# Effect of Calcium and Some Antioxidants treatments on Storability of Le Conte Pear Fruits and its Volatile Components

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**Abstract:** The possibility of calcium nitrate and / or some antioxidants i.e. citric acid and ascorbic acid as preharvest treatment alone or in combination to control decay and its role in improvement the quality of Le Conte pear fruits as well as volatile components under cold storage condition and marketing period during to successive seasons 2007 and 2008.Le Conte pear trees were foliar spraying twice with calcium nitrate at concentration of ( 0.0 and 1700 ppm), citric acid at concentration of (0.0,50 and 100 ppm) and ascorbic acid at concentration of (0.0,50 and 100 ppm), ten treatments were used including control. All treated and untreated pear fruit were stored at 0 ± 1 ºC and 85 – 90% relative humidity (RH) for 75 days and additional one week at room temperature (20-25ºC) as stimulated marketing period. Fruit quality assessments i.e. weight loss and decay percentage, fruit firmness, total soluble solids %, total acidity %, total sugars, fruit calcium content and volatile components were evaluated. Results showed that treated and control fruits withstand free from chilling injury and pathogenic rot up to 45 days of cold storage. While, almost treatments prevented chilling injury symptoms and fruit deterioration up to 60 days of cold storage. Moreover, all treatments alone or in combination decreased the weight loss (%), total acidity % and fruit softening, while increasing fruits content of TSS %, total sugars and calcium (%) as a good keeping fruit conditions for along time. Furthermore, the same trend was observed during marketing period. Therefore, it can be concluded that prolonging storage period of the Le Conte pear fruits by using the considered treatments. However, the combined treatments with calcium nitrate + citric acid, calcium nitrate + ascorbic acid or /and the single treatment of calcium nitrate could be recommended because its gave the best results for keeping fruits and their volatile components under cold storage and marketing period extinction. The headspace volatiles of fresh and stored Le Conte Pear were collected and subjected to GC and GC-MS analysis. 27 volatile components were identified: 15 esters, 8 alcohols, 3 aldehydes and one terpene. Volatile components varied considerably both quantitatively and qualitatively between fresh and stored samples. The best treated samples at fresh were (Ca + CA1) and (Ca + CA2) compared to the control treatments. Although all samples retain a good quality during storage period, Ca(NO3)2, AsA1, (Ca + CA1), (Ca + CA2), and (Ca + AsA1) treated samples were the best compared to the control samples because of the highest content of esters which exhibit it more fruity aroma and cause it more acceptable for consumer. [Nature and Science. 2010;8(5):109-126]. (ISSN: 1545-0740).

**Keywords**: Le Conte pear, Calcium, Citric Acid, Ascorbic Acid, Volatile Components, Storage, Quality Assessments.

## 1. Introduction

Le Conte pear is one of the most important deciduous fruit that shows great success and is widespread in the newly reclaimed areas in Egypt.

Calcium is the most important mineral element determining fruit quality. The multiple roles of Ca associated with the plant cell. Soluble Ca is involved in protein phosphorylation via Ca-Cal- modulin binding. A large portion of the Ca in plant cells is located in the cell wall and plasma membrane where it plays a major role in senescence and ripening. Concentrations of 1-5 mm $Ca^{2+}$ occur in the cell wall region (Poovaian *et al*., 1988). Cell wall – bounded Ca is involved in maintaining cell wall integrity by binding carboxyl groups of polygalacturonate chains, which are mainly present in the middle lamella and primary cell wall (Chardonnet *et al*., 2003). Preharvest Ca treatments used to increase Ca content of the cell wall were effective in delaying senescence, resulting in firmer, higher quality fruit (Serrano *et al*., 2004; Kluter et al., 2006 and Raese and Drake, 2006) that were less susceptible to disease during storage (Hafez and Haggag, 2007).

In recent years there has been a growing interest in all classes of flavonoids as integral antioxidants in the human diet, due in part to their demonstrated ant carcinogenic activity, inhibition of tumor cell proliferation, antioxidant and free radical scavenging capabilities, as well as their effectiveness as metal chelators (Harborne and Williams, 2000). A group of antioxidants, including ascorbic acid (AsA) and citric acid (CA) were screened as possible chemical inhibitors for the reaction (Wang and Mellenthin,

1974). Lin *et al*., 2007 suggested that the effects of AsA treatment on inhibiting core browning and improving post harvest quality in pear cv. Yali may be due to a reduction membrane lipid peroxidation by enhancing the capacity of cells to scavenge reactive oxygen species. Also, Lin *et al*., 2008 found that application of chitosan combined with AsA was more effective than chitosan alone in decreased weight of losses, delayed softening, decreased respiration rate and improved total soluble solids in pear fruits as well as inhibited the incidence core browning throughout storage.

The purpose of this study was to investigate the ability of calcium nitrate and some antioxidant agents i.e. citric acid and ascorbic acid as pre harvest treatments separately or in mixture to control decay and its role in improvement the quality of Le Conte pear fruits as well as their volatile components under cold storage condition and during marketing period.

Volatile components of pear have been investigated with many authors (Kahle *et al*., 2005, Chen *et al*., 2006 (a, b) and Diban, *et al*., 2007).

**Material and Methods:**

**Pear orchard:** Pear trees cv. Le Conte (*Pyrus communis*, L.) in a private orchard at El-Tall El-Kepeer, Ismaalia Governorate. Fruit were picked from five years growen in sandy soil, speased 4x4m, under drip irrigation system, similar in growth and received common horticulture practices, were selected for this investigation. Fertilization, irrigation and other agriculture practices were applied as recommended. The soil texture of the experimental site was used with organic matter 0.36%, pH 8.9, E.C 0.18 $dsm^{-1}$ and $CaCO_3$ 3.6%, P 0.26 mg/100g, K 18.2 mg/100g, Ca 420 mg/100g, Mg 10.2 mg/100g, Na 32 mg/100g, Fe 3.5 ppm , Mn 4.o ppm, Zn 1.6 ppm, and Cu o.4 ppm.

**Treatments:** Preharvest treatments of calcium as form calcium nitrate at 1700 ppm, citric acid (CA) at 50 or 100 ppm and ascorbic acid (AsA) at 50 or 100 ppm were sprayed alone or in combination, ten treatments used including control, on pear trees during 2007 and 2008 seasons. In each season, the foliar spraying treatments were applied at two times. The $1^{ST}$ spraying was at the second week of July. While, the $2^{nd}$ one was at after the first with ten days. All spray solutions contained 0.1% Triton B as a wetting agent and sprayed till run off.

**Storage fruits:** Undamaged mature pear fruits, free from apparent pathogen infection, uniform in shape, weight and color picked separately from each treated pear trees groups. Fruits were harvested at the last week of August during each growing seasons and transported to the laboratory of Agriculture Development System (ADS) Project, Faculty of Agriculture, Cairo University, Egypt. The initial quality measurements were determined.

**Fruit keeping:** The selected fruits were washed with tap water; air dried and then packed in perforated carton boxes in three replicates for each treatment (about 120 fruit/treatment, with 20 fruit/replicates). Each treatment classified into two groups. The first group contains fruits for periodical determination of loss in weight of fruit and fruit decay percentage. The other contained fruits were used for the determination of fruit quality characteristics. Fruit stored at 0 ± 1 °C with relative humidity (RH) 85 – 90 % for 75 days. Assay of the stored fruits was made at 15 days intervals.

**Marketing period:** A sample of 10 fruits of each replicate was taken out at the end of cold storage period and left at room temperature (20 – 24 °C) for one week. Pear fruits quality assessment and fruit decay were assessed.

**Quality assessments:**

**A- Physical characteristics:**

**Weight losses:** Pear fruits were periodically weighted and the losses were recorded for each replicate. Date of weight losses were calculated as percentage from the initial weight.

**Fruit decay percentage:** Evaluated by type, as skin appearance, shriveling, chilling injury and pathogenic rots. In every inspection, decayed fruits were discarded and the number of fruits per replicate was used to express decay percentage.

**Fruit firmness:** Pear fruit firmness was determined as $Lb/inch^2$ by using fruit pressure tester mode. FT 327 (3 – 27 Lbs).

**B- Chemical characteristics:**

**Total Soluble Solids (TSS):** were determined in pear fruit juice using a hand refract meter model (10430 Brix reading 0 – 30 ranges Bausch & lomb Co. Calif., USA) according to A.O.A.C., 1995).

**Total acidity (TA %):** Was estimated as malic acid by titrating 5 ml juice with 0.1Nsodium hydroxide using phenolphthalein as an indicator (A.O.A.C., 1995).

**Total sugars (g/100g fresh weight "F.W"):** Were determined in pear fruits by method described by Smith *et al*.; 1956 using the phenol and sulphoric acid.

**Fruit calcium content:** Samples of fruits pulp were randomly taken from all treatments of each replicate after harvest time and 15 days intervals during storage of periods to determined calcium (Ca %) as described by Shapman and Pratt, 1978.

**C- Volatile components:**

**Isolation and analysis of headspace volatiles:**

The volatiles in the headspace of each sample under investigation were isolated by using a dynamic headspace system according to Fadel et al., 2006.

**Gas chromatographic (GC) analysis:**
GC analysis was performed by using Hewlett-Packard model 5890 equipped with a flame ionization detector (FID). A fused silica capillary column DB5 (60m x 0.32 mm id) was used. The oven temperature was maintained initially at 50°C for 5 min, and then programmed from 50 to 250°C at a rate of 4°C/min. Helium was used as the carrier gas, at flow rate 1.1 ml/min. The injector and detector temperatures were 220 and 250°C, respectively. The retention indices (Kovats index) of the separated volatile components were calculated using hydrocarbon (C8-C22, Aldrich CO.) as references.

**Gas chromatographic-mass spectrometric (GC-MS) analysis:**
The analysis was carried out by using a coupled gas chromatography Hewlett-Packard (5890)/mass spectrometry Hewlett-Packard-MS (5970). The ionization voltage was 70 eV, mass range m/z 39-400amu. The GC condition was carried out as mentioned above. The isolated peaks were identified by matching with data from the library of mass spectra (N1ST) and compared with those of authentic compounds and published data (Adams, 2001). The quantitative determination was carried out based on peak area integration.

**Statistical analysis:** The data were subjected to analysis of variance and the method of Duncan was used to differentiate means**,** Duncan (1955).

## RESULTS AND DISCUSSION

Fruit quality characteristics as affected by calcium and some antioxidant agents treatments of pear cv. Le Conte during cold storage periods:

**Weight loss percentage:**
Effect of calcium and some antioxidant agents treatments on weight loss (%) of Le Conte pear fruits stored at 0 ± 1 º C are listed in table (1). Data showed that the percentage of weight loss was ranged from 1.4 to 7.8 % and from 1.3 to 7.3 % with the nutrition treatments comparing with control ranged from 1.8 to 9.1 % and from 1.8 to 9.4 % in both seasons. It obvious that the fruit weight loss was significant increased gradually with the progress of storage period up to 75 days. The lowest significant values of weight losses percentages were recorded by the combined spray Ca + CA2 (3.4 & 3.8%) respectively in 2007 and 2008 seasons. Followed by the combined spray of Ca + CA1 (4.1%) in the 1st season, while, a single treatment of calcium nitrate (4.0%) in the 2nd season. Came next the alone treatment of calcium nitrate (4.2%) in the first season, but the combined spray with Ca + CA1 and Ca + AsA2 (4.2 & 4.3 %) consecutively in the second season, without significant between them.
The loss in fruit weight is mainly due to water loss as a result of evaporation and transpiration and the amount of dry matter was lost by respiration. Our results are in agreement with Serrano *et al.,* 2004 on peaches and nectarines as well as Hafez & Haggag, 2007 on apple concerning in the effect of calcium treatment, they found that during cold storage, lower levels of weight loss were recorded in treated fruits compared with control fruits. As for the effect of antioxidants treatments, The present result are in agreement with that obtained by Lin *et al.,* 2008, who found that "Yali" pear fruits coating with ascorbic acid and stored deceased respiration rate and decreased weight of loss percentage.

**Decay percentage:**
Data in table (2) clearly revealed that all preharvest treatment with calcium nitrate, citric acid and ascorbic acid either alone or combination reduced decay percent and Le Conte fruits deterioration up to 75 days of cold storage at 0 ± 1 º C compared with untreated fruits (control). In general, to identify the classification of decay injuries influenced by pre harvest treatments, it can be stated that the physiological disorders as chilling injury (CI) and shriveling symptoms were higher percent than pathological rots in all treatments in both seasons. Moreover, it can be noticed from data in Table (2) all treatments including control prevented CI symptoms and pear fruit determination for 45 days at 0 ± 1 º C. However, the preharvest treatments alone or in combination prevented CI symptoms up to 60 days except the alone treatment of AsA1 in the 2nd season, as well as prevented the pear fruit determination up to 60 days except the alone treatment of AsA1 in the 1st season and combined treatment of Ca + AsA2 in the 2nd season. The best treatment prevented CI symptoms and pear fruit determination, as a good keeping fruits for along time (up to 75 days), obtained with the alone treatment of calcium nitrate and the combined treatment of Ca + CA2 in the 1st season, they recorded 100% total healthy. Meanwhile, in the 2nd season the two prevented treatments recorded 100% total healthy fruits after 60 days of cold storage. The alone treatment of Ca superior on this respect, it recorded the lowest significant CI symptoms 4.8% at 75 days. Followed by the combined treatment of Ca + CA2 gave 9.53%.
The results of preharvest treatments of calcium and some antioxidants study confirmed the previous finding of Guy *et al*., 2003 they reported that the pre harvest calcium sulfate application as bud sprays reduced both the progress and severity of gray mould

and increasing vase life of the rose flowers. Also, Richardson & Lombard**,** 1979 revealed that cork spot of pear Cv. "d" Anjou fruits was reduced 20% to 80% with orchard application of calcium at rates ranging from 325 to 350 ppm as chloride or nitrate spray containing surfactant. Late season sprays were more effective than early season sprays. Fruit calcium spray increased fruit calcium concentrations by 15 – 30%, sufficient to decrease the incidence of the disorders. Moreover, Hafez & Haggag, 2007 found that preharvest calcium application resistance to pathological disorders and keeping fruit quality. As for the effect antioxidants in the respect, Lin *et al*., 2007 & 2008 suggested that AsA treatment inhibiting core browning and improving postharvest quality in "Yali" pears may be due to a reduction membrane lipid peroxidation by enhancing the capacity of cells to scavenge reactive oxygen species.

**Fruit firmness (Lb/inch$^2$):**

Fruit firmness as affected by nutrition treatments during 2007 and 2008 seasons are listed in Table (3). Resulted showed that the fruit firmness were 7.8 to 13.8 Lb/inch$^2$ during 2007 season and 8.3 to 14.8 Lb/inch$^2$ during 2008 season compared with 7.5 to 12.4 Lb/inch$^2$ and 7.9 to 12.0 Lb/inch$^2$ in control treatment, respectively, within the storage days. It is clear that fruit firmness was decreased as storage period advanced. Also, it can be noticed from data obtained that all tested treatments had the highest effects on firmness comparing with control, but without any significant differences between them in the 1$^{st}$ season. However, in the 2$^{nd}$ season the highest significant values were obtained from all treatments in this connection. A combined treatment of Ca + CA2 and a single treatment of Ca were significantly increased the fruit firmness (12.2 & 11.62 Lb/inch$^2$) consecutively, but with no significant differ them. Meanwhile, the other treatment with antioxidants alone or with combined with calcium gave the same effect in reducing the rate of fruit softening without significant differences between them. On the other side, the untreated fruits were the lowest significant rate of fruit firmness in 2008 season.

These results might be due to the positive of applying calcium, citric acid and ascorbic acid alone or in combination on treated fruits. The obtained results could be explained by statement of Lin *et al*., 2007 which showed that antioxidants application improving postharvest quality and inhibiting core browning in Yali pears may be due to a reduction membrane lipid peroxidation by enhancing the capacity of cells to scavenge reactive oxygen species. The favorable effect of calcium obtained by Siddiqui and Bangerth, 1995 on Golden Delicious apple, it suggested that the observed effects of $CaCl_2$ on fruit firmness are likely to be associated with the calcium content of the covalently-bound pectin fraction. Also, Benavides *et al*., 2002 on Golden Smoothee apple found that the fruit firmness increased when calcium was applied. Similar results were obtained by Casero *et al*., 2004 on Golden Smoothee apple who indicated that fruit firmness shows positive correlation with fruit Ca content and bitter pit incidence correlates negatively with this nutrient concentration. Further more, Saure (2005) "on fleshes fruit" reported that Ca is known to stabilize cell membranes and in this way may prevent physiological disorders attributed to Ca deficiency. AS only very limited quantities of Ca can be directly supplied to the fruit, reducing excessive gibberellins levels by various means may be the better way to control such disorders. AS well as Montanaro *et al*., 2006 on "Kiwifruit" suggests that transpiration is not the only factor controlling Ca transport, and light also influenced the Ca concentration in xylem sap. Taking into account that auxin is able to stimulate Ca uptake and light promotes the biosynthesis of auxin protecting phenols (hydroxycinnamic acid). So, a new working hypothesis is proposed that light induces the biosynthesis of such phenols, which in directly decreases auxin degradation, and therefore, increases Ca accumulation.

Table (1): Effect 0f calcium and some antioxidant agents treatments on weight loss percentage of Le Conte pear fruits stored for 75 days at 0º C during 2007 and 2008 seasons.

| Treatments | Storage period in days | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 1.8 | 3.6 | 5.1 | 7.3 | 9.1 | 5.4 a |
| $Ca(NO_3)_2$ (1700ppm) | 1.5 | 3.0 | 4.2 | 5.5 | 6.7 | 4.2 cd |
| CA1 (50 ppm) | 1.6 | 3.2 | 5.0 | 6.8 | 7.6 | 4.8 b |
| CA2 (100 ppm) | 1.6 | 3.1 | 4.4 | 5.7 | 7.3 | 4.4 bc |
| AsA1 (50 ppm) | 1.6 | 3.1 | 4.6 | 6.0 | 7.6 | 4.6 b |
| AsA2 (100ppm) | 1.5 | 3.1 | 4.5 | 6.1 | 7.8 | 4.6 b |
| Ca + CA1 | 1.5 | 2.8 | 4.0 | 5.4 | 6.8 | 4.1 d |
| Ca + CA2 | 1.4 | 2.8 | 3.9 | 5.1 | 6.3 | 3.9 e |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ca + AsA1 | 1.4 | 2.9 | 4.3 | 5.7 | 7.2 | 4.3 c |
| Ca + AsA2 | 1.6 | 3.2 | 3.5 | 5.9 | 7.5 | 4.3 c |
| Means | 1.6 e | 3.1 d | 4.4 c | 6.0 b | 7.4 a | |
| | Season 2008 | | | | | |
| Control (water) | 1.8 | 3.8 | 5.6 | 7.3 | 9.4 | 5.6 a |
| $Ca(NO_3)_2$ (1700ppm) | 1.5 | 2.8 | 4.0 | 5.1 | 6.4 | 4.0 e |
| CA1 (50 ppm) | 1.6 | 3.3 | 5.5 | 6.4 | 7.3 | 4.8 b |
| CA2 (100 ppm) | 1.4 | 2.9 | 4.3 | 5.7 | 7.1 | 4.3 d |
| AsA1 (50 ppm) | 1.7 | 3.2 | 4.5 | 5.7 | 7.3 | 4.5 c |
| AsA2 (100ppm) | 1.6 | 3.1 | 4.4 | 6.3 | 7.3 | 4.5 c |
| Ca + CA1 | 1.4 | 3.0 | 4.2 | 5.5 | 6.8 | 4.2 d |
| Ca + CA2 | 1.3 | 2.7 | 3.9 | 5.1 | 6.2 | 3.8 f |
| Ca + AsA1 | 1.4 | 3.0 | 4.4 | 5.8 | 7.3 | 4.4 cd |
| Ca + AsA2 | 1.5 | 3.0 | 4.4 | 5.8 | 7.0 | 4.3 d |
| Means | 1.5 e | 3.1 d | 4.5 c | 5.9 b | 7.2 a | |

Table (2): Effect 0f calcium and some antioxidant agents treatments on decay percentage and types of Le Conte pear fruits stored for 75 days at 0 ºC during 2007 and 2008 seasons.

| Treatments | Storage period in days | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Season 2007 | | | | | | | | |
| | Chilling injury (shriveling) | | | Pathogenic (soft rots) | | | Total healthy fruits | | |
| | 60 | 75 | Means | 60 | 75 | Means | 60 | 75 | Means |
| Control (water) | 9.53 | 14.3 | 4.77 a | 4.8 | 19.1 | 4.78 a | 85.7 | 66.6 | 90.5 b |
| $Ca(NO_3)_2$(1700ppm) | 0.0 | 0.0 | 0.0 a | 0.0 | 0.0 | 0.0 b | 100.0 | 100.0 | 100.0 a |
| CA1 (50 ppm) | 0.0 | 23.8 | 4.76 a | 4.8 | 9.53 | 2.87 a | 95.2 | 66.7 | 92.4 ab |
| CA2 (100 ppm) | 0.0 | 19.1 | 3.82 a | 0.0 | 4.8 | 0.96 b | 100.0 | 76.1 | 95.2 a |
| AsA1 (50 ppm) | 0.0 | 23.8 | 4.76 a | 4.8 | 4.8 | 1.92 b | 95.2 | 71.4 | 93.3 ab |
| AsA2 (100ppm) | 0.0 | 23.8 | 4.76 a | 0.0 | 9.5 | 1.90 b | 100.0 | 66.7 | 93.3 ab |
| Ca + CA1 | 0.0 | 14.3 | 2.86 a | 0.0 | 0.0 | 0.0 b | 100.0 | 85.7 | 97.1 a |
| Ca + CA2 | 0.0 | 0.0 | 0.0 a | 0.0 | 0.0 | 0.0 b | 100.0 | 100.0 | 100.0 a |
| Ca + AsA1 | 0.0 | 23.6 | 4.76 a | 0.0 | 0.0 | 0.0 b | 100.0 | 76.2 | 95.2 a |
| Ca + AsA2 | 0.0 | 19.1 | 3.82 a | 0.0 | 0.0 | 0.0 b | 100.0 | 80.9 | 96.2 a |
| Means | 0.95 b | 15.72 a | | 1.44 b | 4.77 a | | 97.61 a | 79.03 b | |
| | Season 2008 | | | | | | | | |
| Control (water) | 9.53 | 19.1 | 13.32 a | 14.3 | 14.3 | 5.72 | 76.2 | 66.6 | 88.6 c |
| $Ca(NO_3)_2$(1700ppm) | 0.0 | 4.8 | 0.96 d | 0.0 | 0.0 | 0.0 | 100.0 | 95.2 | 99.04 a |
| CA1 (50 ppm) | 0.0 | 23.83 | 4.77 c | 0.0 | 4.8 | 0.96 | 100.0 | 71.4 | 94.3 b |
| CA2 (100 ppm) | 0.0 | 4.8 | 0.96 d | 0.0 | 14.3 | 2.86 | 100.0 | 80.9 | 96.2 a |
| AsA1 (50 ppm) | 4.8 | 33.3 | 7.62 b | 0.0 | 9.5 | 1.9 | 95.2 | 60.5 | 91.1 b |
| AsA2 (100ppm) | 0.0 | 23.8 | 4.76 c | 0.0 | 0.0 | 0.0 | 100.0 | 76.2 | 95.2 ab |
| Ca + CA1 | 0.0 | 19.1 | 3.82 c | 0.0 | 0.0 | 0.0 | 100.0 | 80.9 | 96.2 a |
| Ca + CA2 | 0.0 | 9.53 | 1.91 d | 0.0 | 4.8 | 0.96 | 100.0 | 85.7 | 97.1 a |
| Ca + AsA1 | 0.0 | 14.3 | 2.86 c | 0.0 | 4.8 | 0.96 | 100.0 | 80.9 | 96.2 a |
| Ca + AsA2 | 0.0 | 14.3 | 2.86 c | 4.8 | 0.0 | 0.96 | 95.2 | 85.7 | 96.1 a |
| Means | 1.43 b | 16.7 a | | 1.91 b | 5.3a | | 96.7 | 78.4 b | |

Decay (%) and types in all treatments up to 45 days = 0.0 in both studied seasons.

Table (3): Effect 0f calcium and some antioxidant agents treatments on fruit firmness (Lb/inch$^2$) of Le Conte pear fruits stored for 75 days at 0º C during 2007 and 2008 seasons.

| Treatments | Storage period in days | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 12.4 | 11.5 | 10.3 | 9.9 | 7.5 | 10.3 a |
| $Ca(NO_3)_2$(1700ppm) | 13.3 | 12.5 | 10.7 | 10.1 | 8.6 | 11.04 a |
| CA1 (50 ppm) | 12.4 | 11.6 | 10.3 | 10.0 | 8.3 | 10.52 a |
| CA2 (100 ppm) | 12.6 | 11.9 | 10.4 | 10.0 | 8.3 | 10.64 a |
| AsA1 (50 ppm) | 12.4 | 11.5 | 10.5 | 9.9 | 7.8 | 10.42 a |
| AsA2 (100ppm) | 12.7 | 11.8 | 10.6 | 10.0 | 7.9 | 10.60 a |
| Ca + CA1 | 13.4 | 12.3 | 11.5 | 10.1 | 8.9 | 11.30 a |
| Ca + CA2 | 13.8 | 13.0 | 12.0 | 10.4 | 9.0 | 11.64 a |
| Ca + AsA1 | 12.7 | 12.0 | 11.0 | 10.0 | 8.6 | 11.90 a |
| Ca + AsA2 | 13.0 | 12.7 | 11.1 | 10.2 | 8.8 | 11.20 a |
| Means | 12.9 a | 12.1 b | 10.84 c | 10.1 c | 8.4 d | |
| | Season 2008 | | | | | |
| Control (water) | 12.0 | 10.9 | 9.7 | 8.9 | 7.9 | 9.90 d |
| $Ca(NO_3)_2$(1700ppm) | 13.7 | 13.5 | 11.2 | 10.7 | 9.0 | 11.62 a |
| CA1 (50 ppm) | 13.0 | 12.4 | 10.1 | 9.7 | 8.9 | 10.82 B |
| CA2 (100 ppm) | 13.6 | 12.8 | 10.9 | 10.0 | 9.0 | 11.30 abc |
| AsA1 (50 ppm) | 12.8 | 11.7 | 10.3 | 9.5 | 8.3 | 10.52 c |
| AsA2 (100ppm) | 13.0 | 12.3 | 11.4 | 10.2 | 9.5 | 11.30 abc |
| Ca + CA1 | 13.3 | 12.5 | 12.0 | 10.0 | 9.2 | 11.40 abc |
| Ca + CA2 | 14.8 | 13.0 | 12.3 | 10.9 | 10.0 | 12.20 a |
| Ca + AsA1 | 13.0 | 11.0 | 10.8 | 9.6 | 9.0 | 10.70 bc |
| Ca + AsA2 | 13.6 | 12.0 | 11.1 | 10.7 | 9.6 | 11.40 abc |
| Means | 13.3 a | 12.2 b | 11.0 c | 10.02 d | 9.04 e | |

Table (4): Effect 0f calcium and some antioxidant agents treatments on total Soluble solids (TSS %) of Le Conte pear fruits stored for 75 days at 0 ºC during 2007 and 2008 seasons.

| Treatments | Storage period in days | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 13.5 | 14.7 | 15.3 | 15.5 | 15.9 | 15.0 c |
| $Ca(NO_3)_2$(1700ppm) | 14.7 | 15.2 | 15.5 | 15.6 | 17.0 | 15.6 ab |
| CA1 (50 ppm) | 14.3 | 14.6 | 15.0 | 15.5 | 16.0 | 15.1 ab |
| CA2 (100 ppm) | 14.5 | 15.0 | 15.2 | 16.5 | 17.7 | 15.8 a |
| AsA1 (50 ppm) | 13.8 | 14.6 | 15.3 | 15.8 | 16.5 | 15.2 bc |
| AsA2 (100ppm) | 14.2 | 14.9 | 15.0 | 15.6 | 16.7 | 15.3 bc |
| Ca + CA1 | 15.0 | 15.4 | 15.6 | 16.0 | 17.5 | 15.9 a |
| Ca + CA2 | 15.4 | 15.6 | 16.3 | 17.0 | 17.5 | 16.4 a |
| Ca + AsA1 | 13.4 | 14.5 | 15.0 | 15.7 | 16.9 | 15.1 ab |
| Ca + AsA2 | 13.8 | 14.7 | 15.3 | 16.5 | 19.3 | 15.5 ab |
| Means | 14.3 e | 14.9 d | 15.4 c | 16.0 b | 16.9 a | |
| | Season 2008 | | | | | |
| Control (water) | 13.8 | 14.5 | 14.8 | 15.0 | 15.7 | 14.8 d |
| $Ca(NO_3)_2$(1700ppm) | 14.9 | 15.2 | 15.7 | 16.0 | 17.2 | 15.8 a |
| CA1 (50 ppm) | 14.9 | 15.0 | 15.4 | 15.7 | 16.0 | 15.4 bc |
| CA2 (100 ppm) | 14.9 | 15.0 | 15.5 | 15.7 | 16.2 | 15.5 b |
| AsA1 (50 ppm) | 13.9 | 14.0 | 14.7 | 15.5 | 15.9 | 14.8 d |
| AsA2 (100ppm) | 14.0 | 15.0 | 15.2 | 15.7 | 16.0 | 15.2 bcd |
| Ca + CA1 | 14.8 | 15.5 | 15.8 | 159 | 16.0 | 15.6 ab |
| Ca + CA2 | 14.9 | 15.7 | 16.0 | 16.4 | 17.3 | 16.1 a |
| Ca + AsA1 | 14.0 | 14.5 | 14.9 | 15.3 | 15.8 | 14.9 cd |
| Ca + AsA2 | 14.5 | 14.7 | 15.0 | 15.8 | 16.4 | 15.3 bcd |
| Means | 14.5d | 15.0 c | 15.3c | 15.7 bc | 16.3 a | |

Table (5): Effect of calcium and some antioxidant agents treatments on total Acidity (TA %) of Le Conte pear fruits stored for 75 days at 0ºC during 2007 and 2008 seasons.

| Treatments | Storage period in days | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 0.32 | 0.31 | 0.30 | 0.23 | 0.20 | 0.272 a |
| $Ca(NO_3)_2$(1700ppm) | 0.30 | 0.30 | 0.30 | 0.20 | 20.0 | 0.260 b |
| CA1 (50 ppm) | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| CA2 (100 ppm) | 0.30 | 0.30 | 0.30 | 0.30 | 0.20 | 0.280 a |
| AsA1 (50 ppm) | 0.31 | 0.31 | 0.30 | 0.23 | 0.20 | 0.270 ab |
| AsA2 (100ppm) | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| Ca + CA1 | 0.30 | 0.23 | 0.21 | 0.20 | 0.20 | 0.228 d |
| Ca + CA2 | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| Ca + AsA1 | 0.30 | 0.30 | 0.23 | 0.20 | 0.20 | 0.264 c |
| Ca + AsA2 | 0.23 | 0,23 | 0.20 | 0.20 | 0.13 | 0.198 e |
| Means | 0.299 a | 0.288 b | 0.274 ab | 0.246 b | 0.193 c | |
| | Season 2008 | | | | | |
| Control (water) | 0.32 | 0.31 | 0.30 | 0.23 | 0.20 | 0.272 a |
| $Ca(NO_3)_2$(1700ppm) | 0.30 | 0.30 | 0.30 | 0.20 | 20.0 | 0.260 b |
| CA1 (50 ppm) | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| CA2 (100 ppm) | 0.30 | 0.30 | 0.30 | 0.30 | 0.20 | 0.280 a |
| AsA1 (50 ppm) | 0.31 | 0.31 | 0.30 | 0.23 | 0.20 | 0.270 ab |
| AsA2 (100ppm) | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| Ca + CA1 | 0.30 | 0.23 | 0.21 | 0.20 | 0.20 | 0.228 d |
| Ca + CA2 | 0.31 | 0.30 | 0.30 | 0.30 | 0.20 | 0.282 a |
| Ca + AsA1 | 0.30 | 0.30 | 0.23 | 0.20 | 0.20 | 0.264 c |
| Ca + AsA2 | 0.23 | 0,23 | 0.20 | 0.20 | 0.13 | 0.198 e |
| Means | 0.299 a | 0.288 b | 0.274 ab | 0.246 b | 0.193 c | |

Table (6): Effect of calcium and some antioxidant agents treatments on total sugars (g/100gFW) of Le Conte pear fruits stored for 75 days at 0º C during 2007 and 2008seasons.

| Treatments | Storage period in days | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 8.0 | 8.6 | 9.0 | 9.5 | 9.6 | 8.94 f |
| $Ca(NO_3)_2$(1700ppm) | 9.9 | 10.0 | 10.2 | 10.3 | 11.4 | 10.4 b |
| CA1 (50 ppm) | 8.5 | 9.0 | 9.5 | 9.9 | 10.6 | 9.5 e |
| CA2 (100 ppm) | 8.8 | 9.6 | 9.9 | 10.0 | 10.8 | 9.82 d |
| AsA1 (50 ppm) | 8.5 | 8.6 | 9.9 | 10.0 | 10.5 | 9.5 e |
| AsA2 (100ppm) | 8.6 | 8.8 | 9.5 | 10.3 | 10.7 | 9.6 e |
| Ca + CA1 | 8.9 | 9.3 | 10.0 | 10.5 | 11.4 | 10.02 c |
| Ca + CA2 | 9.4 | 9.7 | 10.3 | 11.6 | 12.0 | 10.72 a |
| Ca + AsA1 | 8.7 | 9.5 | 9.8 | 10.3 | 11.0 | 9.9 d |
| Ca + AsA2 | 9.3 | 9.3 | 10.9 | 11.2 | 11.9 | 10.52 b |
| Means | 8.9 e | 9.24 d | 10.0 c | 10.4 b | 11.01 a | |
| | Season 2008 | | | | | |
| Control (water) | 8.0 | 8.2 | 8.7 | 9.6 | 10.1 | 8.92 a |
| $Ca(NO_3)_2$(1700ppm) | 8.7 | 9.0 | 10.6 | 11.1 | 11.2 | 10.12 b |
| CA1 (50 ppm) | 8.3 | 8.8 | 9.9 | 10.2 | 11.5 | 9.74 d |
| CA2 (100 ppm) | 8.5 | 8.9 | 10.3 | 10.6 | 11.7 | 10.0 bc |
| AsA1 (50 ppm) | 8.4 | 8.5 | 9.3 | 10.3 | 11.3 | 9.6 d |
| AsA2 (100ppm) | 8.6 | 8.8 | 9.5 | 10.6 | 11.6 | 9.82 cd |
| Ca + CA1 | 8.7 | 9.0 | 10.5 | 11.8 | 12.5 | 10.5 a |
| Ca + CA2 | 8.9 | 9.5 | 10.7 | 11.9 | 12.9 | 10.8 a |
| Ca + AsA1 | 8.7 | 8.9 | 10.4 | 11.2 | 11.8 | 10.2 b |
| Ca + AsA2 | 8.8 | 9.3 | 10.6 | 11.9 | 12.7 | 10.7 a |
| Means | 8.6 e | 8.9 d | 10.1 c | 10.92 b | 11.72 a | |

Table (7): Effect of calcium and some antioxidant agents treatments on fruit Ca content (%) of Le Conte pear fruits stored for 75 days at 0º C during 2007 and 2008 seasons.

| Treatments | Storage period in days at | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 | Means |
| | Season 2007 | | | | | |
| Control (water) | 0.024 | 0.026 | 0.026 | 0.028 | 0.029 | 0.0270 c |
| $Ca(NO_3)_2$(1700ppm) | 0.027 | 0.028 | 0.029 | 0.030 | O.O32 | 0.0292 ab |
| CA1 (50 ppm) | 0.024 | 0.025 | 0.026 | 0.027 | 0.027 | 0.0260 d |
| CA2 (100 ppm) | 0.025 | 0.025 | 0.026 | 0.027 | 0.028 | 0.0260 d |
| AsA1 (50 ppm) | 0.024 | 0,026 | 0.027 | 0.028 | 0.029 | 0.0270 c |
| AsA2 (100ppm) | 0.025 | 0.026 | 0.027 | 0.028 | 0.029 | 0.0270 c |
| Ca + CA1 | 0.026 | 0.028 | 0.029 | 0.030 | 0.032 | 0.0290 d |
| Ca + CA2 | 0.027 | 0.029 | 0.029 | 0.030 | 0.032 | 0.0294 ab |
| Ca + AsA1 | 0.027 | 0.028 | 0.028 | 0.029 | 0.033 | 0.0290 b |
| Ca + AsA2 | 0.027 | 0.028 | 0.030 | 0.031 | O.033 | 0.0300 a |
| Means | 0.026 e | 0.029 d | 0.028 c | 0.029 b | 0.030 a | |
| | Season 2008 | | | | | |
| Control (water) | 0.025 | 0.026 | 0.027 | 0.028 | 0.029 | 0.0270 e |
| $Ca(NO_3)_2$(1700ppm) | 0.028 | 0.028 | 0.029 | 0.031 | 0.033 | 0.0300 b |
| CA1 (50 ppm) | 0.025 | 0.026 | 0.027 | 0.028 | 0.029 | 0.0272 d |
| CA2 (100 ppm) | 0.025 | 0.026 | 0.027 | 0.029 | 0.029 | 0.0272 d |
| AsA1 (50 ppm) | 0.025 | 0.026 | 0.028 | 0.028 | 0.029 | 0.0272 d |
| AsA2 (100ppm) | 0.026 | 0.026 | 0.027 | 0.028 | 0.029 | 0.0272 d |
| Ca + CA1 | 0.027 | 0.028 | 0.029 | 0.030 | 0.031 | 0.0290 c |
| Ca + CA2 | 0.028 | 0.029 | 0.030 | 0.031 | 0.032 | 0.0300 b |
| Ca + AsA1 | 0.028 | 0.028 | 0.029 | 0.031 | 0.033 | 0.0300 b |
| Ca + AsA2 | 0.028 | 0.029 | 0.030 | 0.031 | 0.033 | 0.0302 a |
| Means | 0.027 d | 0.027 d | 0.028 c | 0.030 b | 0.031 a | |

Table (8): Effect of calcium and some antioxidant agents treatments on decay (%) and types of Le Conte pear fruits after marketing period during 2007 and 2008 seasons.

| Treatments | For 75 days cold stored fruits +7 days at room temperature | | | | | |
|---|---|---|---|---|---|---|
| | Season 2007 | | | Season 2008 | | |
| | Chilling injury (shriveling) | Pathogenic (soft rot) | Total healthy fruits | Chilling injury (shriveling) | Pathogenic (soft rot) | Total healthy fruits |
| Control (water) | 13.33 a | 26.70 a | 60.00 a | 20.00 a | 33.33 a | 46.70 b |
| $Ca(NO_3)_2$(1700ppm) | 13.33 a | 6.70 ab | 80.00 a | 20.00 a | 6.70 ab | 73.33 ab |
| CA1 (50 ppm) | 26.70 a | 13.33 ab | 60.00 a | 13.33 a | 20.00 ab | 66.70 ab |
| CA2 (100 ppm) | 13.33 a | 6.70 ab | 80.00 a | 20.00 a | 0.00 b | 80.00 a |
| AsA1 (50 ppm) | 20.00 a | 6.70 ab | 73.33 a | 20.00 a | 6.70 ab | 73.33 ab |
| AsA2 (100ppm) | 6.70 a | 6.70 ab | 86.70 a | 13.33 a | 6.70 ab | 80.00 a |
| Ca + CA1 | 13.33 a | 6.70 ab | 80.00 a | 13.33 a | 20.00 ab | 73.33 ab |
| Ca + CA2 | 13.33 a | 0.00 b | 86.90 a | 6.70 a | 0.00 b | 93.33 a |
| Ca + AsA1 | 26.70 a | 0.00 b | 73.33 a | 13.33 a | 13.33 ab | 73.33 ab |
| Ca + AsA2 | 6.70 a | 6.70 ab | 86.70 a | 6.70 a | 6.70 ab | 86.90 a |

Table (9): Effect of calcium and some antioxidant agents treatments on physical characteristics of Le Conte pear fruits stored for 75 days + 7 days at (20 - 24$^0$C) during 2007 and 2008 seasons.

| Treatments | For 75 days cold stored fruits +7 days at room temperature | | | | | |
|---|---|---|---|---|---|---|
| | Season 2007 | | | Season 2008 | | |
| | Weight loss (%) | Firmness (Lb/inch$^2$) | TSS (%) | Weight loss (%) | Firmness (Lb/inch$^2$) | TSS (%) |
| Control (water) | 2.9 a | 7.7 a | 14.20 a | 3.1 a | 6.3 c | 14.33 c |
| $Ca(NO_3)_2$(1700ppm) | 2.6 bc | 8.6 a | 15.90 a | 2.9 ab | 8.0 ab | 16.00 a |
| CA1 (50 ppm) | 2.7 b | 8.0 a | 15.50 a | 2.8 ab | 7.8 b | 15.33ab |
| CA2 (100 ppm) | 2.6 bc | 8.3 a | 15.70 a | 2.7 bc | 8.3 a | 16.00 a |
| AsA1 (50 ppm) | 2.8 a | 7.4 a | 15.00 a | 2.9 ab | 7.5 b | 15.40ab |
| AsA2 (100ppm) | 2.7 b | 7.8 a | 15.73 a | 2.8 ab | 8.0 ab | 15.90 a |
| Ca + CA1 | 2.5 c | 8.4 a | 16.00 a | 2.6 bc | 8.4 a | 15.70 a |
| Ca + CA2 | 2.3 d | 8.8 a | 16.00 a | 2.5c | 9.0 a | 16.00 a |
| Ca + AsA1 | 2.6 bc | 7.8 a | 14.90 a | 2.8 ab | 7.6 b | 15.00 b |
| Ca + AsA2 | 2.5 c | 8.3 a | 15.20 a | 2.7 bc | 8.3 a | 15.33ab |

Table (10): Effect of calcium and some antioxidants treatments on chemicals characteristics of Le Conte pear fruits stored For 75 days + 7 days at (20 - 24$^0$C) during 2007 and 2008 seasons.

| Treatments | For 75 days cold stored fruits +7 days at room temperature | | | | | |
|---|---|---|---|---|---|---|
| | Season 2007 | | | Season 2008 | | |
| | TA (%) | Total sugars (g/100gFW) | Fruit calcium content | TA (%) | Total sugars (g/100gFW) | Fruit calcium content |
| Control (water) | 0.30 a | 9.9 g | 0.029 c | 0.30 a | 11.0 f | 0.029 c |
| $Ca(NO_3)_2$(1700ppm) | 0.31 a | 11.7 c | 0.033 b | 0.31 a | 12.1 c | 0.033 b |
| CA1 (50 ppm) | 0.30 a | 10.7 f | 0.028 d | 0.30 a | 11.3 e | 0.028 d |
| CA2 (100 ppm) | 0.30 a | 11.4 d | 0.029 c | 0.30 a | 11.3 e | 0.029 c |
| AsA1 (50 ppm) | 0.30 a | 9.9 g | 0.029 c | 0.30 a | 11.1 f | 0.029 c |
| AsA2 (100ppm) | 0.30 a | 11.0 e | 0.029 c | 0.30 a | 11.3 e | 0.029 c |
| Ca + CA1 | 0.31 a | 11.3 d | 0.033 b | 0.31 a | 12.0 c | 0.033 b |
| Ca + CA2 | 0.31 a | 14.4 a | 0.034 a | 0.31 a | 14.0 a | 0.034 a |
| Ca + AsA1 | 0.30 a | 11.1 e | 0.033 b | 0.30 a | 11.6 d | 0.033 b |
| Ca + AsA2 | 0.30 a | 12.4 b | 0.034 a | 0.30 a | 13.4 b | 0.034 a |

Table (11): Volatile Compounds Identified in Headspace of Le Conte Pear Fruits in Fresh (Zero time) as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination. (*values expressed as relative area percentages to total identified compounds)

| Peak No | KI[a] | Components | Fresh Treated Samples | | | | | | | | | | Methods of identification[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Control (water) | Ca $(No_3)_2$ | $CA_1$ (50ppm) | $CA_2$ (100ppm) | $A_sA_1$ (50ppm) | $A_sA_2$ (100ppm) | Ca + $CA_1$ | Ca + $CA_2$ | Ca + $A_sA_1$ | Ca + $A_sA_2$ | |
| 1 | 614 | Ethanol | – | 0.22 | 0.22 | – | 0.35 | 0.87 | – | – | – | 0.17 | MS, KI, St |
| 2 | 646 | Ethyl acetate | *15.01 | 0.47 | 0.17 | 13.25 | 16.35 | 1.51 | 10.15 | 3.28 | 0.33 | 12.04 | MS, KI, St |
| 3 | 655 | Methyl propanoate | 1.43 | 1.93 | 1.68 | 1.37 | 24.85 | 2.50 | 4.58 | 16.92 | – | 1.07 | MS, KI, St |
| 4 | 695 | 1-Butanol | 0.82 | 0.97 | 12.00 | 42.00 | 14.75 | 4.21 | 3.55 | – | 19.35 | 9.51 | MS, KI, St |
| 5 | 686 | Methyl-2-methyl propanoate | 0.71 | 0.16 | 0.25 | 1.13 | 2.49 | 0.66 | 0.35 | 0.19 | – | 6.07 | MS, KI |
| 6 | 716 | Ethyl propanoate | 0.69 | 0.11 | 0.66 | 1.44 | 0.55 | 2.44 | 0.63 | 0.10 | – | 1.00 | MS, KI |
| 7 | 722 | Methyl butanoate | 0.46 | – | 0.76 | 1.61 | 6.85 | 1.29 | 0.25 | 0.51 | 0.67 | 0.51 | MS, KI |
| 8 | 737 | 1-Penten-3-ol | 1.36 | 1.80 | 1.72 | 0.84 | 6.70 | 9.56 | 1.56 | 0.87 | 1.07 | 0.86 | MS, KI |
| 9 | 744 | Ethyl-2-methyl propanoate | 4.59 | 0.46 | 0.99 | 1.47 | – | 1.50 | 0.19 | – | – | 1.96 | MS, KI |
| 10 | 748 | 1-Pentanol | 1.38 | – | 0.47 | 7.29 | 6.59 | 4.84 | 1.36 | 0.36 | 0.16 | – | MS, KI |
| 11 | 772 | (E)-2-hexenal | 0.67 | 0.70 | 1.52 | 1.56 | 6.13 | 6.76 | 1.08 | 0.84 | 0.56 | 2.07 | MS, KI |
| 12 | 797 | (Z)-3-hexen-1-ol | 1.40 | 0.26 | 0.55 | 0.71 | – | 0.88 | 0.08 | 0.18 | – | – | MS, KI |
| 13 | 826 | Butyl acetate | 0.78 | – | 0.38 | 0.36 | 0.57 | 2.99 | 0.12 | – | 0.11 | 0.27 | MS, KI |
| 14 | 842 | Ethyl butanoate | 33.06 | 51.40 | 42.65 | 1.32 | 0.87 | 19.47 | 38.40 | 40.28 | 41.00 | 32.27 | MS, KI |
| 15 | 851 | Ethyl-2-methyl butanoate | 1.59 | – | 0.97 | 15.48 | 2.19 | 1.93 | – | – | – | 1.55 | MS, KI |
| 16 | 862 | 1-Hexanol | 1.26 | 1.45 | 0.81 | 1.47 | 1.05 | 1.57 | – | 2.16 | – | 2.46 | MS, KI |
| 17 | 873 | 2-methyl-1-buty acetat | 0.43 | 0.2 | 2.32 | 1.33 | 2.89 | 1.76 | 0.16 | 1.31 | 0.68 | 2.11 | MS, KI |
| 18 | 930 | Methyl hexanoate | 0.50 | 0.35 | 0.28 | 0.34 | 0.63 | 2.36 | 0.09 | 0.18 | 0.47 | 0.39 | MS, KI |
| 19 | 955 | (E) -2-heptenal | 0.11 | 0.16 | 0.33 | 0.06 | 0.16 | 1.28 | – | 0.06 | 0.49 | 0.16 | MS, KI |
| 20 | 977 | 1-heptanol | 1.04 | 2.80 | 3.24 | 0.55 | 0.96 | 3.37 | – | 3.16 | 5.83 | 4.01 | MS, KI |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 999 | Ethyl hexanoate | 16.04 | 19.46 | 17.97 | 1.66 | 0.23 | 5.77 | 27.01 | 18.75 | 18.13 | 11.36 | MS, KI |
| 22 | 1011 | Hexyl acetate | 9.15 | 11.93 | 8.58 | 0.13 | – | 3.06 | 9.23 | 9.40 | 8.49 | 4.63 | MS, KI |
| 23 | 1022 | Octanol | 0.81 | 0.20 | 0.17 | 0.22 | 0.23 | 0.34 | 0.12 | 0.08 | 0.17 | 0.16 | MS, KI |
| 24 | 1353 | (E,E) 2,4-Decadienal | 0.83 | 0.30 | 0.08 | 0.45 | 0.77 | 1.40 | 0.16 | 0.08 | 0.03 | 0.17 | MS, KI |
| 25 | 1372 | Methyl E,Z-2,4-decadienoate | 1.50 | 0.09 | 0.34 | 1.38 | 0.13 | 2.42 | 0.08 | 0.14 | 0.40 | 1.31 | MS, KI |
| 26 | 1449 | Ethyl E,Z-2,4-decadienoate | 2.33 | 1.80 | 0.03 | 1.44 | 2.23 | 12.99 | 0.05 | 0.06 | 1.00 | 1.86 | MS, KI |
| 27 | 1500 | α-Farnesene | 2.04 | 2.77 | 0.85 | 1.13 | 1.47 | 2.26 | 0.79 | 1.08 | 1.05 | 2.02 | MS, KI |

– Not detected.

Compounds listed according to their elution on DB5 column.

[a] Kovats index.

compound identified by GC-MS (MS) and / or by kovats index on DB5 (KI) and / or by comparison of MS and KI of standard compound (St) run under similar

GC-MS conditions.

Table (12): Volatile Compounds Identified in Headspace of Le Conte Pear Fruits cold stored for 75 days +7 days at room temperature as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination. (*values expressed as relative area percentages to total identified compounds)

| Peak No | KI[a] | Components | Cold Stored Treated Samples after 75 days + 7 days at room temperature | | | | | | | | | | Methods of identification |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Control (water) | Ca $(No_3)_2$ | $CA_1$ (50ppm) | $CA_2$ (100ppm) | As $A_1$ (50ppm) | As $A_2$ (100ppm) | Ca + $CA_1$ | Ca + $CA_2$ | Ca+As$A_1$ | Ca+As$A_2$ | |
| 1 | 614 | Ethanol | 27.11 | 22.51 | 19.17 | 22.30 | 2.34 | 15.64 | 23.42 | 30.99 | 26.85 | 17.81 | MS, KI, St |
| 2 | 646 | Ethyl acetate | – | – | – | – | 1.37 | – | – | – | – | – | MS, KI, St |
| 3 | 655 | Methyl propanoate | – | – | – | – | 5.51 | – | – | – | 1.40 | 2.24 | MS, KI, St |
| 4 | 695 | 1-Butanol | – | – | 7.23 | – | – | 0.19 | – | – | 0.67 | 16.60 | MS, KI, St |
| 5 | 686 | Methyl-2-methyl propanoate | – | – | – | – | 0.37 | 1.22 | – | – | 1.61 | 3.83 | MS, KI |
| 6 | 716 | Ethyl propanoate | 0.59 | – | – | – | 1.42 | 0.55 | – | – | – | – | MS, KI |
| 7 | 722 | Methyl butanoate | 0.29 | – | – | 15.43 | – | – | – | 10.82 | – | 4.07 | MS, KI |
| 8 | 737 | 1-Penten-3-ol | 10.84 | 5.89 | 6.39 | - | 0.90 | 1.78 | 16.79 | 4.46 | 3.79 | 6.44 | MS, KI |
| 9 | 744 | Ethyl-2-methyl propanoate | 59.52 | 69.71 | 32.86 | 34.25 | 4.84 | 10.73 | 43.12 | 47.04 | 21.72 | 23.69 | MS, KI |
| 10 | 748 | 1-Pentanol | 0.91 | 1.05 | 8.41 | 18.41 | 7.08 | 35.39 | – | – | – | – | MS, KI |
| 11 | 772 | (E)-2-hexenal | – | – | – | – | 0.34 | – | – | – | – | 0.79 | MS, KI |
| 12 | 797 | (Z)-3-hexen-1-ol | – | – | – | – | 0.35 | – | 0.57 | 0.22 | 0.47 | 5.82 | MS, KI |
| 13 | 826 | Butyl acetate | – | – | – | – | – | – | 0.17 | – | 0.75 | 0.45 | MS, KI |
| 14 | 842 | Ethyl butanoate | 0.29 | 0.50 | 1.17 | 1.32 | 1.94 | 0.27 | – | – | 1.70 | 1.22 | MS, KI |
| 15 | 851 | Ethyl-2-methyl butanoate | – | – | – | – | 29.17 | 25.54 | 5.88 | 2.91 | 2.28 | 0.34 | MS, KI |
| 16 | 862 | 1-Hexanol | – | – | – | – | 0.60 | 0.27 | – | – | 0.51 | 1.35 | MS, KI |
| 17 | 873 | 2-methyl-1-buty acetate | – | – | – | – | – | – | – | – | 0.49 | – | MS, KI |
| 18 | 930 | Methyl hexanoate | – | – | – | – | – | – | – | – | – | 0.30 | MS, KI |
| 19 | 955 | (E) -2-heptenal | – | – | – | – | 2.16 | – | – | – | – | – | MS, KI |
| 20 | 977 | 1-heptanol | – | – | – | – | 17.28 | – | 0.58 | 0.20 | – | 0.78 | MS, KI |
| 21 | 999 | Ethyl hexanoate | – | – | 11.12 | – | 18.80 | 6.75 | 6.16 | 2.65 | 33.68 | 5.59 | MS, KI |
| 22 | 1011 | Hexyl acetate | – | 0.33 | – | – | 1.09 | 0.27 | – | – | 2.76 | 3.09 | MS, KI |
| 23 | 1022 | Octanol | 0.44 | – | – | 1.35 | 0.81 | 0.23 | 3.30 | 0.7 | – | 0.59 | MS, KI |
| 24 | 1353 | (E,E) 2,4-Decadienal | – | – | – | 1.42 | 0.79 | 0.11 | – | – | – | 1.97 | MS, KI |
| 25 | 1372 | Methyl E,Z-2,4-decadienoate | – | – | – | 0.88 | 0.96 | 0.8 | – | – | – | 0.41 | MS, KI |
| 26 | 1449 | Ethyl E,Z-2,4-decadienoate | – | – | 6.89 | 1.53 | 2.21 | 0.14 | – | – | 1.31 | 1.64 | MS, KI |
| 27 | 1500 | α-Farnesene | – | – | 6.75 | 4.61 | 0.84 | 0.63 | – | – | – | 0.37 | MS, KI |

– Not detected.
Compounds listed according to their elution on DB5 column.
[a] Kovats index.
[b] compound identified by GC-MS (MS) and / or by kovats index on DB5 (KI) and / or by comparison of MS and KI of standard compound (St) run under similar
GC-MS conditions.s


Fig. 1. The total area percentages of the main chemical classes of volatile components in the headspace of Le Conte fruits fresh (zero time) as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination.

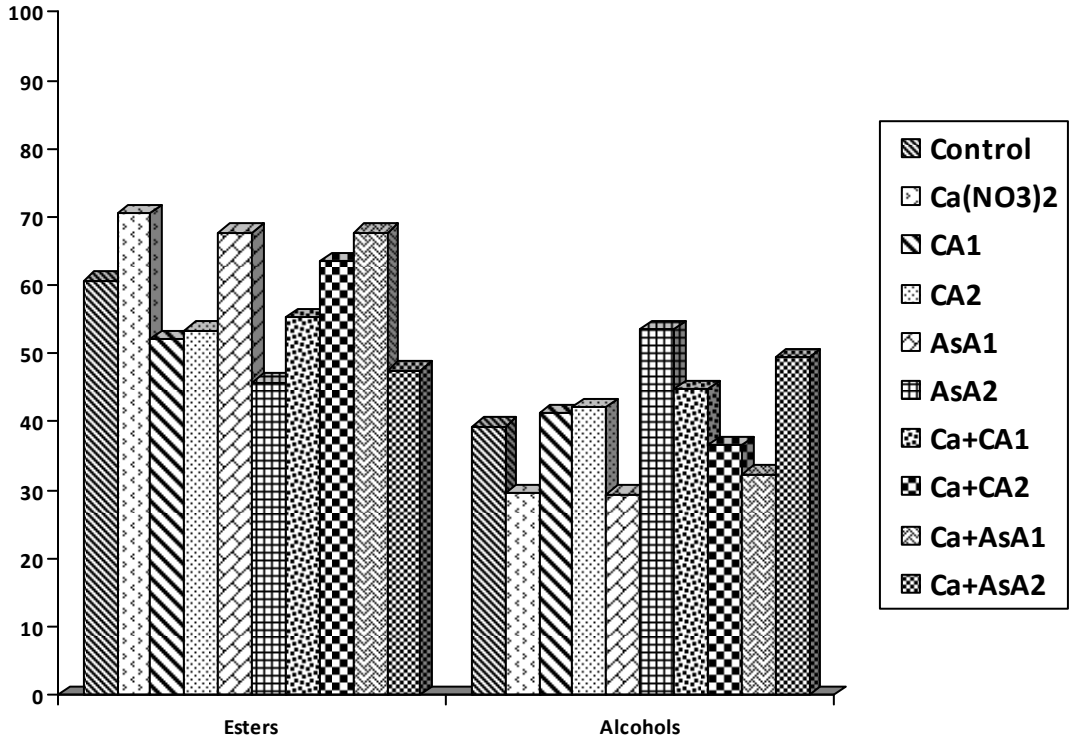


Fig. 2. The total area percentages of the main chemical classes of volatile components in the headspace of Le Conte pear Fruits cold stored for 75 days +7 days at room temperature as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination.

**Total soluble solids percentage (TSS %):**

Total soluble solids percentage were 13.4 to 17.7% and 13.9 to 17.3% developed by nutrition treatments, during 2007 and 2008 respectively comparing with 13.5 to 15.9 % and 13.8 to 15.7 % in the control (Table,4). It is obvious that TSS % was significant increased with all treatment throughout the progress of the storage periods in both seasons. Data presented in Table (4) indicated that all conductive treatments more effective statistically in increasing TSS % at initial or at end of storage, when compared with untreated fruits. These results are true in both studied seasons except the Ca + AsA1treatment in the 1st season after 15 days of storage only. The best results were obtained with Ca + AC2 treatment it recorded the highest significant values of TSS % (16.4 & 16.1 %, consecutively, in both seasons. Followed by Ca + AC1 treatment (15.9 %), CA2 treatment (15.8 %), Ca $(NO_3)_2$ treatment (15.6 %) and Ca + AsA2 treatment (15.5 %) in the 1st season. However, the Ca $(NO_3)_2$ treatment (15.8 %) and the Ca + CA2 treatment (15.6) in the 2nd season. But without any significant differences between them. The other treatments were next. The lowest significant levels of TSS % was detected by the control treatment (15.o & 14.8 %) respectively, in 2007 and 2008 seasons. Also, the AsA1 treatment (14.8 %) in the 2nd season.

These results are in line to those achieved by Nomier, 2000, Montanaro *et al*., 2006 and Lin *et al*., 2008.

**Total Acidity percentage (TA %):**

Data in Table (5) show the effect of calcium nitrate, citric acid and ascorbic acid treatment alone or in combination on the Le Conte pear fruits content of TA %. It can be noticed the same trend and values were recorded from all treatments in both studied seasons. The values of TA % in both seasons varied from 0.13 to 0.31 %, while in the control was varied from 0.2o to o.32 %. The total acidity % of pear fruits showed a slight reduction up to 45 days of cold storage and a gradual statistically decrease as storage period advanced for treated and untreated fruits. The significant reduction in fruits acidity reached maximum with Ca + AsA2 treatment (0.198 %). Followed by Ca + CA1 treatment (0.228 %). The combined treatment at Ca + AsA1 (0.264 %) came next, but with significant among them. On the other hand, the highest statistical value were recorded by CA1 (0.282 %), AsA2 (0.282 %), Ca + CA2 (0.282 %) CA2 (0.280 %) and the control treatment (0.272 %).

The previously results are in agreement with these found by Hafez and Haggag, 2007 mentioned that on Anna apple fruits spraying with calcium decrease the acidity during storage. Also, Mansour *et al.,* 2000 on Tomsson seedless grapevines treated with ascorbic acid reduced the total acidity percentage in berries. Moreover, Lin *et al*., 2008 who found that pear coating with AsA and stored helped maintain titratable acidity compared with control.

**Total Soluble Sugars (g/100g FW):**

The effect spraying of calcium, citric acid and ascorbic acid preharvest application on pear fruit content of total sugars listed in Table (6). Data showed that the nutrition treatments gave the values of total sugars ranged from 8.5 to 12.0 (g/100g FW) and from 8.3 to 12.9 (g/100g FW) during the different storage period in 2007 and 2008 seasons, consecutively as compared with values from 8.0 to 9.6 (g/100g FW) and from 8.0 to 10.1(g/100g FW) in the control treatment. The present results indicated that a continuous steady increased total soluble sugars content of Le Conte fruit during storage at 0 ± 1 º C up to 75 days. This increase took place in all treatments as well as control. Also, this increment was gradually by extension of storage period. At the beginning or the end of storage period, all treatment resulted in higher total sugars than the control for both investigate seasons. The best results had more effective in increasing the total sugars were obtained from the combined treatments of Ca + CA2 (10.72 & 10.8 g/100g FW) respectively, in the two seasons. Also, the Ca + AsA2 and Ca + CA1 treatments (10.7 & 10.5 g/100g FW) consecutively, in the 2nd season. But, without significant differences differ between them. The single treatment of Ca $(NO_3)_2$ (10.4 & 10.12 g/100g FW, respectively in both seasons, as well as Ca + AsA2 (10.52) in 2007 season and Ca + AsA1 (10.2 g/100g FW) in 2008 season come next, with no statistical found them. The signal treatment of antioxidants indicated that the moderately higher sugars contents in both studied seasons. The lowest significant values of fruit total sugars recorded by untreated fruits (8.94 & 8.92 g/100g FW, consecutively) in both seasons.

Effect of application antioxidant agents instead of using auxin for improving yield and fruit quality of various fruit crops is considered important tasks for pomologists. Antioxidants have synergistic action of flowering and productively of fruit trees as well as controlling the incidence of most fungi on fruit trees (Nomeir, 2000 and Mansour, 2000). Furthermore, to prolong storage quality of pears fruit (Lin *et al*., 2007 & 2008).

The great benefits of using antioxidants were observed when it incorporated with macro or micronutrients which were responsible for improving yield and fruit quality of different grapevine (Mansour,

2000). As for the effect of calcium nutrition on increasing the total sugars could be attributed to the balance in the nutrition status of the tree which advanced fruit maturity and ripening. The obtained results are in line with the findings with Hafez & Haggag, 2007 they found that the spraying with $CaCl_2$ treatment increased total sugars of Anna apple fruits at harvest and at end of the storage period.

**Fruit Calcium Content (%):**

Data presented in Table (7) show the effect of calcium, citric acid and ascorbic acid spray alone or in combination on fruit calcium contents during storage periods at 0 ± 1 º C up to 75 days. The rates of fruit calcium content in treated fruits ranged from 0.024 to 0.033% and from 0.025 to 0.033 % in 2007 and 2008 seasons, while in untreated fruit were 0.024 to 0.029 % and from 0.025 to 0.029 %, consecutively. It can be observed that Le Conte pear fruits contents of calcium were significant increased gradually with progress in the period of exposure to cold storage. Moreover, the treated fruits recorded a more concentrate in this respect as compared with control treatment. Also, it can be noticed all combined treatments gave the highest significant values of fruits calcium content. Followed by the single treatment of calcium. The alone treatments of antioxidants came next. These results were true in both investigated seasons.

The previously results are in line with those Tobias *et al*., 1993, found that calcium applied to fruit penetrates primarily through lenticels and increase Ca content of the tissues, mainly in the middle lamella region. Also, Chardonnet *et al*., 2003 mentioned that on "Golden Delicious" apple the effect of calcium infiltration after harvest and throughout storage at 0 ± 1 º C up to 6 months, resulted in an increase in both total and cell wall – bound Ca of the apple tissue during storage, with a maximum reached at 2 % $CaCl_2$ for fruit stored 4 or 6 months. In addition, Richardson and Lombard, 1979 found that fruit calcium sprays increased fruit calcium concentrations by 15 – 30 %, sufficient to decrease the incidence of the disorders.

**Fruit quality assessments after marketing period (MP) as shelf life:**

Effect of calcium and some antioxidant agents treatments alone or in combination on decay percentage & types, physical and chemical characteristics of Le Conte pear fruits after MP during 2007 and 2008 seasons.

On the other side, MP indicator of pear fruit for decay (%) was inspected after 7 days at 20 – 24 º C (Table, 8). The same trend of decay (%) and types of pear fruits were found after MP in all treatments but with slight increase than storage at 0 ± 1 º C in chilling injury symptoms. The pathogenic rots had the opposite trend. The best results were remarkable this respect, the combined treatments of Ca + CA2 and Ca + AsA1 in the 1st season while, Ca + CA2 in the 2nd season.

Concerning physical properties of pear fruits after MP for one week as shown in Table, 9. It can be detected that the lowest significant values of weight loss (%) was recorded with all treatments in stimulate marketing period comparing with control. These results are confirmed in both investigated seasons.

Data in Table (9) also, showed that although all conductive treatments recorded the highest values in fruit firmness after MP, but this increment without significant between them as compared with control in the 2007 season. However, the almost treatments gave higher significant effect in reducing the rate of fruit softening in 2008 season. On the other side, the untreated fruit were soft after MP in 2008 season.

TSS % of pear fruits in MP (Table, 9) revealed that the highest significant values of TSS% were recorded with all treatments when comparing with control in both studied seasons. In general, the alone or combined treatments had great role in increasing TSS% of pear fruits in MP after cold storage. While untreated fruits recorded the lowest rate of TSS% in 2007 and 2008 seasons.

As for the chemical properties of pear fruits after cold storage at 0 ± 1 º C up to 75 days and then 7 days at 20 – 24 º C (MP) as shown in Table (10). Total acidity percentage, no developed significant differences between all treatments in the two seasons.

The sugars content were 9.9 to 14.4g and 11.1 to 14.0g, while in the control treatment were 9.9 and 11.0g, respectively in 2007 and 2008 seasons. The highest significant values were obtained from a combined treatment with Ca + CA 2 (14.4 and 14.0g) consecutively in both studied seasons. Followed by the combined treatment with Ca + AsA2 (12.4 and 13.4g) respectively, in the both seasons. The single treatment with Ca $(NO_3)_2$ come next, it recorded 11.7 and 12.19 respectively, in both seasons, also Ca +CA 1 treatment 12.0g in the 2nd season. Afterwards, the single treatments of antioxidants had high dose then low dose. The CA remarkable on AsA in this respect. On the other hand, the lowest significant value was obtained from untreated fruits 9.9 and 11.0 g, consecutively in both seasons.

Fruit calcium content (%) as show in Table (10) it cleared that all combined treatments and the single treatments of Ca had a great role in increasing the average of fruit calcium content. The highest significant values were recorded from the combined treatments with Ca + CA2 (0.034 %) and Ca + AsA2 (0.034 %). Followed by the single treatment with Ca $(NO_3)_2$ (0.033%) and the combined treatment of Ca +CA1 (0.033 %). The other treatments including control came next (0.29 %). The single treatment of

CA1 had the lowest significant value in fruit calcium content (0.028%). These results are true and steady in both investigated seasons.

The above results are in line with findings found by Hafez and Haggag, 2007 who suggested that spraying Anna apple trees with calcium alone or in combination with boron for improving the fresh quality assessments after cold storage at S0C and after two weeks of marketing period at 20 - 25 $^0$C. Also, Lin *et al*., 2008 found that ability of chitosan coatings with ascorbic acid (AsA) to prolong storage quality of Chinese pear fruits because AsA decreased weight loss, delayed softening, decreased respiration rate and membrane permeability and helped maintaining TSS and titratable acidity compared with controls. Incidence of core browning maintaining quality and reducing core browning and also enhanced fruit AsA contents and antioxidants defense mechanisms (superoxide dismutase, catalase and ascorbate peroxidase activity).

**Volatile components in headspace of fresh (zero time) Le Conte pear fruits as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination:**

Twenty seven volatile compounds were identified by using high resolution gas chromatographic (HRGC) and GC-MS analysis listed with their area percentages in Table (11). The majority of compounds were 15 esters, 8 alcohols, 3 aldehydes and one terpene. The total area percentages of the main chemical classes of volatile components in the headspace of fresh (zero time) control sample and fresh treated pear fruits samples with calcium; citric acid and ascorbic acid at different ratios are shown in Fig. (1). Esters of aliphatic acids were the predominant class of constituents in headspace volatiles of pear in all samples under investigation, it comprised 88.27% in control sample; 88.36% in $Ca(No_3)_2$ sample; 78.03% in citric acid 50ppm (CA1); 43.71% in citric acid 100ppm (CA2); 60.83% in ascorbic acid 50ppm (AsA1); 62-65% in ascorbic acid 100ppm. sample (AsA2); 91.29% in calcium and citric acid 50ppm sample (Ca + CA1); 91.12% in calcium and citric acid 100ppm (Ca + CA2); 71.28% in calcium and ascorbic acid 50ppm sample (Ca + AsA1) and 78.4% in calcium and ascorbic acid 100ppm sample (Ca + AsA2) Fig. (1). As shown from Table (11), the major esters which comprised high concentrations in most samples were ethyl butanoate, ethyl hexanoate, ethyl acetate, hexyl acetate, methyl propanoate; ethyl-2-methyl butanoate and ethyl (E, Z) - 2,4-decadienoate. These results are in accordance with those previously reported by Chen *et al*., 2006 (a, b). The most odour active esters were ethyl butanoate, ethyl hexanoate, hexyl acetate and ethyl-2-methyl butanoate. The odour quality of these compounds is described as an apple, pear and fruit type (Acree and Arn, 2006). Also, we can found that methyl and ethyl (E, Z)-2,4-decadienoate comprised remarkable concentrations in all samples under investigation since ethyl (E, Z)-2,4-decadienoate reached 12.99% in ascorbic acid treated sample 100ppm (AsA2),which responsible for the typical flavour impact of pears (Kahle *et al*.,2005 and Diban *et al*., 2007). Esters are important for the sensory impression because of their type of smell and their low odour thresholds (Pohjanheimo and Sandell 2009).

Alcohols were the second major compounds in headspace volatiles of pear fruits. Their total yield was 8.07% in control sample; 7.7% in Ca(NO3)2 treated sample; 19.18% in CA1 treated sample; 53.08% in CA2 treated sample; 30.63% in AsA1 treated sample; 25.64% in AsA2 treated sample; 26.58% in (Ca + AsA1) and 17.17% in (Ca + AsA2) treated sample Fig (1). These high increases in concentrations of later six samples was attributed to the high increase in major alcohol 1-butanol which comprised 12%, 42.00%, 14.75%, 4.21%, 19.35%, 9.5% in these six treated samples, respectively Table (11), also 1-penten-3-ol comprised a high concentration in AsA1 and AsA2 treated samples since it recorded 6.7% and 9.56% respectively, whereas 1-Pentanol comprised a high concentration in CA2; AsA1 and AsA2 treated samples (7.29%, 6.59% and 4.84% respectively) Table (11). The drop in concentrations of total alcohols in both (Ca + CA1) and (Ca + CA2) to 6.67% and 6.81% the respectively (Fig. 1) is due to the very sharp decrease in concentrations of butanol; 1-Penten-3-ol and 1-Pentanol Table (11). These results are in accordance with Abd El Mageed and Ragheb (2006) who found that butanol was the predominate alcohol and the major compound in headspace volatiles of fresh apple juice (31.31%) and it was considered responsible for the characteristic flavour of fresh apple. 1-Hexanol and (Z)-3-hexen-1-ol comprised considerable concentrations in all samples under investigation Table (11). These two compounds have a typical resinous and green grass aroma, in fresh fruit flavours, they considered as degradation products of lipid (Roberts *et al*., 2004).

(E)-2-hexenal, (E)-2-heptenal and (E, E)-2, 4-decadienal were the three aldehydes identified in headspace volatiles of fresh (control) and in all fresh treated samples Table (1). Their total yield were 1.61% in control sample; 1.16% in Ca $(NO_3)_2$ treated sample; 1.93% in CA1 treated sample; 2.07% in CA2 treated sample; 7.06% in AsA1 treated sample; 9.44% in AsA2 treated sample; 1.24% in (Ca + CA1) treated sample; 0.98% in (Ca + CA2) treated sample; 1.08% in (Ca + AsA1) treated sample and 2.4% in (Ca + AsA2) treated sample Fig (1). The major aldehyde was (E)-2-hexenal

which comprised high concentrations (6.16% and 6.76%) in AsA1 and AsA2 treated samples respectively, (Table 1), It has leaf-like, apple like, green unrip-fruit (concentration dependent) note (Rychlik *et al*., 1998). α- Farnesene was the only sesquiterpene found in headspace volatiles of Le Cont pear with considerable concentration in fresh control and in all fresh treated samples, Table (11). It was the main volatile compound of Japanese pear peel, Shiota *et al.*, 1981.

**Volatile components in headspace of Le Conte pear fruits cold stored for 75 days and 7 days at room temperature (marketing period) as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination:**

The volatile components in headspace of Le Cont pear fruits after marketing period were identified and listed with their area percentages in Table (2).The total area percentages of the main chemical classes of volatile components in the headspace their fruits are shown in Fig. (2).

As shown from Table (12) volatile components varied considerably both quantitatively and qualitatively as effect of storage. Storage of Le Conte pear fruits for 75 days at 0°C + 7 days at 20 – 24 ° C cause a sharp decrease in both number of esters in most samples Table (12) and on their total yield Fig (2), but still esters constitute the predominant ratio of headspace volatiles of stored samples. These results are in accordance with that previously reported by Chen *et al*., 2006 a, b. Although the major esters in all fresh samples were ethyl butanoate, ethyl hexanoate, ethyl acetate and hexyl acetate we found that a very sharp decrease in ethyl butanoate and hexyl acetate and approximately absent for ethyl acetate (Table 12) which meaning a decrease in odour quality (Abd El-Mageed & Ragheb 2005 and Acree & Arn, 2006). Where as at the same time, as shown from (Table 12) we found that ethyl-2-methyl propanoate. Became the major ester in all stored samples also ethyl hexanoate and ethyl-2-methyl butanoate comprised a remarkable increase in most stored samples which compensate the decrease in the above mentioned esters. Takeoka *et al*., 1992 reported that ethyl-2-methyl butanoate, ethyl hexanoate and ethyl-2-methyl propanoate are important contributors to pear aroma. The importance ethyl-2-methyl butanoate is due to its particularly low odour threshold of 0.006 ppb.

Concerning alcohols their total concentration increased in all treated samples including control sample after storage period Fig (2). This increase is due to the high increase in ethanol (which is the major alcohol in most stored samples) and in 1-penten-3-ol in control sample (27.11% and 1.84%) respectively; in $Ca(NO_3)_2$ treated sample; (22.51% and 5.89%) respectively; in (Ca + CA1) treated sample (23.42% and 16.79%) respectively; in (Ca + CA2) treated sample (30.42% and 16.79% respectively; in (Ca + AsA1) treated sample (26.85% and 3.79%) respectively concerning the other samples the increase in total alcohols were due to ethanol, 1-penten-3-ol and 1-pentanol like CA1 treated sample (19.17%, 6.39% and 8.41%) respectively; whereas CA2 sample the increase in alcohols is due to ethanol and 1-pentanol (22.30% and 18.41%); also in AsA2 treated sample (15.64% and 35.39%) respectively. Whereas in (Ca + AsA2) treated sample the increase was due to increase in ethanol, butanol and 1-penten-3-ol (17.81%, 16.6% and 6.44%) respectively Table (12). Aldehydes and α-Farnesene showed remarkable decrease after storage in most samples Table (12). These results are in agreement with previously reported by (Zhang, 1990 and Chen *et al.*, 2006 (a, b)) who found that the volatiles of climacteric fruit accumulated after the respiratory climacteric, but decreased during storage. The major alcohols were ethanol, 1-penten-3-ol, and 1-pentonal. All samples retain good quality during storage period and the best ones storage were AsA1 treated sample and (Ca + AsA1) treated sample and Ca $(No_3)_2$ treated sample which have a highest content of esters which exhipt it more fruity aroma and cause it more acceptable for consumer.

## CONCLUSION

As a conclusion from the results obtained in this work, spraying Le Conte pear trees with the combined treatments of Ca $(NO_3)_2$ + Citric acid at 100 ppm or Ca $(NO_3)_2$ + ascorbic acid at 100 ppm or the single treatment of calcium nitrate are suggested to be a good recommendation for keeping fruit quality under cold storage and in stimulate marketing period as well as the highest content of esters which exhibit it more fruity aroma and cause it more acceptable for consumer.

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