Araştırma Makalesi

www.ziraat.selcuk.edu.tr/ojs
Selçuk Üniversitesi
Selçuk Tarım ve Gıda Bilimleri Dergisi
24 (3): (2010) 87-100
ISSN:1309-0550

EFFECT OF CALCIUM AND SOME ANTIOXIDANTS TREATMENTS ON STORABILITY OF LE CONTE PEAR FRUITS AND ITS VOLATILE COMPONENTS

Omaima, M. HAFEZ[1,4], H. A. HAMOUDA[2], Magda A. Abd- El- MAGEED[3]

[1]Pomology Research Department, National Research Center- Dokki, Giza/Egypt

[2]Fertilizer Technology Department, National Research Center- Dokki, Giza/Egypt

[3]Chemistry of Flavour and Aroma Department, National Research Center- Dokki, Giza/Egypt

(Geliş Tarihi: 22.09.2009, Kabul Tarihi: 27.05.2010)

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 (1700 ppm), citric acid at concentration of (50 and 100 ppm) and ascorbic acid at concentration of (50 and 100 ppm), ten treatments were used including control. All treated and untreated pear fruit were stored at 0 ± 1ºC and 85 – 90% relative humidity (RH) for 75 days and additional one week at room temperature (20-24ºC) as simulated 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. Totally 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 calcium nitrate + citric acid at 50, 100 ppm compared to the control treatments. Although all samples retain in good quality during storage period calcium nitrate, ascorbic acid at 50 ppm, calcium nitrate + citric acid at 50, 100 ppm, and calcium nitrate + ascorbic acid at 50 ppm treated samples were the best compared to the control samples because of in highest content of esters which exhibit it more fruity aroma and cause it more acceptable for consumer.

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

LE CONTE ARMUT MEYVELERİ VE UÇUCU BİLEŞENLERİNİN DEPOLANABİLİRLİĞİ ÜZERİNE KALSİYUM VE BAZI ANTİOKSİDAN MUAMELELERİNİN ETKİSİ

ÖZET

Kalsiyum nitrat veya sitrik asit ve askorbik asit benzeri antioksidanların 2007 ve 2008 sezonlarında hasat öncesi tek başına ve birlikte uygulamalarının soğuk depolama şartları ve market peryodunda Le Conte armut meyvelerinin kalitesini iyileştirme ve çürümeyi kontrol etme olasılığı mevcuttur. Le Conte armut ağaçları 1700 ppm konsantrasyonunda kalsiyum nitrat, 50 ve 100 ppm konsantrasyonunda sitrik asit ve 50 ve 100 ppm konsantrasyonunda askorbik asitle iki kez uygulandı ve kontrol dahil 10 muamele kullanıldı. Bütün muameleli ve muamelesiz armut meyvası 75 gün % 85-90 nispi nemde 0±1 oC'da depolandı ve ayrıca buna ilave olarak 1 hafta markette oda sıcaklığında (20-24 ^{0}C) bekletilmiştir. Ağırlık kaybı ve çürüme oranı, meyve sertliği, toplam çözünür katı madde miktarı (%), toplam asitlik (%), toplam şeker, meyvenin kalsiyum içeriği ve uçucu bileşenleri gibi meyve kalite unsurları değerlendirildi. Uygulamalı ve kontrol meyveleri soğuk depolamanın 45.gününe kadar soğuk zararına ve patojenik çürüklüğe dayanmıştır. Bütün uygulamalar soğuk zararı belirtilerini ve meyve bozulmasını depolamanın 60.gününe kadar önlemiştir. Toplam olarak 27 uçucu bileşenler teşhis edilmiştir: 15 ester, 8 alkol, 3 aldehit ve 1 terpen. Uçucu bileşenler taze ve depolanmış örnekler arasında hem kalitatif hemde kantitatif olarak önemli ölçüde değişmiştir. Taze meyvede kontrolle kıyaslandığında en iyi uygulama dozu olarak 50, 100 ppm de kalsiyum nitrat ± sitrik asit olmuştur. Bütün örnekler depolama peryodu sırasında iyi kalitede olmasına rağmen, kalsiyum nitrat, 50 ppm lik askorbik asit, 50, 100 ppm'lik kalsiyum nitrat ± sitrik asit ve 50 ppm'lik kalsiyum nitrat ± askorbik asit muameleli örnekler kontrol örnekle kıyaslandığında en iyi olanlardır. Çünkü yüksek ester içerikleri daha meyvemsi bir aroma sergilemiştir ve tüketiciler tarafından daha çok beğeni toplamıştır.

Anahtar Kelimeler: *Le Conte Armut, Kalsiyum, Sitrik Asit, Askorbik Asit, Uçucu Bileşenler, Depolama, Kalite Unsurları*

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. One of the most important mineral element determining fruit quality is Calcium. It is associated with many activities in the plant cell e.g. involved in protein phosphorylation via Ca-Cal- modulin binding and plays a major role in senescence and ripening due to its location at cell wall and plasma membrane (Poovaian *et al*., 1988). It is well-Known that, 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

[4]Sorumlu Yazar: omaimahafez@yahoo.com

primary cell wall (Chardonnet *et al*., 2003). Preharvest Ca treatments used to increase Ca content of the cell wall which delaying senescence, resulting in firmer, higher quality fruit (Serrano *et al*., 2004; Kluter *et al*., 2006; Raese and Drake, 2006) with less susceptible to disease during storage (Hafez and Haggag, 2007). Recently 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 loss in weight, delayed softening, decreased respiration rate and improved total soluble solids in pear fruits as well as inhibited the incidence core browning throughout storage. 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; Schmarr and Bernhardt 2010). The purpose of this study was to investigate the ability of calcium nitrate and some antioxidant agents e.g. Citric acid and ascorbic acid as pre harvest treatments separately or in mixture to control decay and their role in improvement the quality of Le Conte pear fruits as well as their volatile components under cold storage condition and during marketing period.

MATERIALS AND METHODS

Pear Orchard

Pear trees cv. Le Conte (*Pyrus communis*, L.) cultivated in a private orchard at El-Tall El-Kepeer, Ismaalia Governorate. Fruit were picked from five years growen in sandy soil, speased 4x4 m, under drip irrigation system, similar in growth and received common horticulture practices and 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, K 18.2, Ca 420, Mg 10.2 and Na 32 mg/100g) and (Fe 3.5 , Mn 4.), Zn 1.6 and Cu 0.4 ppm).

Treatments

Preharvest treatments of calcium nitrate at 1700 ppm, citric acid (CA) at 50(CA1) or 100(CA2) ppm and ascorbic acid (AsA) at 50(AsA1) or 100(AsA2) 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 1st spraying was at the second week of July, while, the 2nd 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 of 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 of fruits was 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 and decay percentage. While the other 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 and decay were assessed.

Quality Assessments

I. Physical Characteristics

Pear fruits were periodically weighted and the losses recorded for each replicate. Date of weight losses were calculated as percentage from the initial weight. Fruit Decay Percentage *was* 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. Pear fruit firmness was determined as Lb/inch^2 by using fruit pressure tester mode (FT 327; 3 – 27 Lbs).

II. Chemical Characteristics

Total Soluble Solids (TSS) was determined in pear fruit juice using a hand refractometer 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/100 g Fresh Weight "F.W") were determined in pear fruits by method described by (Smith *et al*., 1956) using the phenol and sulphuric acid. 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).

III. 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 ± 1ºC 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 % in comparison to control which 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 increased gradually with the progress of storage period up to 75 days in a significant way. The lowest significant values of weight losses percentages were recorded by the combined spray Ca + CA2 (3.4 and 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 recorded (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 and 4.3 %) consecutively in the second season, without significant between them. Our results are in agreement with Serrano *et al.* (2004) on peaches and nectarines, Hafez and Haggag (2007) on apple and Lin *et al.* (2008) on "Yali" pear fruits.

Decay Percentage

Data in Table 2 clearly revealed that all preharvest treatment with calcium nitrate, citric acid and ascorbic acid either alone or as mixtures reduced decay percent and Le Conte fruits deterioration up to 75 days of cold storage at 0 ± 1ºC 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 for 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 ± 1ºC. However, the preharvest treatments alone or as mixtures prevented CI symptoms up to 60 days except for treatment with 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 treatment of calcium nitrate alone and mixture of Ca + CA2 in the 1st season, they recorded 100% total healthy. Meanwhile, in the 2nd season the remaining other treatments recorded 100% total healthy fruits after 60 days of cold storage. The treatment using Ca was superior on this respect, it recorded the lowest significant CI symptoms 4.8% at 75 days, followed by Ca + CA2 gave 9.53%. The results are in harmony with those obtained by Richardson and Lombard (1979), Guy *et al.* (2003), Hafez and Haggag (2007) and Lin *et al.* (2007, 2008).

Fruit Firmness (Lb/inch^2)

Fruit firmness affected by nutrition treatments during 2007 and 2008 seasons are listed in Table 3. Results 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. Fruit firmness was decreased as storage period increased. Also, it can be noticed that all tested treatments had the highest effects on firmness comparing with control, but without significant differences between them in the 1st season. However, during 2nd season highest significant values were obtained by all treatments. Treatment using Ca + CA2 and Ca alone were significantly increased the fruit firmness (12.2 and 11.62 Lb/inch^2) consecutively. Meanwhile, the other treatment with antioxidants alone or mixtures including calcium gave the same effect in reducing the rate of fruit softening without significant differences between them. On the other hand, the untreated fruits were the lowest significant rate of fruit firmness in 2008 season. These results are in agreement with the findings by Siddiqui and Bangerth (1995) on Golden Delicious apple, Benavides *et al*. (2002) on Golden Smoothee apple, Casero *et al*. (2004) on Golden Smoothee apple, Saure (2005) on fleshes fruit, Lin *et al*. (2007) on Yali pears and Montanaro *et al*. (2006) on "Kiwifruit.

Total Soluble Solids Percentage (TSS %)

Total soluble solids percentage was 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 increase significantly 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 for the Ca + AsA1 treatment in the 1st season after 15 days of storage only. The best results were obtained with Ca + AC2 treatment which 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 recorded (15.8 %) and the Ca + CA2 treatment (15.6 %) in the 2nd season. The lowest significant levels of TSS % were detected by the control treatment (15.o & 14.8 %) respectively, in 2007 and 2008 seasons. These results are in line to those achieved by Nomier (2000), Montanaro *et al*. (2006) and Lin *et al*. (2008).

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	

Total Acidity Percentage (TA %)

Data in Table 5 showed the effect of calcium nitrate, citric acid and ascorbic acid treatment alone or as mixtures on the Le Conte pear fruits content of TA %. It can be noticed that, 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 0.20 to 0.32 %. 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 %). Treatment with Ca + AsA1 (0.264 %) came next. On the other hand, the highest statistical values 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 Mansour *et al.* (2000) on Tomsson Seedless grapevines, Hafez and Haggag (2007) on Anna apple fruits and Lin *et al*. (2008) on pear.

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	5.3 a		96.7 a	78.4 b	

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

Total Soluble Sugars (g/100g FW)

The spraying effect of calcium, citric acid and ascorbic acid as a preharvest application on the total sugars content of pear fruit 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) in 2007 season and from 8.3 to 12.9 (g/100g FW) in 2008 season during the different storage period, comparing 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 in both seasons. The present results indicated a continuous steady increased in the total soluble sugars content of Le Conte fruit during storage at 0 ± 1ºC up to 75 days. This increase took place in all treatments as well as control, and fond increment by extension 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 treatments using Ca + CA2 which recorded (10.72 & 10.8 g/100g FW) respectively, in the two seasons. Treatment with Ca $(NO_3)_2$ recorded (10.4 and 10.12 g/100g FW, respectively in seasons, as well as Ca + AsA2 (10.52) in 2007 season and Ca + AsA1 (10.2 g/100g FW) in 2008 season came next. The single treatment using 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.

Fruit Calcium Content (%)

Data presented in Table 7. show the effect of calcium, citric acid and ascorbic acid spray alone or as mixtures on fruit calcium content during storage periods at 0 ± 1ºC up to 75 days. 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 during cold storage. Moreover, the treated fruits recorded a more concentrate in this respect as compared with control treatment. Also, it can be noticed that all treatment with mixters 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 Richardson and Lombard (1979), Tobias *et al*. (1993) and Chardonnet *et al*. (2003).

Fruit Quality Assessments After Marketing Period (MP) as Shelf Life

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

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	

Physical properties of pear fruits after MP for one week are 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 differences 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. Total Soluble Solids (%) 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.

Chemical properties of pear fruits after cold storage at 0 ± 1ºC up to 75 days and then 7 days at 20 – 24 º C (MP) as shown in Table 10. Concerning total acidity percentage, no developed significant differences between all treatments in the two seasons were observed. The sugars content Table 10. was 9.9 to 14.4 g and 11.1 to 14.0 g, while in the control treatment was 9.9 and 11.0 g, respectively in 2007 and 2008 seasons. The highest significant values were obtained through treatment with Ca + CA 2 (14.4 and 14.0 g) consecutively in both studied seasons. Followed by Ca + AsA2 (12.4 and 13.4 g), Ca $(NO_3)_2$ (11.7 and 12.19 g) respectively, in both seasons, however Ca +CA 1 recorded 12.0 g in the 2nd season. 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 (%) is shown in Table 10. it cleared that all treatments had a great role in increasing the average of fruit calcium content. The highest significant values were recorded from treatments with Ca + CA2 (0.034 %) and Ca + AsA2 (0.034 %), followed by Ca $(NO_3)_2$ (0.033%) and Ca +CA1 (0.033 %). Treatment with CA1 had the lowest significant value in fruit calcium content (0.028%). The above results are in line with findings found by Hafez and Haggag (2007) and Lin *et al.* (2008).

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	14.5 d	15.0 c	15.3 c	15.7 bc	16.3 a	

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 Figure1. 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 50 ppm (CA1); 43.71% in citric acid 100 ppm (CA2); 60.83% in ascorbic acid 50 ppm (AsA1); 62.65% in ascorbic acid 100 ppm. sample (AsA2); 91.29% in calcium and citric acid 50 ppm sample (Ca + CA1); 91.12% in calcium and citric acid 100 ppm (Ca + CA2); 71.28% in calcium and ascorbic acid 50 ppm sample (Ca + AsA1) and 78.4% in calcium and ascorbic acid 100 ppm sample (Ca + AsA2) in 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.* (2006a, 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 100 ppm (AsA2), these esters are 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).

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	

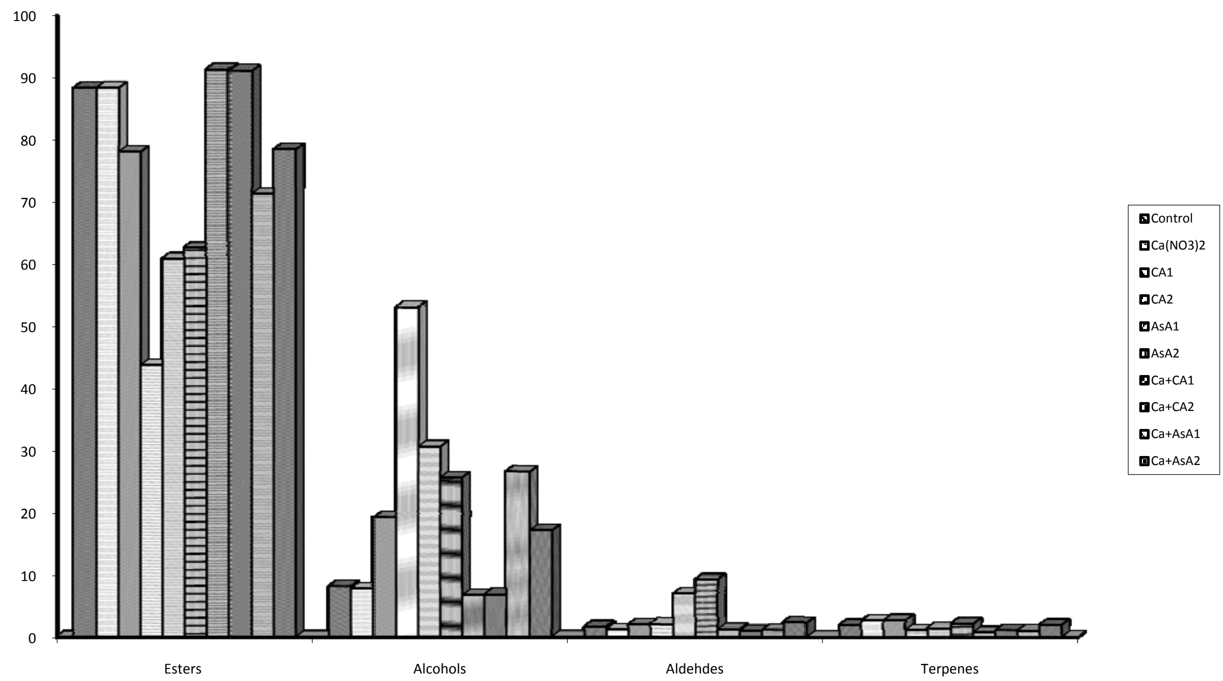

Figure1. The total area percentages of the main chemical classes of volatile components in the headspace of Le Conte fruits fresh (zero time) as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination.

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	

Alcohols were the second major compounds in headspace volatiles of pear fruits. Their total yield was 8.07% in control sample; 7.7% in $Ca(NO_3)_2$ 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 Figure 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% and 9.5% in these six treated samples, respectively in 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 Figure 1. is due to the very sharp decrease in concentrations of butanol; 1-Penten-3-ol and 1-Pentanol inTable 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 inTable 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).

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

(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 11. 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 in Figure 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 11. 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).

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

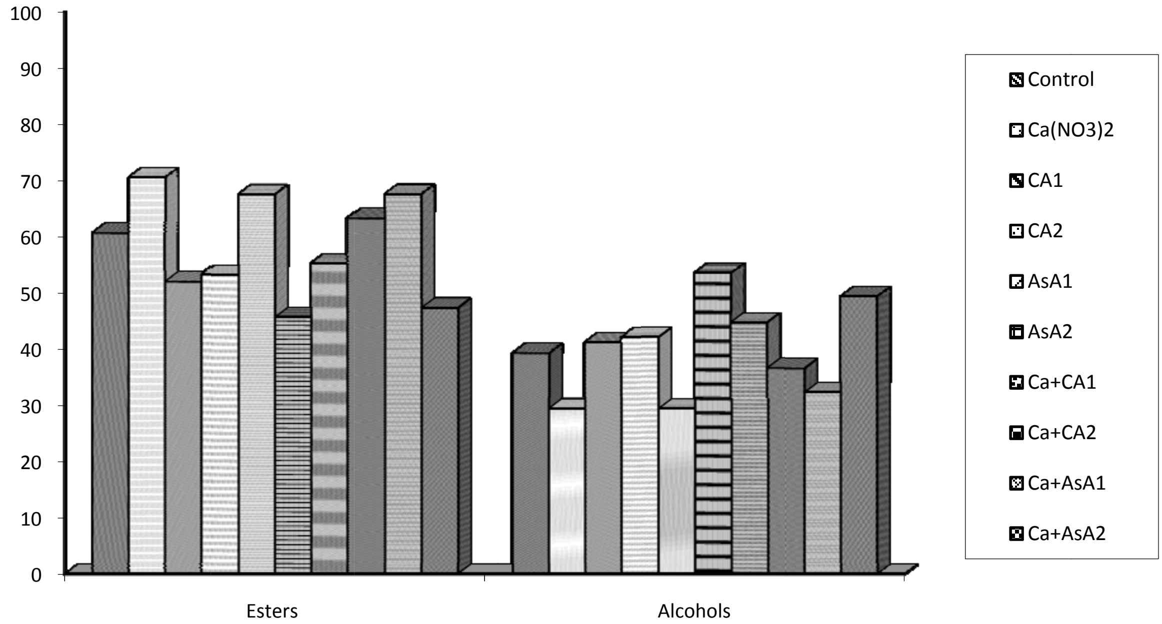

Figure2. The total area percentages of the main chemical classes of volatile components in the headspace of Le Conte pear Fruits cold stored for 75 days +7 days at room temperature as affected by pre harvest treatments with calcium, citric acid and ascorbic acid alone or in combination.

Volatile Components in Headspace of Le Conte Pear Fruits Cold Sored for 75 Days And 7 Days at Room Temperature (Marketing Period) as Affected by Pre Harvest Treatments with Calcium, Ctric Acid and Ascorbic Acid Aone 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 12. The total area percentages of the main chemical classes of volatile components in the headspace their fruits are shown in Figure 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 º C cause a sharp decrease in both number of esters in most samples Table 12. and on their total yield Figure 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.* (2006a, 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 and Ragheb (2005); Acree and Arn (2006). Where as at the same time, as shown from Table 12 we found that ethyl-2-methyl propionate becomes 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 of 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 Figure 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); Chen *et al.* (2006 a, b) who found that the volatiles of climacteric fruit accumulated after the respiratory climacteric, but decreased during storage. All samples retain in good quality during storage period and the best ones storage were treated samples with AsA1, (Ca + AsA1), (Ca + CA2) 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 50 or 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.

REFERENCES

Abd El-Mageed, M.A. and Ragheb, E.E., 2006. Effect of pasteurization and storage on flavour of apple and kiwi fruit blends juice. Arab Universities J. of Agric. Sci. 14(2): 643-660.

Acree, T., and Arn, H. 2006. Flavourent and human odour space. Retrieved 15.12.06. <http://flavornet.org/flavornet.html>.

Adams. R.P., 2001. Identification of essential oil components by gas chromatography/quadru pole spectroscopy. Carol Stream IL, USA: Allured.

Association of Official Analytical Chemists, 1995. Official Methods of Analysis 15th Ed. Published by A.O.A.C. Washington, D.C., pp. 440 -510, USA.

Benavides, A., Recasens, I., Casero, T., Soria, Y. and Puy, J., 2002. Multivariate analysis of quality and mineral parameters on Golden Smoothee apples treated before harvest with calcium and stored in controlled atmosphere**.** Food Science and Technology International.Vol. 8: 139 - 145.

Casero, T., Benavide, A., Puy, J. and Recasens, I., 2004. Relationships between leaf and fruit nutrients an fruit quality attributes in Golden Smotthee apples using multivariate regression techniques. J. of Plant Nutrit.Vol. 27: 313 – 324.

Chardonnet, C.O., Charron, C.S., Sams C. E. and Canway, W.S., 2003. Chemical changes in the cortical tissue and cell walls of calcium – infiltrated “Golden Delicious” apples during storage. Postharvest Biology and Technology.Vol. 28: 97 - 111.

Chen, J.L., Wu, J.H., Wang, Q., Deng, H. and Hu, X.S., 2006 b**.** changes in the volatile compounds and chemical and physical properties of Kuerle Fragrant Pear (Pyrus Serotina Reld) during storage. J. of Agric. Food Chem. 54 (23): 8842 - 8847.

Chen, J.L., Yan, S., Feng, Z., Xiao, L.and Hu, X.S. , 2006 a. Changes in the volatile compounds and chemical and physical properties of Yali pear (*Pyrus bertschneideri* Reld) during storage**.** Food Chemistry. Vol. 97:248-255.

Diban, N., Ruiz, G., Urtiaga A. and Ortiz, I., 2007. Granular activated carbon for the recovery of the main pear aroma compound: viability and kinetic modeling of ethy l- 2, 4-decadienoate adsorption. J. of food Engineering. Vol. 78:1259 - 1266.

Duncan, D.B., 1955. Multiple ranges and multiple F-Test. Biometrics. Vol. 11: 1- 42.

Fadel, H.H.M, Abd El Mageed, M.A., Abdel Kader, M.E., Abdel Samad, M.E. and Lotfy, S.N., 2006. Cocoa substitute: Evaluation of sensor qualities and flavour stability. European Food of Res. Technol.Vol.223:125-131.

Guy, C.; Maffia, L.A., Finger F.L., and Batisla, U.G., 2003. Pre harvest calcium sulfate application effect vase life and severity of gray mould in cut roses. Scientia Horticulturae. Vol. 103: 329-338.

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					
			Control (water)	Ca (No3)$_2$	CA$_1$ (50ppm)	CA$_2$ (100ppm)	A_5A_1 (50ppm)	A_5A_2 (100ppm)
1	614	Ethanol	–	0.22	0.22	–	0.35	0.87
2	646	Ethyl acetate	*15.01	0.47	0.17	13.25	16.35	1.51
3	655	Methyl propanoate	1.43	1.93	1.68	1.37	24.85	2.50
4	695	1-Butanol	0.82	0.97	12.00	42.00	14.75	4.21
5	686	Methyl-2-methyl propanoate	0.71	0.16	0.25	1.13	2.49	0.66
6	716	Ethyl propanoate	0.69	0.11	0.66	1.44	0.55	2.44
7	722	Methyl butanoate	0.46	–	0.76	1.61	6.85	1.29
8	737	1-Penten-3-ol	1.36	1.80	1.72	0.84	6.70	9.56
9	744	Ethyl-2-methyl propanoate	4.59	0.46	0.99	1.47	–	1.50
10	748	1-Pentanol	1.38	–	0.47	7.29	6.59	4.84
11	772	(E)-2-hexenal	0.67	0.70	1.52	1.56	6.13	6.76
12	797	(Z)-3-hexen-1-ol	1.40	0.26	0.55	0.71	–	0.88
13	826	Butyl acetate	0.78	–	0.38	0.36	0.57	2.99
14	842	Ethyl butanoate	33.06	51.40	42.65	1.32	0.87	19.47
15	851	Ethyl-2-methyl butanoate	1.59	–	0.97	15.48	2.19	1.93
16	862	1-Hexanol	1.26	1.45	0.81	1.47	1.05	1.57
17	873	2-methyl-1-buty acetate	0.43	0.2	2.32	1.33	2.89	1.76
18	930	Methyl hexanoate	0.50	0.35	0.28	0.34	0.63	2.36
19	955	(E) -2-heptenal	0.11	0.16	0.33	0.06	0.16	1.28
20	977	1-heptanol	1.04	2.80	3.24	0.55	0.96	3.37
21	999	Ethyl hexanoate	16.04	19.46	17.97	1.66	0.23	5.77
22	1011	Hexyl acetate	9.15	11.93	8.58	0.13	–	3.06
23	1022	Octanol	0.81	0.20	0.17	0.22	0.23	0.34
24	1353	(E,E) 2,4-Decadienal	0.83	0.30	0.08	0.45	0.77	1.40
25	1372	Methyl E,Z-2,4-decadienoate	1.50	0.09	0.34	1.38	0.13	2.42
26	1449	Ethyl E,Z-2,4-decadienoate	2.33	1.80	0.03	1.44	2.23	12.99
27	1500	α-Farnesene	2.04	2.77	0.85	1.13	1.47	2.26

Peak No	KI[a]	Components	Fresh Treated Samples				
			Ca + CA$_1$	Ca + CA$_2$	Ca + A_5A_1	Ca + A_5A_2	Methods of identification[b]
1	614	Ethanol	–	–	–	0.17	MS, KI, St
2	646	Ethyl acetate	10.15	3.28	0.33	12.04	MS, KI, St
3	655	Methyl propanoate	4.58	16.92	–	1.07	MS, KI, St
4	695	1-Butanol	3.55	–	19.35	9.51	MS, KI, St
5	686	Methyl-2-methyl propanoate	0.35	0.19	–	6.07	MS, KI
6	716	Ethyl propanoate	0.63	0.10	–	1.00	MS, KI
7	722	Methyl butanoate	0.25	0.51	0.67	0.51	MS, KI
8	737	1-Penten-3-ol	1.56	0.87	1.07	0.86	MS, KI
9	744	Ethyl-2-methyl propanoate	0.19	–	–	1.96	MS, KI
10	748	1-Pentanol	1.36	0.36	0.16	–	MS, KI
11	772	(E)-2-hexenal	1.08	0.84	0.56	2.07	MS, KI
12	797	(Z)-3-hexen-1-ol	0.08	0.18	–	–	MS, KI
13	826	Butyl acetate	0.12	–	0.11	0.27	MS, KI
14	842	Ethyl butanoate	38.40	40.28	41.00	32.27	MS, KI
15	851	Ethyl-2-methyl butanoate	–	–	–	1.55	MS, KI
16	862	1-Hexanol	–	2.16	–	2.46	MS, KI
17	873	2-methyl-1-buty acetate	0.16	1.31	0.68	2.11	MS, KI
18	930	Methyl hexanoate	0.09	0.18	0.47	0.39	MS, KI
19	955	(E) -2-heptenal	–	0.06	0.49	0.16	MS, KI
20	977	1-heptanol	–	3.16	5.83	4.01	MS, KI
21	999	Ethyl hexanoate	27.01	18.75	18.13	11.36	MS, KI
22	1011	Hexyl acetate	9.23	9.40	8.49	4.63	MS, KI
23	1022	Octanol	0.12	0.08	0.17	0.16	MS, KI
24	1353	(E,E) 2,4-Decadienal	0.16	0.08	0.03	0.17	MS, KI
25	1372	Methyl E,Z-2,4-decadienoate	0.08	0.14	0.40	1.31	MS, KI
26	1449	Ethyl E,Z-2,4-decadienoate	0.05	0.06	1.00	1.86	MS, KI
27	1500	α-Farnesene	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.

Hafez- Omaima, M. and Haggag, K.H.E., 2007. Quality improvement and storability of apple cv. Anna by pre-harvest Applications of Boric acid and Calcium Chloride. J. Ag. Bio. Sci. 2: 176-183.

Harborne, J.B. and Williams, C.A., 2000. Advances in flavonoid research since 1992. Phytochemistry. Vol. 55:481- 504.

Kahle, K., Preston, C., Richling, E., Heckel, F. and Schreier, P., 2005. On-line gas chromatography combustion / pyrolysis isotope ratio mass spectrometry (HRGC-C/P-IRMS) of major volatiles from pear fruit (Pyrus communis) and pear products. Food chemistry. Vol. 91: 449 - 455.

Kluter R.A., Nattress, D.T., Dunne, C.P. and Popper, R.D., 2006. Shelf Life Evaluation of Bartlett Pears in Retort Pouches. J. Food Sci. Vol. 6: 1297 – 1302.

Lin, L., Li, Q.P., Wang, B.G., Cao, J.K. and Jiang, W.B., 2007. Inhibition of core browning in "Yali" pear fruit by post harvest treatment with ascorbic acid. J. of Hort. Sci. Biotech. 82 (3): 397 - 402.

Lin, L., Wang, B.G., Wang, M., Cao, J., Zhang, J., Wu Y. and Jiang, W., 2008. Effect of achitosau-based coating with ascorbic acid on post harvest quality and core browning of "Yali' pears (*Pyrus bretschneideri* Rehd) .J. of Sci. Food Agric. 88 (5): 877 - 884.

Mansour, A.E., Ahmed, F.F, Ali A.H. and Ali, Mervet, A., 2000. The synergistic influence of using some micronutrients with ascorbic acid on yield and quality of Bunaty grapevines. The 2nd Scientific conference of Agric. Sci. Oct. 309 – 316, Assiut.

Montanaro, G., Dichio, B., Xiloyannis C. and Celano, G., 2006. Light influences transpiration and calcium accumulation in fruit of kiwifruit plants (*Actinidia deliciosa* var. deiciosa). Plants Science Vol. 170: 520 - 527.

Nomier- Safaa, A., 2000. Effect of some GA3, vitamins and active dry yeast treatments on vegetative growth, yield and fruit quality of Thompson Seedless grapevines. Zagazig J. of Agric. Res. 27(5): 1267 – 1286.

Pohjanheimo, T.A. and Sandell, M. A., 2009. Headspace volatiles contributing to flavour and consumer liking of wellness beverages. Food Chemistry Article.

Poovaian, B.W., Glenn G.H. and Reddy, A.S.N., 1988. Calcium and fruit softening: Physiology and biochemistry. Hort. Rev.Vol. 10: 107 -152.

Raese J. T. and Drake, S. R., 2006. Calcium Foliar Sprays for Control of Alfalfa Greening, Cork Spot, and Hard End in Anjou' Pears. J.of Plant Nutrition 29 (3): 543 - 552

Richardson, D.G. and Lombard, P.B., 1979. Cark spot of Anjou pear: Control by calcium sprays. Soil Sci. & Plant Analysis.Vol. 10: 383 – 389.

Roberts, J.S., Gentry, T.S. and Bates, A.W., 2004. Utilization of Dried Apple Pomace as a press Aid to Improve the Quality of Strawberry, Raspberry, and Blueberry Juices. J. of Food Sci. 69 (4): 5181-5190.

Rychlik, M., Schieberel, P.and Grosch, W., 1998. Compliation of odour thresholds, odour qualities and retention indices of key food odorants. Deutsche Forschunganstalt fur Lebensmittelchemie and institut fur Lebensmittelchemie der Technischen Univ. Munchen, D-85748 Garching, Germany.

Saure, M.C., 2005. Calcium translocation to fleshy fruit: Its mechanism and endogenous control. Scientia Horticulture Vol. 105: 65 – 89.

Schmar, H.-G. and Bernhardt, J., 2010. Profiling analysis of volatile compounds from fruits using comprehensive two- dimensional gas chromatography and image processing techniques. J. of Chromatography A. Vol. 1217: 565-574.

Serrano, M., Martinez- Romero, D., Castillo, S., Guillen F. and Valero, D., 2004. Effect of preharvest sprays containing calcium, magnesium and titanium on the quality of peaches and nectarines at harvest and during postharvest storage. The Sci. of Food and Agiculture. 84 (11):1270 –1276.

Shiota, H., Minami, T. and Sara, T., 1981. Aroma Constituents of Japanese pear fruit. Kajuu Yoke Ho. Vol. 279: 36 – 40.

Siddiqui, S. and Bangerth, F., 1995. Effect of pre harvest application of calcium on flesh firmness and cell-wall composition of apples. Influence of fruit size. J. of Hort. Sci.Vol. 70: 263 – 269.

Smith, F.A., Gilles, M., Haniltun K.J. and Gedees, A.P., 1956. Colorimetric methods for determination of sugars and related substances. Analysis Chem. Vol. 28: 350.

Takeoka, G. R., Buttery, R.G. and Flath, R. A., 1992. Volatile Constituents of Asian Pear (*Pyrus Serotina*) J. of Agric Food Chem. Vol. 40: 1925 - 1929.

Tobias, R.B., Conway, W.S., Sams, C.E., Gross K.C. and Whitaker B.D.,, 1993. Cell wall composition of calcium reated apple inoculated with *Botrytis cinerea*. Phytochemistry. Vol. 32: 35 – 39.

Wang C.Y. and Mellenthin, W.M. , 1974. Inhibition of friction discoloration on d'Anjou pears by 2-mercaptobenzothiazole. HortScience. 9 (3): 196.

Zhang, W. Y., 1990. The Biological and Physiology of Fruit. Agricultural Publishing Company. China

[4]Sorumlu Yazar: omaimahafez@yahoo.com