Impact of the hybrid on the fatty acid composition and thermal stability of cold-pressed sunflower oils produced from 17 newly cultivated hybrids from the region of North Macedonia

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Cold-pressed and refined sunflower oils rich in linolenic acid, are particularly susceptible to undesirable changes during deep-frying. The main object of this study was determination of physicochemical parameters such free fatty acids, peroxide value, saponification value, iodine number, density, oxidative stability, and fatty acid composition on cold-pressed oils from 17 newly cultivated hybrids from sunflower from the region of North Macedonia. Results from fatty acid methyl esters indicated Experto hybrid as the high oleic sunflower hybrid with 86.2% of oleic acid. Moreover, iodine number for sunflower oil from this hybrid was 87.5 g I_2 per 100 g oil, which was expected due to the high level of monosaturated fatty acid. Negative correlation confirmed inverse relationship between the amounts of oleic acid and values of iodine number (r = –0.896). Opposite, positive correlation between iodine number and amount of linoleic acid (r = 0.892) means that sunflower oils with higher value of iodine number will be thermally unstable and not suitable for deep-frying. Furthermore, the highest value for oxidative stability was measured for cold-pressed sunflower oils obtained from Talento, BG Fil and "Dijamantis hybrids (over 8, 9 and 5 h, respectively). This can be explained by the fact that the oils from those three hybrids had the highest level of oleic acid (83.1, 82.3 and 79.4%, respectively). Monounsaturated fatty acids are more stable then polyunsaturated, which makes sunflower oil suitable for deep-frying. The positive linear correlation between the amount of oleic acid and oxidation stability (r = 0.687) confirmed our statement that a higher amount of monounsaturated fatty acids (as oleic acid) can improve thermal stability and makes the sunflower oils from Talento, Fila BG and Dijamantis hybrids suitable for cooking and deep-frying. The oxidative stability of other examined hybrids at around 3 h can be explained by a dominance of polyunsaturated linoleic acid with levels between 43% and 57.1%. Statistical analysis confirmed our findings due to the negative linear correlation between oxidative stability and amount of polyunsaturated linoleic acid (r = –0.698). We expected higher value for oxidative stability (over 6 h) for cold-pressed sunflower oil from Experto hybrid due to its fatty acid composition. More precisely, the level of oleic acid for this oil was 86.2% and only 4.6% of polyunsaturated linoleic acid. Surprisingly, the oxidative stability of these oils was only 2.64% which can be explained as oxidation of the oil during production. According to the results from our study, we recommended the gap of oleic/linoleic acid as the most important for the determination of the thermal stability of sunflower oils. Finally, physicochemical parameters iodine number and oxidation stability can be a significant parameter for the prediction of the dominance of fatty acids in sunflower oil.

Keywords: cold-pressed sunflower oils, 17 hybrids, free fatty acids, fatty acid composition, iodine number, saponification value, refractive index, oxidative stability

1. INTRODUCTION

Virgin oils are very popular as natural products with a deep colour, typical taste, and smell, produced only with cold pressing and without any step of refining. Cold pressed oils occupy a very popular place in human nutrition due to the high level of polyunsaturated fatty acids (PUFA) and tocopherols [1]. A positive correlation between PUFA-rich vegetable oil consumption and a reduced risk of coronary heart diseases level of LDL, degenerative diseases, and cancer is very well known [2, 3]. However, PUFA-containing edible oils are highly prone to lipid oxidation leading to the formation of potentially toxic compounds, rancid flavour and a reduced shelf life [4]. Vegetable oils high in PUFA, such as sunflower oil and flaxseed oil, might be converted to oils with detrimental health effects. To overcome the adverse effects of lipid oxidation, food manufacturers add antioxidants to vegetable oils thereby enhancing their oxidative stability. While synthetic antioxidants were shown to be very effective, consumers demand natural products since synthetic antioxidants were also associated to the progression of cancer development [5]. Stability of cold-pressed sunflower oil depends not only on the fatty acids composition but also on the content of antioxidants, primary and secondary oxidation products, metals and other contaminants which might accelerate or inhibit oxidation process [6].

Classical sunflower oil fatty acid composition is saturated acids 11% (stearic, palmitic), oleic 20% and linoleic acid 69% [7].

Cold-pressed and refined sunflower oils rich in linolenic acid, are particularly susceptible to undesirable changes during deep-frying [8, 9]. Frying oils made from sunflower have lower stability because of their high polyunsaturated fatty acids and low γ-tocopherol content [10-13].

The working group of Orsavova et al., studied fatty acid composition of some vegetable oils, energy contribution of saturated and polyunsaturated fatty acids, n-3 PUFAs and n-6 PUFAs of analysed oils to recommended dietary intakes for total fat [14]. The research studies of new sunflower oils with modified tocopherol and fatty acid composition developed as feedback for the food industry requirements to offer healthier products, and the two commodity oils available nowadays (normal and high-oleic sunflower oils) can cover the requirements of the food industry without chemical manipulation with the aim of increasing the consumers' quality of life [15]. According to the findings of Cao et al., (2021) compound sodium nitrophenolate can be effective modulator for sunflower seeds growth by boosted the triacylglycerol hydrolysis, promoted the conversion of fatty acids to sugars, and decreased the abscisic acid content during imbibition of aged sunflower seed [16]. Sunflower (*Helianthus annuus* L.) is an important oilseed crop in the world; however, no comprehensive study on exploring the role of FAD family in relation to stress tolerance in sunflower has been studied by Xu et al., (2021) [17]. Blended sunflower (SO) (50-80%) and sesame oils (SEO) (20-50%) were evaluated for thermo-oxidative stability (induction period, IP), oxidation kinetics (rate constant, *k*), synergy and shelf-life (25°C) (IP_{25}) using Rancimat (100, 110, 120, and 130°C) [18, 19]. The aim of the work of research group of Aguirrezábal was to assess the response of oil fatty acid composition of the new high oleic mutation to MNT compared to traditional and Pervenets genotypes [20-22].

The aim of this study is to cultivate hybrids from which we can produce stable high-oleic sunflower oil, which can be used as cooking oil for deep-frying and the thermal processing of food. Furthermore, the goal of this study was to find difference in the composition of fatty acids among the hybrids as well as the overall quality of cold-pressed sunflower oils from 2016 and 2017 harvesting years.

2. MATERIALS AND METHODS

2.1 FIELD TRIALS

Field trials were carried out at the experimental research area in Ovče Pole valley, near Sveti Nikole municipality, in the east-central part of the Republic of North Macedonia. Ovče Pole is a plain situated around the flow of Sveti Nikole's River, which is a tributary to the Bregalnica River, within the following geographic coordinates N: 41°49′21.9″ and E: 21°59′03.9″. The climate in Ovče Pole valley is characterised by hot and dry summers (the temperature is in the range from 31°C to 40°C) and temperate cold winters (the temperature is in the range from -10°C till 7°C), with occasional sharp drops. The experimental area belongs to the continental sub-Mediterranean area. The field experiments were set up during two consecutive growing seasons (2016 and 2017). The investigated area on which the research was conducted is owed by the Faculty of Agriculture, "Goce Delchev" University - Štip, the Republic of North Macedonia. A randomised block system, with three replications for each sunflower hybrid, was used for field research and the plot size was 5 m^2. The distance between the row was 70 cm and 1 metre between the hybrids. Sunflower hybrids were sown by a seed sower in April in both testing years. Pre-sowing soil preparation was conducted in suitable timing, in both years and in accordance with weather conditions. During the vegetative period, standard agronomic practices were applied. The amount of rainfall was also observed, during both years of research. In the first experimental year (2016) 295 l/m^2 rainfall amount was recorded during vegetative period (refer to Hydrometeorological Institute, Skopje). In the second testing year, the rainfall amount was by half less (167 l/m^2) compared to the amount of precipitation in 2016. No additional irrigation was conducted during the field experiment. The sunflower hybrids were harvested by hand in September in both years.

2.2 PLANT MATERIAL

In this research, seventeen sunflower hybrids were used as an experimental material (Experto, Armoni, Fortimi, Adagio, Neoma, Torino, Arisona, Bacardi, Feliks, Neostar, Kondi, Talento, Subaru, Edison, BG Fila, Sumiko and Dijamantis). Feliks hybrids have Serbian origin; BG Fila is Bulgarian hybrid and the rest belong to Syngenta Seed Company. All sunflower hybrids were new varieties and were introduced to our country to be tested. During the vegetative period, in both years of testing, resistance of diseases, drought and lodging were recorded. All seventeen hybrids were included, for the first time, in this type of research to evaluate their potential, qualitative and quantitative properties under environmental conditions in the region of North Macedonia. The samples of 17 hybrids from sunflower oil were not mixed and oils obtained from every hybrid was examined separately from each harvested year.

2.3 APPLIED METHODS

A few parameters were examined to determine the overall quality of 17 hybrids of cold-pressed edible oils from the region of North Macedonia.

2.3.1 Determination of free fatty acid

Determination of free fatty acid was done by a cold solvent method using potentiometric titration (ISO 660:2010). In 10 g mass of test portion 50 ml of the neutralised solvent mixture (ethanol and diethyl ether) was added and the sample dissolved.

2.3.2 Determination of peroxide value

Peroxide value is a measure of the peroxides contained in the oil. Peroxide value is determined by measuring iodine released from potassium iodide. Furthermore, this value is a dynamic value, dependent upon the history of the test sample. The determination of peroxide value is a highly empirical procedure and the value obtained depends on the mass of the test portion. Actually, the determination of peroxide value was done by ISO 27107:2011.

2.3.3 Determination of density of oils

Density was determined by using a pycnometer at 20°C that performed according to ISO 6683:2014 [20].

2.3.4 Determination of iodine value

The determination of the iodine value was performed by ISO 3961:2013. The iodine number is determined by the mass of halogen, expressed as iodine, absorbed by the test portion following the specified procedure, divided by the mass of the examined sample of sunflower oil or more precisely, the iodine number equals the number of mg of iodine required to saturate the fatty acids present in 100 mg of the oil. Usually, iodine number is used to determine the amount of unsaturation in sunflower oils. In fatty acids, unsaturation occurs mainly as a double bond, very reactive towards halogens, iodine in this case. Thus, the higher the iodine value, the more unsaturation are present in the sunflower oil. The iodine number for high-oleic sunflower oil is usually in the range from 78-90 while for high linoleic sunflower oil is normally in the range from 118-141.

2.3.5 Determination of saponification value

The saponification value is determinate by taking 2.0 g mass of test portion in a conical flask to which 25 ml 0.5 mol/L ethanolic potassium hydroxide solution is added. Determination of saponification value was done by ISO 3657:2013.

2.3.6 Determination of oxidative stability of oils

Oxidative stability of oil was evaluated by the Rancimat method. Stability was expressed as the oxidation induction time (h) measured with the Rancimat 743 (Metrohm Co., herisau, Switzerland), using 3 g oil sample heated to 120°C with an air flow of 10 l/h. In general, sunflower oil will be kept at temperature of 120°C by Rancimat instrument. This temperature for our experiments is determined by several reasons. Firstly, frying food at a temperature which is too low results in an increased fat uptake. Water, which is contributed by the foods that are fried in an oil enhances the breakdown of fatty acids which occurs during heating. In addition, hydrolysis results in a poor-quality oil that has a reduced smoke point, a darker colour and altered flavour. During heating, oils also polymerise, creating a viscous oil that is readily absorbed by foods and that produces a greasy product. The more saturated (solid) the oil, the more stable it is to oxidative and hydrolytic breakdown, and the less likely it is to polymerise.

2.3.7 Determination of fatty acid methyl esters

In brief, 2 drops of oil were dissolved in 1 ml of heptane. Furthermore, 50 µL of sodium methylate (2 mol/L) was added and the samples were vigorously mixed for 1 min. Afterwards 100 µL of distilled water was added to each sample. After centrifugation of the samples, the lower phase was removed while the upper phase was mixed with 50 µL of 1 M HCl (with methyl orange for acidification control). After centrifugation at 4500 g for 10 min, the n-heptane phase was transferred to a new vial and the fatty acid methyl esters were analysed using an Agilent 6890 GC-chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a CP7420 Select FAME column (Agilent Technologies, Santa Clara, CA) (100 m 9 0.25 mm i.d. with 0.25 lm film thickness) and FID detector following the ISO standard ISO 5509:2000. The oven temperature was programmed to increase from 150 to 240°C with rate of 1.5°C/min and maintained isotherm at 240°C for 20 min. Pentadecanoic acid was used as an internal standard for quantitative analysis. The injector and detector temperature were both 260°C. Hydrogen was used as the carrier gas at an average velocity of 2 ml/min.

2.4 STATISTICAL DATA PROCESSING

Data collected from both years of the experiment were subjected to variance analysis using JMP statistical software. Fit analysis was performed to obtain the least significant differences (LSD) for tested hybrids by different properties. Based on the LSD data, the sunflower hybrids were statistically processed and grouped.

The statistical one-way ANOVA analysis was applied to see the level of every particular minor and major compound by consideration of the hybrid of oil with the significance level of 0.05. The level of significance of differences between the percentages of free fatty acids, fatty acid methyl esters, peroxide value, iodine value, saponification value, density and oxidative stability mean values was determined at 5% by a one-way ANOVA using the Tukey's test. This treatment was performed by SPSS v.16.0 software (IBM Corporation, USA). The ANOVA results were classified using letters (different letters mean significant differences among results). The letters are a, b, c, d, e and f according to the decrease of the result values.

At the end, a linear correlation between tested physicochemical properties was applied by SPSS statistical software.

3. RESULTS AND DISCUSSION

Results from fatty acid methyl esters presented in table I and values for oxidative stability presented in Tables II and III indicated strong relationship between percentage of oleic acid, iodine number and thermal stability of cold-pressed edible oils produced from 17 newly cultivated hybrids. The percentage of fatty acid composition was determined by every harvested year (by three replications by each sample) and statistically analysed. Statistically significant differences were detected between tested sunflower varieties. Results from the Table I, unequivocally indicated a strong relationship between the fatty acid composition and a variety of sunflower oil. The highest amount of monounsaturated oleic acid was related to 4 varieties: Experto, Talento, BG Fila and Dijamnatis. On the other hand, the next 4 varieties Fortimi, Torino, Felix and Neostar were related with the amount of polyunsaturated linoleic acid with over 50% of all fatty acids. As we can see from Table I, the percentage of oleic acid in cold-pressed edible oils from Experto hybrid was 86.2% and the value for iodine number was 87.5 g I_2/100 g which was expected due to the high level of monosaturated fatty acid. The same tendency was observed for cold-pressed edible oils produced from BG Fila and Dijamantis hybrids. The free fatty acid value of the tested oils varied between 0.10 and 0.60% oleic. Negative correlation confirmed inverse relationship between the amounts of oleic acid and values of iodine number (r = –0.896). Opposite, positive correlation between iodine number and amount of linoleic acid (r = 0.892) means that sunflower oils with higher value of iodine number will be thermally unstable and not suitable for deep-frying (Tab. IV). Furthermore, the highest value for oxidative stability was measured for cold-pressed sunflower oils obtained from Talento, BG Fila and Dijamantis hybrids (over 9 and 5 h, respectively). This can be explained by the fact that the oils from those three hybrids had the highest level of oleic acid (83.1, 82.3 and 79.4% respectively) (Tab. III).

Monounsaturated fatty acids are more stable then polyunsaturated which makes sunflower oil suitable for deep-frying. A positive linear correlation between the amount of oleic acid and oxidation stability (r = 0.687) confirmed our statement that higher amount of monounsaturated fatty acids (as oleic acid) can improve thermal stability and makes the sunflower oils from Fila BG and Dijamantis hybrids suitable for cooking and deep-frying. The oxidative stability of other examined hybrids at around 3 h can be explained by dominance of polyunsaturated linoleic acid with levels between 43% and 57.1% (Tab. I). Statistical analysis confirmed our findings due to the negative linear correlation between oxidative stability and the amount of polyunsaturated linoleic acid (r = –0.698) (Tab. IV). Due to its fatty acid profile, we expected higher value for oxidative stability (over 6 h) for cold-pressed sunflower oil from Experto hybrid. More precisely, the

Table I - Fatty acid methyl esters of 17 hybrids of sunflower oils (%)

	Experto	**Armoni**	**Fortimi**	**Adagio**	**Neoma**	**Torino**	**Arisona**	**Bacardi**	**Felix**
C16:0	4.9±0.3^{d}	5.5±0.1^{c}	6.5±0.4^{b}	5.9±0.2^{b}	5.1±0.1^{c}	7.1±0.3^{a}	5.5±0.1^{c}	6.1±0.4^{b}	5.8±0.1^{b}
C18:0	2.2±0.4^{c}	2.6±0.2^{b}	2.6±0.0^{b}	3.1±0.4^{a}	1.9±0.0^{d}	2.5±0.5^{b}	3.7±0.7^{a}	3.5±0.3^{a}	2.6±0.3^{b}
C18:1	86.2±3.2^{a}	41.8±4.8^{d}	32.0±4.5^{e}	40.8±2.3^{d}	57.7±9.2^{c}	34.0±7.1^{e}	45.8±6.3^{d}	40.4±5.4^{d}	33.7±4.9^{e}
C18:2	4.6±0.2^{f}	49.3±0.3^{b}	57.1±7.1^{a}	48.3±3.0^{b}	32.4±4.1^{d}	53.4±9.8^{a}	42.1±4.1^{c}	48.8±3.9^{b}	55.8±7.7^{a}
C18:3	1.9±0.0^{c}	0.4±0.0^{f}	0.9±0.1^{e}	1.3±0.0^{d}	2.9±0.0^{a}	1.5±0.1^{d}	2.6±0.0^{b}	1.2±0.0^{d}	1.1±0.0^{e}
	Neostar	**Kondi**	**Talento**	**Subaru**	**Edison**	**BG Fila**	**Sumiko**	**Dijamantis**	
C16:0	6.4±0.1^{b}	5.5±0.1^{c}	4.8±0.6^{d}	5.6±0.3^{c}	3.8±0.1^{e}	4.5±0.2^{d}	6.8±0.5^{b}	4.3±0.4^{d}	
C18:0	2.9±0.1^{a}	3.1±0.3^{a}	2.2±0.2^{b}	1.8±0.1^{c}	2.1±0.0^{b}	2.8±0.0^{a}	2.8±0.1^{a}	1.7±0.2^{c}	
C18:1	35.3±4.5^{e}	42.5±2.7^{d}	83.1±5.7^{a}	43.9±5.1^{d}	50.1±7.2^{c}	82.3±9.9^{a}	39.3±5.1^{d}	74.9±6.7^{b}	
C18:2	50.7±4.4^{b}	45.5±2.3^{c}	6.7±0.8^{f}	48.3±4.7^{b}	43.0±6.8^{c}	7.6±1.1^{f}	48.7±6.0^{b}	18.2±3.4^{e}	
C18:3	2.3±0.0^{b}	2.1±0.0^{c}	3.6±0.0^{a}	0.2±0.0^{f}	0.1±0.0^{f}	2.8±0.1^{b}	2.3±0.2^{b}	0.7±0.1^{e}	

Table II - Mean values of free fatty acid, peroxide value and density of different sunflower oils

Hybrids/ Properties	Free fatty acid (%)			Peroxide value (O_2/kg)			Density (mg/cm^3)		
	2016	**2017**	**Mean**	**2016**	**2017**	**Mean**	**2016**	**2017**	**Mean**
Experto	0.42^{c}	0.15^{bcd}	0.29	0.69^{m}	0.78^{i}	0.74	0.912^{h}	0.913^{f}	0.913
Armoni	0.47^{b}	0.16^{b}	0.32	1.21^{de}	0.89^{h}	1.05	0.919^{bcd}	0.919^{a}	0.919
Fortimi	0.22^{j}	0.12^{ef}	0.17	1.14^{f}	1.03^{f}	1.09	0.917^{abc}	0.918^{b}	0.918
Adagio	0.60^{a}	0.12^{ef}	0.36	1.28^{b}	1.14^{d}	1.21	0.915^{ef}	0.918^{b}	0.917
Neoma	0.29^{h}	0.14^{bcde}	0.22	1.07^{h}	0.98^{g}	1.03	0.918^{abc}	0.919^{a}	0.919
Torino	0.25^{i}	0.13^{cde}	0.19	1.14^{f}	0.56^{l}	0.85	0.916^{def}	0.915^{d}	0.916
Arisona	0.36^{de}	0.15^{b}c	0.26	0.99^{j}	0.72^{j}	0.86	0.916^{def}	0.919^{a}	0.918
Bacardi	0.32^{g}	0.14^{bcde}	0.23	0.84^{l}	0.78^{i}	0.81	0.918^{ab}	0.919^{a}	0.919
Feliks	0.33^{fg}	0.12^{ef}	0.23	0.63^{n}	0.65^{k}	0.64	0.916^{def}	0.919^{a}	0.918
Neostar	0.37^{d}	0.14^{bcde}	0.26	1.35^{a}	0.78^{i}	1.07	0.919^{a}	0.919^{a}	0.919
Kondi	0.46^{b}	0.16^{b}	0.31	1.19^{e}	0.77^{i}	0.98	0.916^{def}	0.918^{b}	0.917
Talento	0.30^{h}	0.15^{bcd}	0.23	0.86^{k}	0.78^{i}	0.82	0.913^{gh}	0.914^{e}	0.914
Subaru	0.14^{k}	0.13^{cde}	0.14	1.21^{d}	1.30^{b}	1.26	0.916^{def}	0.916^{c}	0.916
Edison	0.13^{kl}	0.13^{cde}	0.13	1.10^{g}	1.13^{d}	1.12	0.916^{cde}	0.916^{c}	0.916
BG Fila	0.35^{ef}	0.33^{a}	0.34	1.36^{a}	1.34^{a}	1.35	0.912^{h}	0.912^{f}	0.912
Sumiko	0.14^{k}	0.13^{de}	0.14	1.25^{c}	1.23^{c}	1.24	0.918^{ab}	0.918^{b}	0.918
Diamantis	0.11^{l}	0.10^{f}	0.11	1.05^{i}	1.09^{e}	1.07	0.914^{fg}	0.914^{de}	0.914
Average	**0.31**	**0.15**	**0.23**	**1.08**	**0.94**	**1.01**	**0.916**	**0.917**	**0.916**
$LSD_{0.05}$	0.02	0.02		0.02	0.02		0.001	0.001	
CV (%)	3.82	9.90		0.93	1.37		0.12	0.06	

level of oleic acid for this oil was 86.2% and only 4.6% of polyunsaturated linoleic acid. Surprisingly, the oxidative stability of the oils was only 2.64% which can be explained as an oxidation of the oil during production (Tab. III).

Fatty acid composition affects oil oxidative stability [23, 24]. Oils with a high content of polyunsaturated fatty acid are more easily oxidised. Symoiniuk et al. (2018) used 27 different cold press oil samples (linseed, rapeseed, camelina, black cumin, prim-

Table III - Mean values of iodine number, saponification measurement and oxidative stability of different sunflower oils

Hybrids/ Properties	Iodine value (g I_2/100 g)			Saponification value (mg KOH/g)			Oxidative stability (h)		
	2016	**2017**	**Mean**	**2016**	**2017**	**Mean**	**2016**	**2017**	**Mean**
Experto	85^{jk}	90^{l}	87.5	188^{d}	188^{e}	188.0	1.80^{n}	3.48^{f}	2.64
Armoni	123^{c}	138^{b}	130.5	191^{abc}	189^{de}	190.0	2.86^{j}	2.92^{l}	2.89
Fortimi	129^{a}	140^{a}	134.5	190^{abc}	189^{de}	189.5	2.68^{m}	2.86^{m}	2.77
Adagio	120^{def}	131^{e}	125.5	190^{c}	189^{de}	189.5	2.96^{i}	3.17^{h}	3.07
Neoma	127^{b}	135^{cd}	131.0	190^{c}	189^{de}	189.5	2.81^{k}	2.97^{k}	2.89
Torino	109^{h}	121^{g}	115.0	190^{c}	190^{cd}	190.0	3.66^{d}	3.76^{d}	3.71
Arisona	121^{cde}	125^{f}	123.0	191^{abc}	190^{cd}	190.5	2.73^{l}	3.10^{i}	2.92
Bacardi	120^{ef}	136^{c}	128.0	190^{bc}	190^{bc}	190.0	3.59^{f}	2.99^{k}	3.29
Feliks	122^{cd}	136^{bc}	129.0	190^{abc}	190^{cd}	190.0	2.66^{m}	2.98^{k}	2.82
Neostar	122^{cd}	136^{c}	129.0	191^{abc}	189^{de}	190.0	2.66^{m}	2.93^{l}	2.80
Kondi	121^{cde}	134^{d}	127.5	190^{c}	190^{c}	190.0	2.72^{l}	2.88^{m}	2.80
Talento	87^{j}	90^{l}	88.5	191^{ab}	190^{bc}	190.5	8.68^{b}	10.16^{a}	9.42
Subaru	115^{g}	116^{i}	115.5	191^{abc}	191^{ab}	191.0	3.16^{g}	3.20^{g}	3.18
Edison	111^{h}	111^{j}	111.0	190^{abc}	190^{bc}	190.0	3.64^{e}	3.71^{e}	3.68
BG Fila	83^{k}	85^{m}	84.0	191^{abc}	190^{c}	190.5	9.04^{a}	9.10^{b}	9.07
Sumiko	118^{f}	119^{h}	118.5	192^{a}	192^{a}	192.0	3.04^{h}	3.06^{j}	3.05
Diamantis	95^{i}	94^{k}	94.5	191^{ab}	190^{bc}	190.5	5.24^{c}	5.28^{c}	5.26
Average	**112.2**	**119.8**	**116.0**	**190.4**	**189.8**	**190.1**	**3.76**	**4.03**	**3.90**
$LSD_{0.05}$	2.03	1.80		1.52	1.21		0.02	0.03	
CV (%)	1.09	0.90		0.48	0.38		0.36	0.44	

Table IV - Linear correlation between some physicochemical properties and Fatty acid methyl esters of 17 hybrids of sunflower oils

Traits	Free fatty acid	Peroxide value	Density	Iodine value	Sapunification value	Oxidative stability	C16:0	C18:0	C18:1	C18:2	C18:3
Free fatty acid	1	-0.058	-0.034	0.024	-0.410	0.089	0.000	0.524*	0.119	-0.164	0.354
Peroxide value		1	-0.111	-0.051	0.435	0.161	-0.091	-0.138)	-0.009	0.029	0.135)
Density			1	0.951**	0.104	-0.689**	0.562*	0.400	-0.822**	0.814**	-0.162
Iodine value				1	0.013	-0.742**	0.585*	0.395	-0.896**	0.892**	-0.271
Sapunification value					1	0.260	0.161	0.068	-0.197	0.199	0.063
Oxidative stability						1	-0.453	-0.186	0.687**	-0.698**	0.458
C16:0							1	0.433	-0.725**	0.676**	0.023
C18:0								1	-0.412	0.356	0.245
C18:1									1	-0.995**	0.403
C18:2										1	-0.479
C18:3											1

*Correlation is significant at the 0.05 level
**Correlation is significant at the 0.01 level

rose, hempseed, milk thistle, poppy, pumpkin, and sunflower) to determine the fatty acid composition. Their results showed that sunflower oil was characterised by the smallest proportion of saturated fatty acid (linoleic acid was 5.49%). Our results showed the highest abundance of palmitic acid for Torino hybrid (7.1%) while the highest amount of stearic acid was detected for Bacardi hybrid. Oleic acid, one of the monounsaturated fatty acids, was most dominant in sunflower oil (86.52%) compared to the other analysed oils. Also, sunflower oil has the highest value for oxidative stability (102.84 min) [25].

From the results in this paper (Tab. II), Diamantis showed the lowest value for free fatty acid in both years of testing, but, at the same time, had high oxidative stability (5.26 h, Tab. III) and presented a high resistance of diseases and drought. Edison, Sumiko and Subaru also showed lower values for free fatty acid, compared to the other tested varieties. They had a good oxidative stability, around 3 h and a good resistance to diseases. Fortimi showed 0.17% free fatty acid and during the vegetation presented tolerance to drought, lodging and diseases.

On the other hand, the lowest peroxide value was obtained by Feliks, followed by Experto, Bacardi, Talento, Torino and Arisona (Tab. II). Also, Talento showed the highest oxidative stability (9.42 h, Tab. III) and was resistant to lodging and diseases. Torino and Bacardi also had high value for oxidative value (3.71 h and 3.29 h, consequently).

Aşkin (2018) analysed six sunflower hybrids in his research. Major fatty acid composition in tested hybrids agreed with contents mentioned among literatures and registration reports of the food ministry in Turkey. The oleic acid ranges from 36.6% to 87.23%, while linoleic fatty acid from 5.72% to 52.93% [26].

The Mediterranean diet is well-known as a diet with a high consumption of olive oil and a minimal amount of saturated fatty acids. Red meat, whole fat milk products, nuts, and high fat fruits, such as olives and avocados are among the natural sources of monounsaturated fatty acids [27]. For the proper utilisation of sunflower oils in food and other industries, oil, moisture and protein contents, fatty acid compositions and quality characteristics of sunflowers should be quickly and reliably evaluated by analytical tools upon harvesting, marketing, and processing [28]. The fatty acid composition of sunflower, rapeseed, mustard, peanut, and olive oils were subject to examination in Konuskan et al. (2019) research. According to those authors sunflower oils have the highest oleic acid (68.88%) followed by olive oil. Our examinations indicated Experto as the richest hybrid of oleic acid (86.2%) [30]. Kefale et al. (2017) also investigated fatty acid composition in different oils from sunflower and safflower. We agree with their conclusion that sunflower hybrids with low levels of saturated fatty acids were suitable for edible oil processing for edible purposes [29]. The results from the examination of Konuskan et al. (2019) showed that the free fatty acid value of the tested oils varied between 0.43 and 1.36% which is significantly higher than the free fatty acids of all 17 hybrids examined in our study (Tab. II) [30]. Generally speaking, results from Tables II and III indicated better properties of samples of sunflower oils produced from 2017. In the second testing year, the average percentage of free fatty acids was 0.15 compared to the harvesting year 2016 when the average percentage of free fatty acids was double. Furthermore, the average value of peroxide value for 2017 harvesting year was 0.94 O_2/kg while for 2016 was 1.08 O_2/kg. The difference between varieties produced from both harvesting years and values for free fatty acids and peroxide value was the most significant for the Torino and Neostar varieties (Tab II).

A total of 320 edible oils on Indian market were included in research of the working group of Dorni et al (2018). We agree with their statement that every variety of edible oil showed its own unique fatty acid profile with a significant variation within each individual fatty acid [31]. Our findings stated that few hybrids of sunflower oil such as Experto and BG Fila had their unique fatty acid profile with over 80% oleic acid (Tab. I) [32, 33]. Furthermore, the fatty acid composition was studied considering the general groups saturated, unsaturated, monounsaturated, and polyunsaturated. Saturated and unsaturated are influenced by environmental conditions such as temperature, rainfall, and genotypes [34]. Remarkable studies demonstrated that the health beneficial effects of vegetable oils have been often attributed to their antioxidant properties and abilities to increase cellular antioxidant defence system and thereby scavenge free radicals, inhibit lipid peroxidation, and augment anti-inflammatory potential [35]. We assumed that the results of the oxidative stability of examined oils depends on the level of unsaturated fatty acids and the level of natural antioxidants which include α-tocopherol as the most abundant Vitamin-E-active compound in sunflower oil [12, 13, 36]

The results presented by different authors in the last decade have shown that it is possible to obtain sunflower oils of very different qualities combining the genetic variability in the response of the fatty acid composition to temperature and the climatic diversity under which the sunflower is cultivated [23, 37, 38].

Cold-pressed sunflower oil is a rich source of β-sitosterol, campesterol and total phytosterol and might be a better choice for patients with high cholesterol and cardiovascular diseases [39, 40].

4. CONCLUSIONS

Generally speaking, results from free fatty acids and peroxide value indicted better properties of samples of sunflower oils produced from 2017 in comparison to 2016. Furthermore, results from our study showed a strong relationship between the fatty acid composition and the variety of sunflower oil. The highest amount of monounsaturated oleic acid was related to Experto, Talento, BG Fila and Dijamnatis while Fortimi, Torino, Felix and Neostar hybrids were related to the amount of polyunsaturated linoleic acid with over 50%. Due to the fatty acid profile, we recommend the cold-pressed sunflower oils from three hybrids Experto, BG Fila and Dijamnatis as cooking oils suitable for the thermal processing of food. Furthermore, we recommended the gap of oleic/linoleic acid as the most important for the determination of the thermal stability of sunflower oils. Lastly, physicochemical parameters, iodine number and oxidation stability can be significant parameters understand the dominance of fatty acids in sunflower oil.

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