Biochemical Parameters and Oxidative Resistance to Thermal Treatment of Refined and Unrefined Vegetable Edible Oils

Rajko VIDRIH[1], Sergeja VIDAKOVIČ[2] and Helena ABRAMOVIČ[1]

[1]Department of Food Science and Technology, Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia; [2]Emona Nutrition Research and Development Centre, Ljubljana, Slovenia

Abstract

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In human nutrition fats are physiologically important food constituents but also the components most liable to oxidative degradation. The oils included in the study were refined (sunflower, extra-sunflower, soybean, and rapeseed) as well as unrefined (olive and pumpkin-seed) oils. The aim of our study was to determine the fatty acid composition, tocopherol content, and quality parameters such as the free fatty acid content, peroxide value, and induction time. Extra virgin olive oil had the highest average peroxide value, while unrefined pumpkin seed oil had the lowest one. The acid value of the unrefined oils was higher on average than that of the refined oils. Soybean oil had the highest total tocopherol content and extra virgin olive oil the lowest one. The refined oils with higher contents of saturated and monounsaturated fatty acids and lower polyunsaturated fatty acid contents had a high oxidative stability. A negative correlation has been found in the oils between the induction time and polyunsaturated fatty acid content. Among the oils investigated, unrefined pumpkin seed oil was the most oxidatively stable, the other oils following in the decreasing order: extra virgin olive > high oleic sunflower > rapeseed > soybean > sunflower oil. The oxidative stability of the unrefined oils was better than that of the refined oils.

Keywords: vegetable oils; oxidative stability; tocopherols; fatty acid composition

Vegetable oil is regarded as an important component of the diet because it is an important source of energy, as well as of essential fatty acids. The crude oil that is extracted from oilseeds or fruit pulp is a mixture of free fatty acids, mono-, di-, and triglycerides, phosphatides, pigments, sterols, and tocopherols. Trace amounts of metals, flavonoids, tannins, and glycolipids may also be present (O'Brien 2004).

A considerable body of research demonstrates that specific fatty acids, especially long chain polyunsaturated fatty acids (PUFA), are more than just a source of energy. Two types of PUFA, the *n*-6 and *n*-3 fatty acids, are essential substrates in the body for many of the regulatory lipids and structural elements of cell membranes. It can be assumed that all of the *n*-6 and *n*-3 fatty acids found in the body are derived from dietary sources. In recent years, it has become clear that changes of the relative amounts and types of PUFA may change biological processes important in maintaining health and preventing disease. The ratio *n*-6/*n*-3 in the diet, rather than the absolute intake of these PUFA, affects the composition and function of membranes, eicosanoid synthesis, regulates gene expression, controls neurological and retinal de-

velopment, and modulates immune function in health and disease. Most studies suggest that a ratio between 4:1 and 10:1 is needed to achieve health benefits. Today's diet consists mainly of *n*-6 fatty acids with no or very little *n*-3 fatty acids (Simopoulos 1999). The dietary intake studies estimate that nowadays the dietary *n*-6/*n*-3 ratio approaches 14:1 to 20:1.

The quality and stability of edible oil are the main factors that influence its acceptability and market value (O'Brien 2004). In human nutrition, PUFA found in vegetable oil are physiologically important food constituents but also the most susceptible ones to oxidative degradation, and as such may contribute to an overall enhancement of peroxidative stress in the body. Lipid oxidation is a major cause of the deterioration of oils, leading to the loss of nutritional value, and to alteration of sensory properties like flavour, aroma, and colour. During processing or storage of oils, fatty acids are oxidised first to hydroperoxides which are non-volatile, odourless substances. They can easily degrade to secondary oxidation products like epoxides, saturated and non-saturated aldehydes, ketones, acids, etc. (Halliwell & Gutteridge 1999; Biswas *et al*. 2002), that are responsible for the rancid taste and development of unpleasant flavours (Wagner & Elmadfa 2001).

Therefore, the degree of oxidation and the potential for deterioration are important quality parameters of edible oils. The dynamics of oxidation or food deterioration mostly depends upon the fatty acid composition, contents and activities of antioxidants and prooxidants (air, heat, light, presence of trace metals, free fatty acids, various oxidation products, metal ions, and moisture).

Refining of crude vegetable oils, particularly deodorisation at elevated temperatures, diminishes the contents of the naturally present antioxidants such as tocopherols, sterols, and carotenoids (O'Brien 2004). Deodorisation at elevated temperatures causes tocopherols and sterols to be stripped away, while carotenoids are thermally decomposed and removed (O'Brien 2004).

Oxidative stability, known as the resistance to oxidation under defined conditions, is one of the most important indicators in maintaining the quality of edible oils. It has been shown that oxidation of edible oils takes place through a chain reaction that essentially consists of an induction stage. The time before a dramatic increase in the rate of lipid oxidation occurs is the measure of oxidative stability and is referred to as the induction time. It is well known that antioxidants such as tocopherols or other minor components that may be present in oils modulate the susceptibility of PUFA to oxidation and thus maintain the nutritional value of vegetable oils, enhance the keeping quality, and increase their shelf life. In the case of non-refined pumpkin-seed oil, the roasting process may affect the oil stability (Murkovic & Pfannhauser 2000; Yoshida *et al*. 2006).

The aim of this research was to estimate the correlation between important biochemical parameters of refined and unrefined vegetable edible oils (fatty acid composition, free fatty acids, antioxidant content (tocopherols), and peroxide value) and their oxidative resistance to the thermal treatment. The comparison of some biochemical parameters of refined and unrefined oils has also been made.

MATERIALS AND METHODS

Materials. Commercially available vegetable oils were used, i.e. seven samples of refined sunflower oil (one sample originated from the Netherlands, one from Austria, five samples from Slovenia), five samples of refined high oleic sunflower oil (all samples originated from Slovenia), five samples of refined soybean oil (three samples originated from Austria, one sample from Slovenia, one sample from Italy), five samples of refined rapeseed oil (three samples originated from Slovenia, one sample from Hungary, one sample from Austria), six samples of unrefined olive oil (one sample from Italy, one sample from Spain, one sample from Croatia, one sample from Greece, two samples from Slovenia), and five samples of unrefined pumpkin seed oil (all samples originated from Slovenia). The oil samples were obtained from the local supermarket. According to the data presented on the labels, the shelf-life of all oil samples investigated was one year. The oil samples in their original packaging (bottles) wrapped with aluminium foil were stored in a refrigerator at 4°C. After an oil sample was withdrawn for a particular analysis, the bottle was flushed with nitrogen, covered with the original cup and sealed with parafilm. All analyses were performed within three months after bottling. All other chemicals and solvents were of analytical grade.

Peroxide value. Peroxide value (PV) was determined according to AOAC Official Method 965.33

(1999). The method is based on iodometric titration, which measures the iodine produced from potassium iodide by the peroxides present in the oil. PV was expressed as mmol O_2 per kg of oil. The determinations were carried out in triplicates. The standard deviation for each determination was below 2%.

Determination of free fatty acid content. The content of free fatty acids (FFA) was determined according to AOAC Official Method 940.28 (1999). The values were expressed as percentage of oleic acid. These determinations were carried out in triplicates. The standard deviation for each determination was less than 0.01%.

Determination of tocopherol content. The tocopherol content was determined by means of high-performance liquid chromatography (HPLC) according to the method (ISO 9936:1997). The analyses were performed on an Agilent HPLC 1100 chromatography system equipped with a BinPump G1312A binary pump, an ALS G1329A + AlsTherm G1330B automatic liquid sampler, a Phenomenex Luna (250 × 4.60 mm) column packed with silica (5 µm particle size), a Colcolm G1316A column thermostatting system, an FLD G1321A fluorescence detector at the excitation wavelength 290 nm and emission wavelength 330 nm, with a mobile phase of hexane-isopropanol (99.3:0.7 v/v) at a flow-rate of 1.0 ml/minute. For each of the four tocopherol isomers, a calibration graph was used to calculate its concentration. The tocopherol content was given as mg of tocopherol per kg of oil. The analyses were carried out in duplicates. The standard error of the determination was less than 15 mg/kg.

Determination of fatty acid composition. Fatty acids were determined as methyl esters after transesterification according to AOAC Official Methods 969.33 (1999) by gas chromatography on an HP 5890 Hewlett-Packard gas chromatograph, series II instrument (Hewlett Packard Corp., Palo Alto, USA), equipped with a Supelco, SP 2380 (30 m × 0.25 mm and film thickness 0.20 µm) fused silica capillary column. The stationary phase was poly (90% biscyanopropyl/10% cyanopropylphenyl siloxane). The carrier gas was helium at 1 cm^3/minute. The internal standard was heptadecanoic acid. The column temperature was programmed from 150°C to 210°C at 5°C/minute. The injector and flame-ionisation detector temperatures were set at 220°C and 250°C, respectively. The injection volume was 1 µl. The identification was achieved by comparing the retention times of the fatty acid methyl esters of the investigated oil samples to the retention times of fatty acid methyl ester standards (FAME Mix rapeseed oil, Supelco 46961). The reliability and accuracy of the analytical method for the detection of fatty acids was ensured by the use of the certified reference matrix (Oil Reference Standard, AOCS No. 1; Supelco O7006-1AMP), the results having been in good agreement with the certified values. The results were expressed as the weight percentage of total fatty acids. The analysis was carried out in duplicate. The standard error of determination amounted to between 0.01% and 0.25%.

Determination of oxidative stability. The oxidative stability of the investigated oil samples was studied using the Rancimat test (Läubli *et al*. 1988). The test was performed on a 679 Rancimat apparatus (Methrom, Herisau, Switzerland). The oil samples (3 ml) were subjected to a temperature of 110°C at an air flow rate of 20 dm^3/hour. The determination was based on the conductometric detection of volatile acids. The results were expressed as the induction time (IT) in hours. The induction time represents the time needed for the decomposition of hydroperoxides produced by oil oxidation (Läubli *et al*. 1988). The determination was carried out in triplicate. The standard deviation for each determination was less than 0.3 hour.

Statistics. Duncan's multiple range test was performed to evaluate the significance of the difference between the mean values. The significance was considered established at 0.05 level of probability. All computations were made using the statistical analysis system (SAS) program (SAS 1999) with the general linear models (GLM) procedure.

RESULTS AND DISCUSSION

The results, summarised in Tables 1–3, show that the investigated vegetable oils correspond to National Regulations about Edible Vegetable Oils, Edible Vegetable Fats and Mayonnaise Quality (2003) and Olive Oil Regulations (1999).

The content of FFA expressed as % of oleic acid is given in Table 1. The content of FFA in our investigation was below the limiting value for refined oils (0.3%), as well as for unrefined oils (3%). This parameter assesses the treatment of the source material before and during pressing, since FFA are virtually absent in the fats/oils of

Table 1. Chemical composition of oil samples

Oil	*n*	Parametr		
		Peroxide value (mmol O_2/kg)	acidity (% as oleic acid)	induction time at 110°C (h)
Sunflower	21	1.08 ± 0.61$^{d.c}$	0.05 ± 0.097^{c}	6.19 ± 0.82^{d}
min. – max.		0.33 – 1.99	0 – 0.16	5.30 – 7.82
High oleic sunflower	15	2.0 ± 0.19^{b}	0.032 ± 0.025^{c}	12.61 ± 1.07^{b}
min. – max.		1.72 – 2.39	0.015 – 0.055	11.50 – 15.00
Soybean	15	1.48 ± 0.17$^{c.d}$	0.07 ± 0.069^{c}	7.83 ± 0.91$^{c.d}$
min. – max.		1.18 – 1.67	0.029 – 0.13	6.20 – 8.87
Rapeseed	15	1.55 ± 0.65^{c}	0.045 ± 0.056^{c}	8.95 ± 0.93^{c}
min. – max.		0.60 – 2.34	0 – 0.085	7.43 – 10.50
Extra virgin olive	18	5.79 ± 1.18^{a}	0.51 ± 0.39^{a}	15.29 ± 4.90^{a}
min. – max.		3.75 – 7.33	0.19 – 0.75	9.13 – 23.20
Pumpkin seed	15	0.74 ± 0.26^{e}	0.44 ± 0.31^{b}	16.26 ± 4.69^{a}
min. – max.		0.42 – 1.20	0.35 – 0.74	12.80 – 25.70
Significance		***	***	***

Mean values ± standard deviation; min. – max. values; *n* – number of observations; means with a different superscript within groups differ significantly ($P \leq 0.05$); highly statistically significant ***$P \leq 0.001$

living tissue. Hydrolysis of ester bonds in lipids (lipolysis), resulting in the liberation of FFA, may be caused by enzymatic action or by heat and moisture (Nawar 1996). The release of free fatty acids is responsible for the development of the undesirable rancid flavour (hydrolytic rancidity). Furthermore, FFA are more susceptible to oxidation than the glycerol esters of these fatty acids. Therefore, any increase in the acidity of the oil must be absolutely avoided. During the refining process, these constituents are more or less removed from the oil. As can be seen in Table 1, the unrefined oils in our investigation such as extra virgin olive oil and pumpkinseed oil had on average a tenfold higher acidity than the refined oils. The FFA content in the refined oils in our study was on average the highest in soybean oil, amounting to 0.07% expressed as oleic acid. The average values for FFA content in our refined oils was at the level of the minimal value found in the investigation performed on commercial vegetable oils available on the German market (Klein 1999b).

We can also see in Table 1 that a PV of 10 mmol O_2/kg, the upper limit for unrefined oils, and a PV of 7 mmol O_2/kg, the upper limit for refined oils, were not exceeded in the oil samples investigated. Pumpkinseed oil had on average a significantly lower PV amounting to 0.74 mmol O_2/kg, and extra virgin olive oil a higher PV amounting to 5.79 mmol O_2/kg than were the mean PVs for all the other oils investigated. The average PVs of the oils investigated in this study were under the average PVs for the oils studied by Klein (1999b).

The susceptibility of oils to oxidation was measured by means of the Rancimat test and expressed as the induction time. The Rancimat test is a commonly used procedure in the food industry for the examination of the oxidative stability of edible oils and prediction of their shelf life. Gordon and Mursi (1994) reported for rapeseed oil that the induction time of 1 h determined at 100°C was equivalent to 2 days storage at 20°C. Maszewska (2002) found that an induction time of 1 h at 120°C was equal to 5 months storage at 12°C.

The comparison of the mean values of the induction time of the oils in our study presented in Table 1 showed that the unrefined oils, i.e. extra virgin olive oil and pumpkin-seed oil with average values for IT of 15.4 h and 16.3 h, respectively, were more oxidatively stable than the refined oils. Among these, the IT of high oleic sunflower oil amounting to 12.61 h was significantly higher than the ITs of the other refined oils investigated. ITs of other refined oils followed the decreasing order: rapeseed (IT = 8.95 h) > soybean (IT = 7.83 h) > sunflower oil (IT = 6.19 h). Matthäus (1996) in his investigation, as well as Velasco (2004), found a higher IT for rapeseed oil than for sunflower

Table 2. Composition of total fatty acids (%) in oil samples

Oil	*n*	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linolic C18:2	Linolenic C18:3	Arachidic C20:0	Gadoleic C20:1	Behenic C22:0	Lignoceric C 4:0
Sunflower	7	6.01 ± 0.3^{c}	3.76 ± 0.5^{b}	29.92 ± 6.6^{d}	58.44 ± 7.1^{a}	0.85 ± 1.3^{b}	0.13 ± 0.2^{b}	0.099 ± 0.3^{b}	0.61 ± 0.3^{b}	0.077 ± 0.13^{a}
min. – max.		5.48 – 6.22	2.95 – 4.14	26.20 – 44.52	42.67 – 62.58	0.00 – 3.66	0.0 – 0.3	0.00 – 0.69	0.00 – 0.74	0.00 – 0.29
High oleic sunflower	5	3.87 ± 0.2^{d}	3.40 ± 0.6^{b,c}	72.84 ± 4.1^{a}	18.82 ± 3.2^{d}	0^{b}	0.060 ± 0.1^{b}	0.053 ± 0.1^{b}	0.81 ± 0.1^{a}	0.062 ± 0.14^{a1}
min. – max.		3.58 – 4.06	2.35 – 3.71	69.90 – 80.10	13.23 – 21.42	0 – 0	0.0 – 0.3	0.00 – 0.26	0.60 – 0.91	0.00 – 0.31
Soybean	5	10.21 ± 0.9^{b}	3.97 ± 0.7^{b}	28.79 ± 5.9^{d}	50.60 ± 5.2^{b}	6.11 ± 1.2^{a}	0.085 ± 0.2^{b}	0.14 ± 0.3^{b}	0.084 ± 0.2^{c}	0^{a}
min. – max.		8.61 – 10.78	3.19 – 4.89	24.72 – 39.17	41.45 – 54.53	4.45 – 7.14	0.00 – 0.43	0.00 – 0.72	0.00 – 0.42	
Rapeseed	5	5.78 ± 0.8^{c}	2.16 ± 0.2^{d}	53.68 ± 5.4^{b}	30.22 ± 6.2^{c}	6.30 ± 1.3^{a}	0.58 ± 0.06^{a}	1.10 ± 0.2^{a}	0.18 ± 0.2^{c}	0^{a}
min. – max.		5.02 – 6.98	1.98 – 2.48	48.69 – 60.20	22.86 – 36.49	4.91 – 7.87	0.51 – 0.65	0.92 – 1.36	0.00 – 0.46	
Extra virgin olive	5	13.21 ± 2.5^{a}	3.02 ± 0.3^{c}	73.85 ± 5.5^{a}	8.78 ± 3.3^{e}	0.68 ± 0.05^{b}	0.31 ± 0.30^{b}	0^{b}	0^{c}	0^{a}
min. – max.		11.13 – 17.30	2.72 – 3.44	65.60 – 78.20	5.91 – 13.58	0.60 – 074	0.00 – 0.63			
Pumpkin seed	5	11.11 ± 0.7^{b}	5.64 ± 0.5^{a}	35.98 ± 1.7^{c}	46.29 ± 2.9^{b}	0.83 ± 0.2^{b}	0.093 ± 0.2^{b}	0^{b}	0^{c}	0^{a}
min. – max.		10.12 – 11.91	5.28 – 6.48	34.46 – 39.00	41.66 – 49.50	0.64 – 098	0.00 – 047			
Significance		***	***	***	***	***	***	***	***	ns

Mean values ± standard deviation; min. – max. values; *n* – number of observations; means with a different superscript within groups differ significantly ($P \leq 0.05$); highly statistically significant ***$P \leq 0.001$; ns – statistically not significant

oil. Isbell *et al*. (1999) and also Chu and Kung (1998) reported that high oleic sunflower oil is more oxidatively stable than soybean oil. However, it is difficult to compare the absolute values of the induction time obtained in different investigations because the measurements were performed under different conditions. In Table 1 can be seen that within an oil group the differences between minimal and maximal values of IT are much more pronounced in the unrefined oils (coefficient of variation was about 30%) than in the refined oils (coefficient of variation was about 10%).

The contents of fatty acids in the investigated samples are shown in Table 2. Even though the oils were obtained from the same genotype, they exhibited variations in the contents of palmitic, oleic, and linoleic acids, leading to differences in total saturated and unsaturated fatty acids. Besides plant genotype, other factors such as the growth conditions and harvesting time could influence the fatty acid profile of vegetable oils. On average, the content of saturated fatty acids, with palmitic acid predominating, was the highest in pumpkin-seed oil and in olive oil, followed by soybean oil. The average content of oleic acid was significantly higher in extra virgin olive oil (73.85%) and in high oleic sunflower oil (72.84%) compared to the other oils. Oleic acid also predominated in rapeseed oil (53.68%). Compared to the other oils, the content of linoleic acid (58.44%) in sunflower oil was significantly higher. Linoleic acid also predominated in soybean oil and pumpkin-seed oil, amounting to 50.60% and 46.29%, respectively. The content of polyunsaturated linolenic acid (about 6%) was found to be significantly higher in soybean and rapeseed oils as compared to the other oils. As expected, fatty acids such as arachidic, gondoic, and bechenic acids were present in the investigated oils in low quantities or were even absent (Table 2).

The fatty acid profile provides information on oil nutritional quality. WHO (World Health Organization) recommends the *n*-6/*n*-3 fatty acid ratio in the diet to be between 5:1 and 10:1. The most suitable ratios were found in rapeseed oil (*n*-6/*n*-3 = 5:1) and soybean oil (*n*-6/*n*-3 = 8:1). In the other investigated oils, the ratio *n*-6/*n*-3 was less suitable. In sunflower oil it amounted to 69:1, in pumpkin-seed oil to 56:1, and in extra virgin olive oil it was 13:1.

As seen in Table 3, there were differences between the investigated oils in the average values of the content of tocopherols. The average value of total tocopherol content determined in soybean oil (813.38 mg/kg), with γ-tocopherol predominating, was significantly higher than in the other investigated oils. γ-tocopherol also predominated in rapeseed oil and in pumpkin-seed oil, while in the other investigated oils α-tocopherol predominated. β-tocopherol and δ-tocopherol were present in small quantities. An exception was soybean oil that contained a significantly higher amount of δ-tocopherol than the other oils. In Table 3, we can also see that differences occur between minimal and maximal values for tocopherol content, being most noticeable in the case of soybean oil. The actual

Table 3. Content of tocopherols (mg/kg oil) in oil samples

Oil	*n*	α-Tocopherol	β-Tocopherol	γ-Tocopherol	δ-Tocopherol	Total tocopherols
Sunflower	7	441.40 ± 49.02^{a}	11.98 ± 2.01^{b}	42.66 ± 61.44^{c}	5.79 ± 2.77^{b}	501.83 ± 29.09^{b}
min. – max.		351.22 – 493.11	7.59 – 13.62	7.84 – 179.35	2.35 – 9.43	459.24 – 547.59
High oleic sunflower	5	427.59 ± 23.35^{a}	15.59 ± 0.63^{a}	9.71 ± 2.85^{c}	2.74 ± 1.65^{b}	455.63 ± 5.89^{b}
min. – max.		386.95 – 444.38	14.58 – 16.23	6.93 – 12.88	0.00 – 4.09	410.72 – 477.10
Soybean	5	108.64 ± 36.12^{c}	9.10 ± 1.90^{c}	532.05 ± 172.73^{a}	163.59 ± 44.37^{a}	813.38 ± 192.27^{a}
min. – max.		75.92 – 166.77	7.06 – 12.09	273.20 – 689.67	121.96 – 220.53	506.07 – 987.52
Rapeseed	5	241.41 ± 34.04^{b}	3.62 ± 1.27^{d}	304.76 ± 72.67^{b}	11.03 ± 4.03^{b}	560.82 ± 47.65^{b}
min. – max.		190.08 – 273.08	2.34 – 5.10	229.48 – 422.72	7.00 – 15.55	519.96 – 630.91
Extra virgin olive	6	147.28 ± 30.65^{c}	1.90 ± 0.089^{e}	6.32 ± 2.84^{c}	0^{b}	155.50 ± 30.42^{c}
min. – max.		107.82 – 182.78	1.73 – 1.96	3.14 – 11.01		116.77 – 187.87
Pumpkin seed	5	103.61 ± 53.48^{c}	4.75 ± 1.32^{d}	368.47 ± 37.76^{b}	13.57 ± 6.49^{b}	490.41 ± 25.36^{b}
min. – max.		45.47 – 173.43	2.99 – 5.88	319.23 – 419.52	7.87 – 20.87	448.48 – 511.12
Significance		***	***	***	***	***

Mean values ± standard deviation; min. – max. values; *n* – number of observations; means with a different superscript within groups differ significantly ($P \leq 0.05$); highly statistically significant ***$P \leq 0.001$

value of tocopherols content is a consequence of plant genotype, oil processing, and storage conditions. Many authors (Koski *et al*. 2002) as well as Morello *et al*. (2004) have confirmed a decrease of tocopherol content in vegetable oils during storage. However, the contents of tocopherols in sunflower, soybean, and rapeseed oils were within the range indicated in the literature (Klein 1999a) and are characteristic for the respective oil type.

The results obtained for refined oils showed that the contents of PUFA (C18:2 + C18:3) are very important in affecting the oxidative stability. The PUFA contents in sunflower oil (59%) and soybean oil (58%) with low induction times were higher than in the other refined oils with higher induction time values, i.e. high oleic sunflower oil (19%) and rapeseed oil (36%). Figure 1 shows the dependence of the induction time of the investigated oils (except pumpkin-seed oil) on PUFA content. We can see that IT linearly decreases with the increase of PUFA content in the oils (r = –0.971).

It was expected that a higher content of primary oxidation products and the presence of free fatty acids might profoundly lower the oxidative stability of oil.

But the most oxidatively stable of the refined oils, the high oleic sunflower oil, had on average the highest PV. Even if we correlated PV content with IT inside an oil group, we did not obtain statistically significant results, with the exception of sunflower oil (r = –0.688). Similarly, the correlation between FFA content and IT inside an oil group was statistically significant only for high oleic sunflower oil (r = –0.988). Besides PUFA content, the presence of FFA and PV, inherent antioxidants were an important factor influencing the oil stability. Extra virgin olive oil has on average the highest PV and the highest amount of FFA but a long induction time. Tan *et al*. (2002) found that olive oil with its high initial PV had a longer induction time than other common vegetable oils investigated in his study. The increased oxidative stability of extra virgin olive oil is related to the high levels of monounsaturated oleic acid and the presence of natural antioxidants, especially phenolic compounds (Baldioli *et al*. 1996). Among the investigated oils, pumpkinseed oil, despite its appreciable contents of PUFA and FFA, has the highest oxidative stability. Its remarkable stability could be explained by the fact that during roasting of pumpkin seeds products with antioxidative properties are formed (Murkovich & Pfannhauser 2000). Maillard reaction products are well known potent natural antioxidants and could possibly contribute to the high oxidative stability of the oil (Morales & Babel 2002). Soybean oil contains the same amount of oleic (C18:1), a little less linoleic (C18:2) and more linolenic (C18:3) acids than sunflower oil but is rich in γ-tocopherol and therefore has a better oxidative stability than sunflower oil. High levels of tocopherols, especially the γ- isomer, protect soybean oil against oxidation. Rapeseed oil contains less total tocopherols and less γ-tocopherol than soybean oil but has a better oxidative stability than soybeaan oil. Rapeseed oil is oxidatively more stable than soybean oil because of its fatty acid composition. Rapeseed oil contains the same amount of linolenic (C18:3), much less linoleic (C18:2) and much more oleic (C18:1) acids than soybean oil. Sunflower and high oleic sunflower oils contain the same levels of tocopherols, mostly α-tocopherol, but have different induction times. The induction time of sunflower oil is only half that of high oleic sunflower oil. Sunflower oil is oxidatively less stable than high oleic sunflower oil because of its higher content of polyunsaturated linoleic acid. Matthäus (1996) in his investigation performed on some vegetable oils with different degrees of unsaturation found a high correlation (r = 0.985) between total tocopherol content and *IP* determined by the Rancimat method at 120°C. In our investigation no statistical significance was observed for the correlation between total tocopherol content in oil and IT (r = 0.383).

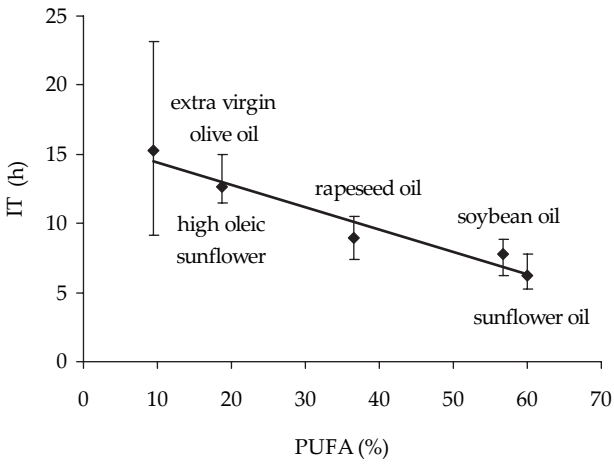

Figure 1. Dependence of average IT on PUFA for investigated oils. Vertical bars represent the standard deviation for each data point

CONCLUSION

It can be concluded that the vegetable oils included in the research have acceptable levels of quality parameters such as PV and FFA. The parameters such as fatty acid composition and tocopherol content are all within the range indicated in the literature. According to their fatty acid profiles, the oils in our investigation could be separated into two groups, those with high oleic acid content (high oleic sunflower oil, extra virgin olive oil) and those in which both oleic and linoleic acid contents were high (sunflower oil, soybean oil, rapeseed oil, pumpkin-seed oil). The results obtained for the refined oils showed that the contents of PUFA are more important than the initial PV and FFA contents in affecting the oxidative stability. The oxidative stability of the unrefined oils (pumpkin seed and extra virgin olive oils) is better than that of refined oils, thus the unrefined oils have a longer hypothetical stability and are more suitable for frying. Among the refined oils, the highest oxidative stability was found in the case of high oleic sunflower oil which is the most appropriate oil for frying, the least suitable being sunflower oil.

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Corresponding author:

Dr. Helena Abramovič, University of Ljubljana, Biotechnical Faculty, Department of Food Science and Technology, 1000 Ljubljana, Slovenia
tel.: + 386 142 311 61, e-mail: helena.abramovic@bf-uni-lj.si