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Oxidative stability of cosmetic argan oil: a one-year study

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Synopsis

The objective of this work is to determine the chemical stability of cosmetic argan oil (INCI: *Argania spinosa* kernel oil). The methodology involves the repeated measurement over a 1-year period of the quality metrics used in the cosmetic industry: acid and peroxide value and specific absorbance. During this year, storage is performed at 40° or 25°C to assess the importance of temperature. In this latter case, oil samples have been either protected or exposed to sunlight. In addition, sterol and fatty acid composition is determined to attest argan oil chemical integrity over 1 year. Storage of argan oil at 40°C results in a rapid loss of quality. Stored at 25°C and protected from sunlight, argan oil quality is still satisfactory after 12 months according to the official Moroccan norm, but storage should not be longer than 6 months to fulfill industrial standards.

INTRODUCTION

The recent worldwide success of edible argan oil is only challenged by the concomitant global success of cosmetic argan oil (INCI: *Argania spinosa* kernel oil, CAS: 223747-87-3) (1). Whereas edible argan oil, which constitutes the basic ingredient of the Amazigh diet (2), is mainly prized for its hypocholesterolemiant properties (3), so far, cosmetic argan oil is sought for its skin antiaging moisturizing and conditioning, and hair-protecting capacity, not to mention its nail strengthening or emollient properties (4). Consequently, cosmetic argan oil is included in various cosmetic formulations as shampoo, lotion, skin-care cream, ointment, and facial makeup. Because of its limited supply and unprecedented success, argan oil has become the most expensive oil in the world in 2011 (1). Edible and cosmetic argan oils are prepared by cold-pressing argan kernels (5). Pressing roasted kernels affords edible argan oil while unroasted kernels are used to prepare cosmetic argan oil that is very pale gold-colored and whose taste is slightly bitter. Edible argan oil is copper-colored and presents a hazelnut taste mostly resulting from the presence of volatile

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compounds formed during kernel roasting (6). Those volatile compounds, produced via oxidation and/or Maillard reaction, are present in very minute amounts but actively participate in the good preservation of edible argan oil (7) whose shelf life is estimated to about 2 years (8). Cosmetic argan oil whose moisture content is slightly higher than that of edible argan oil necessarily lacks these volatile compounds; it presents a much shorter shelf life (7).

For a while, cosmetic argan oil suffered with trust issues due to major adulteration matters, making the cosmetic industry reluctant to use it. A large number of solutions are now available to solve adulteration problems (9–14).

Even though food and cosmetic industries have fundamentally different requirements, the Moroccan Institute of Normalization only recognizes a single norm applicable to both argan oil types (15). In other words, official specifications regarding cosmetic and edible argan oil are strictly similar. Consequently, when purchasing argan oil, cosmetic laboratories generally use requirements that are more severe than those depicted in the official norm (16). These are not only microbiological or hazardous flask-released chemical restrictions but result from the absolute necessity for cosmetic formulations to respect the skin physiological parameters as well as the integrity of the other ingredients. Accordingly, the cosmetic industry is particularly cautious concerning the presence of any source of free radicals or over-oxidation products (17) which requires argan oil peroxide value and E_{270} absorption below 10 meq O_2/kg and 0.2 (16), respectively. Whereas the Moroccan norm stipulates a value below 20 meq O_2/kg and 0.45 (15), respectively, for regular virgin argan oil.

To identify the oxidative phenomena occurring in cosmetic argan oil during its storage, their kinetics, and to understand some of the cosmetic argan oil oxidation processes, we have periodically determined several physicochemical parameters of the same initial batch of cosmetic argan oil placed in different storage conditions. In light of our previous study on edible argan oil (8), one-third of the batch was kept at 25°C and exposed to sunlight, and two-thirds were kept at 25° and 40°C, respectively, and protected from sunlight.

MATERIALS AND METHODS

MATERIALS AND CHEMICALS

Argan oil was prepared by women of the cooperative of Tiout (Taroudant county, Morocco) using their current technology as previously described (18). Kernels were cold-pressed using a Komet DD 85 G press (IBG Monforts Oekotec GmbH & Co. KG, Mönchengladbach, Germany). All reagents used were of analytical or HPLC grade. 2,2,4-Trimethylpentane, heptane, and isopropanol used for chromatography, and cyclohexane used for extinction coefficient determination were purchased from Professional Labo (Casablanca, Morocco). Clear and brown glass bottles were purchased from Cfimu sarl (Casablanca, Morocco).

SAMPLE PREPARATION AND DISTRIBUTION

Immediately after fresh-kernel pressing, cosmetic argan oil was distributed in 60-ml glass bottles. Samples were stored either at 5 ± 1°, 25 ± 2°, or in an oven at 40 ± 1°C. One half of the samples stored at 25°C were in clear glass bottles exposed to daylight,

whereas the other half was in brown glass bottles and stored in a cupboard. Head-space volume for each bottle was 3.5 ml. Analyses were performed just after pressing, then after 1 month of storage, and then every 2 months over 1 year.

ANALYSIS OF OILS

Physicochemical parameters were determined using procedures that we have already repeatedly described (7,8,18,19). In brief, acid and peroxide values were determined using International Standard Organization methods ISO-660 (20) and ISO-3960 (21), respectively. Results are expressed in mg KOH/g and meq O_2/kg, respectively. Iodine index was determined using the International Standard Organization method ISO 3961 (22) or calculated using Carreras' method (23). Results are expressed in gI_2/g. Ultraviolet absorption was determined at l 232 and 270 nm using the International Standard Organization method ISO 3656 (24). Fatty acid (FA) composition was determined using the International Standard Organization method ISO 5508 (25). A gas chromatograph (Varian CP-3800, Varian Inc., Middelburg, The Netherlands) equipped with a FID and a CP- Wax 52CB column (30 m × 0.25 mm i.d.; Varian Inc.) were used. The carrier gas was helium, and the total gas flow rate was 1 ml/min. The initial and final column temperature was 170° and 230°C, respectively. Temperature was increased by steps of 4°C/min. The injector and detector temperature was 230°C. Data were processed using Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA). Results are expressed as the relative percentage of each individual FA present in the sample. Sterol composition was determined using the International Standard Organization method ISO 6799 (26) using a Varian 3800 instrument equipped with a VF-1 ms column (30 m and 0.25 mm i.d.) and using helium (flow rate 1.6 ml/min) as carrier gas. Column temperature was isothermal at 270°C, and injector and detector temperature was 300°C. Injected quantity was 1 μL for each analysis. Data were processed using Varian Star Workstation v 6.30 (Varian Inc.).

STATISTICAL ANALYSIS

Values reported in tables and figures are the means ± S.E. of three replications. The significance level was set at $p = 0.05$. Separation of means was performed by Tukey's test at the 0.05 significance level.

RESULTS AND DISCUSSION

CHANGES IN ACID AND PEROXIDE VALUES AS A FUNCTION OF TIME AND STORAGE CONDITION

Variations in acid and peroxide value as a function of time for the three evaluated storage conditions are presented in Figure 1. Cosmetic industry requires an acid value below 4 mg KOH/g (16). Such value corresponds to the "extra virgin" or "fine virgin" labels of argan oil and excludes the "ordinary virgin" and "lampant" quality according to the official norm (15). Cosmetic argan oil presented an initial acid value of 0.5 mg KOH/g, a low value fully in accordance with our previous results (18). Acid value of cosmetic argan oil stored at 25°C did not significantly change over 12 months whether or not protected

from sunlight. Acid value of oil samples stored at 40°C remained stable for 6 months, and then consistently and almost linearly increased to reach 0.9 mg KOH/g after 12 months of storage. Despite this variation, after 1 year, the acid value of the evaluated samples crossed the low-margin 4 mg KOH/g limit imposed by the cosmetic industry. Change in acid value is a direct marker of the free acid amount formed in the oil as a function of time. Our results show that some amount of the triglycerides of cosmetic argan oil gets hydrolyzed during prolonged storage following a process that is favored by heating, insensitive to light, and whose kinetic is different from that of edible argan oil (7). Therefore, it is very likely that the cosmetic argan oil moisture level is the major factor that governs the observed fast triacylglyceride hydrolysis in cosmetic argan oil. Peroxide value is a primary oxidation marker. Peroxides are feared in the cosmetic domain since, in addition to generating free radical species, they can also increase radical-induced lipid peroxidation, leading to an accelerated rancidity and possibly the formation of off-flavors inappropriate for cosmetic products (17). Peroxides can also alter other oxygen-sensitive components included in cosmetic formulations or react with cosmetic containers. Finally, they might also lead to the formation of mixtures of brownish oxidation compounds unacceptable for cosmetics. For all these reasons, the cosmetic industry has restrictive rules regarding the argan oil peroxide value that must remain below 10 meq O_2/kg (16), whereas the Moroccan norm accepts a peroxide value up to 15 meq O_2/kg (15). The initial peroxide value of cosmetic argan oil was 0.9 meq O_2/kg (Figure 1). This value rapidly increased to reach 4.3 meq O_2/kg after 1 month in oil samples stored at 40°C. In argan oil stored at 25°C and exposed to sunlight, this value reached 3.98 meq O_2/kg after the same delay. When protected from sunlight, a moderate but significant increase was also observed (3.35 meq O_2/kg). Prolonged storage at 40°C led to a continuous and almost linear increase in peroxide value indicating a rapid peroxide formation, and in these conditions, the 10 meq O_2/kg limit value was reached after 5 months of storage. At 40°C, 9 months was necessary to reach the 15 meq O_2/kg limit value imposed by the Moroccan norm. At 25°C, sunlight protection moderately reduced peroxide formation and the 10 meq O_2/kg limit value was reached after 7 months. Interestingly, for oil samples

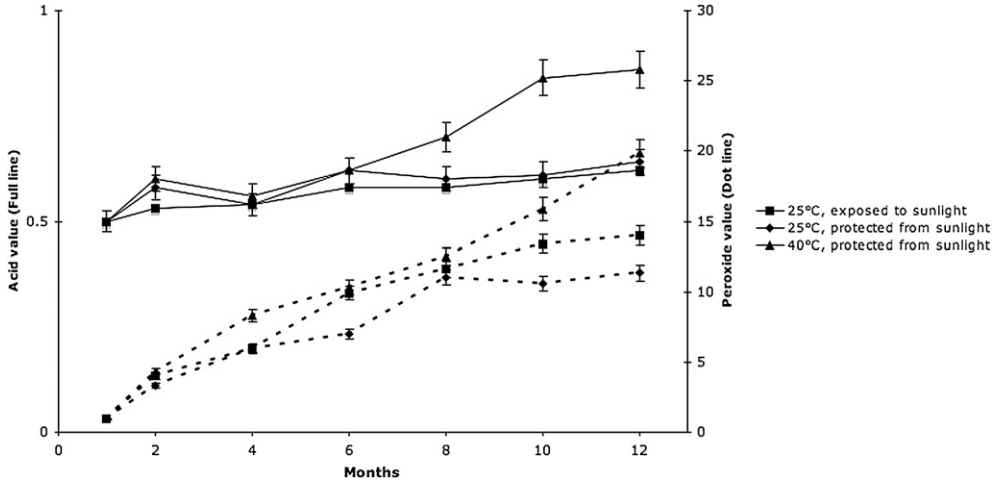

Figure 1. Acid (full line, left axis) and peroxide (dot line, right axis) value of cosmetic argan oil stored at various temperatures as a function of time.

stored at 25°C and sunlight protected, peroxide value reached a plateau after 10 months of storage. Such an event has as a consequence the 15 meq O_2/kg limit value was never reached. It is also evidenced that after some months, the kinetic of FA peroxidation and of secondary oxidation product formation were similar. The peroxide value of sunlight-protected edible argan oil stored at 25°C has been shown to reach 10 meq O_2/kg after 2 years (8). Therefore, our combined results clearly indicate cosmetic argan oil is much more sensitive to peroxide formation than edible argan oil. This not only emphasizes the critical importance of the Maillard's compounds formed during roasting in argan oil overoxidation preservation but also demonstrates that to be introduced in cosmetics, cosmetic laboratories should not store argan oil more than 7 months at room temperature.

In addition to a peroxide value determination, we also monitored primary oxidation product formation from extinction coefficient at 232 nm (E_{232}) even though the cosmetic industry does not impose any rules regarding this analysis (Figure 2, full line). E_{232} underwent a particularly fast increase for cosmetic argan oil stored at 40°C, confirming an important peroxide formation over a 1-year period. At 25°C, sunlight exposure favored primary oxidation product formation, although not as rapidly as at 40°C. Sunlight protection allowed to reduce the rate of formation of primary oxidation product, resulted in a plateau being reached after 8 months. We also determined the extinction coefficient at 270 nm (E_{270}) to evaluate secondary peroxidation product formation (Figure 2, dot line). Because these oxidation products encompass highly chemically reactive compounds such as aldehyde or ketones, a drastic limit of 0.2 is imposed by the cosmetic industry, whereas the limit of the Moroccan norm is 0.35. The 0.2 limit was reached after only 1 month for argan oil stored at 40°C. It was reached between April and June for samples stored at 25°C whether protected or not from sunlight. These measurements indicate that after 6 months of storage at 25°C, cosmetic argan oil is not suitable anymore to be introduced in cosmetic formulation according to industrial requirements, even though, in terms of Moroccan norm, the limit value is not reached after 1 year of storage at 25°C and using sunlight protection.

Cosmetic argan oil properties result from its physicochemical properties and from its specific chemical composition (4). Main components, as unsaturated FA, and minor

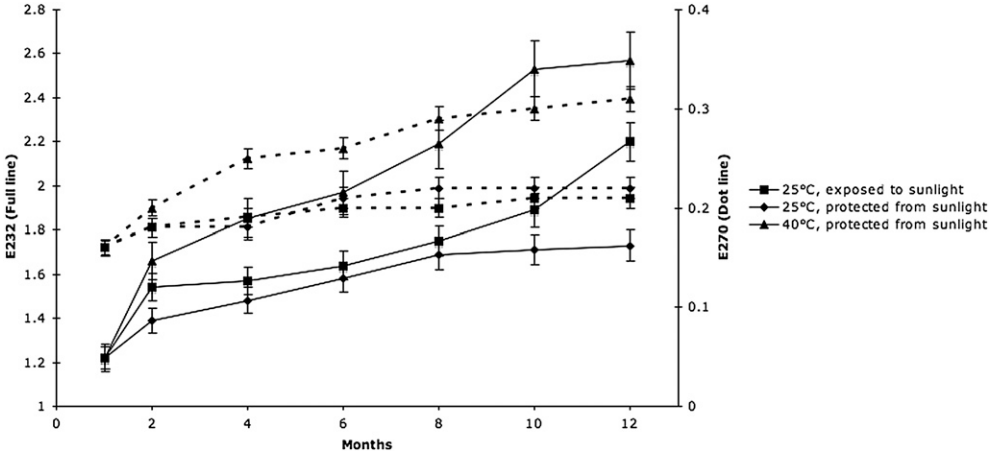

Figure 2. Extinction coefficient at 232 nm (full line, left axis) and 270 nm (dot line, right axis) of cosmetic argan oil stored at various temperatures as a function of time.

Table I
Sterol and Fatty Acid Composition of Cosmetic Argan Oil Immediately after Cold-Pressing and after 6 Months (1 Year) of Storage Sunlight-Exposed or -Protected

		25°C	
	Initial	Exposed	Protected
Sterol (%)			
Schottenol	46.6 ± 2.5	46.5 ± 3.9 (47.8 ± 4.1)	47.5 ± 3.5 (46.2 ± 2.5)
Spinasterol	39 ± 2	36 ± 4 (38.1 ± 6.2)	37 ± 3 (40 ± 4)
Stigma-7[a]	4.2 ± 0.8	5 ± 2 (4.1 ± 1.5)	5 ± 1 (4.3 ± 2.1)
Stigma-8[a]	3.9 ± 0.6	4.1 ± 0.9 (3.8 ± 1.1)	3.8 ± 0.7 (4 ± 1)
Campesterol	0.2 ± 0.1	0.1 ± 0.1 (0.2 ± 0.1)	0.2 ± 0.1 (0.2 ± 0.1)
Fatty acid (%)			
Palmitic	13.2 ± 1.5	13.2 ± 1.8 (13.1 ± 2.1)	13.1 ± 2.5 (13.2 ± 1.8)
Stearic	5.3 ± 0.4	5.6 ± 0.9 (5.5 ± 1.1)	5.2 ± 0.7 (5.7 ± 1.5)
Oleic	48 ± 3	48 ± 4 (48 ± 6)	47 ± 4 (48 ± 4)
Linoleic	33 ± 2	33 ± 2 (33 ± 4)	32 ± 2 (33 ± 4)
Linolenic	0.1 ± 0.1	0.1 ± 0.1 (0.1 ± 0.1)	0.1 ± 0.1 (0.1 ± 0.1)

[a]Stigma-7: Stigma-7,24-dien-3-ol, Stigma-8: Stigma-8,22-dien-3β-ol.

components, as sterols, participate in argan oil cosmetic activity (4). In our physico-chemical analyses indicating a 6-month-limit for argan oil stored at 25°C, we compared the FA and sterol composition of argan oil just after pressing and after 6 months. No significant difference was observed for sterol or FA composition after this period (Table I). Such chemical stability suggests that the dermocosmetic properties of argan oil are fully preserved during the first 6 months of its storage when performed at 25°C.

SUMMARY

Cosmetic argan oil is often presented as possessing low preservation properties. Storage at various temperatures demonstrate that when argan oil is stored at temperatures up to 25°C its quality can be easily ascertained for 12 months according to the Moroccan norm, and for 6 months according to the cosmetic industry norm. Formation of oxidative species is the main reason for argan oil instability, far ahead from triglyceride hydrolysis or sterol loss. Storage of argan oil under inert atmosphere or/and at low temperature should increase argan oil shelf life if necessary. To increase argan oil shelf life, the addition of antioxidants could also be considered, but the resulting product would not satisfy the "extra virgin argan oil" labeling anymore.

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