Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1061-1068

Effect of Drying Conditions on Antioxidant Properties of Rosehip Fruits (*Rosa canina* sp.)

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The objective of this work was to investigate the influence of drying conditions on antioxidants contents and antioxidant activity of rosehips. Freshly harvested rosehips were dried under 3 air temperatures (50, 60 and 70 ºC) at air flow rates of 0.5, 1.0 and 1.5 m s^{-1}. The retention of total phenolics was best at 50 ºC and 1.5 m s^{-1} air flow rate. For the retention of total carotenoids and antioxidant activity, the appropriate drying conditions were found to be 70 ºC and 1.5 m s^{-1} air flow rate. For the highest retention of ascorbic acid, 60 ºC drying temperature and 1.5 m s^{-1} air flow rate was determined to be appropriate.

Key Words: Antioxidant activity, Ascorbic acid, Rosehip fruits.

INTRODUCTION

There is a much interest in the association between fruit and vegetable consumption and human health. Because oxidative stress plays a significant role in most disease processes and aging, the potential health benefits of fruits and vegetables have been largely attributed to their potential antioxidant capacity[1].

Rosehip fruits are one of the richest sources of antioxidant phytochemicals encountered. In addition to ascorbic acid, rosehips are also rich in carotenoids and phenolics[2,3].

Rosehips have been used for the production of herbal tea, nectar and marmelade in Turkey. Freezing, chilling or drying are the methods used for the storage of rosehips before processing by the food industry. Freezing and chilling are the methods used by food factories, drying is the method applied by people living at sunny regions.

There are many literatures aimed to investigate the health benefit effects[4], composition[5-7], antioxidant activity[2,8] and the utilization[9-12] of rosehips. But there is not much work about the losses during processing rosehips into various products[13-16]. Therefore, the objective of this work was to investigate the influence of the drying conditions on antioxidant content and antioxidant activity of rosehips and to find out the most suitable drying temperature and drying air flow rate.

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EXPERIMENTAL

The freshly harvested rosehips (*Rosa canina* sp.) were wholly dehydrated by hot air drying technic using the dehydration system developed[17] at 50, 60 and 70 ºC with air flow rates of 0.5, 1.0 and 1.5 m s^{-1} to achieve moisture content of 10 %. The dehydrated rosehips were put into sealable glass jars and were cooled. Before analysis, the samples were divided into two pieces by using a mortar and they were sorted. The samples which will be used for ascorbic acid determination were ground by the mortar and the others were milled as can pass through 1 mm sieve by using stainless steel mill. The average composition of fresh rosehip samples is given in Table-1. The drying experiments and analyses were duplicated and results were given as mean values.

TABLE-1
AVERAGE COMPOSITION OF FRESH ROSEHIP SAMPLES

Parameters	Mean
pH	3.94
Dry matter (g 100 g^{-1})	38.28
Total sugar (g kg^{-1})*	222.67
Reducing sugar (g kg^{-1})*	205.82
Unreducing sugar (g kg^{-1})*	16.01
Total carotenoids (mg g^{-1})*	0.38
Ascorbic acid (mg g^{-1})*	24.96
Total phenolics (mg g^{-1})*	79.88
Antioxidant activity (FRAP value) (mmol g^{-1})*	9.22

*Dry matter basis.

Determination of dry matter: Dry matter content was determined by heating in a vacuum oven at 70 °C until a constant weight was obtained[18].

Determination of total carotenoids: Total carotenoid determination was carried out according to the method of Chan and Cavaletto[19], with some modifications.

Three grams of the samples were extracted with a mixture of 50 mL acetone and petroleum ether (1:1 by volume), by using a homogenizer (Controls, Milano-Italy) and filtered under vacuum. The residue was extracted until the complete exhaustion of colour (usually 4-5 extractions were enough) with acetone:petroleum ether. The extracts were transferred to a seperatory funnel containing 25 mL of 10 % KOH in methanol (w/v) and allowed to stand for 1 h in darkness. Partition was achieved by adding 75 mL of petroleum ether and 100 mL of 20 % NaCl (w/v) and mixing gently. The hypophasic layer was discarded. The epiphasic layer was washed 3 times with water, passed through anhydrous Na_2SO_4 and made up 250 mL with petroleum ether. Absorption spectra in the visible region, 350-750 nm, were run with a spectrophotometer (Jasco V-530, Japan). Total carotenoid values were calculated[20] from the absorption maxima using an extinction coefficient of 2592 at 453 nm. The results were expressed based on ß-carotene equivalents as mg g^{-1} dry matter.

Determination of ascorbic acid: A sample of 3 g was weighed and homogenized with metaphosphoric acid solution (5 %, w/v) until uniform consistency at room temperature (20 ± 2 ºC), then centrifuged for 10 min at 3000 rpm and filtered under vacuum in a volumetric flask. This procedure was repeated twice. The final volume of the extracted solution was set at 100 mL with the metaphosphoric acid solution. The supernatants were recovered and ascorbic acid immediately measured spectrophotometrically by 2,6-dichlorophenolindophenol dye[21] at 520 nm. L-Ascorbic acid was used to prepare a standard solution (1 mg mL^{-1}). The results were expressed as mg g^{-1} dry matter.

Determination of total phenolics: A ground sample of 1 g weighed and phenolic compounds were extracted with 20 mL of 80 % aqueous methanol for 1 h with agitation (magnetic stirrer) at room temperature (20 ± 2 ºC) and filtered. The residue was extracted again in the same way. The solution was diluted to volume with the methanol. Sample extract was introduced in a 100 mL volumetric flask; 5 mL of Folin Ciocalteau's reagent (Sigma Chemical Co., St. Louis, MO) were added and mixed. The mixture was allowed to stand at room temperature for 5 min. A volume of 10 mL of saturated sodium carbonate solution (7.5 %, w:v) was added to the mixture and then mixed gently. A blank was also made by mixing water and the reagents. The solution was brought to 100 mL with water. After allowing the mixture to stand at room temperature for 0.5 h, the absorbance was read at 760 nm using the spectrophotometer. The experiment was carried out in duplicate. The standard calibration curve was plotted using catechin equivalent and the results expressed as, miligrams per gram of dry matter[22].

Determination of antioxidant activity: To measure antioxidant activity, an aliquot of the acetone/methyl alcohol/water/formic acid (40:40:20:0.1) extracts of rosehip samples were dried at 30 °C under vacuum, using an evaporator (Heidolph 4001, Germany) and redissolved in same volume of water[23]. Aqueous samples were mixed with 0.95 mL of ferric-TPTZ reagent (prepared by mixing 300 mM acetate buffer, pH 3.6, 10 mM 2,4,6-tripyridil-*s*-triazine in 40 mM HCl and 20 mM $FeCl_3$ in the ratio of 10:1:1) and measured at 593 nm. $FeSO_4$ was used as a standard and the antioxidant activity was expressed as mmol g^{-1} FRAP of dry matter[2].

RESULTS AND DISCUSSION

During dehydration of rosehips using different temperature and air flow rate, the time to reach the same dry matter is given in Fig. 1.

As can be seen from Fig.1, the drying time of the samples changed due to air flow rate. As expected, samples dried at 0.5 m s^{-1} air flow rate showed the highest drying time and drying time decreased as the air flow rate increased. Also, drying time increased as the temperature decreased. Similar results were reported by many resarchers[24-27]. According to them, during constant rate period of dehydration, the faster the air, the faster the rate of drying, but during the falling rate period, the factors that control the rate of drying change. Initially the important factors are

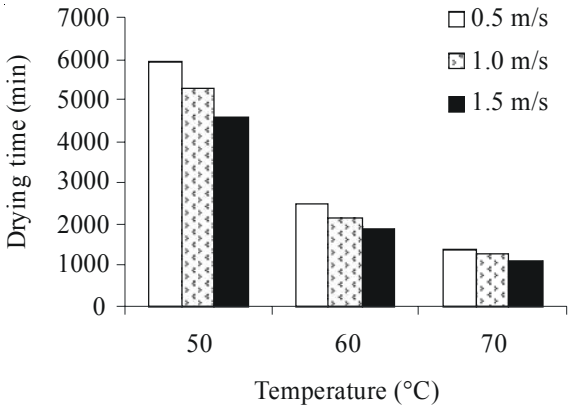

Fig. 1. Relation between air flow rate, drying temperature and drying time

similar to those in constant rate period, but gradually the rate of water movement from the interior of the food becomes the controlling factor. So the effect of air flow rate becomes unimportant. The drying times of samples dehydrated at 50 ºC and all 3 air flow rates were higher than the others. The samples dried at 60 and 70 ºC showed shorter drying times and as will be point out later, drying time significantly affected the antioxidant matters and antioxidant activity.

At the drying temperatures of 60 and 70 °C, the ascorbic acid and total carotenoids contents of the samples were close to each other, but at 50 °C, these values were lower (Figs. 2 and 3). This could be attributed to the fact that the decrease of the drying temperature resulted in the increase of drying time and hence, longer exposure time to the drying air. Same result was found by Rodriguez-Amaya[28] for carotenoids. This was ascribed to the continuation of enzymatic activity. Carotene degradation during drying has been attributed to its high sensitivity to oxidation. In a drying process, the cumulative effect of time-temperature determines the total carotene loss. In the absence of oxygen, formation of *cis*-isomers can also cause degradation of carotene[29]. According to Suvarnakuta *et al.*[26], carotene is degraded by free radical

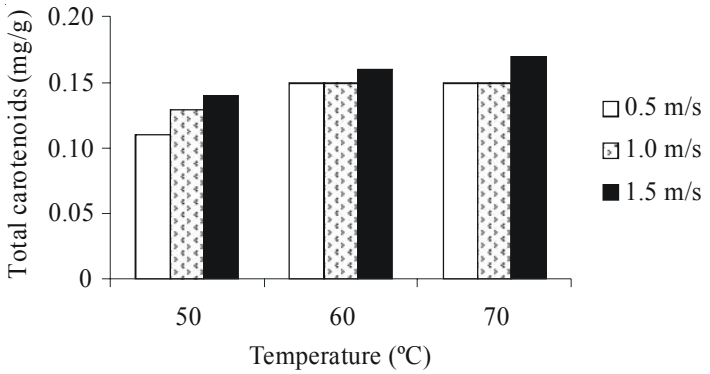

Fig. 2. Influence of air flow rate and drying temperature on total carotenoids

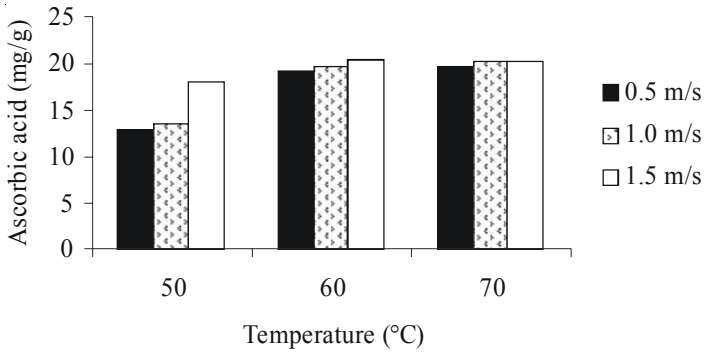

Fig. 3. Influence of air flow rate and drying temperature on ascorbic acid

oxidation mechanism and the degree of oxidation depends on the heating time, heating temperature and oxygen content.

Samples dehydrated at 50 ºC and 0.5 m s^{-1} air flow rate showed the lowest value for total carotenoids as indicated in Fig. 2. The loss was 71.05 %. For all drying temperatures used in this experiment, the samples dried at air flow rate of 1.5 m s^{-1} showed the lowest total carotenoids loss. Between the drying temperatures and air flow rates studied, 70 ºC and 1.5 m s^{-1} caused the lowest (55.26 %) total carotenoids loss.

As seen in Fig. 3, samples dehydrated at 50 °C and 0.5 m s^{-1} air flow rate showed lower ascorbic acid content. For all the experimental drying temperatures, samples dried at 1.5 m s^{-1} air flow rate gave much lower ascorbic acid loss, compared to the other air flow rates. During drying, the ascorbic acid degradation was between 17.65-48.57 %. The lowest loss was determined for 60 °C and 1.5 m s^{-1}, while the highest loss was at 50 °C and 0.5 m s^{-1}. According to Mrkìc *et al.*[30] the ascorbic acid content positively correlated with air flow rate. The present results are in agreement with theirs. Ascorbic acid is easily oxidized and, if the oxidation process continues beyond the stage of dehydroascorbic acid, it becomes irreversible[31].

As shown in Fig. 4, the highest total phenolics content was obtained for the samples dried at 50 °C, as the temperature raised, phenolic matter loss increased. Similar results were reported by several resarchers[32,33]. Kyi *et al.*[33] recorded that the polyphenol degradation rate increased with increasing temperature and the concentration of total polyphenol declined rapidly during drying because of the enzymatic oxidation of polyphenols. The lowest total phenolics loss (32.86 %) was obtained for the samples dried at 50 °C and 1.5 m s^{-1} air flow rate. For all the experimental air flow rates, although the total phenolics loss of samples dried at 60 and 70 °C seem close to each other, the highest loss was determined as 47.21 % for the samples dried at 70 °C and 1.0 m s^{-1} air flow rate conditions.

The highest FRAP value was obtained for the samples dehydrated at 70 °C. This means, total antioxidant activities of analyzed rosehip samples were affected from ascorbic acid and total carotenoids, rather than total phenolics.

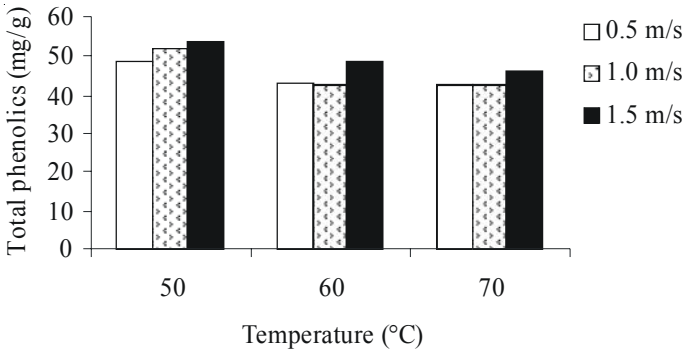

Fig. 4. Influence of air flow rate and drying temperature on total phenolics

When FRAP values examined (Fig. 5), it is observed that, the rosehip samples dehydrated at 70 °C and 1.5 m s^{-1} air flow rate gave the highest values (70.64 % loss), whereas the samples dried at 60 °C and 0.5 m s^{-1} gave the lowest (87.26 % loss) values. Drying time showed a negative effect on antioxidant contents and the antioxidant activity decreased with increase in temperature. Hence, high temperature short time prosess maximized the antioxidant activity of rosehips. This is consistent with the data reported by Mrkìc *et al.*[30] for broccoli. The negative effect of drying time on antioxidant activity could be ascribed to its depleting effect on ascorbic acid and total carotenoids contents.

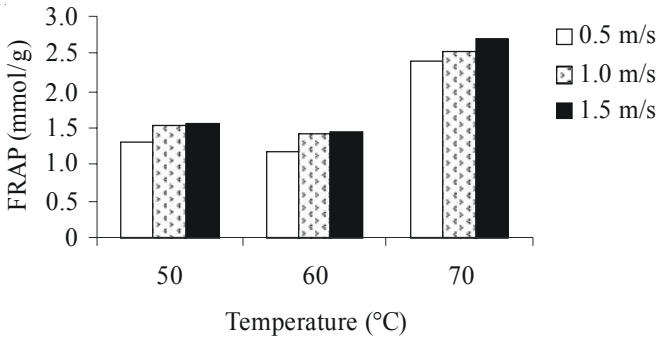

Fig. 5. Influence of air flow rate and drying temperature on FRAP value

Hot-air drying implies a thermal treatment and thermal degradation of polyphenols is expected but the decomposition of polyphenols was proven to depend on the food matrix and the processing conditions. Moreover, this process enhances or depletes the antioxidant activity of products depending on the nature of the substrate. During drying, oxidation reactions could also take place and polyphenols with an intermediate oxidation state can exhibit a higher radical scavenging activity than non-oxidized polyphenols. High temperature drying could further cause the formation of Maillard reaction products that could act as pro- or antioxidants. These compounds

have been shown to act as antioxidants in dried foodstuffs, individually or in synergism with naturally occurring antioxidants, since synergistic effects between antioxidants have been demonstrated[30].

As can be seen from the Figs. 2-5, samples dried at 1.5 m s^{-1} air flow rate showed the highest value of ascorbic acid, total carotenoids, total phenolics and antioxidant activity, whereas the samples being dried at 0.5 m s^{-1} generally gave the lowest values.

Conclusion

The obtained experimental data showed that, retention of ascorbic acid, total carotenoids, total phenolics and antioxidant activity depended on drying temperature, air flow rate and drying time related to these two factors. From the retention point of view, 50 °C dehydrating temperature and 1.5 m s^{-1} air flow rate were found to be the most suitable for drying rosehips in terms of total phenolics retention, whereas 70 °C and 1.5 m s^{-1} were found to be the most suitable dehydration conditions in terms of the retention of total carotenoids and antioxidant activity.

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(*Received*: 15 December 2007; *Accepted*: 19 September 2008) AJC-6875