Article
Storage of the Early Ripe Almonds under Modified Atmosphere to Preserve Kernel Qualitative and Sensory Traits

Riccardo Massantini 1,2, Valerio Cristofori 3 and Maria Teresa Frangipane 1,*

1 Department for Innovation in Biological, Agro-Food and Forest Systems (DIBAF), University of Tuscia, Via San Camillo de Lellis, 01100 Viterbo, Italy; massanti@unitus.it
2 Study Alpine Centre, University of Tuscia, Via Rovigo, 7, 38050 Pieve Tersino, Italy
3 Department of Agriculture and Forest Sciences (DAFNE), University of Tuscia, Via San Camillo de Lellis, 01100 Viterbo, Italy; valerio75@unitus.it
* Correspondence: mtfrangi@unitus.it

Abstract: Almonds are often used both in confectionery products and for fresh consumption. Thus, to enhance the use of early ripe or unripe fresh almonds, it is important to maintain the organoleptic and qualitative traits of the product for a period of time as long as possible. The objective of the research was to study different types of almonds storage, not artificially dried, under a modified atmosphere to maintain quality in almond kernels mainly destined to table consumption. The storage of samples was in a modified atmosphere in 100 ± 1 kPa CO2, 100 ± 1 kPa N2 or air and at +4 °C and +10 °C, respectively for 12 days. Some analytical parameters and sensory analysis were explored. Test results showed that the modified atmosphere of N2 at +4 °C was the most suitable for keeping the chemical, physical and sensorial attributes of fresh almond kernels, maintaining their quality intact for up to almost two weeks of storage.

Keywords: Prunus dulcis Mill. D. A. Webb; postharvest; sensory analysis; nitrogen; carbon dioxide; storage

1. Introduction

The almond (Prunus dulcis Mill. D.A. Webb) is a temperate nut species belonging the genus Prunus (Rosaceae family) and its fruit is a drupe, consisting of an outer fleshy hull surrounding a hard shell, which protects the edible seed [1]. Almond is a cultivated nut crop in the Mediterranean area. World almond production was more than two million tons, and the United States is the leading producing country (1,872,500 tons), followed by Spain (339,033 tons), while Italy ranks sixth with an average production of 79,801 tons [2]. Almond cultivation has increased in recent decades, mainly due to the growing demand for nuts in general, and for their healthy food composition [3,4]. Oliveira et al. [5] highlighted as the major compounds with beneficial properties for health are lipids, predominantly monounsaturated fatty acids, phytosterols, vitamins, minerals, polyphenols and fiber. The abundant polyphenolic heritage bets a notable role in the protection against chronic degenerative diseases. Consuming almonds helps to reduce the risk of various diseases, including hypertension, diabetes mellitus, obesity, and metabolic syndrome [6]. Zahedi et al. [7] suggested that environmental effects might influence the physical and biochemical characteristics of almonds. Additionally, some researchers [8] have shown that differences in physical form of ingested almonds led to variability in the bioaccessibility of almonds’ nutrients, and the potential beneficial almond effects would seem better when consumed as whole kernels. In recent research [9] authors advised adults person to consume around 45 g (g) a day of almonds to protect heart health and to obtain benefits. In vivo experiments on pigs [10] also noted faster gastric emptying of proteins for raw than roasted almonds, probably caused by the protein changes. Besides, a recent work [11] studied the consequence of eating almonds as a bite in the morning compared to the snack savory crackers. The authors showed that...
raw almonds revealed a lower hunger compared to crackers. Maintaining the quality of almonds during storage in ambient conditions is a challenge in emerging export markets all over the world, indeed, fresh almonds can have a long life if correctly stored. Several studies [12–18] have been conducted on the optimal storage conditions of raw almonds. A recent review [19] explored the present acquaintance of the features that affect the shelf life of nuts, including almonds, highlighting as storage has an important effect on the shelf life of both in-shell and shelled nuts. Furthermore, the authors concluded that temperatures ranging from +4 to +15 °C, moisture content about 2.5%, relative humidity ranging from 40% to 60%, oxygen concentration less than 2.5% and the dark are better storage parameters for almost all kinds of nuts. Almond kernels had hygroscopic characteristics such as causing an increase in their moisture content during storage. Mexis et al. [12] studied the influence of modified atmosphere packaging and storage on the quality of raw ground almonds. The authors showed that the best conditions for storage of raw ground almonds were using an oxygen absorber in combination with a barrier packaging material. Another study [14] aimed to determine the best storage conditions for almond kernels highlighted as the best packaging material for the storage of almonds was PA-PE-PE-PA (PA: Polyamide; PE: Polyethylene) laminate, and packaging conditions were vacuum conditions. The effect of temperature and kind of atmosphere (vacuum, CO₂, and normal air) on the oxidation, were studied by Raisi et al. [15]. The authors showed that modified atmosphere of vacuum and CO₂ gave 10 months of shelf life in all samples independent of storage temperature. Therefore, a modified atmosphere was the best type of conservation to preserve the almonds from oxidation. Abda et al. [16] reported how storage temperature and modified atmosphere packaging influenced the quality of fresh green almonds. The authors concluded that modified atmosphere packaging could significantly extend the shelf life of almonds. Maturity at harvest can influence the kernel quality of nuts [20] and an in-depth study of their correlation may help to promote the direct consumption of not completely ripe “green nuts” as currently happening for hazelnut in some traditional growing areas [21]. For this purpose, maintaining quality during storage under modified atmosphere for fresh hazelnuts and chestnuts was investigated [22,23]. Furthermore, as highlighted above, some studies [8–11] have proved the nutritional and dietary validity of consuming raw almonds. However, the main difficulty for fresh nuts is maintaining quality during storage. Therefore, to encourage the use of fresh almonds, it is important to preserve their sensory qualities over time. Given this obvious interest, we applied our research previously made on hazelnuts [23] to almonds. The objective of this study was to analytical investigate the chance to preserve not dried almonds in a modified atmosphere in order to keep the quality intact since almonds are increasingly used for fresh consumption, thanks to their nutritional values and sensory attributes. Moreover, consumer attitudes are slowly changing as demand for healthy and sustainable foods is growing. This could be the right time to identify a packaging capable of guaranteeing the qualitative and sensorial characteristics of fresh almonds intact, with efficiency and sustainability.

2. Materials and Methods
2.1. Almond Samples and Experiments

A sample of about 30 kg of whole raw almonds (Prunus dulcis Mill. D. A. Webb) of the cultivar ‘Tuono’ were randomly picked-up directly from the plants on the third decade August, selecting those that showed the spitted hull. The almond orchard was established in the experimental farm of ARSIAL (Regional Agency for Innovation and Development of Agriculture in Latium) located in the municipality of Tarquinia (Latium region-Italy. Latitude 42°16’20” N; longitude 11°42’26” E; altitude 32 m a.s.l.). After harvesting, the nuts were immediately taken to the laboratory in thermal boxes to maintain them at low temperature (+15 ± 1 °C) during transportation.

Considering the importance of the almond classification based on the forms [24], in order to characterize in advance the almonds for their nut traits, a sample of 50 almonds was tested measuring the nut length (L), width (W), and thickness, as shown in Figure 1.
Considering the importance of the almond classification based on the forms [24], in order to characterize in advance the almonds for their nut traits, a sample of 50 almonds were kept under different modified atmospheres (MA) as follows: (a) 100 ± 1 kPa CO₂ at +4°C; (b) 100 ± 1 kPa CO₂ at +10°C; (c) 100 ± 1 kPa N₂ at +4°C; (d) 100 ± 1 kPa N₂ at +10°C. These conditions were selected considering both the previous work of the authors and the analysis of literature [23,29]. Samples were stored for 12 d in a ventilated and hermetically closed cell (Isolcell, Bozen, Italy) at relative humidity (RH) of 80% ± 1%. The cell atmosphere was controlled by a system (mod. Multiplex, Isolcell, Bozen, Italy). Almond samples were manually cracked in order to measure the thickness (T) and volume (V). Measurements focused the nut and kernel length (L), width (W), thickness (T), geometric mean diameter (Dg), sphericity (Φ) and volume (V) were calculated by using the following equations [25–28]:

\[
D_g = \left(\frac{L \times W \times T}{3}\right)^{1/3} \quad (1)
\]

\[
\Phi = \left(\frac{L \times W \times T}{100L}\right) \quad (2)
\]

\[
V = \left(\frac{\pi \times D_g^3}{6}\right) \quad (3)
\]

All mean values of the nut and kernel traits are reported in Table 1, since they may provide useful data for postharvest handling.

**Table 1. Mean values of nut and kernel traits of almond cultivar ‘Tuono’**.

<table>
<thead>
<tr>
<th>Traits</th>
<th>L (mm)</th>
<th>W (mm)</th>
<th>T (mm)</th>
<th>Dg (mm)</th>
<th>Φ (%)</th>
<th>V (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean ± Std. D.</td>
<td>30.22 ± 0.25</td>
<td>19.85 ± 0.20</td>
<td>12.85 ± 0.27</td>
<td>19.76 ± 0.30</td>
<td>65.45 ± 0.38</td>
<td>3825 ± 22.18</td>
</tr>
<tr>
<td>(C.V.)</td>
<td>(0.52%)</td>
<td>(0.50%)</td>
<td>(0.56%)</td>
<td>(0.62%)</td>
<td>(0.57%)</td>
<td>(1.87%)</td>
</tr>
<tr>
<td>Mean ± Std. D.</td>
<td>21.35 ± 0.28</td>
<td>11.25 ± 0.23</td>
<td>5.41 ± 0.18</td>
<td>10.95 ± 0.28</td>
<td>52.65 ± 0.62</td>
<td>878 ± 5.18</td>
</tr>
<tr>
<td>(C.V.)</td>
<td>(0.61%)</td>
<td>(0.43%)</td>
<td>(0.48%)</td>
<td>(0.51%)</td>
<td>(1.10%)</td>
<td>(0.87%)</td>
</tr>
</tbody>
</table>

Measurements focused the nut and kernel length (L), width (W), thickness (T), geometric mean diameter (Dg), sphericity (Φ) and volume (V). Std. D., standard deviation; C.V., coefficient of variation.

The remaining almonds were cracked in the lab and the kernels with pellicle were then divided into six groups of 1000 g each, in order to carry out analytical determinations after the storage period under different environmental conditions. The storage of samples was the same as other our previously research on hazelnuts [23]. Two almond kernel groups were kept in the air at +4°C and +10°C, respectively, and the other four groups were kept under different modified atmospheres (MA) as follows: (a) 100 ± 1 kPa CO₂ at +4°C; (b) 100 ± 1 kPa CO₂ at +10°C; (c) 100 ± 1 kPa N₂ at +4°C; (d) 100 ± 1 kPa N₂ at +10°C. These conditions were selected considering both the previous work of the authors and the analysis of literature [23,29]. Samples were stored for 12 d in a ventilated and hermetically closed cell (Isolcell, Bozen, Italy) at relative humidity (RH) of 80% ± 1%. The cell atmosphere was controlled by a system (mod. Multiplex, Isolcell, Bozen, Italy). Almond kernel samples of 80 g each were analyzed every four d for all compared storage techniques. All analyses were carried out in three replicates, and the results were expressed as mean ± standard deviation.

2.2. Chemical-Physical Analyses

A spectrophotometer (CM-2600 d, Konica Minolta, Osaka, Japan) was used to estimate the color [30]. In the CIEL*a*b* uniform color space, the color coordinates are: L* the lightness coordinate; a* the red/green coordinate and b* the yellow/blue coordinate. In agreement to the CIEL*a*b* color space it was measured the L* (luminosity), h (hue angle,
h = \tan^{-1} \frac{b^*/a^*} and C* (saturation index or chrome, \(C^* = [a^{*2} + b^{*2}]^{1/2}\)) coordinates. 
L* (lightness, ranging from zero (black) to 100 (white), a* (ranging from +60 (red) to −60 (green) and b* (ranging from +60 (yellow) to −60 (blue) were studied as color parameters and estimated in triplicate. Chrome (C*) measures color saturation and the hue angle (h) describes the relative amounts of redness and yellowness. A redder product was denoted by a lower hue value. According to Wrolstad and Smith [31], hue angle and chrome were estimated by determining a* and b* values. It was also measured the color difference CIE 1976 (\(\Delta E^* = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2}\)) between the color data collected every 4 d from the beginning of the test (day zero) for each sample [32]. Firmness was measured with an Instron Universal Testing Machine mod. 4301 (Instron Corporation, Norwood, MA, USA) equipped with a piston diameter of 8 mm, a crosspiece speed of 15 mm s\(^{-1}\), and a compression force of 5 N [33]. The moisture in the kernel was determined by drying the almonds at +103 ± 1 °C, and the water content was expressed as a percentage of the fresh weight. The extraction of enzymes and their activity were assessed as reported in the previous research [23]. The respiration rate (\(\mu\text{mol CO}_2 \text{ g}^{-1} \text{ h}^{-1}\)) was evaluated using an infrared analyzer mod. Oxy carb (Isocell, Bozen, Italy). The enzymes were extracted according to Serra Bonvehì and Serrano Rosà [34]. Polyphenol oxidase (POD) activity was estimated spectrophotometrically by analyzing 1 mL of enzymatic extract, 1 mL of 2.2-azino-bis-(3-ethylbenz-tiazoline)-6-sulfonic acid solution (ABTS) and 1 mL of 35% formaldehyde. The samples were registered at 430 nm for 5 min. The enzyme activity was expressed as absorbance (ABS) \(\text{min}^{-1} \text{ mg}^{-1}\) of protein. Peroxidase (PPO) activity was tested spectrophotometrically at 540 nm for 5 min by using 1 mL enzyme extract added to 1 mL 0.05 M catechol. Both POD and PPO enzyme activity was expressed as ABS \(\text{min}^{-1} \text{ mg}^{-1}\) of protein.

2.3. Sensory Analysis

The sensory analysis was performed at the end of the test period (12 d) by a group of 20 trained judges who had no peanut or tree-nut allergies. Unnamed almond kernel samples were served in a covered 30 mL plastic cup and each one was randomly coded with three digits. Sensory analysis was conducted in a properly equipped laboratory according to the ISO 8589 [35] standards. The samples were submitted to the panelists in a randomized block design to avoid bias. Three almond kernels of cultivar ‘Tuono’ were tested by each panelist during two sessions. Instructions were given to judges for using the samples during sensory analysis. Crackers and water were served to purify their palate. Between each sample, a pause of 5 min was carried out. Scoring was carried out on paper ballots using a hedonic scale set from 9 (high intensity) to 1 (low intensity) that accounted almond kernels for appearance, aroma, flavor intensity and crispness [15,36]. The “appearance” of the almond kernel was visually considered and the integrity of the skin was assessed by carefully looking at the skin and surface of the kernel; the higher the score, the more intact the skin appearance from a score of 9 (excellent) to 1 (poor). Regarding “almond aroma” it was considered the aromatics reminiscent of almond kernel from a score of 9 (typical) to 1 (atypical). Similarly, for “crispiness” was intended the intensity of audible noise at first chew with molars from a score of 9 (crispy) to 1 (soft).

2.4. Statistical Analyses

A two-way within-subjects analysis of variance (ANOVA) with atmosphere composition as subject, the temperature of storage and time of storage as factors were performed for each parameter. The honestly significant difference (Tukey’s HSD) was calculated for \(p \leq 0.05\). All statistical tests were performed using JMP statistical software package, version 4 (SAS Institute Srl, Milano, Italy).
3. Results
3.1. Chemical-Physical Analyses

Figure 2 shows the color variations observed through the hue angle values which tended to decrease significantly during the storage especially in samples stored in air at +10 °C. These samples showed on day 12 of storage average values of hue angle approximately 71, significantly lower than those observed in almond kernels stored under nitrogen at +4 °C and +10 °C that did not show undergone color variations during the same storage period. Almond kernels stored under carbon dioxide at +4 °C and +10 °C showed a pellicle browning higher than those stored in air at +4 °C, while samples stored in air at temperatures of +10 °C had the highest degree of browning.

The CIEL \(a^*b^*\) color measurements showed as the best samples were those stored under nitrogen. At the end of the experiment, the lowest color differences were observed in the samples stored under nitrogen with no significant differences between +4 °C and +10 °C (Figure 3). Almond kernels stored in air at +4 °C showed a lower E value than those treated in carbon dioxide at +4 °C. Both the air and carbon dioxide storage showed noticeable color differences only after four d storage at +10 °C. Through all storage time, it was observed that samples stored in air and carbon dioxide showed greater color differences at +10 °C than at +4 °C.

The results obtained could be due to the high dehydration and lignification of the pellicle, deeper when the sample was stored in the air; this fact could be since the need for oxygen for the final stage of lignin biosynthesis [37]. Nevertheless, though to a lower degree, the browning was observed in samples stored under carbon dioxide. As noted by some researchers [38], the high degree of carbon dioxide increased phenylalanine ammonialyase activity that caused higher brown and lignification of the pericarp with its color change. Tissue lignification seems to progress even at low oxygen levels due to the indirect effect of specific enzymes involved in the biosynthesis of lignin such as PAL, whose activity tends to increase following the physiological stress caused by low temperatures [39]. These findings were in agreement with those of Wang et al. [40] who reported that modified atmosphere packaging treatments increased phenylalanine ammonialyase (PAL) activity.
in the green shell of fresh nuts inside the hull stored at −0.5 to +1.0 °C for 60 d. However, the low temperatures controlled the color variation of the samples, as also reported by Labavitch [41] who found that almonds keep very well at temperatures between +4 and +8 °C, as they are not susceptible to chilling injury. It was observed that, generally, the increase of a* and b* parameters with a parallel decrease of L* parameter seem bonded to higher temperatures and oxygen concentrations. Such changes result in an almond darkening which could be ascribed to the oxidation of some phenolic compounds [42]. It is important to underline that almond kernels can darken during storage and this defect inevitably reduces the marketability of the product. Ledbetter and Palmquist [43] studied different almond varieties packaging during storage at +2, +22 and +32 °C. Their results showed that storage temperature is very important for darkening the skin of almonds, regardless of the almond variety. In contrast, we took over that in our samples stored under nitrogen, no significant color variations were observed in both applied temperatures.

More recently, in a study conducted across five sites located in the main almond production regions of Morocco, Sakar et al. [44] found that all factors, such as cultivar, growing season, and site, impacted significantly kernel color indices. Nevertheless, the cultivar effect was the principal variability source. On the other hand, as highlighted by Yaghini et al. [45], the basic color indices are related to the kinds and quantities of pigments accumulated in fruits during their development.

The nitrogen and carbon dioxide treatments confined the respiratory activity. Likewise, Wang et al. [46] also evidenced that a balanced concentration of O₂ and CO₂ in MA could inhibit the falling of fresh walnuts. All samples stored under MA at +4 °C and +10 °C exhibited a similar respiration rate, without being affected by the two different storage temperatures (Figure 4).
The result excluded possible differences between the samples, storage in air at +4 °C, demonstrated a slowed respiration due to the decrease in temperature. As expected, respiratory activity was higher in almonds stored in the air at +10 °C, showing CO₂ mean values of 0.48, 0.32, 0.30, and 0.21 µmol g⁻¹ h⁻¹ f.w. after 0, 4, 8 and 12 d of storage, respectively.

Almond kernels stored in air lost higher moisture than MA samples at the same storage temperatures. After 12 d, the loss of moisture was minor in the +4 °C MA samples (1% in both nitrogen and carbon dioxide atmospheres). This result was probably bonded to decreasing tissue transpiration caused by temperature lower with the absence of oxygen. The greatest loss of moisture was observed in kernels stored in air at +10 °C (3.85% ± 0.44). The result excluded possible differences between the samples, storage in air at +4 °C (1.62% ± 0.35), under nitrogen at +10 °C (1.48% ± 0.29) and under carbon dioxide at +10 °C (1.40% ± 0.43) (data not shown). According to these results, the kernel moisture content was principally affected by two factors: temperature and atmosphere. This aspect is particularly important since the packaging method had a strong effect on the changes in kernel moisture content, also in agreement with Wu et al. [18] who demonstrated that for the raw almonds. The authors showed as PE bags effectively reduced environmental effects also highlighting as the psychrometric properties of the air and the type of packaging had a great influence on the exchange of moisture between the environment and the almond kernels. Shirmohammadi et al. [47] conducted tests on almonds with different levels of moisture content from 5.5 to 14.1 g/100 g on wet. Almond fruits are exposed to different mechanical stresses during all production lines. The reduction of mechanical damage appeared to be strongly controlled by the moisture content of the kernel. Their results also showed that the samples with a higher moisture content were able to withstand more deformation than dry kernels. Based on this consideration, preserving moisture allows samples not to become soft over time, maintaining their quality.
Firmness, measured using almond kernel deformation, remained almost constant for the samples stored under nitrogen and carbon dioxide at +4 °C (Figure 5).

Through the experiment, it was found that the MA controlled the maintenance of kernel firmness, whereas, as expected, in air-stored kernels, firmness was not maintained. In fact, also at a temperature of +10 °C, both under nitrogen and carbon dioxide the firmness was preserved. Instead, the firmness of kernel decreased during storage at +10 °C in the air for all samples. Maintaining the firmness of almond kernels during MA treatments is supposed the consequence of slower degradation of the cell walls compared to samples stored in the air, also according to Wang et al. [18] who demonstrated the inhibitory effect of MA on the activities of enzymes related to cell wall degradation.

The activity of POD (Figure 6) and PPO (Figure 7) for all samples under MA over the 12 d storage period was constant and similar, whereas the almonds stored in the air showed a decrease in enzymatic activity over time. It has been observed that the storage temperature influences the PPO and POD activity trend only in the presence of oxygen.
stored in the air, also according to Wang et al. [18] who demonstrated the inhibitory effect of MA on the activities of enzymes related to cell wall degradation.

The activity of POD (Figure 6) and PPO (Figure 7) for all samples under MA over the 12 d storage period was constant and similar, whereas the almonds stored in the air showed a decrease in enzymatic activity over time. It has been observed that the storage temperature influences the PPO and POD activity trend only in the presence of oxygen.

Figure 6. Peroxidase activity (POD) over 12 days of storage at +4 °C and +10 °C in air, 100 ± 1 kPa of CO₂, and 100 ± 1 kPa of N₂, respectively.

Interestingly, the samples under MA did not show significant differences between the storage temperatures, while for the samples stored in air a decrease in enzymatic activity was observed only at +4 °C. The oxygen-free environments therefore effectively slowed down the activity of the two enzymes. Sheikhi et al. [48] evaluated the prospective of modified atmosphere packaging, utilizing multiple O₂, CO₂, and N₂ concentrations, considering fresh in-hull pistachios. The authors observed that the PPO activity increased steadily in fresh pistachio hulls under all treatments stored for 45 d at +4 °C. In addition, it can be assumed that also variables such as the physiological phase of the fruit, variety, cultivation method and geographical origin have influences on the POD and PPO activities [49]. Jiang et al. [50] highlighted that the activity of the POD enzyme was nearly connected to antioxidant protection and browning. This could help explain the maintenance of quality in MA preserved samples of our study. As reported by Terefe et al. [51], POD played an essential role as a protective antioxidant enzyme, in resisting membrane damage by eliminating reactive oxygen species. In a previous study [52], a lower PPO activity was the cause of the effect of MA treatment on the alleviation of peel browning.

3.2. Sensory Analysis

In general, data obtained from sensory analysis (Table 2) highlighted as the best sensory characteristics were perceived by panelists for samples stored at +4 °C. All Samples stored at +10 °C scored lower due to an evident loss of crispness of the kernels. In samples stored in MA at +4 C°, both under nitrogen and carbon dioxide, the crispness maintained

Figure 7. Polyphenoloxidase activity (PPO) 12 days of storage at +4 °C and +10 °C in air, 100 ± 1 kPa of CO₂, and 100 ± 1 kPa of N₂, respectively.
Interestingly, the samples under MA did not show significant differences between the storage temperatures, while for the samples stored in air a decrease in enzymatic activity was observed only at +4 °C. The oxygen-free environments therefore effectively slowed down the activity of the two enzymes. Sheikhi et al. [48] evaluated the prospective of modified atmosphere packaging, utilizing multiple O₂, CO₂, and N₂ concentrations, considering fresh-in-hull pistachios. The authors observed that the PPO activity increased steadily in fresh pistachio hulls under all treatments stored for 45 d at +4 °C. In addition, it can be assumed that also variables such as the physiological phase of the fruit, variety, cultivation method and geographical origin have influences on the POD and PPO activities [49].jiang et al. [50] highlighted that the activity of the POD enzyme was nearly connected to antioxidant protection and browning. This could help explain the maintenance of quality in MA preserved samples of our study. As reported by Terefe et al. [51], POD played an essential role as a protective antioxidant enzyme, in resisting membrane damage by eliminating reactive oxygen species. In a previous study [52], a lower PPO activity was the cause of the effect of MA treatment on the alleviation of peel browning.

### 3.2. Sensory Analysis

In general, data obtained from sensory analysis (Table 2) highlighted as the best sensory characteristics were perceived by panelists for samples stored at +4 °C. All Samples stored at +10 °C scored lower due to an evident loss of crispness of the kernels. In samples stored in MA at +4 °C, both under nitrogen and carbon dioxide, the crispness maintained values significantly higher than those stored in MA at +10 °C, whereas the air-stored almonds showed low values in crispness at both +4 and +10 °C (Table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Appearance</th>
<th>Almond Aroma</th>
<th>Flavor Intensity</th>
<th>Crispness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+4 °C</td>
<td>+10 °C</td>
<td>+4 °C</td>
<td>+10 °C</td>
</tr>
<tr>
<td>Air</td>
<td>7.90ₐ</td>
<td>6.77ₜ</td>
<td>6.15ₐ</td>
<td>6.05ₐ</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.18ₐ</td>
<td>8.02ₜ</td>
<td>7.20ₐ</td>
<td>7.22ₐ</td>
</tr>
</tbody>
</table>

Air: air storage as control; CO₂: modified atmosphere storage with 100 ± 1 kPa CO₂; N₂: modified atmosphere storage with 100 ± 1 kPa N₂. [Appearance: poor (1)—excellent (9); Almond aroma: atypical (1)—typical (9); Flavor intensity: low intensity (1)—high intensity (9); Crispness: soft (1)—crispy (9)]. Values followed by a different letter are significantly different (p < 0.05).

This finding is interesting as it is believed that crunchiness/softness belongs to texture attributes easily assessed by consumers, who prefer crunchiness fresh almonds [53] and in accordance with Contador et al. [54] who showed that the most relevant parameters for defining almond quality were those associated with the texture (such as “crispness”). Their study demonstrated that a trained panel characterized and discriminated between raw almond the texture attributes in different cultivars. Even in recent research [54], it was shown that almond varieties differed in their sensory profiles, particularly in texture. They deduced that this sensory difference could have been presented to producers and consumers in choosing the most suitable almond varieties for different uses. Table 2 showed as samples stored in MA received high scores. This finding highlighted the greater flavor intensity and between samples in nitrogen respect these in carbon dioxide, significant differences were found. Particularly, it was evident that the most suitable one for maintaining the flavor intensity of the almonds overtime was nitrogen at +4 °C. This could be explained precisely since exposure to high temperatures and oxygen decreases the shelf life of almonds since promotes lipid oxidation and the formation of off flavors with widespread fermentation (rancidity). The appearance of the kernel was strongly influenced by the preservation in the air, as shown in Table 2. The air-stored almonds at +10 °C received the worst scores with respect to almonds preserved in MA and to those stored
in air at +4 °C (6.77 versus 7.90). After 12 d of storage, the almond aroma was preserved in all of the samples stored under MA, but the highest scores were recorded for almonds stored under nitrogen, giving a score of 8.20 at +4 °C and 8.05 at +10 °C, respectively. Almonds stored at air had lower scores in almond aroma (score of 6.15 at +4 °C and 6.05 at +10 °C, respectively) than those stored at MA, regardless of the storage temperature. Our results are in agreement with those of Mexis et al. [36], who showed that benzaldehyde, the main volatile compound responsible for the characteristic almond aroma, decreased during unprotected almond storage. In the protected products without oxygen, the variations in benzaldehyde concentration were insignificant (p > 0.05) with consequent maintenance of the characteristic taste of the almond even after 12 months of storage. On the other hand, it is difficult to assess which compounds are important to the raw almond aroma and which are not, since the aroma effect will depend on their concentration and smell intensity of the volatile compound. Moreover, the general classes of volatile compounds identified in raw almonds by various authors [1,12,55,56] are highly variable. Almonds stored in nitrogen at +4 °C received higher scores in both almond aroma and crispness (Table 2) and this result is interesting since, as recently described by Lipan et al. [57], the purchase choice of international consumers was based above all on the almond aroma and crunchiness which are the best parameters required by consumers. These findings, along with those that consumers were willing to pay more for hydrosoistantable almonds [58], encourage the almond industry to bet on using MA to stored fresh almonds and simultaneously maintain their functional and sensory quality.

4. Conclusions

In order to identify better conditions to ensure maintenance of the qualitative and sensory characteristics of almonds for fresh consumption, the modified atmosphere used in the experiment was efficacious for the 12 days storage period. The comparison of the different atmospheres applied in this research highlighted as the most suitable MA for maintaining chemical, physical and sensory characteristics of the almonds overtime was nitrogen at +4 °C. Therefore, the recommended conditions for better-storing almonds are using a modified atmosphere of N₂ at +4 °C. This allows maintaining their quality intact for up to almost two weeks of storage. Almonds stored in nitrogen showed no changes in pellicle color, intensity of respiration and POD and PPO enzymatic activity, after 12 d storage. At the temperature of +4 °C, the crispness of the almonds under nitrogen and carbon dioxide during the 12 d was preserved. Besides, it was found that storage at +10 °C for all samples caused a low quality. The saturated carbon dioxide atmosphere produced almonds with lower quality than the saturated nitrogen atmosphere. Finally, it was highlighted that respiration rates and POD and PPO activities were influenced by storage temperature only for samples stored in air and not for those in MA. Nitrogen in MA at +4 °C has been very effective in extending more than ten d the shelf life of raw almonds for commercial purposes, demonstrating a relevant industrial relevance. The results of this research will help almond producers use the best modified atmosphere for almond storage, which was the most suitable for keeping the chemical, physical, and sensorial attributes of fresh almond kernels. This study can also be useful to enhance the use of early ripe fresh almonds, maintaining their organoleptic and qualitative traits. Our findings may entice consumers to increase the use of fresh almonds thanks to the improvement of their shelf life while keeping quality traits and their known human health benefits intact. The use of a nitrogen modified atmosphere at 4 °C has been very effective in extending more than ten days the shelf life of raw almonds for commercial purposes, demonstrating a relevant industrial relevance. This could be the right time to identify an excellent modified atmosphere capable of ensuring the maintenance of the qualitative and sensory characteristics of fresh almonds, with efficiency. The next step in improving the preservation of fresh almonds could be to study the effect of packaging films and micro-perforation techniques.
Author Contributions: All authors contributed to manuscript writing. Conceptualization, review and editing, R.M. and M.T.F.; supervision, R.M. and V.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable for studies not involving humans or animals.

Informed Consent Statement: Not applicable for studies not involving humans.

Data Availability Statement: The data presented in this study are available on request from the co-author, Maria Teresa Frangipane.

Acknowledgments: The author gratefully acknowledge the ‘Departments of excellence 2018’ program (i.e., ‘Dipartimenti di eccellenza’) of the Italian Ministry of Education, University and Research for the financial support through the ‘Landscape 4.0 food, wellbeing and environment’ (DIBAF Department of University of Tuscia, Italy).

Conflicts of Interest: The authors declare no conflict of interest.

References


