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Advances in the use of white light on broccoli and kale postharvest shelf life

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ABSTRACT

In this work, the effect of irradiation with three different intensities of white light-emitting diodes (LED) on the quality and senescence of refrigerated broccoli and green and red kale was studied. A high increase in weight loss was observed in samples exposed to high (80 μmol m^{-2} s^{-1}) and low (10 μmol m^{-2} s^{-1}) LED intensity. Samples stored under mid-intensity (30 μmol m^{-2} s^{-1}) significantly reduced the change of total color (ΔE), hue angle, and lightness (L*) values. Broccoli florets and green kale subjected to mid-intensity illumination retained higher chlorophyll levels than the other treatments ($P < 0.05$), and about 30% more compared to the dark stored samples. These differences were even more evident in red kale. Mid-intensity illumination also markedly reduced sugar losses and improved carotenoid contents. As a whole, results show that the selected intensity of white light used for postharvest illumination has a key influence on treatment efficacy.

Industrial relevance: Postharvest shelf life of green vegetables is very limited and there is a need to use environmentally friendly tools to extend it. The use of white light during storage has been proven to be a clean and non-chemical methodology to delay vegetable senescence, but the appropriate illumination conditions to maximize the quality of unprocessed vegetables are still unknown. In the present work, the effect of different lighting conditions on the visual and nutraceutical quality of refrigerated broccoli and green and purple kale was studied, and the best condition was defined. The selected light intensity may be considered for fresh market storage.

1. Introduction

Brassicaceae is one of the most reputed families, mainly because its species constitute valuable sources of phytochemicals with nutraceutical properties (Di Gioia et al., 2020; Šamec, Urlić, & Salopek-Sondi, 2019). Broccoli, cauliflower, cabbage, brussels sprouts, and rocket are some of the most widespread products. The anciently cultivated kale leaves have also started to gain popularity in recent years for their unique thick green or purple leaves which can be used either raw or processed. Nonetheless, like broccoli, kale is highly perishable and senesces very rapidly upon harvest. Cold storage can improve postharvest life, but even under proper refrigeration, extensive chlorophyll catabolism, sugar degradation, and antioxidant losses would still occur within a few days (Sripong, Janjob, Uthairatanakij, & Jitareerat, 2017). The increasing concern of many consumers on the chemical substances used in the food chain has expanded the interest in physical clean postharvest techniques which can prolong the shelf-life of harvested commodities while reducing the use of synthetic additives.

Proper visible light application along the postharvest chain has been proposed as a simple tool that can offer some benefits in terms of quality maintenance in some commodities (Ilić & Fallik, 2017). The use of Light Emitting Diodes (LED) particularly boosted this possibility, due to their improved energy efficiency, reduced heat production, and longer life-span compared to traditional incandescent sources (Khan & Abas, 2011). Some studies have provided evidence of the utility of lighting treatments to extend the shelf-life of green vegetables such as broccoli and spinach held at room temperature (Ilić & Fallik, 2017; Jin, Yao, Xu, Wang, & Zheng, 2015). Bárcena, Martínez, and Costa (2019) showed that illumination with fluorescent red, and white light delayed the deterioration of red kale leaves stored at 25 °C and 50% RH. Whether or

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not these treatments are still effective under cold storage must be determined, if considered an accurate light treatment as a supplementary strategy to proper temperature management.

White, blue, green and red light were found to improve chlorophyll content and to delay senescence during the postharvest of vegetables (Perera, Navaratne, & Wickramasinghe, 2022). Taking this into account, the use of white light is feasible since in its broad spectrum it contains the aforementioned wavelengths and that applied together can improve the performance of postharvest treatment. On the other hand, the white light source in general is easier to obtain and does not have a negative visual impact on the illuminated vegetables as monochromatic lighting could have.

The outcome of light treatments to delay senescence has shown large variations depending on both the type of vegetable and the radiation conditions applied. In a previous work (Pintos, Hasperué, Vicente, & Rodoni, 2020) we showed that the radiation intensity is one of the main factors determining the efficacy of white illumination to delay senescence in minimally processed broccoli. To the best of our knowledge, the proper intensity required to delay the senescence of most green commodities including whole broccoli inflorescences and kale leaves under refrigerated storage has not been determined yet. Therefore, the present work aims to explore how white LED radiation intensity influences senescence and quality maintenance of fresh broccoli heads and kale leaves.

2. Materials and methods

2.1. Plant material and light treatments

Broccoli heads (*Brassica oleracea* var. *Italica* cv. Legacy), and 18 cm length ± 2 curly kale leaves (*Brassica oleracea* L. convar. *Acephala* (DC) cultivars Darkibor F1 (green kale) and Redbor F1 (red kale) grown in La Plata, Argentina, were harvested at 8:00 AM and transported to the laboratory. Samples were washed for 2 min with NaClO 100 mg L^{-1} adjusted to pH 6.5 and drained for 3 min at room temperature. For storage, selected broccoli heads were conditioned per treatment and arranged vertically in plastic cups wrapped with PVC to avoid excessive dehydration and perforated to prevent gas accumulation. The kale leaves were packed in plastic trays and covered with perforated PVC to reduce dehydration while preventing atmosphere change during illumination. Four broccoli heads and four trays with six leaves each were used for each treatment and storage time. The vegetables were properly arranged in the chambers to assure the same light exposure in all the samples. Broccoli heads and kale trays were stored at 5 °C and 90 ± 1% humidity for 17 days (broccoli) or 11 days (kale) in complete darkness or under the following continuous white LED regimes: a) Low-intensity: 10 μmol m^{-2} s^{-1}; b) Mid-intensity: 30 μmol m^{-2} s^{-1}; c) High-intensity: 80 μmol m^{-2} s^{-1} (around 740, 2300, and 6000 lx respectively for the LED sources used). The trays were directly exposed to the white LED panels (SMD 15 W for low-intensity, SMD 35 W for mid-intensity, and SMD 70 W for high-intensity, Triano, color temperature 4400 K), at a certain distance to reach the mentioned light dose. The LED emission spectrum was determined with a spectrometer (model: AvaSpec-ULS3648- USB2-UA-25, Avantes) (Supplementary Fig. 1). The photonic fluxes reaching the vegetable surface were measured with a light sensor (Radlogger RAD 1, Cavadevices). After 0, 11, and 17 days (broccoli) or 0, 7, and 11 days (kale), samples were taken and immediately analyzed or frozen in liquid nitrogen and stored at −80 °C until use. The frozen broccoli material was the flower buds separated by a scalpel. The entire experiment was repeated twice.

2.2. Weight loss

Broccoli samples were weighed at 0, 11, and 17 days, and kale samples at 0, 7, and 11 days. The percentage of weight loss (WL) was calculated from initial weight (IW) and final weight (FW) as follows: WL (%) = [(IW − FW)/ IW] x 100. Four broccoli heads and six random kale leaves were taken per treatment and per storage day for WL measurements.

2.3. Superficial color

The superficial color was determined with a colorimeter (Minolta CR-300) to obtain the L*, a*, and b* coordinates. The total color difference (ΔE*) was calculated according to Lindbloom (2016). The hue angle was calculated as $H^{\circ} = 180^{\circ} + \tan^{-1}$ (b*/a*). For each storage day, 30 measurements per treatment were recorded for broccoli and 36 for kale.

2.4. Chlorophylls and carotenoids

On each sampling day, three pools of frozen broccoli florets and kale leaves were immersed in liquid nitrogen to obtain a fine and uniform powder after grinding. Then, 1 g (for broccoli) or 0.5 g (for kale) of the obtained powder was mixed with 5 mL of acetone/water (80/20). The homogenate was stirred for 3 min and centrifuged at 5500 ×*g* for 15 min at 4 °C. The supernatant was collected, and the procedure was repeated. For both broccoli and kale, the supernatants of the two extractions were pooled, and total chlorophyll *a*nd carotenoid content were determined in a spectrophotometer, according to Lichtenthaler (1987). Three extracts were done per treatment and sampling date. Results were expressed in mg kg^{-1} on a fresh weight basis.

2.5. Sugars

Frozen tissues were ground as described for chlorophylls and carotenoids, and 0.6 g of the powder was homogenized with 5 mL of ethanol 96% in a vortex for 1 min. The same procedure was followed for broccoli florets and for kale leaves. The mixture was centrifuged at 5000 ×*g* for 10 min at 4 °C. From the ethanolic extract obtained, the total content of soluble sugars was determined by the anthrone method according to Hasperué, Guardianelli, Rodoni, Chaves, and Martínez (2016). Briefly, it was prepared the anthrone reagent by mixing 0.025 g of anthrone, 99 mL of 98% H_2SO_4 (*w*/w), and 51 mL of distilled water. One mL of the reagent was added to 10 μL of ethanol extract, homogenized, and kept at 100 °C in a water bath for 10 min. It was then allowed to cool in the water for 20 min and the absorbance at 620 nm was measured using a spectrophotometer. Three measurements were done per treatment and sampling date. For quantification, a standard glucose solution was used, and the results were expressed in fresh weight as g kg^{-1}.

2.6. Folin-Ciocalteu reactive substances (FCRS)

The ethanolic extract obtained as described in the previous section was used, and the content of reactive substances to Folin-Ciocalteu reagent was determined according to Singleton, Orthofer, and Lamuela-Raventós (1999) with slight modifications. Briefly, 50 μL of the supernatant was added to 950 μL of distilled water and 50 μL of Folin-Ciocalteu reagent diluted 1: 1 in water. After 3 min, 100 μL of a solution of 20% Na_2CO_3 (m/v) in 0.1 M NaOH was added and the resulting solution was incubated at 25 °C for 90 min. Absorbance was measured with a spectrophotometer at 630 nm. Substances that react with FC reagent were quantified using gallic acid (GA) as standard and expressed as FCRS. Three measurements were done per treatment and sampling date. Results were expressed as g GA kg^{-1} of fresh weight.

2.7. Statistical analysis

A factorial design was used, with the factors as the illumination treatment (dark stored Control, Low, Mid, or High-intensity white LED treatments) and storage time (0, 11, 17 days for broccoli, and 0, 7, 11 days for kale). Data were subjected to ANOVA and the means were

compared by Fisher's LSD test using InfoStat software (Di Rienzo et al., 2020) at a significance level of $P < 0.05$. Besides, to have a better interpretation of the data, a Principal Component Analysis (PCA) was done. This multivariate statistical analysis summarizes the high dimensional space of the data set into a smaller set of variables (the principal components, PC) based on correlations with the original variables (Petriccione et al., 2015). PCA identifies similarities between the samples and their associations with the parameters studied. Moreover, the cophenetic correlation coefficient (CCC) was determined as a measurement of how accurately the PCA preserved the original Euclidean distances among data points. Before the analysis, data was standardized and centered.

3. Results

3.1. Weight loss

During storage, the WL was higher in kale than in broccoli ($P < 0.05$). In broccoli, the highest %WL was observed in the samples subjected to low and high LED treatments, while a slower rate of WL was observed in the mid LED and the controls samples, reaching day 17 of storage with WL near 6% for mid-intensity and controls and around 10% for samples treated with low and high-intensity. Comparing kale cultivars, at the end of storage a higher WL was found in red kale than in green kale in all treatments except for the mid-intensity samples (Table 1). In green kale, low and high-intensity treatments exceeded 34% WL at day 11, reaching the end of storage visibly deteriorated. However, in mid-intensity and controls the WL was around 23%. In red kale, it was observed even a higher WL, and the differences observed in controls and mid-intensity treated samples against the low and high-intensity samples were higher than those observed for green kale. In red kale, we observed the same behavior as in green kale and broccoli but with a higher WL. At the end of storage, it was the mid-intensity treatment that caused the lowest WL, even lower than the observed in the controls.

3.2. Surface color

The color was globally assessed in broccoli and kale by determining the total change (ΔE*), which describes the distance from the initial color within the three-dimensional color space. All samples showed an increase in ΔE* parameter throughout storage, but there were clear differences among treatments (Table 2). In broccoli heads, the highest ΔE* was observed for the low-intensity treatment during all storage time. At 17 days of storage, the mid-intensity samples had the lowest ΔE* values, followed by the controls and the high-intensity treated samples. In green kale, it was observed a similar trend in ΔE* among treatments, with the exception that the mid-intensity treatment was effective to maintain lower ΔE* throughout the storage. In green tissues, that is, broccoli and green kale, the differences in color between mid-intensity and the control samples were greater at the last sampling date and were quite evident even with the naked eye. Alike other senescing green tissues, an increase in lightness (L*) along with a drop in the hue angle was recorded during storage in all broccoli and green kale samples (Table 2). In red kale samples, lower increases in the a* values were observed in mid-intensity samples during storage, indicating a slower change from initial red-green to red (Supplementary Table 1). In broccoli and green kale, mid-intensity treated samples showed the lowest increase in L* and maintained higher hue angles in line with better maintenance of green color.

3.3. Chlorophylls

In broccoli, although the chlorophyll content decreased with the storage time, the treatment with mid-intensity LED delayed chlorophyll degradation, followed by the high-intensity. The reduction in chlorophyll content from the pre-storage period until 17 days was below 35% in mid and high-intensity samples, against 57 and 71% for controls and low-intensity respectively (Fig. 1). In kale, there was a decrease in the chlorophyll content during storage in all samples and, as observed in broccoli, mid-intensity treated leaves showed the highest total chlorophyll retention. This was mainly due to a decreased rate of chlorophyll *a* degradation (Fig. 2). In green kale, at day 7 mid-intensity treated samples had 33% more chlorophyll than controls, although that difference was reduced to 19% at day 11. Even though at day 7 the high-intensity samples had more chlorophylls than the controls, they had a more accelerated chlorophyll degradation towards day 11. In red kale, the decrease in chlorophylls was more pronounced than in green kale (Fig. 2). However, higher chlorophyll retention was observed in the samples treated with mid-intensity LED, which had contents 2.5 times higher than the controls. The low and high-intensity red kale samples had higher chlorophyll contents than the controls, although lesser than the mid-intensity treatment.

3.4. Sugar content

Mid and high-intensity treatments induced an increase in sugar content in both broccoli and kale leaves, and an opposite trend was observed in controls. In broccoli, the samples treated with mid and high-intensity had at day 11 storage 17% more sugars than the initial day and reached day 17 with similar contents to that measured at the beginning of the experiment (Fig. 3A). Compared to the controls, at day 11 the samples under mid and high-intensity LED had sugar contents 34 and 32% higher respectively, while at day 17 those differences increased to 50 and 44% respectively. The samples treated with low-intensity LED had the strongest decrease in the sugar content during storage, showing at the end of storage even lower levels than the controls. In the case of kale (both green and red), while in treated samples sugars increased from the harvest to the end of storage, in controls it decreased (Fig. 3B, C). In green kale, samples treated with mid and high-intensity LED doubled at day 7 the sugars measured at the beginning of storage, while low-intensity LED and controls almost did not show differences during this period of storage (Fig. 3B). Towards day 11, the total sugars decreased in all samples, but light treatments reduced that loss, mainly the mid and high-intensity LED. Different from what was observed in green kale, in red kale the sugar content increased at 7 and 11 days of storage, mainly in mid and high-intensity LED treatments (Fig. 3C). Regarding the control samples, as it was observed in green kale, they had

Table 1
Percentage of weight loss (%WL) in broccoli heads and green and red kale stored in darkness or treated with low, mid, or high-intensity white LED during storage at 5 °C for 17 or 11 days for broccoli and kale, respectively. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

	Broccoli			Green kale		Red kale	
Time (d)	11	14	17	7	11	7	11
Control	2.15 ± 0.92 a	4.17 ± 0.42 a	5.26 ± 0.49 a	17.5 ± 4.8 a	22 ± 2.4 a	20.9 ± 5.7 a	34.2 ± 6.8 b
Low-Intensity	4.12 ± 0.99 b	7.42 ± 1.09 b	9.36 ± 1.41 b	24.8 ± 6.6 b	35.8 ± 12.2 b	28.7 ± 8.2 b	47.4 ± 7.3 c
Mid-Intensity	2.66 ± 0.47 a	5.14 ± 0.69 a	6.03 ± 0.38 a	15.7 ± 3.8 a	24.6 ± 6 a	15.8 ± 7.5 a	26.2 ± 5.4 a
High-Intensity	5.05 ± 0.63 c	8.28 ± 0.99 b	10.43 ± 1.05 b	24.6 ± 2.8 b	34.3 ± 3.2 b	32.3 ± 8.3 b	49.9 ± 2.5 c

Table 2
Total color change (ΔE), lightness (L*), and Hue in broccoli heads and green and red kale stored in darkness or treated with low, mid, or high-intensity white LED during storage at 5 °C for 17 or 11 days for broccoli and kale, respectively. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

	Broccoli				Green kale			Red kale		
Time (d)	0	11	14	17	0	7	11	0	7	11
ΔE										
Control	0.0 ± 0.0	3.90 ± 2.30 a	6.01 ± 2.64 a	10.43 ± 4.09 b	0.0 ± 0.0	12.83 ± 2.27 b	18.07 ± 1.88 b	0.0 ± 0.0	5.38 ± 1.12 a	9.46 ± 1.99 a
Low-Intensity		5.64 ± 2.96 b	13.83 ± 2.93 c	17.33 ± 3.22 c		12.01 ± 2.99 ab	16.30 ± 6.14 b		5.17 ± 0.55 a	9.98 ± 1.93 a
Mid-Intensity		4.54 ± 1.18 a	5.41 ± 1.87 a	7.42 ± 3.05 a		8.36 ± 3.45 a	11.47 ± 2.42 a		5.64 ± 3.62 a	7.79 ± 2.82 a
High-Intensity		4.15 ± 1.31 a	7.99 ± 2.98 b	10.72 ± 3.26 b		13.77 ± 5.73 b	19.21 ± 5.56 b		7.34 ± 1.75 b	10.61 ± 2.19 a
L*										
Control	40.5 ± 1.6	40.7 ± 2.65 b	42.8 ± 2.61 ab	46.45 ± 4.24 b	27.94 ± 8	42.16 ± 8.86 b	47.02 ± 8.29 b	26.54 ± 2	29.98 ± 1.62 c	32.46 ± 2.60 c
Low-Intensity		43.2 ± 3.55 c	50.2 ± 3.11 c	52.53 ± 3.46 c		41.13 ± 8.48 ab	45.51 ± 10.48 b		28.79 ± 1.74 b	31.16 ± 3.36 bc
Mid-Intensity		38.6 ± 1.89 a	41.8 ± 2.30 a	43.44 ± 3.90 a		37.22 ± 7.64 a	39.92 ± 5.28 a		28.23 ± 1.78 ab	29.13 ± 2.82 a
High-Intensity		38.6 ± 1.88 a	44.2 ± 3.52 b	47.04 ± 3.73 b		43.56 ± 10.27 b	48.24 ± 8.51 b		27.97 ± 1.34 a	29.96 ± 4.21 b
HUE										
Control	127.2 ± 4	129.7 ± 5.06 b	121.5 ± 4.17 c	109.9 ± 6.38 b	128.7 ± 2.6	122.0 ± 5.47 ab	115.6 ± 7.65 b	–	–	–
Low-Intensity		122.9 ± 7.07 a	105.5 ± 7.93 a	94.2 ± 5.78 a		123.4 ± 5.36 bc	117.7 ± 7.97 b		–	–
Mid-Intensity		133.6 ± 4.09 c	126.8 ± 4.42 d	119.5 ± 7.32 c		124.8 ± 5.18 c	119.5 ± 6.18 b		–	–
High-Intensity		128.5 ± 4.35 b	117.2 ± 6.14 b	108.5 ± 8.86 b		120.1 ± 8.11 a	109.1 ± 8.32 a		–	–

a decrease in sugar contents throughout storage. On day 11 of storage, mid and high-intensity LED samples almost tripled the sugar content compared to the controls, and almost doubled the content in comparison to low-intensity LED samples.

3.5. Hydrophilic and lipophilic antioxidants

3.5.1. Folin-Ciocalteu reactive substances (FCRS)

Antioxidant substances measured by the Folin-Ciocalteu method slightly decreased during storage in broccoli and green kale but increased in red kale (Table 3). In broccoli, while at day 7 the mid-intensity treated samples retained more FCRS than the other light treatments but not the controls, at day 17 had the highest FCRS. In green kale, FCRS decreased during storage in all samples, mainly in the low-intensity ones, which had at the end of storage, lower contents than mid-intensity and controls. In red kale, the FCRS increased during storage in all samples except for the high-intensity samples. On both day 7 and day 11, the mid-intensity samples had higher levels of FCRS than the controls, and at the end of storage were the high-intensity samples which had the least FCRS content.

3.5.2. Carotenoids

In broccoli, the carotenoids increased during storage in the samples treated with mid and high-intensity LED while in the controls there were no changes (Table 3). These variations were not observed on day 11 but on day 17 when it was observed in the mid and high-intensity treatments an increase in carotenoid content by 25% compared to controls. On day 17, in broccoli there were no differences in carotenoid content between low-intensity LED and controls. In kale, both green and red, the difference between treatments in carotenoid content was also observed towards the end of the storage. While in green kale the carotenoid content was maintained in the samples treated with mid-intensity, it decreased in the controls and high-intensity samples ($P < 0.05$). Regarding red kale, although carotenoids decreased in all samples during storage, towards day 11 the samples treated with mid-intensity showed a tendency to preserve the carotenoid content to a greater extent than high-intensity and control samples ($P < 0.1$).

3.6. Principal component analysis and correlation analysis

To assess the efficacy of the LED treatments on the three groups of samples analyzed, a PCA with the physical (color and %WL) and the chemical (carotenoid, chlorophylls, sugar content, and FCRS) parameters was performed. The scores plot (which defines the position of the mean values of the original data in the new space) and the loading plots (which indicate the direction of each original variable) are displayed in Fig. 4a and b, while the reports of the loadings of the variables and the accumulated variation for the main components, can be found in the Supplementary Information. The CCC value was = 0.9, which indicates that an accurate reduction was achieved with the analysis (Schenk, Ferrario, & Guerrero, 2018). Besides, the eigenvalues revealed that the two main principal components (PC) accounted for 75.9% of the total variance in the dataset and the samples could be correctly classified into 3 different clusters which corresponded to broccoli, green, and red kale.

The lightness (L*) was positively correlated to PC1, while the chemical parameters carotenoids, and chlorophylls were negatively correlated. As previously explained (Section 3.2), during senescence the lightness of the samples increased, while the chlorophylls and carotenoids degraded. Therefore, it could be concluded that the main PC was correlated with the parameters that best reflect deterioration throughout storage. In line with this idea, in all the samples, the storage time increased in the horizontal direction of PC1.

On the other hand, the parameters positively associated with PC2 were b* and ΔE, whereas hue and a* were negatively associated. This

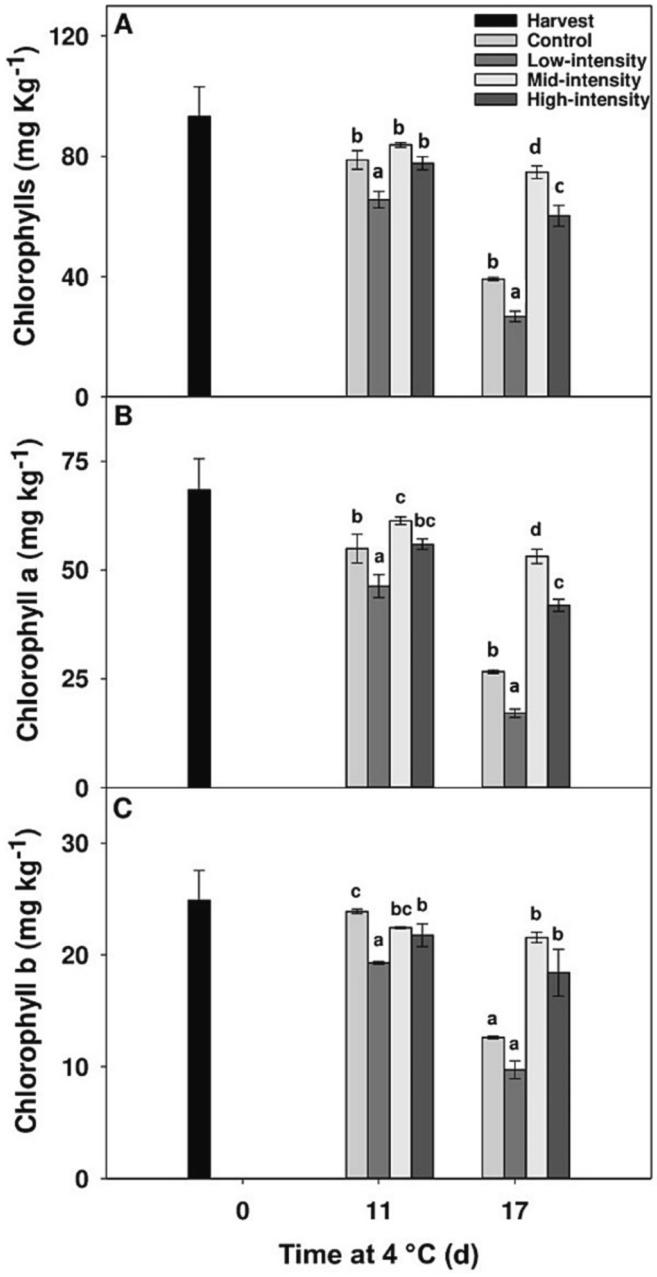

Fig. 1. Chlorophyll content in broccoli. (A) Total chlorophylls, (B) Chlorophyll *a*, (C) Chlorophyll *b* stored at 5 °C in darkness or treated with low, mid, or high-intensity white LED for 11 or 17 days. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

indicates that PC2 was better related to the color parameters. A detailed inspection of the disposition of the broccoli samples in Fig. 4a suggests that the ripening of this product could be followed not only by the increase in PC1 but also in PC2. This indicates that broccoli senescence can be described by the color changes during storage: an increase in b*, and a reduction in a* and hue, and a similar tendency was observed in green kale. In contrast, red kale deterioration was not properly related to PC2, this indicates that its senescence is better described by the chemical parameters and L* accounted in PC1 and not by the color parameters in PC2 such as hue. Finally, in all the cases the mid-intensity light was the condition that best preserved the biocomposites at levels similar to the initial ones.

4. Discussion

Previous studies have shown diverse responses to postharvest white light treatments, from no benefits (Aliniaeifard, Falahi, Dianati Daylami, Li, & Woltering, 2020; Mastropasqua, Tanzarella, & Paciolla, 2016) to real improvement (Casajús et al., 2021; Hasperué, Guardianelli, et al., 2016; Hasperué, Rodoni, Guardianelli, Chaves, & Martínez, 2016; Liu et al., 2015). This is probably due to differential responses depending on the type of product, degree of processing, and variations in the lighting conditions themselves. In this sense, it is essential to know the best light conditions (i.e. light intensity) for each plant species to delay the loss of quality of the product during postharvest, which is generally represented as weight loss, superficial color, and nutraceutical quality. In this work, the illumination, as well as the light intensity, were factors that strongly influenced the postharvest quality. The color is the main quality attribute in all green vegetables, which undergo an increase in luminosity during storage, and chlorophyll catabolism is in most cases the key reaction leading to limiting the shelf life of these products (Büchert, Civello, & Martínez, 2011; Koukounaras, Siomos, & Sfakiotakis, 2007). In broccoli or green kale, high-intensity treated samples showed similar or lower hue values than the control, indicating that improper choice of light intensity for postharvest illumination could lead to deleterious effects on quality retention. In the case of red kale, which had heterogeneity in the leaf blade color due to the presence of anthocyanins, the hue angle was not accurate to rate the color evolution. In green tissues, the main pigment that provides color is chlorophyll. In the present work, the effect of light treatment on color both in broccoli and in kale appears not to have been due to a difference in synthesis but to a delay in chlorophyll degradation. This could be due in part to the inhibitory effect of light on the expression of genes of enzymes related to chlorophyll degradation, such as pheophytinase (Büchert et al., 2011), given i) the potential for photosynthesis to proceed under low temperatures is very restricted and that ii) under the illumination conditions usually used, the plant tissue would be under the light compensation point (amount of light required for the rate of photosynthesis to be equivalent to the rate of respiration). Based on that chlorophyll content declined under far-red light while red light delayed its degradation, Costa, Montano, Carrión, Rolny, and Guiamet (2013) suggested that retarding effect on senescence of postharvest illumination may be mediated by phytochromes and not for net photosynthesis. This is still speculative because there could be effects without the mediation of light receptors i.e., metabolic modifications by modulation of endogenous reactive oxygen species levels and redox state at the cellular level. In future studies, it would be interesting to evaluate the response of light receptor mutants to postharvest illumination to deepen the understanding of the role of phytochromes, cryptochromes, or other photoreceptors in the visual appearance of treated vegetables.

The marked protective effect of irradiation treatments on sugar levels deserves special attention. In both broccoli and kale, we observed throughout storage a higher sugar content in samples treated with the highest light intensities. The increase in metabolic rate with senescence is well-known and it is associated with an increase in the energy required for the reactions of "organized disorganization" that it involves. If we excluded the possibility of a significant contribution of postharvest photosynthesis, that could partly explain why during storage, non-illuminated samples showed a reduction of the sugar content while this was not observed in some light-treated samples which showed a slowdown of senescence. However, the sugars measured in broccoli in the mid and high-intensity LED samples at day 11 were even higher than at the beginning of storage, and the same was observed for those treatments in green and red kale on days 7 and 11 of storage. Similar results were obtained by Noichinda, Bodhipadma, Mahamontri, Narongruk, and Ketsa (2007) who found that the use of a fluorescent white source on chinese kale during cold storage, increased the sugar content with respect to day 0. These results contrast with those reported by Favre, Bárcena, Bahima, Martínez, and Costa (2018) in broccoli, and

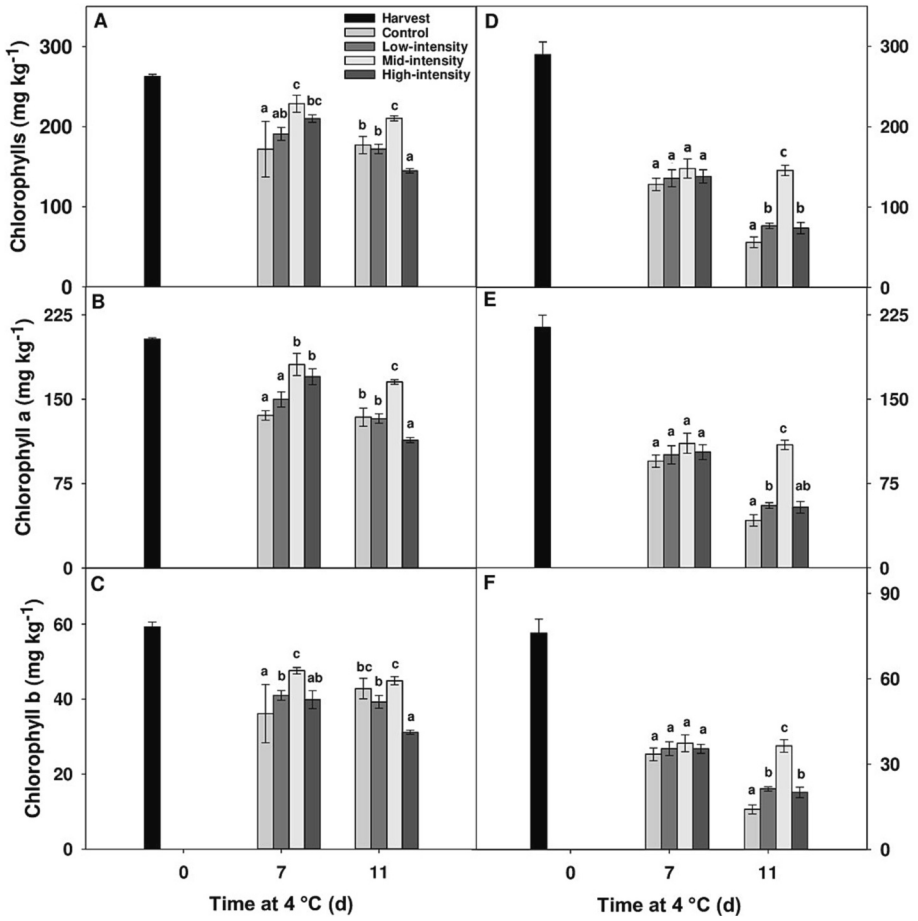

Fig. 2. Chlorophyll content in green (A, B, C) and red (D, E, F) kale. (A, D) Total chlorophylls, (B, E) Chlorophyll *a*, (C, F) Chlorophyll *b* stored at 5 °C in darkness or treated with low, mid, or high-intensity white LED for 7 or 11 days. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

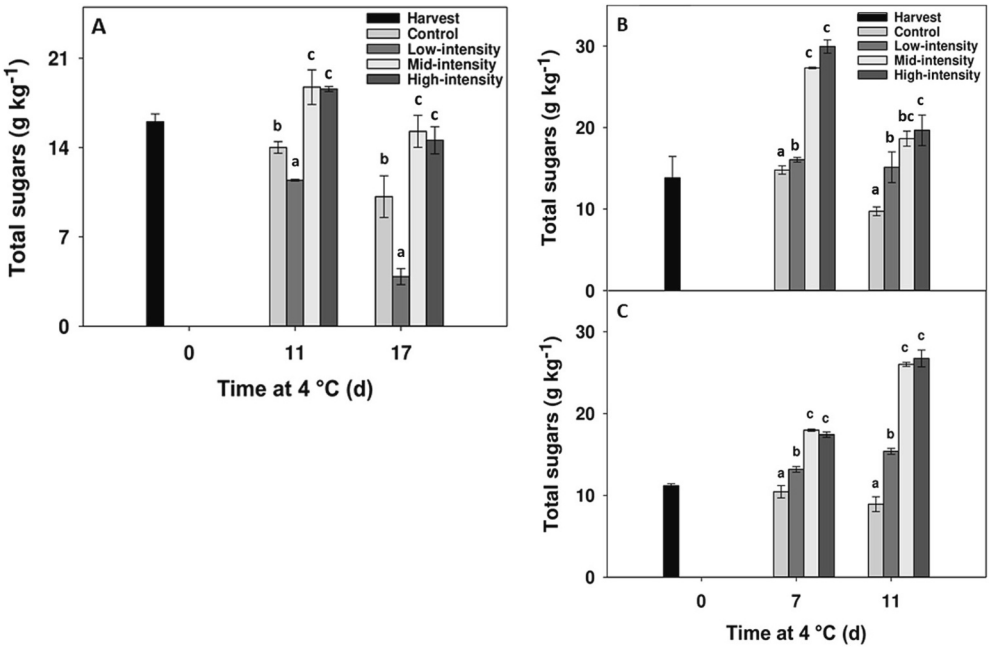

Fig. 3. Total sugars in broccoli (A), green (B) and red (C) kale stored at 5 °C in darkness or treated with low, mid, or high-intensity white LED during storage. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

Table 3
Hydrophilic (FCRS) and lipophilic (carotenoids) antioxidants in broccoli heads and green and red kale stored in darkness or treated with low, mid, or high-intensity white LED during storage at 5 °C for 17 or 11 days for broccoli and kale, respectively. FCRS are expressed in mg g^{-1}, and carotenoids in mg kg^{-1}. Data represent means ± standard deviation. Different letters along a single storage day indicate significant differences based on a LSD test at a significance level of $P < 0.05$.

	Broccoli			Green kale			Red kale		
Time (d)	0	11	17	0	7	11	0	7	11
FCRS									
Control	5.6 ± 0.12	5.7 ± 0.04 c	5.0 ± 0.06 b	3.0 ± 0.12	2.9 ± 0.11 a	2.6 ± 0.22 b	1.9 ± 0.19	2.1 ± 0.08 a	2.7 ± 0.05 b
Low-Intensity		5.2 ± 0.02 a	4.8 ± 0.01 a		2.4 ± 0.26 a	2.1 ± 0.06 a		2.5 ± 0.03 bc	2.5 ± 0.08 b
Mid-Intensity		5.7 ± 0.03 c	5.5 ± 0.08 c		2.5 ± 0.12 a	2.5 ± 0.05 b		2.6 ± 0.09 c	3.2 ± 0.04 c
High-Intensity		5.4 ± 0.09 b	4.8 ± 0.08 ab		2.8 ± 0.36 a	2.3 ± 0.13 ab		2.2 ± 0.22 ab	1.7 ± 0.10 a
Carotenoids									
Control	16.6 ± 5.36	16.7 ± 1.33 a	16.0 ± 0.42 a	47.3 ± 7.76	41.2 ± 1.16 a	39.3 ± 2.45 ab	50.5 ± 1.92	34.4 ± 3.9 a	26.4 ± 3.7 a
Low-Intensity		18.9 ± 1.54 a	17.6 ± 1.09 a		47.4 ± 2.39 b	43.5 ± 2.28 bc		37.2 ± 2.98 a	31.0 ± 0.70 ab
Mid-Intensity		18.3 ± 0.23 a	21.9 ± 0.79 b		44.0 ± 2.08 ab	48.5 ± 3.03 c		39.0 ± 3.87 a	35.4 ± 1.38 b
High-Intensity		18.0 ± 0.30 a	22.2 ± 0.24 b		44.7 ± 2.15 ab	35.5 ± 0.24 a		34.9 ± 1.08 a	26.9 ± 3.3 a

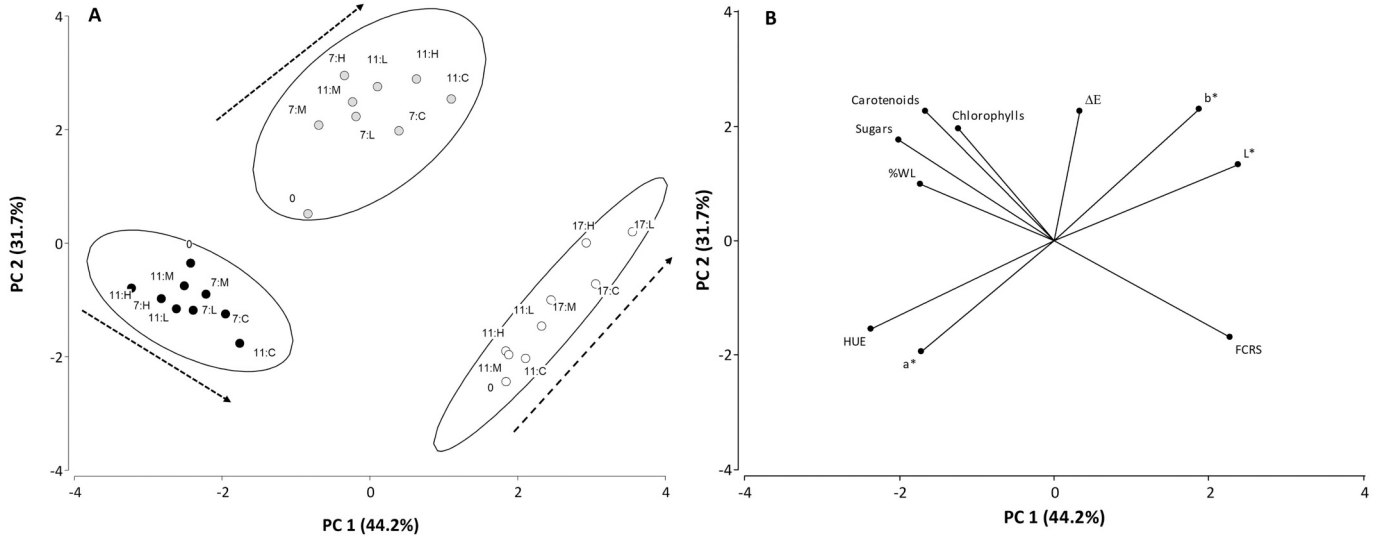

Fig. 4. Principal Component Analysis (PCA) scatter plots of (A) broccoli (0, 11 or 17 days), green and red kale (0, 7 or 11 days) stored at different light conditions (C: no light; L: low; M: mid or H: high intensity) and the loading plots (B) of the chemical parameters and color. The dashed line indicates the direction of the senescence for each vegetable in the new space.

Bárcena et al. (2019) in red kale, which found higher sugar contents in light-treated samples compared to controls in dark, but the measured contents were lower than those observed at the beginning of the storage. This discrepancy may be explained by the refrigeration conditions we used during the storage, which caused a slowdown in metabolism that could favor sugar accumulation. It could be speculated that the higher sugar levels measured in the illuminated samples could be due to differences in amylase activity, or the degradation of cell wall polysaccharides. However, in kale, not only an increase in glucose and fructose was determined, but also in sucrose (data not shown). This sugar accumulation leads us to speculate also that at least part of the carbohydrates measured in the illuminated samples came from photosynthesis during storage, mainly in the treatments with higher light intensity.

Beyond the clear positive response of the mid-intensity treatment on broccoli and kale quality attributes, it is of interest to analyze in more detail the different responses of high and low-intensity treatments. Although these conditions were not as effective as mid-intensity, both showed a certain positive effect concerning controls stored in the dark, but in well-differentiated quality attributes: low-intensity lighting did not improve green color retention, although it favored sugar retention to a lesser extent. In contrast, high-intensity lighting was more favorable in the retention of sugars, and strikingly not beneficial in color retention and the delay of yellowing. It seems that at very low intensities the modification of plant metabolism by light was not enough to maintain quality, added to a greater loss of water through transpiration, probably due to a greater stomata opening in postharvest illuminated tissues (Martínez-Sánchez, Tudela, Luna, Allende, & Gil, 2011). On the other hand, under high light intensity, the plant showed signs of deterioration, possibly due to oxidative stress due to exposure to this light intensity (Glowacz, Mogren, Reade, Cobb, & Monaghan, 2015).

Considering all the parameters evaluated, classical statistical analysis and PCA indicated that mid-intensity white illumination was the condition that most effectively prevented tissue yellowing in whole broccoli heads and green and red kale leaves. It is still a challenge to find an adequate way of sending adequate radiation to post-harvest products since on many occasions they are packaged and stacked so that the light does not easily reach inside the packages. In developing countries, broccoli and kale are commonly marketed fresh in more or less compact tied according to the supplier. Light application in these cases is more feasible since vegetables are not covered by a container and storing the packages properly on the shelves can allow access to the light. Although the installation costs of a lighting system must be considered, it is worth highlighting the long life of LED sources compared to incandescent sources. On the other hand, in markets where these products are sold in individual compact packages, for example, a greater headspace of these

packages could be considered to favor movement of the product within the package, so that allows alternating exposure to the lighting. In these cases, a rotation of containers with a certain frequency in the gondola should be considered.

5. Conclusions

Exposure to white light at a proper intensity is beneficial in extending the shelf life of broccoli and kale even under refrigerated conditions. In any case, it is crucial to establish the optimal intensity to use since this factor is central in determining the efficacy of the treatments. Mid-intensity (≈30 μmol m^{-2} s^{-1}) illumination proved to be effective to delay yellowing and prevent sugar losses in broccoli heads and kale leaves. This was especially significant in red and green kale, in which the treatment was more effective. Lower or higher light intensities are not as effective as the mid-intensity in delaying leaf quality deterioration, and the choice of inappropriate light intensity can increase vegetable deterioration. The use of white light during broccoli and kale storage at proper intensities may be useful to supplement the benefits of refrigeration. In the case of packaged presentations, turning the packets of vegetables on different days of storage could improve the treatment uniformity. Also, further analysis aimed at the development of packing settings with better light penetration in bulk packages can be useful to increase the technological relevance of this clean postharvest technology.

CRediT authorship contribution statement

Federico Pintos: Formal analysis, Investigation. **Luis Rodoni:** Investigation. **Mariela Patrignani:** Formal analysis. **Pablo Ixtaina:** Resources. **Ariel Vicente:** Conceptualization, Writing – review & editing, Funding acquisition. **Gustavo Martínez:** Conceptualization, Writing – review & editing. **Joaquín Hasperué:** Conceptualization, Formal analysis, Investigation, Writing – original draft, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ifset.2023.103373.

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