Original article

**Tocopherol content, peroxide value and sensory attributes in roasted peanuts during storage**

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(Received 24 December 2009; Accepted in revised form 16 April 2010)

**Summary** The objective of this study was to determine changes in tocopherol content, peroxide value (PV) and sensory attributes from roasted peanuts during storage at 40 °C. There were no differences in tocopherol contents between roasted and raw peanuts except in α-tocopherol content that decreased after roasting. All tocopherol contents decreased during storage. On the contrary, lipid oxidation indicators such as PV and the intensity ratings of oxidised and cardboard flavour increased during storage. On the other hand, the intensity ratings of roasted peanutty flavour decreased with storage time. Good correlations were observed between tocopherol contents and PVS. Tocopherol contents could be used as indicator of oxidative state in peanut products.

**Keywords** Peanut, peroxide, sensory, stability, storage, tocopherol.

**Introduction**

Argentina is one of the three major world peanut exporters along with China and the United States of America. The quality of Argentinean peanuts and peanut products is well recognised all over the world. Peanut-containing foods have high consumer acceptance because of their unique roasted peanut flavour. Typical peanut flavour is produced by roasting peanut kernels at a high temperature for an appropriate period of time (Johnsen et al., 1988; Bett & Boylston 1992). Peanut flavour is greatly influenced by oxidation of the lipid component. Lipid oxidation is usually involved as the primary cause of decreased shelf life, adverse tastes and generation of undesirable aromas during extended storage of roasted peanuts (Johnsen et al., 1988).

The consumer perception is a remarkable aspect that needs to be included in the definition of the product quality (Grosso & Resurreccion, 2002). The oxidation reactions that happen during storage affect the overall quality of the flavour and the shelf-life of peanut products. Lipid oxidation, occurring during storage of peanut products and contributing to the development of undesirable flavours, is not being accepted by the consumers (Grosso & Resurreccion, 2002). Cardboard and oxidised flavours are sensory attributes associated with chemical changes that occur during lipid oxidation (Grosso & Resurreccion, 2002; Talcott et al., 2005).

Tocopherols are considered as a lipid-soluble natural antioxidant (Shintani et al., 2002). Several studies make reference to the protective effect of the tocopherols against lipid oxidation (Warner et al., 1996; Nawar 2000; Holownia et al., 2001; Frankel 2005). They stabilise polyunsaturated fatty acids within membrane lipid bilayers protecting them from lipoygenase attack and scavenge lipid radicals to form relatively stable products (Holownia et al., 2001). Tocopherols also contribute to shelf-life and stabilise the quality of the stored peanut product. Four different types of tocopherols are synthesised in mature peanuts, alpha (α-), beta (β-), gamma (γ-) and delta (δ-), that differ from one another based on the number of methyl groups and the position of these methyl groups (Shintani et al., 2002). On the basis of initial rates of oxidation of styrene in chlorobenzene solution in the presence of azo-bis (isobutyronitrile) as initiator, the relative activities as vitamin E of homolog tocopherols are 100%, 40%, 10% and 1% in α-, β-, γ- and δ-tocopherols, respectively (Nawar 2000; Shintani et al., 2002). However, the relative antioxidant activity of δ-tocopherol when tested in fats and oils is higher followed by γ-, β- and α-tocopherols (Shintani et al., 2002).

The objective of this study was to determine the changes in tocopherol contents, peroxide values (PVS) and intensity ratings of sensory attributes during storage.

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in roasted peanut samples coming from the Argentinean production area.

Materials and methods

Materials

Nine samples of peanuts cv Florman-INTA (Runner), crop 2003 collected in the main production area, Córdoba province, Argentina coming from the following localities: General Roca, Juarez Celman, Rio Cuarto and San Martin. They were roasted in the oven (model 600; Memert, Schwabach, Germany) at T = 170 °C for 25 min. Peanuts were heated to a medium roast or an average Hunter colour lightness (L) value of 50 ± 1.0 (Johnsen et al., 1988).

Storage conditions and samplings

After peanuts were roasted, the samples were stored at T = 40°C. Samples of each product were removed from storage for evaluation: chemical and descriptive analyses. Sampling days were at 33, 56 and 84 days. Samples were also evaluated on day “zero”.

Chemical analysis

Tocopherol analysis.

Oil extraction was done according to AOCS (1998). Tocopherols (α-, β-, γ- and δ-) were analysed by high-performance liquid chromatography AOCS (1998) using a Zorbax RX-SiL of 4.6 × 250 mm (5u) column (Agilent Technologies, Palo Alto, CA, USA), mobile phase of 0.5% isopropanol in hexane and detected at 298 nm. Tocopherol peaks were identified by their retention time corresponding to standards that were purchased from Sigma-Aldrich (St Louis, MO, USA).

Peroxide value

It was evaluated according to AOAC (1990). PV was expressed as milliequivalents of active oxygen per kilogram of oil (meqO₂ kg⁻¹) and calculated with the formula: PV (meqO₂ kg⁻¹) = (volume in mL of Na₂S₂O₃) × (0.1 N) × (1000)/(g oil).

Descriptive analysis

A total of 11 trained panellists (nine female and two male) participated in the descriptive analysis of roasted peanuts. All panellists had 3 years of experience evaluating peanut products and were selected according to the following criteria: (i) people with natural dentition, (ii) people without food allergies, (iii) non-smokers, (iv) people between 18 and 64 years old, (v) people who consume roasted peanuts and/or peanut products at least once a month, (vi) people available for all sessions, (vii) people interested in participating, and (viii) people able to verbally communicate the observations regarding the product (Plemmons & Resurreccion, 1998). For panellist selection, a screening test was performed for descriptive analysis. All panellists before being qualified showed a perfect score in a taste sensitivity test and the ability to identify five of seven commonly found food flavours (Meilgaard et al., 1991). All 11 panellists were trained and calibrated in four training sessions during 4 days. Each training session lasted 2 h. A hybrid descriptive analysis method consisting of the quantitative descriptive analysis (Tragon Corp., Redwood City, CA, USA) and the Spectrum TM analysis (Sensory Spectrum, Inc., Chatham, NJ, USA) methods were used for training and evaluation sessions as reported by Grosso & Resurreccion (2002). A 150-mm unstructured line scale was used for sample evaluation. A list of definitions and a sheet with warm-up and reference intensity ratings (Table 1) were developed during the training sessions (Grosso & Resurreccion 2002; Olmedo et al., 2008, 2009). The attributes definitions were based on peanut lexicon (Johnsen et al., 1998).

All samples were evaluated in partitioned booths under fluorescent light at room temperature. Ten grams of the product sample were placed into plastic cups with lids coded with three-digit random numbers. Panellists evaluated nine samples and the warm-up sample per day. Before beginning the evaluation of the samples, the panellists retested all references and the warm-up sample. The final lists of warm-up and reference intensity ratings and definitions were posted in the booths for all test sessions. Samples were tested using a randomised complete block design. The data were registered on paper ballots.

Statistical analysis

The data were analysed using the InfoStat software, version 1.1 (Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Córdoba, Argentina). Means and standard deviations were calculated. Analysis of variance was used to detect significant difference between variables. LSD test was used to find significant differences (α = 0.05) between means. Linear regression equations in the regression analyses were used to determine if the independent variables (time) had an effect on the sensory attributes, PVS and tocopherol contents (Sokal & Rohlf, 1994).

Results and discussion

Tocopherols in raw and roasted peanuts

Tocopherol contents are shown in Table 2. α-Tocopherol content was higher in raw peanuts than in roasted
peanuts. This content decreased significantly (\(a = 0.05\)) for the roasting process. The other tocopherols (\(\beta\), \(\gamma\) and \(\delta\)) did not have significant differences between raw and roasted peanuts. This result indicates that \(\alpha\)-tocopherol is more sensitive to deterioration for heating process. The mean value of total tocopherol was lower in roasted peanuts, however significant differences between raw and roasted peanuts were not found. Other authors (Li et al., 1996) observed a decrease in tocopherols in flax, palm and sunflower oils after heating at 110 \(\degree C\). Holownia et al. (2001) detected that \(\alpha\)-, \(\beta\)-, \(\gamma\)- and \(\delta\)-tocopherols in peanut oil decreased from 14.1 to 11.16 mg per 100 g oil, from 0.3 to 0.18 mg per 100 g oil, from 12.4 to 8.12 mg per 100 g oil and from 0.75 to 0.62 mg per 100 g oil, respectively, 24 h after frying. Other authors (Barrera-Arellano et al., 1999) also observed a decrease in tocopherol contents after a heating process in a triglyceride model finding that \(\gamma\)-tocopherol was the most stable and \(\alpha\)-tocopherol the least stable.

**Storage study**

Only roasted peanut samples were analysed for tocopherol contents, PVs and intensity rating of sensory

### Table 1 Definitions of attributes, standard references and warm-up intensity ratings used in descriptive analysis of roasted peanuts

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Definition</th>
<th>Reference</th>
<th>Reference Intensity</th>
<th>Warm-up Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – Brown colour</td>
<td>The intensity or the strength of brown colour from light to dark brown.</td>
<td>Cardboard (lightness value, (L = 47 \pm 1.0))</td>
<td>61</td>
<td>44</td>
</tr>
<tr>
<td>2 – Roughness</td>
<td>The appearance associated with uneven surface.</td>
<td>Corn flakes</td>
<td>85</td>
<td>38</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 – Roasted peanutty</td>
<td>The aromatic associated with medium roasted peanuts.</td>
<td>Dry roasted peanuts</td>
<td>69</td>
<td>56</td>
</tr>
<tr>
<td>4 – Oxidised</td>
<td>The aromatic associated with rancid fats and oils.</td>
<td>Rancid peanuts</td>
<td>75</td>
<td>15</td>
</tr>
<tr>
<td>5 – Cardboard</td>
<td>The aromatic associated with wet cardboard.</td>
<td>Moist cardboard</td>
<td>65</td>
<td>13</td>
</tr>
<tr>
<td>Tastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 – Sweetness</td>
<td>Taste on the tongue associated with sucrose solutions.</td>
<td>2% sucrose solution</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>7 – Saltiness</td>
<td>Taste on the tongue associated with sodium chloride solutions.</td>
<td>0.2% NaCl solution</td>
<td>25</td>
<td>7</td>
</tr>
<tr>
<td>8 – Soursness</td>
<td>Taste on the tongue associated with acid agents such as citric acid solutions.</td>
<td>0.05% citric acid solution</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>9 – Bitterness</td>
<td>Taste on the tongue associated with bitter solutions such as caffeine.</td>
<td>0.05% caffeine solution</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>Texture</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 – Hardness</td>
<td>Force needed to compress a food between molar teeth.</td>
<td>Almonds</td>
<td>75</td>
<td>45</td>
</tr>
<tr>
<td>11 – Crunchiness</td>
<td>Force needed and amount of sound generated from chewing a sample with molar teeth.</td>
<td>Corn flakes</td>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>

*Attributes listed in order as perceived by panellists.
*The attributes definitions were based on a lexicon for peanut samples Muñoz et al. (1992).
*Intensity ratings are based on 150 mm unstructured line scales.
*Corn flakes, Granix, Buenos Aires, Argentina.
*Dry roasted peanuts, type Runner, JL SA, Tucino, Cordoba, Argentina.
*Dry roasted peanuts (type Runner, JL SA, Tucino, Cordoba, Argentina) stored at 40 °C during 60 days 6 months (intensity rating = 75).
*Moist cardboard: 1 mL distilled water absorbed by 0.5 g cardboard.
*Almonds, Grandiet, Cordoba, Argentina.
Medium roasted peanuts (lightness value, \(L = 50 \pm 1\), Type Runner, Blanched, Tucino, Cordoba, Argentina.

### Table 2 Tocopherol content in raw and roasted peanuts

<table>
<thead>
<tr>
<th>Tocopherol</th>
<th>Raw peanuts (mg per 100 g oil)</th>
<th>Roasted peanuts (mg per 100 g oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total tocopherol</td>
<td>44.45 ± 1.29a</td>
<td>40.26 ± 0.72a</td>
</tr>
<tr>
<td>(\alpha)-Tocopherol</td>
<td>20.21 ± 0.8a</td>
<td>15.62 ± 1.41b</td>
</tr>
<tr>
<td>(\beta)-Tocopherol</td>
<td>0.40 ± 0.05a</td>
<td>0.47 ± 0.04a</td>
</tr>
<tr>
<td>(\gamma)-Tocopherol</td>
<td>22.23 ± 0.88a</td>
<td>22.94 ± 0.77a</td>
</tr>
<tr>
<td>(\delta)-Tocopherol</td>
<td>1.60 ± 0.30a</td>
<td>1.24 ± 0.06a</td>
</tr>
</tbody>
</table>

Means followed by the same letter within each row are not significantly different at \(a = 0.05\).
attributes during storage because it is the way the product is consumed by people. The results of the contents of the tocopherol composition during storage are shown in Fig. 1. The content of tocopherols (α-, β-, γ- and δ-) decreased with time of storage (α = 0.05). The major antioxidants in vegetable oils are the tocopherols that are capable of quenching free radicals. Thus, tocopherols protect triglycerides, phospholipids and cholesterol against oxidation and subsequent breakdown to potentially harmful, chemical reactive products. Because of that, it is very important to preserve these kinds of antioxidant compounds in food products (Sherwin 1978; Hudson & Mahgoub, 1981). Other authors (Li et al., 1996) observed that the level of tocopherol decreased during storage in vegetable oils.

Considering from day 0 to day 84 in this study, tocopherol contents were from 40.26 to 19.6 mg per 100 g oil in total tocopherol, from 22.94 to 11.4 mg per 100 g oil in γ-tocopherol, from 15.62 to 7.08 mg per 100 g oil in α-tocopherol, from 1.24 to 0.95 mg per 100 g oil in δ-tocopherol and from 0.47 to 0.34 mg per 100 g oil in β-tocopherol. According to the regression equation (Table 3) and the results observed in Fig. 1, total tocopherol showed the highest decrease (β₁ = −2.46) during storage followed by γ (β₁ = −1.37) and α (β₁ = −1.03) tocopherols. The lowest decrease was exhibited by β- and δ- (β₁ = −0.03) tocopherols. The decrease was because of the lipid oxidation that occurred during storage. Lipid oxidation is usually implicated as the primary cause of decreased shelf-life and generation of undesirable flavours (Talcott et al., 2005; Nepote et al., 2006a,b; Ryan et al., 2008). This oxidation process leads to loss of antioxidants like tocopherols. These molecules are a class of compounds that function as lipid-soluble antioxidants that are extremely potent quenchers of singlet and free radical species (Frankel, 2005). Therefore, the amounts of tocopherol present in vegetable oils (Holownia et al., 2001) or in roasted peanuts could indicate the degree of stability or degradation of the product.

Peroxide value is an indicator of primary lipid oxidation. This parameter increases when the lipid deterioration advances during the storage of a food product (Navar, 2000; Frankel, 2005; Ryan et al., 2008). In this study, PVs increased during storage in roasted peanuts (Fig. 2a). PVs were from 3.52 to 57.15 meqO₂ kg⁻¹ oil. Peanut products are susceptible to develop rancid and off-flavours through lipid oxidation because of their fatty acid composition: 30-35% and 45-50% of the oil being linoleic and oleic acids, respectively (St Angelo, 1996). Lipid oxidation occurs during storage of peanut products and contributes to the development of undesirable flavours in foods where peanuts are an ingredient (Bett & Boylston 1992; Frankel, 2005).

Peroxide values had a high slope (β₁ = 0.65) in the regression equation. Therefore, the lipid oxidation in roasted peanuts increased rapidly during storage. The adjusted $R^2$ was 0.81 in roasted peanuts. This indicates that PVs are good predictors to determine shelf-life in these products. The Argentinean Food Code allows for up to 10 meqO₂ kg⁻¹ PV in peanut oil (CAA, 1996). There is no legislation for other peanut products in Argentina. For that reason, 10 meqO₂ kg⁻¹ is considered an adequate limit for shelf-life in peanut products. Using the prediction equation, PVs higher than 10 - meqO₂ kg⁻¹ were reached after 13.8 days in this storage condition.

Table 3 Regression coefficients from predictions equations of tocopherols, peroxide values (PV) and sensory attributes (oxidised, cardboard and roasted peanut flavours) in roasted peanuts

<table>
<thead>
<tr>
<th>Chemicals Variable</th>
<th>$\beta_0$</th>
<th>$\beta_1$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Tocopherol</td>
<td>15.00</td>
<td>0.10</td>
<td>0.80</td>
</tr>
<tr>
<td>β-Tocopherol</td>
<td>0.46</td>
<td>−0.03</td>
<td>0.82</td>
</tr>
<tr>
<td>γ-Tocopherol</td>
<td>22.51</td>
<td>−1.37</td>
<td>0.86</td>
</tr>
<tr>
<td>δ-Tocopherol</td>
<td>1.23</td>
<td>−0.03</td>
<td>0.77</td>
</tr>
<tr>
<td>Total tocopherol</td>
<td>38.78</td>
<td>0.24</td>
<td>0.89</td>
</tr>
<tr>
<td>Peroxide value</td>
<td>0.01</td>
<td>0.85</td>
<td>0.81</td>
</tr>
<tr>
<td>Oxidised</td>
<td>9.30</td>
<td>0.10</td>
<td>0.22</td>
</tr>
<tr>
<td>Roasted peanut</td>
<td>56.21</td>
<td>−0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Cardboard</td>
<td>11.70</td>
<td>0.05</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Regression coefficients for the general equation: $Y = \beta_0 + \beta_1 X$, where $Y$ is dependent variable (α-, β-, γ-, δ- and total tocopherol, peroxide value, oxidised, roasted peanut, cardboard), $X$ is independent variable (days of storage).*

![Figure 1 Tocopherol content (mg per 100 g oil) in roasted peanut during storage at 40 °C. (a) α-, γ- and Total-tocopherol. (B) β- and δ-tocopherol.](image-url)
It was clearly observed that tocopherol contents decreased at the same time as PVs increased during storage. That meant a high negative correlation higher than −0.80 using a Pearson correlation coefficient between these parameters. The highest negative correlation (−0.93) was between PV and γ-tocopherol followed by the negative correlation between PV and total tocopherol (−0.91). High positive correlation was detected between tocopherol contents (total, α-, β-, γ- and δ-tocopherols). That meant that all tocopherol contents decreased with storage. Higher correlation was exhibited between total tocopherol and γ-tocopherol contents (0.97). These results indicate that tocopherol contents could be used as indicators of the degree of oxidative deterioration in roasted peanuts.

Eleven sensory attributes from descriptive analysis were evaluated in roasted peanuts from day 0 to day 84 of storage. Some sensory attributes such as brown colour, roughness, sweetness, saltiness, bitterness, sourness, hardness and crunchiness showed similar results to the warm up reference (Table 1) and did not change their intensity ratings with storage time. Other works also observed similar values in these attributes from roasted peanuts prepared with American (Grosso & Resurreccion, 2002) and Argentinean (Nepote et al., 2006a,b) peanut kernels. In those researches, it was also detected that these attributes did not change significantly. The other sensory attributes such as roasted peanutty, oxidised and cardboard flavours also had similar values to the warm up reference at day 0 but the intensity ratings changed during storage (Fig. 2b). Cardboard and oxidised flavours are sensory attributes that are directly related to the rancidity process and to lipid deterioration. Therefore, both these sensory attributes are responsible for off-flavours in peanut product. The lipid oxidation reactions lead indirectly to the formation of numerous aliphatic aldehydes, ketones and alcohols. Simultaneously, these flavours increase in such peanut products (Bett & Boylston, 1992; Frankel, 2005). The intensity ratings (0–150 unstructured line scale) of oxidised and cardboard flavours increased from 10.06 to 17.8 and from 10.84 to 15.72 during storage, respectively. A higher positive slope (Table 3) was observed in the oxidised flavour ($\beta_1 = 0.10$) than in the cardboard flavour ($\beta_1 = 0.05$). Nepote et al. (2006a,b) also reported that the intensities of cardboard and oxidised flavours increased and roasted peanutty flavour decreased during storage in roasted peanuts prepared with regular and high-oleic peanuts. Other authors (Bett & Boylston, 1992) detected that cardboard flavour intensity in roasted peanuts had a linear increase across storage time. Muego-Gnanasekharan & Resurreccion (1992) also detected that oxidised and cardboard flavour intensities exhibited a linear increase during storage time in peanut paste.

On the contrary, roasted peanutty intensity ratings decreased from 56.59 at day 0 to 51.33 at day 84 during storage. Therefore, this attribute had a negative slope ($\beta_1 = −0.06; \text{Table } 3$). Roasted peanutty flavour is considered a positive sensory attribute in peanut products (Nepote et al., 2009). This flavour is related to a group of compounds called alquilpyrazines that are produced in the roasting process as a consequence of the reactions between the amine group of proteins and sugars. It was shown that a decrease in this sensory attribute is correlated with a decrease in the alquiplpyrazine content (Bett & Boylston 1992). In a previous study, the intensity rating of roasted peanutty flavour also decreased on roasted peanuts prepared with normal and high oleic peanuts during storage (Nepote et al., 2006a,b).

**Conclusion**

In conclusion, roasting process in peanuts affected the tocopherol content, especially the α-tocopherol content. This tocopherol could be more sensitive to heat treatment. During storage, all tocopherols’ contents decreased and, simultaneously, PVs increased during storage. This correlation indicates that the lipid oxidation process was advancing despite the antioxidant activity from tocopherols. This lipid oxidation in roasted peanuts during storage was also detected for sensory panel for descriptive analysis that perceived an increase in the intensity ratings of oxidised and cardboard flavours and a decrease in the intensity of the characteristic roasted peanutty flavour. The deterioration process in roasted peanut during storage implies...
losses in tocopherol content that reduces the antioxidant capability of these molecules in protecting this product from lipid oxidation reaction. Therefore, tocopherol contents could be used as an indicator of oxidative state in peanut products.

Acknowledgments

We thank INTA, CONICET and SECYT-UNC for financial support. In addition, we also thank Ferrayolli and Turco from CEPROCOR for technical support.

References


