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β-Carotene Stability and Some Physicochemical Properties of Apricot Juice Powders Obtained by Using Maltodextrins with Different Dextrose Equivalents

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In this study, apricot juice powders (AJPs) are obtained via freeze-drying using different maltodextrins (MDs) as carrier agents. The Hacıhaliloğlu cultivar, which is the most common variety in Turkey, is used as an apricot sample. Three different MDs: low (4–7), medium (13–17), and high (17–20) dextrose equivalence (DE) are used as the carrier agent. The powders obtained are subjected to accelerated oxidation at 55 °C, and the stability of β-carotene in the AJPs is determined. Some physicochemical properties, such as the glass transition temperature, microstructure, bulk density, color, moisture, solubility, degree of caking, and hygroscopicity, are also determined. The results show that after a 20 day period of oxidation, the remaining β-carotene in the control sample is 24% of the initial value, whereas for low, medium, and high DE MD samples, it is measured to be 47%, 60%, and 57% of the initial concentration, respectively. There is no significant difference in the content of surface carotenoids between the control and the samples with added MD. In contrast, according to other quality attributes like hygroscopicity, caking, moisture content, and solubility, the best results are obtained from the low DE MD sample.

1. Introduction

Carotenoids are important phytochemicals with health-promoting activities along with their coloring properties. The intense color of the carotenoids is caused by the multiple conjugated double bonds they possess. Due to the tendency of those double bonds to oxidize, carotenoids are easily lost during processing and storage.[1] β-carotene is the most commonly found carotenoid, and vegetables such as carrot, pumpkin, sweet potato and fruits such as apricot, plum, durian, papaya, and mango, are important sources of this compound in the human diet.[2] It has been reported that β-carotene is the major carotenoid found in apricot and fresh fruit containing up to 16 mg kg^{-1} of β-carotene, mostly in the form of trans isomers.[3]

Fruit powders are classed as intermediate products in the food industry because they can be incorporated in many food formulations, such as ice cream, biscuits, cakes, beverages, fruit yoghurt, and milk. High stability, dispersibility, and a low weight/volume ratio make fruit powders important ingredients over fresh and whole dried fruits.[4] Fruit powders can be produced via spray drying, drum drying, foam-mat drying, freeze-drying, etc. Among these methods, freeze-drying is considered to be one of the most advantageous processes for manufacturing high quality dehydrated products.[5]

Due to the high concentration of simple sugars in fruits, drying aids should be used to prevent caking during the production and storage of fruit powders. Apricot is rich in glucose, fructose, and sucrose,[6] therefore it is technically difficult to convert apricot flesh to a free flowing powder without using drying aids.

Carbohydrates such as maltodextrin (MD) and gum Arabic, which has a high glass transition temperature (T_g), are typical drying aids that are frequently used in fruit powder production.[7] The MD, which is obtained by partial hydrolysis of starch, is a water-soluble, white-colored, tasteless substance and is defined as a product with dextrose equivalence (DE) values lower than 20 by the Food and Drug Administration agency.[8] Due to the presence of glucose oligomers, MDs also act as encapsulating agents and can protect bioactive compounds from degradation during processing and storage.[9] Commercially, different MDs are available with different DE values according to the chain length of the glucose polymers.[10] Several studies have shown that MDs can protect bioactive compounds such as carotenoids,[9,11] anthocyanins,[12] and ascorbic acid[13] from degradation via encapsulation. However, to the authors' best knowledge there is no report on the stability of β-carotene and other quality characteristics of apricot juice powders (AJPs) produced by using MD.

The aims of this study were therefore to 1) investigate the stability of β-carotene and 2) to assess some physicochemical characteristics in AJPs produced by using MDs with different DE values.

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DOI: 10.1002/star.201900318

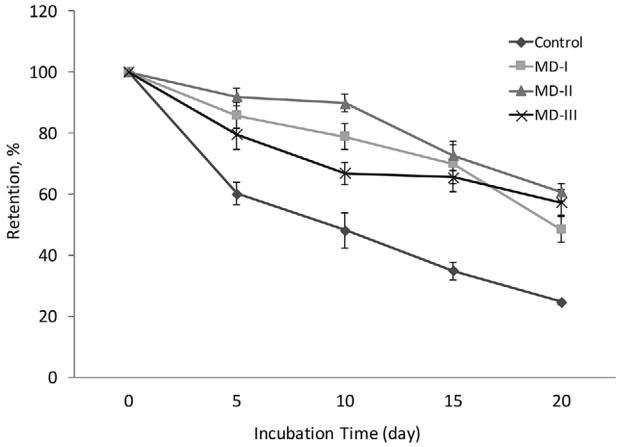

Figure 1. Total β-carotene retention during accelerated oxidation conditions.

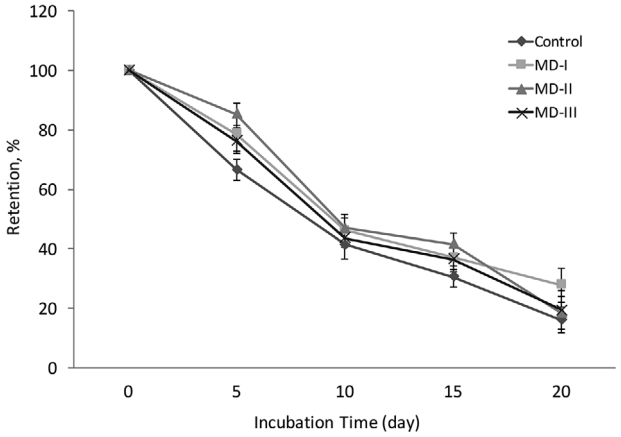

Figure 2. Surface β-carotene content during accelerated oxidation conditions.

2. Results and Discussion

As fruit juice powders have large surface areas, they are exposed to plenty of air, which causes isomerization or molecular cleavage of β-carotene during production and storage.[14] To prevent this degradation, in situ encapsulation of β-carotene by using MD, which is a drying aid in addition to its encapsulation potential, was studied. With this aim, AJPs were subjected to accelerated oxidation conditions to predict the effect of different MDs on β-carotene retention, and then compared to the control sample during long-term storage. HPLC analyses results showed that all the samples with added MD have higher β-carotene stability compared to the control sample (**Figure 1**). The initial carotenoid content was assumed to be 100%, and the decrease in β-carotene content was calculated as a percentage during the oxidation period. At the end of the storage period, the control sample lost 75% of its initial β-carotene content while this value was less than 52% for samples with added MD. Among the samples, MD-II was found to be the best carrying agent for the protection of β-carotene during the first 10 days of the accelerated oxidation experiment (Figure 1). This was followed by MD-I and MD-III. After that period, the total amount of β-carotene retained for samples incorporating MD fluctuated. Carotenoids are known to be susceptible to oxidation and can easily be degraded over time. It is known that the protection of core materials in capsules is quite dependent on the chemical and physical properties of the wall material.[11] During the preparation of apricot puree with MDs, β-carotene molecules were probably covered with MD chains along with the other constituents present in apricot fruit. After freeze-drying, most of the carotenoids were encapsulated in the matrix composed of this complex mixture. As the three types of MDs differ in the molecular weight of the glucose oligomers they contain, it can be stated that oligomers with a medium chain length have a better capacity to encapsulate carotenoids. It is known that with increasing molecular weight, the polarity of the glucose polymers decrease and it is assumed that they have better emulsification capacity, which enhances encapsulation efficiency of non-polar compounds.[15] However, this is not the case in our study and the highest protection was provided by medium chain MD. This unexpected result could be explained by the presence of simple sugars coming from both the apricots and the MDs. The concentration and molecule size of the simple sugars affects the permeability of capsules as they act as the building blocks of the wall material by filling the pores in the MD network.[16] Reduction of the pore size means less oxygen penetration into the capsules and less carotene degradation. Przybysz et al.[9] studied the retention of β-carotene in microcapsules produced by using gum Arabic, OSA-type modified starch, and MD. They reported that, at the end of the 65-day storage period, only 44% percent of β-carotene was retained in the control sample, whereas it was much higher in encapsulated samples. The researchers highlighted that the pores in the capsule material are quite important for oxygen penetration and should be minimized for longer shelf life.

During accelerated oxidation tests, the surface β-carotene content was also monitored as a percentage of the initial value. As can be seen in **Figure 2**, unlike the total β-carotene retention, there was no statistically significant difference in the retention of β-carotene in samples incorporating MD compared to the control ($p > 0.05$). As the surface carotenoids are readily exposed to the air and light, it is not surprising to find out that they are degraded faster compared to the encapsulated carotenoids.[17]

Fruit powders are expected to be free flowing and not be caked during their shelf life. One of the most important factors affecting this attribute is the moisture content. Although all AJP samples were obtained via the same freeze-drying conditions, significant differences in moisture content were observed among the samples (**Table 1**). The highest moisture content was found in the control sample and was probably due to the relatively higher rate of simple sugars in this sample compared to those containing MD (Table 1). It is known that the main sugars in apricot fruit are glucose and fructose. [18] On the other hand, MDs contain a significant amount of oligosaccharides derived from partial hydrolysis of starch along with a relatively lower amount of monosaccharide glucose.[19] Thus, it is quite possible that during drying, simple sugars were accumulated on the surface of the particles and an impermeable glassy surface was formed that prevented removal of moisture. The gradual increase in moisture content of samples containing MD corresponding to their DE value supports this idea. In agreement with our

Table 1. Physical characteristics of apricot juice powders.

Characteristic	Control	MD-I	MD-II	MD-III
Moisture [%]	8.87 ± 0.41a	4.19 ± 0.02c	5.37 ± 0.55b	5.67 ± 0.20b
Solubility [%]	85.42 ± 0.34c	95.15 ± 0.87a	93.96 ± 0.22b	94.56 ± 0.28ab
pH	4.82 ± 0.01a	4.76 ± 0.01b	4.76 ± 0.02b	4.76 ± 0.00b
Bulk density [g mL^{-1}]	3.28 ± 0.02a	2.63 ± 0.07b	2.05 ± 0.00c	1.65 ± 0.00d
L	66.7 ± 0.07d	80.7 ± 0.14a	77.3 ± 0.10b	75.1 ± 0.13c
a	8.6 ± 0.08a	2.2 ± 0.08d	4.0 ± 0.05c	5.3 ± 0.00b
b	29.2 ± 0.08a	21.7 ± 0.13d	24.0 ± 0.10c	26.1 ± 0.15b
Hygroscopicity [%]	64.1 ± 0.14a	41.1 ± 0.70d	46.3 ± 0.35b	43.7 ± 0.42c
Degree of caking [%]	40.0 ± 0.35a	11.6 ± 0.21d	29.4 ± 0.70b	17.3 ± 0.85c
Glass transition temperature [T_g, °C]	−4.74 ± 0.01d	89.33 ± 0.02a	79.62 ± 0.03b	79.08 ± 0.02c

Different letters indicate statistical groups determined by one-way ANOVA test ($p < 0.05$).

findings, increasing DE was reported to cause a clear increase in moisture content of spray dried tomato powders.[10]

Fruit powders are mostly consumed after being reconstituted in water or incorporated in different water-based foods; thus, solubility is an important quality attribute. According to our results, it was found that MD-I had the highest solubility among the samples followed by MD-III, MD-II, and the control sample, respectively (Table 1). The lower solubility of the control sample might have been due to the relatively higher percentage of the insoluble fibers from the apricot fruit. Incorporation of MD caused a significant increase in the solubility, although the DE value was not found to be directly related to the powder solubility. In a similar manner, it was reported that acai pulp with MD had a higher solubility compared to the control sample.[20]

Our results have also revealed that, with added MD, the pH value was decreased regardless of the DE values (Table 1). In contrast, it was reported that the presence of MD caused an increase in the pH of soursop fruit powder.[17] However, it is known that apricot is a relatively non-acidic fruit[21] and a decrease in pH with added MD was to be expected.

Bulk density is the measure of the weight per unit volume of powder. The control sample had the highest bulk density and the presence of MDs with increasing DE value caused a clear decrease (Table 1). In agreement with our findings, it was reported that date powder with MD had lower bulk density compared to the powders without MD.[7] On the other hand, it was stated that with the increasing DE of MD, the bulk density of black mulberry juice powder was increased.[22] These inconsistent results might be related to the different sugar/fiber composition of different fruits, the final moisture content and the method used in powder preparation.

The color of AJP is yellowish due to its high β-carotene content.[23] As expected, incorporation of MDs caused a significant ($p < 0.05$) increase in the L^* value by diluting β-carotene in the final product. Decreasing DE, lower L^*, and higher a^* and b^* values were measured, probably as a result of the presence of higher molecular weight glucose polymers that are better at masking carotenoids. In addition, the surface morphology of the particles were also reported to affect the color properties.[11] As seen in **Figure 3**, among the samples with added MD, MD-I had the minimum roughness and flake-like surface, whereas MD-II and MD-III had more roughened particles. This could also be the reason for the slightly lighter color of MD-I compared to MD-II and MD-III.

Hygroscopicity, which is directly related to the moisture content and caking, is another important property of fruit juice powders. According to our results, the control AJP was found to be the most hygroscopic sample, with lower hygroscopicity measured in samples with added MD. It was also reported by Tonon et al.[20] that MD caused a decrease in hygroscopicity compared to a control sample. A positive correlation between DE and hygroscopicity was reported by Goula and Adamopoulos[10]; whereas, in our study, among the samples with added MD, the highest values were obtained from MD-II. The reason for this unexpected result can be explained with the particle morphology because MD-II had smaller particles that increased the surface area and the degree of exposure to moisture (Figure 3). A similar trend was observed for the caking measurement where the control sample was the most susceptible to caking and was followed by MD-II, MD-III, and MD-I (Table 1).

The glass transition temperature values for AJPs were measured by determining the point where a sudden shift in the baseline of the DSC thermogram occurred. In **Figure 4**, the DSC thermogram of the control sample is given as a representative example. The control sample T_g was measured at −4.74 ± 0.01 and with MD incorporated, the glass transition temperature of the samples increased dramatically. As expected, with an increase in the MD's DE value, the glass transition temperature decreased (Table 1). Some important properties of fruit juice powders, such as stickiness and caking are directly related to T_g, or can easily be predicted by measuring it. It is well known that simple sugars have relatively lower T_g values and they can be increased by adding high T_g materials such as MD and gum Arabic.[24]

In order to explore the microstructure of AJPs, SEM images were recorded. As seen in Figure 3, AJP particles have irregular flake-like shapes, unlike the spherical particles reported for spray dried powders.[4] During freeze-drying, microbubbles were formed due to water sublimation from the fruit puree. At the crushing stage, those microbubbles were broken and irregular crystal-like shapes might have formed. A similar formation was observed in powders obtained from grape juice[25] and blueberry juice powder obtained by the foam-mat freeze-drying process.[4] Yamashita et al.[12] commented that their 10DE sample had more friability and thus, smaller particles compared to their 20DE

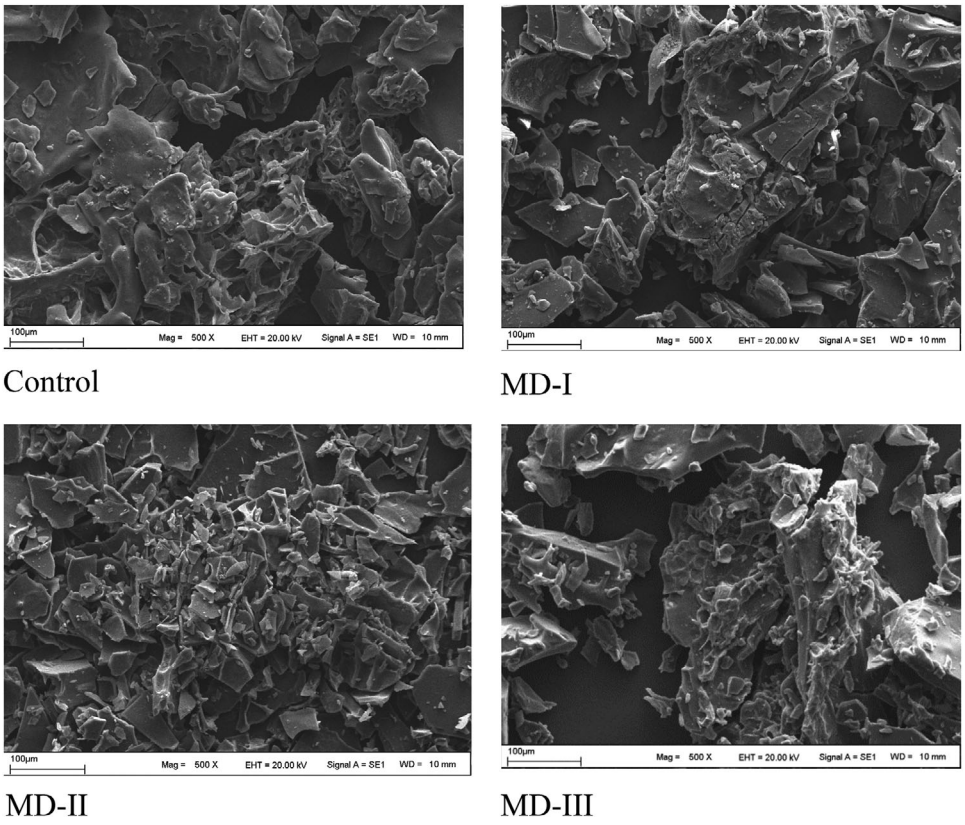

Figure 3. SEM images of apricot juice powders.

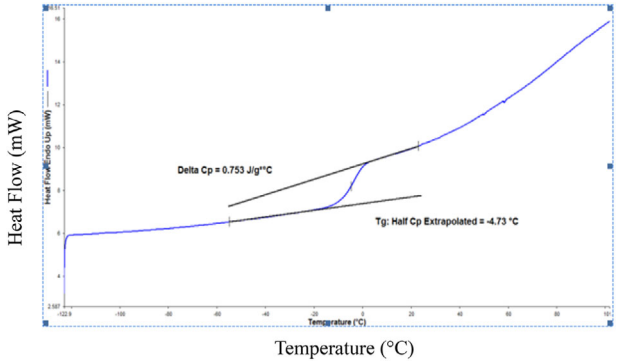

Figure 4. Differential scanning calorimetry thermogram of the control sample.

sample, which in turn provided better protection for encapsulated bioactive compounds. This finding is quite consistent with our results and the MD-II sample, which had a DE value of 13 to17, evidently had smaller particles compared to the other samples (Figure 3) investigated and provided better protection for β-carotene.

3. Conclusions

The presence of MDs caused a significant increase in the retention of β-carotene in AJP during accelerated oxidation conditions. Among the samples with added MD, Medium DE MD was superior in protecting β-carotene. Compared to the control sample, all AJPs obtained by using different MDs with different DE values were found to show better quality attributes, including the glass transition temperature, the degree of caking, the solubility, the hygroscopicity, etc. In future studies, different drying aids, such as gum Arabic, modified starch, etc., can be studied comparatively to find the best solutions for industrial production of AJP.

4. Experimental Section

Materials and Sample Preparation: All chemicals used in this study were obtained from Sigma-Aldrich (St. Louis, MO, USA). Apricots of the Hacıhaliloğlu variety were kindly provided by the Apricot Research Institution (Malatya, Turkey). Apricots were immediately brought to the laboratory and their stones removed. To prepare apricot puree, 100 mL of deionized water was added to 400 g of apricots and crushed in a Waring blender (Şimşek Laborteknik, Turkey) for 1 min at a speed of 18 000 rpm. This puree was divided into four equal parts, and 100 mL of water containing 30% MDs with different dextrose equivalents (MD-I: 4.0 to 7.0, MD-II: 13.0 to 17.0, and MD-III: 16.5 to 19.5) were added to three of those samples while the remaining portion of the puree samples was mixed with just water as the control sample. These amounts were determined by doing some pre-experiments where the necessary amount of MD was assessed to obtain a free flowing powder. Final mixtures, including the control sample, were further homogenized at 24 000 rpm for 2 min using a high speed homogenizer (Ultra-Turrax, IKA, Germany). The resulting pulps were poured into stainless steel containers to produce an 0.5 cm-thick layer and immediately frozen to −20 °C. After 24 h,

the frozen puree samples were freeze-dried in a lyophilizer (Armfield, UK) at a condenser temperature of −55 °C under a 30 mTorr vacuum for 12 h. The freeze-dried samples were then ground in a coffee grinder (Tefal, Turkey), sieved through a 500 micron sieve, and stored at +4 °C in plastic bags.

Determination of β-Carotene Stability: In order to determine the stability of β-carotene during accelerated oxidation conditions, vials (amber colored, 22.5 × 75 mm) containing 1 g of AJP were placed in an oven set to 55 °C. At 5 day intervals, the vials were subjected to a β-carotene analysis. To extract surface carotenoids, 5 mL of hexane containing 10 mM of butylated hydroxyanisole (BHA) was added to the vials by pipette and stirred for 10 min at a speed of 100 rpm with a magnetic stirrer (Velp, Italy). The suspension was filtered through an 0.45 micron syringe filter and 100 µL of the filtrate was dried under nitrogen gas and re-dissolved in acetonitrile to inject into an HPLC system. An 0.5 g amount of AJP was re-hydrated with 3 mL of distilled water for 2 h at +4 °C in the darkness under a nitrogen atmosphere, and carotenoids were extracted with 3 mL of a hexane : ethanol mixture (2:1) containing 10 mM of BHA using a homogenizer (Heidolph, Germany) at 10 000 rpm for 1 min.[26] The suspensions were centrifuged at 2500 rpm for 15 min, then the upper layer was collected and the precipitant was re-extracted until it became colorless. A 100 µL of the combined extracts were dried under nitrogen, dissolved in 1 mL of acetonitrile and 10 µL was injected into an HPLC system (Shimadzu Prominence, Tokyo, Japan) equipped with an Inertsil ODS-3 (5 µm, 250 × 4.6 mm) column. An acetonitrile : methanol : THF (50:10:40) mixture containing 0.05 M of ammonium acetate was used as a mobile phase at an isocratic flow rate of 1.0 mL min^{-1} at 30 °C. β-Carotene was detected using a UV diode-array detector at a wavelength of 450 nm and quantified by using a calibration curve plotted with different concentrations of external standard.

Determination of Quality Characteristics: To determine the moisture content, 1 g of AJP sample was weighed in an aluminum cup and placed in an oven (Şimşek Laborteknik, Turkey) maintained at 102 ± 2 °C until a constant weight was obtained. The moisture content of the AJP samples was then determined gravimetrically. The pH was measured using a pH-meter (Thermo, USA) after suspending 3 g of AJP in 50 mL of deionized water at 20 °C. The solubility of the AJPs was determined by the method described by Ceballos with some modifications.[17] A further 10 g of AJP was added to 100 mL of distilled water in a flask and mixed by using a magnetic stirrer at 200 rpm for 5 min. This suspension was transferred to test tubes and centrifuged at 4500 rpm for 10 min. A 25 mL amount of the supernatant was transferred to a pre-weighed petri dish and dried in an oven at 102 ± 2 °C for 12 h. The solubility (%) was calculated from the weight difference. To assess bulk density, AJPs were loaded into a 25 mL graduated cylinder and the volume occupied was recorded after tapping a few times. Bulk density was calculated as described elsewhere (Sablani et al., 2008). The color of the AJP samples was determined by using a Minolta CR-10 Chroma Meter (Minolta, Japan) calibrated with a white standard tile. AJPs (10 g) were put on petri plates and measurements were taken from underneath the plates. Results were expressed using the Hunter color values of L*, a*, and b*, where L* indicates lightness, a* redness and greenness, and b* yellowness and blueness.[27] Hygroscopicity was expressed as the final moisture content attained after exposing the powder to humid air. Approximately 5 g of powder was spread uniformly on a petri dish and placed in a chamber (30 × 30 × 30 cm). The relative humidity was established by using a saturated solution of potassium nitrate. Powders were weighed every day until a constant weight was reached.[28]

The humid sample obtained from the hygroscopicity assay was placed in an oven set at 70 °C and dried until a constant weight. After cooling in a desiccator, the samples were transferred to a 500 micron sieve, and it was then agitated for 5 min. The remaining powder was weighed and the degree of caking was calculated.[29]

The glass transition temperature was determined by using a Differential Scanning Calorimeter (Shimadzu DSC-60). Indium (PerkinElmer standards) was used to calibrate the instrument, and an empty aluminum pan was used as the reference. A 5 mg sample of AJP was placed in the aluminum pan and scanned from −120 to 100 °C at a rate of 10 °C min^{-1}.[7] The shift in the base line in the DSC thermograph was recorded as the glass transition (T_g) point.

The particle morphology was evaluated by using scanning electron microscopy (SEM, LEO, EVO 40).[20] For this purpose, powder was attached to a piece of double-sided adhesive tape mounted on SEM stubs, coated with 3 to 5 mA of gold/palladium under a vacuum and examined at 500-fold magnification.

Statistical Analysis: All experiments were replicated at least three times and the data obtained were subjected to analysis of variance (ANOVA) using SPSS 16.0 software. Duncan's multiple range test was used to determine the difference between the means ($p \leq 0.05$).

Acknowledgements

This study was supported by İnönü University Scientific Research Council under project number 2012/06. The authors are also grateful to Malatya Apricot Research Institute for the apricot samples.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

β-carotene, apricots, juice powders, maltodextrin

Received: December 17, 2019
Revised: March 27, 2020
Published online: May 19, 2020

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