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Kinetic parameter determination of roasted and unroasted argan oil oxidation under Rancimat test conditions

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SUMMARY: The present study investigated the Kinetic parameter determination of edible argan oil (cold-pressed from roasted argan kernels) and cosmetic argan oil (cold-pressed from unroasted argan kernels) under the Rancimat test conditions. The physicochemical parameters of edible and cosmetic argan oil immediately after preparation and after accelerated oxidation test Rancimat at different temperatures 90 °C, 100 °C, 110 °C, 120 °C, 130 °C and 140 °C were determined and compared. The natural logarithms of the kinetic rate constant (kvalue) varied linearly with respect to temperature. An increasing rate of oxidation could be observed as temperature increased. On the basis of the Arrhenius equation and the activated complex theory, frequency factors A, activation energies Ea, Q10 numbers, activation enthalpies ΔH, and activation entropies ΔS for oxidative stability of the vegetable oils were calculated. The accelerated oxidation and Kinetic parameters have shown that edible argan oil can be stored much better than cosmetic oil.

***KEYWORDS**: Argan oil; Kinetic parameters; Oxidative stability; Rancimat; Roasting*

RESUMEN: ***Determinación de parámetros cinéticos de la oxidación mediante Rancimat de aceites de argán tostado y sin tostar***. En presente estudio se determinaron los parámetros cinéticosde aceites de argán comestible (prensado en frío a partir de granos tostados de argán) y cosmético (prensado en frío a partir de granos de argán sin tostar) bajo las condiciones del método Rancimat. Se determinó y comparó los parámetros físico-químicos de aceites de argán comestible y cosmético inmediatamente después de la preparación y después de la oxidación acelerada mediante Rancimat a temperaturas de 90 °C, 100 °C, 110 °C, 120 °C, 130 °C y 140 °C Los logaritmos naturales de la constante de velocidad cinética (valor k) variaron linealmente con respecto a la temperatura. Se pudo observar un valor creciente de la oxidación conel aumento de la temperatura. Se calculó para la estabilidad oxidativa de los aceites vegetalesy sobre la base de la ecuación de Arrhenius y la teoría del complejo activado, la frecuencia de los factores A, energías de activación Ea, los valores de Q10, lasentalpías de activación ΔH, y las entropías de activación ΔS. La oxidación acelerada y los parámetros cinéticos han demostrado que el aceite de argán comestible se puede almacenar mucho mejor que el aceite cosmético.

***PALABRAS CLAVE**: Aceite de argán; Estabilidad oxidativa; Parámetros cinéticos; Rancimat; Tostado*

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1. INTRODUCTION

Argan oil, a typical Moroccan product, is prepared from the fruits of argan trees (*Argania spinosa* L. Skeels). It is extracted by pressing the argan kernels through a multistep process (Charrouf *et al*., 2002; Matthaus *et al*., 2010). Edible argan oil is obtained when the kernels are slightly roasted prior to grinding (Gharby *et al*., 2011). Unroasted kernels are used to prepare a cosmetic oil (Faez *et al*., 2013; Guillaume and Charrouf, 2011).

For years, argan oil has been prepared exclusively by Berber women through a traditional multistep process (Charrouf *et al*., 2002).

Unfortunately, this method is time consuming for producing oil batches with different organoleptic properties due to the non-reproducible roasting (Charrouf *et al*., 2006) and chemical composition of oil batches (Matthaus *et al*., 2010; Gharby *et al*., 2011). In addition, bacteriological concerns are frequently raised (Gharby *et al*., 2011).

Recently,in the women's cooperatives,argan oil has been extracted using mechanical presses producing a high quality of oil on a large scale (Charrouf *et al*., 2002). At present, the production of high quality argan oil is particularly important since it has been reported to promote several benefits for human health (Charrouf and Guillaume 2008). However, as a consequence of its high degree of unsaturation, argan oil is very susceptible to oxidation (Gharby *et al*., 2011).

Lipid oxidation in vegetable oils is one of the most important reactions that can cause the deterioration of their quality. The oxidation process of edible oil results in the development of undesirable flavors which affect the sensory quality and considerably reduce the pharmaceutical and food use of these oils (Jacobsen and Nielsen 2008; Matthaus *et al*., 2010). Therefore, the monitoring of the oxidative stability of argan oil is of great importance for producers and manufacturers in order to control and optimize the production process and to predict the shelf-life of the final oil (Gharby *et al*., 2011).

A number of accelerated methods have been developed to test the resistance of edible fats and oils to oxidation. All these accelerated methods involve the use of elevated temperatures because it is known that the rate of the reaction is exponentially related to temperature (Reynhout, 1991). Among them, the Rancimat test, due to its ease of use and reproducibility, has become frequently used and reviewed (Hasenhuettl and Wan 1992; Matthäus 1996; Mendez *et al*., 1996; Anwar *et al*., 2003; Kowalski *et al*., 2004; Gonzaga *et al*., 2007; Farhoosh 2007; Gharby *et al*., 2012).

This test allows for the determination of the induction period (IP) or oil/oxidative stability index (ISO-6886), which is the time before rapid deterioration of the oil occurs. The oxidative stability index can be determined at various temperatures and, therefore, the relative oxidative stability of edible fats and oils can be evaluated in a range of temperatures. In addition, previous studies have demonstrated the correlation between the stability data obtained by the Rancimat test and those determined by other sensory and/or analytical methods (Anwar *et al*., 2003; Adhvaryu *et al*., 2000; Kowalski *et al*., 2004; Gordon and Mursi, 1994).

A number of kinetic parameters can be determined under the Rancimat test conditions. Kinetic data can be used to characterize the differences or similarities in the oils. These data are very useful for predicting the oxidative stability of vegetable oils under various heat processing, storage, and distribution conditions (Tan *et al*., 2001). Also, a whole series of experiments and calculations of kinetic data for each argan oil under the Rancimat test conditions can be performed relatively quickly.

The aim of the present study was to determine the relative oxidative stabilities of argan oil obtained from roasted and unroasted kernels and the kinetic parameters of their oxidation under the Rancimat test conditions.

2. MATERIALS AND METHODS

2.1. Materials

Argan fruits (600 Kg) were collected in Ait Baha, (Province of Chtouka Ait baha, Morocco). The fruit was dried and peeled using the argan-cooperative traditional technique (Charrouf and Guillaume, 2008). Argan nuts were manually opened using the traditional method and a fraction of the kernels (150 Kg) was roasted at 110 °C for 25 min (Harhar *et al*., 2011, El Manfalouti *et al*., 2013). The argan oil was produced by mechanical pressing of kernels according to the method described by Hilali *et al*. (2005). Therefore, two types of argan oil were analyzed: (1) argan oil from unroasted kernels (UAO); (2) argan oil from roasted kernels (RAO).

All chemicals and solvents used were of analytical reagent grade (Merck, Darmstadt, Germany).

2.2. Chemical analysis

The determination of physicochemical parameters (acidity, peroxide value, UV-light absorption (K232 and K270), was carried out according to the analytical methods described by Regulation EEC/ 2568/91 and EEC/ 1429/92 of the European Union Commission (1991, 1992). Acidity, given as percentage of oleic acid, was determined by titration of a solution of oil dissolved in EtOH/Et_2O (1:1) with 0.1 M KOH in EtOH. To determine the peroxide value, expressed as milli-equivalents of active oxygen per kilogram of oil (meq $O_2 \cdot kg^{-1}$), a mixture of oil and iso-octane–acetic acid was left to react

with a solution of KI in the dark; the free iodine was then titrated with a sodium thiosulfate solution. UV-light absorption (K270 and K232) was measured in cyclohexane using a Cary 100 Varian UV spectrophotometer as previously described (Harhar *et al.*, 2010).

For the determination of fatty acid composition, the methyl esters were prepared by cold transmethylation in a basic medium (IOOC, 2001) and were analyzed in a gas phase chromatograph (HP 6890, Agilent) fitted with aCP-Wax52CB column (30 m 0.25 mmi.d.) using helium (flow rate 1 $mL \cdot min^{-1}$) as the carrier gas. The initial oven temperature was set at 170 °C; the injector temperature at 200 °C; and the detector temperature at 230 °C. The injected quantity was 1 µL for each analysis.

The tocopherol content was determined on the basis of the AOCS Official method Ce8-89 (AmericanOil Chemists'Society, 1993). Tocopherols were analyzed by HPLC using Shimadzu instruments equipped with a C18-Varian column (25 cm×4 mm). Detection was performed using a fluorescence detector (excitation wavelength 290 nm, detection wavelength 330 nm). The eluent used was a 99:1 isooctane/isopropanol (V/V) mixture at a flow rate of 1.2 $mL \cdot min^{-1}$. Phosphorus content was determined using the NF T60-227 recommendation (Paquot and Hautfenne, 1987). Beta-Carotene content was determined using a PFX-995 lovibond tintometer (cell length 10 mm).

2.3. Rancimat test

A Metrohm Rancimat model 743 (Herisau, Switzerland) was used. In order to establish air-saturated conditions in the oil samples, the tests were carried out with 3 g of the oil samples at temperatures of 90 °C, 100 °C, 110 °C, 120 °C, 130 °C and 140 °C at an airflow rate of 20 L/h. Samples for all determinations were randomized on their position in the heating block.

The glassware was rigorously cleaned between runs to avoid any contamination that would catalyze peroxidation. Measuring vessels, electrodes, and connecting tubes were cleaned several times with alcohol and distilled water, and were blown out with nitrogen before the experiment (Farhoosh *et al.*, 2008).

2.4. Statistical analysis

All Rancimat experiments and measurements were carried out in triplicate, and the data were subjected to analysis of variance (ANOVA). ANOVA and regression analyses were performed according to the SPSS software. Significant differences between means were determined by Duncan's multiple range Tests; p values less than 0.05 were considered statistically significant.

3. RESULTS AND DISCUSSION

The initial compositions of the argan oils studied are summarized in Table 1. All samples fulfil the requirements of Moroccan Regulations for extra virgin argan oil (EVAO): acidity, PV and K270 (SNIMA 2003). The amount of free FAs is an indicator of the quality and is traditionally used as an indicator for the classification of the different commercial types from EVAO (Gharby *et al.*, 2012). It can be seen that at the beginning of this study, all EVOO varieties showed an acidity index of 0.3%, which is much lower than the regulated 0.8% as the maximum for any EVOO. Concerning PV, this index is considered to be an indicator of primary oxidation (Gharby *et al.*, 2011). The two argan oils considered here showed low PV values, with the cosmetic argan oil yielding the highest value at 0.9 meq $O_2 \cdot kg^{-1}$. In any case, none of the analyzed oils surpassed 15 meq $O_2 \cdot kg^{-1}$ oil, which is the limit established for EVAO (SNIMA 2003). Another quality index specified in Moroccan Regulations is K270 (Rahmani, 2005). An increase indicates that oil oxidation has begun, which could be due to some factors affecting storage conditions or to an inadequate EVAO processing (Cayuela *et al.*, 2008). In this study, K270 coefficients were less than 0.2, compared to a maximum established by Moroccan Regulations for EVAO of 0.35.

We also found that there was no statistically significant difference among the percentages of saturated fatty acids SFA and unsaturated fatty acids (MUFA+PUFA) of the roasted and unroasted argan oil.

The initial content of tocopherol, in the oil prepared from roasted seeds was 791.2 ppm; it differs significantly from the corresponding values in oils from unroasted seeds of 667.04 ppm. The beta-carotene

Table 1. Initial quality characteristics and fatty acid composition of the argan oils

	RAO	UAO
Acid Value (%)	0.18±0.01	0.38±0.01
Peroxide value (meq $O_2 \cdot kg^{-1}$)	0.54±0.06	0.98±0.02
K232	1.38±0.026	1.25±0.01
K270	0.25±0.023	0.22±0.01
β-carotene (ppm)	19,96±0.13	8.62±0.14
Phosphorus (ppm)	42.81±0.14	2.06±0.03
Phospholipid ($mg \cdot 100\ mg^{-1}$)	0.3	0.006
SFA ($mg \cdot 100\ mg^{-1}$)	19±0.7	19.45±0.17
MUFA ($mg \cdot 100\ mg^{-1}$)	46.35±0.72	46. 25±0.37
PUFA ($mg \cdot 100\ mg^{-1}$)	34.65±0.72	34.30±0.37
Tocopherols (ppm)	791.91	667.04

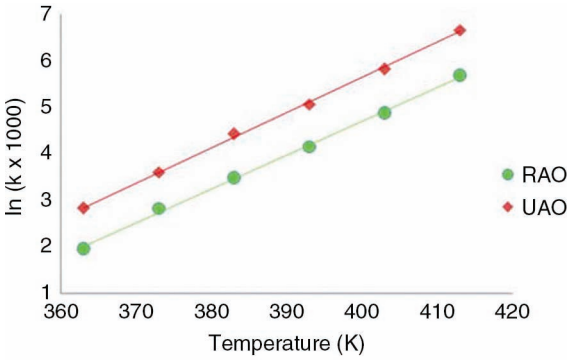
SFA: Saturated fatty acid; MUFA: Mono unsaturated fatty acid; PUFA: Polyunsaturated fatty acid.

TABLE 2. The reaction rate constants (k) of the argan oils at different temperatures

	K±SD ($\times 10^3$)[h^{-1}]					
Oil	**90**	**100**	**110**	**120**	**130**	**140**
Roasted Argan Oil	7.09±0.15	16.69±0.69	32.26±0.25	63.13±0.89	131.58±0.98	294.12±0.85
Unrosted Argan Oil	16.89±0.72	36.66±0.34	83.33±0.48	158.73±0.57	335.57±0.84	781.25±0.75

SD, Standard deviation.

and the phosphorus/phospholipid contents were significantly lower in the beauty oil than in the edible oil. Beta-Carotene is a very lipophilic molecule that is known to present antioxidant properties in synergy with α-tocopherol (Palozza and Krinsky, 1992). However, no precise results can be given concerning the influence ofbeta-carotene onthe oxidative stability of edible argan (Gharby *et al*., 2011). The phospholipid content of the edible argan oil was found to be ten-times higher than that of the beauty oil (0.3 vs 0.006 mg·100 mg^{-1}, respectively). Interestingly, the phosphorus/phospholipid content of the beauty oil was found to be as low as that of artisanally-prepared argan oil (Gharby *et al*., 2011), the extraction of which is completed by a water-assisted stage. Such a hypothesis is fully consistent with the known fact that the simultaneous presence of phospholipids, β-carotene and tocopherols, which are abundant in argan oil, act synergistically as antioxidants in oils (Weng and Gordon, 1993; Lee *et al*., 2004; Steel *et al*., 2005). The k values for lipid oxidation of each argan oil at each temperature are presented in Table 2. By studying the rates of lipid oxidation as a function of temperature, an increasing rate of oxidation can be observed as temperature increases (Gharby *et al*., 2011). As shown in Fig. 1, the semi-logarithmic relationship between k and T values in all argan oils showed a linear dependency with good correlation of determination (R^2>0.99). The lipid oxidation at low and high temperatures may go through different steps or reaction pathways, depending on the reactivity of metal ions and antioxidants at different temperatures (Tan *et al*., 2001). Moreover, the oil temperature affects the degree of oxygen solubility in vegetable oils which decreases by almost 25% for each 10 °C rise in temperature (Robertson, 2000). The T_{Coeff} values calculated from the linear functions in Fig. 1 for the argan oils ranged from 7.2×10^{-2} to 7.5×10^{-2} K^{-1}. These values could be interpreted as quantities representative of the argan oils studied. Our values are in accordance with Farhoosh and Moosavi (2007), who reported such values between 6.5×10^{-2}



Ln(k)=a(T)+b

	a	b	R^2	T_{coef} x 10^{-2} (k^{-1})
•RAO	0.072	–24.43	0.998	7.2
♦UAO	0.075	–24.59	0.998	7.5

FIGURE 1. Semi-logarithmic relationship between k and T values for lipid oxidation of the argan oils.

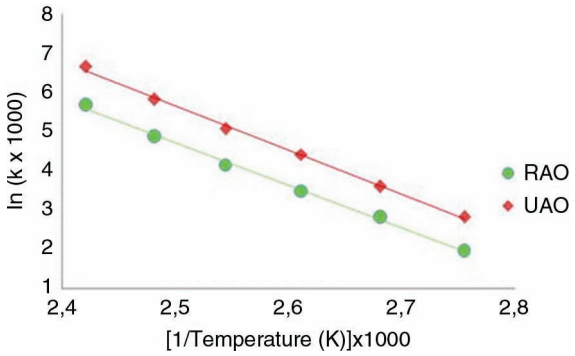


FIGURE 2. Semi-logarithmic relationship between k and (1/T) values for lipid oxidation of the argan oils.

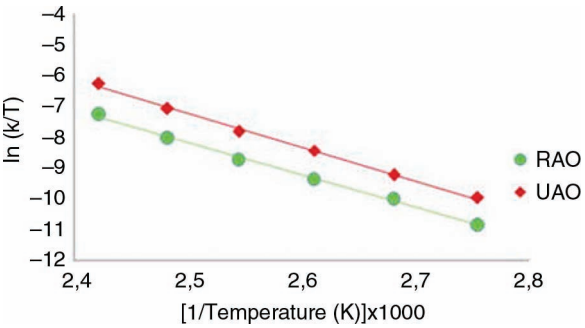


FIGURE 3. Semi-logarithmic relationship between (k/T) and (1/T) values for lipid oxidation of the argan oils.

TABLE 3. Regression parameters for Arrhenius relationships between the reaction rate constant and the temperature for the argan oils

	ln (k)=ln(A)−(Ea/R)*(1/T)					
	a	b	R^2	Ea	A	Q_{10}
•RAO	−10.91	32	0.997	90.71	7.89 10^{13}	2.11
♦UAO	−11.32	33.97	0.997	94.12	5.66 10^{14}	2.16

TABLE 4. Activation enthalpies ΔH and entropies ΔS for lipid oxidation of the argan oils

	ln (k/T)=ln (k_B/h)+(ΔS/R) – (ΔH/R)×(1/T)				
	a	b	R^2	ΔH	ΔS
•RAO	−10.52	18.13	0.996	87.47	−46.81
♦UAO	−10.93	20.11	0.997	90.87	−30.35

to 7.4×10^{-2} K^{-1} (mean value: 7.17×10^{-2} K^{-1}) in the case of other oils (canola, soybean, sunflower, olive and corn oils) (Farhoosh *et al*., 2008).

Table 3 provides the regression parameters for Arrhenius relationships between the reaction rate constant and the temperature for the argan oils studied. Using these regression parameters, the frequency factors, activation energies, and Q_{10} numbers for the formation reaction of the secondary oxidation products under the Rancimat test conditions (volatile acids, mostly formic acids, with lesser amounts of acetic, propionic, and other acids) were calculated (de Man *et al*., 1987). These quantities for the lipid oxidation of the argan oils under the Rancimat test conditions differed significantly. This implies that the production of volatile acids under these conditions was dependent on the oil source, so it affected the assessment of the relative stability of the argan oils (Mendez *et al*., 1996).

The results obtained showed that a high content of β-Carotene, Phospholipid and Phosphorus would improve resistance to lipid oxidation (increase the Ea value). These would result in delaying the onset of the initial oxidation process where bond scission takes place to form primary oxidation products. The B Carotene, Phospholipid and Phosphorus contents of the argan oils (Table 1) explain the observed trends in various activation energies (Table 3) to a certain extent. However, it was observed that several other factors affecting the oxidative stability, e.g. the tocopherol content influenced the susceptibility to oxidative degradation to varying extents. The frequency factors with a trend similar to that of the Ea values for the argan oils studied increased from 7.89 10^{13} for RAO to 5.66 10^{14} for UAO.

The magnitude of the temperature effect on the oxidation rate of the argan oils was evidenced by the Q_{10} numbers. In general, a higher Q_{10} number implies that a smaller temperature change is needed to induce a certain change in the rate of lipid oxidation. As can be seen in Table 3, the Q_{10} number increased from 2.11 for RAO to 2.16 for UAO.

The ΔH and ΔS values estimated based on the activated complex theory and the corresponding regression parameters are summarized in Table 4. The high correlation of determination (R^2>0.99) indicated an adequate fit and characterization of the temperature dependence of lipid oxidation using the activated complex theory.

The ΔH and ΔS values for the argan oils studied ranged from 87.47 kJ·mol^{-1} and −46.81 J·mol^{-1}·K^{-1} for roasted argan oil to 90.87 kJ·mol^{-1} and −30.35 J·mol^{-1}·K^{-1} for unroasted Argan oil, respectively. In their study on the determination of the oxidative stability of rapeseed, sunflower and soybean oils by the Rancimat test, Kowalski *et al*., calculated the amounts of 82 kJ·mol^{-1} and −52.7 J·mol^{-1}·K^{-1}, 84 kJ·mol^{-1} and −42.8 J·mol^{-1}·K^{-1}, and 74.9 kJ·mol^{-1} and −70.2 J·mol^{-1}·K^{-1} for their ΔH and ΔS values, respectively (Kowalski *et al*. 2004). The negative values for ΔS indicate that the activated complexes are more ordered than the molecules of the reactants, and its greater negative values indicate fewer numbers of species in the activated complex state, and hence a lower probability of the activated complex toward lipid oxidation and therefore a slower rate.

CONCLUSIONS

The experimental results allowed us to draw the following conclusions: An increasing rate of oxidation could be observed as temperature increases and, edible argan oil can be stored much better than cosmetic oil.

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