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Quality preservation of walnut kernels using edible coatings

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SUMMARY: The objective of this work was to evaluate the performance of various edible coatings for preserving the quality of walnut kernels (W) during storage. Three edible coatings based on carboxymethyl cellulose (CMC), methyl cellulose (MC) and whey protein isolates (WP) were prepared. Coated and uncoated walnuts (WC) were stored for 210 days at room temperature (23±2 °C). After 210 days, WC presented the highest peroxide value (PV = 3.06 meqO2/kg), conjugated dienes (CD = 3.01) and trienes (CT = 0.31), pentanal, nonanal, hexanal, and decane, 5,6-bis (2,2-dimethylpropylidene) contents. Meanwhile, WMC showed the lowest PV (1.20 meqO2/kg), CD (2.26) and CT (0.17) and the lowest decrease in carotenoid content (0.60 mg/kg). The L* value measured in walnut oil decreased in all samples. MC, CMC and WP coatings showed protection on walnuts against the deterioration process. MC coating displayed the best performance.

KEYWORDS*: Coatings; Oxidation; Preservation; Walnuts*

RESUMEN: ***Conservación de la calidad de los granos de nueces utilizando recubrimientos comestibles.*** El objetivo de este trabajo fue evaluar el comportamiento de cubiertas comestibles para preservar la calidad de nueces (W). Tres tipos de cubiertas fueron estudiadas: carboximetilcelulosa (CMC), metilcelulosa (MC) y aislados proteicos de suero de leche (WP). Las nueces con y sin cobertura (WC) fueron almacenadas durante 210 días a temperatura ambiente (23 ± 2 °C). WC presentó los valores más altos para indicadores químicos de oxidación lipídica (índice de peróxidos (PV) = 3,06 meqO_2/kg; dienos conjugados (CD) = 3,01 y trienos conjugados (CT) = 0,31) y para volátiles de oxidación (pentanal, nonanal, hexanal y decane,5,6-bis(2,2-dimethylpropylidene). Por el contrario, WMC presentó los menores PV (1,20 meqO2/kg), CD (2,26) y CT (0,17) y la menor desaparición de carotenoides (0,60 mg/kg). El valor L* medido en el aceite de nuez decreció en todos los tratamientos. Las cubiertas comestibles MC, CMC y WP exhibieron efecto protector en el deterioro de las nueces. MC fue la que presentó mejor comportamiento.

PALABRAS CLAVE*: Cubiertas comestibles; Nueces; Oxidación; Preservación*

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1. INTRODUCTION

The walnut (*Juglans regia* L.) is a crop of high economic importance for the food industry (Martínez *et al.,* 2013). For this reason, the cultivated area is rapidly growing in many countries (Christopoulos and Tsantili, 2011). The crop is only harvested once a year, so it is very important to preserve the chemical and sensory qualities of the kernels until the next year's harvest. The most abundant chemical component of walnut kernels is the oil, which constitutes 52 to 70% of the kernel mass (Zwarts *et al*., 1999; Grosso *et al.,* 2017). Walnut oil is considered unique because it presents high levels of polyunsaturated fatty acids (PUFA), with a perfect balance of n-6 and n-3 PUFAs. The consumption of oils containing the ideal ratio of these fatty acids (4:1) has been shown to decrease the risk of cardiovascular disease (Martínez *et al.,* 2011). PUFAs have also been associated with other health-promoting properties. The lipid oxidation of walnuts results in losses of essential fatty acids and vitamins, the appearance of off-flavors, and the generation of toxic compounds and color changes which decrease their nutritional, sensory, chemical and economic value and limit the shelf-life of walnut kernels (Salcedo *et al.,* 2010; Grosso *et al.,* 2017).

Product stability depends on the preservation of quality parameters during storage and is a key issue when determining shelf-life and distribution logistics. Previous studies have demonstrated that the sensory, microbiological and chemical quality of different types of foods and their raw materials can be preserved by applying an edible coating. Edible coatings are a type of biodegradable active packaging material that can extend shelf-life and enhance the functional properties of food products by improving the stability of their lipids (Gayol *et al.,* 2009; Embuscado and Huber, 2009; Grosso *et al.,* 2017; Riveros *et al.,* 2018; Larrauri *et al.,* 2016). Previous research has focused on the effect of chitosan added with green tea extract on walnuts (Sabaghi *et al.,* 2015), soy protein isolates (Kang *et al.,* 2012), pea starch, whey protein isolate, and carnauba wax coating (Mehyar *et al.,* 2012) on the nut's quality. The research makes a contribution to the knowledge about the preservation of the chemical quality parameters of walnuts using commercial edible coatings for an extended period of time. The objective of this work was to evaluate the performance of various edible coatings in preserving the quality of walnut kernels during 210 days of storage at room temperature (23 ± 2 °C), by studying physical and chemical variables.

2. MATERIALS AND METHODS

2.1. Materials

Fresh butterfly walnut kernels (Chandler variety) harvested in April, 2016 were provided by Nogales S.R.L, Argentina. The walnuts were stored (warehouse) at room temperature until they were bought in May, 2016. Then, they were stored in the freezer (-20 °C) until the beginning of the experiment.

Carboxymethyl cellulose (CMC) (Parafarm ®) and methyl cellulose (MC) (Parafarm ®) were obtained from SAPORITI S.A.C.I.F.I.A. (Buenos Aires, Argentina), and whey protein isolates (WP) were purchased from Todo Droga (Córdoba, Argentina) to prepare the coatings.

2.2. Methods

2.2.1. Edible coating preparation

CMC coating: A 0.5% (w/v) solution of CMC was prepared and glycerol was added as a plasticizer (1.9%, w/v) (Grosso *et al.,* 2017).

MC coating: A 2% (w/v) solution of MC was prepared and glycerol was added as a plasticizer (1.9%) (Grosso *et al.,* 2017).

WP coating: A 11% (w/w) solution of WP was prepared and 11 g glycerol were added to the solution (Grosso *et al.,* 2017).

Walnuts were immersed in containers with the corresponding coating solution (CMC, MC, and WP) for 5 minutes. After that, they were removed and put in a strainer for 5 minutes to let the excess solution drip off. Finally, the coated walnuts were placed at room temperature under hood for 24 h to dry off the excess moisture. The final moisture contents (%) in the walnut kernels after the drying process were: 4.05 in WC, 4.52 in WCMC; 5.94 in WMC and 4.24 in WWP. Four treatments were prepared using unshelled walnuts: uncoated walnuts (WC, control sample); and coated walnuts with CMC (WCMC), MC (WMC), and WP (WWP).

2.2.2. Storage study

The walnuts (WC, WCMC, WMC, and WWP) were stored in 15 x 25 x 5 cm plastic containers (Tupperware, Buenos Aires, Argentina) at room temperature (23±2 °C) under normal atmosphere conditions (20-21% O_2; 60-70% RH) for 210 days, which are the usual conditions for storing these products. Each container was loaded with 1 kg of walnut kernels. The samples were analyzed for physical-chemical parameters (peroxide value, carotenoid content, conjugated dienes and trienes and 4 volatile compounds) at 0, 35, 70, 105, 140, 175 and

210 storage days. The experimental design consisted of 4 treatments (WC, WWP, WCMC, and WMC) x 3 replicates of each treatment x 10 chemical variables x 7 periods of time. The physical variable (color) was determined at the beginning and at the end of storage.

2.2.3. Chemical analysis: Peroxide value, conjugated dienes and trienes, and carotenoid content

These analysis were performed on walnut oil. The oil was obtained by cold pressing 20 g of walnuts, using a 20-ton press (HE-DU, Hermes I. Dupraz S.R.L., Córdoba, Argentina). Peroxide value was measured according to AOAC (2010). Conjugated dienes and trienes were measured at 232 nm and 268 nm, respectively (COI, 2001). Carotenoid contents were analyzed at 470 nm following the procedures described by Mosquera *et al.,* (1991).

2.2.4. Volatile analysis

The volatile compound analysis of the walnut samples was performed in walnut kernels by headspace solid phase microextraction fiber (HS-SPME) according to Martin et al. (2016). The SPME fiber used was divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm, StableFlex, 1-cm long (Supelco). Raw walnut kernels (2 g) were ground using a mill (FBR 3 ® Decalab S. R. L, Buenos Aires, Argentina) and placed in vials at 70 °C for 20 min. The fiber was exposed to the vial headspace for 10 min and then injected into a Gas Chromatograph (Perkin Elmer Clarus 600) coupled with a mass detector. An ELITE 5MS (30 * 0.25 mm i.d., 0.25 mm film thickness; Perkin Elmer) column was used. Chromatographic responses of detected volatile compounds (peak area electronic counts) were monitored for comparison of each compound among samples (Quiroga, Asensio and Nepote, 2014).

2.2.5. Physical analysis: walnut oil color

Color measurements were taken on the oil samples on a white background with a Minolta colorimeter (Minolta CM-508d, Tokyo, Japan). The CieLab parameters (L*, a* and b*) for each sample were measured at least in five random positions. The measurements were performed at 3 different periods of time: 0, 105, 210 days.

2.2.6. Statistical analysis

Three replicates of the experiment were made. The data were analyzed using InfoStat software, version 2016p. A two-way analysis of variance (factors: 'treatment' and 'time') and LSD-Fisher was used to detect significant differences among treatments (ANOVA, $\alpha = 0.05$). Pearson coefficients were calculated to establish correlations among dependent variables. A principal component analysis (PCA) was performed on the correlation matrix of normalized data. The objective of the PCA analysis was to explore associations among treatments and variables. A Cluster Analysis (CA) was carried out to obtain groups of walnut treatments with similar characteristics. Sample similarities were calculated using the Euclidean distance, and groups of walnut treatments with similar characteristics were obtained using the unweighted pair-group method (UPGMA).

3. RESULTS AND DISCUSSION

3.1. Chemical analysis: Peroxide value, conjugated dienes and trienes, and carotenoid content

The changes in the PV and CD and CT of WC, WCMC, WMC and WWP are illustrated in Figure 1. Peroxide formation proceeds slowly in the initial stages of oxidation. However, in the later stages, it acts as a catalyst in oil oxidation (Moslehi *et al.,* 2015). In this study, the PV increased for all walnut samples during the storage period. The increase was the highest in WC (Figure 1a). The PV measured on the first day of storage (0 days) was 0.37 meqO_2/kg, and no significant differences among the treatments were detected ($\alpha > 0.05$). In the middle of the storage period (day 105), differences in the mean values among treatments began to appear. The Argentinean Food Code allows for a maximum of 10 meqO_2/kg for nut products (Riveros *et al.,* 2013). Moreover, correlation coefficients higher than 0.6 were observed among the chemical variables (PV, AV and CD) and the sensory variables (oxidized and cardboard flavors) related to the lipid oxidation process (Olmedo *et al.,* 2009). On the last day of storage (day 210), WMC exhibited the lowest PV (1.20 meqO_2/ kg), followed by WCMC (2.26 meqO_2/ kg), and WWP (2.53 meqO_2/ kg). WC experienced the highest increase in PV (3.06 meqO_2/ kg). These results showed that the application of the CMC, MC and WP coatings to walnut samples generated a protective effect on the product during the storage period. In terms of the PV, the coating that had the most significant protective effect was MC. Methyl cellulose is a flexible and transparent polysaccharide tailored from cellulose. It was reported to have moderate strength, resistance to oil and fat migration, and acts as moderate barrier to moisture and oxygen (Maftoonazad and Ramaswamy, 2005). Because of these factors, it can be assumed that methyl cellulose inhibits oxidation in the coated walnut kernels.

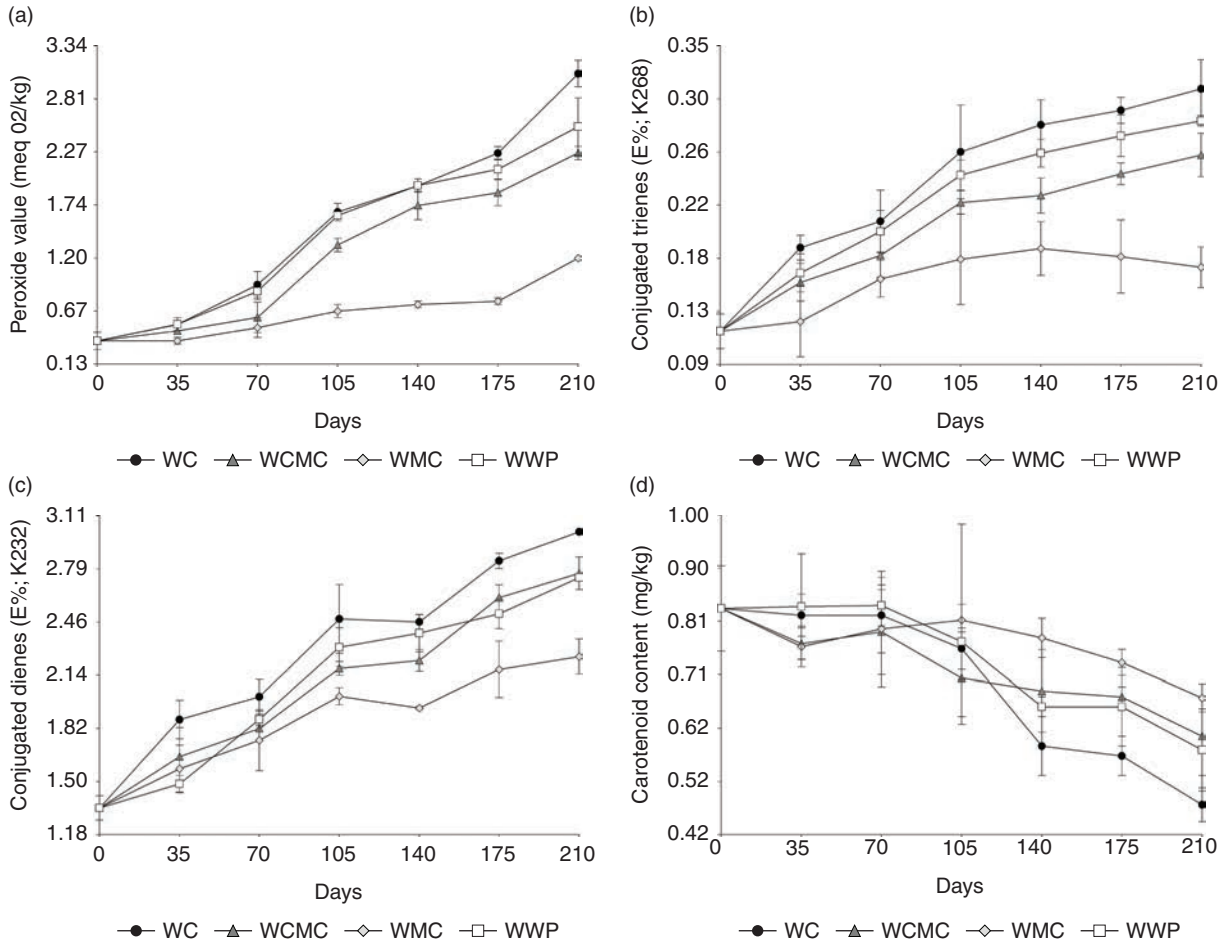

FIGURE 1. (a) Peroxide value (meq O2/kg), (b) Conjugated trienes (E1%, K268), (c) Conjugated dienes (E1%, K232), (d) Carotenoid content (mg/kg) in walnut samples coated with carboximethyl cellulose (WCMC), methyl cellulose (WMC) and whey protein (WWP); and walnuts without coating (WC) analyzed during 210 days of storage (n = 3; α = 0.05).

Moslehi *et al.,* (2015) found that pistachios coated with MC had the lowest PV after four months of storage, and Grosso *et al*., (2017) found that MC coating had a preserving effect in the intensity of the characteristic walnut flavor which reduced the development off-flavors related to lipid oxidation. In a different study, the maximum PV occurred in non-coated control samples; walnuts coated with chitosan and green tea extract had significantly ($p < 0.05$) lower PV value after 18 weeks of storage (Sabaghi *et al.,* 2015). Other works have shown that CMC coatings also provide significant protection against lipid oxidation in other food products such as almonds (Larrauri *et al.,* 2016) and peanuts (Riveros *et al.,* 2013).

The CD is related to the formation of hydroperoxides, conjugated dienes and carboxylic compounds, while CT reflects the concentrations of secondary oxidation products formed from the initial compounds detected at 232 nm (Ancin Azpilicueta and Martínez Remírez, 1991) The samples showed an increase in both parameters during the storage period (Figure 2.b). On storage day 0, there were no significant differences among the treatments ($p \leq 0.001$). Significant differences were found at subsequent storage periods. On the last day measured, WMC exhibited the lowest values for CD and CT (2.26 and 0.17, respectively) while, WC displayed the greatest values for these parameters (3.01 and 0.31, respectively). Once more, MC acted as a barrier between walnuts and the atmosphere, preventing gas exchange and, as a consequence, lipid oxidation. This was previously studied in coated pistachios (Moslehi *et al.,* 2015) and avocados (Maftoonazad and Ramaswamy, 2005) where MC coating lessened moisture losses and respiration rates. Other studies have also found lower values of CD in products protected with edible coatings.

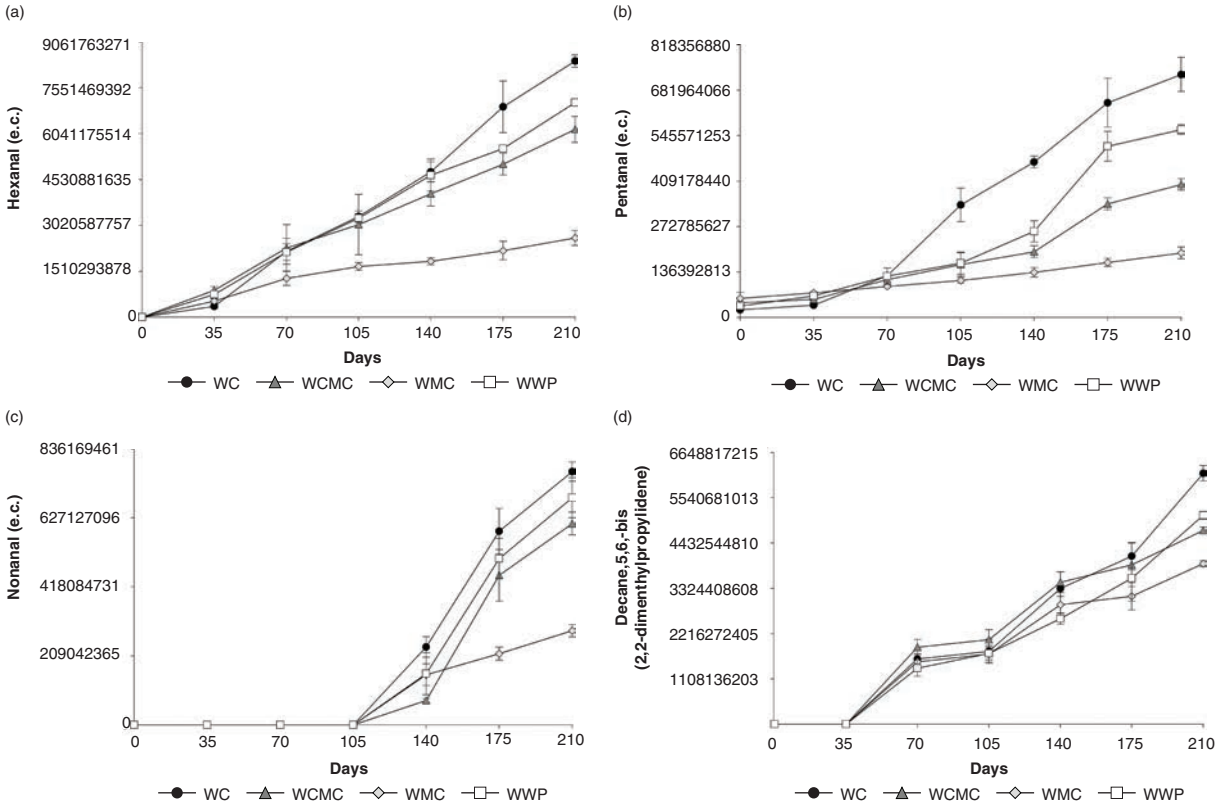

FIGURE 2. (a) Hexanal, (b) Pentanal, (c) Nonanal, (d) Decane, 5,6-bis (2,2-dimethylpropylidene) measured in electronic counts in walnut samples coated with carboximethyl cellulose (WCMC), methyl cellulose (WMC) and whey protein (WWP), and walnuts without coating (WC) analyzed during 210 days of storage (n = 3; α = 0.05).

Riveros *et al.,* (2013) reported that peanuts coated with CMC presented the lowest CD after 56 days of storage, followed by samples coated with MC. In a different work, Riveros *et al.,* (2016) also reported that sunflower seeds without coating had higher CD than sunflower seeds coated with CMC.

Carotenoids are compounds that play an important role in the oxidative stability of walnuts because they can act as antioxidants (Özrenk *et al.,* 2012). The main cause of carotenoid loss is oxidation (Dias, Camões and Oliveira, 2014). The carotenoid content of the samples decreased during the storage period, although no significant differences in the mean values were detected until storage day 140 (Fig 1.d). On the last day of storage, the sample with the lowest carotenoid content was WC (0.48 mg/kg), followed by WCMC, WMC, and WWP (0.60, 0.67, and 0.58 mg/kg, respectively). This indicates that the WC sample suffered greater oxidation, while the coated samples were protected against the oxidation of carotenoids. In a research investigating the effect of edible coatings consisting of native and modified maize and cassava starches on carotenoid retention in pumpkin during drying showed that carotenoid degradation was minimized and therefore, a significant improvement was found in the carotenoid contents of dehydrated pumpkin slices which were previously coated with native and modified maize and cassava starches (Yousuf *et al.,* 2018).

3.2. GC-MS volatile compounds analysis

In the present study, different volatile compounds were detected in walnut kernels by GC/MS analysis. Table 1 summarizes the compounds identified in the walnut treatments on the first day of storage. During the storage period, the quantities of the volatile compounds changed (Figure 2). The most remarkable changes occurred in pentanal, nonanal, hexanal, and decane,5,6-bis (2,2-dimethylpropylidene). These compounds increased during the storage period and reached their maximum values on the last day measured (day 210). The presence of hexanal and nonanal is directly related to the development of rancid flavors in lipid-rich foods (Quiroga, Asensio and Nepote, 2014). On day 0, neither hexanal nor nonanal were found in any of the samples (Table 1). During the storage period, hexanal

TABLE 1. Volatile compounds (electronic counts 10^6) per gram of walnuts coated with carboximethyl cellulose (WCMC), methyl cellulose (WMC) and whey protein (WWP), and walnuts without coating (WC) analyzed in fresh product (storage day 0).

	Treatment			
Volatile compound	**WC[a]**	**WCMC[a]**	**WMC[a]**	**WWP[a]**
Alcohols				
Cyclopropyl carbinol	42.22±5.78 a	49.29±0.73 a	49.73±3.25 a	46.40±4.97 a
Aldehydes				
Pentanal	22.62±3.59a	44.22±4.55b	56.93±7.73b	34.27±1.45a
Butanal	56.23±4.40 b	40.83±3.36 a	44.87±1.83 a	50.46±3.28 ab
Aliphatic hydrocarbons				
Nonane	99.08±9.90 a	107.54±4.69 a	109.54±6.74 a	125.14±9.72 a
Tridecane	82.52±5.61 a	88.78±1.17 a	85.12±7.33 a	77.14±1.50 a
Tetradecane	1005.19±103.91 a	1037.93±28.97 a	1061.90±128.28 a	958.26±60.88 a
Pentadecane	973.34±46.06 a	1096.18±74.28 a	919.53±10.06 a	1035.50±97.56 a
Hexadecane	1340.96±2.65 a	1611.12±83.74 a	1457.32±111.56 a	1354.51±120.74 a
Pentadecane, 2-6-10-14-tetramethyl	54.70±9.77 a	50.58±4.75 a	44.89±2.92 a	49.27±4.41 a
Dodecane, 2,6,10-trimethyl-	362.98±55.88 a	420.24±26.98 a	377.04±12.37 a	384.61±18.52 a
Decane,5,6-bis(2,2-dimethylpropylidene)	ND	ND	ND	ND
Aromatic hydrocarbons				
Benzene, 1-methyl-2-(1-methylethyl)-	295.43±57.90 a	292.79±30.65 a	261.32±20.61 a	264.78±4.81 a
Benzene derivates				
Benzothiazole	39.26±17.74 ab	75.34±14.48 a	64.43±6.96 b	90.05±13.12 b
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-, methylcarbamate	124.89 a	199.30±5.75 b	138.08±11.43 a	145.48±11.67 a
Organic acids				
Oxalic acid	35.77±4.21 a	3.502±1.75 a	30.79±2.38 a	32.21±1.17 a
Oxalic acid, allyl pentadecyl ester	106.29±7.49 a	125.97±6.52 a	102.30±6.51 a	112.81±8.59 a
Amines				
N-Thio-valero-morpholine	351.97±33.29 a	356.50±31.21 a	277.33±31.18 a	299.98±18.01 a
Terpenes				
3-Cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)-	148.04±20.35 a	135.19±2.55 a	132.32±13.91 a	135.63±14.31 a
Esters				
Sulfurous acid, cyclohexylmethyl hexyl ester	743.95±24.09 a	888.97±69.30 a	691.59±108.10 a	775.98±69.26 a

ND = Not detected
[a] Mean values ± standard deviations followed by different letters in each row indicate significant differences at $\alpha = 0.05$ (n = 3, LSD Fisher).

started to increase from day 35, while nonanal was detected from day 126 (Figures 2.a and 2.c). On the last day of measurement, significant differences among walnut treatments were found ($p \leq 0.001$). WC presented the highest values for hexanal, nonanal and pentanal. On the other hand, WMC was the treatment which presented the lowest amounts of volatile compounds related to lipid oxidation. Larrauri *et al.,* (2016) reported for roasted coated almonds stored for 126 days at 40 °C that hexanal and nonanal increased in all samples. However, almonds coated with CMC and CMC+antioxidants had significantly lower levels of these compounds. Crowe *et al.,* (2002) showed that the levels of hexanal (aldehyde) increased as walnut sensory quality deteriorated. Elmore *et al.,* (2005) reported that hexanal was the volatile compound present in the highest quantities in walnut samples, followed by 1-pentanol, pentanal, 1-hexanol and 1-penten-3-ol. Most of these compounds are mainly formed from the oxidation of linoleic acid.

Another compound that showed intriguing behavior was decane,5,6-bis (2,2-dimethylpropylidene)

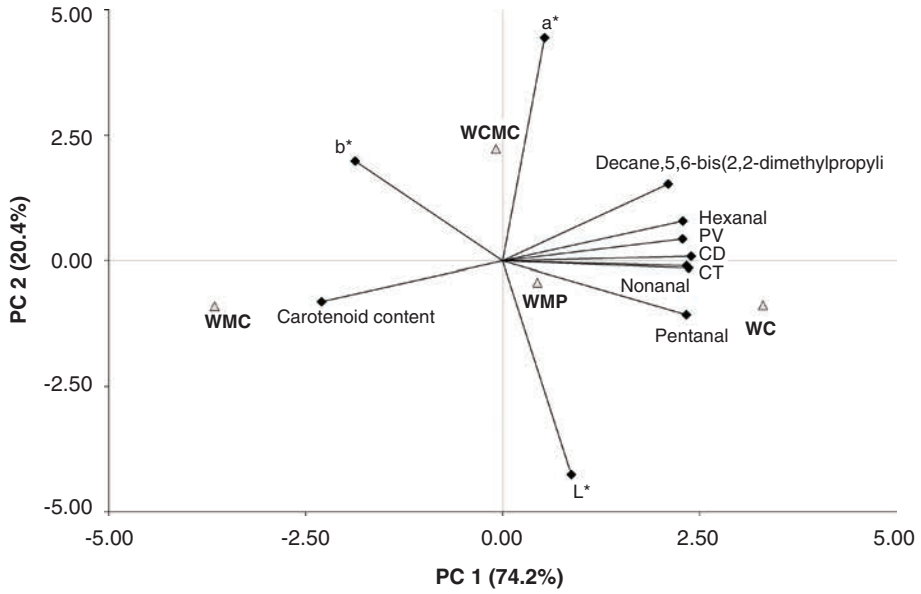

FIGURE 3. Bi-plots of principal component analysis. Independent variables: peroxide value (PV), conjugates dienes (CD), conjugated trienes (CT), hexanal, nonanal, pentanal, decane, 5,6-bis (2,2-dimethylpropylidene)-, a*, b*, L* and carotenoid content. Treatments: walnuts coated with carboximethyl cellulose (WCMC), methyl cellulose (WMC) and whey protein (WWP), and walnuts without coating (WC).

(Figure 2.d.) Martin *et al.,* (2016) reported that this compound was found in peanut kernels stored in different types of packaging. Decane, 5,6-bis (2,2-dimethylpropylidene) showed an increase from day 0 to day 210. On the first day of measurement, this compound was not found in any of the treatments, while on the last day measured, WC presented the highest amount, followed by WWP and WCMC. WMC contained the lowest quantity.

3.3. Physical analysis: Color

Walnut color has a direct relationship with pigment and phenolic contents which are contained mainly in the skins of the seeds (Christopoulos and Tsantili, 2011). These compounds play an important role in protecting fatty acids from oxidation (Salcedo, López de Mishima and Nazareno, 2010). On the other hand, it is known that lipoxygenase (LOX) catalyses the hydroperoxidation of lipids containing free fatty acids with an activated methylene group between the two double bonds such as linoleic and α-linolenic acids, and has a significant effect on the stability, taste and color of plant-based products (Baysal and Demirdoven, 2007). Like most enzymes, LOX activity is accelerated by adding water or solutions to food products and can affect their color. Color changes in walnut kernels during storage were evaluated by analyzing the changes in lightness (L value), green/red components (a* value), and blue/yellow components (b* value). At the beginning of the experiment, the color parameters of WC, WCMC, WMC and WWP showed negative values for a*, positive values for b* and a high lightness value (L*). At the end of storage, the a* value was more negative in WC (-1.145) suggesting an increase in its greenness, followed by WMC and WWP and WCMC. This change could be attributed to the oxidation of skin pigments. Opposite results were found in coated avocados with MC where the a* value was more negative in coated samples, indicating the avocado skin to be greener; then, with the passing of time, the color shifted towards a positive a* value, which indicates more redness in color as a result of ripening (Maftoonazad and Ramaswamy, 2005). In the case of b*, there was an increase compared to the first day, but no significant differences were found among samples. Finally, the L* value decreased for all samples. On the last day measured (210), WMC (70.46) and WCMC (70.37) presented the lowest values, followed by WWP (70.66) and WC (70.75). This color change in the L* value indicated lower brightness due to storage time. Manzocco *et al.,* (2001) also reported that the L* in walnuts decreased during storage. In addition, Maftoonazad and Ramaswamy (2005) found that coated samples with MC presented lower decreases in L* values. A descriptive study about the sensory qualities of walnuts with edible coatings (Grosso *et al.,* 2017) also showed that the color intensity of the kernels increased during storage. In addition, a

direct relationship between this attribute and oxidized flavor was found. In this research, the browning and color quality deterioration which occurred in the samples probably occurred because of LOX enzymatic oxidation.

3.4. Principal component analysis

A PCA was conducted in order to understand the behavior of the different treatments with respect to their ability to preserve the oxidative stability of walnuts during storage. The biplot obtained from the first two principal components (PC) in the PCA is presented in Fig. 3. The first two PC explained 94.4% data variability over the 210 storage days. CD, CT, PV, L*, a*, b*, nonanal, hexanal, pentanal and decane,5,6-bis (2,2-dimethylpropylidene) were placed on the right side (PC1) of the biplot. There was a positive association among these variables; and they were negatively related to carotenoids and b*. WC was placed on the right side of the plot close to the volatile compounds and to the lipid oxidation indicators. On the other hand, WMC and WCMC were placed on the left side of the plot opposite these indicators and the WC sample. This behavior was consistent with the obtained results, where edible coatings presented a better performance in protecting walnuts from deterioration, and in particular, the sample coated with MC. In the plot, WMC was positively associated with carotenoid content, which is an indicator of product quality preservation.

These associations were confirmed by the correlation analysis (Pearson coefficients). Pentanal and hexanal showed the strongest correlation of all the volatile compounds analyzed, represented by a coefficient of 0.93. Pentanal and hexanal were also highly correlated with nonanal with coefficients of 0.86 and 0.84, respectively. Decane, 5,6-bis (2,2-dimethylpropylidene) was most strongly correlated with hexanal (0.86). Larrauri *et al.,* (2016) also found a positive correlation between hexanal and nonanal in a storage study performed on coated almonds. In the current study, chemical lipid oxidation indicators were also correlated. For example, PV showed a 0.89 correlation coefficient with CD, and 0.84 with CT. CD was highly correlated with CT (0.87). Martin *et al*., (2016) also found a positive correlation between CD and PV in a storage study on peanut samples stored in different types of packaging, while Asensio *et al.,* (2011) found a similar correlation of PV with CD and CT in a stability study on olive oil flavored with oregano essential oil. In the present study, these chemical indicators were also correlated with the volatile compounds. Hexanal was correlated with PV and CD (Pearson's coefficients of 0.95 and 0.89, respectively). Quiroga, Asensio and Nepote (2014) reported a positive association between hexanal content and oxidation indicators (peroxide value) in a storage study on sunflower seeds with the addition of antioxidants. In the present study, carotenoids were negatively correlated with the chemical oxidation indicators mentioned above. Asensio *et al.,* (2011) also found negative correlations for carotenoid content with CD, CT and PV in samples of extra-virgin olive oil with added oregano essential oil.

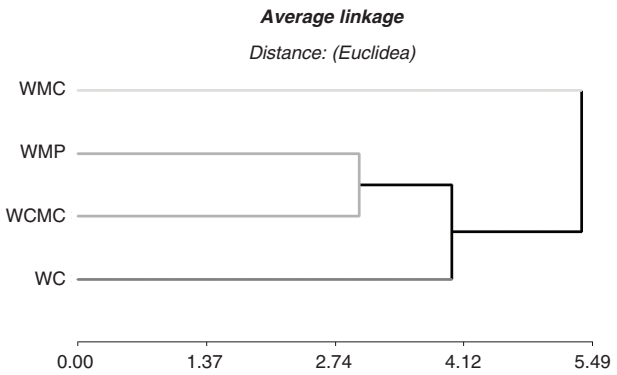

FIGURE 4. Dendrogram from cluster analysis of walnuts coated with carboximethyl cellulose (WCMC), methyl cellulose (WMC) and whey protein (WWP), and walnuts without coating (WC) considering physical and chemical variables measured during storage.

3.5. Cluster analysis (CA)

The results from the CA, which consider the dependent variables studied, are presented as a dendogram (Fig. 4). Three groups were identified in the cluster analysis. Group 1 was formed by WC; Group 2 was formed by WCMC and WWP; and Group 3 was formed by WMC. These results indicate that the control sample, which experienced the greatest changes during storage, was the most oxidized sample and different from the rest of the treatments. Based on the measured indicators, WCMC and WWP showed intermediate behavior. WMC was alone in Group 3 due to its different performance during storage. This treatment was the least affected by the oxidation process. This result was in accordance with the PCA, in which WMC was the sample most separated from other samples in the bi-plot and was placed on the opposite side of the graph with respect to the lipid oxidation indicators.

4. CONCLUSIONS

In general, the use of carboxy methyl cellulose, methyl cellulose and whey protein edible coatings on walnuts helps to prolong the shelf-life of the kernels by preserving their chemical and physical quality properties. The use of methyl cellulose coating lessens the deterioration of walnut kernels.

Therefore, the use of edible coatings, especially those containing methyl cellulose, can be used in the food industry as an alternative method to prolong the overall quality and shelf-life of walnuts.

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