Antioxidant properties of milk chocolate assortments enriched with dried fruit

Diana Moigradean*, Mariana-Atena Poiana, Diana-Veronica Dogaru, Ionela Ciurica

Banat’s University of Agricultural Sciences and Veterinary Medicine „King Michael I of Romania” from Timisoara, Faculty of Food Processing Technology, Calea Aradului 119, Timisoara, RO 300645, Romania

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Abstract
The purpose of this study was to obtain homemade milk chocolate assortments enriched with dried fruit such as prunes, apricots and figs and investigate the antioxidant properties of the dried fruit and of the chocolate samples. Dried fruits are resulted from fresh fruit dehydrated at 65°C for 12 h; edible portions were cut into small pieces and were added in chocolate in different percentages (10% and 15% of total weight).

The total antioxidant capacity was measured by FRAP assay and to assess the total polyphenol content was used the Folin–Ciocalteu method. The prunes contain the highest total antioxidant capacity followed by apricots and figs. Based on the results obtained from this study, we can observe that the chocolate assortments with 15% addition of prunes has highest values of total antioxidant capacity (18.22 mM Fe²⁺/100 g DM) and total polyphenol content (3.30 mM GAE/100 g DM). The order of total polyphenol content in the chocolate assortments showed a similar trend as the total antioxidant capacity.

Keywords: homemade milk chocolate, antioxidant properties, dried fruit, prunes, apricots, figs

1. Introduction
Chocolate is one of the most loved foods all over the world [1]. Chocolate, derived from the cacao bean, has many beneficial compounds that can contribute to good health. The addition of ingredients in the manufacturing of milk chocolate decreases the nutritional value of chocolate and makes of this food less healthy than its dark chocolate [2]. Recently, it has been shown that chocolate is one of the most polyphenol rich foods along with tea and wine [1].

Fresh fruits are processed by various techniques to become dried fruits to prolong their shelf life [3]. Drying is one of the most widely used methods for fruit preservation [4]. Dried fruits are a concentrated form of fresh fruits, albeit with lower moisture content than that of their fresh counterparts since a large proportion of their moisture content has been removed through various modern drying techniques [3]. Sun drying is the most common method, because it uses a natural resource/source of heat: sunlight [5] but it is known that vacuum drying may allow obtaining high quality products [4, 6]. During the drying process, it is well known that numerous physical, chemical and nutritional changes occur in the fruits, which can affect their quality attributes [4]. The dried fruits without additives offer numerous health benefits. Some dried fruits are a good source of certain antioxidants. Phenols, a type of antioxidant, are more abundant in fruits like dates and figs than in some fresh fruits, leading researchers to advise that more dried fruits be included in the diet [7].

The raisins, figs, dates, prunes and apricots are the most common dried fruits in the marketplace [8]. Dried apricots contain vitamin C, which is important for the teeth and bones, the skin,
connective tissues, helps in iron absorption, and protects against colds and flu. The dried apricots are rich in antioxidants called polyphenols. These compounds reduce oxidative stress in your body and may help to prevent cardiovascular and other diseases [9]. Prunes promote healthy bones. They are rich in phenolic compounds, which may inhibit bone resorption and stimulate bone formation as well as function as antioxidants [10]. Figs and dried plums have the best nutrient score among the dried fruits. Processing to produce the dried fruit significantly decreases the phenols in the fruits on a dry weight basis [11].

Our study investigated the antioxidant properties of the dried fruit (prunes, apricots and figs) and the some milk chocolate assortments enriched with these fruit.

2. Materials and Methods

2.1. Dried fruits used as additives in chocolate

Fresh fruits were purchased from supermarket and then were dried in laboratory. The dehydration process was carried out with Food Dehydrator with 4 shelves by Heinner/Germany at the temperature of 65°C and were continued until to reach approximately the same moisture content (20% wet basis) for 12 hours.

A knowledge of the moisture content is often necessary to predict the behavior of foods during processing, e.g. mixing, drying, packaging [12]. It can also be used to confirm whether or not the drying process of foods is finished.

Moisture content (MC) is a measurement of the total amount of water contained in a food and is usually expressed as a percentage of the total weight:

\[ MC = \frac{w - d}{w} \times 100 \]  

[1]

In this equation \( w \) = wet weight and \( d \) = dry weight [13].

2.2. Obtaining chocolate assortments

It was obtained, in homemade condition, the plain milk chocolate (no added) - PMC and the milk chocolate assortments enriched with prunes - MCP, with figs - MCF and apricots - MCA; added in chocolate after our recipe. Recipes also influence the properties of chocolate [14]; the basic ingredients required for the manufacturing of chocolate are sugar, milk powder, butter, cocoa powder. Different percentages of dried fruit (10% and 15% of total weight, respectively) are used in making different chocolate assortments.

2.3. Chocolate recipe

The recipe, for preparing 1000 g chocolate, contains the following ingredients: 420 g sugar; 100 mL water; 50 g cocoa mass; 250 g milk powder; 200 g butter with 65% fat; 100 g dried fruit (prunes or apricots or figs).

The milk powder and the cocoa powder are mixed. The sugar with the water boil for 10 minutes. After melting the sugar, add the butter. Mixed until the butter melts, remove from heat and add the mixture of milk powder and cocoa. Stir continuously until smooth. In the meantime, the dried fruit is added. Pour the melted chocolate on a round silicone molds. After 2-3 hours checked if the chocolate is cool and remove from the molds, packaged and remained at 18°C.

2.4. Chemical analysis

Dried fruit samples (5 g) and chocolate samples (5 g) were grinded and were dissolved in 20 mL ethanol-water solution 45:55 (v/v), at room temperature.

After 30 minutes, the samples was filtered and centrifuged for 10 min at 5000 rpm with Mikro 200 Microliter Centrifuges by Hettich Lab Technology / Germany. The supernatant were analyzed to determine the total phenolic content and the total antioxidant activity.

The total antioxidant capacity was measured by FRAP assay (Benzie and Strain 1996) [15]. FRAP reagent was prepared freshly by 10 mM TPTZ (2,4,6-Tris(2-pyridyl)-s-triazine) solution (diluted in HCl 40 mM), 20 mM FeCl₃·6H₂O solution and 300 mM sodium acetate buffer at pH 3.6 in the ratio of 1:1:10. Was added 0.5 mL hydroalcoholic extract samples diluted in the ratio 1:10 (v/v) in distilled water and 2.5 mL FRAP reagent.

Absorbance was read at 593 nm, after 30 minutes, using an aqueous solution of FeSO₄ as standard. Correlation coefficient (r²) for calibration curve was 0.9993. Total antioxidant capacity was expressed as mM Fe²⁺/100 g DM (dry matter).

The total polyphenol content was determined by Folin-Ciocalteu method (Singleton and al., 1999) [16]. Briefly, 0.5 mL hydroalcoholic extract samples diluted in the ratio 1:50 (v/v) in distilled water

132
water, 2.5 mL of Folin-Ciocalteu reagent (diluted 1:10 in distilled water) and 2.0 mL Na₂CO₃ sol. 7.5% was stirred and was kept at room temperature. After 2 hours, the absorbance was read at UV-VIS Spectrophotometer SPECORD 205 by Analytik Jena at wavelength λ = 750 nm using gallic acid for calibration curve ($r^2 = 0.9982$).

The results were expressed as milligrams of gallic acid equivalents per 100 g dry matter (mg GAE/100 g DM).

All tests were performed in triplicate.

### 2.5. Statistical analysis

Simple linear regression analysis was applied using the Origin 8.0 software program for obtaining some correlations between the antioxidant properties of PMC and milk chocolate assortments with dried fruit.

### 3. Results and Discussions

Usually, the moisture content of dried fruit is 31% water [13], but our moisture content was smaller. After drying process, was observed a massive percent water loss, in the range of 80-85% in fresh fruit up to the range of 18-25% in dried fruit (Table 1).

Are presented in Table 2 the sensory properties of chocolate assortments enriched with dried fruit.

The addition of dried fruits in milk chocolate recipe was improved, in a pleasant manner, the sensory characteristics of the chocolate assortments with the advantage that it helps to diversify the range of chocolate speciality.

Based on the data presented in Table 3 are given values of total antioxidant capacity and total polyphenol content of the dried fruit used in technological chocolate recipe to obtain different chocolate assortments.

#### Table 1. The moisture in fruit before and after dehydration

<table>
<thead>
<tr>
<th>Dried fruit</th>
<th>Initial moisture (%)</th>
<th>Final moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prunes</td>
<td>81.78</td>
<td>25.16</td>
</tr>
<tr>
<td>Figs</td>
<td>80.06</td>
<td>18.39</td>
</tr>
<tr>
<td>Apricots</td>
<td>84.96</td>
<td>21.42</td>
</tr>
</tbody>
</table>

#### Table 2. The chocolate sensory properties

<table>
<thead>
<tr>
<th>The sensory properties</th>
<th>Appearance-exterior</th>
<th>Appearance-interior</th>
<th>Color</th>
<th>Consistency</th>
<th>Taste and Smell</th>
<th>The finesse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polished surface, without stains, scratches or air gaps.</td>
<td>Chocolate with added dried fruits; Are they evenly distributed and homogeneous consistency.</td>
<td>Dark-brown.</td>
<td>Hard and brittle.</td>
<td>Pleasant, taste and odor dried fruit added.</td>
<td>The product is unctuous.</td>
</tr>
</tbody>
</table>

#### Table 3. Total antioxidant capacity and total polyphenol content of the dried fruit

<table>
<thead>
<tr>
<th>Dried fruit</th>
<th>Total antioxidant capacity (mM Fe²⁺/100 g DM)</th>
<th>Total polyphenol content (mM GAE/100 g DM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prunes</td>
<td>32.71</td>
<td>4.32</td>
</tr>
<tr>
<td>Figs</td>
<td>23.54</td>
<td>2.15</td>
</tr>
<tr>
<td>Apricots</td>
<td>29.30</td>
<td>3.75</td>
</tr>
</tbody>
</table>

In the drying process, the protection of phenolic content is a very important issue because of the known antioxidant activity of the phenolic compounds [4].

In our studies, the prunes contain the highest total antioxidant capacity (32.71 mM Fe²⁺/100 g DM) followed by apricots (29.30 mM Fe²⁺/100 g DM) and figs (23.54 mM Fe²⁺/100 g DM). The total antioxidant capacity and the total polyphenolic compounds in dried fruit decreased in the order of prunes > apricots > figs (Table 3). These results are in compliance from other authors.

Pellegrini and al. (2006) [17] determined the total antioxidant activity of some dried fruits (apricots,
figs, prunes and raisins) in which prunes had the highest value (60.54 mM Fe$_{2+}$/kg) followed by apricots (36.64 mM Fe$_{2+}$/kg) and figs (14.43 mM Fe$_{2+}$/kg).

A study by Kamiloglu and al. (2014) [18] the antioxidant activities of dried fruit were in the descending order of raisins > apricots > figs and the total polyphenol content (expressed as mg GAE/g) decreased in the order of prunes > raisins > figs > dates [19].

Vinson and al. (2005) [11] mentioned that dried figs have superior quality of antioxidants, called phenols, compared to other fruits that attribute their antioxidant property; but it's not our case.

If have investigated the antioxidant capacity and total polyphenol content of the PMC it was found to be 15.67 mM Fe$_{2+}$/100 g DM and 3.12 mM GAE/100 g DM, respectively.

The total antioxidant capacity values and total polyphenol content of all the milk chocolate samples analyzed were higher than the PMC. The addition of more dried fruit will give the PMC a high antioxidant capacity values, thereby increasing with the percentage proportion of dried fruit (Table 4 and Table 5). Its values were also influenced by the type of dried fruits used as enriched. Total polyphenol content in chocolate assortments with 10% addition of dried fruit vary from 3.02 mM GAE/100 g DM in MCF to 3.24 mM GAE/100 g DM in MCP.

The order of total polyphenol content in the chocolate assortments showed a similar trend as the total antioxidant capacity.

The chocolate sample with the highest antioxidant activity is MCP 15% (18.22 mM Fe$_{2+}$/100 g DM), followed by MCA 15% (17.71 mM Fe$_{2+}$/100 g DM) and MCF 15% (16.85 mM Fe$_{2+}$/100 g DM) (Table 5).

Table 4. Antioxidant capacity and total polyphenol content of chocolate assortments with 10% addition of dried fruit

<table>
<thead>
<tr>
<th>The chocolate assortments</th>
<th>Total antioxidant capacity (mM Fe$_{2+}$/100 g DM)</th>
<th>Total polyphenol content (mM GAE/100 g DM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMC</td>
<td>15.67</td>
<td>3.12</td>
</tr>
<tr>
<td>MCP</td>
<td>17.37</td>
<td>3.24</td>
</tr>
<tr>
<td>MCF</td>
<td>16.46</td>
<td>3.02</td>
</tr>
<tr>
<td>MCA</td>
<td>17.03</td>
<td>3.18</td>
</tr>
</tbody>
</table>

Table 5. Antioxidant capacity and total polyphenol content of chocolate assortments with 15% addition of dried fruit

<table>
<thead>
<tr>
<th>The chocolate assortments</th>
<th>Total antioxidant capacity (mM Fe$_{2+}$/100 g DM)</th>
<th>Total polyphenol content (mM GAE/100 g DM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMC</td>
<td>15.67</td>
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<tr>
<td>MCP</td>
<td>18.22</td>
<td>3.30</td>
</tr>
<tr>
<td>MCF</td>
<td>16.85</td>
<td>2.98</td>
</tr>
<tr>
<td>MCA</td>
<td>17.71</td>
<td>3.21</td>
</tr>
</tbody>
</table>
Figure 1. The relationships between the antioxidant properties of plain milk chocolate and milk chocolate assortments with prunes (A), figs (B) and apricots (C).

All equations were revealed a positive relationship between the antioxidant properties of the PMC and the milk chocolate assortments, regardless of the fruit used and regardless of the dried fruit percentage added.

Figure 1 shows that there is a very good correlation between the antioxidant properties of the PMC and the MCP (Figure 1A) and MCA (Figure 1C) with the coefficient of determination $R^2 = 0.9643$; while the coefficient of determination calculated for the MCF is 0.9631(Figure 1B).

4. Conclusion

The drying process conditions housekeeping ($65^\circ$C) as figs, apricots and prunes is a simple method for preserving fruit with keeping their antioxidant properties.

The addition of different percentages of dried fruit in the chocolate assortments not induce negative changes in the sensory properties of chocolate, particularly its texture and consistency.

Our study showed that all milk chocolate assortments enriched with dried fruit have higher antioxidant properties about plain milk chocolate. Also, the highest values for antioxidant capacity and total polyphenol content were identified in chocolate samples with 15% addition of dried fruit, especially in milk chocolate assortments with prunes. The milk chocolate assortments enriched with dried fruit are the best in terms of antioxidant properties and can be consumed as a dessert.

Since the plums and the apricots are romanian native fruits and these is available in large quantities, it is recommended their valorification as dried fruit in chocolate industry.

Compliance with Ethics Requirements. Authors declare that they respect the journal’s ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.
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