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Studies of the physico-chemical characteristics and fatty acid composition of commercially available Algerian frying edible oils

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In the present study various physical and chemical characteristics have been studied and may be used for quality control of the main edible vegetable oil brands sold on the Algerian market, namely: Afia, elio, fleurial, La Belle, Oleor. The result obtained indicate that all the oils were consistent with the norms established indicative of edible oils with a good quality: Free Fatty Acid ranged from 0.044 to 0.054 %, the peroxide value varied from 1.61 to 2, the iodine value ranged from 124.07 to 129.91, the saponification value (189.01 to 192.21), the density at 20°C (0.917-0.921) and the refractive index at 40°C (1.4663-1.4670). However, the oils recorded a high PUFA content (mean 60%) suggesting that our oils are highly unsaturated and may be susceptible to rancidity. "Fleurial" oil can be more sensitive to oxidation and thermal alteration when compared with the others; this oil had the lowest induction period (8.27h), the lowest activation energy (438.16KJ/mol) and the highest PUFA content (mean 65%); however, at the factory, this oil was enriched by vitamins A and D, which makes it suitable for use as a salad oil.

Keywords: frying vegetable oils, Algeria, characterization

INTRODUCTION

Vegetable oils are substances derived from oil plants; they are composed of triglycerides which contain primarily polyunsaturated and monounsaturated fatty acids. Oil is extracted primarily from seeds. However, the crude oil obtained needs to be refined in order to transform it into a range of useful products for industry and consumers.

Oils improve the flavor, lubricity, texture, and satiety to foods. They have also been found to have a major role in human nutrition. Oils and fats have the highest energy in comparison to carbohydrates and proteins, carriers of oil soluble vitamins and many contain fatty acids essential for health, that are not manufactured by the human body [1].

Algeria has a large deficit in edible oils. The main oil produced is olive oil. But production hardly covers the needs and that makes it highly dependent on imports to supply the market. Thus, high quantities of crude oil are imported. After refining, the oil is sold under different brands. Some oils are pure and others are a blend of two oils. These oils are sold at different prices and used in cooking, notably for frying.

The main objective of this study was to characterize the refined vegetable oils used for frying commercialized in Algeria and improve the understanding as regards the oil quality, stability and applicability.

MATERIALS AND METHODS

Samples for examination represent all (five) Algerian manufacturers, i. e. Cevital Bejaïa (two oils: Fleurial and elio), C.O.G.B/La Belle Bejaïa (one oil: La Belle) and Afia International Oran (two oils: Oleor and Afia). The five refined edible vegetable oils analyzed in this study were acquired from a supermarket, Tizi-Ouzou, Algeria. These oils were submitted to the following tests: Free Fatty Acid, peroxide value, iodine value, saponification value, fatty acid composition, density, UV absorbance, Rancimat test, activation energy and refractive index assessment using the methods given in Table 1. The Data obtained was statistically analyzed using analysis of variance (ANOVA).

Free Fatty Acids content (FFA)

FFA content is a conventional expression of the percentage mass-fraction of the oil total. In view of the results shown in Table 2, the percentages of FFA (calculated as oleic acid) of the vegetable oils sold on the Algerian market were very low. The results obtained were in the range of 0.044%±0.003 ("elio" oil), 0.050±0.001 ("Afia" oil), 0.051±0.003 ("Oleor" oil), 0.051±0.005 ("fleurial" oil) and 0.054±0.003 ("La Belle" oil). These values were under the value of 0.2%, which is the maximum established by the

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Algerian standard 1169 (1990) for refined oils. The values were lower than those reported for Slovene sunflower oils (0.043) by Tasic and Klofutar [2]. The low values can be attributed to the efficient removal of the FFA during the refining of crude oil.

Table 1. Methods of analyses

Chemical analysis
Free Fatty Acids *(AFNOR NF T60-204, 1988).*
Peroxide value *(AFNOR NF T60-220, 1988).*
Iodine value *(AFNOR – NFT60 – 203, 1968).*
Saponification value *(AFNOR T60-206, 1968)*
Physical analysis
Refraction index *(ISO 6320, 2000)*,
Density *« DMA 4500 » densimeter*,
Ultraviolet spectrophotometry *(AFNOR T60-223, 1968)*,
Fatty acid composition *(AFNOR ISO 5509, 1978)*,
Rancimate test *(ISO 6886)* «Rancimat 743»,
Activation energy « NETZSCH STA 449C »

RESULTS AND DISCUSSION

Chemical properties

The mentioned chemical and physical characteristics of refined oils in our country are shown in Table 2. As shown, significant differences were found between these edible oils.

Iodine value

The iodine value (IV) is an indicator of the degree of unsaturation of fats and oils. The IV is the mass of iodine in grams that is consumed by 100 grams of oil. The IV provides an overall status of the unsaturation of the oils. The iodine value increases with the increase of unsaturation of oil. As in the measurement of the FFA %, our oils have acceptable values of IV in comparison with the range established by the Algerian Official Journal (120-143gI_2/100g oil) and Codex STAN 210, 1999 (118-141). In addition, these values are in agreement with those suggested by Pocklington [3] for edible oils of good quality.

Nevertheless, frying vegetable oils in our country are more unsaturated than those commercialized in Romania; Chira et al. [4] obtained the values of 113, 122 and 128 for canola oil, sunflower and soybean oil respectively. Our results were also higher than those of Tasic and Klofutar [2] for oils commercialized in Slovenia. The high IV indicates a high degree of unsaturation of our oils. From the oils studied, "fleurial" oil is characterized by the greatest IV; this may result from the fact that this oil has a higher content of polyunsaturated fatty acids. Its established unsaturated character affects the stability of the oils and as a result, leads to the appearance of degradation effects during storage.

Peroxide value

The peroxide value of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. This parameter expresses the oxidation in its early stages. The values obtained were low (mean 1.826) compared to the maximum acceptable value of 10meq KOH/g by the Codex Alimentarius Commission for oleaginous seed. The oils under investigation were purchased the same day these were received by the supermarket, which explains the lowest peroxide value. The low values of PV are indicative of the low levels of oxidative rancidity of the oils.

Otherwise, our fresh oils are less peroxidized than those commercialized in Bulgaria; Marinova et al. [5], that report values of 8.8 and 4 meq for sunflower and soybean oil, respectively. Bazlul Mobin et al. [6] report the values of 2.5 and 5 meq for our oils in Malaysia. Tasic and Klofutar [2] determined that the average of the peroxide values for four brands of our sunflower oil in Slovenia was 2.090.

Saponification value

The saponification value (SV) is an indicator of the average molecular weight and hence chain length. It is inversely proportional to the molecular weight of the lipid [7]. The results for the SV of the refined oils analyzed in this study were similar. These values were in agreement with the Algerian Official Journal (189-195) and Codex STAN 210, 1999 (188-194).

It was established that a high SV (>194) for the fats and oils is due to the predominantly high proportion of shorter carbon chain lengths of the fatty acids [8]. Our oils contain fatty acids with the same number of carbon atoms; four fatty acids are present in significant quantities: palmitic, stearic, oleic and linoleic acids which are all basically medium chain fatty acids and account for the high SV values.

The SV of the "fleurial" oil is lower than the result of Chira et al. [4] for sunflower oil in Romania (mean 204), but higher than that found by Tasic and Klofutar [2] for sunflower oils commercialized in Slovenia (192.077).

Table 2. Physical and chemical properties of the refined oils studied.

	Oil brands :				
	La Belle	Oleor	elio	Afia	Fleurial
Free fatty acids (%)	0.054±0.003	0.051±0.003	0.044±0.003	0.050±0.001	0.051±0.005
Peroxide value (meq kg^{-1})	2.00±0.20	1.97±0.12	1.70±0.20	1.85±0.10	1.61±0.21
Iodine value (g $100g^{-1}$)	127.05±2.07	124.07±4.10	125.14±4.82	126.25±4.03	129.91±2.78
Saponification value (mg g^{-1})	191.06±1.41	189.32±0.77	192.21±1.49	189.22±0.96	189.01±0.62
Refractive index at 40°C	1.4664	1.4664	1.4667	1.4663	1.4670
Densities at 20°C	0.921	0.920	0.917	0.920	0.920
A_{232nm}(1%)	3.03	2.93	3.07	2.93	2.52
A_{270nm}(1%)	1.74	2.00	2.34	1.75	2.06
A_{232}/A_{270}	1.74	1.46	1.30	1.67	1.22

Table 3. Saturated fatty acid composition of different types of vegetable oils (% w/w).

Type of Oil	C14	C16	C18	C20	C24
La Belle	0.080±0.000[a]	10.611±0.016[d]	3.984±0,0016[c]	0.423±0.003[b]	0.201±0.001[c]
Fleurial	0.070±0.000[e]	6.472±0.008[f]	3.857±0.004[e]	0.273±0.001[f]	0.245±0.005[a]
Oleor	0.080±0.000[b]	10.637±0.003[c]	3.919±0.000[d]	0.432±0.002[a]	0.202±0.003[c]
Afia	0.070±0.000[c]	10.749±0.012[b]	4.493±0.003[b]	0.358±0.000[d]	0.124±0.002[e]
Elio	0.070±0.000[d]	8.050±0.001[e]	3.517±0.000[f]	0.288±0.002[e]	0.213±0.002[b]

Means ± SD (standard deviation) within a column with the same lower case letters are not significantly different at $P < 0.05$; C14, myristic acid; C16, palmitic acid; C18, stearic acid; C20, behenic acid; C24, lignoceric acid

Table 4. Unsaturated fatty acid composition of different types of vegetable oils (% w/w).

Type of Oil	C18:1 n-9	C18:1 n-7	C18:2 n-6	C18:3 n-3	C20:1 n-9
La Belle	28.055±0.030[a]	1.458±0.002[a]	49.366±0.020[f]	5.199±0.003[d]	0.250±0.001[b]
Fleurial	23.266±0.004[d]	0.699±0.002[f]	64.442±0.043[a]	0.327±0.001[f]	0.152±0.001[f]
Oleor	27.184±0.012[b]	1.441±0.006[b]	50.240±0.027[e]	5.297±0.001[c]	0.266±0.006[a]
Afia	20.977±0.003[e]	1.335±0.001[c]	55.063±0.007[c]	6.376±0.000[b]	0.183±0.001[d]
Elio	23.537±0.002[c]	1.059±0.003[e]	60.475±0.002[b]	2.320±0.000[e]	0.173±0.003[e]

Means ± SD (standard deviation) within a column with the same lower case letters are not significantly different at $P < 0.05$; C18:1, oleic acid; C18:2, linoleic acid; C18:3, linolenic acid; C20:1, paullinic acid

Table 5. The content of SFA, MUFA, PUFA (% w/w) and the values of P/S indexes in different types of vegetable oils.

Type of Oil	Total SFA	Total MUFA	Total PUFA	P / S	n-6 / n-3
La Belle	15.331±0.023[c]	29.763±0.033[a]	54.565±0.023[f]	3.560±0.006[f]	9.494±0.004[c]
Fleurial	10.959±0.016[f]	24.117±0.005[d]	64.769±0.042[a]	5.909±0.013[a]	195.271±0.121[a]
Oleor	15.281±0.013[d]	28.891±0.012[b]	55.537±0.028[e]	3.633±0.004[e]	9.474±0.005[c]
Afia	15.797±0.010[b]	22.495±0.003[e]	61.439±0.007[c]	3.890±0.004[c]	8.630±0.000[d]
elio	12.188±0.000[e]	24.769±0.002[c]	62.795±0.003[b]	5.150±0.001[b]	26.060±0.000[b]

Table 6. Densities, UV absorption, induction period and activation energies of refined edibles vegetables oils analyzed.

Oils	Densities at :				A_{232nm}/ A_{270nm}	IP (h)	Activation energies (KJ / mol)
	283.17K (10°C)	293.14K (20°C)	303.14K (30°C)	313.14K (40°C)			
M1	0.926	0.921	0.916	0.913	1.741	10.15	550.09
M2	0.926	0.920	0.916	0.912	1.465	14.05	581.52
M3	0.922	0.917	0.912	0.909	1.311	13.46	570.50
M4	0.926	0.920	0.916	0.912	1.674	13.25	570.03
M5	0.926	0.920	0.916	0.912	1.223	08.27	438.16

M1: La Belle; M2: Oleor; M3: elio; M4: Afia and M5: fleurial

Physical properties

The physical properties of vegetable oils depend primarily on the composition (and hence the biological origin) and temperature [9]. They can be used to assess the purity or quality of lipid material with reference to the known standards or preferred characteristics [10].

Fatty acid composition

FA contents (as % of total FA) of all oils were significantly different. The percentage of the total saturated fatty acid (SFA) contents changed from 10.959±0.016% ("fleurial" oil) to 15.797±0.010 ("Afia" oil) (Table 3). These results are logical considering the nature of these oils."Fleurial" oil is constituted only of sunflower oil, while "Afia" oil is 100% soybean oil. It seems that soybean oils contain the highest percentage of SFA from sunflower oils. Indeed, Kostik et al. [11]; Tasan et al. [12]; Zambiazi et al. [13] reported that soybean oils were more saturated when they were compared to sunflower oils; the values obtained were respectively 13.5% *v.s* 8.8%, 14.24% *v.s* 9.45% and 15.10 *v.s* 12.36%; consequently, soybean oil may be more resistant to oxidation spoilage in comparison to sunflower oil. Otherwise, these values were lower than those found by Asgary et al. [14] for edible Iranian frying oils (18.9%). In consideration of SFA content, our oils are not suitable for frying. It has been indicated that only saturated oils are considered good sources for cooking and short term frying processing, due to their relatively higher SFA content and consequently higher stability [15, 16]. In addition, palmitic acid (C16:0) was the major SFA for all our oils, followed by stearic acid (C18:0). The values of our oils are lower than those of Iranian frying oils; these common SFAs that jointly constitute 21.8% in Iranian frying oils, but only 10.329% in our "fleurial" oil. The distribution patterns of myristic (C14:0) and behenic (C22:0) are almost the same for all vegetable oils and are independent of the oil origin, only traces were found. However, arachidic (C20:0) and lignoceric (C24:0) were found in considerable amounts in all our oils. Besides, our vegetable commercialized oils don't contain lauric acid (C12:0). This result is in line with Gregorio[17] and Gopala et al. [18]; these authors reported that only coconut oil is a major source of lauric acid.

The mean values of total unsaturated FAs (UFAs) of our oils varied from 83.934% ("Afia" oil) to 88.886% ("fleurial" oil) of the total FAs for all refined vegetable oils used in our study. Oleic (C18:1, ω9) and linoleic (C18:2) acids were the major UFA present in all studied oils (Table 4). "fleurial" oil and pure sunflower oil, contain a low proportion of palmitic acid as well as a considerable quantity of oleic acid and very high content of linoleic acid which give it a higher UFA content than other oils. This result is in accordance with Kostik et al.[11]; Tasan et al. [12] and Zambiazi et al. [13]. Hence, our commercialized oils are much unsaturated than those used in Iran: frying (72.3%), cooking (83.4%) and hydrogenated oils (34.9%). The oleic acid content of our oils was the lowest in comparison to Iranian edible oils: cooking (41.7%) and frying oils (40.2%). However, considering the linoleic acid content, ours oils appears to be superior; whereas frying, cooking and hydrogenated Iranian oils contain only 28.4%, 37.5% and 7.3% respectively.

The relationship between SFA and PUFA content is expressed as the P/S index. All the vegetable oils analyzed present a total PUFA higher than the SFA content (Table 5); these oils had a P/S ratio which varied from 3.560 ("La Belle" oil) to 5.909 ("fleurial" oil); these values were higher compared to Iranian frying oil (1.66), but similar to the cooking oils used in this country (4.351). All the refined vegetable oils used in our country are highly unsaturated. The refined oils have a higher total PUFAs content than the oils used in Iran (60.07% *v.s* 31.5% for frying oils), which make our oils suitable for use as a salad oil. Our commercialized vegetable oils, despite containing significantly higher amounts of PUFA, were used in frying. "Fleurial" oil showed a high PUFA (C18:2 + C18:3) content (64.769%) with linoleic acid being the major FA (64.442%) and α-linolenic acid the minor one, when compared with all other oils; consequently, this oil presented the highest n-6/n-3 ratio (195.271%). It is obvious, that due to the high content of PUFAs our oils are more prone to oxidation. Thus, none of these oils is suitable for frying.

Refractive index

Both the iodine value and refractive index (RI) are important characteristics which determine the degree of saturation or unsaturation of fats and oils. The RI of oils depends on their molecular weight, fatty acid chain length, degree of unsaturation and degree of conjugation [10]. The mean (1.466), obtained at 40°C, for the oils under investigation was within the range established by Codex alimentarius(1992) (1.466-1.470). As for the iodine value, "fleurial"oil showed a high value for the RI (1.467) in comparison to other oils.

Density

Density is one of the important characteristics of a vegetable oil. This parameter is dependent on their PUFA content, oxidation and polymerization level [19]. In this study, the density was determined for temperatures ranging from 283.17K (10.17°C) to 313.14K (40.14°C). The density variation with temperature for the studied oils was presented in Table 6. It can be observed that blindedoil ("elio") has a lower density than the others which have similar densities.

Otherwise, it was observed from this study that the densities of pure sunflower oil ("fleurial" oil) and pure soybean oil ("La Belle" and "Oleor" oils) are comparable to those of pure soybean oils. These values are within the range established by Codex STAN 210 (1999) at 20°C (0.918-0.923 for sunflower oil and 0.919-0.925 for soybean oil). From Table 6, it can be seen that the density of all oils decline with the rise in temperature. These values are lower than those obtained by Bazlul Mobinet al.[6] for our sunflower oil (0.932) and soybean oil (0.931) in Malaysia.

Rancimate test and activation energy

The oil stability index directly relates to the oxidative resistance of oil. This quality is proportional to the induction period. This latter represents the time needed for decomposition of hydroperoxides produced by oil oxidation [20]. The Rancimat induction time at 98°C for oils under investigation varied from 8.27 h to 14.05 h (Table 6); the minimum and maximum of the oxidative stability belongs to "fleurial" and "Oleor) oils, respectively.

It can also be seen that pure soybean oil is more stable than pure sunflower oil. "Oleor" oil**,** with a higher induction time, was probably more stable in comparison to others. "Fleurial" oil recorded a low induction period and a high iodine value suggesting that this oil may be particularly sensitive to oxidation. The sensibility of this oil ("fleurial" oil) is most likely due to its FA composition which contains a high proportion of PUFA (nearly 65%) (Table 5).

However, the induction times of our oils were found to be higher than those in most countries. Marinova et al. [5] noted a value of 6.7h and 11.5h respectively for sunflower and soybean oils sold in Bulgaria.

The activation energy represents the minimum energy required to start a chemical reaction. It is expressed, in this study, in units of kilojoules per mole (kJ/mol). The two parameters (activation energy and Rancimat test) showed a good agreement when the results were compared. From Table 6 it is seen that the energies values ranged from 438.16 KJ/mol ("fleurial" oil) to 581.52 KJ/mol ("Oleor" oil). The results reveal that the minimum energy required for "fleurial" oil to undergo deterioration reactions when compared to other oils is an indication of the bad oxidative stability of this oil. The energy activation of "fleurial" oil has a direct relationship with the Rancimat test and the high degree of unsaturation of this oil.

CONCLUSIONS

The quality and properties of freshly refined vegetable oils sold in Algeria were evaluated through this study using different parameters. The results obtained indicate that there are significant differences in all the physical and chemical parameters analyzed of these oils. All the refined vegetable oils had a very high IV. This is an indication of high unsaturation in these oils and thus they become more vulnerable to oxidation, making these oils unsuitable for deep-fat frying purposes notably "fleurial" oil. This oil had the highest PUFA content, mainly represented by linoleic acid, which makes it particularly sensitive to oxidation. In addition, its induction time and energy activation were very low; this is also another reason to make this oil more vulnerable to oxidation and thermal processing such as frying. However, this oil ("fleurial" oil) has nutritional advantages; indeed, during its refining, vitamins A and D were incorporated, which makes this oil suitable for use as a salad oil.

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ИЗСЛЕДВАНЕ НА ФИЗИКО-ХИМИЧНИТЕ ХАРАКТЕРИСТИКИ И СЪСТАВА ОТ МАСТНИ КИСЕЛИНИ НА ТЪРГОВСКИ АЛЖИРСКИ ХРАНИТЕЛНИ РАСТИТЕЛНИ МАСЛА

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(Резюме)

В настоящата работа са изследвани различни физични и химични характеристики на главните хранителни растителни масла и смеси, предлагани на алжирския пазар: Afia, elio, fleurial, La Belle, Oleor. Тези характеристики може да послужат за качествен контрол на маслата.

Получените резултати показват, че всички масла отговарят на нормите за хранителни масла с добро качество: съдържанието на свободни мастни киселини е в границите от 0.044 до 0.054 %, пероксидното число варира от 1.61 to 2, йодното число е в интервала от 124.07 до 129.91, числото на осапунване е от189.01 до 192.21), плътността при 20°C е между 0.917 и 0.921, а индекса на пречупване при 40°C е между 1.4663-1.4670. Обаче, съдържанието на поли-ненаситени мастни (PUFA) достига средно 60%, което показва, че маслата са склонни към гранясване. Маслото "fleurial" е най-чувствително спрямо окисление и термични въздействия; то има най-кратък индукционен период (8.27 часа), най-ниска активираща енергия (438.16 kJ/mol) и най-високо съдържание на PUFA (средно 65%). Но то е богато на витамините A и D, което го прави подходящо за консумация.