

Production of Grape Juice Powder Obtained by Freeze-drying after Concentration by Reverse Osmosis

Poliana Deyse Gurak^{1,4*}, Lourdes Maria Correa Cabral² and Maria Helena Rocha-Leão³

¹Instituto de Química; Universidade Federal do Rio de Janeiro; RJ - Brasil. ²Embrapa Tecnologia de Alimentos - RJ - Brasil. ³Escola de Química; Universidade Federal do Rio de Janeiro; RJ - Brasil. ⁴Departamento de Engenharia Química; Universidade Federal do Rio Grande do Sul; Porto Alegre; RS - Brasil

ABSTRACT

This study aimed to evaluate the freeze-drying process for obtaining grape juice powder by reverse osmosis using 50% grape juice pre-concentrated (28.5 °Brix) and 50% hydrocolloids (37.5% maltodextrin and 12.5% arabic gum). The morphology of the glassy food showed the absence of crystalline structure, which was the amorphous wall that protected the contents of the powder. The samples were stored in clear and dark containers at room temperature, evaluated for their physical (X-ray diffraction) for 65 days and chemical (polyphenol content) stability for 120 days. During the storage time in plastic vessels, samples remained physically stable (amorphous) and the phenolic concentration was constant, indicating the potentiality of this technique to obtain a stable product with a high concentration of phenolic compounds. Therefore, the freeze-drying process promoted the encapsulation of concentrated grape juice increasing its stability and shelf life, as well as proving to be an applicable process to food industry.

Key words: phenolic compounds, maltodextrin, arabic gum, X-ray diffraction, scanning electron microscopy

INTRODUCTION

Grape juice has many compounds with healthy energetic, nutritional and bioactive effects. Natural antioxidants present in the grapes include anthocyanins and others flavonoids, which are ubiquitously distributed in the vegetable kingdom as secondary plant metabolites (Paganda and Rice-Evans 1997). Many studies have suggested that ingesting phenolic compounds can help prevent diseases (Scalbert and Williamson 2000; Park et al. 2003; Houston et al. 2007; Spormann 2008; Russell et al. 2009). Since grape juice has almost three times the total polyphenolic concentration of orange or grapefruit, there are large differences between the classes of juice flavonoids (Russell et al. 2009). The discovery of a high amount of

polyphenolics in this juice has increased the interest in studying its behavior in various industrial processes. According to Houston et al. (2007), juice powder made primarily of multiple fruits, vegetables and berries, is seen in a favorable light for the treatment of several cardiovascular diseases. Rho and Kim (2006) studied the freeze-drying used for powders of *Vitis labruscana* Bailey grapes, grape pomace and grape juice. When included in male rats' diet, it showed a possible delay of onset of various degenerative diseases such as cancer, and of the aging process caused by the accumulation of free radicals in body cells. Encapsulation by freeze-drying can be used in the food industry to protect the nutraceuticals by preventing the oxidation, reducing the losses of volatile substances, making handling easier,

* Author for correspondence: gurak@enq.ufrgs.br

facilitating or making more difficult the premature interaction with other ingredients, and regulating food bioactive content during its industrialization processes (Shahidi and Han 1993; Pothakamury and Barbosa-Cánovas 1995). In addition, it keeps them stable in storage at room temperature and ensures the release of an appropriate dosage in a gastric or intestinal pH (Andreev 2004).

Depending on the encapsulation process used, matrices present various shapes (films, spheres, irregular particles) and various physical structures (amorphous or crystalline dehydrated solid, rubbery or glassy matrix) that influence the diffusion of core or external substances (oxygen, solvent), as well as food product stability during the storage. In the food industry, the wall materials most used to encapsulate the nutraceutical substances include carbohydrates, cellulose and its derivatives, lipids, some proteins, and gums (Shahidi and Han 1993). The hydrocolloids, such as maltodextrin and arabic gum, were chosen because they are, among the wall materials, most commonly used by different encapsulation techniques. Righetto and Netto (2005); Zhang et al. (2007); Valduga et al. (2008); used maltodextrins and arabic gum as the carrier agents in the fruit juice encapsulation process. According to Valduga et al. (2008), who studied how to produce a natural pigment (anthocyanin) from "Isabel" grape bagasse powder with the use of spray drying, the combination of maltodextrin with arabic gum was the best choice among the formulations studied. Similarly, Zhang et al. (2007) showed that procyanidins extracted from the grape juice waste and wine productions were microencapsulated with maltodextrin (60%) and arabic gum (40%). The ratio of such core substance to wall material was 30:70 (w/w) and the content of the slurry was 20% (w/v). The analysis of the product showed that the procyanidin microcapsule membrane was not busted or pierced; proving the stability of the products was improved.

There are other studies related to encapsulation polyphenolic extracts. Tonon et al. (2010) evaluated during 120 days the anthocyanin stability and antioxidant activity of powdered açai juice produced by spray drying using maltodextrin 10 DE and 20 DE, gum arabic and tapioca starch as carrier agents. The samples were stored at different temperatures (between 25 and 35°C) and water activities (between 0.328 and 0.529). Anthocyanin degradation exhibited two first-order

kinetics the first one, with higher reaction rate constant, up to 45 – 60 days of storage, and the second one, after this period, with lower degradation rate, with both temperature and water activity negatively affecting anthocyanin stability. Antioxidant activity also decreased with the increase of water activity, but was higher for the powders stored at 35°C. Maltodextrin 10 DE was the carrier agent that showed the best pigment protection and the highest antioxidant activity for all the conditions studied. Other studies also showed the benefits of the encapsulation process for the protection of food additives used as functional food. Zheng et al. (2011) produced bayberry microcapsules by a phase separation method using ethyl cellulose as a coating material. Pitalua et al. (2010) produced beetroot juice using gum Arabic as wall material; Bakowska-Barczak and Kolodziejczyk (2010) produced black currant microcapsules.

Juice powder may act as a functional substance, a natural additive, a natural coloring, or as masking colors and flavors, which do not correspond to the consumers' preference, among other applications. In this context, the objective of this study was the production of grape juice powder pre-concentrated by reverse osmosis and evaluation of its capsules wall behavior during the storage period.

MATERIALS

Grape juice was obtained from the Embrapa Uva e Vinho, Brazil[®]; maltodextrin DE 20 from the MOX-REX 1920 - Corn Products, Brazil[®]; and arabic gum from the Isofar-Micro Med - Ind. and Com. Prod. Químicos, Brazil[®]. All other reagents used were analytical grade.

METHODS

Production of grape juice powder and water activity

Whole grape juice produced at the industrial processing unit of Embrapa Uva and Vinho was used as raw material. The process of concentration by reverse osmosis was conducted on a batch fed using 20 L of juice. The module used was the type plate and frame (DSS), with a 0.65 m² permeation area (membrane HR98PP - DDS, Denmark). The best process was at 50°C and 60 Bar (Gurak et al. 2010), giving a 28.5 °Brix concentrated juice. The evaluation of the concentrated juice quality

revealed that there was a proportional concentration increase to the VCF (volumetric concentration factor) of physical-chemical and quality parameters assessed, such as the total acidity, intensity of color, anthocyanins content and phenolic compounds (Gurak et al. 2010). In addition, the reverse osmosis pre-concentrated juice was freeze-dried in a Labconco FreeZoneR Freeze Dry System - model 740020 – under 46 mbar and - 47°C. The formulation used was 50% of grape juice concentrated by RO (28.5 °Brix) and 50% of hydrocolloids (37.5% of maltodextrin and 12.5% of Arabic gum) as proposed by Rigueto and Netto (2005). The solution of the hydrocolloids and the concentrated grape juice were mixed during 60 min and stored in an isolated container. This sample was then rapidly iced with liquid nitrogen and immediately submitted to the freeze-drying process. Besides, reverse osmosis, freeze-drying process, during the different stages of the experimental procedure, the water activity (A_w) was measured (triplicate) in Aqualab Series 3TE (Decagon Devices Ind., Pullman, Washington, DL, USA).

Evaluation of the phenolic compounds and X-ray diffraction in the grape juice powder

The powder obtained after the freeze-drying was transferred to Falcon® tubes and stored in clear and dark containers at room temperature. During the storage period, the stability of the amorphous surface and the powder were evaluated by X-ray diffraction and phenolic compound. The first was performed using the methodology proposed by the diffractometer manufacturer (HCZ - 4 high resolutions, with a generator ID3000 Seifert), the powder samples were carefully pressed on double-face tape covering aluminum trays and exposed to CuK α radiation ($\lambda = 15418 \text{ \AA}$) at diffraction angles of 2θ , from 10 to 100°C (step size 0.05, time per step 1.0 s) at every 15 days. The phenolic compound content was analyzed every seven days (in triplicate) according to Singleton and Rossi (1965) and the result were expressed in gallic acid equivalent (g/kg).

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to investigate the structure of the glassy food model and the morphology of the powder referred previously in this work. The dried samples were prepared through direct deposition on a conductive carbon tape covering aluminum stubs, gold-

sputtered (Bal-Tec SC 050, Germany), and examined by Jeol Scanning Microscope (JSM-5310), operated at 15 kV with a working-distance of 10 mm.

Statistical analysis

The results were statistical analyzed by the linear model analysis of variance (ANOVA) and Tukey test ($p < 0.05$) for the main effects of storage time between the matrices using software Microcal Origin™ 7.0 version (Origin Lab Corporation, Northampton, USA).

RESULTS AND DISCUSSION

Production of grape juice powder

The grape juice pre-concentrated by reverse osmosis was freeze-drying with and without the hydrocolloids; however, under the second condition, the powder was not obtained. The grape juice drying process by spray-drier was difficult due to its high sugar content. Valduga et al. (2008) during anthocyanins spray-drying microencapsulation observed losses of the core material because a large part of was retained in the walls of the drying chamber, which showed that the freeze-drying process with the addition of hydrocolloids was an interesting viable alternative. The humidity of the powder remained lower than 5% and there was a significant increasing of 86% in the total solids content compared to the whole grape juice (Table 1). The water activity decreased from 0.98 to 0.43, increasing the product shelf life significantly, reducing powder contamination by the microorganisms and increasing their applicability as ingredients in food industry.

As reports about the stability and water activity of grape juice powder have not been reported, the present results were compared to other encapsulated raw materials. The water activity of the concentrated green *Maliphigia* juice was added with maltodextrin and arabic gum. These two ingredients were added in the same proportion applied to the grape juice in the present work, ranging from 0.21 in the spray-drying to 0.23 in the freeze-drying. The microcapsules were 6.3 and 7.0% humidity, respectively (Righetto and Netto 2005). Barros and Stringheta (2006) reported that the encapsulated anthocyanins extracted from *Mellinis minutiflora* presented the humidity of 4% when mixed with 30% maltodextrin, while the combination of 25% maltodextrin and 5% arabic

gum increased the powder humidity to 4.6%. The freeze-dried samples of pomace containing anthocyanin and maltodextrin DE20 showed good

shelf life stability during the storage on 50°C/0.5 a_w for two months.

Table 1 - Water activity, humidity and total solids samples of grape juice in different steps submitted.

Samples	Water activity [†]	Temperature (°C) [†]	Humidity [†]	Total solids [†]
Grape juice	0.98	24.4	85.23	14.77
Grape juice pre-concentrated by RO	0.96	24.5	69.82	30.18
Grape juice concentrated by RO and hydrocolloids	0.93	24.5	31.58	68.42
Powder	0.43	25.0	4.79	95.21

[†]Mean of three replications.

Scanning Electron Microscopy

Figure 1 shows x70, x1000 and x2000 zooms of the grape juice encapsulated. The close-up images proved that it was possible to obtain an amorphous structure that retained the core. The powder showed irregular structures of different sizes that eventually formed aggregations, because the ground was dry in mortar. The physical reactions to speed up the degradation of the core material were not detected.

Desobry et al. (1997) also obtained different

shaped microcapsules for the encapsulated β -carotene, which was produced by freeze-drying process. Farias et al. (2007) studied the encapsulated alpha-tocopherol in a glassy food model applying rapid freeze and freeze-drying. The results of these experiments were capsules with a slightly smooth surface and a rather fragile and porous structure due to cavities formed by ice crystal during the freezing process and the absence of crystalline structure.

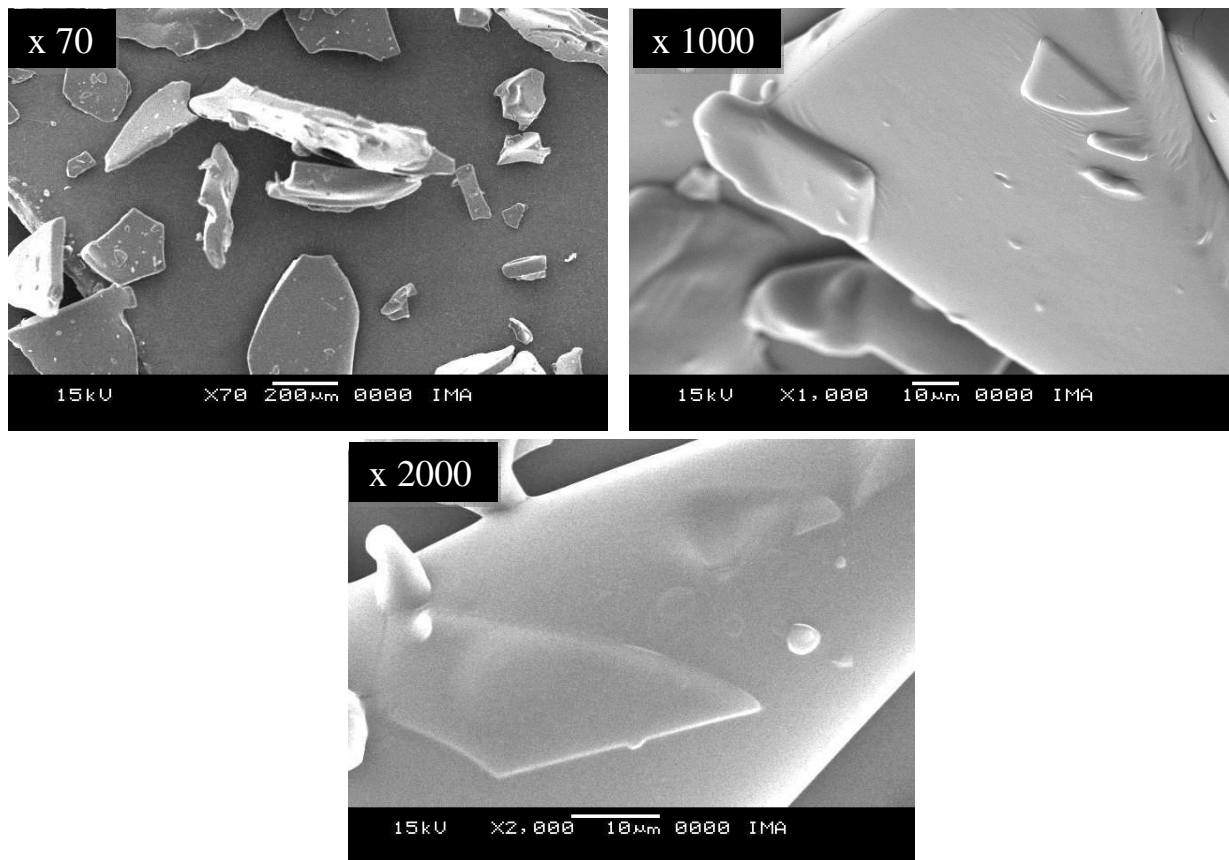


Figure 1 - Scanning electron microscopy shown with different zooms (x70, x1000 and x2000 times, respectively) in encapsulated grape juice with gum arabic and maltodextrin.

Evaluation of the phenolic compounds and X-ray diffraction in the grape juice powder

The evaluation of the stability behavior of the powder by the analysis of phenolic compound showed that there was no significant difference (5% significance level) in the samples stored at room temperature in the clear or dark containers during 120 days (Fig. 2). However, black carrot microcapsules encapsulated by spray-drying and containing maltodextrin as wall material had their amount of anthocyanin reduced to 33% at the end of 64 days storage at 25°C (Ersus and Yurdagel 2006).

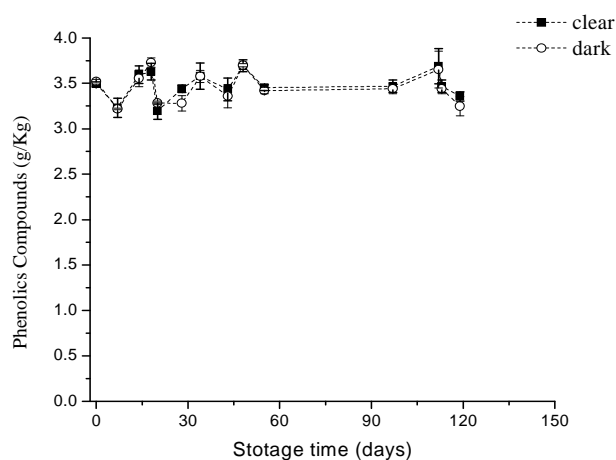


Figure 2 - Analysis of phenolic compounds in grape juice powder stored in clear and dark containers during 120 days.

The analysis by X-ray diffraction showed the presence of diffused and large peaks containing amorphous material due to the fact that in the amorphous state the molecules were disorderly displayed, producing disperse bands whereas crystalline materials yielded sharp and defined peaks, since they were presented in a highly ordered state (Cano-Chauca et al. 2005). The X-ray diffraction spectrum showed the presence of many rustling and peaks without definition or uniform behavior, which was not characteristic of crystalline samples. Figure 3 shows the spectrum of the grape juice powder storage in clear and dark containers at room temperature on the first day of storage. The spectra of the samples stored for 22 and 45 days (data not shown) and 65 days (Fig. 4), respectively showed the same profile and behavior of Figure 3, i.e., the powder remained with no crystalline regions in the amorphous matrix as confirmed by the presence of large, no-defined

peaks with much rustling, and no damage was observed in the different conditions of storage.

It is important to state that the X-ray diffraction profile behavior in this work was similar to those observed by Cano-Chauca et al. (2005), which showed that the powders of the mango juices obtained through spray drying process using the carries maltodextrin and arabic gum presented surfaces of amorphous particles. Similarly, Farias et al. (2007), studying the encapsulation of the alpha-tocopherol in glassy food model matrix using the solutions of maltodextrin and gelatin by freeze-drying, showed that capsules remained stable during 90 days storage at 25 and 35°C. The presence of amorphous material could be due to the fact that during the drying process, the material did not crystallize because the arabic gum had high molecular weight and high viscosity that increased the glass transition temperature, turning the surface amorphous. Such change from this state to crystalline state occurred above the glass transition temperature (Cano-Chauca et al. 2005).

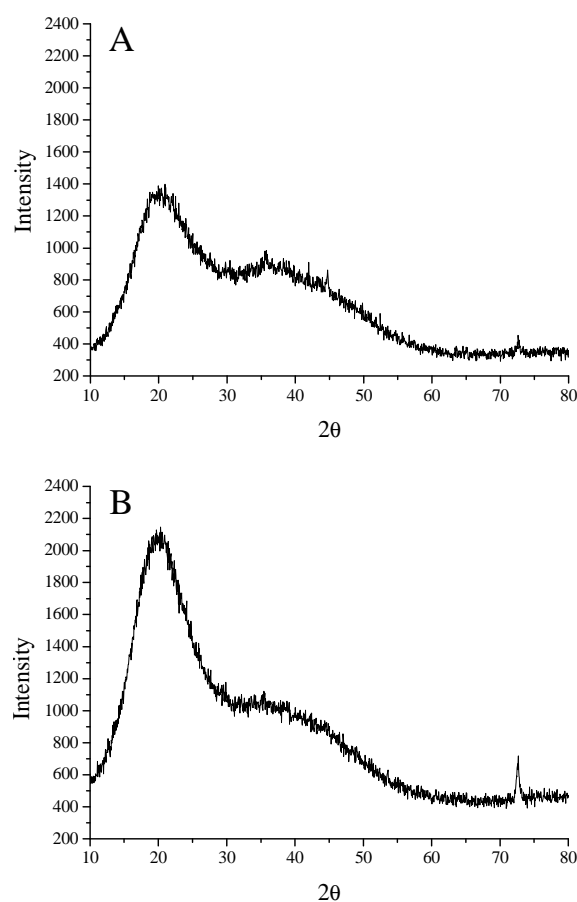


Figure 3 - Spectra of the powder at room temperature in clear (a) and dark (b) after freeze-drying.

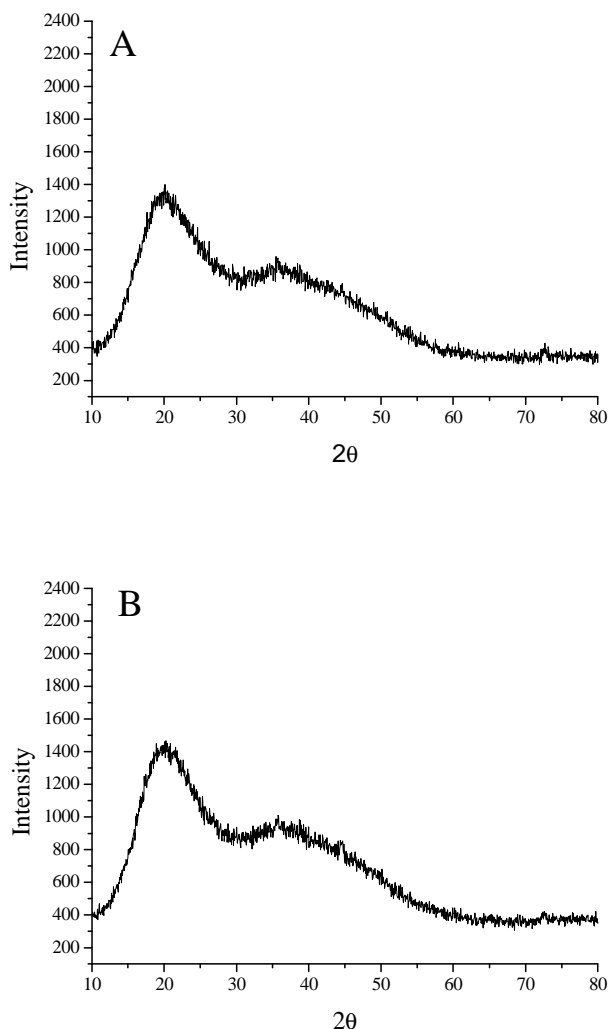


Figure 4 - Spectra of the powder at room temperature in clear (a) and dark (b) after 65 storage days.

CONCLUSION

It was possible to use the freeze-dry process to concentrate the grape juice with the addition of hydrocolloids. The phenolic compound content in the grape juice powder remained stable during 120 days of storage in clear and dark containers at room temperature. The X-ray diffraction analysis during 65 days did not show changes in the powder shell in its crystallized appearance. Therefore, the freeze-drying process promoted the encapsulation of the reverse osmosis concentrated grape juice, while increasing its stability and shelf-life as well as proving to be an applicable process to food industry.

ACKNOWLEDGMENTS

The authors are grateful to Silvia Albuquerque (CBPF) for her help on freeze-drying and analysis of X-ray diffraction, IMA/UFRJ for scanning electron microscopy analysis. CAPES for the financial support.

REFERENCES

- Andreev PV. Drug synthesis methods and manufacturing technology using modified starch in the Russian pharmaceutical industry (a review). *Pharm Chem J.* 2004; 38: 447-451.
- Bakowska-Barczak M, Kolodziejczyk PP. Black currant polyphenols: Their storage stability and microencapsulation. *Ind Crop Prod.* 2010; 34: 1302-1309.
- Barros FAR, Stringheta PC. Microencapsulamento de antocianinas [internet]. 2006 [cited 2012 may 2]; *Revista Biotecnologia Ciência e Desenvolvimento* 36: Available from: http://www.biotecnologia.com.br/revista/bio36/microencapsulamento_36.pdf.
- Cano-Chauca M, Stringheta PC, Ramos AM, Cal-Vidal, J. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. *Innov Food Sci Emerg Tech.* 2005; 6: 420-428.
- Desobry SA, Netto FM, Labuza, TP. Comparison of spray-drying, drum-drying and freeze-drying for β -carotene encapsulation and preservation. *J Food Sci.* 1997; 62: 1158-1162.
- Ersus S, Yurdagel, U. Microencapsulation of anthocyanin pigments of black carrot (*Daucuscarota L.*) by spray drier. *J Food Eng.* 2006; 80: 805-812.
- Farias MC, Moura ML, Andrade L, Rocha-Leão MH. Encapsulation of the alpha-tocopherol in a glassy food model matrix. *Mat Research.* 2007; 10: 57-62.
- Gurak PD, Cabral LMC, Rocha-Leão MH, Matta VM, Freitas SP. Quality evaluation of grape juice concentrated by reverse osmosis. *J Food Eng.* 2010; 96: 421-426.
- Houston MC, Cooil B, Olafsson BJ, Raggi P. Juice powder concentrate and systemic blood pressure, progression of coronary artery calcium and antioxidant status in hypertensive subjects: A pilot study. *eCAM.* 2007; 4: 455-462.
- Paganda G, Rice-Evans CA. The identification of flavonoids as glycosides in human plasma. *FEBS Letters.* 1997; 401: 78-82.
- Park YK, Park E, Kim JS, Kang MH. Daily grape juice consumption reduces oxidative DNA damage and plasma free radical levels in healthy Koreans. *MUT Research.* 2003; 529: 77-86.

- Pitalua E, Jimenez M, Vernon-Carter EJ, Beristain CI. Antioxidative activity of microcapsules with beetroot juice using gum arabic as wall material. *FBP*. 2010; 88: 253-258.
- Pothakamury UR, Barbosa-Cánovas GV. Fundamental aspects of controlled release in foods. *Trends in Food Sci Technol*. 1995; 6: 397-407.
- Rho KA, Kim MK. Effects of difference grape formulations on antioxidative capacity lipid peroxidation and oxidative DNA damage in aged rats. *J Nutr Sci Vitaminol*. 2006; 52: 33-46.
- Righetto AM, Netto FM. Effect of encapsulating materials on water sorption, glass transition and stability of juice from immature acerola. *Int J Food Prop*. 2005; 8: 337-346.
- Russell WR, Labat A, Scobbie L, Duncan GJ, Duthie GG. Phenolic acid content of fruits commonly consumed and locally produced in Scotland. *Food Chem*. 2009; 115: 100-104.
- Scalbert A, Williamson G. Dietary intake and bioavailability of polyphenols. *J Nutr*. 2000;130: 2073S-2085S.
- Shahidi F, Han X-Q. Encapsulation of food ingredients. *Crit Rev Food Sci Nutr*. 1993; 33: 501-547.
- Singleton VL, Rossi JA. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *AJEV*. 1965; 20: 144-158.
- Spormann TM. Anthocyanin/polyphenolic-rich fruit juice reduces oxidative cell damage in an intervention study with patients on hemodialysis. *CEBP*. 2008; 17: 3372-3380.
- Tonon RV, Brabet C, Hubinger MD. Anthocyanin stability and antioxidant activity of spray-dried açai (*Euterpe oleracea Mart.*) juice produced with different carrier agents. *Food Res Int*. 2010; 43: 907-914.
- Valduga EL, Lima L, Prado R, Padilha FF, Treichel H. Extração, secagem por atomização e microencapsulamento de antocianinas do bagaço da uva isabel (*Vitis labrusca*). *Ciênc Agrotec*. 2008; 32: 1568-1574.
- Zhang L, Mou D, Du Y. Procyanidins: extraction and micro-encapsulation. *J Sci Food Agric*. 2007; 87: 2192-2197.
- Zheng L, Ding Z, Zhang M, Sun J. Microencapsulation of bayberry polyphenols by ethyl cellulose: Preparation and characterization. *J Food Eng*. 2011; 104: 89-95.

Received: October 16, 2012;
Accepted: August 20, 2013.