Growing season weather impacts on the physicochemical properties and quality of sunflower oils cold-pressed from hybrids grown in the Republic of North Macedonia

Ivan DONEV[1*]
Natalija MARKOVA RUZDIK[2]
Sanja KOSTADINOVIĆ VELIČKOVSKA[3]
Ljupco MIHAJLOV[2]
Emilija ARSOV[4]
Saša MITREV[4]

[1]UNI Service DOOEL Agro
Faculty of Agriculture
University "Goce Delchev"
Stip, Republic of North Macedonia

[2]Department for Plant Production
Faculty of Agriculture
University "Goce Delchev"
Stip, Republic of North Macedonia

[3]Department for Food Technology
Faculty of Agriculture
University "Goce Delchev"
Stip, Republic of North Macedonia

[4]Department for Plant and Environmental Protection, Faculty of Agriculture
University "Goce Delchev"
Stip, Republic of North Macedonia

(*) CORRESPONDING AUTHOR:
E-mail: sanja.kostadinovik@ugd.edu.mk

Received: July 27, 2019
Accepted: June 15, 2020

The purpose of the research was to determine the physicochemical properties of sunflower oils extracted from hybrids cultivated under environmental conditions in the Republic of North Macedonia. During 2016 and 2017, twelve sunflower hybrids were used as an experimental material in order to analyse some physicochemical properties of sunflower oils, such as free fatty acid, peroxide value, density, iodine measurement, saponification value and oxidative stability. The results were evaluated by LSD test, principal component analysis, linear correlation and cluster analysis. The free fatty acid values of the tested sunflower oils varied between 0.17% and 0.36%. The average value for peroxide measurement for all analysed oils was 0.93 O_2/kg. Fortimi and Neoma had the highest iodine value (134.5 and 131.0 g I_2/100 g, consequently) and the lowest was recorded by Experto (87.5 g I_2/100 g), followed by Talento (88.5 g I_2/100 g).
Significant differences were noticed between oils on their oxidative stability. Talento hybrid showed the highest oxidative stability for both years, which can be linked with high-oleic sunflower oil as more suitable for frying and thermal processing of food. Drastically lower oxidative stability for other sunflower oils might be an indication for high-linoleic sunflower oils which are usually recommended for thermally non processed food. Although Experto and Talento hybrids had the lowest iodine values which caused separation in the same cluster, the value of oxidative stability was drastically lower for Experto hybrid which can be linked with high-linoleic sunflower oils or lower amount of Vitamin-E-active compounds and phenolic compounds presented in sunflower oil as natural antioxidants.
Principal component analysis was utilised to examine the variation and to estimate the relative contribution of analysed properties to total variability. Three main components with Eigen value greater than one were extracted and contributed 88.44% of the total variability. PC1 accounted 44.88% of the total variability and showed positive factor loading for iodine value (0.59) and density (0.57). PC2 accounted 25.99% of the total variation and was positively correlated with saponification value (0.67) and oxidative stability (0.42) but with high negative factor loading for free fatty acid (-0.52) at the same time. The third PC component had 17.57% of variance and was positively linked with free fatty acid (0.59), peroxide value (0.52) and oxidative stability (0.47). On the other site, significant positive correlation was established between iodine value and density (r = 0.935). Oxidative stability was in negative correlation with iodine number (r = - 0.621).

Keywords: Physicochemical properties. Cold-pressed sunflower oils. Hybrids. Multivariate analyses

1. INTRODUCTION

Sunflower (*Helianthus annuus* L.) is one of the major oilseed crops in the world and is in fourth place among vegetative oils after soybean, oil palm and rapeseed

[1]. Sunflower is an important edible vegetative oil due to its nutritive value and use. It is one of the most widely cultivated oil crops in the world due to its ability to grow in large semiarid conditions without irrigation thanks to its root system that is well developed and has power to penetrate deeply in the soil [2]. Cultivation of sunflower has significantly increased in the last years, mainly due to the quality of its oil, which plays a significant role in human nourishment and for biodiesel production [3]. The sunflower seeds contain a high amount of oil (38.0% - 54.4%), protein (28% - 32%) and the most important vitamins and minerals [4]. A number of factors have been reported to affect oil quality [5].

Vegetable oil quality is mostly dependent on its resistance to oxidation. Oxidative and hydrolytic degradation are main reactions occurring during and after oil processing that reduce shelf life and result in low quality products [6].

O'Brien (2004) reported that the quality of the vegetable oils is one of the most important factors that affect their acceptability and market value [7]. Vegetative oils are a complex mixture of various saturated and unsaturated fatty acids, pigments, phosphatides, sterols and tocopherols. The rate of saturated to unsaturated fatty acid is important for human nutrition [8]. Higher rate of saturated fatty acid is important for oil stability while higher rate of unsaturated fatty acid is important to decrease the concentration of low-density lipoproteins [9].

Starting from this point, the study of physicochemical properties is needed to monitor the compositional quality of oils [10]. Free fatty acid, iodine value, saponification measurement, density and peroxide number can be used to evaluate the purity and quality of oils [11].

Principal Component Analysis (PCA) is one of the statistical tools used to assess and evaluate genetic diversity in many varieties. The results of PCA will be of greater benefit to identify the parents to improve various traits or characters and it can also be exploited in planning future breeding program [12]. On the other hand, Cluster Analysis (CA) has been suggested for categorising entries of germplasm collections based on a degree of similarity and dissimilarity [13]. Ghaffoor and Tayaba (2009), Rehman et al. (2013), Uzma and Muhammad (2014) and Hussain et al. (2017) demonstrated the effectiveness of PCA and CA in the selection of the best hybrids or hybrids in their experiments [14 - 17].

The main goal of this research is to determine the physicochemical parameters such, free fatty acid, saponification value, peroxide measurement, iodine value and oxidative stability in different sunflower cold pressed oils extracted from sunflower hybrids cultivated under agro-ecological condition in the Republic of North Macedonia.

2. MATERIALS AND METHODS

2.1. EXPERIMENTAL DESIGN

The trial was set up in the Ovche Pole region, near Sveti Nikole, on an experimental area owned by the Faculty of Agriculture, "Goce Delchev" University – Stip, Republic of North Macedonia during 2016 and 2017. The sunflower hybrids were laid out in a random block system, 5 m^2 plot per hybrid.

The field experiment was conducted without additional irrigation and the following agro-technical measurements were applied during the period of study (autumn and spring ploughing, fertilisation, bleaching, sowing, valuing, herbicide treatment, further fertilisation, intercropping and finally harvesting). The sunflower plants were physiologically matured when the back of the head turned from green to yellow, about 30 to 45 days after blooming. In both years of study, manual harvesting method was used, and the harvest took place in September. During the growing period, presence and absence of diseases was recorded. 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. In the second testing year, the rainfall amount was by half less (167 l/m^2) compared to the amount of precipitation in 2016.

2.2. SOURS OF SUNFLOWER HYBRIDS

Twelve sunflower hybrids (Experto, Armoni, Fortimi, Adagio, Neoma, Torino, Arisona, Bacardi, Feliks, Neostar, Kondi and Talento) were used as an experimental material in this research. Except Feliks, which has Serbian origin, all other tested hybrids were obtained from the Syngenta Company. All sunflower hybrids had not been tested in our country, they are new varieties to the market and were included in this type of examination for the first time. All hybrids were introduced and included in the research to test their physicochemical properties under agro ecological conditions in the Republic of North Macedonia.

2.3. PURIFICATION AND COLD-PRESSING

In order to produce cold-pressed edible oils, the cold-pressing experiment was performed in triplicate. The purification process of sunflower seeds started with the removal of broken and damaged seeds.

After pressing at 40ºC, the fresh cloudy oils were purified from solid impurities in the tanks by sedimentation within 20 days at 17ºC. The crude oils were removed from buffer storage tanks and pumped through a polishing filter to give crystal clear oils. The quantity of plant material was collected only for this experiment and the yield of each cold pressed edible oil was lower than 750 g. After sedimentation, the collected oil was filtrated by using the protection filter and bottled in dark 250 mL bottles. The oils were preserved by adding rosemary extracts supplied by Naturex, France with a dosage 30 mg/kg oil.

2.4. DETERMINATION OF PHYSICOCHEMICAL PROPERTIES OF SUNFLOWER OILS

All physicochemical properties were determined at the laboratory "UNILAB" that is a part of the Faculty of Agriculture, "Goce Delchev" University – Stip, Republic of North Macedonia.

2.4.1 Determination of the free fatty acid

The determination of free fatty acid was done by cold solvent method using potentiometric titration (ISO 660:2010) [18]. To the10 g mass of test portion was added 50 ml of the neutralised solvent mixture (ethanol and diethyl ether) and the sample was dissolved.

2.4.2 Determination of the peroxide value

Peroxide value is a measure of peroxides contained in the oil. Peroxide value is determined by measuring iodine released from potassium iodide. Furthermore, this value is a dynamic value, depending on the history of the test sample. The determination of the peroxide value is a highly empirical procedure and the value obtained depends on the mass of the test portion. The determination of peroxide value was carried out by ISO 27107:2011 [19].

2.4.3 Determination of the density of oils

Density was determined by using a pycnometar at 20°C carried out according to ISO 6683:2014 [20].

2.4.4 Determination of the iodine value

The determination of the iodine value was carried out by ISO 3961:2013 [21].

2.4.5 Determination of the saponification value

The saponification value was determined 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 was added. Determination of the saponification value was carried out by ISO 3657:2013 [22].

2.4. 6 Determination of the oxidative stability of oils

Oxidative stability of oil was evaluated by the Rancimat method (Gutierrez, 1989). 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 10l/h [23].

2.5. STATISTICAL ANALYSIS

Physicochemical properties were estimated for years and hybrids using the JMP 5.0.1 program. Fit analysis was performed to obtain the least significant differences (LSD values) for tested hybrids for years. Based on the LSD data, the hybrids were grouped and those with the highest values of the studied trait belong to group a. In order to evaluate the relationship between the tested physicochemical traits of sunflower oils and to analyse the contribution of each trait on the total variation, multivariate analyses were applied. Principal Component Analysis and Cluster Analysis were carried out by Statgraphis 2.1, while the linear correlation was calculated according to Singh and Chaudhary (1985) using SPSS (2010) software.
The one-way ANOVA statistical analysis was applied in order to see the abundance of residue after 8 days of sedimentation of crude oil by consideration of the type of hybrid with the significance level of 0.05. The significance level of differences between the mm of residue mean values was determined at 5% by a one-way ANOVA using Tukey's test. This treatment was performed by SPSS v.16.0 software (IBM Corporation, USA).

3. RESULTS AND DISCUSSION

The physicochemical properties of cold press oils extracted from sunflower hybrids are given in Table I and Table II.
Free fatty acid contains an important oil quality parameter [24]. The free fatty acid composition depends on the hybrid but also from environmental conditions, planting and harvesting time [25, 26]. Oils with higher free fatty acids content have poor quality and significant losses occur during the refining process [27].
From our research, free fatty acid for all samples varied between 0.17% and 0.36%, during the period of study (Tab. I). The highest average value for free fatty acid was recorded by Adagio hybrid (0.36%) followed by Armoni (0.32%). Fortimi hybrid had the lowest value for free fatty acid (0.17%). The mean value for this trait for all tested hybrids during the period of study was 0.26%.
Konuskan et al. (2019), reported low value for free fatty acid in sunflower oil (0.81%) [28]. Esuoso and Odetokun (1995) stated that free fatty acid contents of oils should not exceed 5% in order to be suitable for edibility. According to this view, all tested sunflower hybrids, from our experiment have value in ranges [29].
Peroxide value is used as a measure of the extent to which rancidity reactions have occurred during storage and it could be used as an indication of the quality and stability of fats and oil [30, 31]. Actually, peroxide number is used as an indicator for primary oxidation and rancidity of the oils [32]. The fresh vegetable oils normally have peroxide values below 10 meq O_2/kg [33]. High peroxide value could resulte from high degree of unsaturation and found to increase with the storage time, temperature, light and contact with atmospheric oxygen [11].
In our study, the average peroxide value for all analysed hybrids in the first year was 1.03 O_2/kg and the coeffi-

Table I - 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^{ab}	0.29	0.69^{h}	0.78^{e}	0.74	0.912^{e}	0.913^{e}	0.913
Armoni	0.47^{b}	0.16^{a}	0.32	1.21^{c}	0.89^{d}	1.05	0.919^{a}	0.919^{a}	0.919
Fortimi	0.22^{h}	0.12^{c}	0.17	1.14^{d}	1.03^{b}	1.09	0.917^{b}	0.918^{b}	0.918
Adagio	0.60^{a}	0.12^{c}	0.36	1.28^{b}	1.14^{a}	1.21	0.915^{d}	0.918^{b}	0.917
Neoma	0.29^{f}	0.14^{abc}	0.22	1.07^{e}	0.98^{c}	1.03	0.918^{b}	0.919^{a}	0.919
Torino	0.25^{g}	0.13^{ab}	0.19	1.14^{d}	0.56^{h}	0.85	0.916^{c}	0.915^{c}	0.916
Arisona	0.36^{d}	0.15^{ab}	0.26	0.99^{f}	0.72^{f}	0.86	0.916^{c}	0.919^{a}	0.918
Bacardi	0.32^{e}	0.14^{abc}	0.23	0.84^{g}	0.78^{e}	0.81	0.918^{ab}	0.919^{a}	0.919
Feliks	0.33^{e}	0.12^{c}	0.23	0.63^{i}	0.65^{g}	0.64	0.916^{c}	0.919^{a}	0.918
Neostar	0.37^{d}	0.14^{abc}	0.26	1.35^{a}	0.78^{e}	1.07	0.919^{a}	0.919^{a}	0.919
Kondi	0.46^{b}	0.16^{a}	0.31	1.19^{c}	0.77^{e}	0.98	0.916^{c}	0.918^{b}	0.917
Talento	0.30^{f}	0.15^{ab}	0.23	0.86^{g}	0.78^{e}	0.82	0.913^{e}	0.914^{d}	0.914
Average	0.37	0.14	0.26	1.03	0.82	0.93	0.916	0.917	0.917
$LSD_{0.05}$	0.02	0.03		0.01	0.02		0.001	0.001	
CV (%)	2.70	1.71		0.87	1.59		0.07	0.07	

cient of variation was small (0.87%). In 2017, the highest peroxide value was recorded by Adaigo (1.14 O_2/kg), followed by Fortimi (1.03 O_2/kg) and the smallest was obtained from Torino hybrid (0.56 O_2/kg). Significant differences were noticed for all tested sunflower hybrids in both years of research using LSD test (Tab. I). The mean peroxide measurement for all tested hybrids in the second experimental year was 0.82 O_2/kg with a 1.59% coefficient of variation.

Generally, all analysed sunflower hybrids had low average value for peroxide measurement (from 0.64 O_2/kg to 1.21 O_2/kg). Adagio (1.21 O_2/kg), Fortimi (1.09 O_2/kg), Neostar (1.07 O_2/kg) and Armoni (1.05 O_2/kg) exhibited higher values than 1 O_2/kg. The lowest peroxide number was recorded by Feliks hybrid (0.64 O_2/kg). The mean peroxide measurement for all tested hybrids was 0.93 O_2/kg (Tab. I) during the period of research. A higher moisture of the oils in 2016 is expected due to more intense rainfalls causing higher peroxide values for oils produced in 2016 in comparison to the oils from the same hybrids produced in the harvested year 2017 [57].

According to Konuskan et al. (2019), the peroxide value was 4.19 meq O_2/kg, which indicates that the tested oil was fresh [28]. Oils with peroxide value higher than 9 meq O_2/kg cause undesirable health problems by increasing reactive oxygen species as well as secondary products of lipid peroxidation that stimulate cardiovascular diseases [34]. Generally, oils with peroxide levels higher than 10 meq O_2/kg are considered to be less stable and have short shelf life. According to Awatif and Shaker (2014), the peroxide value ranges between 1.66 to 2.17 meqO_2/kg, while Mengistie et al. (2018) had reported 8.80 meq/kg peroxide number for tested sunflower oil [35, 36].

Even the values for density were very similar, significant differences were recorded between tested hybrids in both years of research using LSD (Tab. I). Experto and Talento showed the smallest average values for density (0.913 mg/cm^3 and 0.914 mg/cm^3, consequently). The average value for all analysed sunflower hybrids was 0.917 mg/cm^3.

Table II - 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^{g}	90^{h}	87.5	188^{c}	188^{c}	188.0	1.80^{i}	3.48^{c}	2.64
Armoni	123^{c}	138^{b}	130.5	191^{ab}	189^{bc}	190.0	2.86^{e}	2.92^{g}	2.89
Fortimi	129^{a}	140^{a}	134.5	190^{ab}	189^{bc}	189.5	2.68^{h}	2.86^{h}	2.77
Adagio	120^{e}	131^{e}	125.5	190^{b}	189^{bc}	189.5	2.96^{d}	3.17^{d}	3.07
Neoma	127^{b}	135^{cd}	131.0	190^{b}	189^{bc}	189.5	2.81^{f}	2.97^{f}	2.89
Torino	109^{f}	121^{g}	115.0	190^{b}	190^{ab}	190.0	3.66^{b}	3.76^{b}	3.71
Arisona	121^{de}	125^{f}	123.0	191^{ab}	190^{ab}	190.5	2.73^{g}	3.10^{e}	2.92
Bacardi	120^{e}	136^{c}	128.0	190^{ab}	190^{a}	190.0	3.59^{c}	2.99^{f}	3.29
Feliks	122^{cd}	136^{bc}	129.0	190^{ab}	190^{ab}	190.0	2.66^{h}	2.98^{f}	2.82
Neostar	122^{cd}	136^{c}	129.0	191^{ab}	189^{bc}	190.0	2.66^{h}	2.93^{g}	2.80
Kondi	121^{cde}	134^{d}	127.5	190^{b}	190^{a}	190.0	2.72^{g}	2.88^{h}	2.80
Talento	87^{g}	90^{h}	88.5	191^{a}	190^{a}	190.5	8.68^{a}	10.16^{a}	9.42
Average	115	126	120.5	190	189	189.5	3.32	3.68	3.50
$LSD_{0.05}$	1.96	1.77		1.59	1.26		0.02	0.03	
CV (%)	1.01	0.83		0.49	4.05		0.42	0.54	

The iodine number equals the number of mg of iodine required to saturate the fatty acids in 100 mg of the oil or fat. Actually, the iodine number determines the stability of oils to oxidation [37]. Oils rich with saturated fatty acids have low iodine value. Decrease in iodine value shows decrease in the number of double bonds and it indicates the oxidation of the oil. In many papers, the main goal of the research was the determination of the iodine value that is used to measure the amount of unsaturated fatty acids [38 - 40].

The results for iodine value from our experiment are indicated in Table II. Significant differences were recorded between tested sunflower hybrids during both years of testing (Tab. II). In 2016 and 2017, the highest value for iodine measurement was obtained by Fortimi (129 g I_2/100 g in first testing year and 140 g I_2/100 g in second experimental year) and the lowest was obtained by Experto (85 g I_2/100 g in 2016 and 90 g I_2/100 g in 2017). In both years of study, the coefficients of variation were small (1.01% and 0.83% consequently). The average iodine value for all tested hybrids during the period of study was 120.5 g I_2/100 g (Tab. II).

Codex Alimentarius Commission (1993) recommended standard for iodine value in sunflower variety ranges from 110 to 143 g of iodine/100g of oil [41]. According to Konuskan et al. (2019), the iodine value in sunflower oil was 102.02 g I_2/100 g [28]. Awatif and Shaker (2014) examined the physicochemical properties of oil extracted from seven sunflower hybrids [35]. In their research the iodine number ranges between 86.10 to 105.50 g/100 g. Aşkın (2018) also studied the iodine value in six sunflowers hybrids grown in Trakya Agricultural Research Institute in Edirne [42]. The value for this trait ranges between 89 to 129 g I_2/100 g oil. According to Antia (1989), the iodine measurement of sunflower oil ranges between 125 to 136 g of iodine/100g of oil, while Neelam Khetarpaul et al. (2007) had been reported 135.47% for this trait [43, 44].

Saponification value is an important parameter for characterising the industrial use of oil, specifically for soap production [45]. Oils with low SV value can be used to produce soap, candles, and raw materials for lubricants [46]. Saponification value measures the average chain length of the fatty acid that makes up the oil. This means that the saponification value is useful in providing information as to the quantity, type of glycerides and mean weight of the acids in the oil sample [47, 11]. Saponification value is an index of average molecular mass of fatty acid in the oil sample.

The average values for saponification measurement in 2016 and 2017 were 190 mg KOH/g and 189 mg KOH/g, consequently (Tab. II). Even the results show similar values for saponification measurements, significant differences were obtained between tested sunflower hybrids, using LSD test.

Similar results were obtained by Aşkın [42]. According to Mengistie et al. (2018) sunflower oil has 197.14 mg KOH/g oil saponification value, while Neelam Khetarpaul et al., (2007) reported 192.65 mg KOH/g oil saponification number [36, 44].

Oxidative stability is an important oil factor used to assess oil quality, determining its resistance to the oxidation process. All the samples under study differ in their oxidative stability and belong to different groups based on LSD value (Tab. II). The hybrid Experto showed the lowest average oxidative value (2.64 h) and was followed by the hybrid Fortimi which showed a slightly higher value (2.77 h). The hybrid Torino had high mean oxidative stability (3.71 h) but among all hybrids, Talento performed the best result, with the highest oxidative stability value of 9.42 h (Tab. II).

Awatif and Shaker (2014) reported higher values for oxidative stability compared to results obtained with this study [35].

The variety appeared to have a significant effect on physicochemical properties and significantly affected the oil, iodine value as well as the oxidative stability. As we can see from the Table II, a lower iodine number is not always linked by higher oxidative stability. This behaviour can be explained by the fact that a higher oxidative stability can be related to a higher level of monounsaturated fatty acids (in particular, oleic acid) and a lower level of polyunsaturated fatty acids (such linoleic acid). Furthermore, the values of free fatty acids and peroxide numbers are linked by the degree of oxidation which can affectto the oxidative stability of oils. Higher amount of free fatty acids and peroxide values means that oils are partially oxidised that can reduce the oxidative stability of the oil.

Regarding the growing season's weather, the most significant is the impact of rainfall on the level of free fatty acids. According to the findings of Japir et al. (2017), the currently evolving climate, torrential rainfall, humidity and inadequate storage result in the breakdown of TAGs and release free fatty acids in crude palm oil [56]. As we can see from the Table I, the higher rainfall rate can be linked to higher humidity that can give rise to yeast and moulds. On the other hand, the second reason for higher level of free fatty acids can be linked to the unsuitable storage of the seeds [48].

Multivariate analyses like the Principal Component Analysis (PCA), linear correlation and Cluster Analysis (CA) are necessary for the proper examination and analysis of agro-morphological and physicochemical properties. According to Mohammadi and Prasanna (2003) most frequently used approaches are Principal Component Analysis and Cluster Analysis, which are used for the estimation of genetic diversity in various crops like wheat, sorghum and sunflower [49 - 53]. The objective of the Principal Component Analysis is the reduction of dimensionality of a data set with a large number of correlated variables of traits [54].

Table III - Principal Component Analysis and factor loading of tested physicochemical traits

	PC1	PC2	PC3
Eigen value	2.69	1.56	1.05
Percentage of variance (%)	44.88	25.99	17.57
Cumulative percentage (%)	44.88	70.87	88.44
Physicochemical traits	**Factor loading of tested traits**		
Free fatty acid	0.06	-0.52	0.59
Peroxide value	0.37	-0.22	0.52
Density	0.57	0.21	-0.07
Iodine value	0.59	0.10	-0.10
Saponification value	0.16	0.67	0.38
Oxidative stability	-0.40	0.42	0.47

In this study, the Principal Component Analysis was used to examine the variation and estimate the relative contribution of tested traits for the total variability. Principal Component Analysis was carried out by using twelve sunflower hybrids and six traits. Three main components were extracted with Eigen value greater than one (Tab. III). The result showed that 88.44% of the variability was explained by three main components. The first and the second components explained 44.88% and 25.99% of the total variation, respectively. The third PC component had 17.57% of the total variance. Two main components with a cumulative variability of 73.7% were reported by Hussain et al. (2017). Density and iodine value were the important traits positively contributing to the first main component (Tab. III). On the other side, the oxidative stability showed a negative factor loading in PC1 (-0.40). The second main component was highly linked to the saponification value (0.67) and oxidative value (0.42) but, at the same time, had a negative factor loading with free fatty acid (-0.52). Free fatty acid, peroxide value and oxidative value showed positive factor weights by PC3 (0.59, 0.52 and 0.47, respectively).
The Principal Component Analysis and the factor loaded with tested physicochemical traits indicated an inverse relationship between free fatty acids and peroxide value on one hand and oxidative stability on the other hand (Tab. III). More precisely, higher values for free fatty acids and peroxide number indicated oxidation in oil which resulted in a smaller oxidative stability. Furthermore, the highest linear correlation coefficient for iodine value and oxidative stability (-0.621) confirm that sunflower oils with lower value for iodine number

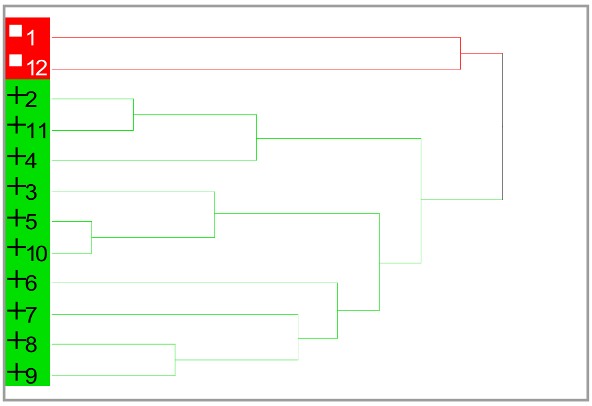

Figure 1 - Cluster analysis of sunflower hybrids based on some physicochemical properties.
Legend:
1 Experto. 2 Armoni. 3 Fortimi. 4 Adagio. 5 Neoma. 6 Torino. 7 Arisona. 8 Bacardi. 9 Feliks. 10 Neostar. 11 Kondi. 12 Talento

had higher oxidative stability (Tab. IV).
Manu researches used a linear correlation to determine the interaction between physicochemical properties in sunflower seeds [42, 56].
The results of the linear correlation are depicted in Table IV. The iodine value was highly and significantly in positive correlation with density (r = 0.935). A significant negative correlation was established between the oxidative stability and iodine value (r = - 0.621).
Two cluster groups were extracted by Cluster Analysis based on tested physicochemical properties (Fig. 1). The analysis showed that cluster one included two sunflower hybrids (Experto and Talento). Experto and Talento have the lowest values for iodine measurement. The second cluster group contained the remaining hybrids. The smallest distance was noticed between Neoma and Neostar. Those hybrids have similar peroxide value and oxidative stability.
With the exception of the Felix hybrid, the results for 11 hybrids, after 8 days of sedimentation, (presented in Tab. V) indicated significantly less residue and higher quality of oils for the 2017 harvest year. The amount of residues was in the range from 68 mm for the Torino hybrid to 203 mm for the Neoma one. This statement can be linked to less rainfall in 2017 in comparison to 2016. The cold-pressed edible oil from the Felix hybrid is the only sample that showed significantly smaller residue for the 2016 harvest year when rainfall was higher.

Table IV - Linear correlation coefficient between some physicochemical properties in sunflower oils

	Free fatty acid	Peroxide value	Density	Iodine value	Saponification value	Oxidative stability
Free fatty acid	1	0.339	-0.071	-0.035	-0.175	-0.187
Peroxide value		1	0.393	0.478	0.015	-0.215
Density			1	0.935**	0.423	-0.500
Iodine value				1	0.321	-0.621*
Saponification value					1	0.388
Oxidative stability						1

* Statistical significance of differences at P<0.05; ** Statistical significance of differences at P<0.01

Table V - Mean values of residue after 8 days of sedimentation in mm

Hybrids	Mean values of residue after 8 days of sedimentation in mm	
Harvest year	***2016***	***2017***
Experto	92 ± 7[a]	69 ± 9[b]
Armoni	137 ± 12[a]	69 ± 7[b]
Fortimi	121 ± 9[a]	86 ± 5[b]
Adagio	108 ± 11[a]	89 ± 4[b]
Neoma	203 ± 21[a]	77 ± 10[b]
Torino	68 ± 5[a]	53 ± 3[b]
Arisona	182 ± 14[a]	96 ± 4[b]
Bacardi	157 ± 13[a]	69 ± 8[b]
Feliks	***98 ± 4[b]***	***149 ± 14[a]***
Neostar	178 ± 17[a]	70 ± 7[b]
Kondi	146 ± 14[a]	63 ± 6[b]
Talento	102 ± 10[a]	66 ± 8[b]

4. CONCLUSIONS

Free fatty acid, peroxide value, density, iodine number, saponification value and oxidative stability of twelve sunflower oils extracted from different sunflower hybrids were determined. From all tested sunflower hybrids, Talento had the lowest value for iodine number and the highest measurement for oxidative stability. The average values for free fatty acids and peroxide number for 2016 were 0.37% and 1.03 0_2/kg, which were significantly higher values in comparison to the same parameters for 2017 (0.14% and 0.82 0_2/kg, respectively) (Tab. I). Our results confirmed that rainfalls had a significant impact on the values of free fatty acids and peroxide value since higher results we obtained from 2016 when rainfalls were intense. The values of the iodine number were linked to the oxidative stability due to the ratio of monounsaturated and polyunsaturated fatty acids. Furthermore, the abundance of residue for 11 hybrids indicated higher quality of oils from 2017 in comparison to 2016. The only exception was cold-pressed edible oil from Felix hybrid that had higher sediment for 2017 harvest year. The Principal Component Analysis was utilised to estimate the relative contribution of different traits for total variability. The results of the PCA revealed that 88.44% of the total variability was explained by the three main components. PC1 accounted 44.88% of the total variability and showed positive factor loading for density and iodine value. Also, positive significant linear correlation between those traits was established. PC2 accounted 25.99% of the total variation and the third component had 17.57% of total variability. Actually, the results for all tested physicochemical properties were within the range as explained in literature. It can be concluded that all analysed sunflower oils had an acceptable level of physicochemical quality. The results from our study indicated Talento as the best sunflower hybrid with the highest oxidative stability of cold-pressed sunflower oil and the lowest value for iodine and peroxide number. Frying oils made from sunflower have lower stability due to their high polyunsaturated fatty acids; however, high-oleic sunflower oils are suitable frying oils. The oxidative stability above 8h can be a good indication that Talento hybrid can be linked with high-oleic sunflower oil. The lowest value of Iodine value is not always an indication that oil will be stable during oxidation. Experto and Talento hybrid was classified in the same cluster (Fig. 1), but oxidative stability was drastically lower in comparison to the Talento hybrid. Iodine value can be used to measure the degree of unsaturation of oil while the oxidative stability except from the iodine value also depends on Vitamin-E-active compounds, polyphenols and other natural antioxidants presented in the oil. Our future study will be on the fatty acid composition of all hybrids in order to estimate high-oleic sunflower oils with better stability during frying and better quality for thermally processed food.

REFERENCES

[1] A. Gouzy, A.P. Massol, Z. Mouloungui, O. Merah. Effects of technical management on the fatty-acid composition of high-oleic and high-linoleic sunflower cultivars. Oilseeds and fats, Crops and lipids, *23*(5), D502, (2016)

[2] G. Piva, A. Bouniols, G. Mondies. Effect of cultural conditions on yield, oil content and fatty acid composition of sunflower kernel. In: Proc 15th International Sunflower Conference, Toulouse, France, 61-66, (2000).

[3] R. John Evans, S.L. Bandemer. Nutritive value of some oil seed protein. Cereal Chem. *44*(3), 417-426, (1967).

[4] M.M. Keshta, T.Y. Rizk, E.T. Abdou. Sunflower response to mineral nitrogen, organic and bio-fertilisers under two different levels of salinity. In: Velasco, L. (ed.), Proceedings of the 17th International Sunflower Conference, Cordoba, Spain, June *8*(12), 451-454 (2008).

[5] G. Justyna, W. Waldermar. Trends in edible vegetable oils analysis. Part A. Determination of different components of edible oils-a review. Pol. J. Food Nutr. Sci. *61*(1), 33-43 (2011).

[6] V. Rajko, V. Sergeja, A. Helena. Biochemical parameters and oxidative resistance of thermal treatment of refined and unrefined vegetable edible oils. Czech J. Food Sci. *28*(5), 376-384 (2010).

[7] R.D. O'Brien. Fats and Oils: Formulating and Processing for Applications. CRC Press, Boca Raton, 1-147 (2004).

[8] K. Ganesan, K. Sucalingam, B. Xu, Impact of

consumption and cooking manners of vegetable oils on cardiovascular diseases–a critical review. Trends Food Sci. Technol. *71*, 132-154, (2018).
[9] D. Dzisiak. New oils reduce saturated and trans fats in processed foods. Cereal Foods World, *49*(6), 331-333 (2004).
[10] K. Mousavi, S. Shoeibi, M. Ameri. Effects of storage conditions and PET packaging on quality of edible oils in Iran. Advances Environ. Biol. *6*(2), 694-701, (2012).
[11] I.H.A Mohammed, T.B. Ali. Physicochemical characteristics of some imported edible vegetable oils in Iraq. Res. J. Pharm. Biol. Chem. Sci. *6*(5), 488-494, (2015).
[12] B. Venujayakanth, A.S. Dudhat, B. Swaminathan, M.L. Anurag. Assessing crop genetic diversity using principle component, Trends in Biosci. *10*(2), 523-528, (2017).
[13] H.S.B. Mustafa, F. Jehanzeb, H. Ejaz, B. Tahira, M. Tariq. Cluster and principle component analyses of maize accessions under normal and water stress conditions. J. Agric. Sci. 60(1), 33-48, (2015).
[14] A. Ghaffoor, S. Tayaba. Botanical and morphological characters, yield and oil contents. Pak. J. Bot. *44*, 687-690, (2009).
[15] R. Rehman, N.S. Kausar, M. Shahid, M. Arshad, A. Ghafoor. Genetic divergence among Pakistani bread wheat varieties and advanced lines for randomly amplified polymorphic DNA (RAPD) markers. Pak. J. Bot. *45*(S1), 327-332, (2013).
[16] A. Uzma, F.K. Muhammad, B. Sanam. Investigation of genetic divergence in local sunflower hybrids and inbred lines by applying morphological markers. Int. J. Agron. Agric. Res. *5*(2), 154-163, (2014).
[17] F. Hussain, M. Rafiq, M. Ghais, R. Qamar, M.K. Razzaq, A. Hameed, S. Habib, H. Saad, H.S. Bin Mustafa. Genetic Diversity for Seed Yield and its Components Using Principal Component and Cluster Analysis in Sunflower (Helianthus annuus L.) Life Science J. *14*(5), 71-78, (2017).
[18] ISO 660:2010. Determination of acid value and acidity. 9 pages.
[19] ISO 27107:2011. Determination of peroxide value – potentiometric and point determination. 10 pages.
[20] ISO 6683:2014. Determination of density. 10 pages.
[21] ISO 3961:2013. Determination of iodine value (ISO 3961:2013). 10 pages.
[22] ISO 3657:2013. Determination of saponification value. 10 pages.
[23] ISO 6886:2016. Animal and vegetable fats and oils - Determination of oxidative stability (accelerated oxidation test). 13 pages
[24] C.R. Moschner, B. Biskupek-Korell. Estimating the content of free fatty acids in high oleic sunflower seeds by near-infrared spectroscopy. Eur. J. Lipid Sci. Technol. *108*, 606-613, (2006).
[25] H. Baydar, S. Erbas. Influence of seed development and seed position on oil, fatty acids and total tocopherol contents in sunflower (Helianthus annuus L.). Turk. J. Agric. For. *29*, 179-186 (2005).
[26] J. Roche, A. Bouniols, Z. Mauloungui, T. Barranco, M. Cerny. Management of environmental crop conditions to produce useful sunflower oil components. Eur. J. Lipid Sci. Technol. *108*(4), 287-297 (2006).
[27] J.A. Cornelius. Some technical aspects influencing the quality of palm kernels. J. Sci. Agric. *17*, 57-61, (1966).
[28] D.B. Konuskan, M. Arslan, A. Oksuz. Physicochemical properties of cold pressed sunflower, peanut, rapeseed, mustard and olive oils grown in the Eastern Mediterranean region. Saudi J. Biol. Sci. *26*, 340-344, (2019).
[29] K.O. Esuoso, S.M. Odetokun. Proximate chemical composition and possible industrial utilization of Blighiasapida seed and seed oils. Riv. Ital. Sostanze Grasse, *72*, 311-313, (1995).
[30] F.C. Ekwu, A. Nwagu. Effect of processing on the quality of cashew nut oils. J. Agric. Sci. Food Technol. *4*, 105-110, (2004).
[31] J.G. Nangbes, J.B. Nvau, W.M. Buba, A.N. Zukdimma. Extraction and characterization of castor (Ricinus communis) seed oil. Int. J. Eng. Sci. *2*(9), 105-109, (2013).
[32] M. Poiana. Oxidative stability of sunflower oil during convective and microwave heating using grape seed extract. Int. J. Molecular Sci. *13*, 9240-9259, (2012).
[33] A.B. Orhevba, A.N. Efomah. Extraction and characterization of cottonseed (*Gossypium*) oil. J. Basic Appl. Sci. Res. *1(2)*, 398-402, (2012).
[34] V. Lobo, A. Patil, A. Phatak, N. Chandra. Free radicals, antioxidants and functional foods: Impact of human health. Pharmacogn. Rev. *4*, 118-126, (2010).
[35] I.I. Awatif, M.A. Shaker. Quality characteristics of high-oleic sunflower oil extracted from some hybrids cultivated under Egyptian conditions. Helia, *37*(60), 113-126, (2014).
[36] T. Mengistie, A. Alemu, A. Mekonnen. Comparison of physicochemical properties of edible vegetative oils commercially available in Bahir Dar, Ethiopia. Chem. Int. *4*(2), 130-135, (2018).
[37] J.E. Asuquo, A.C.I. Anusiem, E.E. Etim. Extraction and characterization of rubber seed oil. Int. J. Mod. Chem. *1*(3), 109-115, (2012).
[38] J. Chebet, Th. Kinyanjui, K.P. Cheplogoi. Impact of frying on iodine value of vegetable oils before and after frying in different types of food in Kenya.

J. Sci. Innov. Res. *5*(5), 193-196, (2016).
[39] K.A. Bayz, N.H. Rasul. Investigation of the composition of sunflower seeds oil and their physicochemical properties in different zones in Iraqi Kurdistan region. ZANCO J. Pure Appl. Sci. *29*(4), 310-321, (2017).
[40] E. Zahir, R. Saeed, M.A. Hameed, A.Yousuf. Study of physicochemical properties of edible oil and evaluation of frying oil quality by fourier transform-Infrared (FT-IR) spectroscopy. Arab. J Chem. *10*, 3870-3876, (2017).
[41] Codex Alimentarius Commission (1993). Joint FAO/WHO Food Standards Programme. Report of the fourteenth session of the codex committee on fats and oils, London, United Kingdom, Rome, Italy.
[42] B. Aşkin. Determination of chemical and physical properties for seeds and oils of some different oleic and linoleic sunflower types. Selcuk J. Agric. Food Sci. *32*(1), 73-80, (2018).
[43] P.F. Antia. Clinical dietetics and nutrition. Third edition, Oxford University Press, Bombay, India. (1989).
[44] P. Neelam Khetarpaul, S. Jood, R. Goyal. Fatty acid composition and physic-chemical characteristics of cooking oils and their blends. J. Dairy Food Home Sci. *26*(3/4), 202-208, (2007).
[45] A.S. Olanrewaju, O.E. Moriyike. Physicochemical Characteristics and the effect of packaging materials on the storage stability of selected Cucurbits oils. Am. J. Food Nutr. *1*, 34-37, (2013).
[46] C. Agatemor. Studies of selected physicochemical properties of fluted pumpkin (Telfairia occidentalis Hook F.) seed oil and tropical almond (*Terminalia catappia* L.) seed oil. Pak. J. Nutr *5*, 306-307, 2006.
[47] W. Fazal, K.B. Musa, N. Mohsan, K. Khakemin. Comparison of some physico-chemical properties of different oils available in the local market in Pakistan. Int. J. Recent Res. Aspects, *2*(2), 93-98, (2015).
[48] U.N. Ekwenye. Chemical characteristics of palm oil biodeterioration. Biokemistri *18*, 141-149 2006.
[49] S.A. Mohammadi, B.M. Prasanna. Analysis of genetic diversity in crop plants: Salient statistical tools and consideration. Crop Sci. *43*, 1235-1248, (2003).
[50] F. Hailu, A. Merker, H. Singh, G. Belay, E. Johansson. Multivariate analysis of diversity of tetraploid wheat germplasm from Ethiopia. Genet. Resour. Crop Ev. *54*, 83-97, (2006).
[51] A. Ayana, E. Becele. Multivariate analysis of morphological variation in sorghum (*Sorghum bicolor* L. *Moench*) germplasm from Ethiopia and Eritrea. Genet. Resour. Crop Ev. *46*, 273-284, (1999).
[52] M. Kholghi, I. Bernousi, R. Darvishzadeh, A. Pirzad, H.H. Maleki. Collection, evaluation and classification of Iranian confectionary sunflower (*Helianthus annuus* L.) populations using multivariate statistical techniques. Afr. J. Biotechnol. *10*(28), 5444-5451, (2011).
[53] N. Markova Ruzdik, I. Karov, S. Mitrev, B. Gjorgjieva, B. Kovacevik, E. Kostadinovska. Evaluation of sunwflower (*Helianthus annuuus* L.) hybrids using multivariate statistical analysis. Helia, *38*(6), 175-187, (2015).
[54] I.T. Jolliffe. Principal component analysis. 2nd Edn., Springer-Verlag, New Your, USA. (2002).
[55] A.A. Neagu, I Niță, E. Botez. Correlation between some physic-chemical properties of sunflower oil. Ovidius University Annals of Chemistry, *25*(2), 71-74, (2014).
[56] A.A.W. Japir, J. Salimon, D. Derawi, M. Bahadi, S. Al-Shuja'a, M.R. Yusop. Physicochemical characteristics of high free fatty acid crude palm oil. Oilseeds, fats, crops and Lipids *24*(5), (2017).
[57] R. Akinoso, S.A. Aboaba, TMA Olayanju. Effect of moisture content and heat treatment on peroxide value and oxidative stability of un-refined sesame oil. African J. Food Agric. Nutr. Develop. *10*(10), 4268-4285, (2010).