Effect of processing on the quality of edible argan oil

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Abstract

Sensory quality of edible oil is essential to get the consumer acceptance. Modifications during processing can alter edible oil sensory quality. The storage stability and sensory quality of argan oil prepared from (1) mechanically pressed unroasted kernels, (2) mechanically pressed roasted kernels, (3) hand-pressed roasted kernels, and (4) hand-pressed roasted kernels coming from goat-digested fruits was studied at room temperature and under accelerated conditions (60 °C). The roasting process had a positive effect on storage stability of the resulting oils, while argan oil prepared from mechanically pressed roasted kernels provides the optimum storage stability. Oil from hand-pressed roasted kernels originating from goat-digested fruits was not suitable for human consumption because of the unpleasant taste and odour. Only oil from mechanically pressed roasted kernels did not produce negative sensory attributes like fusty or Roquefort cheese.

1. Introduction

Argan tree (Argania spinosa) is only endemic in Southwestern Morocco where the argan forest was recognised as a biosphere reserve by the UNESCO in 1998. The argan forest is currently covering slightly more than 800,000 ha, but its extension was twice as large at the end of the nineteenth century (Morton & Voss, 1987). To avoid further deterioration and favour its sustainable development, an increase of its economic value is an absolute necessity. Argan oil has rapidly emerged as the only produce able to bring more wealth to the Berber population (Charrouf, Harhar, Haddad, Gharby, & Guillaume, 2008), leading to oil batches of work are necessary to get 2–2.5 L of oil), leading to oil batches having variable organoleptic properties due to non-reproducible reactions once the oil has been bottled. In this latter case, tocopherols (vitamin-E-active compounds) and sterols have been shown to be important factors involved in the sensory quality of olive oil
Up to now, very little is known about the influence of each processing step on the quality of argan oil during storage even though the involvement of tocopherols and sterols on oil quality has been suggested (Verhé, 2009). Therefore, we evaluated the concentration of these two types of compounds in argan oil as a function of storage time; the ultimate aim of the present study being to determine the effects of the production conditions on the sensory quality and storage stability of edible argan oil. Storage was at 20 °C for up to 20 weeks to relate to real storage conditions and at 60 °C for up to 35 days to accelerate the storage condition.

2. Material and methods

2.1. Production of argan oil

Peeled argan fruits (300 kg) were collected in Tiout (Province of Taroudant, Morocco) in 2007. Fruits were sun-dried for two weeks and then mechanically dehulled (SMIR Technotour, Agadir, Morocco). Argan nuts were manually opened using the traditional two-stone method (Charrouf et al., 2002) to get the kernels. A fraction of the nuts was roasted at 110 °C for 30 min (roaster: SMIR, Technotour Agadir, Morocco). Afterwards, oil extraction was carried out as done traditionally or mechanically using a Komet DD 85 G press (IBG Monforts Oekotec GmbH & Co. KG, Mönchengladbach, Germany). Goat-digested argan fruits (120 kg) were treated as peeled collected fruits but argan oil was traditionally extracted.

Therefore, four types of argan oil were analysed: (1) argan oil from unroasted kernels, mechanically extracted; (2) argan oil from roasted kernels, mechanically extracted; (3) argan oil from roasted kernels, traditionally extracted; and (4) argan oil from goat-digested seeds, roasted and traditionally extracted.

For each oil type, 2.5 L of oil were prepared and kept in 200 mL brown glass bottles, resulting in the production of eleven bottles for each oil sample.

2.2. Storage of the oils

One bottle was used to evaluate the initial state of the oils with regard to the sensory quality and the oxidative state. Five bottles of a given oil type were stored at 20 °C ± 1 °C for 20 weeks and the five remaining bottles were stored at 60 °C ± 1 °C for 35 days. From the bottles stored at 20 °C, one bottle was used for sensory analysis and investigation of its chemical parameters every four weeks. For the bottles stored at 60 °C, one bottle was used for investigation of its chemical parameters every seven days.

2.3. Sensory evaluation

The sensory evaluation of the oil samples stored at 20 °C was carried out according to the DGF method C-II 1 (07) (DGF, 2008) with a panel of four trained tasters.

In order to perceive the aroma of the argan oils, the oils were tasted in special blue coloured glasses typical for the sensory evaluation of olive oils. They were covered with a watch glass to gather/keep the volatile aroma compounds for the time of the sensory assessment session. Every glass was filled with the same amount of about 15 mL of oil to ensure that the oil develops an intense headspace aroma and the volatile compounds diffuse in the covered glass. The oils were evaluated at room temperature. The flavour and taste of the oils were characterised according to a sensory description form, previously developed by the sensory panel over a period of 3 years and assessment of nearly 300 different argan oils from different locations, production facilities, and types of processes. A scoring system with a scale from 0 (not detectable) to 5 (strongly detectable) was used to characterise the typical (nutty, roasty) and atypical (Roquefort cheese, rancid, wood-like, bitter, burnt, musty, yeasty-like, fusty, and others) attributes.

The data sets obtained from the sensory assessments were statistically evaluated in order to improve the reliability and repeatability of the results. Since the mean of the results for one attribute is influenced by every single result, especially by outliers, in the data set the median has been calculated as the best result. In addition, the relative coefficients of variation of the results were calculated in order to get a rough estimation whether the final result is an unanimous result or a heterogeneous one. The relative coefficient of variation for the different attributes has to be below 15%.

2.4. Peroxide and anisidine values

The peroxide and anisidine value were determined following the DGF method C-VI 6a and DGF method C-VI 6e, respectively (DGF, 2008).

2.5. Vitamin-E-active compounds

For the determination of vitamin-E-active compounds a solution of 250 mg oil in 25 mL n-heptane was used for HPLC analysis. The analysis was conducted using a Merck–Hitachi low pressure gradient system, fitted with a L-6000 pump, a Merck–Hitachi F-1000 Fluorescence Spectrophotometer (detector wavelengths for excitation 295 nm, for emission 330 nm) and a D-2500 integration system. The sample (20 µL) was injected by a Merck 655-A40 autosampler onto a Diol phase HPLC column 25 cm × 4.6 mm ID (Merck, Darmstadt, Germany) used with a flow rate of 1.3 mL/min and heptane/tert-butyl methyl ether (99:1, v/v) as mobile phase (Balz, Schulte, & Thier, 1992; DGF, 2008). Results are given as mg vitamin-E-active compounds/kg oil.

2.6. Sterol composition

Sterol composition was evaluated by GLC-FID/capillary column. Briefly, sterols purified from the unsaponifiable matters by HPLC were transformed into their trimethylsilyl ethers counterparts using pyridine, hexamethyldisilazane, and trimethylchlorosilane 9:3:1 (v/v/v). The sterol profile was analysed using a gas-phase chromatograph fitted with a chroma pack CP Sil 8 C B column (30 m × 0.32 mm i.d.) and a flame ionisation detector. The temperature of the injector and detector were both 300 °C. The column temperature was 200 °C and programmed to increase at the rate of 10 °C/min to 270 °C. The carrier gas was dry oxygen-free nitrogen, and the internal pressure was 8.6 bar. Sterol quantification was achieved by use of an internal 0.2% chloroform solution of α-cholesterol.

2.7. Content of hexanal

Hexanal was determined by the method of dynamic headspace concentration (Brühl & Fiebig, 2005): About 200 mg of oil were weighed exactly into a 20 mL headspace vial, sealed and put into a PTA3000 (Axel Semrau, Sprockhövel, Germany) autosampler. Volatiles were purged with nitrogen at 10 PSI with a stream of 20 mL/min over the sample surface at 80 °C and trapped in an on-line Tenax trap (eight fold volume) at -65 °C using carbon dioxide/cooling. After 20 min of trapping, all volatiles were removed by heating the trap to 200 °C for 10 min. The purge valve was held at 150 °C and the transfer line (uncoated fused silica) at 200 °C in order to avoid recondensation without any water trap in the system.
The heating jacket of the transfer line was connected to a split/splitless injector of a HP5890 GC instead of the septum cap and the transfer line was lead through the injector directly into the oven where it was connected to a guard column 1 m Carbowax, 0.32 mm ID 0.25 μm film thickness and a separating column CP-Sil 19 (14% cyanopropyl-phenyl + 86% dimethylpolysiloxane, 60 m, 0.32 mm ID, 1 μm FD; The column was connected to a flame ionisation detector at 280 °C. The oven temperature was held for 5 min. at 40 °C, with no additional cold trap focusing necessary, 3 °C/min to 245 °C, 10 min isotherm.

2.8. Statistical analysis

Student’s t-test to evaluate the statistical significance for independent and variables interactions was performed with two-tailed t-tests at P = 0.01. The data was evaluated using a computer program (Statgraphics, Rockville, MD, USA).

3. Results

3.1. Sensory evaluation

An essential parameter for the evaluation of edible oils is its sensory quality. Available standards on edible oils, such as Codex Alimentarius Standard for Named Vegetable Oils (Codex Alimentarius, 1993) or German Guidelines for edible fats and oils (Leitsätze, 1997), define the sensory evaluation as the predominant parameter for assessing quality of edible oils. Depending on their initial preparation process, each argan oil sample had a different taste and smell at the beginning of the storage experiment (Fig. 1). While oil samples from unroasted seeds had a nutty taste, oil samples from roasted seeds were characterised by the appearance of nutty and roasty attributes. In oil from goat-digested seeds a slight fusty attribute was also perceivable.

During storage the sensory sensations of oil from unroasted seeds changed very fast and within 4 weeks attributes like fusty as well as Roquefort cheese appeared resulting in oil judged as inedible for humans because of their unacceptable taste. A similar judgement was expressed for argan oil obtained from roasted seeds by traditional extraction. Just after extraction, the typical nutty and roasty attributes characterising fresh argan oil were found with no attribute negatively affecting the oil quality. However, during storage the nutty attribute disappeared within 16 weeks of storage and Roquefort cheese taste developed. The roasty attribute was still perceivable after 20 weeks of storage, but due to a Roquefort cheese taste the oil was considered inedible after 12 weeks of storage. No change of the sensory characteristics was found for roasted kernel oils obtained by mechanical extraction. Over a 20 week storage period at 20 °C only the typical sensory attributes nutty and roasty were perceivable. Only a slight decrease in the intensity of these attributes was noted at the end of the experiment.

Oils from goat-digested seeds behaved differently. Fresh oil obtained from goat-digested fruit was characterised by a typical smell and taste for Roquefort cheese whose intensity increased with the storage time. Since tasters identified the attribute Roquefort cheese only in oil samples prepared either with improper raw material (goat-digested seeds) or whose quality had decreased during storage, this attribute is a clear indication for improper argan oil quality.

3.2. Hexanal

Hexanal content is a key component to evaluate the oxidative deterioration of linoleic acid-containing oils. Since a hexanal
concentration of 1.0 mg/kg of oil can result in the perception of the attribute rancid by a trained panel (unpublished result), hexanal level is consequently of the upmost importance for the sensory description of argan oils. Fig. 2 shows the influence of storage time and process on the formation of hexanal. At the beginning of the storage experiment, argan oil prepared from mechanically extracted roasted seeds displayed the highest hexanal level (0.35 mg/kg) likely due the roasting process and/or the heat resulting from mechanical extraction. After 35 days of storage at 60 °C, the hexanal content in this latter oil increased only slightly to reach 0.6 mg/kg. The largest increase (from 0.1 to 3.75 mg/kg) was found for argan oil prepared from unroasted argan seeds. For the other oils, after 35 days, the hexenal concentration was found to be above the 1.0 mg/kg threshold value, oil from unroasted seeds reaching this value after only 28 days. Storage at 20 °C remarkably reduced the rate of formation of hexanal. After 20 weeks of storage only a very small increase of hexenal level was found in all oils, from 0.02–0.04 to 0.1 mg/kg.

3.3. Oxidative state

Lipid oxidation has been identified as the main factor responsible for deterioration of edible oil quality and oxidised lipids can further accelerate the deterioration of sensory quality in oil and decrease the consumer acceptance (Jacobsen, 1999). For commercialisation of edible oils, the shelf life of the products is essential to ascertain a period of time sufficient to bridge the time gap separating the production and the consumer, within the given legislative regulations for the oxidative state.

Several parameters describe the oxidative state of edible oils. One is the peroxide value which increases with progressive oxidation of the oil until the rate of degradation of the formed hydroperoxides exceeds the formation of new hydroperoxides. In contrast to the peroxide value, the anisidine value measures secondary decomposition products such as carbonyl compounds (aldehydes and ketones) affecting negatively the taste and smell of edible oils.

Peroxide value strongly depends on the extraction method, seed treatment, and geographical origin (Cayuela et al., 2008; Marfil et al., 2008). Traditionally extracted oils from roasted and unroasted seeds showed a 1.5-fold higher peroxide value than the semi-automatically prepared ones (Cayuela et al., 2008). Higher mean peroxide values for oil obtained by the semi-automatic method in comparison with the traditional method have been reported (Marfil et al., 2008), but samples prepared by the traditional method showed a wider peroxide value range.

Our study revealed that production conditions influence the oxidative stability of argan oil, especially at high storage temperatures. Indeed, storage at 20 °C resulted in a noticeable increase of the peroxide value for the different samples, but none of them reached the limits of 10 or 15 meq O2/kg of oil given by different standards (Codex Alimentarius, 1993; Leitsätze, 1997) within the storage time of 20 weeks (results not shown). Interestingly, the roasting process seems to improve the oxidative stability of argan oil; oil from unroasted seeds showing a significantly faster increase ($P \leq 0.01$) of its peroxide value during storage than oils from roasted seeds (Fig. 3). At storage temperature of 60 °C, the effect of roasting on the peroxide value was more pronounced. Indeed, the peroxide value of argan oil from unroasted seeds increased up to 40 meq O2/kg whereas that for other oils was significantly lower ($P \leq 0.01$). Nevertheless, oil from traditionally extracted roasted kernels and traditionally extracted goat-digested seeds reached the limit of 10 meq O2/kg within 28 days of storage at 60 °C. Only the mechanically extracted oil from roasted kernels remained below the limit during all the storage experiment.

The increase in secondary oxidation products was only very small during storage at 60 °C and, after 35 days, the oil samples only reached anisidine values between 0.8 and 1.0. After 20 weeks of storage at 20 °C, the anisidine values ranged between 0.2 and 0.7 (results not presented).

3.4. Vitamin-E-active compounds

The amount of vitamin-E-active compounds in mechanically extracted argan oil generally ranges between 400 and 775 mg/kg (Hilali et al., 2005) and consisted of about 85% of γ-tocopherol (Charrouf & Guillaume, 2007).

The highest initial amount α-tocopherol, γ-tocopherol, and δ-tocopherol in the oil prepared from mechanically extracted roasted seeds was 16.6, 403.2, and 37.3 mg/kg, respectively, even though this content did not significantly differ from corresponding values in oils from unroasted seeds or roasted seeds after traditional processing (Table 1). Conversely, the total amount of vitamin-E-active compounds in oil from goat-digested seeds was significantly lower (α-tocopherol, γ-tocopherol, and δ-tocopherol: 30.6, 283.7, and 21.0 mg/kg, respectively). Storage at 20 °C did not significantly decrease the amount of vitamin-E-active compounds in the different oils. After 20 weeks of storage, the oils contained approximately the same concentration of vitamin-E-active compounds as at the initial time (results not shown). Under accelerated storage conditions, more contrasted results were observed (Table 1). Quantitatively, the most dramatic decrease in vitamin-E-active
Table 1
α, γ, and δ-tocopherol levels (mg/kg) in argan oil during storage at 60 °C (decimal have been omitted for ease of presentation).

<table>
<thead>
<tr>
<th>Storage time (days)</th>
<th>Unroasted, mechanical extraction</th>
<th>Roasted, mechanical extraction</th>
<th>Roasted, traditional extraction</th>
<th>Roasted, goats, traditional extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>γ</td>
<td>δ</td>
<td>α</td>
</tr>
<tr>
<td>0</td>
<td>16 ± 1.6e</td>
<td>382 ± 38.2c</td>
<td>21 ± 2.1f</td>
<td>16 ± 1.6e</td>
</tr>
<tr>
<td>7</td>
<td>16 ± 1.6e</td>
<td>374 ± 37.4c</td>
<td>19 ± 1.9df</td>
<td>11 ± 1.1e</td>
</tr>
<tr>
<td>14</td>
<td>14 ± 1.4e</td>
<td>375 ± 37.5e</td>
<td>11 ± 1.1c</td>
<td>11 ± 1.1e</td>
</tr>
<tr>
<td>21</td>
<td>10 ± 1.0e</td>
<td>355 ± 35.5e</td>
<td>11 ± 1.1c</td>
<td>11 ± 1.1e</td>
</tr>
<tr>
<td>28</td>
<td>11 ± 1.1b</td>
<td>302 ± 30.2c</td>
<td>12 ± 1.2c</td>
<td>11 ± 1.1e</td>
</tr>
<tr>
<td>35</td>
<td>9 ± 0.9b</td>
<td>202 ± 20.2d</td>
<td>13 ± 1.3ce</td>
<td>12 ± 1.2c</td>
</tr>
</tbody>
</table>

Values bearing different superscripts are significantly (P ≤ 0.01) different.

Table 2
Sterol levels (mg/100 g of oil) during storage at 60 °C (decimal have been omitted for ease of presentation).

<table>
<thead>
<tr>
<th>Storage time (days)</th>
<th>Unroasted, mechanical extraction</th>
<th>Roasted, mechanical extraction</th>
<th>Roasted, traditional extraction</th>
<th>Roasted, goats, traditional extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>St8^*</td>
<td>Sp^*</td>
<td>Sc^*</td>
<td>St7</td>
</tr>
<tr>
<td></td>
<td>5 ± 0.3^e</td>
<td>39 ± 2.0^d</td>
<td>44 ± 2.2^df</td>
<td>6 ± 0.3^b</td>
</tr>
<tr>
<td>7</td>
<td>4 ± 0.2^b</td>
<td>41 ± 2.1^d</td>
<td>43 ± 2.2^ef</td>
<td>5 ± 0.3^a</td>
</tr>
<tr>
<td>14</td>
<td>4 ± 0.2^b</td>
<td>40 ± 2.0^d</td>
<td>49 ± 2.5e</td>
<td>4 ± 0.2^b</td>
</tr>
<tr>
<td>21</td>
<td>5 ± 0.3^e</td>
<td>43 ± 2.2^d</td>
<td>52 ± 2.6^ef</td>
<td>5 ± 0.3^b</td>
</tr>
<tr>
<td>28</td>
<td>4 ± 0.2^b</td>
<td>50 ± 2.5^e</td>
<td>47 ± 2.4^f</td>
<td>4 ± 0.2^b</td>
</tr>
<tr>
<td>35</td>
<td>3 ± 0.2^b</td>
<td>39 ± 2.0^d</td>
<td>50 ± 2.5^e</td>
<td>3 ± 0.2^b</td>
</tr>
</tbody>
</table>

Values bearing different superscripts are significantly (P < 0.01) different.

* St8, stigmasta-8,22-dien-3-ol; Sp, spinasterol; Sc, schottenol; and St7, stigmasta-7,24-dien-3-ol.
compounds was found for the oil from unroasted seeds for which, after 35 days of storage at 60 °C, the concentration in vitamin-E-active compounds was nearly 50%. Qualitatively, all three types of tocopherols were affected by the oxidative process, but their relative distribution remained almost unchanged: α-tocopherol, γ-tocopherol, and δ-tocopherol: 4.2%, 88.2%, and 5.8%, respectively. Oils from roasted seeds (mechanical and traditional extraction) also showed a significant decrease in vitamin-E-active compounds after 35 days of storage at 60 °C, even though it was not as strong as for the oil from unroasted seeds. The tocopherol level in oil from seeds coming from goat digestion, that was already initially lower than in the other oils, showed also a significant decrease, but in comparison to the other oils, the effect was notably reduced.

3.5. Sterol composition

Argan oil sterol fraction contains five compounds (Hilali et al., 2005), mainly stigmasta-8,22-dien-3-ol (St8), spinasterol (Sp), scarletenol (Sc), and stigmasta-7,24-dien-3-ol (St7). Campesterol is also found but at a low concentration close to 0.3%. Therefore, we decided to quantify the four main sterols during our study. Surprisingly, the initial sterol content in argan oil from goat-digested seeds was much higher than that in the three other oil samples (197.2 mg/100 g of oil vs. 143.5 ± 8.2 mg/100 g of oil). Nevertheless, the sterol fraction composition remained qualitatively and quantitatively constant during storage evaluation and no significant variations were observed over a 20-week storage period at 20 °C or 35 days under accelerated storage conditions (Table 2). These results suggest that the sterol fraction is neither actively involved in the preservation of argan oil nor in its taste. Also, the fact that sterol fraction composition is unaffected during the storage period is an important factor considering the pharmacological properties attributed to this class of compounds (Trautwein & Deumonty, 2007).

4. Discussion

Treatment of the argan kernels and processing has a significant (P < 0.01) influence on the sensory quality and oxidative state of argan oil. Although differences in the oxidative state or stability amongst different oil samples are more pronounced at 60 °C than at room temperature, our results show that oils from roasted kernels were significantly less susceptible to oxidation during storage as shown by the evaluation of peroxide value and the formation of hexanal as one key compound of oxidative deterioration.

The high stability of argan oil toward oxidation can be in part explained by its high tocopherol content. Phenolic compounds are well known to provide high resistance to autoxidation and since our study does not clearly indicate the involvement of a specific tocopherol in this process, it is likely to result from the synergistic action of α-, γ-, and δ-tocopherols, possibly together with other minor phenolic compounds (Shahidi & Wanasundara, 1992). The better stability of argan oil prepared from roasted seeds could be explained by a better extractability of antioxidative compounds from the kernels or the formation of such compounds such as Maillard reaction products (MRPs) during the roasting step. During roasting, temperatures above 100 °C are used, resulting likely in remarkable changes in the structure of the seed material with disruption of oil-bearing cells. Such temperatures are also sufficient for the formation of MPRs. Several of these compounds are described with a high antioxidative effect (Eichner, 1980; Lingert & Eriksson, 1981).

Although the differences amongst oil samples stored at 20 °C were minor, with regard to parameters describing the oxidative behaviour of the oils, major differences were revealed by the sensory evaluation. According to food official standards, oil samples from goat-digested seeds were not suitable for human consumption because of a strong perception of attributes like fusty and Roquefort cheese even at the beginning of the storage experiment. In oil from unroasted seeds the development of the unpleasant fusty and Roquefort cheese attributes was quick, covering the perception of the nutty attribute that was only slightly perceivable at the beginning of the experiment. In traditionally extracted oils from roasted kernels, negative attributes were reported after 12 weeks of storage at 20 °C. Despite a strong roasty aroma the development of the fusty and Roquefort cheese attributes became perceivable, while in oil from mechanically extracted roasted seeds, no negative organoleptic attributes were detected even after 20 weeks of storage. The reason for this difference between the two types of roasted oils may originate from the existing differences in different extraction methods of the oil. Use of water in combination with handwork, result likely in “worse” initial conditions for the oxidative stability of the oil (Hilali et al., 2005).

References


