA 2007, PTASZNIK 2006). It is supposed that the quality features of olive oil may be affected by flavour additives, such as herbs (basil, thyme, estragon) and the addition of other vegetable oils (AMBROSEWICZ et al. 2011).

Growing interest in olive oil stems mainly from its beneficial effect on human health. Although oil contains small amounts of polyunsaturated fatty acids, it has a strong protective effect on the circulatory system and a beneficial effect on the function of the heart by reducing blood viscosity, coagulability and inhibits atherosclerosis (WATERMAN and LOCKWOOD 2007). A high content of oleic acid and antioxidants in oil, i.e. phenolic compounds (hydroxytyrosol, tyrosol and oleuropein), sterols and squalene, prevents formation of free radicals and peroxides, which slows down the ageing processes and explains its anticancer properties (WATERMAN and LOCKWOOD 2007, BENDINI et al. 2006, FLACZYK et al. 2004, PROCYK 2001, KOLANOWSKI 1998). The presence of those

compounds is also important for inhibition of oil oxidation, extending its shelf life period as compared to other oils. It has also been found that hydroxytyrosol, tyrosol and oleuropein have antibacterial properties with regard to strains which cause infections of the intestines and the respiratory system (WATERMAN and LOCKWOOD 2007).

Due to an increasing number of olive oil producers and the multitude of products on the market, the aim of the product was to compare the quality of two classes of olive oil, *extra virgin* with refined *olive oil* and *pomace*, available on the Olsztyn market.

Materials and Methods

Study material

Four *extra virgin* oil samples and 4 samples of refined oil, including 2 of *olive oil* and 2 of *pomace* oil were used as the study material (Table 1). They differed in shelf life period and type of packaging. All the oils were purchased at retail outlets in June 2010.

Table 1

Characterisation of the study material

Oils sample	Oil type	Packaging type	Usability period at the time of analyses (months)
O_1	*extra virgin* – oil extracted from fresh olives at the temperatures < 25°C within 24 h of harvest, with no chemical processes applied. Required acidity <0.8%	clear, light glass bottle	1
O_2	*extra virgin* – as above	clear, light glass bottle	15
O_3	*extra virgin* – as above	clear, light glass bottle	3
O_4	*extra virgin* – as above	clear, light glass bottle	17
O_5	*olive oil* – oil which contains refined oil and extra virgin oil	clear bottle made of emerald glass	1
O_6	*olive oil* – as above	clear bottle made of emerald glass	15
O_7	*pomace* – refined oil extracted from olive pomace	clear, light glass bottle	1
O_8	*pomace* – as above	clear, light glass bottle	11

Methods

The study involved determination of antioxidants (phenolic compounds, tocopherols, squalene), degree of hydrolysis (acid value), degree of oxidation (peroxide number, anisidine number, content of coupled diene and triene fatty acids and fatty acid composition.

The phenolic compound content was determined by the spectrophotometric method described by RIBEREAU-GAYON (1972). Samples for analysis were prepared by the method described by KANIA et al. (2004). Absorbance was measured by a UNICAM UV/Vis UV2 spectrophotometer. The total phenolic compound content was calculated from the standard curve prepared for different concentrations of D-catechol.

Tocopherols were determined by RP-HPLC using the method described by GIMENO et al. (2000). The compounds were separated with a liquid chromatography analyser (manufactured by Agilent Technologies, series 1200) and a fluorescence detector (a LiChrospher Si 60,5 μm column [250 mm × 4 mm] by Merck) and 0.7% solution of isopropanol in hexane as the mobile phase. Tocopherol isomers were identified by their retention times determined for the standards of those compounds, supplied by Merck.

Squalene content was determined by the method described by CZAPLICKI et al. (2009). The analysis was performed with a liquid chromatography analyser manufactured by Agilent Technologies, series 1200, and a photodiode detector and a LiChrospher RP-18, 5 μm column (250 × 4.6 mm). A mixture of isopropanol, acetonitrile, hexane was used as the mobile phase. Squalene detection was conducted at the wavelength of 218 nm. The quantitative analysis was based on the standard curve plotted for a standard supplied by Sigma-Aldrich.

The degree of hydrolysis of the olive oils was found by determination of the acid values in accordance with the standard PN-ISO 660:1998 (*Oleje i tłuszcze*. PN-ISO 660:1998).

The degree of oxidation of the olive oils was determined by determination of the peroxide number (*Oleje i tłuszcze*. PN-ISO 3960:1996), anisidine number (*Tłuszcze*. PN-93/A-86926) and the content of coupled diene and triene acids (*Ultraviolet*. AOCS Standard. Official method Cd 7-58:1973).

Fatty acid composition in olive oils was determined in accordance with PN-EN ISO-5508:96, by preparing methyl esters in accordance with *Oleje i tłuszcze.* PN-EN ISO-5509:2001.

Statistical analysis

Obtained results of researches were statistically analyzed using the Statictica 9.0 PL (StatSoft Poland) program. In order to indicate significance of differences between oils of peanut samples unvaried analysis of variance (ANOVA) with Tukey's test of $p \leq 0.05$ significance level was used. Moreover, there were determined Pearson correlation coefficients (r) between individual quality factors.

Results and discussion

Antioxidants

The content of antioxidants, i.e. phenolic compounds, tocopherols and squalene, varied significantly in the olive oils under study (Table 2).

Table 2

The content of phenolic compounds, α-tocopherol and squalene in olive oils

Specification	Olive oils							
	extra virgin				oilve oil		pomace	
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8
Phenolic compounds [mg kg^{-1}]	$19.4^{b} \pm 2.92$	$52.6^{d} \pm 4.90$	$30.0^{bc} \pm 0.95$	$40.1^{c} \pm 3.25$	$1.8^{a} \pm 0.66$	$3.1^{a} \pm 0.69$	$4.2^{a} \pm 0.59$	$4.7^{a} \pm 0.08$
α-tocopherols [mg 100 g^{-1}]	$35.9^{e} \pm 0.28$	$32.4^{a} \pm 0.58$	$32.1^{a} \pm 0.34$	$23.0^{b} \pm 0.79$	$27.2^{d} \pm 0.30$	$24.1^{c} \pm 0.21$	$73.5^{g} \pm 0.28$	$71.1^{f} \pm 0.30$
Squalene [mg 100 g^{-1}]	$458.6^{h} \pm 1.23$	$406.8^{g} \pm 2.20$	$248.9^{f} \pm 0.45$	$212.8^{e} \pm 0.53$	$118.9^{d} \pm 2.63$	$66.3^{a} \pm 0.42$	$109.3^{c} \pm 2.61$	$96.7^{b} \pm 0.65$

The content of phenolic compounds varied within a broad range from 1.8 to 52.6 mg kg^{-1} (Table 2). The highest and the most varied content of those compounds was found in *extra virgin* oils (O_1–O_4, 19.4–52.6 mg kg^{-1}), while the lowest, 2.4 mg kg^{-1} on average, in *olive oil* O_5 and O_6. The content of phenolic compounds in samples of *pomace* oil O_7 and O_8 was equal to 4.2 and 4.7 mg kg^{-1}, respectively. OWEN and TUCK and HAYBALL (cit. WATERMAN and LOCKWOOD 2007) report that, in general, *extra virgin* oils contain more phenolic compounds than refined oils. GÓMEZ-CARAVACA et al. (2007) and TSIMIDOUR et al. (2005) examined the effect of filtration of olive oil on phenolic compounds content and their oxidative stability and found non-filtered oils to contain more such compounds and are oxidised more slowly than filtered oils.

Phenolic compounds present in oil are responsible for its stability, smell and bitterish taste. They inhibit oxidation processes through various mechanisms, for example, by free radical sweeping, transfer of a hydrogen atom and by chelating metal ions (BENDINI et al. 2007). OWEN et al. (cit. WATERMAN and LOCKWOOD 2007) report that phenolic compounds present in oil can remove free radicals formed in faeces matrix, which prevents development of colorectal cancer.

An analysis of tocopherol content revealed only the presence of α-tocopherol. The isomer content in the oils under study ranged from 23.0 mg kg^{-1} (*extra virgin* oil O_4) to 73.5 mg kg^{-1} (*pomace* oil O_7) (Table 2). The differences in α-tocopherol content were also found to exist both between two classes of olive oil and within samples of the same class. E*xtra virgin* oils (O_1–O_4) differed by about 13.0 mg content of the compound per kg of oil. O*live oils* contained three times less α-tocopherol than pomace oils. GLISZCZYŃSKA-ŚWIGŁO et al. (2007) analysed tocopherol content, e.g. in *extra virgin* oil, and found a much higher value for the α form (163.0 mg kg^{-1}) as well as the presence of other isomers, i.e. β, γ and δ. PSOMIADOU et al. (2000) analysed tocopherol content in 25 samples of Greek oil and found 15 of them to contain more than 200 mg of tocopherol per kg. BASUNY et al. (2008) showed that the tocopherol content in extra virgin oil depended on the olive variety and on whether olives were stoned prior to oil extraction. The authors found olive oils from unstoned olives to contain less tocopherol than oils from stoned fruit. ANTONOPOULOS et al. (2006) found the decrease in tocopherol content in refined oils to be a result of using steam, high temperature and pressure in oil deodorisation.

Tocopherols are natural antioxidants which protect oils from free radicals, reactive oxygen species and peroxides (STUCHLÍK and ŽÁK 2002). The main physiological functions of tocopherols include preventing peroxidation of lipids during the seeds' resting period, their germination and early development of seedlings (SATTLER et al. 2004). According to AZZI and STOCKER (cit. GLISZCZYŃSKA-ŚWIGŁO et al. 2007) they may have a beneficial effect on human health by prevention of such diseases as atherosclerosis, cataract, cancers and neural tube defects.

Squalene content in the oils under study ranged from 66.28 to 458.59 mg/100 g (Table 2). The highest, and at the same time the most varied, content of the compound was found in the four extra virgin oil samples, with O_1 and O_2 samples containing 406.8–458.6 mg/100 g, while O_3 and O_4 contained nearly twice less of it (212.8 and 248.9 mg/100 g, respectively). Squalene content in *olive oil* O_5 and O_6 samples was equal to 66.28 and 118.94 mg/100 g, whereas in the *pomace* oil O_7 and O_8 samples – about 103 mg/100 g. OWEN et al. (cit. WATERMAN and LOCKWOOD 2007) report that *extra virgin* oils contain only a little more of the compound as compared to refined oils.

Squalene is a three-pentene hydrocarbon and the main mediator in the synthesis of plant and animal steroids. According to NEWMARK (1997), the content of the compound in olive oil is about 0.7%, whereas it ranges from 0.002 to 0.03% in other animal and plant oils (LIU et al. 1976). NEWMARK (1997) also reported that food control units use the compound assay as an indicator of commercial purity of olive oil. Squalene has antioxidant properties and owing to its structure it is more effective in sweeping singlet oxygen species than hydroxyl radicals (WATERMAN and LOCKWOOD 2007). Its highest concentration in the human body was found in the skin (12%), whereas its content in the adipose tissue ranges from 0.001 to 0.04%. There is a high probability of the presence of a reactive singlet oxygen species in skin exposed to high levels of UV radiation, but a high concentration of the squalene in it may produce a chemopreventive effect (NEWMARK 1997). OWEN et al. (cit. WATERMAN and LOCKWOOD 2007) report that epidemiological studies conducted on a population using a Mediterranean diet with a high squalene content have confirmed that the compound reduces the risk of skin cancer occurrence.

Degree of hydrolysis

The acid values for the oils under study ranged from 0.14 to 1.03 mg KOH g^{-1} (Table 3). The highest values were found for the *extra virgin* oils (O_1–O_4), but they did not exceed the highest acceptable value for extra virgin edible oils, i.e. 4 mg KOH g^{-1} (*Tłuszcze*. ZN-94/SGO-01). Samples of *olive oil* (O_5 and O_6) and *pomace* oil (O_8) had low values of the degree of hydrolysis, indicated by the acid values, which did not exceed the highest acceptable value for refined vegetable oil – 0.3 mg KOH g^{-1} (*Oleje i tłuszcze*... PN-A-86908:2000). Only a sample of oil O_7 did not meet the criteria set out in the standard, which can be attributed to the fact that the oil was at the end of its shelf life (1 month) and to probable failure to meet the required storage conditions by the trade entities, i.e. wholesalers and retailers. The lower acid values of refined olive oil were probably caused by the removal of free fatty acids in the refinement process, i.e. in dehydration. TAŃSKA and ROTKIEWICZ (2003) analysed two commercial *extra virgin* oils and found higher acid values of 1.68 and 1.75 mg KOH g^{-1}. TYNEK and SZUKALSKA (2006) analysed, *inter alia*, *extra virgin* and *pomace* oils and found the values of the quality feature similar to those determined in this study.

Table 3

Discriminate of olive oils technological value

Gualitative discriminants	Olive oils							
	extra virgin				oilve oil		pomace	
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8
Acid value [mg KOH g^{-1}]	$0.67^{e} \pm 0.001$	$0.53^{d} \pm 0.040$	$1.03^{g} \pm 0.041$	$0.83^{f} \pm 0.001$	$0.17^{a} \pm 0.000$	$0.14^{a} \pm 0.040$	$0.44^{c} \pm 0.003$	$0.22^{d} \pm 0.001$
Peroxide value [mEq O_2 kg^{-1}]	$0.62^{a} \pm 0.045$	$0.51^{b} \pm 0.001$	$0.58^{a} \pm 0.001$	$0.57^{ab} \pm 0.003$	$1.60^{f} \pm 0.033$	$1.51^{e} \pm 0.070$	$1.31^{d} \pm 0.018$	$1.01^{c} \pm 0.010$
Anisidine value	$9.18^{e} \pm 0.27$	$5.39^{b} \pm 0.15$	$7.04^{c} \pm 0.05$	$7.06^{c} \pm 0.83$	$6.27^{d} \pm 0.35$	$3.43^{a} \pm 0.07$	$5.42^{b} \pm 0.02$	$3.62^{a} \pm 0.07$
Conjugated compounds [%]								
Diene	$0.12^{bc} \pm 0.003$	$0.12^{bc} \pm 0.004$	$0.21^{ad} \pm 0.004$	$0.11^{b} \pm 0.047$	$0.16^{cd} \pm 0.012$	$0.22^{a} \pm 0.000$	$0.22^{a} \pm 0.041$	$0.23^{a} \pm 0.014$
Triene	$0.001^{e} \pm 0.000$	$0.000^{a} \pm 0.000$	$0.014^{d} \pm 0.000$	$0.000^{a} \pm 0.000$	$0.000^{a} \pm 0.000$	$0.000^{a} \pm 0.000$	$0.009^{b} \pm 0.000$	$0.012^{c} \pm 0.001$

Degree of oxidation

The peroxide number ranged from 0.51–1.60 mEq O_2 kg^{-1}, which indicates a very low degree of the oils oxidation (Table 3). Samples of *extra virgin* oils had similar values of the feature, ranging from 0.51 to 0.62 mEq O_2 kg^{-1}. The highest acceptable peroxide number for extra virgin oils is 10 mEq O_2 kg^{-1} (*Tłuszcze...* ZN-94/SGO-01). The peroxide number for refined olive oils did not exceed the highest acceptable value of 5 mEq O_2 kg^{-1} (*Oleje i tłuszcze...* PN-A-86908:2000) (Table 3).

The values of anisidine number, which describes the content of secondary oxidation products (JERZEWSKA 1991), were statistically different for individual oils and ranged from 3.43 to 9.18 (Table 3). MAKAREVICIENE and JANULIS report that the maximum value of the anisidine number for extra virgin oils should not exceed 3 units. The samples of extra virgin oils analysed in this study had much higher values of the feature (5.39–9.18) – Table 3. The high degree of oxidation of the oils was probably caused by the use by the producer of packages which did not protect the oils against light and the final part of the shelf life of two samples: O_1 and O_3 (1 and 3 months). The anisidine numbers for refined olive oils did not exceed 8, which is the highest value accepted by the standard for refined oils. TYNEK and SZUKALSKA (2006) analysed extra virgin oils and pomace oils and found the feature to have a lower value for extra virgin oils. TAŃSKA and ROTKIEWICZ (2003) found much higher values of the anisidine number for *extra virgin* (about 13).

The content of coupled diene acids in oils was low and ranged from 0.11 to 0.23% (Table 3). A generally higher content of such compounds was found in refined *olive oil* and *pomace oil*. TAŃSKA and ROTKIEWICZ (2003) analysed two *extra virgin* olive oils and found coupled diene acids at similar content.

The content of coupled triene acids in oils was low and it did not exceed 0.014% (Table 3). Of the eight analysed olive oils, those compounds were not found in four of them (O_2, O_4, O_5 and O_6). Olive oils analysed by TAŃSKA and ROTKIEWICZ (2003) also contained coupled triene acids at low concentrations.

Fatty acids' composition

The analysis results revealed significant differentiation of the fatty acids; composition in olive oils (Table 4).

Table 4

The share [%] of fatty acid of olive oils [%]

Olive oils		Fatty acids						
		$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	others
Extra virgin	O_1	$11.19^{b} \pm 0.02$	$0.53^{a} \pm 0.06$	$3.23^{c} \pm 0.07$	$80.42^{h} \pm 1.00$	$4.23^{c} \pm 0.34$	$0.34^{bc} \pm 0.00$	$0.06^{a} \pm 0.01$
	O_2	$14.13^{e} \pm 0.04$	$0.81^{c} \pm 0.07$	$2.78^{ab} \pm 0.06$	$76.52^{d} \pm 5.41$	$5.41^{e} \pm 0.06$	$0.33^{b} \pm 0.04$	$0.00^{a} \pm 0.00$
	O_3	$14.81^{g} \pm 0.071$	$0.93^{b} \pm 0.04$	$2.86^{b} \pm 0.04$	$77.57^{f} \pm 0.07$	$3.83^{b} \pm 0.00$	$0.00^{a} \pm 0.00$	$0.00^{a} \pm 0.00$
	O_4	$14.70^{f} \pm 0.01$	$0.97^{b} \pm 0.00$	$2.44^{d} \pm 0.01$	$74.84^{b} \pm 0.07$	$7.04^{a} \pm 0.08$	$0.00^{a} \pm 0.00$	$0.00^{a} \pm 0.00$
Olive oil	O_5	$12.60^{d} \pm 0.07$	$0.61^{a} \pm 0.06$	$3.13^{c} \pm 0.03$	$79.25^{g} \pm 0.06$	$4.41^{d} \pm 0.04$	$0.00^{a} \pm 0.00$	$0.00^{a} \pm 0.00$
	O_6	$17.16^{h} \pm 0.09$	$1.66^{d} \pm 0.01$	$2.69^{a} \pm 0.09$	$67.56^{a} \pm 0.13$	$10.52^{g} \pm 0.00$	$0.40^{c} \pm 0.00$	$0.00^{a} \pm 0.00$
Pomace	O_7	$12.41^{c} \pm 0.06$	$0.59^{a} \pm 0.04$	$2.81^{ab} \pm 0.11$	$76.84^{e} \pm 0.03$	$7.04^{a} \pm 0.00$	$0.00^{a} \pm 0.00$	$0.31^{b} \pm 0.09$
	O_8	$10.42^{a} \pm 0.03$	$0.54^{a} \pm 0.06$	$3.24^{c} \pm 0.03$	$75.33^{c} \pm 0.04$	$9.94^{f} \pm 0.06$	$0.52^{d} \pm 0.04$	$0.01^{a} \pm 0.00$

Oleic acid, which accounts for 67.56 (O_6) to 80.42% (O_1) of the total (Table 4), is the dominant fatty acid in the oils under study. Its highest average content, 74.84 to 80.42%, was found in *extra virgin* oils O_1–O_4. The lowest and the most varied content of oleic acid was found in *olive oils* O_5 and O_6 (79.25 and 67.56%). This acid accounted for 76.84 and 75.33% of total acids in *pomace* oils O_7 and O_8. The results in this study were similar to the findings of studies by TYNEK and SZUKALSKA (2006) as well as by TAŃSKA and ROTKIEWICZ (2003).

A molecule of oleic acid contains one double bond, so it is regarded as less susceptible to oxidation than polyunsaturated fatty acids (WATERMAN and

LOCKWOOD 2007). According to literature data, the oxidation rate of the acid is 10–40 times lower than linoleic acid (DROZDOWSKI 2002, FREGA et al. 1999). Owing to a high content of oleic acid, olive oil is regarded as an oil with high oxidative stability, which gives it a long shelf life (BENDINI et al. 2006). Monounsaturated fatty acids are thought to reduce the risk of cardiovascular diseases by lowering the level of triacylglycerols, total cholesterol and its LDL fraction (GILL et al. 2003, KRIS-ETHERTON et al. 1999). Literature reports contain some information about the anticancer properties of oleic acid, but the data are inconclusive (WATERMAN and LOCKWOOD 2007).

Polyunsaturated fatty acids in the oils under study were represented by linoleic acid, which accounted for 3.83–10.52% of the total fatty acids (Table 4). The most varied content of the acid was found in samples of *olive oil* (O_5 and O_6), where the difference was as high as about 6.0 percentage points. Linoleic acid accounted for 3.83–7.04% of total acids in *extra virgin* oils and for 7.04 and 9.94% in *pomace* oils O_7 and O_8.

Of the eight oil samples, the presence of h-linolenic acid was not found in four of them (O_3–O_5 and O_7). In the other samples, the acid accounted for 0.33–0.52% of the total acids.

In total, saturated fatty acids, palmitic and stearic, accounted for 13.66 (O_8) to 19.85% (O_6) of all the acids, with palmitic acid dominating and accounting for >76% of total saturated acids (Table 4). The average content of saturated fatty acids in *extra virgin* O_1–O_4 was about 16.5%, whereas in *pomace* oils O_7 and O_8 it was 14.4%. The most varied in this regard were *olive oils* O_5 and O_6, in which the percentage of the acids was 15.22 and 13.66%, respectively. Both TYNEK and SZUKALSKA (2006) and TAŃSKA and ROTKIEWICZ (2003) found a lower content of saturated fatty acids in the oils they analysed.

Correlations

An analysis of correlation coefficients between the features which describe the degree of hydrolysis and the degree of oxidation of olive oils and the content of antioxidants revealed the existence of significant relationships only in several cases (Table 5). Acid value was negatively correlated with the content of phenolic compounds and squalene, for both: r = -0.86. The peroxide number increased with a decrease in squalene content (r = -0.78). The content of coupled diene acids was negatively correlated with the content of phenolic compounds and squalene.

Tabela 5
Significant correlation between individual quality factors of olive oils (Pearson correlation coefficients – *r*)

Discriminants	Phenolic compounds [mg kg^{-1}]	Tocopherols [mg kg^{-1}]	Squalene [mg/100 g]	Oleic acid [%]	Linoleic acid [%]
Acid value [mg KOH g^{-1}]	-0.86	–	-0.86	–	–
Peroxide value [mEq O_2 kg^{-1}]	–	–	-0.78	–	–
Anisidine value	–	–	–	0.73	-0.82
Conjugated diene fatty acids [%]	-0.71	–	-0.75	–	–
Conjugated triene fatty acids [%]	–	–	–	–	–

Conclusion

Extra virgin oils have considerably higher nutritional value than refined oils (*olive oil*, *pomace oil*). Higher nutritional value of *extra virgin* oils is a result of much higher content of phenolic compounds and squalene, which protects oil from excessive hydrolysis and oxidation, thereby protecting a consumer from consuming toxic oxidation products. This is indicated by the negative correlation coefficients between those compounds and the numbers which describe the degree of hydrolysis and degree of oxidation. A lower α-tocopherol content in *extra virgin* oils seems to be of lesser importance because no significant correlation was found to exist between the compound content and the characteristic numbers for the oils. Growing consumer awareness of the wholesomeness of olive oil, which results from a high content of antioxidants and oleic acid, has led to an increase in interest in the product. Producers want to increase the competitiveness of olive oils by producing refined oils with additives, i.e. spices and flavours, to persuade consumers to buy their product. However, one should think about whether such oils meet consumers' expectations not only with respect to their flavour and taste, but also to their nutritional value and durability.

Translated by JOANNA JENSEN

Accepted for print 24.11.2011

References

ANTONOPOULOS K., VALET N., SPIRATOS D., SIRAGAKIS G. 2006. *Olive oil and pomace olive oil processing*. Grasas y aceites, 57(1): 56–67.

AMBROSEWICZ M., ROTKIEWICZ D., TAŃSKA M. 2012. *Evaluation method of labellimg of vegetable oils on the Olsztyn mosket*. Pol. J. Natur. Sc., 27(1): 67–79

Analiza estrów metylowych kwasów tłuszczowych metodą chromatografii gazowej. PN-EN ISO 5508.

BASUNY A.M.M., DALIA A.M.S., MOSTFA M.M. 2008. *Virgin olive oil quality: relationship between bioactive components and organoleptic evaluation*. Alex. J. Fd. Sci. & Tchnol., *special volume conference*, 21–29.

BENDINI A., CERRETANI L., CARRASCO-PANCORBO A., GÓMEZ-CARAVACA A., SEGURA-CARRETERO A., FERNÁNDEZ-GUTIÉRREZ A., LECKER G. 2007. *Phenolic molecules in virgin olive oils: a survey of their sensory properties, health effects, antioxidant activity and analytical methods. An overview of the last decade*. Molecules, 12: 1679–1719.

BENDINI A., CERRETANI L., VECCHI S., CARRASCO-PANCORBO A., LERCKER G. 2006. *Protective effects of extra virgin olive oil phenolics on oxidative stability in the presence or absence of copper ions*. J. Agric. Food Chem., 54: 4880–4887.

CZAPLICKI S., ZADERNOWSKI R., OGRODOWSKA D. 2009. *Triacylglycerols from viper bugloss (Echium vulgare L.) seed bio-oil*. Eur. J. Lipid Sci. Technol., 111: 1266–1269.

DROZDOWSKI B. 2002. Lipidy. Rozdział 7. [In:] W.E. Sikorski, *Chemia żywności*. Warszawa, WNT.

FLACZYK E., RUDZIŃSKA M., GÓRECKA D., SZCZEPANIAK B., KLIMCZAK S., KORCZAK J. 2004. *Ocena wybranych wskaźników jakościowych przechowywanej oliwy „extra virgin"*. Rośliny Oleiste, 25(1): 213–224.

FREGA N., MOZZON M., LERCKER G. 1999. *Effect of free fatty acids on oxidative stability of vegetable oil*. J. Amer. Oil Chem. Soc., 76(3): 325–329.

GILL J., BROWN J., CASLAKE M., WRIGHT D., COONEL J., BEDFORD D., HUGHES D.A., STANLEY J.C., PACKARD CH.J. 2003. *Effects of dietary monounsaturated fatty acids on lipoprotein concentrations, compositions, and subfraction distributions and on lipoprotein concentrations, compositions, and subfraction distributions and on VLDL apolipoprotein B kinetics*. Am. J. Clin. Nutr., 78(1): 47–56.

GIMENO E., CASTELLOTE A., LAMUELA-RAVENTOS R., DE LA TORRE M. 2000. *Rapid determinatoin of vitamin E in vegetable oils by reversed-phase high-performance chromatography*. J. Chromatogr. A., 881: 251–254.

GLISZCZYŃSKA-ŚWIGŁO A., SIKORSKA E., KHMELINS I., SIKORSKI M. 2007. *Tocopherol content in edible plant oils*. Pol. J. Food Nutr. Sci., 4(A): 157–161.

GÓMEZ-CARAVACA A., CERRETANI L., BENDINI A., SEGURA-CARRETERO A., FERNÁNDEZ-GUTIÉRREZ A., LERCKER G. 2007. *Effect of filtration systems on the phenolic content in virgin olive oil by HPLC-DAD-MSD*. Am. J. Food Technol., 2(7): 671–678.

IOOC. 2011. International Olive Oil Council. www.internationaloliveoil.org.

JELNICKA K., PTASZNIK S. 2008. *Ocena sensoryczna wybranych gatunków oliwy z oliwek extra virgin*. Tłuszcze Jadalne, 43(3–4), 77–88.

JERZEWSKA M. 1991. *Wprowadzenie metody oznaczenia liczby anizydynowej i współczynnika Totox w olejach roślinnych do krajowej praktyki laboratoryjnej*. Rocz. Inst. Przem. Mięs. Tłuszcz., 28: 108–117.

KANIA M., MICHALAK M., GOGOLEWSKI M., HOFFMANN A. 2004. *Antioxidative potential of substances contained in cold Pressem soybean oil and after each chase of refining process*. Acta Sci. Pol., Technol. Aliment., 3(1): 113–121.

KOLANOWSKI W. 1998. *Oliwa czy olej oliwkowy – podstawa diety śródziemnomorskiej. Charakterystyka, klasyfikacja, znaczenie zdrowotne*. Żywność, Żywienie a Zdrowie, 3: 285–290.

KRIS-ETHERTON P., PEARSON T., WAN Y., HARGROVE R., MORIARTY K., FISHELL V., ETHERTON T.D. 1999. *High – monounsaturated fatty acids diets lower both plasma cholesterol and triacyloglicerol concentration*. Am. J. Clin. Nutr., 70(6): 1009–1015.

KWIATKOWSKA E. 2007. *Właściwości zdrowotne oliwy z oliwek*. Postępy Fitoterapii, 3: 168–171.

LIU C., AHRENS E., SCHREIBMAN H., CROUSE R. 1976. *Measurement of squalene in human tissues and plasma: validation and application*. J. Lipid Res., 17: 38–45.

MAKAREVICIENE V., JANULIS P. *Analiza jakości olejów jadalnych oraz obowiązkowe wymagania*. Tłuszcze Jadalne, 34(1–2): 15–32.

NEWMARK H. 1997. *Squalene, olive oil, and cancer risk: a review and hypothesis*. Cancer Epidemiol. Biomarkers Prev., 6: 1101–1103.

Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczby kwasowej i kwasowości. PN-ISO 660:1998.

Oleje i tłuszcze roślinne oraz zwierzęce. Oznaczanie liczny nadtlenkowej. PN-ISO 3960:1996.

Oleje i tłuszcze roślinne oraz zwierzęce. Przygotowanie estrów metylowych kwasów tłuszczowych. PN-EN ISO-5509:2001.

Oleje i tłuszcze roślinne oraz zwierzęce. Rafinowane oleje roślinne. PN-A-86908:2000.

PROCYK A. 2001. *Oliwa europejska.* Wiadomości Zielaskie, 43(5): 3–16.

PSOMIADOU E., TSIMIDOU M., BOSOKU D. 2000. *Alpha-tocopherol content of Greek virgin olive oils.* J. Agric. Food Chem., 48(5): 1770–1775.

PTASZNIK S. 2006. *Oliwa z oliwek – historia a rzeczywistość, skład chemiczny i aspekty jakościowe*. Tłuszcze Jadalne, 41(1–2): 3–16.

SATTLER S., GILLILAND L., MAGALLANES-LUNDBACK M., POLLARD M., DELLAPENN D. 2004. *Vitamin E is essential for seed longevity and for preventing lipid peroxidation during germination*. The Plant Cell, 16: 1419–1432.

STUCHLÍK M., ŽÁK S. 2002. *Vegetable lipids as components of functional foods*. Biomed. Papers, 146(2): 3–10.

TAŃSKA M., ROTKIEWICZ D. 2003. *Stopień przemian lipidów wybranych olejów roślinnych i konsumpcyjnych nasion oleistych.* Tłusz. Jad., 38(3/4): 147–155.

Tłuszcze roślinne jadalne. Oleje tłoczone na zimno. ZN-94/SGO-01.

Tłuszcze roślinne jadalne. Oznaczanie liczby anizydynowej oraz obliczanie wskaźnika oksydacji tłuszczu Totox. PN-93/A-86926.