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Effect of traditional sun-drying and oven-drying on carotenoids and phenolic compounds of apricot (*Prunus armeniaca* L.)

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ABSTRACT

Background: The indubitable role of phytochemicals such as carotenoids and phenolic compounds in human health has prompted the researchers to study the factors affecting the stability and the availability of these compounds. **Aims**: This study investigates the effect of two drying processes; oven-drying (OD) and traditional sun-drying (TSD) on carotenoids and phenolic compounds of apricots. **Methods and Material**: OD was performed at 65°C, and TSD was performed by direct exposure of apricot to sunlight at daytime temperatures around 40°C and relative humidity between 25 and 35%, following an Algerian traditional method of drying. Carotenoids and phenolic compounds were extracted, and then total carotenoids (TC), total phenolic compounds (TPC), total flavonoids (TF) and total tannins (TT) were spectrophotometrically quantified. The free radical scavenging activity (FRSA) of the phenolic extracts was measured by the DPPH method. **Results**: Carotenoids and phenolic compounds were significantly affected by both drying methods. OD decreased TC and TT by 44% and 12%, respectively, and increased TPC and TF by 4%. TDS affected negatively all the measured components, where TC, TPC, TF, and TT decreased by 67%, 15%, 43%, and 36%, respectively. However, the highest FRSA was reported for the TSD apricots (40%) followed by OD apricots (36%), and fresh apricots (32%). **Conclusions**: Carotenoids and phenolic compounds were significantly affected by both drying methods. OD decreased TC and TT by 44% and 12%, respectively, and increased TPC and TF by 4%. TDS affected negatively all the measured components, where TC, TPC, TF, and TT decreased by 67%, 15%, 43%, and 36%, respectively. However, the highest FRSA was reported for the TSD apricots (40%) followed by OD apricots (36%), and fresh apricots (32%).

Keywords: Apricot, traditional sun-drying, oven-drying, carotenoids, phenolic compounds.

1. INTRODUCTION

Fruits are excellent sources of macro and micronutrients, particularly bioactive compounds such as vitamins and antioxidants. Nowadays, it's clear that antioxidants as phenolic compounds, carotenoids, and vitamin C impart numerous health benefits, where the prevention of some socially significant diseases (like cancer and cardiovascular diseases), has been associated with consumption of fresh fruits and vegetables [1,2]. Plant antioxidants are phytochemicals that can prevent the oxidation of a biological substrate. Thus, protecting food and tissues from damages that can be caused by free radicals [3]. Apricots are widely distributed fruits, due to their specific sweet flavor and color. Every year, more than 4.2 million tons are produced [4]. Furthermore, apricot constitutes one of the most cultivated fruits in the North African region, particularly in Algeria, which covers more than 6 % of the world's production [4]. Apricots provide significant health benefits because of their high content in antioxidants, primarily phenolic compounds and carotenoids [5,6]. Phenolics represent the predominant phytochemicals

present in apricots [5]. These compounds are a structurally diverse class of phytochemicals and they occur as plant secondary metabolites, they are defined by the presence of at least one aromatic ring bonded directly to one or more hydroxyl groups [2]. Along with their antioxidant activity, Phenolics showed several further biological characteristics such as antimicrobial, anti-inflammatory, and immuno-stimulatory activities [7]. Flavonoids are water-soluble phenolics that show strong antioxidant activities, they constitute the largest group of polyphenols, with more than 5000 identified compounds [8]. Carotenoids are a large family of lipophilic compounds that are responsible for the orange color of apricots; they play a significant role in light-harvesting and in protection against photodamage in plants [9]. Carotenoids have been found to exhibit important antioxidant activity and help in preventing chronic diseases such as cardiovascular disease and skin cancer [10]. Furthermore, they are referred to as provitamin A since they can be transformed *in vivo* to active vitamin A[9, 10].

Apricots are climacteric fruits that undergo fast maturation after harvesting, which considerably limits their period of storage. Thus, different preservation methods such as drying and canning are habitually applied to preserve the fruits. Drying is the most common method to preserve apricots and extend their availability [11]. The process reduces the moisture content of apricots to a degree that allows safe storage for a longer period [12]. However, several studies reported that the antioxidant content of fresh fruits can be affected by processing techniques, which can increase or decrease their content [8, 13, 14].

Sun-drying of fruits and vegetables is one of the oldest forms of food preservation methods. In Algeria, traditional sun-drying of apricot remains the most practiced method. The reason behind this is that sun-drying is a simple method, requiring low capital, simple equipment, and low energy input. The traditional process of drying, applied in Algeria, is different from that usually reported in the literature, where apricots are neither blanched, nor treated with sulfates to prevent browning. Instead, apricots are treated with salt as a preservative agent and then dried. This method provides to the dried apricots specific organoleptic properties, where the color of the product is brown to dark with a salty flavor. Thus, there is a lack of knowledge on the effect of this traditional procedure on apricot antioxidants. For this reason, the current work investigates the effects of traditional sun-drying (TSD) on apricot antioxidants, primarily polyphenols, flavonoids, tannins, and carotenoids. The effect of oven drying (OD) was also investigated for comparison.

2. MATERIAL AND METHODS

2.1. Plant materials

Fruits of *Prunus armeniaca* L. (cv. Louzi) were collected from the N'gaous region of Algeria at commercial maturity. Apricots were directly transported to the laboratory, rinsed with tap water and stored at 4°C until utilization.

2.2. Drying process

2.2.1. Oven-drying

Fruits were dried in a ventilated laboratory oven (Memmert ULE 600, Germany) at a drying temperature of 65°C (Figure 1). The temperature of 65°C constitutes the average temperature used by food technologists to dry apricot [15-18]. Samples of fresh apricots were halved, pitted, and then placed in the oven, on the steel sieved trays, which were designed to increase air passage from both surfaces. Before starting the drying process, the oven was run for 30 min to obtain steady-state conditions. The suitable dryness level (moisture around 25 %, according to *CODEX STAN 130-1981*) was reached in 14 to 15 hours. Dried apricots were placed into polyethylene bags and stored at 4°C until subsequent analysis.

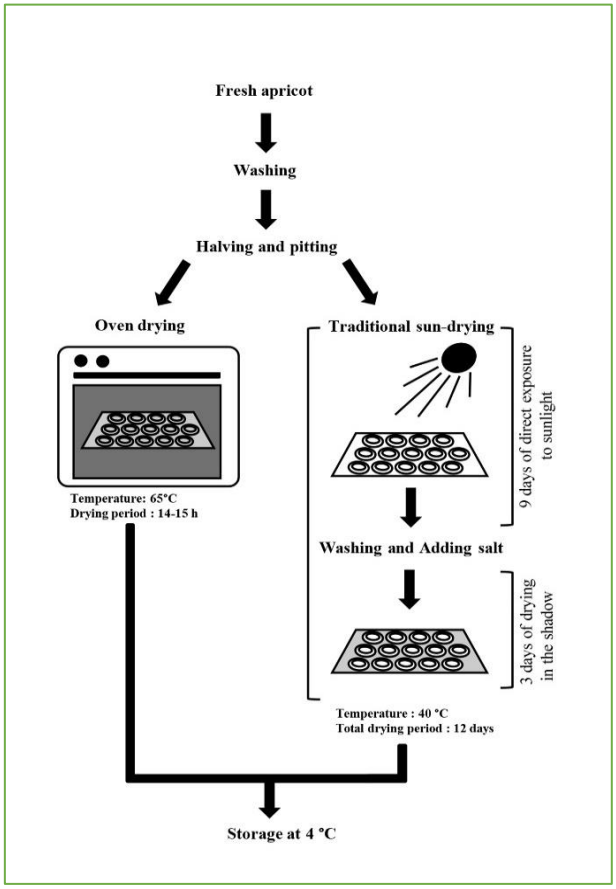

Figure 1: Simple schematization of the drying processes

2.2.2. Traditional sun-drying

Fresh apricots were halved, pitted, divided on a metal plate (covered with a cloth) and then dried by direct exposure to sunlight, with an overall maximum daytime air temperature of around 40°C for nine days (starting from mid-June). After that, dried apricots were washed, treated with salt by pulverization, and then, dried for three other days in the shadow to evaporate the residual water from the washing step (Figure 1). Dried apricots were placed into polyethylene bags and stored at 4 °C until subsequent analysis. During the drying process, the relative humidity of the air was between 25 and 35%, the days were sunny with no precipitation. This traditional sun-drying method is a common process applied by the farmers and the families in several regions in Algeria, aiming to preserve the excess of production and make apricots available for longer periods.

2.3. Chemical properties

Aiming to facilitate the extractability of apricot antioxidants and to standardize the analysis conditions for all samples, dried apricots were rehydrated for 24 h at room temperature. The exact and identical amount of water lost during the drying process was added during the rehydration (to reach the same water content as the fresh fruit), while the fresh samples were directly analyzed [19]. Before analysis samples were homogenized for two minutes using a Hand Blender Beaker. The following analyses were performed on the obtained purees: moisture content (MC) and dry-matter content (DM). They were measured (%) in a vacuum oven for 3 h at 105 °C (NF V 05-108, 1970) (for fresh, dried and rehydrated fruit), pH, measured using a digital pH meter (NF V 05-108, 1970). Acidity was determined as gram of citric acid per 100 g of samples by titration with 0.1 N sodium hydroxide to endpoint (pH 8.3) (NF V 05-101,1974). Ash content (%) was obtained using a muffle furnace at 550 °C for 5 hours (NF V 05-113,1972).

2.4. Measurement of total carotenoids

Total carotenoids were extracted according to the method of Rodriguez-Amaya [20] with optimization. Five grams of sample were extracted with 100 mL of methanol/petroleum ether (1:9, v/v) by using a high-speed homogenizer, and the mixture was transferred to a separating funnel. The petroleum ether layer was filtrated through sodium sulfate, transferred to a volumetric flask, and then the volume was completed to 100 mL with petroleum ether. Finally, the total carotenoid content was measured at 450 nm using a Shimadzu 1600- UV spectrophotometer. The results were expressed in mg β-carotene equivalent (β-CE/100 g DM).

2.5. Phenolic compounds analysis

2.5.1. Phenolic extract preparation

Phenolic compounds were extracted using the method described by Ali *et al.* [21]. Five grams of fruit puree was taken from the homogenate and diluted to 30 mL with 80% methanol and clarified by centrifugation (SEGMA 3-30K) at 10,000 × g for 15 min. The extract was filtered through a Whatman no. 1 filter paper.

2.5.2. Total *phenolic compounds* measurement

Total phenolic compounds (TPC) were measured by using the Folin–Ciocalteu assay as described by Singleton *et al.* [22] with minor modification. The crude phenolic extract, 0.5 mL was first diluted to 5 mL with 80% methanol, then 0.5 mL of 2 N Folin–Ciocalteu reagent and 0.5 mL of 20% sodium carbonate solution were added. The mixture was then allowed to stand for 60 min at room temperature and the absorbance was measured at 765 nm using a Spectrophotometer. Total phenolics were estimated by calibration curve prepared with concentrations of 0.01-0.25 mg/mL of gallic acid. The results were expressed in mg gallic acid equivalent (GAE) / 100 g DM.

2.5.3. Total flavonoids measurement

Total flavonoids (TF) were determined using the colorimetric method described by Bahorun *et al.* [23]. From the crude phenolic extract, 1 mL was mixed with 1 mL of a 2% $AlCl_3$-$6H_2O$ solution. After 10 min, the absorbance was measured immediately at 430 nm using a Spectrophotometer. The results were expressed as mg quercetin equivalent (QE) /100 g DM, according to a calibration curve prepared with concentrations of 1-40 µg/mL of quercetin.

2.5.4. Total tannins measurement

The estimation of the total tannins (TT) content was carried out by the method described by Hagerman & Butler [24]. 1 mL of the phenolic extract was mixed with 2 mL of bovine serum albumin solution (1 mg/mL) prepared in 200 mM acetate buffer, pH 4.9. After immediate stirring and incubation for 24 hours at 4 °C, the mixture was centrifuged for 15 min at 4000 rpm. The supernatant was discarded and the pellet was recovered and washed with 200 mM acetate buffer, pH 4.9. The resulting precipitate was dissolved in 4 mL of sodium-dodecyl-sulfate/*Tri-ethanol-amine* (1:5, w/v) solution, pH 9.5, and then 1 ml of the ferric chloride solution (100 mM HCl, 10 mM $FeCl_3$) was added. After incubation for 15 min, the absorbance was read at 510 nm on a Spectrophotometer. The amount of tannins was calculated by a calibration curve prepared with tannic acid (0.1-1.25 mg/ml). The results are expressed in mg tannic acid equivalent (TAE)/100 g DM.

2.5.5. Free radical scavenging activity measurement

Free radical scavenging activity (FRSA) was measured using DPPH (2,2-diphenyl-l-picrylhydrazyl) free radical according to the protocol described by Kuskoski *et al.* [25]. 0.1 ml of crude phenolic extract was taken in the test tube and 3.9 mL of 100 µM DPPH (2,2-diphenyl-l-picrylhydrazyl) solution was added, then the mixture was shaken vigorously and incubated for 30 minutes at room temperature. Absorbance was measured at 517 nm using a Spectrophotometer. The DPPH solution, freshly prepared with 80% methanol, gives an absorbance of 1.1 at 517 nm. Radical scavenging activity was calculated as % inhibition of DPPH radical using formula (01):

$$\%\text{Inhibition} = \frac{A_{control} - A_{sample}}{A_{control}} \times 100 \quad \ldots\ldots\ldots (01)$$

$A_{control}$: Absorbance of the control reaction (blank with methanol and DPPH solution).

A_{sample} : Absorbance of the sample reaction (phenolic extract with methanol and DPPH solution).

2.6. Statistical analysis

All analyses were carried out in triplicate and the experimental data were reported as means ± standard deviation (SD). The data were subjected to an analysis of variance (one-way ANOVA). The significant difference was determined by Tukey's multiple range test ($p \leq 0.05$) using XL-STAT software Version 2009.

3. RESULTS

The aim of the current study is to investigate the effect of traditional sun-drying (TSD) and oven drying (OD) on apricot antioxidants (carotenoids and phenolic compounds). Prior to the measurements on antioxidants, fresh and dried apricot were first assayed for humidity, ash content, pH and acidity. The results are shown in table 1.

Table 1: Chemical properties of fresh and dried apricots

Drying process	MC (%)	DM (%)	Ash (%)	pH	TA (%)
FA	85.24 ± 0.23	14.76 ± 0.23	0.734 ± 0.08	3.94 ± 0.07	0.59 ± 0.06
TSD	21.05 ± 0.56	79.95 ± 0.56	4.26 ± 0.18	4.03 ± 0.17	3,62 ± 0,13
OD	26.06 ± 0.74	73.94 ± 0.74	2.82 ± 0.08	4.16 ± 0.05	2.87 ± 0.08

FA, fresh apricot; TSD, traditional sun drying; OD, oven drying; MC, moisture content; DM, dry matter content; TA, titratable acidity. All the values are means of three replications +SD.

Moisture content decreased from 85.24% for fresh apricot to 21.05% and 26.06% for TSD and OD dried apricots, respectively. As a result, dry matter and ash content decreased after the drying processes, as well as TA. However, a slight increase in pH was observed for the dried apricots (Table 1).

Total Carotenoids (TC) were assessed before and after the drying processes. Data are reported on a DM basis in figure 2. Significant differences between the TC of fresh and dried apricots ($p<0.0001$) were reported. OD had remarkably affected TC content of apricots; the drying process decreased TC from 46.4 ± 6.2 mg β-CE/100 g DM to 25.8 ± 2.4 mg β-CE/100 g DM, which represents a loss of 44%. Furthermore, compared to OD, TSD was much harmful to TC, where the traditional process provoked a more significant decrease of 67%.

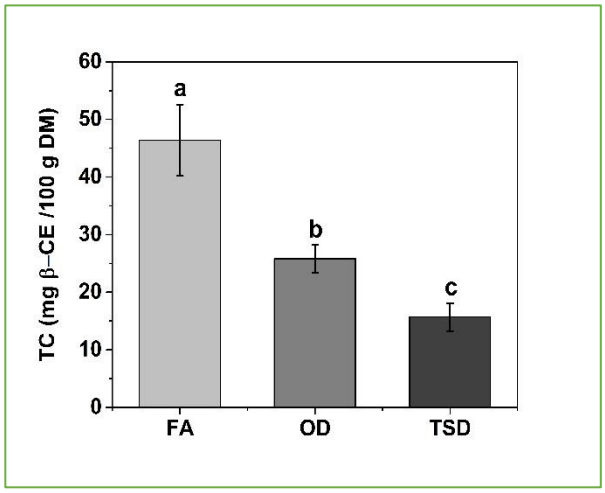

Figure 2: Effects of oven-drying (OD) and traditional sun-drying (TSD) on apricot total carotenoids (TC)
FA, fresh apricot; β-CE, β-carotene equivalent; DM, dry matter content. All the values are means of three replications +SD. The same letters indicate the absence of significant differences ($p<0.05$).

The effects of TSD and OD on total phenolic compounds (TPC), total flavonoids (TF), total tannins (TT), and Free radical scavenging activity (FRSA) of apricots are reported on a DM basis on figure 3. All measured parameters were significantly affected ($p<0.05$) by both drying methods (TSD and OD). TSD decreased remarkably the amount of TPC (Figure 3.a), TF (Figure 3.b), and TT (Figure 3.c) of apricots. The drying process caused significant losses of 15%, 43%, and 36%, respectively. However, for the OD, a decrease of 12% in TT after the drying process was recorded, while a slight increase of 4% was observed in TPC and TF.

FRSA (%) results are presented on figure 3.d. In contrast to our previous results (TPC, TF, and TT), FRSA increased significantly in dried apricot, and the heist FRSA was reported for the TSD. The methanolic extract of the dried apricot showed a radical scavenging activity of 40.1 ± 0.8%, followed by OD (35.9±1.7%), and fresh apricot (31.7 ± 1.2%).

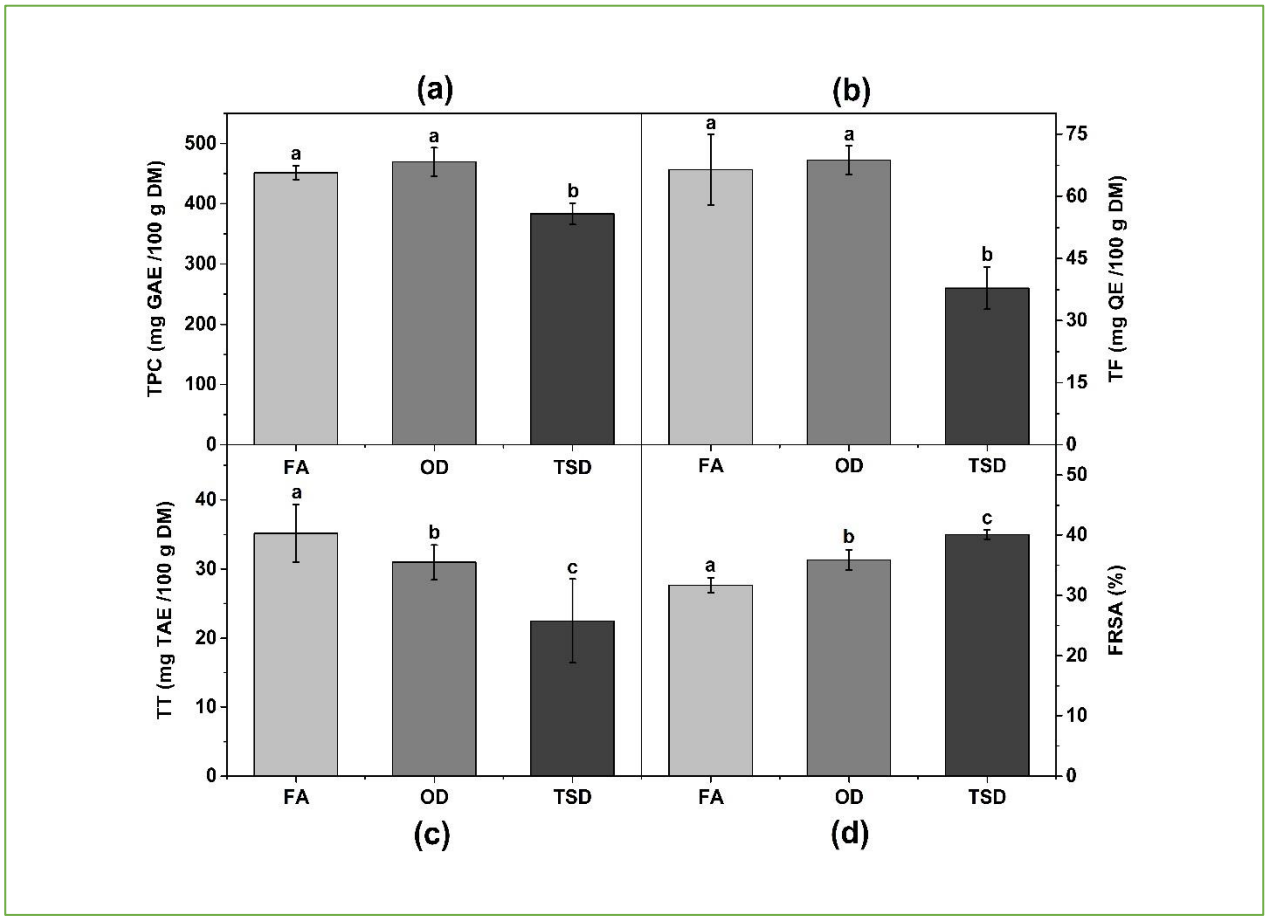

Figure 3: Effects of oven-drying (OD) and traditional sun-drying (TSD) on apricot total phenolic compounds (TPC), total flavonoids (TF), total tannins (TT), and Free radical scavenging activity (FRSA)

a: TPC, b: TF, c: TT, d: FRSA. FA, fresh apricot, DM, dry matter content, β-CE: β-carotene equivalents, GAE: gallic acid equivalent, QE: quercetin equivalent, TAE: tannic acid equivalent. All the values are means of three replications +SD. The same letters indicate the absence of significant differences ($p<0.05$).

4. DISCUSSION

The comparison between our findings and the different works on apricots showed that our values are included in the ranges reported by Akin *et al.* [26] for the humidity (74.19 - 88.17%) and ash content (0.50% - 0.89%), and the intervals indicated by Leccese *et al.* [6] for pH (3.35 - 4.41) and acidity (0.48 - 2.28%). The important loss of water during the drying process resulted in a concentration of the different components of apricot, which explains the increase in ash content and acidity (Table 1). The titratable acidity of apricot after the TSD (3.62%) was higher than the titratable acidity of apricot after the OD (2.87%). This can be due to the difference in drying conditions (mainly time and temperature) between the two processes, where apricot (climacteric fruit) can carry on the post-harvest maturation during TDS [11]. The drying temperatures (40°C) during TDS promote the physiological and biochemical reactions, including organic acids synthesis. However, the drying temperatures (65°C) during OD are relatively high, thus the physiological and the biochemical reactions are restrained. High acidity for sun-dried apricots was also reported by Madrau *et al.* [15] (4.67 - 7.33%) and Bolin [27] (3.8%). The ash content of the traditional sun-dried apricots was superior then the ash content of the oven-dried apricots too. This difference is mostly caused by the salt added during the process. Contamination by dust during the TSD may have also contributed to the ash content increase. Both drying methods have significantly decreased the carotenoids content of apricots (Figure 2). OD decreased apricot carotenoids by 44% of the initial content. These results are comparable to those of Fratianni *et al.* [16], where they reported significant losses of 50 % in total carotenoids for apricots dried at temperatures between 60 and 70 °C. In the same context, Karabulut *et al.* [17] recorded a decrease of 40% in β-carotene content after drying at 70 °C, and surprisingly they reported more losses (60%) by decreasing the drying temperature to 60 °C. The thermal damages caused by drying were directly proportional to the temperature used and the time operated in the process. It was mentioned that the heat applied during drying softens the cell walls, making them fragile and easily separated [16,17]. Therefore, the

carotenoids, usually stable within the original structure, become highly sensitive to external agents such as heat, oxygen, and light [16]. However, carotenoids were more sensitive to TSD. The traditional process caused the most significant losses, where the measurement of total carotenoid has highlighted a more significant decrease of 67% compared to OD. It has been reported that oven drying and additional conventional drying methods have several advantages over sun-drying. García-Martínez *et al.* [19] related these advantages to the fact that conventional drying methods are more rapid and the fruits are not in contact with the open environment during the process. Our results are consistent with those of Korekar *et al.* [28], where the authors reported a loss of 65% of β-carotene content for the sun-dried apricots. Furthermore, in a recent study, performed by Vega-Gálvez *et al.* [18] on the effect of hot-air drying temperatures (40-80°C) on apricot bioactive compounds, the results showed that the increase of drying time led to more damage than the increase of temperature. Moreover, the same authors reported the more significant carotenoids content decrease (53% loss) at the lowest temperature (40°C). The principal cause of carotenoids degradation, during the TSD, was the direct exposure of apricot to oxygen and sunlight. The destructive effect of oxygen and sunlight on carotenoids was confirmed by several authors [16-19, 29]. The exposure to oxygen during drying causes the generation of peroxides and oxidizing free radicals, which can cause a serious carotenoids loss [29]. Yang *et al.* [30] reported that carotenoids are sensitive to oxidation and can decompose, even if the samples were kept in the presence of traces of oxygen. The degradation of carotenoids can also result from photo-oxidation in the presence of light [31].

The investigated apricots in the current study were found to be a suitable source of phenolic compounds (451.6 ± 11.3 mg GAE / 100 g DM). The comparison with other studies shows that our results are higher than the ranges (319 and 413 mg GAE / 100 g DM) as reported by Milošević *et al.* [32]. As shown on figure 3.a, drying methods affected significantly apricots' phenolic compounds. In the last decades, numerous works investigated the effect of different treatments on phenolic compounds. Yet, data are not to seem correlated and even contradictory [33]. Most researchers reported a negative effect (decrease in phenolic compounds concentration) of heat treatments on phenolic compounds [13, 34,35]. On the other hand, several authors stated an increase in phenolic compounds after heat treatments. In our study, we witnessed both effects, where OD caused a slight increase in TP and TF, while TSD led to a significant decrease in TP, TF, and TT.

The increase, detected in TPC and TF after OD, was also reported in a previous study on apricot by Hussain *et al.*[36], where the authors detected an increase of 11.6-16.4% in the phenolic compounds concentration after drying. In the same angle, Santos *et al.* [37] studied the effect of drying at 60 °C on the phenolic compounds of pears, and reported an increase of 2.4-15% in TPC. However, Madrau *et al.* [15] reported a decrease in TPC of apricots dried at a lower temperature (55°C). In addition, Vega-Gálvez *et al.* [18] reported a significant decrease of TPC (>73%), and TF (>61%) for dried apricots at temperatures between 60 and 70 °C. The increase of TPC and TF can be explained by the improvement of phenolic compounds extractability, due to the relatively high temperature (70 °C) during the drying process, where it has been reported that high temperature facilitates the extraction of phenolic compounds [38-40]. Phenolic cosmpounds occur more often conjugated in soluble and insoluble forms, covalently bound to structural components of the cell wall (cellulose, hemicelluloses, and lignin). Bound phenolic compounds constitute an average of 24% of the fruits TPC, and heat treatments are likely to release those bound phenolic compounds [41]. Brunton [42] reported that, in addition to the better extractability of phenolic compounds during drying, the increase of TPC and TF can be due to the depolymerization of phenolic compounds with high molecular weights such as tannins. This statement agrees with our findings, where the increase of TPC and TF after OD was accompanied by a decreased in TT.

Unlike OD, TSD has caused significant losses of apricots phenolic compounds, where TPC, TF, and TT decreased by 15%, 43%, and 36%, respectively. This decrease can be explained by the enzymatic oxidation of phenolic compounds. Madrau *et al.* [15] reported that drying apricots for a long period in the presence of oxygen promotes the degradation of phenolic compounds by polyphenol oxidase (PPO). This enzyme is responsible for the oxidation of phenolic compounds to quinines. The enzymatic oxidation is followed by non-enzymatic polymerization of the resulted quinones into dark/brown polymers called melanins [43]. Apricot PPO remains active at drying temperature below 55 °C [44], and since TSD was performed at temperatures ~ 40 ° C, enzymatic browning is mostly the main cause of phenolic compounds decrease in TSD apricots. This was also visually confirmed, where the dried apricots had dark colors. Our results are in agreement with the results obtained by Vega-Gálvez *et al.* [18], where the authors attributed the decrease in TPC and TF observed during drying at 40 °C to the PPO activity.

The antioxidant activity increased significantly after the OD, this can be explained by the increase reported previously in TPC and TF, where phenolic compounds are known for their FRSA. However, while the expectations shifted toward a decrease in FRSA after TSD, surprisingly, the results showed a significant increase in FRSA (Figure 3.d). These results are similar to those of Madrau *et al.* [15] and Hussain *et al.* [36], the authors reported a significant increase in FRSA for dried apricots, despite the reduction in TPC. However, Vega-Gálvez *et al.* [18] reported a decrease in FRSA for dried apricots at temperatures between 40 and 80°C. According to Pokorny & Schmidt [45], FRSA of processed fruits may be enhanced by the development of new antioxidants, such as the products of browning reactions. Furthermore, Gan *et al.* [46] reported an increase in the antioxidant activity for the dried mung bean, which was also accompanied by an increase in browning. The same findings were reported by Lee *et al.* [47] for dried onions, the authors indicated that the antioxidant activity depends more on browning during drying than on phenolic content.

5. CONCLUSION

The main obtained results showed that TSD conditions, such as direct sunlight exposure and the longtime of the drying process, are parameters that affect negatively carotenoids and phenolic compounds of apricots. These conditions promoted the carotenoids photo-oxidation and the enzymatic oxidation of phenolic compounds (by PPO). Thus, OD caused less damage to carotenoids and phenolic compounds compared to TSD. The advantages of OD are the short period of drying, and the fruits are not exposed to open air, which has resulted in better preservation of carotenoids and phenolic compounds. However, despite the destructive effect of TSD on carotenoids and phenolic compounds, the process increased the FRSA of the phenolic extract. The enzymatic oxidation of the phenolic compounds during TSD promoted the generation of new compounds with high antioxidant properties. Thereby, the traditionally sun-dried apricots are a better source of antioxidants.

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