Vol. 16, No. 3 (2017) 813-825
Revista Mexicana de Ingeniería Química

IMPACT OF OPEN SUN DRYING AND HOT AIR DRYING ON CAPSAICIN, CAPSANTHIN, AND ASCORBIC ACID CONTENT IN CHILTEPIN (*Capsicum annuum* L. var. *glabriusculum*)

IMPACTO DEL SECADO AL SOL Y POR CONVECCIÓN FORZADA SOBRE CAPSAICINA, CAPSANTINA Y EL CONTENIDO DE ÁCIDO ASCÓRBICO EN CHILTEPÍN (*Capsicum annuum* L. var. *glabriusculum*)

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Received March 8, 2017; Accepted May 26, 2017

Abstract

Chiltepin is recognized for its pungency and deep red color. The purpose of this study was to evaluate the impact of open sun drying and hot air drying methods, as well as pretreatments on capsaicin, capsanthin, and ascorbic acid content in chiltepin. Chiltepin was dried using open sun and hot air drying. Raw chiltepin showed capsaicin (C) and capsanthin (CAPS) content of 5,560 μg/g dry weight (dw) and 58.7 μg/g dw, respectively; ascorbic acid (AA) concentration (140 μg/g dw) was lower to that reported in other peppers. Open sun drying affected the concentrations of CAPS (12.09 μg/g dw) and AA (3.5 μg/g dw), but not C (5,500 μg/g dw). In hot air drying, the lowest temperature (35 °C) favored retention of bioactive compounds of 90%, 52%, and 35% (C, CAPS, and AA, respectively). These results suggest that C is the most stable compound. Thus, hot air drying can be recommended for a higher retain of CAPS and AA compounds.

Keywords: chiltepin, capsaicin, capsanthin, ascorbic acid, open sun drying, hot air drying.

Resumen

El chiltepín es reconocido por su característico sabor picante y su intenso color rojo. En este estudio, se analizó el impacto de los métodos de secado, sobre el picante proporcionado por capsaicinoides como capsaicina en mayor proporción, el color, dado por capsantina y además el contenido de ácido ascórbico; considerados todos ellos como compuestos bioactivos. Se utilizaron los métodos de secado al sol y de convección forzada. El chiltepín como materia prima mostró una concentración de capsaicina (C) y capsantina (CAPS) de 5,560 mg/g y 58,7 mg/g respectivamente; la concentración de ácido ascórbico (AA) (140 mg/g peso seco) fue menor a la reportada en otros chiles. El secado al sol no afectó la concentración de C (5,500 mg/g), sin embargo CAPS y AA disminuyen hasta 12,09 mg/g y 3,5 mg/g respectivamente. En el secado por convección forzada, la temperatura más baja (35 ° C) favorece la retención de compuestos bioactivos en el 90%, 52% y 35% (C, CAPS y AA, respectivamente). Los resultados sugieren que C es el compuesto más estable. Por lo tanto, el método de secado por convección forzada puede ser recomendado para una mayor retención de CAPS y AA.

Palabras clave: chiltepín, capsaicina, capsantina, ácido ascórbico, secado al sol, convección forzada.

1 Introduction

Chili peppers (*Capsicum annuum*) are the oldest and most popular vegetables used as spice around the world (Giuffrida *et al*., 2013). The main producer of chili peppers is China, followed by Mexico, Turkey, United States, and Spain (FAO, 2010; SAGARPA, 2011). Chiltepin (*Capsicum annuum* L. var. *glabriusculum*) is a type of wild chili and is considered the father of chilies due to the assumption that several varieties have emerged from it (Raju *et al*., 2010). Moreover, chiltepin is recognized for its pungent flavor and deep red color (Fig. 1a), which are the most important food quality parameters in chili peppers. Thus, different methods have been

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employed to preserve the quality and microbiological safety of these foods. In chiltepin, drying is the main process of preservation, which is mainly carried out under. Drying food products is complicated due to the physical and chemical biochemical transformations that may occur, some of which are desirable. In this process, several conditions must be considered: processed product, drying purpose, and methodology (Domínguez-Niño *et al*., 2016).

The pungent metabolites in the fruits of *Capsicum* species are called capsaicinoids, which are a group of 12 or more alkaloids with a structure of vanillylamide of branched fatty acids with 9-11 carbons (Suzuki & Iwai, 1984), but capsaicin (C) [(E)-N-(4-hydroxy-3-methoxybenzyl)-8-methyl-6-nonenamide] and dihydrocapsaicin are responsible for more than 90% of the pungency (Cisneros-Pineda *et al*., 2007; Wahyuni *et al*., 2013). The red color is due to carotenoids, which are based on a C40 tetraterpenoid skeleton and are 50% capsanthin (CAPS) (Topuz and Özdemir, 2004; Giuffrida *et al*., 2013). Although chiltepin is considered among the most pungent (Montoya-Ballesteros *et al*., 2010), its content of C and/or CAPS has not been yet reported to our knowledge. In addition to C and CAPS, *Capsicum annuum* also contains ascorbic acid (AA) (Raju *et al*., 2010).

The antioxidant activity of these bioactive compounds has increased its study on beneficial health effects (Wahyuni *et al*., 2013). In addition, C has been used in pharmaceutical industry and CAPS as a natural colorant in the food industry. In recent years, the use of natural food colorants has increased due to the negative effects of synthetic colorants on health. However, the content of these compounds vary according to cultivar and processing conditions (Wahyuni *et al*., 2013). They are susceptible to oxidation, which is dependent to factors such as temperature, light, enzymes, water activity, and endogenous antioxidants (Santos and Silva, 2008; Rodriguez-Amaya, 2010). Therefore, it has been necessary to establish process conditions according to each cultivar.

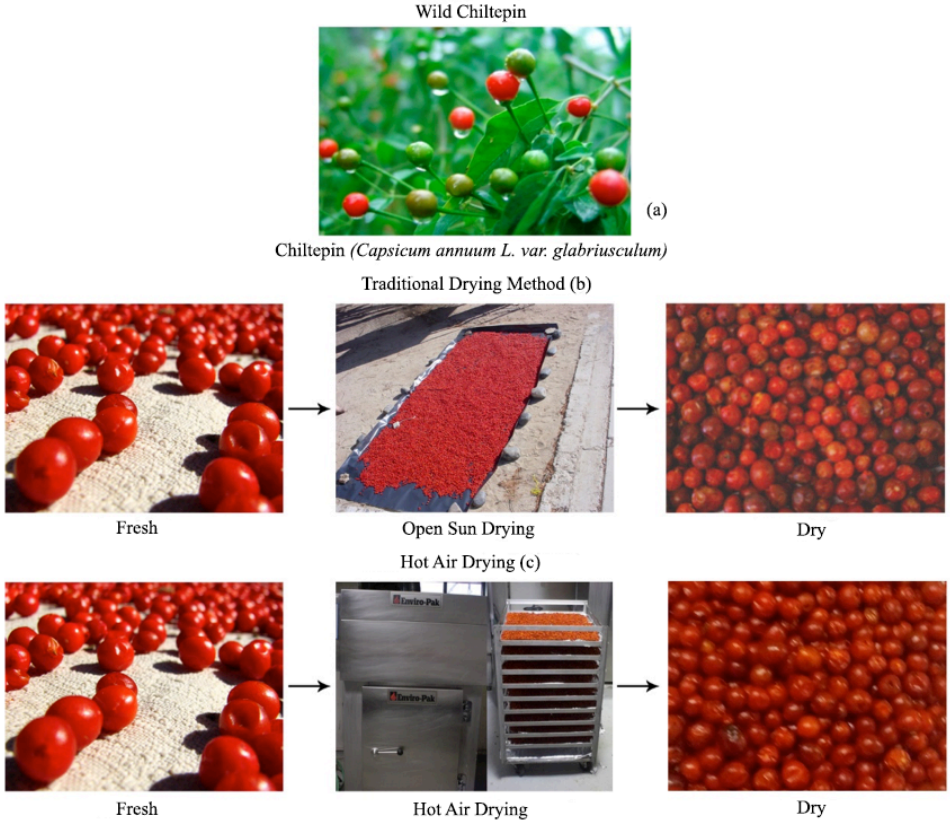

Fig. 1. (a) Chiltepin (*Capsicum annuum* L. var. *glabriusculum*), (b) traditional drying method: open sun drying chiltepin, and (c) hot air drying chiltepin.

In chili peppers, it has been reported that high temperature and short drying periods result in high losses of C and CAPS (Topuz *et al*., 2011). In contrast, losses decrease with long periods at a low-temperature processing (Mínquez-Mosquera *et al*., 1994), and CAPS is stable at temperatures lower than 60 °C, while C decreases at high temperatures (90 °C) (Daood *et al*., 2006). Moreover, the effect of light in open sun drying with long processing periods is very deleterious, resulting in losses of 79% of CAPS and 24.6% of C (Topuz and Özdemir, 2004). One important stage of the drying process is blanching, characterized for inactivation of enzymes responsible for color and flavor loss (Fellows, 2000), which have not been described in chiltepin. In addition, water activity is also an important factor in color stability of chilies (Govindarajan and Salzer, 2009).

It has been reported in chili peppers that using hot air drying at high temperatures, losses of AA are greater than 50% (Daood *et al*., 2006; Vega-Gálvez *et al*., 2009). Few studies have described the effects of open sun and hot air drying, blanching prior to drying, or light exposure in chiltepin. Therefore, the aim of this study was to evaluate the impact of these drying methods and pretreatments on C, CAPS, and AA content in chiltepin.

2 Materials and methods

All solvents used in C, CAPS, and AA analysis were HPLC-grade. Standards of C and AA were obtained from Sigma Aldrich Chemical Co. (St Louis, Mo. USA). Standards of C and AA were obtained from Brand Carotene Nature, Switzerland. Separation of C and CAPS was achieved through a Nova-Pak® C18 column, 4 μm, 3.9 x 150 mm, 60 Å, (Waters Corporation, Ireland). Separation of AA was using an Amino μBondapak^{TM} NH212, 5 Å, 10 μm 3.9 x 300 mm HPLC column (Waters Corporation, Ireland).

2.1 Raw material

Wild chiltepin (*Capsicum annuum* L. var. *glabriusculum*) was collected in a northwestern region of Mexico (coordinates: 29°0'23.3" N 110° 8'19.5" W), with a height of 544 m above sea level and semiarid climate. Since there is a lack of knowledge about the stages of its maturity, a bright red color of chiltepin was use as an indicator for harvesting. Samples of red color chiltepin were stored at 5 °C before processing. Thus, two harvest seasons were used for the study: November 2011 and November 2012.

2.2 Drying processes

Two drying methods were applied, open sun and hot air drying in dark conditions at different temperatures. Each drying process was stopped at an equilibrium moisture of 0.03 g of water/g of dry solid.

2.2.1 Open sun drying

Open sun drying was used with the first harvest, in which a batch of 10 kg of chiltepin was exposed to sunlight, method most traditionally used. This batch, without blanching as generally performed, was place on the ground using a polyethylene contact surface (Fig. 1b). It was exposed for 8 hours a day, and every two hours; a random sample was taken for moisture and bioactive content analyses. After 8 h of daily exposure, each batch was stored overnight at a room temperature. In the drying process, the chiltepin's internal temperature was measure during day and night using thermocouples MesaLabs Model Micropack III temperature data Loger.

2.2.2 Hot air drying

The hot drying air method was used in the second harvest (Fig. 1c). The experiment consisted of two batches of 30 kg of chiltepin to be dried. The first batch of samples was unblanched (OB), while the other batch was previously blanched (WB).

2.2.2.1 Blanching

Samples were blanched by immersion in hot water at a temperature of 85 °C for 8 min. Relationship chiltepin:water was of 1:2. Consequently, blanched samples were chilled by water immersion at a temperature of 20 °C. These conditions were established by previous studies with an optimized response surface methodology by a central composite rotational design (CCRD) configuration for two factors: a temperature of 75-95 °C and for a time of 4-12 min. The dependent variables were enzymatic activity of peroxidase (POD), C, and color (L*, a*, b*). The optimal conditions for a temperature 85 °C for 8 min resulted in POD activity reduced from 0.85 UA/mg protein/mL to 0.6 UA/mg protein/mL, C concentration remained in 5,5 μg/g dry weight (dw) to 5,4 μg/g dw, and no apparent color effect. The

desirability analysis for this optimization was with a function d = 0.67.

2.2.2.2 Drying

Using hot air drying, three constant temperatures were maintained: 35 °C, 45 °C, and 55 °C. The rate of airflow was 3 m/s with a parallel flow for the 3 temperatures. A batch of 10 kg for each drying temperature was used. Each batch was placed on trays drilled forming a monolayer. During the drying process, samples were taken every two hours for the analyses of moisture and C, CAPS, and AA content. A Micro-Pak Series MP500 drying cabinet (Enviro-Pak, Clackamas, OR) was used, in which the drying chamber was operated under conditions of darkness.

2.3 Analytical methods

2.3.1 Moisture content

Moisture content was determined according to the official method 934.06 Moisture in Dried Fruits of the Association of Official Agricultural Chemists (AOAC), which is based on weight difference (AOAC, 2013).

2.3.2 Water activity

Water activity was determined at 25 °C, using a portable Rotronic model HygroPalm AW1, CH -8303 indicator (Grindelstrasse, Bassersdorf, Switzerland).

2.3.3 Peroxidase (POD) activity

POD activity was measured in raw and blanched chiltepin using a modified method of Orak and Demirsi (2005). Three grams (3 g) samples were crashed in liquid nitrogen, homogenized in cold acetone and filtered under a vacuum using cold acetone until a colorless powder was obtained. The powder was then dried under vacuum and stored at -20 °C or below for the enzyme activity assay. Extraction was performed from acetone powders and homogenized with 25 ml of phosphate buffer pH 7 (0.2 M). Homogenates were centrifuged at 3,380 g for 20 min at 5 °C.

2.3.4 Capsaicin (C)

C concentration was determined according to the technique described by the method 21.3 of the American Spice Trade Association (ASTA, 1997). For its extraction, 25 g samples of chiltepin were weighed out into a flask and consequently, 200 mL of absolute ethanol was added. Several glass beads were added and the solution was mildly refluxed for 5 hours. Quantification was performed by HPLC (Varian 920 LC, Agilent Technologies Palo Alto, CA, USA). Separation was achieved through a Nova-Pak® C18 column, at a flow rate of 1.5 mL/min and a temperature of 35°C. The detector was UV-Vis, using a wavelength of 280 nm. The mobile phase consisted of acetonitrile-water mixture (40:60) under isocratic conditions, and the injection volume was 20 μL. C quantification was achieved by the external standard method and was made from peak area ratio, which was based on a calibration curve generated from standard C.

2.3.5 Capsanthin (CAPS)

CAPS extraction was performed with a modified method of Mínguez-Mosquera *et al*., (1994). Ten grams of sample were mixed with cold acetone, consequently, several washes were performed to extract the pigments, and then the extract was saponified using 100 g of potassium hydroxide in 500 ml of methanol. Quantification was performed by reversed phase HPLC (Varian 920 LC, Agilent Technologies, Palo Alto, CA, USA), using a C18 column, at a flow rate of 1.5 mL/min and temperature of 35°C. The detector used was a UV-Vis spectrophotometer and the measurement wavelength was 478 nm. Mobile phase A consisted of methanol-water mixture (85:15), and phase B consisted of acetone-methanol mixture (50:50). The following gradient program was used: 0 min 0 % B, 20 min 45 % B, 33 min 100 % B, 42 min 0 % B, and 47 min 0 % B; the injection volume was 5 μL. CAPS quantification was achieved by the external standard method and was made from peak area ratio, which was based on a calibration curve generated from standard CAPS.

2.3.6 Ascorbic acid (AA)

For the determination of AA, samples of 10 g of chiltepin were mixed with metaphosphoric acid and glacial acetic acid and consequently, macerated for 2.5 minutes, filtered and then centrifuged at 9,727 g at 5 °C for 25 minutes (Doner and Hicks 1981). Quantification was performed using HPLC (Varian 920 LC, Agilent Technologies, Palo Alto, CA, USA) with a UV-Vis detector using an Amino μBondapak^{TM} NH212 column, and a wavelength of 268 nm. The mobile phase consisted of acetonitrile-phosphate of

monobasic potassium mixture (75:25) under isocratic conditions, with a flow rate of 1.0 mL/min, a temperature of 35°C, and 10 μL of injection. AA quantification was achieved by the external standard method from peak area ratio, which was based on a calibration curve generated from standard AA.

2.4 Kinetics of degradation

The first order reaction kinetic was established by observing a straight line when plotting data on semi log paper. A linear regression was applied to calculate a slope to obtain the degradation rate constant (k) and half-live times.

2.5 Statistical analysis

All treatments (open-sun drying and forced convective drying) were carried out in duplicate. For the analysis of each bioactive compound during drying, a random sample was taken until the final moisture every two hours. Each bioactive was extracted in duplicate for every sample. The data were subjected to one-way analysis of variance (ANOVA) for open-sun drying and forced convective drying (for each drying temperature); where independent variable was drying time and dependent variable C, CAPS, and AA. When significant differences were observed ($p \leq 0.05$), Tukey-Kramer test was used to determine the differences among means (NCSS, version 2008, NCSS, LLC, Kaysville, Utah, USA).

3 Results and discussion

3.1 Raw chiltepin

3.1.1 Moisture content

Chiltepin had initial moisture of 46.16 % ± 1.53 (0.88 g of water/g dw) in the first harvest and 49.62% ± 0.05 (0.93 g of water/g dw) in the second one. These results are lower than that reported for other red raw chili peppers (Bernardo *et al*., 2008; Vega-Gálvez *et al*., 2009). These differences in moisture could be attributed to different maturity stages, which have not yet been established for chiltepin and other red chili peppers. These results are lower than that reported for other red raw chili peppers (Bernardo *et al*., 2008; Vega-Gálvez *et al*., 2009).

3.1.2 Water activity

Although chiltepin has low moisture, its water activity was higher for the two harvest seasons (0.955 ± 0.004 and 0.931 ± 0.008), which makes it vulnerable to microbial growth and enzymatic activity reactions (Labuza *et al*., 1970). The water activity is similar to those of other chili peppers such as red, golden, and white habaneros, as well as those of tabascos, jalapeños, and serranos (Giuffrida *et al*., 2013).

3.1.3 Bioactive compounds

The concentration of bioactive compounds in raw chiltepin for the two harvest seasons was different. In the first harvest season, C concentration was 5,500 μg/g dw (5.5 mg/g dw) and 4,400 μg/g dw (4.4 mg/g dw) in the second one, similar to that reported for red Habanero type I (4.9 mg/g dw) and lower than the golden habanero (8.17 mg/g dw), but higher than the jalapeño (1.1 mg/g dw), tabasco (0.9 mg/g dw), and serrano (0.7 mg/g dw) (Topuz *et al*., 2011; Giuffrida *et al*., 2013). The concentration of CAPS was also different for the two harvest seasons (first: 48.81 μg/g dw; second: 58.7 μg/g dw). These results were similar to other varieties of red chili peppers such as the Sole cultivar (*Capsicum annuum*) (54.61 μg/g dw) and Idealino cultivar (*Capsicum annuum*) (49.7 μg/g dw) (Pugliese *et al*., 2014). Regarding AA, the concentrations also differed [first harvest season: 950 μg/g dw (0.95 mg/g dw) and second harvest season: 140 μg/g dw (0.14 mg/g dw)]. Those concentrations were lower with respect to other peppers as red pepper *Capsicum annuum*, L. var. Hungarian (6.8 mg/g dw) (Vega-Gálvez *et al*., 2009), spice red peppers cultivated under indoor conditions, Jeromin (4.4 mg/g dw), hybrids Remény (1.90 mg/g dw), and SP 20 Ba (0.9 mg/g dw) (Daood *et al*., 2014). However, this value is higher than that reported for the Fresno de la Vega (0.018 mg/g dw) and Benavente-Los Valles (0.010 mg/g dw) chilies (Bernardo *et al*., 2008). Chiltepin, like other chili peppers, vary in their chemical composition, which depends on the maturity, harvest time, variety, agricultural practices, and environmental factors such as weather conditions (Howard *et al*., 2000; Pérez-López *et al*., 2007).

3.2 Drying process

3.2.1 Open sun drying

In the open sun drying (Fig. 2), during the night, with temperature variations from 23 °C to 42 °C and

relative humidity variations between 70% and 10%; an internal temperature of 26 °C was obtained and the time required for desirable humidity was of 32 h of sun exposure.

3.2.2 Effect of drying on the moisture, water activity, and concentration of bioactive compounds

3.2.2.1 Moisture

The initial humidity of the samples that were open sun dried (OB) was of 0.90 g of water/g of dry solid. After samples were blanched by hot water immersion, humidity was increased in a 0.96 to 1.54 g of water/gram of solid dry, initiating the drying with the most humidity in comparison to previous dryings.

3.2.2.2 Water activity

Fig. 3 shows the water activity versus drying time of chiltepin samples under all drying conditions. After a period of 16 h of sun drying, the water activity of the samples was below 0.6 (Fig. 3a). Enzymatic activity is low when water activity is below 0.6, but values between 0.6 and 0.85 favor it (Labuza *et al.*, 1970), and higher values increases microbial reactions. However, it depends on the food matrix. Water activity in blanched samples increased from 0.93 to 0.95, effect not observed in the OB samples. In samples dried by hot air (Fig. 3b and 3c), the period

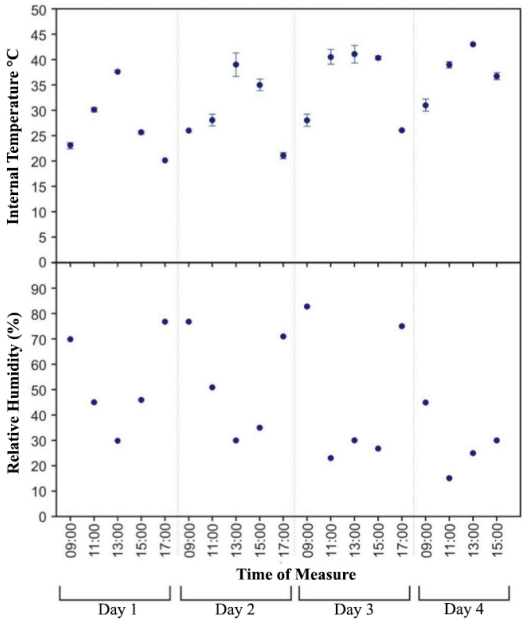

Fig. 2. Internal temperature and relative humidity of chiltepin during open sun drying.

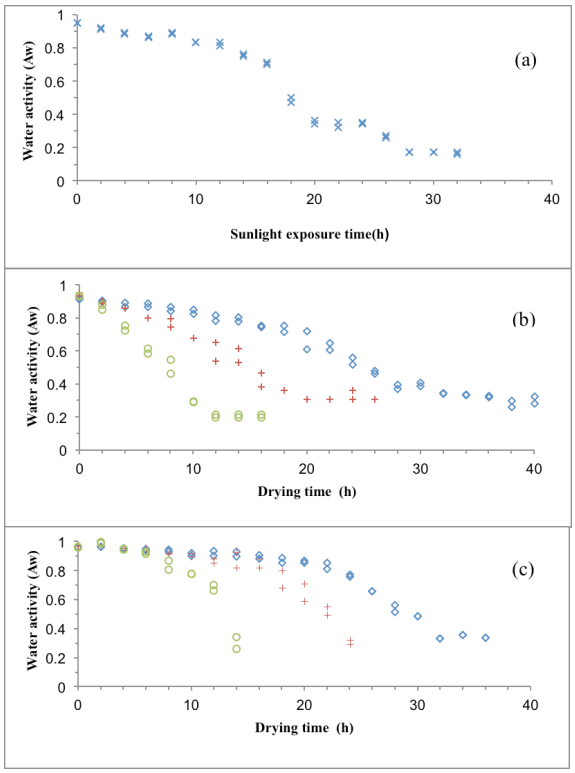

Fig. 3. (a) Open sun drying, (b) hot air drying at different temperatures without blanching (OB), and (c) hot air drying at different temperatures with blanching (WB) and after hot air drying. ×: Open sun drying, ◇: hot air drying at 35 °C, +: hot air drying at 45 °C, and *o*: hot air drying at 55 °C. Each point reflects the average of duplicates.

of high water activity was longer in samples where blanching was performed before drying. This effect is probably due to the blanching by water immersion, where samples could absorb water in the process.

Water activity in blanched samples increased from 0.93 to 0.95, effect not observed in the OB samples. In samples dried by hot air (Fig. 3b and 3c), the period of high water activity was longer in samples where blanching was performed before drying. This effect is probably due to the blanching by water immersion, where samples could absorb water in the process.

3.2.2.3 Bioactive compounds

In our study, C losses (less than 10 %) were not as strong as CAPS (50 %) and AA (70%). The kinetics of degradation of CAPS and AA followed a first order reaction, with linear correlation coefficients (R^2) ranging from 0.901 to 0.979 (Table 1).

Table 1. Degradation kinetics of bioactive compounds.

Bioactive compounds	**Temperature (°C)**	$\mathbf{k^{-1}}$**(** $\mathbf{h^{-1}}$**)**	$t_{1/2}$**(h)**	R^2	Q_{10}	E_a **(kJ/mol K)**
(CAPS)	35 OB	0.015	46.2	0.958		
(CAPS)	45 OB	0.025	27.7	0.976	1.66 (35-45 °C)	
(CAPS)	55 OB	0.045	15.4	0.956	1.8 (45-55 °C)	46.09
(CAPS)	35 WB	0.033	21	0.971		
(CAPS)	45 WB	0.038	18.2	0.906	1.15 (35-45 °C)	
(CAPS)	55 WB	0.078	8.8	0.935	2.05 (45-55 °C)	35.86
(AA)	35 OB	0.025	27.7	0.901		
(AA)	45 OB	0.038	18.2	0.975	1.52 (35-45 °C)	
(AA)	55 OB	0.065	10.6	0.975	1.71 (45-55 °C)	40.06
(AA)	35 WB	0.027	25.6	0.979		
(AA)	45 WB	0.033	21	0.959	1.22 (35-45 °C)	
(AA)	55 WB	0.067	10.3	0.979	2.03 (45-55 °C)	37.93

k_{-1}: Degradation rate constant, Q_{10}: Temperature coefficient, $t_{1/2}$: Half-life time, CAPS: Capsanthin, AA: Ascorbic acid, OB: Without Blanching, WB: With Blanching, E_a: Activation energy.

This first-order reaction for CAPS and AA with significant losses has already been reported by other authors in the drying of other foods such as carrot, papaya, and tomato (Jarén-Galán and Mínguez-Mosquera, 1997; Kurozawa *et al*., 2014).

3.2.2.3.1 Capsaicin (C)

Fig. 4 shows C concentration versus drying time. In the open-sun drying treatment (Fig. 4a) and unblanched (OB) samples dried by forced convection at 35 ºC, 45 ºC, and 55 ºC (Fig. 4b, 4c and 4d), the C concentration decreased ($p \leq 0.05$) during the first hours of drying (between 4 and 8 h). Samples from a batch drying process (2-10 h) showing a lower content of C cannot result with higher C concentrations at the end of the drying, similar to the initial concentration. We think that C concentrations of these samples undergo a POD oxidation since there are the condition of an activity of 0.85 UA/mg protein/mL of POD and also high AW (0.9-0.8). During the process of analysis in this condition, maceration promote these loss of C. Sample maceration may cause an oxidation reaction by POD, an oxidation reaction by POD (Kirschbaum-Titze *et al*., 2002). In peppers, soluble POD constitutes about 95% of the total POD activity (Estrada and Bernal, 2000; Schweiggert *et al*., 2006). This enzyme has an affinity for C at a pH near 6, which is found in chiltepin peppers (Contreras-Padilla and Yahia, 1998). After this period of slight drop of C concentration, water activity was reduced below 0.8, C concentration is not affected by maceration at these condition.

This effect can be compared with blanched samples (WB) (Figure 4b, 4c, 4d) where C concentrations were not significant ($p \geq 0.05$) during drying time; C did not show any loss. After blanching, the samples showed a reduction of POD activity, from 0.85 UA/mg protein/mL to 0.60 UA/mg protein/mL.

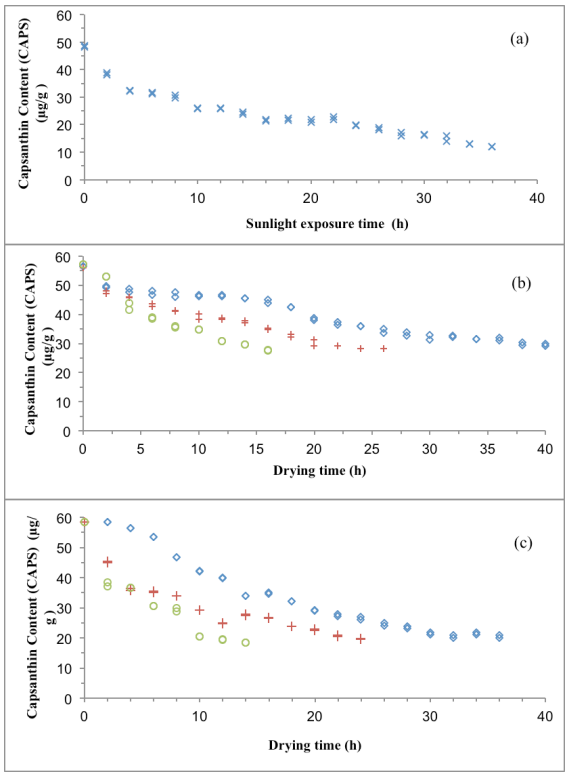

Fig. 4. (a) Open sun drying, (b) hot air drying at 35 °C, (c) hot air drying at 45 °C, and d) hot drying at 55 °C. x: unblanched samples (OB), □: blanched samples (WB). Each point reflects the average of duplicates.

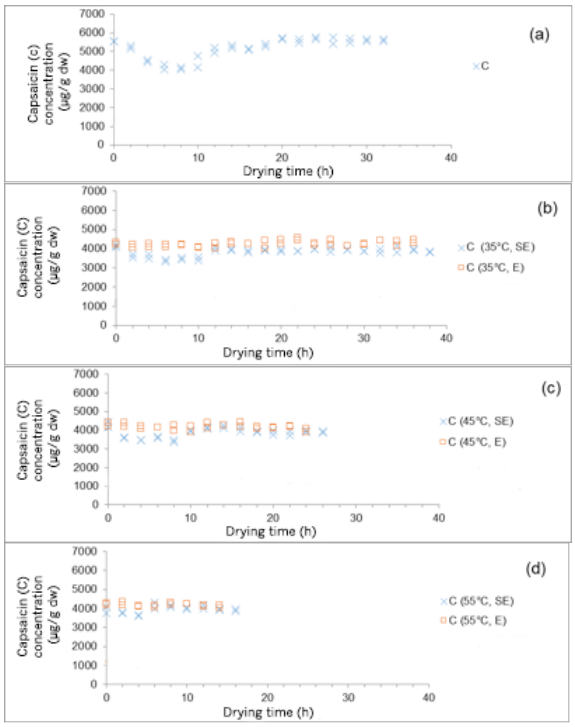

Fig. 5. (a) Open sun drying, (b) hot air drying at different temperatures without blanching (OB), and (c) hot air drying at different temperatures with blanching and after hot air drying. ×: Open-sun drying, ⋄: hot drying at 35 °C, +: hot drying at 45 °C, and o: hot drying at 55 °C. Each point reflects the average of duplicates.

3.2.2.3.2 Capsanthin (CAPS)

Fig. 5 shows the concentration of capsanthin versus drying time of chiltepin samples under both drying conditions. The concentration of capsanthin during open-sun drying decreased significantly ($p \leq 0.05$) from 48.81 μg/g to 12.1 μg/g (75.2% loss) (Fig. 5a). This effect might be due to the exposure time to temperature and sunlight. There are few reports on the effect of solar drying on capsanthin, but it is known that high losses (79.5%) may occur in the drying of the ground pepper during long sun exposure time (5-7 days) (Topuz and Özdemir, 2004). A fading color appears upon prolonged exposure to temperature and light, which is due to isomerization reactions shifting from *trans* to *cis* configurations (Gregory *et al*., 2008). Environmental conditions such as light, unsaturated lipid content, and exposure time can generate free radicals, where capsanthin may be acting as an antioxidant, capturing free radicals (Giuffrida *et al*., 2013).

During hot air drying of unblanched samples (OB), CAPS concentration decreased with drying time ($p \leq 0.05$) for each draying temperature (Fig. 5b). The concentration values decreased from 58.7 μg/g to 29.0 μg/g (50.6% loss) at 35 °C, 28.1 μg/g (52.1% loss) at 45 °C, and as low as 27.6 μg/g (52.9% loss) at 55 °C. Degradation rate constants (Table 1) were lower at the lowest drying temperature, presenting the largest degradation at a temperature of 55 °C, with a half-life of 15 h. When the temperature increased from 45 to 55 °C, the degradation rate of CAPS was more affected than the other temperature (35 to 45 °C). To measure this change, we calculated its temperature coefficient (Q_{10}) to describe CAPS sensitivity to temperature change. This behavior could be explained by the effect of the drying temperature, which can lead to isomerization of the stable *trans*-capsanthin form to *cis*-capsanthin (Gregory *et al*., 2008); *cis*-capsanthin in paprika increased by increasing the drying temperature from 30 to 60 °C (Pérez-Gálvez and Garrido-Fernández, 1997). *Trans*-

capsanthin is isomerized to the cis form by the effect of heat, in accordance with the absorbed energy. In samples dried at 55 ºC, the effect of temperature is higher due to the higher energy absorbed. Therefore, CAPS isomerization may also be higher. Thus, the degradation constant is greater with a shorter half-life than for other treatments (Table 1).

In hot air drying of WB samples (Figure 5c), CAPS concentration didn´t decrease with the blanching temperature and time (58.4 μg/g dw), but it did with the drying time ($p \leq 0.05$) for each drying temperature. Even though blanching temperature is higher (85 °C) than drying, the time was lower (8 min). CAPS is a water-insoluble carotenoid and it would probably be more affected during drying because of the increased time of temperature exposure.

Losses observed at each drying temperature, increased relatively to unblanched samples. In this case, the concentrations decreased from 58.4 μg/g dw to 20 μg/g dw, 19 μg/g dw, and 18 μg/g dw, depending on the drying temperature. At temperatures of 35 °C, 45 °C, and 55 °C, CAPS decreases up to 69 %. As in the unblanched samples, CAPS degradation rate increased depending on the drying temperature (Table 1). The degradation rates during drying at temperatures of 35 and 45 °C are very similar, but at a 55 °C, a two-fold increase was observed. Meanwhile, the half-life is reduced dramatically with the increasing drying temperature (Table 1). When the temperature increased from 45 to 55 °C, the degradation rate of CAPS in blanched samples was more affected than the other temperatures (35 to 45 °C). To measure this change, we used the temperature coefficient (Q_{10}) value to describe CAPS sensitivity to temperature change. This effect is probably due to blanching, where the applied temperature might alter the cell wall causing a great extraction of compounds such as CAPS, which is exposed to drying temperature (Fellows, 2000). During blanching, an excessive autoxidation of carotenoids and discoloration occur in chili peppers (Schwarts and Von Elbe, 2008). It has been reported that blanching helps reducing losses (Gupta *et al*., 2002), but the effect depends on the product and the temperature used.

The activation energy (E_a) required for OB samples was greater (46.09 kJ/mol K) than WB samples (35.86 kJ/mol K) (Table 1). This difference is probably due to the blanching temperature, which might alter the wall cell, facilitating the release of compounds, and requiring less Ea; in contrast to WB that has a firmer wall cell, requires more Ea (Fellows, 2000).

The effect of temperature and time on carotenoids has already been reported; it is known that isomerization of its conformation from *trans* to *cis* occurs, which causes the color fading (Schwarts and Von Elbe, 2008). However, in our study, CAPS concentration in the chiltepin's drying process in unblanched and blanched samples, had lower losses than those reported for paprika dried in an oven at 70 °C (Topuz and Özdemir, 2004). The temperature and time required in both drying process, depends on the variety, environmental conditions, and stage of maturity of the chili peppers. For some varieties, shorter drying times at high temperatures are favorable, while others present greater losses. The carotenoid level in paprika of some varieties such as 'Jaranda', 'Jeromin', 'Joriza', and 'Remény', dried at 90 °C for 6 h, did not differ significantly from the content found in samples dried at 50 °C. However, in the hybrid 'Délibáb' and the variety 'SZ-178', the retention of color was significantly higher following a high-temperature treatment (Daood *et al*., 2014). Fig. 5b shows a typical chromatogram of the pepper CAPS obtained by HPLC methodology.

3.2.2.3.3 Ascorbic acid (AA)

The open-sun drying method had a significant effect ($p \leq 0.05$) on the content of AA. During the first 2 hours of drying, losses in AA concentration were over 90% (from 95 to 3.5 μg/g dw). It is noteworthy that during this two-hour period, the water activity remained at high levels (0.95 to 0.8) (Fig. 3a) and the internal temperature, throughout the drying process, ranged between 20 and 40 °C with a relative humidity between 20 and 80%. This drastic effect on the concentration of AA could be attributed to two major factors: light intensity and water activity. Studies on the sensitivity of AA to light report that the concentration depends on light intensity and product type (De Tullio *et al*., 2007; Santos and Silva, 2008); an increase in light intensity leads to an increase in ascorbic acid oxidase activity, which oxidizes AA (De Tullio *et al*., 2007). The concentration of AA also depends on water activity. The AA degradation is greatest when water activity is high and it has been reported that the highest loss of AA is with a value of 0.84 (De Tullio *et al*., 2007); this value is within the range found in our study (0.9-0.8) where losses of AA were of 90%.

The AA concentration reduction, during drying by hot air drying under darkness, depends on the drying time ($p \leq 0.05$). An increase in the drying time reduces

the concentration of AA (from 142 to 45 μg/g dw). In unblanched samples, the values of AA ranged from 14 μg/g dw to 48 μg/g, 47 μg/g, for 35 °C and 45 °C respectively, with the lowest value obtained at 55 °C (46 μg/g). AA losses reached up to 75% at this temperature, while at 35 °C the reduction was 65%. In blanched samples, AA was reduced in 30% of the concentration from 142 μg/g to 100 μg/g. During the drying process the losses were similar to unblanched samples, ranging between 54 and 72% (from 100 to 38 μg/g dw). The AA degradation rate constants were in the range of 0.025-0.067 h^{-1} and increased with the drying temperature (Table 1). The AA half-life time ($t_{1/2}$) in unblanched samples was 27.7 h at 35 °C, but it decreased to 10.6 h at 55 °C; an increase in Q_{10} with the increase in drying temperature was observed. The E_a required for OB samples was greater (40.06 kJ/mol K) than WB samples (37.93 kJ/mol K) (Table 1). This difference is also probably due to the blanching temperature, as CAPS activity energy (Fellows, 2000). AA degradation is complex, but its sensitivity to temperature is well known, and may be due to both non-enzymatic and enzymatic reactions. AA can be oxidized and also act as an anti-oxidant (Daood *et al*., 2006).

Regarding chili pepper, it has been was reported that high AA losses (98.2%) occur with drying air temperatures of 90 °C, which is similar to those found for open-sun drying in our study (Vega-Gálvez *et al*., 2009). Other studies reported losses greater than 60 % during drying by hot air drying, mainly at high temperatures (Daood *et al*., 2006; Vega-Gálvez *et al*., 2009). Another important parameter to be considered in the AA degradation is water activity. We observed the highest losses of AA concentration in the range of water activity between 0.7 - 0.9 at 35 °C, and between 0.4 - 0.9 at 45 and 55 °C (Fig. 3b). In previously blanched samples, this range was reduced from 0.8 - 0.9 for all temperatures (Fig. 3c). In our study, during drying, losses of AA in chiltepin pepper could have been due to the endogenous antioxidant action of AA itself, which may also have prevented the oxidation of carotenoids (Daood *et al*., 2006). This action might also contribute to retention of CAPS during the first stage of drying due to its losses occurred at longer times of drying, where AA reduction was the greatest. AA losses in sun drying are greater than those in hot air drying; therefore, the effect of light is important.

Conclusions

Raw chiltepin has a substantial content of C and CAPS, and a low content of AA. In this study, the drying conditions mainly affected CAPS and AA concentrations. Particularly in open sun drying, the contents of AA and CAPS were reduced to a greater extent than in hot air drying. Blanching prior to hot air drying increased losses, particularly CAPS and AA. The C concentration during the drying process was more stable than those of CAPS and AA. In hot air drying, the lowest temperature (35 °C) favored the retention of CAPS and AA in chiltepin. Thus, the hot air drying method is recommended to retain higher content of CAPS and AA compounds in chiltepin.

Nomenclature

C	capsaicin
CAPS	capsanthin
AA	ascorbic acid
dw	dry weight
OB	unblanched
WB	blanched
CCRD	central composite rotational design
POD	peroxidase
AOAC	association of official agricultural chemists
ASTA	American spice trade association
k	degradation rate constant
R^2	linear correlation coefficient
Q_{10}	temperature coefficient
E_a	activation energy
$t_{1/2}$	half-life time

Acknowledgements

The authors acknowledge the help provided by CONACyT, CIAD A.C., and UNIDA of ITV of Mexico, as well as the technical support by Maribel Yael Valencia Tapia, Anahi Guadalupe Cozaín Montiel, and Francisco Alfonso Aguilar Valenzuela.

References

ASTA. (1997). *Official analytical methods of the ASTA: method 21.3, pungency of Capsicum and their oleoresins*. 5th ed., New Jersey.

AOAC. (2013). Association of Official Agricultural Chemists. Official Method 934.06 Moisture in Dried Fruits. Available at: http://files.foodmate.com/2013/files_2914.html. Accessed at: May 26, 2017.

Bernardo, A., Martínez, S., Álvarez, M., Fernández, A., and López, M. (2008). The composition of two Spanish pepper varieties (Fresno de la Vega and Benavente-los Valles) in different ripening stages. *Journal of Food Quality 31*, 701-716.

Carvajal, M., Giménez, J.L., Riquelme, F., and Alcaraz, C.F. (1998). Antioxidant content and colour level in different varieties of red pepper (*Capsicum annuum* L.) affected by plant-leaf Ti4 + spray and processing. *Acta Alimentaria 27*, 365-375.

Cisneros-Pineda O., L. W. Torres-Tapia, L. C. Gutiérrez-Pacheco, F. Contreras-Martín, T. González-Estrada, and S. R. Peraza- Sánchez. (2007). Capsaicinoids quantification in chili peppers cultivated in the state of Yucatán, México. *Food Chemistry 104*, 1755-1760.

Contreras-Padilla, M., and Yahia, E.M. (1998). Changes in capsaicinoids during development, maturation, and senescence of chili peppers and relation with peroxidase activity. *Journal of Agricultural Food Chemistry 46*, 2075-2079.

Daood, H.G., Kapitány, J., Biacs, P., and Albrecht, K. (2006). Drying temperature, endogenous antioxidants and capsaicinoids affect carotenoid stability in paprika (red pepper spice). *Journal of the Science of Food and Agriculture 86*, 2450-2457.

Daood, H.G., Palotás, G., Palotás, G., Somogyi, Z., Pék, Z., and Helyes, L. (2014). Carotenoid and antioxidant content of ground paprika from indoor-cultivated traditional varieties and new hybrids of spice red peppers. *Food Research International 65(Part B)*, 231-237.

De Tullio, M.C., Ciraci, S., Liso, R., and Arrigoni, O. (2007). Ascorbic acid oxidase is dynamically regulated by light and oxygen. A tool for oxygen management in plants? *Journal of Plant Physiology 164*, 39-46.

Domínguez-Niño, A., Buendía-González, A.N., Cantú-Lozano, D., Andrade-González, I., and Luna-Solano G. (2016). Efecto del secado por lecho fluidizado sobre las propiedades fisicoquímicas y microbiológicas de queso fresco mexicano. *Revista Mexicana de Ingeniería Química 15*, 869-881

Doner, L.W., and Hicks, K.B. (1981). High-performance liquid chromatographic separation of ascorbic acid, erythorbic acid, dehydroascorbic acid, dehydroerythorbic acid, diketogulonic acid, and diketogluconic acid. *Analytical Biochemistry 115*, 225-230.

Estrada, B., and Bernal, M.A. (2000). Fruit development in *Capsicum annuum*: changes in capsaicin, lignin, free phenolics, and peroxidase patterns. *Journal of Agricultural and Food Chemistry 48*, 6234-6239.

FAO. Comisión del Codex Alimentarius. Programa conjunto FAO/OMS sobre normas alimentarias comité del codex sobre frutas y hortalizas frescas. (2010). Available at: ftp://ftp.fao.org/codex/meetings/CCFFV/ccffv14/ff14_10s.pdf. Accessed at: May 10, 2016.

Fellows, P. (2000). *Food Processing Technology Principles and Practice*. CRC Press, Boca Raton, Florida.

Giuffrida, D., Dugo, P., Torre, G., Bignardi, C., Cavazza, A., Corradini, C., and Dugo, G. (2013). Characterization of 12 *Capsicum* varieties by evaluation of their carotenoid profile and pungency determination. *Food Chemistry 140*, 794-802.

Govindarajan, V., and Salzer, U. (2009). *Capsicum* - production, technology, chemistry, and quality - part II: processed products, standards, world production and trade. *Critical Reviews in Food Science and Nutrition 23*, 207-288.

Gregory, F. (2008). Vitamins. In Damodaran, S., Parkin, K., and Fennema O. (Eds.). *Fennema's Food Chemistry* (4th ed.). Pp. 441-515, CRC Press/Taylor & Francis; Boca Raton, FL.

Gupta, P., Ahmed, J., Shivhare, U.S. and Raghavan, G.S.V. (2002). Drying characteristics of red chili. *Drying Technology 20*, 1975-1987.

Howard, L.R., Talcott, S.T., Brenes, C.H., and Villalon, B. (2000). Changes in Phytochemical and antioxidant activity of selected pepper cultivars (*Capsicum* species) as influenced by

maturity. *Journal of Agricultural and Food Chemistry 48*, 1713-1720.

Jarén-Galán, M., and Mínguez-Mosquera, M.I. (1997). β-Carotene and capsanthin co-oxidation by lipoxygenase, kinetic and thermodynamic aspects of the reaction. *Journal of Agricultural and Food Chemistry 45*, 4814-4820.

Kirschbaum-Titze, P., Hiepler, C., Mueller-Seitz, E., and Petz, M. (2002). Pungency in paprika (*Capsicum annuum*): 1. Decrease of capsaicinoid content following cellular disruption. *Journal of Agricultural and Food Chemistry 50*, 1260-1263.

Kurozawa, L.E., Terng, I., Hubinger, M.D., and Park, K.J. (2014). Ascorbic acid degradation of papaya during drying: effect of process conditions and glass transition phenomenon. *Journal of Food Engineering 123*, 157-164.

Labuza, T., Tannenbaun, S., and Karel, M. (1970). Water content and stability of low moisture and intermediate moisture foods. *Food Technology 24*, 543-544.

Lee, S.H., and Labuza, T.P. (1975). Destruction of ascorbic acid as a function of water activity. *Journal of Food Science 40*, 370-373.

Mínguez-Mosquera, M.M., Jarén-Galán, M., and Garrido-Fernández, J. (1994). Influence of the industrial drying processes of pepper fruits (*Capsicum annuum* cv. *Bola*) for paprika on the carotenoid content. *Journal of Agricultural and Food Chemistry 42*, 1190-1193.

Montoya-Ballesteros, G.B., Ayala-Chávez, G.M., Martínez-Núñez, Y.Y., and Robles-Ozuna, L.E. (2010). Capsaicinoides y color en chiltepín (*Capsicum annuum var. Aviculare*): efecto del proceso sobre salsas y encurtidos. *Revista Mexicana de Ingeniería Química 9*, 197-207.

Orak, H., and Demirsi, M. (2005). Effect of different blanching methods and period of frozen storage on enzyme activities and some quality criterias of hot and sweet red peppers (*Capsicum annuum* L.). Pak. *Journal of Biological Science 8*, 641-648.

Pérez Gálvez, A., and Garrido Fernández, J. (1997). Termodegradación de carotenoides en el pimentón. *Grasas y Aceites 48*, 290-296.

Pérez-López, J., López-Nicolás, J.M., Núñez-Delicado, E., Del Amor, F. and Carbonell-Barrachina, A. (2007). Effects of agricultural practices on color, carotenoids composition, and minerals contents of sweet peppers, cv. *almuden*. *Journal of Agricultural and Food Chemistry 55*, 8158-8164.

Pugliese, A., O'Callaghan, Y., Tundis, R., Galvin, K., Menichini, F., O'Brien, N., and Loizzo, M.R. (2014). *In vitro* assessment of the bioaccessibility of carotenoids from sun-dried chili peppers. *Plant Foods for Human Nutrition 69*, 8-17.

Raju, P.S., Chauhan, O.P., and Brawa, A.S. (2010). Chili flavor. In HUI Y. (Ed.). *Handbook of Fruit and Vegetable Flavors*. Hoboken; New Jersey: John Wiley & Sons, Inc.

Rodriguez-Amaya, D.B. (2010). Quantitative analysis, *in vitro* assessment of bioavailability and antioxidant activity of food carotenoids-a review. *Journal of Food Composition and Analysis 23*, 726-740.

SAGARPA. (2011). Mantiene México liderazgo en la producción mundial de chile. Secretaria de Agricultura, Ganadería, Desarrollo Rural, Pesca y Alimentación, México. Available at: http://www.sagarpa.gob.mx/Delegaciones/yucatan/Boletines/Paginas/201208B058.aspx&source=gmail&ust=1463159607067000&usg=AFQjCNE2BaGsr3k3G2Zl2zLh5-aAWBMxcA. Accessed at: May 10, 2016.

Santos, P., and Silva, M.A. (2008). Kinetics of L-ascorbic acid degradation in pineapple drying under ethanolic atmosphere. *Drying Technology 27*, 947-954.

Schwarts, J.S., and Von Elbe, G.M. (2008). Colorants. In: Damodaran, (S., Parkin, K., and Fennema, O.R. eds.), Pp. 571-632. *Fennema's Food Chemistry* (4th ed.), CRC Press/Taylor & Francis; Boca Raton, FL.

Schweiggert, U., Schieber, A., and Carle, R. (2006). Effects of blanching and storage on capsaicinoid stability and peroxidase activity of hot chili peppers (*Capsicum frutescens L.*). *Innovative Food Science and Emerging Technologies 7*, 217-224.

Topuz, A., Dincer, C., Özdemir, K.S., Feng, H., and Kushad, M. (2011). Influence of different drying methods on carotenoids and capsaicinoids of paprika (Cv., *Jalapeno*). *Food Chemistry 129*, 860-865.

Topuz, A., and Özdemir, F. (2004). Influences of gamma irradiation and storage on the capsaicinoids of sun-dried and dehydrated paprika. *Food Chemistry 86*, 509-515.

Vega-Gálvez, A., Di Scala, K., Rodríguez, K., Lemus-Mondaca, R., Miranda, M., López, J., and Pérez-Won, M. (2009). Effect of air-drying temperature on physico-chemical properties, antioxidant capacity, colour and total phenolic content of red pepper (*Capsicum annuum*, *L. var. Hungarian*). *Food Chemistry 117*, 647-653.

Vega-Gálvez, A., Lemus, M.R., Bilbao, S.C., Yagnman, F., and ROJAS, A. (2007). Mass transfer kinetics during convective drying of red pepper var. Hungarian (*Capsicum annuum*). Mathematical modeling and evaluation of kinetic parameters. *Journal of Food Process Engineering 31*, 120-137.

Wahyuni, Y., Ballester, A.R., Sudarmonowati, E., Bino, R.J., and Bovy, A.G. (2013). Secondary metabolites of *Capsicum* species and their importance in the human diet. *Journal of Natural Products 76*, 783-793.