Effect of traditional dehydration processing of pepper jalapeno rayado (Capsicum annuum) on secondary metabolites with antioxidant activity

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ABSTRACT

Jalapeno rayado peppers (Capsicum annuum) are usually subjected to a traditional smoke-dehydration process using Quercus sp. This treatment provides peppers with their characteristic functional attributes. To differentiate the production of antioxidant metabolites during the dehydration-smoking process, this process was compared with convective dehydration, both at 60°C. A higher antioxidant activity in smoke-dried pepper was observed due to the increase in concentration of phenolic compounds, flavonoids and Maillard products in the last hours of the process and was related to the presence of radicals with m/z (-) values: 585.32, 292.2, 326.18, 653.28, 240.11 and 210.14, generated during both dehydration processes. The change in colour was mainly due to the increase of Maillard compounds. Convective dehydration favoured the extraction of capsaicinoids, whereas no significant change was observed in smoke-dehydration, and carotenoid degradation was 40% with either process. A similar final moisture content was achieved in both processes.

Efecto del proceso de deshidratación artesanal del chile jalapeño rayado Capsicum annuum, en los metabolitos secundarios con actividad antioxidante

RESUMEN

El chile jalapeño (Capsicum annuum) suele ser sometido a un proceso de deshidratación-ahumado tradicional empleando leña de Quercus sp. Este tratamiento le confiere atributos funcionales característicos. Para diferenciar la producción de metabolitos antioxidantes durante el proceso de deshidratación-ahumado, este proceso se comparó con deshidratación convectiva, ambos a 60°C. Una mayor actividad antioxidante en chile deshidratado-ahumado se observó debida al incremento en la concentración de compuestos fenólicos, flavonoides y productos de Maillard en las últimas horas del proceso, y se relacionó con la presencia de radicales con valores m/z (-): 585.32, 292.2, 326.18, 653.28, 240.11 y 210.14, generados en ambos procesos de deshidratación. El cambio de color se debió principalmente al aumento de compuestos de Maillard. La deshidratación convectiva favoreció la extracción de capsaicinoides, mientras que en el deshidratado-ahumado no se observó un cambio significativo, y con ambos la degradación de carotenoides fue de 40%. En ambos procesos se alcanzó un contenido de humedad final similar.

Introduction

The genus Capsicum is characterized by metabolites with antioxidant properties and proven effects against diseases such as carotenoids, capsaincoids and phenolic compounds (Oboh, Puntel, & Rocha, 2007). Hitherto, 52 carotenoids have been identified in chilies (Giuffrida et al., 2013), which determine the characteristic colour of the fruits; as well as 8 different capsaincoids responsible for the pungency, though 90% is due to capsainc and dihydrocapsainc (Kozukue et al., 2005). In chili peppers, vanillic, benzoic, caffeic, ferulic, synapic, and p-coumaric acids, quercetin, rutin, luteolin, apigenin and their respective glucosides have been reported (Mohktar et al., 2015; Morales-Soto, Gómez-Caravaca, García-Salas, Segura-Carretero, & Fernández-Gutiérrez, 2013). During the dehydration of chili, heat treatment can improve the extraction of several compounds; however, there are some undesirable modifications in some metabolites as moisture is decreased (Topuz, Dincer, Özdemir, & Kushad, 2011; Turkmen, Sari, & Velioglu, 2005).

Pepper jalapeno rayado (Capsicum annuum var. annuum) differs from commercial jalapeno pepper given the ripe ‘jalapeno rayado’ has clear brown lines of jagged texture, denominated “corchosidades”. This variety is widely processed and consumed in the state of Hidalgo, Mexico (21°04’23”N and 98°48’25”W). During harvesting, the environmental conditions are high relative humidity and constant drizzle, preventing the use of solar energy, which has led to the preference for more than a century of the use of smoke-drying in craft furnaces for 3-4 days. In these furnaces, smoke generated by the combustion of oak wood is used. The dehydration with evergreen oak wood allows the conservation or small losses of carotenoids in the form of paprika de La Vera from Spain (Pérez-Gálvez, Hornero-Méndez, & Mínguez-Mosquera, 2005). Velázquez et al. (2014) showed that smoke-drying of chili for the production of paprika preserves the antioxidant activity of the paprika for a longer time, attributed to the methoxyphenols of the smoke that are incorporated into the product. During the
dehydration of chili, the formation of Maillard compounds is induced (Ruñán-Henares, Guerra-Hernández, & García-Villanova, 2013). These compounds are indicators of protein degradation and/or damage; on the other hand, sugars–amino acids and rutin–lysine chemical reaction models have shown to increase antioxidant capacity (Vhangani & Van Wyk, 2016; Zhang et al., 2016). Therefore, it is important to identify the antioxidant metabolites of chili and the formation of Maillard products, which contribute to the functional and colour attributes in the final product, when the pepper jalapeno rayado is dehydrated and smoked with oak wood; it is important also to differentiate between this kind of peppers and those treated by convective dehydration, which require hot air at the same temperature.

Material and methods

Raw material and reagents

Chili peppers jalapeno rayado (C. annuum) were used at commercial ripeness, when more than half of the fruit acquires a red colour and shows light brown lines in the pericarp, from here this state is referred as “fresh-red”. All the reagents used were analytical grade, and the solvents for UPLC-MS were spectrophotometry grade.

Dehydration treatments

Convective dehydration

In order to discriminate the effect of smoke-drying, 7 kg of jalapeno rayado peppers at commercial maturity were placed in a 1.2 m × 1.2 m metal mesh fashioning a 5-cm layer and dehydrated in a convective dryer (VEMAG, Germany) maintaining a drying inlet-air temperature of 60°C for 36 hours. Under these conditions the fruit surface temperature was between 47°C and 55°C during the process, which was measured with a laser thermometer (Raynger®ST, Raytek, USA), performing 10 measurements at random positions, every 180 min.

Smoke-drying

The traditional oven was built with wood and clay, with rectangular shape of 1.2 m × 1.2 m and 1 m height. At the bottom front, it had a 40 cm × 40 cm gap where the firewood was placed. At the top, a wooden grid was placed to support the chili peppers. Samples of 150 kg of fresh-red peppers were dried, keeping the drying air inlet temperature at 60°C, as measured at the base of the drying chamber. In the artisanal oven using firewood of Quercus sp. and free convection, the average surface temperature of chili peppers was between 42°C and 52°C, measured with a laser thermometer, performing 10 measurements at random positions, every 180 min, for 3 days.

Randomly, 100 fruits were placed on the surface of the drying grid, determining weight loss every 180 min. Lots (n = 10) were formed after 10% weight loss intervals. At the end batches of n = 30 were formed. The samples were freeze dried, after removing seeds and peduncles; afterwards, they were ground and stored in amber flasks at −80°C for further analysis.

Water activity (a_w) and moisture content

The determinations were made in whole smoke-dried chili without peduncle using an analyzer (Model Aqualab 4T, Decagon, USA) at 25°C. The moisture content was determined according to AOAC methods (934.06, 1997).

Extraction and quantification of capsaicinoids

The extraction was carried out according to Collins, Wasmund and Bosland (1995) with some modifications, by placing 0.5 g of sample and 5 mL of acetonitrile at 80°C for 4 h. The extract was filtered through 0.22 μm membrane prior to injection to HPLC (Agilent 1200 Infinity®, Agilent, USA). The chromatographic method was carried out according to Igbal, Amjad, Asi and Ariño (2013) using an isocratic mobile phase (acetonitrile:water, 60:40) with a flow rate of 0.8 mL/min, for 15 min. The column was C18 (Zorbax SB-C18, 5 μm, 4.6 × 150 mm, Agilent, USA) at 30°C. Detection was set at 280 nm. Calibration curves were performed by the external standard method using capsaicin and dehydrocapsaicin.

Extraction and quantification of carotenoids

Placing 0.3 g of chili sample with 30 mL of acetone in a stirrer at 100 rpm for 1 h. The blend was filtered and the residue was re-suspended in 20 mL of acetone under the same conditions for 30 min. Both extracts were transferred to 10 mL of petroleum ether. The extract was saponified for 1 h with 1 mL of 10% KOH in methanol, washed with water up to neutral pH, and dried with Na2SO4. The spectrophotometric quantification (Thermo Scientific, USA) of carotenoids in petroleum ether was expressed in mg equivalents of β-carotene/g of sample d.b., according to Rodríguez-Amaya (2001).

\[
\text{Total carotenoids (μg)} = \frac{A_y \times 10^6 \times FD}{A_{1\%1cm}^{100}}
\]

Where y is the capacity volume (mL); FD, the dilution factor; A is absorbance at 450 nm; A1%1cm is the specific absorption coefficient of β-carotene in petroleum ether (2592).

Extraction of phenolic compounds

The method proposed by Alvarez-Parrilla, De La Rosa, Amarowicz and Shahidi (2011), with some modifications, was used. Portions of 0.5 g were sonicated (Bransonic® 5210, USA) with 10 mL of 80% methanol for 30 min; the supernatant was removed and the residue was extracted once more with 10 mL of 80% methanol. Both extracts were combined and filtered. The extract was evaporated to dryness and suspended in 10 mL of distilled water.

Quantification of phenolic compounds

Total phenolics

These were determined by the Folin-Ciocalteau method (Medina-Juárez, Molina-Quijada, Del Toro Sánchez, González-Aguilar, & Gámez-Meza, 2012) after some modifications: a sample of 20 μL of diluted extract was placed in a U-bottom translucent microplate and mixed with 90 μL of the Folin-Ciocalteau reagent and 90 μL of Na2CO3 solution (60 g/L) were added; then, it was incubated for 90 min. Absorbance was measured at 750 nm using a microplate reader (Synergy H1, Biotek, USA). The total content of phenolic compounds was reported as mg equivalents of gallic acid (EAG)/g d.b.
Total flavonoids
The colorimetric method was used according to Alvarez-Parrilla et al. (2011) using a spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific, USA). Total flavonoid content was reported as mg equivalents of quercetin (EQ)/g d.b.

Extraction and quantification of Maillard compounds
Portions of 0.05 g of sample were extracted with 5 mL of deionised water, sonicating for 10 min, accordingly to Delgado-Andrade, Morales, Seiquer, and Pilar Navarro (2010).

Browning index
The extract was 4-fold diluted and its absorbance was read at 420 nm using a microplate reader (Kim & Lee, 2009).

Fluorescent Maillard compounds
The lysine–glucose reaction was prepared in duplicate (0.05 M and 0.075 M, respectively), according to the methodology of Yamaguchi, Nomi, Homma, Kasai and Otsuka (2012), with some modifications. Lysine and glucose were placed in 10 mL of 0.2 M sodium phosphate buffer (pH 6) at 93°C (boiling point at 585 mmHg) for 120 min. On the other hand, the extracts in deionized water were 6-fold diluted and were placed in a black plate for the microplate reader. The excitation and emission spectrum in lysine-glucose and extracts were scanned. The excitation/emission maxima at 350/415 nm were determined to measure the fluorescence intensities in the extracts.

Colour
A colour reader (CR-10, Konica Minolta, USA) was used to determine L, a and b parameters in powder samples using D65 illuminating conditions at 10°. Then \( L^*, a^*, b^* \) were obtained to calculate \( \Delta E \), where \( L_0^*, a_0^*, b_0^* \) are parameters of fresh-red pepper:

\[
\Delta E = \left[ (L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2 \right]^{0.5}
\]

Antioxidant capacity
Portions of 0.05 g of sample were placed in 10 mL of different solvents, namely (a) distilled water and (b) 80% methanol. Samples were sonicated for 15 min and filtered.

DPPH (1,1-diphenyl-2-picrylhydrazyl) Radical Scavenging Activity
The method reported by Medina-Juárez et al. (2012) was followed, which was set to 3.9 mL of DPPH (0.08 mg/mL) with 0.1 mL of extract. After 30 min, samples were read at 515 nm in a spectrophotometer (Genesys 10S UV-Vis, Thermo Scientific, USA).

Oxygen Radical Absorbance Capacity (ORAC) assay
The extracts were 300-fold diluted, and the ORAC assay was done according to Alvarez-Parrilla et al. (2011), using a microplate reader. A Trolox calibration curve was obtained, expressing the values as \( \mu \text{mol} \) of Trolox/g d.b. The solutions and dilutions of the sample were prepared using sodium phosphate buffer at pH 7.4.

Identification of antioxidant compounds by UPLC–ESI–MS
Extracts were prepared in water and 80% methanol by mixing 1 g of sample with 10 mL of solvent and sonicating for 30 min; the extraction was repeated and both extracts were combined. The water extract was evaporated to 1 mL and filtered before being injected. While the extract with 80% methanol was purified according to the method of Materska and Perucka (2005); with a SEP-PAK C18 * cartridge (Waters, USA) with 100% water and then 40% methanol. Both fractions were mixed and filtered before being injected.

The chromatography separation was performed on an Acquity H Class UPLC® (Waters, USA) equipment with Acquity H Class UPLC® BEH C18 (2.1 x 50 mm, 1.7 μm) using as mobile phase A: water with 0.01% formic acid, B: acetonitrile; under the following gradient elution: 0 min, 100% A and 0% B; 1.7 min, 92% A and 8% B; 7.3 min, 80% A and 20% B; 9 min, 62% A and 38% B; 10 min, 100% A and 0% B, holding for 2 min. The flow rate was 0.4 mL/min. The injection volume was 5 μL. The injection was performed in duplicate. The chromatographic system was coupled to a Xevo G2-XS TOF® spectrometer, with an ESI interface, using the negative ionization mode in a range from 100 to 2000 Da. The capillary voltage and cone voltage were set at 1.95 kV and 30 V, respectively. The desolvation gas was set to 554 L/h at 200°C, there was no cone gas, and the source temperature was at 150°C.

Statistical analysis
One-way ANOVA test, one-way ANOVA with factorial arrangement and Tukey’s test were performed. The software InfoStat (ver. 2015) was used (Di Rienzo et al., 2015), setting a level of significance \( \alpha = 0.05 \).

Results and discussion
The moisture content of the fresh-red pepper was 6 g/g d.b., in the dehydrated product this parameter was 0.76 g/g d.b., whereas in the smoke-dried product it was 0.89 g/g d.b.

Table 1 shows the content of the main antioxidant metabolites present in chili pepper jalapeno rayado, as well as after the processing of dehydration and smoke-drying. An increase in the content of total phenolics, capsaicin and dihydrocapsaicin as an effect of the dehydration process was found. The smoke-drying process favoured the increase

| Concentration (mg/g d.b.) | Fresh-red | Dried | Smoke-dried |
|---------------------------|-----------|-------|-------------|
| Total phenolics (gallic acid equivalents) | 1.98 ± 0.06 | 4.82 ± 1.93 | 11.34 ± 0.77 |
| Capsaicin | 1.20 ± 0.12 | 2.48 ± 0.41 | 1.74 ± 0.18 |
| Dihydrocapsaicin | 0.46 ± 0.03 | 1.04 ± 0.12 | 0.61 ± 0.04 |
| Total carotenoids (β-carotene equivalents) | 1.43 ± 0.18 | 0.82 ± 0.08 | 0.83 ± 0.03 |

Table 1. Antioxidant metabolites of jalapeno rayado peppers fresh-red, dried and smoke-dried.
of the content of phenols and flavonoids, in a ratio of 2:1 and 10:1, respectively, while the content of capsaicinoids was not modified. Both treatments decreased carotenoid content by 40%.

**Capsaicinoids**

Fresh-red jalapeno rayado pepper has 1.2 and 0.46 mg/g d.b. of capsaicin and dihydrocapsaicin, respectively. Similar concentrations of capsaicinoids have been reported in this genotype (Giuffrida et al., 2013; Kozukue et al., 2005). The convective dehydration process increased twice the concentration of both capsaicinoids, compared to fresh-red pepper (Table 1). Yaldız, Ozguven and Sekeroglu (2010) found an increase in capsaicin content after in-cabinet dehydration processing with drying air temperatures between 40°C and 60°C; although similar temperatures were reached in convective dehydration and smoke-drying in the present work, no significant change was found in the latter. This increase in the convective-dehydrated product may be due to the release of capsaicinoids from the food matrix due to thermal damage, while in the smoke-dried one, a longer exposure to heat might induce oxidation of these released capsaicinoids (Topuz & Ozdemir, 2004) and, consequently, no change was observed in the final content of capsaicinoids. Comparable results have been reported for chipotle production, where even a loss occurs after a period of smoke-drying for 4 days (Moreno-Escamilla et al., 2015).

**Carotenoids**

Red chili had an initial content of 1.37 mg of β-carotene/g d.b.; the loss of carotenoids was not significantly different between convective dehydration and smoke-drying. In both cases, processed chilies showed a 40% loss in relation to fresh-red chili (Table 1); contrary to Moreno-Escamilla et al. (2015), who mentioned that there was no change in the carotenoid content of jalapeno peppers after dehydration (transformation to chipotle).

With a water activity of 0.975 at 21 h of dehydration (see Table 2), an 8% increase in carotenoid content was observed. Carotenoid synthesis has also been reported during natural convective drying in jalapeno pepper and in paprika de La Vera (Pérez-Gálvez et al., 2005; Topuz et al., 2011). In those works, the results have been related to an incomplete ripening of harvested fruits, which ends during the early stages of dehydration; nevertheless, in the following stages of the traditional drying process, there is a significant loss of carotenoids, such as was observed in smoke-drying process. According to Schweigert, Schieber and Carle (2005) is because of the action of lipoxygenases continues given these enzymes require a temperature higher than 90°C for their inactivation.

**Phenolic compounds**

In the fresh-red state, jalapeno-rayado pepper contained 9.45 mg of GAE/g d.b., 14.76 mg GAE/g d.b. in dehydrated chili, while in smoke-dried 19.14 mg GAE/g d.b. were found (Table 1). Regarding the total flavonoids, there was no significant increase due to convective dehydration. However, an increase in total flavonoids was obtained in the smoke-dried product. The phenolics and total flavonoids were similar to that reported by Moreno-Escamilla et al. (2015) in chili chipotle. This increase was obtained due to damage of the cell structure, which allowed the release of these metabolites from the plant matrix, for instance, because of the exposition of the samples to both thermal treatments (Turkmen et al., 2005). Nonetheless, the smoke-drying treatment was more aggressive since the highest increase of phenolics and total flavonoids were observed after 59 h of smoke-drying, when water activity was below 0.761 (Table 2). Additionally, Ornelas-Paz et al. (2010) found that thermal treatments such as roasting increase the phenolic content in pungent chilies, contrary to what happened in non-pungent varieties, so that this increase of phe- nolic compounds and flavonoids observed after dehydration and smoke-drying is favoured by the protective effect of the capsaicinoids of jalapeno rayado pepper.

**Maillard compounds**

Table 3 shows that the absorbance value at 420 nm in dehydrated and smoke-dried chili was increased 1.8-fold with respect to fresh-red pepper; nonetheless, there is no difference between the two dehydration treatments. The non-enzymatic browning index is often measured at 420 nm in foods subjected to heat treatment and is related to the appearance of end products such as melanoidins (Delgado-Andrade et al., 2010). Fluorescence techniques have been more sensitive for determining the presence of Maillard compounds (Yamaguchi et al., 2012). Aqueous extracts of fresh-red, dehydrated and smoke-dried pepper were compared to the fluorescence spectra of a lysine-
When comparing fluorescence intensity, it was observed that smoke-dried chili showed 29% more intensity than when only convective dehydration was used (Table 3). The type of heat treatment determines the generated amount of compounds, as reported by Yamaguchi et al. (2012); furthermore, the exposure time favours the generation of these compounds.

Table 3. Indicators of Maillard reaction products and colour attributes of jalapeno rayado peppers fresh-red, dried and smoke-dried.

| Attribute                        | Fresh-red | Dried   | Smoke-dried |
|----------------------------------|-----------|---------|-------------|
| Browning intensity (A420 nm)     | 0.201 ± 0.01 * | 0.380 ± 0.01 b | 0.382 ± 0.04 c |
| Maillard’s products (RFU)        | 15,308 ± 580 a | 47,933 ± 3566 b | 71,325 ± 2803 c |
| L                                | 30.2 ± 0.68 a | 24.3 ± 0.42 b | 20.7 ± 0.21 a |
| a                                | 26.10 ± 1.01 a | 15.10 ± 0.40 b | 8.40 ± 0.36 a |
| b                                | 22.77 ± 0.74 a | 13.77 ± 0.45 b | 9.27 ± 0.25 a |
| al                               | 789.55 ± 48.61 a | 366.45 ± 12.86 b | 174.21 ± 9.19 a |
| ΔE                               | 15.42 ± 1.94 a | 24.20 ± 1.26 b | 22.77 ± 0.74 a |

Different letters in each column indicate statistically significant difference (p ≤ 0.05 and n = 3), by Tukey’s test. A420 nm: Absorbance at 420 nm; RFU: relative fluorescence units; ΔE: total colour change.

A glucose reaction model (80°C) at 0 and 120 min times (Figure 1). The spectra from convective-dehydrated and smoke-dried chilies matched in the presence of maximum emission/excitation peaks of 350/415 nm, which were absent in the spectra from fresh-red pepper and lysine–glucose mixture without heating (0 min).

![Figure 1](image_url)
 compounds (Figure 2) because there is a significant increase after 59 h of smoke-drying, corresponding to a water activity of 0.761 (Table 2).

**Colour**

Respect to the colour variables, the smoke-drying treatment had a greater effect on the fresh-red chilli than the convective drying (Table 3). The smoke-dried product lost more luminosity; in chillies, this has been associated with non-enzymatic browning (Rhim & Hong, 2011). The value of colour parameter \(a\) was more affected in the smoke-dried peppers, which indicates loss of reddish tone; nevertheless, a better evaluation index is the product \(aL\) proposed by Ramakrishnan and Francis (1973). This index allows to classify the colour of chilli when it is submitted to a heat treatment; values of \(aL\) greater than 500 are characteristic of red fruits, like fresh-red peppers; from 300 to 500 are medium-red and correspond to those chillies dehydrated by convection at 60°C, whereas browned chillies have \(aL\) values below 300, as it was for the smoke-dried product. The colour ratio \((aL)\) and the decrease or increase of carotenoids and Maillard compounds during the smoke-drying process can be seen in Figure 2. The first significant colour change occurred when the fruit lost more than 30% of carotenoids, after 44 h. Browned dehydrated chilli was obtained after 59 h of processing, where the loss of carotenoids had less influence compared to a 300% increase in Maillard compounds, when the water activity was lower than 0.761 (Table 2). The total colour difference (\(\Delta E\)) presented by chillies submitted to both thermal processes with respect to fresh-red was higher than that reported by Vega-Gálvez et al. (2009), when the chillies were exposed to dehydration with temperatures at 50°C and 90°C. Additionally, it was observed that smoke-dehydrated chillies had a greater colour change than those dehydrated by convection, 24.20 ± 1.26 and 15.42 ± 1.94, respectively (Table 3).

**Antioxidant capacity and characterization of extracts by mass spectrometry**

The main antioxidant compounds that increased during the smoke-dehydration process were the phenolic compounds and flavonoids; also, a higher production of Maillard compounds was observed. Efficient extraction of these compounds has been reported in solvents such as water and 80% methanol (Alvarez-Parrilla et al., 2011; Delgado-Andrade et al., 2010), so it was interesting to compare its antioxidant activity. There was a significant difference in the antioxidant activity depending on the extraction solvent and the dehydration method \((p < 0.05)\) (Table 4). Using ORAC, extracts in methanol 80% reported 3–5 times greater antioxidant activity than extracts in water; while with DPPH, the extracts in water had slightly higher antioxidant activity. Both methods have been used for determining antioxidant activity attributed to phenolic and capsaicinoid compounds (Alvarez-Parrilla et al., 2011; Medina-Juárez et al., 2012) and products of the Maillard reaction (Kim & Lee, 2009). The value obtained with DPPH analysis in fresh-red pepper was in the range reported by Alvarez-Parrilla et al. (2011); however, in smoke-dried chilli, the antioxidant capacity was higher than that found in literature (Table 4). The antioxidant activity by ORAC was also higher than that reported by Alvarez-Parrilla et al. (2011) in fresh-red and smoke-dried chilli. Among the different varieties of Capsicum fresh jalapeno pepper (C. annuum) has a lower antioxidant capacity (Medina-Juárez et al., 2012; Oboh et al., 2007); nevertheless, artisanal processing significantly improved the antioxidant properties of the final product.

With the exception of higher antioxidant activity by DPPH in the methanolic extract of dehydrated chilli by convection, no significant difference was observed in the antioxidant capacity between fresh-red and convective-dehydrated peppers. In all cases, the smoke-dried chillies showed the highest
antioxidant activity with respect to fresh-red and convective-dehydrated ones. This is due to the longer exposure to the heat treatment, thus more damage to the chili matrix, to the accentuated release of phenolic compounds and generation of Maillard compounds after 59 h of processing (Kim & Lee, 2009; Vhangani & Van Wyk, 2016).

The compounds present in extracts obtained using 80% water and methanol were compared by UPLC–MS–ESI (Table 5), from which seven metabolites were found in fresh-red peppers that were preserved after the heat treatment; only the radicals with m/z values of 191.09, 355.16 and 329.14 have been reported and may correspond to quinic acid or citric acid, feroloyl glucoside (Morales-Soto et al., 2013), and vanillic acid glycoside (Mokhtar et al., 2015), respectively; while a compound of m/z value of 405.19 was no longer detected after dehydration. It has been stated that the incorporation of antioxidant compounds from the smoking treatment favours the antioxidant activity (Velázquez et al., 2014); however, six compounds were generated by the heat treatment and were present in both extracts (m/z values: 585.32, 292.20, 326.18, 653.28, 240.11 and 210.14), and no new compounds were present in smoke-dried chili. Therefore, a greater antioxidant activity in this type of extracts may be due to the increase of the thermal exposure time under the conditions of the traditional dehydration process.

### Table 4. Antioxidant activity of water and methanol 80% extracts of jalapeno rayado peppers fresh-red, dried and smoke-dried.

| Treatment       | Extract          | ORAC μmol Trolox equivalents/g d.b. | DPPH μmol Trolox equivalents/g d.b. |
|-----------------|------------------|-----------------------------------|------------------------------------|
| Fresh-red       | Water            | 154.16 ± 24.9^a                   | 40.39 ± 0.24^c                     |
| Fresh-red       | Methanol 80%     | 684.63 ± 34.2^c                   | 32.52 ± 0.89^a                     |
| Dried           | Water            | 145.82 ± 8.0^c                    | 41.19 ± 0.51^c                     |
| Dried           | Methanol 80%     | 731.31 ± 11.3^c                   | 37.58 ± 0.30^b                     |
| Smoke-dried     | Water            | 262.93 ± 41.3^b                   | 68.97 ± 1.22^a                     |
| Smoke-dried     | Methanol 80%     | 838.3 ± 63.2^d                    | 63.73 ± 0.40^d                     |

Variation factor: Treatment <0.0001, Extract <0.0001, Treatment*extract 0.3952, 0.0006.

d.b.: Dry weight basis. Different letters in each row indicate statistically significant difference (p ≤ 0.05 and n = 3), in a completely randomized analysis with factorial arrangement and by Tukey’s test.

d.b.: Peso en base seca. Letras diferentes entre líneas indican diferencia significativa (p ≤ 0.05 y n = 3), en un análisis completamente al azar con arreglo factorial y prueba de Tukey.

### Table 5. Molecular radicals identified by UPLC–MS–ESI (-) in water and methanol 80% extracts of jalapeno rayado peppers fresh-red, convective-dried and smoke-dried.

| Time (min) | m/z (-) | Water | Methanol 80% | Water | Methanol 80% | Water | Methanol 80% |
|-----------|---------|-------|--------------|-------|--------------|-------|--------------|
| 0.44      | 133.07  | ●     | ●            |       | ●            |       | ●            |
| 0.51      | 173.07  | ●     | ●            |       | ●            |       | ●            |
| 0.71      | 191.09  | ●     | ●            |       | ●            |       | ●            |
| 1.27      | 585.32  | ●     | ●            |       | ●            |       | ●            |
| 1.54      | 292.20  | ●     | ●            |       | ●            |       | ●            |
| 2.10      | 326.18  | ●     | ●            |       | ●            |       | ●            |
| 2.10      | 405.19  | ●     | ●            |       | ●            |       | ●            |
| 2.11      | 653.28  | ●     | ●            |       | ●            |       | ●            |
| 2.40      | 240.11  | ●     | ●            |       | ●            |       | ●            |
| 2.84      | 329.14  | ●     | ●            |       | ●            |       | ●            |
| 3.40      | 337.21  | ●     | ●            |       | ●            |       | ●            |
| 3.89      | 355.16  | ●     | ●            |       | ●            |       | ●            |
| 3.91      | 210.14  | ●     | ●            |       | ●            |       | ●            |
| 4.09      | 431.24  | ●     | ●            |       | ●            |       | ●            |

● Molecular radical is present during treatment.
● Presencia del ion molecular en el tratamiento.

### Conclusions

The chili pepper jalapeno rayado has carotenoids, capsaicinoids and phenolic compounds, which are antioxidant metabolites that become modified during the process of smoke-drying in traditional ovens that use evergreen oak wood. The content of capsaicinoids is not modified by the traditional process. While the reduction of carotenoid content is related to the loss of red colour after 44 h of dehydration processing. The generation of brown colour is due to the development of Maillard compounds, which was emphasised after 59 h of dehydration, with a water activity of 0.761.

Six compounds generated during convective dehydration and smoke-drying were identified, with molecular radicals of m/z values of 585.32, 292.20, 326.18, 653.28, 240.11 and 210.14. This study provides a first approach to the knowledge of the chili metabolites whose content increased as a consequence of traditional dehydration processing, which conferred greater antioxidant activity compared to fresh-
red and convective-dehydrated jalapeno rayado peppers. The last six hours of processing favoured the maximum increase of phenolic compounds, flavonoids, and Maillard compounds, in addition to the decrease in water activity (0.606), resulting in a final moisture content of 0.89 g/g d.b in smoke-dried chili.

Acknowledgements

This work was financially supported through the project SIP-IPN 20171286; CONACYT-PDCPN2013-01 No. 216044-1010/393/2014. The first author thanks to the Mexican National Council for Science and Technology (CONACYT) for the Ph.D. grant provided.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Consejo Nacional de Ciencia y Tecnología [PDCPN2013-01 No. 216044-1010/393/2014]; Secretaría de Investigación y Posgrado, Instituto Politécnico Nacional SIP20171286; SIP20170428.

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