Mediterranean Journal of Nutrition and Metabolism 11 (2018) 331–342
DOI:10.3233/MNM-18208
IOS Press

Nutritional quality and safety of algerian margarines: Fatty acid composition, oxidative stability and physicochemical properties

Saida Bentayeb Ait Lounis[a,b,*], Lakhdar Mekimène[a], Damia Mazi[b], Thinhinane Hamidchi[b], Samir Hadjal[c], Samia Boualit[c] and Mohamed Benalia[a]

[a]*Laboratoire de Technologie Alimentaire et de Nutrition Humaine, Ecole Nationale Supérieure Agronomique "ENSA". Algérie*
[b]*Faculté des sciences biologiques et des sciences agronomiques, UMMTO, Algérie*
[c]*Cévital spa, nouveau quai, port de Béjaia, Béjaia, Algérie*

Received 18 February 2018
Accepted 27 March 2018

Abstract.
BACKGROUND: Margarine is a widely consumed product in Algeria. Few or no studies have been conducted to estimate its safety and nutritional quality.
OBJECTIVES: This study aims to evaluate some algerian margarines. Particular interest is given to their oxidative stability and fatty acid composition.
METHODS: Twelve margarines are selected, including tub and stick margarines, puff pastry margarines and vegetable smen. We evaluate physicochemical parameters (water content, pH, salt content, melting point and solids content with RMN), oxydative stability with Rancimat and fatty acid composition with GLC.
RESULTS: The analyzed products are mostly in conformity with standards. The estimation of the oxidative stability revealed that tub margarines are the least stable. Fatty acid composition showed that practically all the analyzed products are rich in SFA.
CONCLUSION: Large amounts of highly saturated oils such as palm oil, coconut and palm kernel are used. The fact that the *trans* fatty acids content is not very high in Algerian margarines and vegetable smen is not due to the legislation applied but to the awareness of few industries and especially to the import price exerted on different types of fat. So it is in view of profitability that industries choose raw material and not in a health concern.

Keywords: Margarine, vegetable smen, oxidation, SFC, fatty acid profile, SFA, *trans* FA

1. Introduction

Margarine, a fat-based food product, was formulated in the 19th century as a substitute for butter, due to the inability of the lower social classes to afford butter, of dairy origin. Although the raw material for the original margarine formulation was animal fat, shortages in beef fat supply along with advances in plant material hydrogenation, led to its replacement by hydrogenated vegetable oils [1].

*Corresponding author: Saida Bentayeb Ait Lounis, Faculté des Sciences Biologiques et des Sciences Agronomiques. UMMTO, Tizi-Ouzou, Algérie. Tel.: +213 661 47 90 76; E-mail: bentayebsaida@yahoo.fr.

ISSN 1973-798X/18/$35.00

Margarine can be defined as a stable emulsion (water-in-oil type), consisting mainly of vegetable oil and water, possibly with milk. It also contains emulsifiers, flavors, coloring, preservatives (pH correction, antioxidants), vitamins. It can be used as fat spread, for cooking and making bakery products.

From a microbiological point of view and because of its composition, margarine can be considered a healthy product. However, it can undergo chemical or physical deterioration, of which oxidation is the most important. It results in rancidity, and presents nutritional, sensory and hygienic disadvantages. This reduces its shelf life and causes it to be rejected by the consumer.

Over the last decades, the composition of margarine has changed significantly to increase its Healthiness; particularly with regard to cardiovascular diseases. Hydrogenation of vegetable oils has therefore been strongly discouraged, since it leads to the production of *trans* unsaturated fatty acids which increase LDL levels, decrease HDL ones and increase the risk of coronary heart disease. The use of tropical vegetable oils, including palm oil, palm kernel and coconut oil, which are rich in saturated fatty acids, gradually reduces hydrogenation in the production of margarine. This does not diminish the health risk. Indeed, epidemiological studies have shown that excessive consumption of SFA also promotes the risk of cardiovascular disease. SFA, particularly C12:0, C14:0 and C16:0, increase plasma cholesterol levels, including LDL-cholesterol, considered as a major risk factor [2].

While Denmark has restricted the level of *trans* fatty acids to 2% in oils and fats since 2003, and while several countries (Austria, Latvia, Hungary, etc.) have introduced measures to limit the consumption of *trans* fatty acids, no law or text makes any reference to it in Algeria. Moreover, the Algerian consumer ignores the existence of these *trans* fatty acids and their health impact, due to the total absence of awareness campaigns. As a result, the Algerian industry is not restricted in the selection of the fat it uses. Does it then go for hydrogenated vegetable fat or vegetable oils naturally rich in saturated fatty acids?

This study makes it possible, inter alia, to answer this question, given that no data are available on the composition of Algerian margarines or on their quality and that no study has been published on this subject unlike other countries [3–7].

2. Material and methods

2.1. Samples

Our approach to proceed to this study is aligned with the methodology followed by different authors [5, 8–11], For sample selection, we chose stratified random sampling, which advocated small surveys to ensure that the selected products are the most available in the market [10] and [11]. Thus, we selected twelve (12) margarines produced and marketed in Algeria, including three (03) tub margarines (MB) and four (04) stick margarines (MP), two (02) puff pastry margarines (MF) and (03) three Samples of vegetable smen (SM) (vegetable fat without water addition for cooking and bakery). These margarines and vegetable smen are produced by eight (08) factories : *Cévital (Béjaia)* : Medina (SM2), La Parisienne (MF1), Fleurial (MP4), *Groupe COGB La Belle (Béjaia) :* La belle (MB1), *SARL Traveps (Blida)* : Star (MP2) and Bonjour (MP1), *SARL SOFAMAR (Boumerdes) :* Many (MB2) and Mliha (MF2), SARL LES PRODUITS NOUNOURS : Nounours (SM3), *SARL CEBON (Tipaza)* : El mordjane (SM1), SARL *PROLIPOS (Oum El Bouaghi)* : Lyna (MB3), *SARL MATEG (Oran)* : Benina (MP3).

Sampling of the selected margarines is carried out by referring to several studies [8, 9, 12]. Three samples from three different batchs are purchased in supermarkets to form a representative sample of each brand. They are prepared according to the method recommended in [13] and [14]. A quantity of 30 g is taken per batch. The mixture is melted in a water bath at 50°C, homogenized, dried using anhydrous sodium sulfate and stored at –20 °C until analyze. All analysis are carried out in three replicates before the expiration date.

2.2. Methods

2.2.1. Determination of physicochemical properties

2.2.1.1. The water content. It is determined by the gravimetric method in an oven at $103 \pm 2\ ^{\circ}$ [15].

2.2.1.2. pH. pH of the aqueous phase is determined by the potentiometric method.

2.2.1.3. The sodium chloride (NaCl) content. It is determined by the titration of chlorides with silver nitrate in the presence of potassium chromate according to the Mohr method [16]. 5 g of margarine is dissolved in 100 ml of boiling distilled water. After cooling, few drops of potassium chromates (5%) are added. The mixture is then titrated with the silver nitrate solution (0.1N) until the color changes to red brick. The salt content is calculated as follows: Salt level (%) = [(N × V × Eq.g NaCl) / (P × 10)], where N:Normality of AgNO3 (0.1N), V: volume (ml) Of the $AgNO_3$ solution used for the titration, Eq.g NaCl: 58.5 g / mol, P: Weight of the sample (g).

2.2.1.4. Determination of acidity. It is based on hot neutralization of free fatty acids by NaOH solution in the presence of phenolphthalein [17]. 10 g of margarine is dissolved in 75 ml of neutralized ethanol in the presence of few drops of phenolphthalein (1% ethanolic solution). After heating, the mixture is titrated with sodium hydroxide solution (0,1N) until the pink color persists for at least 10 seconds. The acidity is determined as follows : A% = (M × N × V)/(10 × P) where M: molar mass of oleic acid = 282 g/mol, N: normality of the NaOH solution (0.1N), P: weight of the sample (g), V: volume of the NaOH solution used for the titration.

2.2.1.5. Determination of the peroxide value. It is based on the treatment of a sample in acetic acid and chloroform solution with a solution of potassium iodide (KI) and the titration of iodine released by a solution of sodium thiosulfate in the presence of a starch solution as a colored indicator [18]. 5 g of margarine is dissolved in 12 ml of chloroform, 18 ml of acetic acid and 1 ml of the saturated solution of potassium iodide. The mixture is Stirred for 1 min and leaved 1 mn in the dark, between 15 and 25°C. 75 ml of distilled water is added and stirred vigorously in the presence of a few drops of starch solution (1%) as a colored indicator. The mixture is titrated with sodium thiosulfate solution (0.01N) until the color disappears. Blank test is performed. The peroxide number is determined by the following formula: PV = (V-V_0) / P × 1000 where PV: peroxide value (meq of active O_2 / Kg), V: volume of sodium thiosulfate used to titration V_0: the volume of Sodium thiosulfate to titrate the blank and P: weight of the sample (g).

2.2.1.6. The iodine value. It is determined from the fatty acid composition using constants of the most common unsaturated fatty acids required for its calculation. The iodine value is determined by multiplying the percentage of each unsaturated fatty acid by its constant and adding the results. It yields two results from a single analysis [19]. Iodine index = % C 16:1 × 0.9525 + % C 18:1 × 0.8620 + % C18:2 × 1.7358 + % C 18:3 × 2.6216 + % C 20:1 × 0.7872.

2.2.1.7. The determination of solid fat content (SFC). It is carried out using a nuclear magnetic resonance (NMR) (MQ20 NMR Analyseur Bruker Mini Spectre). The percentage expressed represent an important physical characteristic influencing the technological and sensory properties of fatty substances. This determination is carried out according to [20]. Margarine is melted at 70°C, filtered and dried in the presence of anhydrous sodium sulfate. 3 tubes are filled to 2 cm, then incubated in a water bath for 30 minutes at 20°C, 30°C, and 40°C. After that, they are placed in the NMR apparatus. The curve (SFC%) is traced as a function of the temperature (°C).

2.2.1.8. The melting point. It is the temperature at which solidified fat in a capillary tube softened to the point that it rises in the tube. Its determination is based on the passage of fat from the solid state to the liquid state under the effect of heat at a certain temperature. The temperature chosen corresponds to the melting point of margarine,

expressed in degrees Celsius (°C) [21]. Two glass capillary tubes are introduced to a height of 1 cm, in the fat phase of the sample, previously filtered. Then, they are cooled in the freezer for 20 min. The two capillaries are immersed in water heated to 0.5°C/min. The melting temperature is noted when fat begins to rise in the capillary tube.

2.3. Determination of oxidative stability : Rancimat test

The principle of this test is the passage of purified air stream through the sample brought to a specified temperature. The gases released during the oxidation process are blown by the air in a vial containing deionized or distilled water in which a conductivity measuring electrode is immersed. The electrode is connected to a measuring and recording device. The end of the induction period is indicated when the conductivity begins to increase rapidly. This accelerated increase is caused by the accumulation of volatile fatty acids produced during oxidation. The method of the Rancimat test is carried out with 743 Metrohm Analysis, according to [22]. This is a conductimetric determination of the dissociation products of volatile acids (mainly formic acid and acetic acid) during oxidation. 3 g of margarine is introduced into the air oxidation flask. The air flow is adjusted to 10l/h. Temperature is maintained at 100°C. Measurement is stopped when the signal reaches 100% of the scale of the recorder. The induction time (IP) is given in hours.

2.4. Determination of fatty acids composition by GLC

2.4.1. Preparation of Fatty acid methyl esters (FAME)

The method chosen is used by several authors [23] and [6]. 3 ml of hexane is added to 100 mg of sample and stirred. 0.1 ml of 2M methanolic KOH is added and shaked for 2 minutes. Leave to rest for 15 minutes. The hexane phase is recovered in a test tube for GLC analysis.

2.4.2. Analyse of FAME by GLC

The principle of gas chromatography (GC) consists in driving FAME through a column containing an inert liquid at a high temperature, so that according to the partition between the training gas and the liquid, the various esters leave the column at different times. The operating conditions applied for the analysis of FAME are as follows : Chromopack CP 9002 chromatograph, FID detector, column (DB23 50% cyanopropyl, 30 m). The fatty acids are identified by their retention times in comparison with a reference chromatogram of a standard mixture of methyl esters of known composition and concentration. The mixture of standards used is NLEA FAME MIX containing 28 compounds, ranging from C4:0 methyl butyrate to C22:6 methyl docosahexaenoate (Ref. Resteck Catalog n° 35078 Lot n° AO71785). The fatty acid content is expressed as a percentage of the total fatty acids.

2.4.3. Statistical analysis

Statistical treatment of physicochemical analysis results (peroxide index, acidity, salt content, moisture, Rancimat test) is carried out using STATBOX software 6. It consists of an analysis of variance (one factor : brand) (ANOVA) for MB, MP and SM and the Student test for MF (comparison of two averages). The significant p value is 5%.

3. Results and discussions

3.1. Physicochemical properties

The results of physicochemical analysis are given in Tables 1 and 2. MB2, MB3 and MP3 margarines have a water content corresponding to the standard set by codex *alimentarius* for spread margarines, which is 16%.

Table 1
Physicochemical parameters and oxidative stability of margarines and vegetable smen

Samples		Iodine value (g I_2/100 g)	Water content (%)	pH	NaCl content (%)	Acidity (%)	Peroxide value (meO_2/kg)	Induction period (h)
MB	MB1	88,99	$8,51 \pm 3,12^{b}$	4,88	$0,42 \pm 0,09^{b}$	$0,18 \pm 0,02^{a}$	$1,8 \pm 0,8^{c}$	$23,28 \pm 1,26^{b}$
	MB2	66,08	$17,2 \pm 0,36^{a}$	4,52	$0,34 \pm 0,14^{b}$	$0,25 \pm 0,08^{a}$	$18 \pm 1,83^{a}$	$35,61 \pm 4,40^{a}$
	MB3	73,87	$15,91 \pm 0,29^{a}$	6,33	$0,72 \pm 0,03^{a}$	$0,34 \pm 0,12^{a}$	$13,73 \pm 3,11^{b}$	$23,18 \pm 1,48^{b}$
MP	MP1	62,62	$3,17 \pm 0,85^{c}$	–	$0,18 \pm 0,01^{c}$	$0,2 \pm 0,028^{c}$	$6,73 \pm 0,50^{b}$	$45,22 \pm 1,13^{a}$
	MP2	49,14	$1,88 \pm 0,87^{c}$	–	$0,2 \pm 0,07^{c}$	$0,3 \pm 0,04^{b}$	$3,07 \pm 0,99^{c}$	$1,5 \pm 0,11^{b}$
	MP3	47,57	$15,71 \pm 0,05^{a}$	5,94	$0,52 \pm 0,03^{a}$	$0,23 \pm 0,03^{c}$	$12,2 \pm 1,11^{a}$	$59,14 \pm 20,57^{a}$
	MP4	59,00	$12,6 \pm 1,28^{b}$	4,58	$0,36 \pm 0,01^{b}$	$0,4 \pm 0,02^{a}$	$2,33 \pm 0,4^{d}$	$36,92 \pm 3,835^{a}$
MF	MF1	55,06	$5,1 \pm 1,31^{b}$	–	$0,61 \pm 0,02^{a}$	$0,21 \pm 0,03^{a}$	$10,6 \pm 2,00^{a}$	$41,33 \pm 5,36^{a}$
	MF2	54,98	$11,84 \pm 0,33^{b}$	3,93	$0,8 \pm 0,18^{a}$	$0,35 \pm 0,07^{a}$	$0,93 \pm 0,31^{b}$	$51,58 \pm 5,76^{a}$
SM	SM1	47,38	$0,43 \pm 0,15^{a}$	–	$0,05 \pm 0,01^{b}$	$0,26 \pm 0,04^{b}$	$0,4 \pm 0,2^{b}$	$68,16 \pm 12,31^{b}$
	SM2	37,28	$0,56 \pm 0,17^{a}$	–	$0,08 \pm 0,01^{b}$	$0,25 \pm 0,03^{b}$	$0,4 \pm 0,2^{b}$	$92,19 \pm 4,23^{a}$
	SM3	41,27	$0,32 \pm 0,12^{a}$	–	$0,13 \pm 0,02^{a}$	$0,37 \pm 0,03^{a}$	$11,67 \pm 0,61^{a}$	$21,48 \pm 0,21^{c}$

MB : Tub margarine. MP : Stick margarine. MF : Puff pastry margarine. SM : Vegetable smen. Values with the same letters have no significant difference. $a > b > c$ at $p \leq 0,05$ are determinated for three categories separatley (Spread margarines : MB+MP, Puff pastry margarine : MF and vegetable smen : SM).

Table 2
Solid fat content (SFC %) and Melting point (°C) of margarines and vegetable smen

Sample	SFC (%)			Melting point (°C)
	20°C	30°C	40°C	
MB1	17,1	6,7	0,5	35,9
MB2	19,4	7,5	0	35,2
MB3	20	8,4	0,5	35,6
MP1	28,7	13,6	4,4	39,4
MP2	26,1	10,6	3,4	39,6
MP3	29,1	12,8	3	41,5
MP4	30,3	14,1	4,2	39,6
MF1	45,1	25,4	9,7	42,2
MF2	49,4	29,2	14,1	45,4
SM1	34,3	14,7	4,8	41
SM2	36	15,8	5,4	41,3
SM3	36,2	15,9	5	39,2

MP have a lower water content than MB. The water content of MB1 is very low 8.51%. It is a margarine that is experiencing a very strong demand on the Algerian market thanks to its use qualities. The different vegetable smen record the lowest values (less than 0.6%). This is compatible with vegetable smen formulation which is almost free of aqueous phase.

pH is a very important parameter because it prevents the risk of microbial contamination. A low pH value can inhibit the growth of most microorganisms. The pH value is corrected by adding an acidity corrector (citric acid, lactic acid and their sodium and calcium salts [24]. The results obtained for samples are given in Table 1. pH of MB1, MB2 and MP4 correspond to the standard generally set between 4 and 5.5 [24], while pH of MB3

and MP3 are above the standard. pH of puff pastry margarine MF2 is 3.93. According to [25], this last type of margarines can have values ranging between 3.0 and 3.5.

Salt content of margarines and vegetable smen, given in Table 1, corresponds to the standard values which vary between 0.1 and 1% or even 2% [24], with the exception of SM1 (0.05%) and SM2 (0.08%) which have slightly lower values. Salt is an important additive which, through its bacteriostatic properties, can contribute to the protection of the product against microbiological degradation and at the same time improve the palatability of the product for consumption. It also plays a very important role in the stability of emulsion. The amount of salt added depends on the use of margarine and its texture, as well as the culinary habits and consumer category [24].

Acidity measurement is one of the good way to determine the fatty substance alteration by hydrolysis. Except MB1 and MP1, the samples showed an acidity, shown in Table 1, slightly higher than the value recommended (0.2%) [25].

Peroxide concentration, usually expressed as peroxide value (PV), is a measure of oxidation or rancidity in its early stages. It is one of the most commonly used chemical tests for determining the quality of fats and oils [19]. The results for samples are given in Table 1. PV of MB2, MB3, MP3, SM3 and MF1 exceeds NE standards set at 5 meq O_2/Kg [25]. However, it is necessary to be aware that oxidation is an evolutionary factor and that a single measurement at a given time does not always indicate the actual oxidation state or progress stage of reaction. It is therefore interesting to measure oxidation resistance with accelerated tests such as the Rancimat [26]. Since all samples are purchased during the same period, stored under the same conditions and analyzed well before the expiration date, the fact that some have a much higher PV than the standard can be explained by the fact that the auto-oxidation depends on:

- Initial quality of oils used in the formulation of margarines, in particular the hydroperoxide concentration, which will reduce the induction time when it is high. The hydroperoxides then acting as radical initiators, especially if they are in contact with metal ions [27].
- Presence of minor compounds with pro and antioxidant activity (minerals, tocopherols, carotenes, chlorophyll) [27].
- Unsaturated fatty acids composition. Thus, the most unsaturated oils are the least stable to oxidation, especially since the number of double bonds is high [27].

The iodine value (IV) is shown in Table 1. Tub margarines have the highest IV with a maximum recorded in MB1 margarine (88.99%). Vegetable smen have the lowest values with a minimum recorded in SM2 (37.28%). A high iodine value corresponds to a highly unsaturated oil [19]. The type of oils used in the formulation of margarines and vegetable smen depends on the application and/or type of packaging.

Melting point depends on the degree of unsaturation, the length of the carbon chain, the isomeric forms of fatty acids, and the Molecular configuration [19]. Generally, fats and oils containing long chain saturated fatty acids have higher melting points than those containing polyunsaturated or short chain fatty acids [28]. The melting point of samples is shown in Table 2. Puff pastry margarines have the highest melting points with a maximum of 45.4°C (MF2). However, they correspond to industry standards (42–48°C). The melting points of vegetable smen samples correspond to the standards (37–42°C). The standard for the melting point of spread margarine varies between 33 and 37°C, which means that margarine can quickly melt in mouth and be firm at room temperature to withstand mechanical work during its spreading. The melting points of MB margarines have values close to the upper limit of the standard, whereas MP margarines show values above the standard. The melting points of MB are higher than the values found in tub margarines in [29] (31.5–32.5°C) and in the margarines analyzed in [4] (31.2–34.9°C). The melting point of the MP are also higher than the values found in stick margarines analyzed in [29], (34.5–37°C). The melting point gives an indication of the temperature at which spread margarine should melt in mouth. It therefore allows an organoleptic appreciation of the product. Algerian factories opt for margarine recipes with high melting points, thus avoiding product deterioration during transport and distribution.

The solid/liquid ratio obtained by NMR, designated as SFC, is expressed as a percentage, where 0% corresponds to a totally liquid sample and 100% to a totally solid sample [30]. Each type of margarine (cooking, spreading, creaming, puff pastry) corresponds to a specific type of solid curve [24]. Determination of SFC is not an absolute method. In fact, there is no reference fat that can be used as a standard to provide a defined or known SFC value [30]. The SFC of the margarines for different temperatures is given in Table 2. SFC at 40°C vary between 0°C and 5.4°C, except for MF which have the highest SFC (9.7–14.1%). These high values may be due to a high content of saturated fatty acids and long chain monounsaturated fatty acids. This is a sought-after property in puff pastry margarine which must be highly plastic to allow thin lamination without any breakage, not melting too quickly at the cooking temperature and being able to stabilize the air cells during cooking to obtain large bakery products [4].

The solid content of MB decreases rapidly with increasing temperature to reach 0–0.5% at 40°C. These margarines have a good tendency to "melt". This may be explained by the use of oils rich in unsaturated fatty acids (UFA) and short-chain SFA (coconut oil, palm kernel, etc.) which melt rapidly with temperature increase.

It is also observed that the solid content of stick margarine is higher than that of tub margarines. This is because MP need to be harder to prevent margarine flowing and packaging deformation at ambient temperatures.

SM samples have intermediate melting point and solid content with spreadable and puff pastry margarines. This gives them a consistency that is neither too hard nor too soft, allowing them to be stored at room temperature and facilitating their use in various culinary preparations (cooking, bakery, etc).

3.2. Oxidative stability by Rancimat test

Lipid oxidation tends to reduce product shelf life, palatability, functionality and nutritional quality. Oxidative stability can be evaluated by oxidative acceleration methods as Rancimat test. Some parameters may induce a rise in temperature, pressure and/or air flow (oxygen) through the sample. This test can predict product shelf life [31].

Induction period (IP) of samples is given in Table 1. MB1, MB3 and SM3 have the lowest IP (23.28 h, 23.18 h and 21.48 h, respectively). However, these results correspond to the standard which places an optimal induction period between 6 h and 24 h [22]. Short IP means low oxidative stability due to the presence of PUFA. SM2 shows the highest IP (92,19 h). It is therefore the product which has the best oxidative stability because of its high SFA content. Indeed, oil that contains a higher SFA content and a lower UFA content has a longer induction period. In spreading margarine category, stick margarines have better oxidation stability.

3.3. Fatty acids composition

Fatty acid analysis provides a fast and accurate way to determine the fatty acid distribution of fats and oils. This information is beneficial to all aspects of product development, process control, and marketing because the types and proportions of fatty acids and their position on glycerol influence the physical, chemical, and nutritional characteristics of fats and oils [19].

Due to growing nutritional concerns and scientific awareness regarding health consequences of saturated fatty acids (SFA), *trans* fatty acids (TFA), and essential fatty acids (PUFA: n-3 and n-6), composition of dietary fats is of great interest [32].

The relative proportions (expressed as % of total fatty acids) of the saturated, monounsaturated, polyunsaturated and *trans* fatty acids present in margarines and vegetable smen are shown in Table 3. The identified FA correspond to carbon numbers ranging from 8 (caprylic acid C8:0) to 20 (arachidic acid C20:0). The results of the analysis show the presence of *trans* fatty acids (TFA), especially C18:1*t* in five samples: MB1 (8.18%), MF1 (5.60%), MB3 (3.08%) and MP3 (2.64%). C18:2*t* and C18:3t are also present but with low values in all products (between 0.05% and 0.72%). These contents are much lower than those found by many authors; up to 39.4% in Turkish margarines [4], 10–15% in margarines in Costa Rica [5], up to 28.84% in Serbian hard margarines [6].

Table 3
Fatty acid composition (FAME %) of margarines and vegetable smen

Fatty Acid	MB			MP				MF		SM		
	MB1	MB2	MB3	MP1	MP2	MP3	MP4	MF1	MF2	SM1	SM2	SM3
C8:0	–	0,26	–	–	–	–	0,47	0,17	–	–	0,09	–
C10:0	–	0,196	–	0,15	0,67	–	0,38	0,15	–	–	0,08	–
C12:0	–	2,50	0,36	2,26	3,29	6,93	3,34	2,07	0,55	0,19	0,94	0,24
C14:0	0,25	1,39	0,68	1,52	3,84	3,13	2,60	1,34	0,71	0,90	1,01	0,89
C16:0	17,72	33,12	30,43	36,92	40,20	31,94	38,33	35,88	45,31	47,48	57,12	53,96
C16:1	–	–	0,42	0,38	0,36	–	0,45	–	–	0,53	0,07	–
C17:0	–	–	0,41	0,18	0,21	–	–	–	–	0,21	0,07	–
C18:0	7,18	5,75	5,91	5,54	6,02	7,72	4,60	8,81	5,50	4,70	6,29	4,95
C18:1t	8,18	0,65	3,08	–	–	2,64	–	5,60	–	–	–	–
C18:1	29,88	32,93	32,58	33,49	31,67	28,24	29,29	27,67	31,88	35,91	24,32	30,80
C18:2t	0,26	0,55	0,18	0,35	0,39	–	0,33	0,37	–	0,72	0,05	0,08
C18:2t	0,26	–	–	–	0,23	–	–	0,22	–	–	–	–
C18:2	30,26	19,19	22,55	17,19	11,02	12,07	18,53	15,58	15,46	8,61	8,65	8,26
C18:3t	–	0,54	0,52	0,35	0,25	0,20	–	0,18	–	–	0,09	0,06
C18:3	4,08	1,67	2,38	1,36	0,90	0,87	0,44	1,58	0,26	0,37	0,47	0,14
C20:0	0,27	0,33	0,31	0,31	0,26	0,29	0,26	0,27	0,34	0,37	0,46	0,38
SFA %	25,42	43,55	37,68	46,70	54,28	50,01	49,97	48,69	52,41	53,65	65,98	60,42
TFA %	8,70	1,75	3,77	0,70	0,87	2,84	0,33	6,36	0,00	0,72	0,14	0,14

The high content of SFA in margarines and vegetable smen is due to high proportions of palmitic acid C16:0, particularly in SM and puff pastry margarines. For spreadable margarines, C16:0 content is higher in MP than in MB. The minimum value is 17.72% in MB1 and the maximum one is 40.20% in MP2. Many authors have also reported the dominance of C16:0 but at lower levels : 12.28% in Spanish margarines [23], 11.8–31.3% in Turkish margarines [29], 8.3–15.3% in MG-HVNH/NHVO and 5.1–10.5% in MG-HVPH/PHVO) in Canadian margarines [33], 16.9–33.8% in Pakistani margarines [34]. Bayard and Wolff describe as reasonable a C16:0 content in margarines less than or equal to 15% [35].

This strong presence of C16:0 indicates a large contribution of palm oil in margarine recipe. This is in agreement with results found in [29, 34] and [36]. It is probably related to culinary preparations but dramatically increases the intake of saturated fatty acids in the diet.

According to [29], high stearic acid content (5.6–9.4%), suggests that an interesterified or partially hydrogenated oil rich in stearic acid is mixed with liquid oils to obtain the desired solids level.

The highest average contents in MUFA are attributed to SM1 (36.44%), followed by MP1 (33.86%), MB3 (33%) and MB2 (32.93%). MUFA content in the margarines analyzed is higher than that found in [34] (4.2–19.4%).

PUFA are of major importance for biological and nutritional value of foods. In this study, the average PUFA content in MB, MP, MF and SM is 26.71%, 15.59%, 16.44% and 8.83%, respectively. In spreadable margarine, the average is about 21.15%, almost 2 times lower than those recorded in [37] (36.30%), [35] (39.91%) and [23] (41.48%).

PUFAs are mainly represented by C18:2. According to margarine classification in [13], only MB1 and MB3 can be considered semi-soft. The other samples are rather hard margarines.

According to [29], a linolenic acid content of 3.9–4.3%, comparable to that of MB1 which is 4.08%, suggests that the margarines are formulated with approximately 50% non-hydrogenated soybean or canola oil.

Table 4
Ratios between fatty acids of margarines and vegetable smen

Fatty acid	MB			MP				MF		SM		
	MB1	MB2	MB3	MP1	MP2	MP3	MP4	MF1	MF2	SM1	SM2	SM3
SFA	25,42	43,55	37,68	46,70	54,28	50,01	49,97	48,69	52,41	53,65	65,98	60,42
TFA	8,70	1,75	3,77	0,70	0,87	2,84	0,33	6,36	0,00	0,72	0,14	0,14
MUFA	29,88	32,93	33,00	33,86	32,03	28,24	29,75	27,67	31,88	36,44	24,39	30,80
PUFA	34,35	20,86	24,93	18,55	11,92	12,94	18,97	17,17	15,71	8,98	9,12	8,41
UFA	64,23	53,79	57,93	52,41	43,95	41,18	48,71	44,84	47,59	45,42	33,51	39,20
SFA+TFA	34,12	45,30	41,45	47,40	55,15	52,85	50,30	55,05	52,41	54,37	66,12	60,56
SFA/UFA	0,40	0,81	0,65	0,89	1,23	1,21	1,03	1,09	1,10	1,18	1,97	1,54
trans/cis FA	0,14	0,03	0,07	0,01	0,02	0,07	0,01	0,14	0,00	0,02	0,00	0,00
PUFA/SFA	1,35	0,48	0,66	0,40	0,22	0,26	0,38	0,35	0,30	0,17	0,14	0,14
PUFA/SFA+TFA	1,01	0,46	0,60	0,39	0,22	0,24	0,38	0,31	0,30	0,17	0,14	0,14
PUFA+MUFA/SFA+TFA	1,88	1,19	1,40	1,11	0,80	0,78	0,97	0,81	0,91	0,84	0,51	0,65
$\omega 6/\omega 3$	7,41	11,48	9,48	12,67	12,20	13,95	41,91	9,83	60,17	22,96	18,24	57,01
Ratio I3	2,41	1,39	1,63	1,26	0,90	0,92	1,08	0,98	1,02	0,91	0,56	0,71

The ratios between fatty acids are given in Table 4. We note the presence of TFA in 5 samples: MB1 (8.7%), MB2 (1.75%), MB3 (3.77%), MP3 (2.84%) and MF1 (6.36%). There is consistent evidence of the adverse effects of industrial *trans* fats (TFAs) on the development of cardiovascular disease (CVD) as they lead to an increase in very atherogenic lipoprotein, LDL-cholesterol and total cholesterol, and a decrease of HDL-cholesterol, cardioprotective. Thus, WHO recommends that SFA and TFA intake should be limited to less than 10% and 1% of daily energy requirements, respectively [6]. Different approaches have been implemented to reduce the amount of TFA in processed foods. Restricting industrial TFA content has been applied in some countries, such as Denmark since 2003, followed by Austria, Switzerland, Iceland, Norway, Hungary, while others have mandatory labeling (Canada, US, Brazil, etc.), along with nutrition recommendations and awareness programs on the adverse effects of TFA [38]. Denmark has set the most stringent standards, which limit the TFA content in fats and oils to 2 g TFA/100 g. Fats or oils containing less than 1 g of TFA/100 g are considered "TFA-free" [36, 40]. Seven (7) samples can be considered as "TFA-free", containing less than 2% *trans* fatty acids.

We observe high SFA content, exceeding 30% for all products and reaching or even exceeding 50% except for MB1 margarines (25,42%). SFA/UFA ratio is close to or greater than 1 in stick margarines, puff pastry margarines, and vegetable smen. This ratio in MP (0.89–1.23%) is higher in comparison with MB (0.40 and 0.81%) and margarines analyzed in [37] (0.31–0.72%). A high ratio indicates a high proportion of SFA, as observed in [34] (0.82–1.41). The prevalence of unsaturated FA on SFA (low ratio) is considered positive from a nutritional impact point of view [34, 37]).

SFA and TFA fraction, incriminated in the increase of blood cholesterol, is present in high proportion in the samples. It represents more than 30% of total fatty acids in MB, with an average of 40.29% and more than 50% in MP, MF and SM, with averages of 51.42%, 53.73% and 60.35% respectively.

SFA and TFA content in spread margarines did not reach values found in [34] (54.8–84.5%). One of the consequences of improved margarine production conditions is the increased substitution of saturated fatty acids [39]. Replacing PUFA by SFA to reduce TFA content results in an increase in overall fat saturation. This strategy leads to a decrease of PUFA/SFA ratio which conflicts with dietary guidelines and causes elevated plasma cholesterol and triglyceride levels. These same authors emphasize that a PUFA/SFA ratio of 1 is recommended. On the other hand, the mean PUFA-*cis*/SFA ratio recommended by the British Department of Health is 0.45 [34]. The lowest averages of the PUFA/SFA ratio are attributed to SM (0.15), MP (0.31) and MF (0.32). Only

the MB1 has a ratio greater than 1 (1.35). The mean value of PUFA/SFA ratio for margarines in this study is 0.53 greater than those found in [34] (0.36) and [39] in 55% of the margarines analyzed (<0.5).

The most commonly indices used for expressing the nutritional value of dietary fats are I1 = PUFA-cis/(SFA+TFA) and I2 = (PUFA-cis+MUFA-cis)/(SFA+TFA). The lowest average ratios are obtained in SM (0.15), MF (0.30) and MP (0.30). The best ratio is recorded in MB (0.69). In margarines, the ratios I1 and I2 are 0.47 and 1.16 respectively. These values are higher than those of Pakistani margarines analyzed in [34] (0.23 and 0.46) and those of margarines analyzed in [32] (0.25 and 0.76).

I3 ratio = Σ Cis isomers of C18:1, C18:2, C18:3 (Fatty acids lowering cholesterol)/ Σ (SFA (Σ C12:0, C14:0, C16) and *trans* FA (increasing cholesterol). MF and SM have, on average, I3 ratios close to 0.72 and 0.73 respectively, lower than MP (1.06) and MB which have a much better ratio of 2.28. Tub margarines have a better fatty acid profile than stick margarines, which is in agreement with the results found in [36].

The *trans/cis* ratio of margarines represents the degree of formation of the TFA generated during the hydrogenation process from the natural *cis* forms of the UFA. This ratio is quite negligible in all samples analyzed (0.00–0.14). This is not in agreement with the results found in [34] where most margarines had a ratio of 0.5–1.8 expressing a high TFA content.

According to [40], n-6/n-3 ratio as close as possible to 1 is considered to have a protective effect against degenerative diseases. However, an FAO report [41] concludes that it would not be rational to recommend a specific n-6/n-3 ratio if the recommended nutrient intake (NFA) of n-6 (2-3% of QI) and n-3 (0.5% of QI) are not met. This is also the opinion of Health and welfare Canada [29]. A moderate level of C18:3(n-3) varies from 4.8 to 8.8 and that a favorable C18:2(n-6)/C18:3(n-3) ratio is between 2.2–6.0 [33]. However, in this study, the values found are not in agreement with those proposed as being favorable. In SM, a low presence (0.14–0.47) of C18:3 is observed, supported by a "highly" unbalanced n-6/n-3 ratio, reaching 57.01 in SM3.

All n-6/n-3 ratios exceed the standard, only MB1, MB3 and MF1 have acceptable ratios of 7.41, 9.48 and 9.83, respectively.

4. Conclusion

The physicochemical parameters (water content, pH, salt content, melting point and solids content) revealed that most of the products analyzed are in compliance with current standards. Tub Margarines are the least stable from an oxidative point of view, unlike vegetable smen. The determination of the fatty acid profile showed that all the products analyzed are rich in saturated fatty acids. The *trans* fatty acids content exceeds the standards established by some countries such as Denmark. The situation in Algeria is still different from that of other countries (Turkey, Malaysia, Morocco, Canada, Australia, Serbia, Switzerland, USA, etc.). Indeed, in these countries, studies have revealed the presence of large quantities of *trans* fatty acids in different margarines. This has led health authorities to sound the alarm and for some to legislate to minimize the presence of TFA in food. Algerian consumer, country legislation alike, ignores the debate on the deleterious effect of *trans* fatty acids.

Acknowledgments

None. No funding to declare.

References

[1] Clark P. The marketing of margarine. Paper presented to a seminar on Marketing and Advertising in the 20th Century at Central London Polytechnic. Emeral Backfiles. 1983;54.

[2] Astorg P-O, Bougnoux P, Calvarin J, Chalon S, Dallongeville J, Dumas C, Friocourt P, Gerber M, Guesnet P, Kalonji E, Lapillonne A, Morise A, Lecerf J-M, Margaritis I, Moulin P, Pieroni G, et Legrand P. Actualisation des apports nutritionnels conseillés pour les acides gras. Rapport d'expertise collective. Anses. 2011;1-327.

[3] Stender S, Dyerberg J. The influence of trans fatty acids on health Fourth edition. A report from the Danish Nutrition Council. ISSN n°0909-9859. 2003;39-61.

[4] Karabulut I, Turan S. Some properties of margarines and shortenings marketed in Turkey. Journal of Food Composition and Analysis. 2006;19:55-8.

[5] Baylin A, Siles X, Donovan-Palmer A, Fernandez X, Campos H. Fatty acid composition of Costa Rican foods including trans fatty acid content. Journal of Food Composition and Analysis. 2007;20:182-92.

[6] Vucic V, Arsic A, Petrovic SA, Milanovic S, Gurinovic M, Glibetic M. Trans fatty acid content in Serbian margarines: Urgent need for legislative changes and consumer information. Food Chemistry. 2015;185:437-40.

[7] Garsetti M, Balentine DA, Zock PL, Blom WAM, Wanders AJ. Fat composition of vegetable oil spreads and margarines in the USA in 2013: A national marketplace analysis. Int J Food Sci Nutr. 2016;67:372-82.

[8] Tavella M, Peterson G, Espeche M, Cavallero E, Cipolla L, Perego L, Caballero B. Trans fatty acid content of a selection of foods in Argentina. Analytical, Nutritional and Clinical Methods Section. Food Chemistry. 2000;69:209-13.

[9] Martin CA, Carapelli R, Visantainer JV, Matsushita M, Evelazio de Souza N. Trans fatty acid content of Brazilian biscuits. Food Chemistry. 2005;93:445-48.

[10] Karabulut I. Fatty acid composition of frequently consumed foods in Turkey with special emphasis on trans fatty acids. International Journal of Food Sciences and Nutrition. 2007;58:619-28.

[11] Saunders D, Jones S, Devane GJ, Scholes P, Lake RJ, Paulin SM. Trans fatty acids in the New Zealand food supply. Journal of Food Composition and Analysis. 2008;21:320-25.

[12] Greenfield H, Southgate DAT. Données sur la composition des aliments production, gestion et utilisation. Seconde édition. Organisation des Nations Unies pour l'alimentation et l'agriculture. 2007.

[13] Ovesen L, Letha T, Hansen K. Fatty acid composition and contents of trans monounsaturated fatty acids in frying fats, and in margarines and shortenings marketed in Denmark. JAOCS. 1998;75:1079-83.

[14] Letha T, Bysteda A, Hansenb K, Ovesen L. Trans FA Content in Danish Margarines and Shortenings. J10419 in JAOCS. 2003;80 (5):475-8.

[15] ISO International Standard. Method 662. Animal and vegetable fats and oils. Determination of moisture content and volatile matter. 1998.

[16] AOAC. Official methods of analysis (15th ed.). 1990. N 960.29, Arlington, VA.

[17] ISO International Standard. Method 660. Animal and vegetable fats and oils. Determination of peroxide index. Determination of acid value and acidity. 1996.

[18] ISO International Standard. Method 3960, Animal and vegetable fats and oils. Determination of peroxide index. 1998.

[19] O'Brien RD. Fats and oils: Formulating and processing for applications. Ed: CRC Press, CRC Press, Taylor & Francis Group, Boca Raton London New York. 2004.

[20] ISO International Standard. Method 8292 (F). Animal and vegetable fats and oils. Determination of the solids fat by the method of pulsed nuclear magnetic resonance (2nd ed.). 1995.

[21] ISO International Standard. Method 6321, Animal and vegetable fats and oils. Determination of melting point. 2002.

[22] ISO International Standard. Method 6886. Animal and vegetable fats and oils. Determination of the oxidation stability (accelerated oxidation test) (2nd ed.). 2006.

[23] Alonso L, Fraga MJ, Juarez M. Determination of trans fatty acids and fatty acid profiles in margarines marketed in Spain. Journal of the American Oil Chemists' Society. 2002;77:131-6.

[24] Faur L. IN Karleskind A. Manuel des corps gras. Ed : Tech et Doc. Lavoisier. Paris, 1992;SNB : 2-85-206-662-9, 938-987.

[25] Karleskind A. Manuel des corps gras. Ed : Tech et Doc. Lavoisier. Paris, 1992;ISNB : 2-85-206-662-9.

[26] Cuvelier ME, Maillard MN. Stabilité des huiles alimentaires au cours de leur stockage. OCL. 2012;19:125-32.

[27] Crapiste GH, Brevedan MIV, et Carelli AA. Oxidation of Sunflower Oil During Storage. JAOCS. 1999;76:1437-43.

[28] Ghotra BS, Dyal SD, et Narine SS. Lipid shortenings: A review. Food Research International. 2002;35:1015-48.

[29] Tekin A, Cizmeci M, Karabacak H, et Kayahan M. Trans FA and Solid Fat Contents of Margarines Marketed in Turkey. JAOCS. 2002;79:443-5.

[30] Ribeiro ANB, Basso RC, Grimaldi R, Gioielli LA, Gonçalves LAG. Instrumental Methods for the Evaluation of Interesterified Fats. Food Analytical Methods. 2009;2:282-302.

[31] Hidalgo FJ, Leon MM, Et Zamora R. Antioxidative Activity of Amino hydrogenated soybean, rapeseed and sunflower oils. Food Chemistry. 2006;102:827-33.

[32] Anwar F, Bhanger MI, Iqbal S, Sultana B. Fatty acid composition of different margarines and butters from pakistan with special emphasis on trans unsaturated contents. Journal of Food Quality. 2006;29:87-96.

[33] Ratnayake WMN, Gagnon C, Dumais L, Lillycrop W, Wong L, Meleta M, Calway P. trans Fatty Acid Content of Canadian Margarines Prior to Mandatory trans Fat Labelling. J Am Oil Chem Soc. 2007;84:817-25.

[34] Kandhro A, Sherazi STH, Mahesar SA, Bhanger MI, Talpur MY, Rauf A. GC-MS quantification of fatty acid profile including trans FA in the locally manufactured margarines of Pakistan. Analytical Methods. Food chemistry. 2008;109:207-11.

[35] Bayard CC, Wolff RL. Trans-18:1 Acids in French Tub Margarines and Shortenings: Recent Trends. JAOCS. 1995;72:1485-9.

[36] Hernandez-Martinez M, Gallardo-Velazquez T, Osorio-Revilla G. Fatty Acid Profile Including Trans Fatty Acid Content of Margarines Marketed in Mexico. J Am Oil Chem Soc. 2011;88:1485-95.

[37] Tsanev R, Russeva A, Rizov T, Dontcheva I. Content of trans-fatty acids in edibles margarines. JAOCS. 1998;75:143-5.

[38] Costa N, Cruz R, Graça P, Breda JD, Casal S. Trans fatty acids in the Portuguese food market. Food Control. 2016;64:128-34.

[39] Wagner K-H, Auer E, Elmadfa I. Content of trans fatty acids in margarines, plant oils, fried products and chocolate spreads in Austria. Eur Food Res Technol. 2000;210:237-41.

[40] Russo GL. Dietary n-6 and n-3 polyunsaturated fatty acides: From biochemistry to clinical implication in cardiovascular prevention. Biochimical Pharmacology. 2009;77:937-46.

[41] Astrup AV, Bazinet R, Brenna JT, Calder PC, Crawford MA, Dangour A, Donahoo WT, Elmadfa I, Galli C, Gerber M, Henry CJ, Kornsteiner-Krenn M, Lapillonne A, Melanson EL, Miller J, Mozaffarian D, Ratnayake WMN, Sanders TAB, Sinclair AJ, Skeaff CM, Smit LA, Uauy R, Wolmarans P, Willet W. Fats and fatty acids in human nutrition. Report of an expert consultation. FAO Food and Nutrition Paper. Food and Agriculture Organization of The United Nations. 2010.