horticulturae

MDPI

Article

Effect of Combination of $KMnO_4$ Oxidation and UV-C Radiation on Postharvest Quality of Refrigerated Pears cv. 'Ercolini'

Ramiro Alonso-Salinas [1], José Ramón Acosta-Motos [2,3,*], Antonio J. Pérez-López [1], Luis Noguera-Artiaga [4], Estrella Núñez-Delicado [2], Francisco Burló [4] and Santiago López-Miranda [1]

[1] Department of Food Technology and Nutrition, UCAM Universidad Católica de Murcia, Avenida de los Jerónimos 135, Guadalupe, 30107 Murcia, Spain
[2] Chair of Entrepreneurship in the Agri-Food Sector UCAM-Santander, UCAM Universidad Católica de Murcia, Avenida de los Jerónimos 135, Guadalupe, 30107 Murcia, Spain
[3] Group of Fruit Tree Biotechnology, Department of Plant Breeding, CEBAS-CSIC, Campus Universitario de Espinardo, 30100 Murcia, Spain
[4] Research Group "Food Quality and Safety", Centro de Investigación e Innovación Agroalimentaria y Agroambiental, Miguel Hernández University of Elche, Carretera de Beniel km 3.2, 03312 Orihuela, Spain
* Correspondence: jracosta@ucam.edu; Tel.: +34-968-278756

Abstract: This present study proposes an improvement for the postharvest preservation of the 'Ercolini' pear, a fruit that is little tested in the field, using a combination of ethylene elimination methods. The techniques used were potassium permanganate filters in devices with ultraviolet radiation and constant air flow to favour the contact of ethylene with the oxidising agents. The analysis carried out included weight, diameter, firmness, soluble solids content, total acidity, maturity index, ascorbic acid concentration, total phenolic compounds, antioxidant capacity via the ORAC method and a descriptive sensory analysis using experts. In addition, the ethylene removal method was tested at two storage temperatures: 1 °C, near optimal temperature, and 8 °C, the standard temperature for transport and storage of fruit on a commercial scale. The results showed a marked improvement in the maintenance of postharvest physicochemical quality using the proposed combination of methods. The sensory analysis confirmed what was observed in the laboratory, with higher organoleptic quality values observed in pears treated with the complete system under study consisting of filter and machine, highlighting the greater presence of flavours and odours related to green fruit. Ultimately, this innovation could be highly relevant for the food industry.

Keywords: climacteric fruit; fruit storage; potassium permanganate; *Pyrus communis*; UV-C

Citation: Alonso-Salinas, R.; Acosta-Motos, J.R.; Pérez-López, A.J.; Noguera-Artiaga, L.; Núñez-Delicado, E.; Burló, F.; López-Miranda, S. Effect of Combination of $KMnO_4$ Oxidation and UV-C Radiation on Postharvest Quality of Refrigerated Pears cv. 'Ercolini'. *Horticulturae* **2022**, *8*, 1078. https://doi.org/10.3390/horticulturae8111078

Academic Editor: Hongliang Zhu

Received: 14 October 2022
Accepted: 12 November 2022
Published: 16 November 2022

1. Introduction

The presence of ethylene in preservation atmospheres has been shown to be detrimental to the quality and shelf life of fruit and vegetables. In the case of climacteric fruits, ethylene accelerates the ripening processes, a highly undesirable aspect for their optimal commercialisation, leading to waste in a world that is becoming increasingly populated and more demanding of high-quality food. Fruit ripening is a complex process that promotes both physical and physiological changes, leading to a progressive deterioration of the products. Postharvest ripening cannot be stopped but it can be slowed down [1–3].

According to the report on the "DOP Pera Ercolina de Jumilla" carried out by Jesús García Brunton in 2011, pears of the variety 'Ercolini' belong to the group of climacteric fruits. This variety is characterised for having a medium size, as compared to other varieties such as 'Bosc Kobak' [4,5], with white and juicy flesh. Its skin is green and turns yellow when it ripens, a process that takes place very quickly. For this reason, it is essential to store them correctly in atmospheres without ethylene. Its maximum storage time is 3 weeks. The annual production of the 'Ercolini' pear in the Region of Murcia is approximately

22,000 tonnes, 48% of the Spanish national production, and 24% of the European production of this variety, and is, therefore, a crop of national importance [5].

It is known that the exposure to ethylene produces undesirable effects on fruit. In stone fruits such as apricot or peach, other authors have shown that their conservation without ethylene elimination leads to loss of weight, firmness, total acidity (TA), organoleptic qualities, and an increase in soluble solid content (SSC) [6]. In tomato, Mansourbahmani and collaborators showed a similar effect when comparing the application of various ethylene removal methods; these authors concluded that ethylene removal treatments could be a useful tool for reducing spoilage and maintaining fruit quality [7]. In pears, Charoenchongsuk et al., showed a relationship between colour loss, chlorophyll degradation, and softening of Russet pear, due to high ethylene exposure [8]. This effect may be related to the production of reactive oxygen species (ROS) in the degradation processes associated with ripening. Therefore, it would be interesting to study the evolution of the antioxidant activity in this product.

According to Alonso-Salinas [9,10], Kim [11], and Wei [12], ethylene removal by potassium permanganate ($KMnO_4$) oxidation is the most interesting method in terms of cost-effectiveness. This oxidising agent is anchored in active adsorbent materials such as zeolites, activated carbon, carbon nanospheres, and silica gel, to keep $KMnO_4$ and ethylene in contact [13]. These metal-coated porous materials are often used as fillers or active ingredients to be added to packaging films or paper, or as carriers where other ethylene scavengers can be incorporated [14].

Photocatalysis is also a suitable technique for ethylene removal [11,15,16]. UV light has been extensively studied as part of an ethylene degradation system, which is mainly attributed to its photochemical reactivity. Ethylene photo-degradation starts with the radiation of UV-C light, which generates oxidizing agents [11,17]. Although it is true that the efficiency of this ethylene removal method is not the best [18–20], it is sufficiently versatile to be incorporated as a support to other methods, to improve their overall effectiveness.

However, the above options to remove ethylene and avoid its action on fruits are not the only methods used. For example, the most widely studied in recent years is the treatment with 1-methylcyclopropene (1-MCP), a chemically synthesised molecule formed by a small hydrocarbon very similar to ethylene that competes with this gas for its receptor binding points (Ad-ERS1a, Ad-ETR2 and Ad-ETR3) inhibiting the expression of several transcription factors associated with ethylene (Ad-ERF4, Ad-ERF6, Ad-ERF10 and Ad-ERF14). This largely prevents the ripening of climacteric fruits by avoiding the action of ethylene even if it is still in the preservation atmosphere [12,21]. Nevertheless, not a few authors have doubts about its effectiveness compared to other methods such as $KMnO_4$ or palladium [7,10,12,22]. Another method of ethylene removal briefly studied is the application of palladium as an ethylene oxidising agent, acting in a similar way to $KMnO_4$. Nevertheless, although Smith et al. [23] indicate that it is more efficient than $KMnO_4$, its industrial application is complicated, since the cost of this metal is very high in the current market.

The aim of this study was to determine the effect of a novel combined ethylene removal method ($KMnO_4$ and UV-C radiation) on the postharvest quality and sensory analysis of pear cv 'Ercolini' preserved at two refrigeration treatments (1 °C and 8 °C).

2. Materials and Methods

2.1. Plant Material

Forty kilograms of 'Ercolini' pears (*Pyrus communis* L.) were supplied by "Cooperativa Hortofrutícola Campos de Jumilla" (Jumilla, Murcia, Spain). This variety has D.O.P. certification in Jumilla. The pears were harvested in the traditional way and preserved at 1 ± 1 °C for a day until laboratory transport for subsequent analysis. On the day of harvesting (26 July 2022), the supplying company classified the produce by calliper, and on the same day, the harvest index analyses were carried out to check the homogeneity of the pears. All the harvest index analyses were performed on 15 pears randomly selected

from those supplied by the company and in the same way as the subsequent studies. The harvest indexes are shown in Table 1. Then, the pears were cooled and transported the following day (27 July 2022) to the laboratory to start the study.

Table 1. Harvest indexes. The means ± standard error of the means (SEM) are shown. n = 15.

Parameters	Weight (g)	Calliper (mm)	Firmness (N)	Soluble Solid Content (SSC) (%)	Total Acidity TA (%)	Colour
Data	116 ± 10	54.3 ± 2.5	52.6 ± 4.5	11.8 ± 0.9	0.35 ± 0.06	a *: −10.9 ± 2.8 b *: 40.3 ± 4.8 L *: 70.1 ± 3.6
Method	Navigator Balance, Ohaus Europe Gmbh (Nänikon, Switzerland).	Mitutoyo 530-122, Mitutoyo Spain (Guipúzcoa, Spain).	CT3 texturometer, AMETEK Brookfield (Middleboro, MA, USA).	Pocket Brix-Acidity meter, Atago (Tokyo, Japan).	Pocket Brix-Acidity meter, Atago (Tokyo, Japan).	Colourpin II, Natural Color System (Stockholm, Sweden).

2.2. Experimental Design

A total of 340 pears (40 kg) were randomly distributed into six 150 L (volume) conservation chambers (CCs) (Eurofred Cool Head RCG200, Eurofred S.A., Barcelona, Catalonia, Spain) for ethylene removal and temperature treatments.

According to Alonso-Salinas [9], the filters used were composed of $KMnO_4$ anchored to the active centre of zeolite, which allowed for a better interaction of this oxidizing substance with ethylene. The composition of the filters in terms of granulometry and other adsorbent substances was patented in Spain by the company "Nuevas Tecnologías Agroalimentarias KEEPCOOL" (Molina de Segura, Spain), patent No. 2548787 (2016). The adsorbing material was covered by a semi-permeable paper, which enables the entry of ethylene-rich air and the output of air clean of this phytohormone. Conversely, this kind of paper prevented the intrusion of water or other particles that could interfere with the process. Ethylene filters were installed inside an M-CAM 50 device (KEEPCCOL, Molina de Segura, Spain), which is an air-flow-forcing machine, to ensure that all the air in the CC passes through the filter. The volume of air moved inside the system is 750 L/min, which means that all the ethylene inside the CC is removed in 12 s, since the chamber has a capacity of 150 L.

In addition, this system incorporates a photocatalytic ultraviolet light system UV-C (TUV 254 nm, Philips, Amsterdam, Netherland) to aid the $KMnO_4$ filters in the removal of ethylene. The ultraviolet light is focused on the air coming out of the filters, not on the fruit. Throughout the article, the machine, filter and UV-C light combination will be referred to as the filter-device (FD).

According to Yildirim [24], UV-C exposure may have a negative effect on food quality. To avoid this possible adverse effect, the light beam was focused on the ethylene and not on the fruit since the device is completely closed, except for two air inlet and outlet openings, the UV-C radiation does not leave the system. To clarify the operation of this process, a diagram of the system is shown in Figure 1.

The combination of KMnO4 and UV-C radiation was chosen due to $KMnO_4$ being more effective than 1-MCP according to the literature [7,10,12,22] and easier to implement in the food industry than palladium due to its low cost. In addition, UV light was added because of its easiness of application and its support to $KMnO_4$.

Two treatments at 1 °C and 8 °C were set-up. These temperatures were selected because they are the standard storage temperatures utilised by fruit distribution companies.

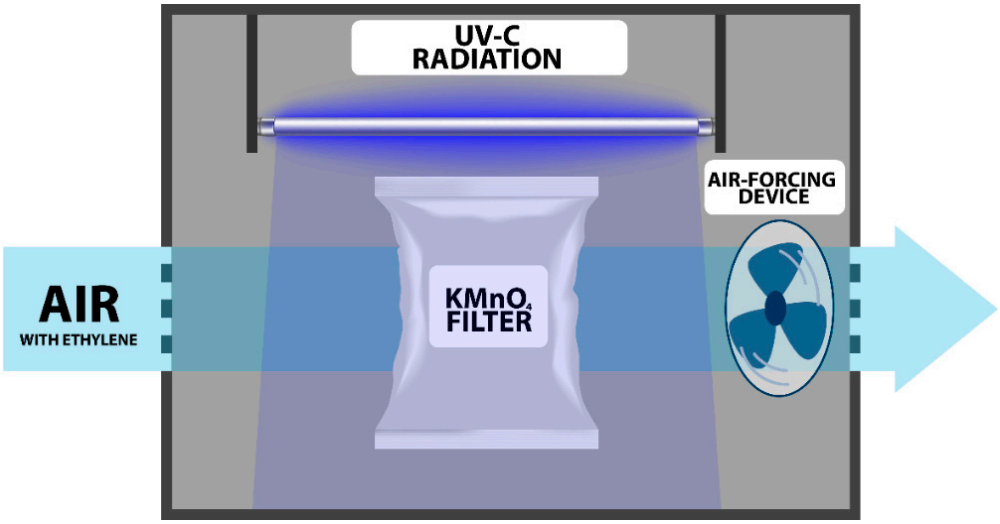

Figure 1. Ethylene scavenger diagram. Own source.

In terms of ethylene removal, preservation temperature and relative humidity the treatments were classified as follows (Table 2):

Table 2. Classification of the treatments applied according to storage temperature (°C), relative humidity (%) and the presence or absence of ethylene scavengers.

Treatments	1 °C-C	1 °C-F	1 °C-FD	8 °C-C	8 °C-F	8 °C-FD
Temperature	1 °C	1 °C	1 °C	8 °C	8 °C	8 °C
Relative humidity	90%	90%	90%	90%	90%	90%
Ethylene scavenger	None	Filter	Filter + Device	None	Filter	Filter + Device

2.3. Physicochemical Variables

All physicochemical analyses were carried out in triplicate on each pear, on five pears per treatment and per day (n = 5) throughout the entire storage period on the following days: 0, 7, 14, 21 and 28 (from 27 July 2022 to 24 August 2022). The shelf life (28 days) was established according to the optimum commercial life of the 'Ercolini' pear suggested by the supplying company. Similar storage times were also observed in other studies [3,25–27].

The ethylene (C_2H_4) concentration was measured using a Gas Analyzer (Felix Three F-950, Felix Instruments, Camas, WA, USA) and expressed as nmol kg^{-1} h^{-1}. The measuring flow rate of the Gas Analyser was 1 mL s^{-1} and 5 measurements were carried out for each day of analysis and treatment. A sealed access to the CCs was opened so that a sonde could be inserted to measure the ethylene concentration without disturbing the internal atmosphere of the chambers. The resolution of the Gas Analyzer was 0.1 ppm and the lower limit of detection is 0.15 ppm. Since at the time of arrival of the pears in the laboratory the ethylene concentration inside the CCs was 0, in order to observe possible differences, ethylene measurements on day 0 were made 6 h after the start of the study.

The weight was measured using a precision balance (Navigator Balance, Ohaus Europe Gmbh Nänikon, Switzerland), expressed in grams. The calliper of the pears was measured with a vernier calliper Mitutoyo 530-122, Mitutoyo Spain (Guipúzcoa, Spain) and expressed in millimetres. The calliper was considered as the equatorial diameter of the pears.

The firmness of the pears was measured with a CT3 texturometer (AMETEK Brookfield, Middleboro, MA, USA) equipped with a cylindrical probe measuring 35 mm height and 6 mm in diameter, which penetrated into the fruit 10 mm at a speed of 0.5 mm s^{-1}. Pear firmness was considered as the maximum force (N) measured during probe penetration.

The soluble solid content (SSC), pH, and total acidity (TA) were measured on fruit samples using the method adapted from Zhang [28]. Twenty grams of pear (without differentiating between skin and flesh) were taken and added to 20 mL of distilled water, then homogenised with a mixer (Ultra turrax T25, LabWare Wilmington, DE, USA) for 30 s. The homogenate was centrifuged at 3600× *g* for 10 min in a centrifuge at 4 °C (Eppendorf Centrifuge 5810, Hamburg, Germany), and the supernatant, mentioned in the rest of the manuscript as pear extract, was used to obtain SSC, pH, TA, ascorbic acid, TPC and antioxidant capacity according to ORAC.

The SSC of the pear extract was determined with a digital refractometer (Pocket Brix-Acidity meter, Atago Tokyo, Japan).) at 20 °C and expressed as a percentage (sugar equivalents in g 100 g^{-1}). The pH of the pear extract was determined with a pH-meter (Testo 206-pH2, Testo, Barcelona, Spain).

The determination of TA of the pear extract was made according to [28] with a Pocket Brix-Acidity meter, Atago (Tokyo, Japan). The results were expressed as g L^{-1}.

The maturity index (MI) was determined by dividing SSC (%) by TA (%). The expression of this parameter is dimensionless.

The ascorbic acid analysis was adapted from the Nielsen [29] method. First, two different solutions were prepared:

- Acid solution: 30 g of metaphosphoric acid (Acrós Organics, Geel, Belgium) and 80 mL of acetic acid (Panreac, Castellar del Vallés, Barcelona, Spain) were added in a 1 L flask and levelled.
- Dichlorophenol solution: 250 mg 2,6-dichlorophenol indophenol (Scharlab S.L., Barcelona, Spain), 210 mg sodium hydrogen carbonate (Panreac, Castellar del Vallés, Barcelona, Spain) were weighed, dissolved and levelled in a 1 L flask.

Ascorbic acid reduces 2,6-dichlorophenol indophenol from purple to a colourless solution. Thus, a 2 mL aliquot of the pear extract was taken and 5 mL of the acid solution was added. Subsequently, the resulting mix was titrated with the 2,6-dichlorophenol indophenol solution under constant stirring until a change in colour to pink was observed. The amount of ascorbic acid was determined by the following formula (F = 0.1):

$$Ascorbic\ acid\ \left(\text{mg L}^{-1}\right) = \frac{F * \text{ mL } used\ of\ 2,6-DCF * \text{ 1000 mL } of\ juice}{Sample\ (\text{mL})} \quad (1)$$

F = titter of dye (0.1 = mg ascorbic acid equivalent to 1.0 mL indophenol standard solution). Ascorbic acid was expressed as milligrams per 100 mL of pear juice (mg 100 mL^{-1}).

The total phenolic content (TPC) of the pear was determined colorimetrically at 765 nm using the Folin–Ciocalteau reagent according to a modification of the Kidron [30] method. The Folin–Ciocalteau reaction was performed by mixing 100 µL of the pear extract, 150 µL of Folin–Ciocalteau reagent, 450 µL of 20% Na_2CO_3, and 2300 µL of distilled water. After 2 h of reaction in dark, the absorbance of the sample was measured against a blank with a spectrophotometer (Shimadzu model UV-1603, Japan). Three measurements were made per pear and 5 pears were analysed for each treatment and day. The calibration curve (y = 0.5206x + 0.0899; R^2 = 0.998) was made using gallic acid as the standard at the range of 25–250 µg mL^{-1}. TPC was expressed in grams of gallic acid equivalents per kilograms of fresh pear (g kg^{-1}).

The antioxidant capacity of the pear extract was measured with ORAC (Oxygen Radical Absorbance Capacity) method following the one described by [31]. It was carried out with a SpectraMax ID3 multidetector microplate reader, from Bio-Tek Instruments, Inc. (USA), using 96-well polystyrene microplates with black sides and clear bottoms. To each well were added 100 mL of fluorescein (from a solution of 1.32 mg fluorescein in 1 L of distilled water), 50 mL of phosphate buffer (1%) and 20 uL of the pear extract diluted 1-10. After 30 min incubation in the dark at 37 °C, 30 uL of 2,2′-azobis(2-methylpropionamidine) dihydrochloride was added and the reaction started and finished after 2 h. Fluorescence was read through the clear bottom every minute of the reaction, with an excitation wavelength of

485 nm and an emission filter of 528 nm. The plate reader was controlled by SoftMax Pro 7.1 software. All reaction mixtures were prepared in triplicate and at least three independent assays were performed for each pear. A total of 5 pears were analysed for each treatment per day. The results were expressed in µmol of Trolox equivalents per kilograms of fresh pear (µmol kg^{-1}). The net area under the curve (AUC) for each well was calculated by subtracting the AUC for the blank from its AUC.

2.4. Descriptive Sensory Analysis

A trained panel consisting of 10 highly trained panellists (aged 25 to 55 years; 6 female and 4 male) from the Food Quality and Safety research group (Universidad Miguel Hernández de Elche, UMH, Orihuela, Spain) conducted the descriptive sensory analysis. Each panellist had more than 1000 h of experience with fruits. The methodology used for the descriptive sensory analysis was that previously described by Noguera-Artiaga [32] and the lexicon used was developed according to Gittins [33]. The scale used ranged from 10 (extremely high intensity) to 0 (no intensity) with 0.5 increments. The samples were served in odour-free disposable plates, at room temperature (~22 °C), and were coded using 3-digit numbers. Mineral water and unsalted crackers were provided to panellists to clean their palates between samples. The analyses were run in triplicate (n = 3). The descriptive sensory analysis was carried out at the beginning (establishing a control at day 0) and at the end of the study comparing the pears after 28 days (24 August 2022) of storage of the 6 treatments described.

2.5. Statistical Analysis

The descriptive statistics (mean and standard error of the mean [SEM] and the different tests described below were performed using the StatGraphics Centurion XV software (StatPoint Technologies, Warrenton, VA, USA). The Shaphiro-Wilk test was performed to check the normality of the data. In addition, to check the homogeneity of variance, Bartlett's test was applied. The six treatments were compared according to 10 variables analysed using a two-way analysis of variance (ANOVA) on days 7, 14, 21 and 28 of the experiment. Pearson's correlation coefficient (r) was calculated to measure the linear relationship between pairs of variables in the correlation matrix (at the end of the experiment, 28 days). A principal component analysis (PCA), followed by a partial least squares discriminant analysis, was conducted to assign the principal components displaying eigenvalues greater than or equal to 1.0, which led to the identification of two principal components that explained 78% of the variation within the data set (at the end of the experiment, 28 days). The sensory analysis was analysed using an analysis of variance (One-way ANOVA), comparing day 0 with day 28 of the experiment. Finally, Tukey's Multiple Range Test was utilised to separate the means and detect significant differences between the treatments (p-value < 0.05).

3. Results and Discussion

3.1. Ethylene

Pear is a climacteric fruit, which means that the ripening process continues once harvested, and this is highly affected by the presence of ethylene. Climacteric fruits increase the production of ethylene during post-harvest ripening, with this gas being responsible for the coordination of the ripening process. Ethylene has an autocatalytic feedback effect, i.e., a higher presence in the storage environment implies a higher ethylene production in the fruit. Therefore, it is crucial to maintain low ethylene levels to ensure an adequate shelf-life and quality of pears [9]. Furthermore, according to Hu [34], pear has a high ethylene sensitivity between 0.03 and 0.1 µL L^{-1}, which indicates that the presence of ethylene exceeding this threshold can cause significant damage to the product.

Figure 2 shows the ethylene concentration throughout preservation of 'Ercolini' pears. This parameter increased steadily in all treatments. However, it was affected by the different storage temperatures and by the use of the $KMnO_4$ filters or the complete ethylene removal system (filter + UV).

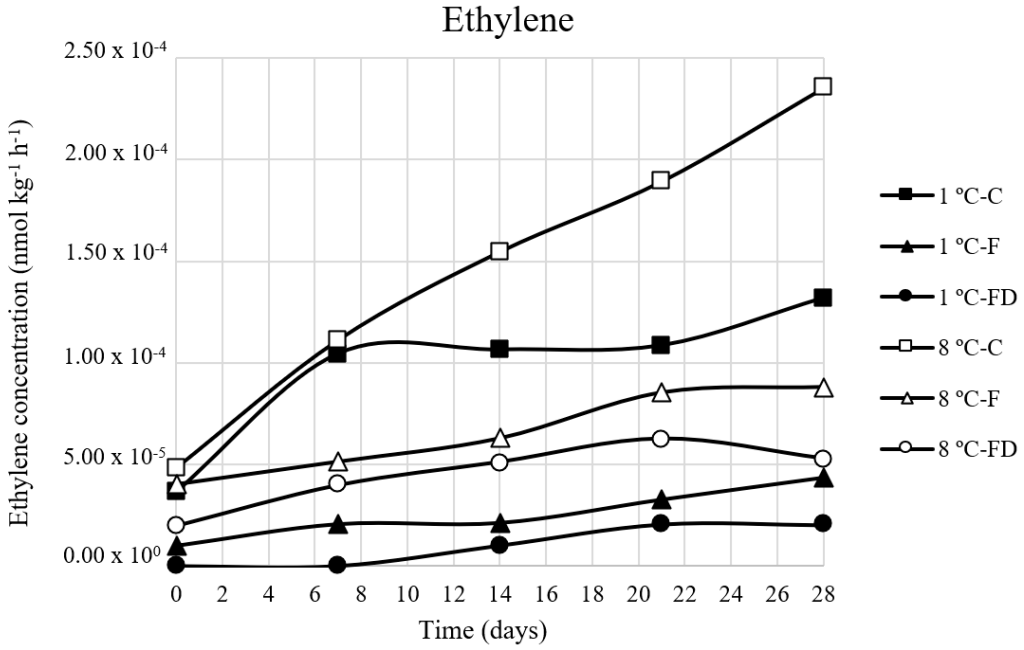

Figure 2. Ethylene concentration expressed as nmol kg^{-1} h^{-1} over the storage time in pears subjected to the different treatments: 1 °C-C (Control), 1 °C-F (Filter), 1 °C-FD (Filter + Device), 8 °C-C (Control), 8 °C-F (Filter) and 8 °C-FD (Filter + Device).

In the treatments kept at 1 °C, differences were observed from day 0 onwards. Treatment 1 °C-C (control) showed higher values than treatments 1 °C-F and 1 °C-FD. The 1 °C-C treatment reached its maximum value on day 28 with $1.32 \cdot 10^{-4}$ nmol kg^{-1} h^{-1}. The 1 °C-F treatment reached its maximum value of $4.37 \cdot 10^{-5}$ nmol kg^{-1} h^{-1} on day 28 as well, 3-fold lower than the control treatment. However, with the 1 °C-FD treatment, ethylene concentrations were obtained that barely exceeded $2 \cdot 10^{-5}$ nmol kg^{-1} h^{-1} throughout the entire storage time, between 5 and 7-fold lower than the control treatment.

In the treatments stored at a more stressful temperature (8 °C), higher levels of ethylene concentration were observed on average. The 8 °C-C treatment reached its maximum on the 28th day of analysis, $2.35 \cdot 10^{-4}$ nmol kg^{-1} h^{-1}. This value highly differed from the treatments in which different ethylene removal methods were used. On the one hand, for the treatment in which $KMnO_4$ filters were exclusively used (8 °C-F), the maximum ethylene concentration levels of $8.84 \cdot 10^{-5}$ nmol kg^{-1} h^{-1} were recorded on day 28, almost 3-fold lower than 8 °C-C. On the other hand, for the treatment in which the complete ethylene elimination system was used, the maximum concentration of this phytohormone was observed on day 28, with a value of $5.29 \cdot 10^{-5}$ nmol kg^{-1} h^{-1}, 2-fold lower than 8 °C-F and close to 10-fold lower than 8 °C-C.

From an overall point of view, the use of $KMnO_4$ filters (treatments 1 °C-F and 8 °C-F) achieved a reduction in ethylene concentration of 69.91% and 62.38% compared to the control treatments at 1 °C and 8 °C, respectively, on day 28. However, the use of the complete system (treatments 1 °C-FD and 8 °C-FD) reduced the concentration by 84.77% and 77.48% compared to the control treatments, at 1 °C and 8 °C, respectively, at the end of the trial.

These results are in agreement with the existing literature. According to Bower [1], it is certainly desirable to minimise ethylene concentrations around stored pears to reduce the incidence of scald and internal breakdown. Alonso-Salinas [9] reported a reduction in the ethylene concentration of 52% in peaches stored at 1 ± 1 °C, using the same ethylene elimination system as in the present study. Other researchers showed the effect of $KMnO_4$ and ultraviolet light as ethylene scavengers separately [19,35,36], nevertheless, their individual effectiveness is lower than that seen in this study as a combination.

Álvarez-Hernández [6] described the effect of applying $KMnO_4$-based ethylene scavengers on apricots stored at 2 °C, indicating a reduction of close to 100; these data are similar to those found in the present manuscript. However, Nguyen [4] reported that using 0.14% of 1-MCP, (a synthetic molecule that competes with ethylene for its receptors), achieved a reduction in the ethylene concentration in 'Bosc Kobak' pears between 5% and 60% compared to the control, depending on the starting day of treatment; similar data have been seen in other studies [3,37]. The use of this molecule, 1-MCP, is shown to be less effective in ethylene removal than those based on potassium permanganate.

3.2. Physico-Chemical Variables Analysed

Table 3 shows the evolution of the physico-chemical variables of pears from the beginning to the end of the conservation period for each treatment. In this table, the 1 °C-FD treatment had a better preservation performance and/or longer shelf life than the rest of the treatments at the end of the experiment (day 28), with a higher weight percentage (97.1%), higher calliper percentage (92.5%), except for 8 °C-FD treatment (95.4%), higher firmness (44.9 N), lower SSC (12.0%), higher TA (3.27 g L^{-1}), lower MI (39.4), higher ascorbic acid concentration (4.4 mg 100 mL^{-1}), higher TPC concentration (0.39 g kg^{-1}), and higher antioxidant capacity measured with ORAC (3.14 µmol kg^{-1}). All of these results are indicative of a less advanced ripening stage and a consequent prolongation of pear shelf life. The raw data are presented in the Supplementary Materials Tables S1–S3 which include the results of the parameters analysed on days 0, 7, 14, 21, and 28 separated into physical variables (Table S1), biochemical variables (Table S2), and bioactive variables (Table S3).

The order of treatments in terms of effectiveness is as follows: 1 °C-FD, 1 °C-F, 8 °C-FD and 1 °C-C. This suggests that the increase in temperature followed by a correct elimination of ethylene (8 °C-FD) slows down the loss of post-harvest quality of the pear, as compared to the control treatment at normal refrigeration temperature (1 °C-C).

In regard to the weight and calliper variables, Charoenchongsuk [8] reported a 20% loss in 'Gorham' pear firmness after 20 days of storage at 20 °C, and a delay in the softening of Russet pears using 1-MCP (1 µL L^{-1}) related to water and weight loss. This effect has also been observed by other authors in various fruit species such as melon [38], apricot [6,39], peach [9,40,41] or kiwifruit [42,43]. In terms of firmness, Nguyen [4] showed that the use of 1-MCP (0.14%) was able to maintain the firmness of the pears cv 'Bosc Kobak' for 14 days without a significant variation. However, Argenta [44] observed a decrease of about 40% of firmness in 1-MCP-treated treatments (0.42 mmol m^{-3}) after 30 days of storage. Escribano [45] reported that after 24 days of application of 0.6 µL L^{-1} of 1-MCP, the firmness of treated 'Bartlett' pears was reduced by about 80%. Until day 12 of the trial, the firmness was maintained. However, on day 14 and subsequent days, the firmness dropped sharply from 80 N on day 12 to 15 N on day 24 of storage.

In relation to the biochemical variables, both of those directly related to maturity and those related to bioactive compounds, Nguyen [4] observed significant differences through the application of 1-MCP (0.14%) to inactivate the action of ethylene on 'Bosc Kobak' pears; Chiriboga [46] showed that, by applying 1-MCP (300 nL L^{-1}), it is possible to preserve the ability to remove reactive oxygen species (ROS) in 'Conference' pears by blocking the autocatalytic feedback effect of ethylene. These researchers analysed electrolyte leakage (EL), total peroxidase (POX), superoxide dismutase (SOD) and catalase activity (CAT) to reach this conclusion. Using $KMnO_4$ as ethylene scavengers, Álvarez-Hernández [47] and Salamanca [48] observed similar effects, but on apricot and in 5 different varieties of tomato, respectively. Alvarez-Hernandez et al. [6] and Salamanca et al. [48] obtained alike results to those presented in this manuscript, supporting the findings reported here. However, Chiriboga et al. [46] obtained lower oxidation protection results than those observed in this study, corroborating that potassium permanganate-based ethylene scavengers are more effective in protecting the bioactive activity of pears than 1-MCP.

Table 3. Evolution from day 0 to day 28 of the physicochemical variables in pears subjected to the different treatments: 1 °C-C (Control), 1 °C-F (Filter), 1 °C-FD (Filter + Device), 8 °C-C (Control), 8 °C-F (Filter) and 8 °C-FD (Filter + Device). The variables measured were: weight expressed as average percentage compared to day 0 (being day 0 the 100% of average weight value of each treatment individually); calliper expressed as percentage compared to day 0 of each treatment; firmness expressed in Newtons; SSC expressed as percentage; pH; TA expressed as g L^{-1}, MI as the SSC (%)/TA (%) ratio; ascorbic acid content expressed as mg 100 mL^{-1}; total phenolic compounds expressed as $g_{galic\ acid}$ kg^{-1} and antioxidant capacity measured with the ORAC method expressed as $\mu mol_{Trollox.Eq.}$ kg^{-1}. The means ± standard error of the means (SEM) are shown. Different letters for each treatment represent statistically significant differences according to Tukey's test, n = 5 per treatment and day. The parameters have also been analysed by factors: ethylene (E), temperature (T) and the interaction of both ethylene × temperature (E × T).

Treatments	Weight (%)		Calliper (%)		Firmness (N)	
	Day 0	Day 28	Day 0	Day 28	Day 0	Day 28
1 °C-C	100	82.9 ± 3.5 b	100	82.5 ± 1.5 b	48.9 ± 1.7	34.4 ± 1.6 c
1 °C-F		91.7 ± 6.3 a		91.6 ± 1.5 a		43.4 ± 1.6 ab
1 °C-FD		97.1 ± 8.3 a		92.5 ± 0.7 a		44.9 ± 2.1 a
8 °C-C		89.9 ± 4.4 a		83.3 ± 2.0 b		26.1 ± 2.6 d
8 °C-F		91.1 ± 2.8 a		89.9 ± 1.7 a		33.0 ± 1.8 c
8 °C-FD		93.2 ± 1.6 a		95.4 ± 2.7 a		37.4 ± 2.1 bc
Ethylene (E)	-	**	-	***	-	***
Temperature (T)	-	n.s.	-	**	-	***
E × T	-	**	-	n.s.	-	n.s.

Treatments	SSC (%)		TA (g L^{-1})		MI	
	Day 0	Day 28	Day 0	Day 28	Day 0	Day 28
1 °C-C	12.5 ± 0.42	15.5 ± 0.65 ab	3.69 ± 0.47	1.76 ± 0.29 c	34.4 ± 2.44	95.9 ± 16.2 ab
1 °C-F		12.5 ± 0.29 c		2.93 ± 0.29 ab		43.7 ± 3.7 c
1 °C-FD		12.0 ± 0.41 c		3.27 ± 0.46 a		39.4 ± 6.3 c
8 °C-C		17.5 ± 0.65 a		1.51 ± 0.22 c		125.5 ± 22.0 a
8 °C-F		15.3 ± 1.10 b		1.93 ± 0.29 bc		84.1 ± 12.1 abc
8 °C-FD		15.0 ± 0.41 b		2.09 ± 0.29 bc		75.7 ± 10.1 bc
Ethylene (E)	-	***	-	***	-	***
Temperature (T)	-	***	-	***	-	***
E × T	-	n.s.	-	n.s.	-	n.s.

Treatments	Ascorbic Acid (mg 100mL^{-1})		TPC (g kg^{-1})		Antioxidant capacity (µmol kg^{-1})	
	Day 0	Day 28	Day 0	Day 28	Day 0	Day 28
1 °C-C	5.0 ± 0.47	2.9 ± 0.37 bcd	0.49 ± 0.03	0.26 ± 0.02 cd	4.17 ± 0.08	2.18 ± 0.14 c
1 °C-F		3.8 ± 0.28 ab		0.35 ± 0.04 ab		2.83 ± 0.06 ab
1 °C-FD		4.4 ± 0.21 a		0.39 ± 0.03 a		3.14 ± 0.22 a
8 °C-C		1.7 ± 0.22 d		0.21 ± 0.04 d		1.78 ± 0.14 d
8 °C-F		2.0 ± 0.39 cd		0.29 ± 0.05 bc		2.21 ± 0.05 c
8 °C-FD		3.1 ± 0.48 abc		0.36 ± 0.05 ab		2.56 ± 0.19 bc
Ethylene (E)	-	***	-	***	-	***
Temperature (T)	-	***	-	**	-	***
E × T	-	n.s.	-	n.s.	-	n.s.

Levels of statistical significance are: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$. n.s.: no significant differences.

However, Mansourbahmani [7] observed no significant differences between the application of 1-MCP (0.14%), $KMnO_4$ (20%) or 5% palladium as ethylene scavengers in AA, TPC, and antioxidant capacity (ORAC) during 35 days of tomato preservation. The data presented in this study contradict the findings of Mansourbahmani et al. [7] since we have seen differences in the application of $KMnO_4$ and UV-C radiation in these parameters.

3.3. Sensory Analysis

After the descriptive sensory analysis of pear samples, statistically significant differences were found in 18 of the 23 sensory descriptors studied (Table 4).

Table 4. Descriptive sensory analysis of pears. Number of panellists: 10. n = 3.

Sensory Descriptor	ANOVA	Day 0	1 °C (Day 28)			8 °C (Day 28)		
			C	F	FD	C	F	FD
COLOUR								
External	**	9.0 a	6.0 c	7.0 bc	8.5 b	2.0 e	3.0 de	4.0 d
Internal	***	8.0 a	6.0 b	6.0 b	7.5 a	2.0 c	2.0 c	5.0 b
Spotting	*	1.0 c	8.0 a	5.5 b	3.0 c	8.5 a	9.0 a	6.0 b
ODOUR								
Pear	***	7.0 a	4.0 c	5.5 b	7.0 a	1.5 d	2.0 d	2.0 d
Fruity (Green)	***	8.0 a	4.0 bc	5.0 b	8.0 a	1.0 c	1.0 c	3.0 c
Fruity (ripe)	***	4.0 d	8.0 bc	8.0 bc	5.0 d	9.0 a	9.0 a	7.0 b
Floral	**	3.0 a	1.0 b	1.0 b	2.5 a	1.0 b	1.0 b	2.5 a
Earthy	n.s.	1.5	3.0	3.0	1.0	3.5	4.0	3.0
FLAVOUR								
Pear	**	8.5 a	4.0 b	4.5 b	7.0 a	1.5 d	1.5 d	2.5 c
Fruity (Green)	***	8.5 a	5.0 b	6.0 b	7.0 a	0.5 d	1.0 d	3.0 c
Fruity (ripe)	***	2.0 d	4.0 c	4.0 c	2.5 d	9.5 a	9.5 a	7.0 b
Floral	*	3.0 a	1.5 b	2.0 b	3.0 a	1.0 b	1.0 b	2.0 b
Earthy	*	3.0 a	4.5 a	4.0 a	2.5 bc	1.0 b	2.0 b	2.0 b
Sweet	*	4.0 b	3.0 c	3.5 c	5.0 a	4.5 b	5.5 a	5.0 a
Sour	n.s.	1.0	1.0	1.0	1.5	2.0	2.5	2.0
Bitter	*	0.5 c	0.5 c	0.5 c	0.5 c	3.0 a	2.0 b	2.0 b
Astringent	n.s.	1.0	1.0	1.0	1.0	2.0	1.5	1.5
Aftertaste	**	4.0 a	2.0 b	2.5 b	4.5 a	1.0 b	1.5 b	2.5 b
TEXTURE								
Hardness	***	9.0 a	6.0 c	6.0 c	7.5 b	2.0 e	2.5 e	4.5 d
Crunchiness	***	9.0 a	6.0 c	5.5 c	7.5 b	1.0 d	1.5 d	3.0 d
Solubility	***	9.0 a	7.0 bc	6.5 bc	8.0 b	6.0 c	7.5 b	8.0 b
Residual particles	n.s.	3.0	5.0	4.5	2.5	3.5	4.0	3.5
Fibrousness	n.s.	1.0	3.0	3.0	1.0	3.0	3.0	3.0

Levels of statistical significance are: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$. n.s.: no significant differences. Values (mean of 3 replications) followed by the same letter, within the same sensory descriptor, were not significantly different ($p > 0.05$), according to Tukey's least significant difference test.

The colour of the fruits was affected by the ethylene treatments studied, both externally and internally. Samples from the 1 °C-FD treatment were the most preserved as compared with the initial colour values (control sample, day zero), while samples from the 8 °C-C treatment changed the most. Initially, the fruits had an intense green external colour, which gradually turned brown in the samples with less intensity. Similar changes were observed in the internal colour of the fruit, but in this case, the colour changed from a characteristic white to yellow-brown. Regarding staining, it was intense in the 8 °C-C, 8 °C-FD, 8 °C-F and 1 °C-C samples, while it remained practically null in the rest of the samples.

Regarding the odour, again, the 1 °C-FD sample obtained intensity values close to the control sample, demonstrating that this treatment is capable of very effectively preserving the characteristic odour of the product for a longer period. In the rest of the treatments, a change was observed in terms of the perception of the fruity odour, with the appearance of high intensities of fruitiness characteristic of ripe fruits. These perceptions were maintained when the same descriptors were analysed via the retro nasal route. Fruit aroma plays a well-established role in determining the final sensory quality, and is a strong determinant of consumer preference for a fruit. Thus, the longer the initial aroma of the fruit is preserved, the more market possibilities it has [49]. Volatile esters are a mayor group of volatile organic

compounds contributing to the aroma of pears and, although ripening is inhibited during refrigeration, the release of volatile compounds still proceeds [50]. The results reported here indicate that the 1 °C-F treatment slowed the loss of these compounds.

If we analyse the results related to sweetness, sourness, astringency, and aftertaste, we again observed that the 1 °C-FD treatment maintained the intensities of the control fruit, while the 8 °C-C treatment had the most altered organoleptic properties.

Finally, when analysing the results obtained after the texture analysis, no differences were found in the content of residual particles and the fibrousness of the samples. However, differences appeared in hardness, crunchiness, and solubility in the mouth. With respect to hardness and crunchiness, the 1 °C-FD treatment presented intensities closest to the control, although slightly lower, followed by the 1 °C-F and 1 °C-C treatments. As for the solubility in the mouth, all the treatments were affected in their intensity with respect to the control sample.

Some authors have shown that the synthesis of esters may be related to the production of ethylene [50–52]. In the case of pears, this connection occurs through the expression of the PuAAT1 gene, which is responsible for the synthesis of these aromatic compounds [53]. The results obtained after the use of $KMnO_4$ and UV light, may indicate that as the fruit is producing ethylene naturally, the production of esters is also being activated. However, by eliminating the excess of ethylene in the chamber, the ripening of the fruit is stopped, but the synthesis of esters continues, which is why the conservation is prolonged, maintaining the typical flavour of the fruit.

These sensory results allow us to conclude that the 1 °C-FD treatment reduced the ripening of the pears for a longer period of time, preserving the odour, flavour, and texture of samples.

3.4. Correlation Matrix and Principal Component Analysis

In order to study the association between the variables studied, a correlation matrix was created (Table 5). The results can be separated into physical variables (weight, calliper, and firmness), biochemical variables (SSC, pH, TA, and MI) and bioactive variables (ascorbic acid, total phenolic compounds, and antioxidant capacity measured with ORAC).

Table 5. Pearson's correlation matrix (r) for analysed. Significant interactions are highlighted in bold. The parameter r represented in this table ranges from 1 to −1 depending on whether the correlations between parameters are positive or negative respectively. The variables analysed were: weight (W), calliper (C), firmness (F), soluble solid content (SSC), pH, total acidity (TA), maturity index (MI), ascorbic acid (AA), total phenolic compounds (TPC) and antioxidant capacity (ORAC). The data used are from the final day of the study (day 28).

	W	C	F	SSC	pH	TA	MI	AA	TPC
C	**0.5976 ****	-	-	-	-	-	-	-	-
F	0.1449 $^{n.s.}$	0.2914 $^{n.s.}$	-	-	-	-	-	-	-
SSC	−0.1510 $^{n.s.}$	**−0.3793 ***	**−0.8344 *****	-	-	-	-	-	-
pH	−0.0620 $^{n.s.}$	−0.2884 $^{n.s.}$	**−0.7391 *****	**0.8209 *****	-	-	-	-	-
TA	0.2226 $^{n.s.}$	0.2732 $^{n.s.}$	**0.7369 *****	**−0.6806 ****	**−0.6353 ****	-	-	-	-
MI	−0.2499 $^{n.s.}$	−0.3314 $^{n.s.}$	**−0.8158 *****	**0.7661 *****	**0.7083 *****	**−0.8862 *****	-	-	-
AA	0.1693 $^{n.s.}$	0.3262 $^{n.s.}$	**0.7097 *****	**−0.6896 ****	**−0.6577 ****	**0.6204 ****	**−0.6240 ****	-	-
TPC	0.2170 $^{n.s.}$	**0.5682 ***	**0.7509 *****	**−0.6930 ****	**−0.7238 *****	**0.6594 ****	**−0.7129 *****	**0.6207 ****	-
ORAC	0.1422 $^{n.s.}$	**0.4062 ***	**0.8681 *****	**−0.8010 *****	**−0.6596 ****	**0.6980 ****	**−0.7054 *****	**0.8058 *****	**0.7003 *****

Levels of statistical significance are: * $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$. $^{n.s.}$: no significant differences.

Regarding the physical variables, a moderate correlation between weight and calliper was observed. In addition, a weak correlation was also observed between calliper and some of the biochemical and bioactive variables, such as SSC, ORAC and, TPC. Firmness stands out from the rest of the variables, as it maintained a strong relationship with all the internal variables, both biochemical and bioactive compounds.

As for the biochemical variables, a strong correlation was observed between them and with the compounds involved in antioxidant capacity. SSC had a strong correlation with pH, MI, and antioxidant capacity (ORAC), and a moderate correlation with TA,

ascorbic acid (AA), and TPC. pH had a moderate correlation with TA, AA, and ORAC, and a strong correlation with MI and TPC. TA had a strong correlation with MI and a moderate correlation with all compounds related to antioxidant activity. All of these variables represent compounds involved in fruit biochemical processes that are more dependent on fruit maturity.

The bioactive compounds correlated amongst themselves. AA concentration showed a strong correlation with ORAC and a moderate correlation with TPC. ORAC was strongly correlated with both variables. This can be explained by the fact that the ORAC method is a generic way of determining antioxidant activity, which together with other compounds, depends on the concentration of AA and the action of TPC, and therefore its correlation with them was strong.

Tables 4 and 5 show a relationship between the data from both sets of analyses. Some examples are given below; the panellists of the descriptive sensory analysis concluded that those pears with higher flavour and fruity odour (green) were those that matched with the lowest maturity indexes (MI) in the treatments 1 °C-F and 1 °C-FD; the same happens with the treatments preserved at 8 °C. Also, panellists found that the highest hardness fits with those treatments that presented the highest firmness. This allows us to have two ways of confirming the efficacy of the applied treatments. Moreover, the sensory point of view (more related to commercial acceptance) is entirely linked to the physicochemical one in this manuscript. Therefore, this method of ethylene elimination can be very useful as a tool to be applied at industrial level. Álvarez-Hernández et al. [6], described a similar effect applying a $KMnO_4$-based ethylene scavenger on apricot.

In addition, to be able to indicate which set of variables explained the greatest variability in the experiment, and how the different treatments were separated, a principal component analysis (PCA) was carried out.

The purpose of the analysis is to first obtain a small number of linear combinations of the 8 variables studied (W, C, F, pH, MI, AA, TPC and ORAC) that explain the greatest variability in the data. In this case, 2 components were extracted, since these 2 components had eigenvalues greater than or equal to 1.0. These components are principal component 1 (PC1) which explains 61.09% of the variability of the experiment, and principal component 2 (PC2) which explains 17.41% of the variability of the experiment. Together they explained 78.51% of the variability in the original data (Table S4 and Figure S1). The second step is to indicate, for each extracted component, which variables had more weight or were the most important (variables with a higher absolute value). In PC1, the variables with the most weight, from high to low, were: F > ORAC > FC > MI > pH > AA. It can be concluded that PC1 contained all the internal quality variables that ultimately affect firmness according to the observed ethylene concentrations; this suggests that firmness, in this study, was the priority marker of the internal quality of the fruit, and was also notably important in the physical quality of the pears. Following the same criteria, in PC2 the variables with the most weight, from highest to lowest, were: W > C. It can be concluded that the PC2 included all variables related with water loss, and therefore those that were affected by the different temperatures applied (Table S5).

Although no references to other similar correlation studies have been found, the findings of this manuscript are indirectly corroborated by the existing literature. Many authors consider firmness [4,54,55] and antioxidant capacity [46,56–58] as the main markers of fruit quality, which supports what was observed in this study, as they are the two parameters with more weight in PC1 of the analysis by principal components.

As indicated above, the other objective is to be able to locate the treatments in a scatter diagram (Figure 3) or bigraphic (Figure S2). These figures are achieved through of the principal component table where for each treatment (5 per treatment for a total of 30 data), the scores obtained for each component are represented. In addition, the average score for each of the six treatments is added (Table S6a).

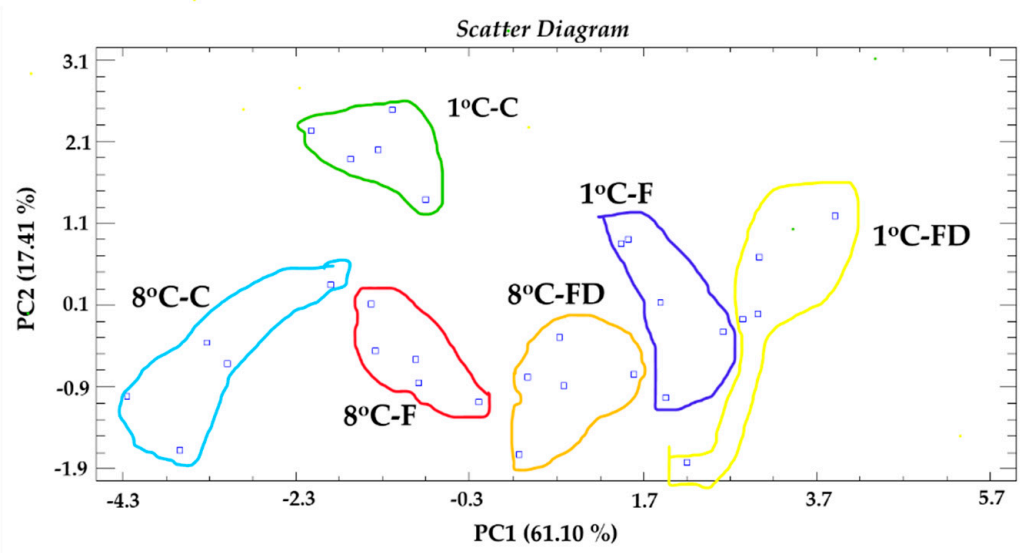

Figure 3. A principal component analysis applied to the different treatments (1 °C-C, 1 °C-F, 1 °C-FD, 8 °C-C, 8 °C-F and 8 °C-FD). Two principal components (PC1 and PC2) resulted in a model that explained 78.5% of the total variance.

The scatter plot shows that the treatments were well separated with the two PCs, but PC1 was the best, with a value of F = 75.72 ***, which allowed us to classify the treatments into four clusters (Table S6b): the first cluster is shaped by the 1 °C-FD and 1 °C-F treatments; the second cluster only includes the 8 °C-FD treatment; the third cluster is composed of the 8 °C-F and 1 °C-C treatments; and the fourth cluster only contained the 8 °C-C treatment (Table S6c). Regarding PC2, the treatments were not as well separated, with a value of F = 10.46 ***, which allowed us to classify the treatments into three clusters (Table S6d): the first cluster only formed by the 1 °C-C treatment; the second cluster included the 1 °C-F, 1 °C-FD, 8 °C-F and 8 °C-C treatments; and the third cluster only the 8 °C-FD treatment. These scores reconfirm the results described in the previous paragraph, which indicated that in PC1, the elimination of ethylene was essential in the preservation of the postharvest quality of the 'Ercolini' pear. Meanwhile, in PC2, a separation of the treatments was observed in relation to the temperature used for storage (Table S6e).

4. Conclusions

In this study, we carried out a complete evaluation of the effects of ethylene removal by $KMnO_4$, UV-C radiation and continuous air flow during the postharvest quality preservation, as well as the sensory analysis of 'Ercolini' pears at 1 °C and 8 °C. Based on the results described above, it can be concluded that the use of the combination of the aforementioned ethylene elimination methods maintained very low levels of this phytohormone, with values close to 0. As for the condition of the pears, those preserved using the complete ethylene elimination system (FD treatments) showed a higher physicochemical quality than the rest of the treatments, including increased weight, calliper, firmness, TA, ascorbic acid, TPC and antioxidant capacity retention and lower levels of SSC and MI, especially in the treatment with low temperature (1 °C-FD). In addition, that treatment had higher scores in the evaluation through sensory analysis. On the other hand, in the treatment with a more stressful preservation temperature, with the complete system of ethylene removal (8 °C-FD), the pears showed a state of maturity equal or lower than the control treatment at optimum temperature (1 °C-C). These results prove that the correct elimination of ethylene with the methods described here, delays the postharvest ripening of 'Ercolini' pears extending its shelf life.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/horticulturae8111078/s1, Figure S1: Sedimentation graph; Figure S2: Graphical representation of the principal components marking with lines for each variables and wit points for each score; Table S1: Evolution during storage time of the physical variables in pears subjected to the different treatments: 1 °C-C (Control), 1 °C-F (Filter), 1 °C-FD (Filter + Device), 8 °C-C (Control), 8 °C-F (Filter) and 8 °C-FD (Filter + Device); Table S2: Evolution during storage time of the biochemical variables in pears subjected to different treatments: 1 °C-C (Control), 1 °C-F (Filter), 1 °C-FD (Filter + Device), 8 °C-C (Control), 8 °C-F (Filter) and 8 °C-FD (Filter + Device); Table S3: Evolution during storage time of the bioactive compounds in pears subjected to different treatments: 1 °C-C (Control), 1 °C-F (Filter), 1 °C-FD (Filter + Device), 8 °C-C (Control), 8 °C-F (Filter) and 8 °C-FD (Filter + Device); Table S4: Principal Component Analysis; Table S5: Table of Component Weights; Table S6a: This table shows the scores of the principal components; Table S6b: ANOVA table for the component 1 scores according to the treatments; Table S6c: Multiple comparisons test for the component 1 scores by treatments using Tukey HSD method; Table S6d: ANOVA table for the component 2 scores according to the treatments; Table S6e: Multiple comparisons test for the component 2 scores by treatments using Tukey's HSD method.

Author Contributions: Conceptualization, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; methodology, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; software, R.A.-S., J.R.A.-M. and L.N.-A.; validation, E.N.-D. and F.B.; formal analysis, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; investigation, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; resources, J.R.A.-M., S.L.-M. and L.N.-A.; data curation, R.A.-S., J.R.A.-M., A.J.P.-L. and L.N.-A.; writing—original draft preparation, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; writing—review and editing, R.A.-S., J.R.A.-M., S.L.-M. and A.J.P.-L.; visualization, A.J.P.-L., J.R.A.-M. and S.L.-M.; supervision, J.R.A.-M., S.L.-M. and F.B.; project administration, S.L.-M. and E.N.-D.; funding acquisition, E.N.-D. and J.R.A.-M. All authors have read and agreed to the published version of the manuscript.

Funding: Nuevas Tecnologías Agroalimentarias (KEEPCOOL): CFE/KE/76-19; "Cátedra Emprendimiento en el Ámbito Agroalimentario" from Universidad Católica San Antonio de Murcia (UCAM) and Banco Santander: CFE/KE/76-19.

Acknowledgments: The authors gratefully acknowledge Antonio Cerdá (Cátedra UCAM-Banco Santander de Emprendimiento en el Ámbito Agroalimentario director), Cooperativa Hortofrutícola Campos de Jumilla from FECOAM ("Federación de Cooperativas Agrarias de Murcia"), especially Antonio Sanz and Lola Mondéjar for supplying the pears D.O.P "Ercolini" used in this study. Mario Fon for his help with English editing. and finally, Miriam Monje for her help with graphical abstract and figures.

Conflicts of Interest: The Doctoral Thesis (Ph.D.) of Ramiro Alonso Salinas, co-author of this work, is being co-financed by the company Nuevas Tecnologías Agroalimentarias (KEEPCOOL), within the UCAM Universidad Católica de Murcia Industrial Doctorate Program. The rest of the authors of the article declare that their contribution to this research was carried out in the absence of commercial or financial relationships that could be constructed as a possible conflict of interest.

References

1. Bower, J.; Biasi, W.; Mitcham, E. Effect of Ethylene in the Storage Environment on Quality of 'Bartlett Pears'. *Postharvest Biol. Technol.* **2003**, *28*, 371–379. [CrossRef]
2. Hiwasa, K.; Kinugasa, Y.; Amano, S.; Hashimoto, A.; Nakano, R.; Inaba, A.; Kubo, Y. Ethylene Is Required for Both the Initiation and Progression of Softening in Pear (*Pyrus communis* L.) Fruit. *J. Exp. Bot.* **2003**, *54*, 771–779. [CrossRef] [PubMed]
3. Horak, M.; Golias, J.; Balik, J.; Nemcova, A.; Snurkovic, P.; Koziskova, J. Changes in Asian and European Pear Cultivars Fruit after Harvest in Various Storage Conditions. *III Balk. Symp. Fruit Grow. Acta Hortic.* **2016**, *1139*, 609–615. [CrossRef]
4. Nguyen, L.L.; Pham, T.T.; Syium, Z.H.; Zsom-Muha, V.; Baranyai, L.; Zsom, T.; Hitka, G. Delay of 1-MCP Treatment on Post-Harvest Quality of 'Bosc Kobak' Pear. *Horticulturae* **2022**, *8*, 89. [CrossRef]
5. Jesús, G.B.; de Murcia, R. Informe sobre los parámetros de la calidad, contenido en Sólidos solubles (azucares) y Firmeza, 495 de los frutos de peral variedad 'Ercolini', cultivados en las condiciones medio ambientales de la comarca de Jumilla 'Altiplano' 496 (Murcia) en los años 2006, 2007 y 2008. *Región Murcia Cons. Agric. Y Agua* **2011**, 1–6.
6. Álvarez-Hernández, M.H.; Martínez-Hernández, G.B.; Avalos-Belmontes, F.; Miranda-Molina, F.D.; Artés-Hernández, F. Postharvest Quality Retention of Apricots by Using a Novel Sepiolite–Loaded Potassium Permanganate Ethylene Scavenger. *Postharvest Biol. Technol.* **2020**, *160*, 111061. [CrossRef]

7. Mansourbahmani, S.; Ghareyazie, B.; Zarinnia, V.; Kalatejari, S.; Mohammadi, R.S. Study on the Efficiency of Ethylene Scavengers on the Maintenance of Postharvest Quality of Tomato Fruit. *J. Food Meas. Charact.* **2018**, *12*, 691–701. [CrossRef]
8. Charoenchongsuk, N.; Matsumoto, D.; Itai, A.; Murayama, H. Ripening Characteristics and Pigment Changes in Russeted Pear Fruit in Response to Ethylene and 1-MCP. *Horticulturae* **2018**, *4*, 22. [CrossRef]
9. Alonso-Salinas, R.; Acosta-Motos, J.R.; Núñez-Delicado, E.; Gabaldón, J.A.; López-Miranda, S. Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures. *Agronomy* **2022**, *12*, 616. [CrossRef]
10. Alonso-Salinas, R.; López-Miranda, S.; Pérez-López, A.J.; Noguera-Artiaga, L.; Carbonell-Barrachina, Á.A.; Núñez-Delicado, E.; Acosta-Motos, J.R. Novel Combination of Ethylene Oxidisers to Delay Losses on Postharvest Quality, Volatile Compounds and Sensorial Analysis of Tomato Fruit. *LWT* **2022**, *170*, 114054. [CrossRef]
11. Kim, S.; Jeong, G.H.; Kim, S.-W. Ethylene Gas Decomposition Using ZSM-5/WO3-Pt-Nanorod Composites for Fruit Freshness. *ACS Sustain. Chem. Eng.* **2019**, *7*, 11250–11257. [CrossRef]
12. Wei, H.; Seidi, F.; Zhang, T.; Jin, Y.; Xiao, H. Ethylene Scavengers for the Preservation of Fruits and Vegetables: A Review. *Food Chem.* **2021**, *337*, 127750. [CrossRef]
13. Janjarasskul, T.; Suppakul, P. Active and Intelligent Packaging: The Indication of Quality and Safety. *Crit. Rev. Food Sci. Nutr.* **2018**, *58*, 808–831. [CrossRef]
14. Esturk, O.; Ayhan, Z.; Gokkurt, T. Production and Application of Active Packaging Film with Ethylene Adsorber to Increase the Shelf Life of Broccoli (*Brassica oleracea* L. Var. Italica). *Packag. Technol. Sci.* **2014**, *27*, 179–191. [CrossRef]
15. Ibhadon, A.; Fitzpatrick, P. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts* **2013**, *3*, 189–218. [CrossRef]
16. Keller, N.; Ducamp, M.-N.; Robert, D.; Keller, V. Ethylene Removal and Fresh Product Storage: A Challenge at the Frontiers of Chemistry. Toward an Approach by Photocatalytic Oxidation. *Chem. Rev.* **2013**, *113*, 5029–5070. [CrossRef]
17. Kaewklin, P.; Siripatrawan, U.; Suwanagul, A.; Lee, Y.S. Active Packaging from Chitosan-Titanium Dioxide Nanocomposite Film for Prolonging Storage Life of Tomato Fruit. *Int. J. Biol. Macromol.* **2018**, *112*, 523–529. [CrossRef]
18. Pathak, N.; Caleb, O.J.; Geyer, M.; Herppich, W.B.; Rauh, C.; Mahajan, P. V Photocatalytic and Photochemical Oxidation of Ethylene: Potential for Storage of Fresh Produce—A Review. *Food Bioprocess Technol.* **2017**, *10*, 982–1001. [CrossRef]
19. Pathak, N. *Photocatalysis and Vacuum Ultraviolet Light Photolysis as Ethylene Removal Techniques for Potential Application in Fruit Storage*; Technische Universität Berlin: Berlin, Germany, 2019.
20. Tytgat, T.; Hauchecorne, B.; Abakumov, A.; Smits, M.; Vinken, K.; Verbruggen, S.; Lenaerts, S. Photocatalytic Process Optimisation for Ethylene Oxidation. *Chem. Eng. J.* **2011**, *209*, 494–500. [CrossRef]
21. Liu, J.; Yang, J.; Zhang, H.; Cong, L.; Zhai, R.; Yang, C.; Wang, Z.; Ma, F.; Xu, L. Melatonin Inhibits Ethylene Synthesis via Nitric Oxide Regulation To Delay Postharvest Senescence in Pears. *J. Agric. Food Chem.* **2019**, *67*, 2279–2288. [CrossRef]
22. Álvarez-Hernández, M.H.; Artés-Hernández, F.; Ávalos-Belmontes, F.; Castillo-Campohermoso, M.A.; Contreras-Esquivel, J.C.; Ventura-Sobrevilla, J.M.; Martínez-Hernández, G.B. Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food Bioprocess Technol.* **2018**, *11*, 511–525. [CrossRef]
23. Smith, A.; Poulston, S.; Rowsell, L.; Terry, L.; Anderson, J. A New Palladium-Based Ethylene Scavenger to Control Ethylene-Induced Ripening of Climacteric Fruit. *Platin. Met. Rev.* **2009**, *53*, 112–122. [CrossRef]
24. Yildirim, S.; Röcker, B.; Pettersen, M.K.; Nilsen-Nygaard, J.; Ayhan, Z.; Rutkaite, R.; Radusin, T.; Suminska, P.; Marcos, B.; Coma, V. Active Packaging Applications for Food. *Compr. Rev. Food Sci. Food Saf.* **2018**, *17*, 165–199. [CrossRef] [PubMed]
25. Makkumrai, W.; Sivertsen, H.; Sugar, D.; Ebeler, S.E.; Negre-Zakharov, F.; Mitcham, E.J. Effect of Ethylene and Temperature Conditioning on Sensory Attributes and Chemical Composition of "Comice" Pears. *J. Agric. Food Chem.* **2014**, *62*, 4988–5004. [CrossRef] [PubMed]
26. Cruz-Hernández, A.; Paredes-López, O. Fruit Quality: New Insights for Biotechnology. *Crit. Rev. Food Sci. Nutr.* **2012**, *52*, 272–289. [CrossRef]
27. Gamrasni, D.; Ben-Arie, R.; Goldway, M. 1-Methylcyclopropene (1-MCP) Application to Spadona Pears at Different Stages of Ripening to Maximize Fruit Quality after Storage. *Postharvest Biol. Technol.* **2010**, *58*, 104–112. [CrossRef]
28. Zhang, B.; Peng, B.; Zhang, C.; Song, Z.; Ma, R. Determination of Fruit Maturity and Its Prediction Model Based on the Pericarp Index of Absorbance Difference (IAD) for Peaches. *PLoS ONE* **2017**, *12*, e0177511. [CrossRef]
29. Nielsen, S.S. *Vitamin C Determination by Indophenol Method BT—Food Analysis Laboratory Manual*; Nielsen, S.S., Ed.; Springer International Publishing: Cham, Switzerland, 2017; pp. 143–146. ISBN 978-3-319-44127-6.
30. Kidron, M.; Harel, E.; Mayer, A.M. Catechol Oxidase Activity in Grapes and Wine. *Am. J. Enol. Vitic.* **1978**, *29*, 30–35.
31. López-Miranda, S.; Serrano-Martínez, A.; Hernández-Sánchez, P.; Guardiola, L.; Pérez-Sánchez, H.; Fortea, I.; Gabaldón, J.A.; Núñez-Delicado, E. Use of Cyclodextrins to Recover Catechin and Epicatechin from Red Grape Pomace. *Food Chem.* **2016**, *203*, 379–385. [CrossRef]
32. Noguera-Artiaga, L.; Salvador, M.; Fregapane, G.; Collado, J.; Wojdyło, A.; López Lluch, D.; Carbonell-Barrachina, A. Functional and Sensory Properties of Pistachio Nuts as Affected by Cultivar. *J. Sci. Food Agric.* **2019**, *99*, 6696–6705. [CrossRef]
33. Gittins, C.; Calvo, P.; Miranda, M.J.; Barda, N. Developing a Sensory Descriptive Panel for Pear Quality Evaluation. *Acta Hortic.* **2011**, *909*, 617–624. [CrossRef]

34. Hu, B.; Sun, D.-W.; Pu, H.; Wei, Q. Recent Advances in Detecting and Regulating Ethylene Concentrations for Shelf-Life Extension and Maturity Control of Fruit: A Review. *Trends Food Sci. Technol.* **2019**, *91*, 66–82. [CrossRef]
35. Gaikwad, K.K.; Singh, S.; Negi, Y.S. Ethylene Scavengers for Active Packaging of Fresh Food Produce. *Environ. Chem. Lett.* **2020**, *18*, 269–284. [CrossRef]
36. Sammi, S.; Masud, T. Effect of Different Packaging Systems on the Quality of Tomato (*Lycopersicon esculentum* Var. Rio Grande) Fruits during Storage. *Int. J. Food Sci. Technol.* **2009**, *44*, 918–926. [CrossRef]
37. Shinozaki, Y.; Hao, S.; Kojima, M.; Sakakibara, H.; Ozeki-Iida, Y.; Zheng, Y.; Fei, Z.; Zhong, S.; Giovannoni, J.J.; Rose, J.K.C.; et al. Ethylene Suppresses Tomato (*Solanum lycopersicum* L.) Fruit Set through Modification of Gibberellin Metabolism. *Plant J.* **2015**, *83*, 237–251. [CrossRef]
38. Le Nguyen, L.P.; Zsom, T.; Dam, M.S.; Baranyai, L.; Hitka, G. Evaluation of the 1-MCP Microbubbles Treatment for Shelf-Life Extension for Melons. *Postharvest Biol. Technol.* **2019**, *150*, 89–94. [CrossRef]
39. Fan, X.; Shu, C.; Zhao, K.; Wang, X.; Cao, J.; Jiang, W. Regulation of Apricot Ripening and Softening Process during Shelf Life by Post-Storage Treatments of Exogenous Ethylene and 1-Methylcyclopropene. *Sci. Hortic.* **2018**, *232*, 63–70. [CrossRef]
40. Emadpour, M.; Ghareyazie, B.; Kalaj, Y.R.; Entesari, M.; Bouzari, N. Effect of the Potassium Permanganate Coated Zeolite Nanoparticles on the Quality Characteristic and Shelf Life of Peach and Nectarine. *Int. J. Agric. Technol.* **2015**, *11*, 1411–1421.
41. Crisosto, C.H.; Gugliuzza, G.; Garner, D.; Palou, L. Understanding the Role of Ethylene in Peach Cold Storage Life. In Proceedings of the Acta Horticulturae; International Society for Horticultural Science (ISHS), Leuven, Belgium, 30 June 2001; pp. 287–288.
42. Hu, Q.; Fang, Y.; Yang, Y.; Ma, N.; Zhao, L. Effect of Nanocomposite-Based Packaging on Postharvest Quality of Ethylene-Treated Kiwifruit (*Actinidia deliciosa*) during Cold Storage. *Food Res. Int.* **2011**, *44*, 1589–1596. [CrossRef]
43. Atkinson, R.G.; Gunaseelan, K.; Wang, M.Y.; Luo, L.; Wang, T.; Norling, C.L.; Johnston, S.L.; Maddumage, R.; Schröder, R.; Schaffer, R.J. Dissecting the Role of Climacteric Ethylene in Kiwifruit (*Actinidia chinensis*) Ripening Using a 1-Aminocyclopropane-1-Carboxylic Acid Oxidase Knockdown Line. *J. Exp. Bot.* **2011**, *62*, 3821–3835. [CrossRef]
44. Argenta, L.C.; Mattheis, J.P.; Fan, X.T.; Amarante, C.V.T. Managing "Bartlett" Pear Fruit Ripening with 1-Methylcyclopropene Reapplication during Cold Storage. *Postharvest Biol. Technol.* **2016**, *113*, 125–130. [CrossRef]
45. Escribano, S.; Lopez, A.; Sivertsen, H.; Biasi, W.V.; Macnish, A.J.; Mitcham, E. Impact of 1-Methylcyclopropene Treatment on the Sensory Quality of 'Bartlett' Pear Fruit. *Postharvest Biol. Technol.* **2016**, *111*, 305–313. [CrossRef]
46. Chiriboga, M.A.; Bordonaba, J.G.; Schotsmans, W.C.; Larrigaudiere, C.; Recasens, I. Antioxidant Potential of "Conference" Pears during Cold Storage and Shelf Life in Response to 1-Methylcyclopropene. *LWT* **2013**, *51*, 170–176. [CrossRef]
47. Álvarez-Hernández, M.H.; Martínez-Hernández, G.B.; Avalos-Belmontes, F.; Castillo-Campohermoso, M.A.; Contreras-Esquivel, J.C.; Artés-Hernández, F. Potassium Permanganate-Based Ethylene Scavengers for Fresh Horticultural Produce as an Active Packaging. *Food Eng. Rev.* **2019**, *11*, 159–183. [CrossRef]
48. Salamanca, F.A.; Balaguera-López, H.; Herrera, A. Effect of Potassium Permanganate on Some Postharvest Characteristics of Tomato "Chonto" Fruits (*Solanum lycopersicum* L.). *Acta Hortic.* **2014**, *1016*, 171–176. [CrossRef]
49. Willner, B.; Granvogl, M.; Schieberle, P. Characterization of the Key Aroma Compounds in Bartlett Pear Brandies by Means of the Sensomics Concept. *J. Agric. Food Chem.* **2013**, *61*, 9583–9593. [CrossRef]
50. Yao, M.; Zhou, X.; Zhou, Q.; Shi, F.; Wei, B.; Cheng, S.; Tan, Z.; Ji, S. Low Temperature Conditioning Alleviates Loss of Aroma-Related Esters of "Nanguo" Pears by Regulation of Ethylene Signal Transduction. *Food Chem.* **2018**, *264*, 263–269. [CrossRef]
51. Chai, J.; Liao, B.; Li, R.; Liu, Z. Changes in Taste and Volatile Compounds and Ethylene Production Determined the Eating Window of 'Xuxiang' and 'Cuixiang' Kiwifruit Cultivars. *Postharvest Biol. Technol.* **2022**, *194*, 112093. [CrossRef]
52. Yao, M.; Zhou, X.; Ji, Y.; Luo, M.; Sun, Y.; Zhou, Q.; Ji, S. Potential of Ethylene in Alleviating Cold-Induced Volatile Esters Loss of 'Nanguo' Pears by Regulating the Lipoxygenase Pathway. *Environ. Exp. Bot.* **2022**, *194*, 104723. [CrossRef]
53. Li, X.; Gao, S.; Yang, L.; Yin, M.; Li, J.; Zhang, H.; Ji, S. Ethylene Promotes Ester Biosynthesis through PuERF13/PuDof2.5 Synergically Activated PuAAT1 during Ripening of Cold-Stored 'Nanguo' Pear. *Postharvest Biol. Technol.* **2023**, *195*, 112108. [CrossRef]
54. Serra, S.; Anthony, B.; Masia, A.; Giovannini, D.; Musacchi, S. Determination of Biochemical Composition in Peach (*Prunus persica* L. Batsch) Accessions Characterized by Different Flesh Color and Textural Typologies. *Foods* **2020**, *9*, 1452. [CrossRef]
55. Álvarez-Hernández, M.H.; Martínez-Hernández, G.B.; Avalos-Belmontes, F.; Rodríguez-Hernández, A.M.; Castillo-Campohermoso, M.A.; Artés-Hernández, F. An Innovative Ethylene Scrubber Made of Potassium Permanganate Loaded on a Protonated Montmorillonite: A Case Study on Blueberries. *Food Bioprocess Technol.* **2019**, *12*, 524–538. [CrossRef]
56. Anton, D.; Bender, I.; Kaart, T.; Roasto, M.; Heinonen, M.; Luik, A.; Püssa, T. Changes in Polyphenols Contents and Antioxidant Capacities of Organically and Conventionally Cultivated Tomato (*Solanum lycopersicum* L.) Fruits during Ripening. *Int. J. Anal. Chem.* **2017**, *2017*, 2367453. [CrossRef]
57. Javanmardi, J.; Kubota, C. Variation of Lycopene, Antioxidant Activity, Total Soluble Solids and Weight Loss of Tomato during Postharvest Storage. *Postharvest Biol. Technol.* **2006**, *41*, 151–155. [CrossRef]
58. Rai, G.; Kumar, R.; Singh, A.; Rai, P.; Rai, M.; Chaturvedi, A.K.; Rai, A. Changes in Antioxidant and Phytochemical Properties of Tomato (*Lycopersicon Esculentum* Mill.) under Ambient Condition. *Pak. J. Bot.* **2012**, *44*, 667–670.