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Composition and Thermogravimetric Characterization of Components of Venezuelan Fermented and dry Trinitario Cocoa Beans (*Theobroma cacao* L.): Whole Beans, Peeled Beans and Shells

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Abstract

Some important chemical and thermal characteristics of components of fermented and dry Venezuelan Trinitario cocoa beans (*Theobroma cacao L.*) were determined. Average bean shell weight (as percent of whole bean weight) was 15.5%, with an average thickness 0.310 mm. Its moisture content (d.b.: dry basis) was significantly higher ($p \leq 0.05$) than that of whole and peeled beans. In spite of the shell higher moisture content, its water activity (a_w) was lower than that of peeled and whole beans, evidencing higher water binding capacity. Crude fat content (d.b.) was higher in whole beans than in peeled beans and significantly larger than that in shells. Crude protein content (d.b.) exhibited a decreasing order for whole beans, peeled beans and shells. The ash content (d.b.) was significantly higher in the shell than in whole and peeled beans. Cocoa bean constituents, exhibited similar thermal properties, as evidenced by their melting and pyrolysis behavior obtained by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) techniques.

Keywords: cocoa beans; shells; water activity; DSC; TGA.

Composición y Caracterización Termogravimétrica de los Componentes de Habas de Cacao Trinitario Venezolano (Theobroma cacao L.) Fermentado y Seco: Habas Enteras, Peladas y Cascarillas

Resumen

Se determinaron algunas características químicas y térmicas del cacao Trinitario venezolano (*Theobroma cacao L.*). El peso promedio de la cascarilla del haba de cacao (como porcentaje del peso del haba entera) fue del 15.5%, con un espesor promedio de 0.310 mm. Su contenido de humedad (b.s.: base seca) fue significativamente mayor ($p \leq 0.05$) que el de las habas enteras y sin cascarilla. A pesar de que la cascarilla tiene un mayor contenido de humedad, su actividad de agua (aw) fue menor que la de las habas enteras y sin cascarilla, lo que demuestra una mayor capacidad de adsorción de humedad. El contenido de grasa cruda (b.s.) fue mayor en habas enteras que en las habas sin cascarilla y significativamente mayor que en las cascarillas. Se encontró que el contenido de proteína (b.s.) disminuyó en el siguiente orden: habas enteras, habas sin cascarilla y cascarillas. El contenido de cenizas (b.s.) fue significativamente mayor en la cascarilla que en las habas enteras y sin cascarilla. Los constituyentes de las habas de cacao exhibieron propiedades térmicas similares, de acuerdo con los datos de fusión y pirólisis obtenidos mediante calorimetría diferencial de barrido (DSC) y técnicas de análisis termogravimétrico (TGA).

Palabras clave: habas de cacao; cascarillas; actividad de agua; DSC; TGA.

Introduction

Trinitario fermented cocoa beans (a hybrid of Criollo and Forastero types), represent an important commodity in the international trade of cocoa in Venezuela. This cocoa type is appreciated as fine flavor beans capable of improving flavor of chocolate and other cocoa products. It is usually well fermented; sun dried and packaged in new jute bags.

Fowler [1] in a pioneer work, analyzed the composition of cocoa bean shells (the thin skin immediately surrounding the cocoa nib that is removed after roasting the beans) of various origins, including Venezuelan beans. Since the cocoa bean shell is essentially waste material, some research works have proposed its incorporation along with cocoa pod husks as agro-fillers in different poly-lactic acid polymer matrices [2]. Besides the work of Fowler [1] on cocoa bean shell composition, no information about the composition and water activity (a_w) of peeled cocoa beans and shells was found in the literature consulted. It has been established that a water activity (a_w) of less than 0.70 in cocoa beans is required for microbiological stability [3, 4]. This water activity level was associated with moisture content in whole beans of 7.10% to 7.34% (dry basis). Wood and Lass [5], suggested a moisture content of 6-7% for long safe storage of whole cocoa beans. Other authors indicated a moisture level of less than 8% (wet basis) to guarantee microbiological stability during storage [6, 7].

There are some studies regarding the thermal characteristics of cocoa products mainly associated to different types of chocolate and chocolate-related products [8-10], rather than on the raw material used in their production (i.e., cocoa beans). Du *et al*. [11] studied the pyrolysis behavior of cocoa bean shells identifying the different compounds evolving from thermal decomposition of this materials under a temperature range of 25-1000°C, using thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy. No information about the thermal characterization of Venezuelan cocoa beans has been found in the literature reviewed. These data are needed to explore future application and uses of this product, as an alternative energy source.

In view of the limited information in the scientific literature reviewed regarding the composition and thermogravimetric properties of whole and peeled cocoa beans, and cocoa bean shells, the aim of this research work is to determine such properties particularly for Venezuelan Trinitario type cocoa beans.

Experimental Section

Raw material and sample preparation

Fermented cocoa beans (*Theobroma cacao L.*) variety Trinitario, were grown and harvested in 2014, at Cúpira (Pedro Gual municipality), Miranda state, Venezuela, and packed in new clean jute sacks. The cocoa beans were graded as well fermented fine first grade (*Fino de Primera*) by *Cacao de Origen*, Hacienda La Trinidad, Caracas, Venezuela, according to the Venezuelan standard for cocoa beans [12]. A composite sample of about 5 kg of cocoa beans was provided by the same. Approximately 720 g of sample was selected at random for peeling to obtain the cocoa bean shells and the peeled cocoa beans. A similar amount was separated to be used as a whole bean sample. Cocoa beans were carefully peeled by hand in the laboratory to separate the cocoa bean shell. To carry out the proximate analysis and thermal characterization all samples were individually ground in a motorized mill (Wiley N°4), using a 2-mm sieve.

Proximate analysis and water activity

Proximate analysis of whole beans, peeled beans and cocoa bean shells were carried out according to the procedures presented in AOAC [13]. Moisture was determined by the atmospheric oven method (100-102 °C for 16 h), until constant weight. Protein content was determined by the micro-Kjeldahl method, using a nitrogen conversion factor of 6.25. Crude fat was determined using the Soxhlet method with hexane as solvent and ash by ignition in a muffle for 30 min at 550 °C were also determined. All the analyses were done by triplicate. Water activity (aw) was measured using a Decagon CX-1 device, previously calibrated.

Relative weight of peeled beans and shells and shell thickness

For this purpose, the following procedure was followed [14,15]: Five 100-bean samples were formed from beans selected at random. The cocoa beans were peeled manually. The weight of whole cocoa beans, shells and peeled beans was determined separately using an analytical balance Ohaus™ model Adventurer (± 0.0001 g) and the percent shell calculated in relation with the weight of whole un-peeled beans. The shell thickness was determined by selecting at random 42 pieces of shells and measuring their thickness in triplicate with a digital micrometer (± 0.001 mm).

Thermal Characteristics of whole cocoa beans, peeled beans and shells

Thermal characteristics of whole cocoa beans, peeled beans and cocoa bean shells, were determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC analysis of ground whole cocoa beans, peeled cocoa bean and cocoa bean shells was carried out separately using a DSC 7 (Perkin Elmer™), previously calibrated with Indium. An amount of approximately 10 ± 1 mg was weighed in hermetically sealed aluminum pans and heated, under pure nitrogen ambient, from -20°C to 200°C at a rate of 5 ºC/min. An empty pan was used as a reference.

Mass changes during heating of ground whole cocoa beans, peeled cocoa bean and cocoa bean shells were measured using a Thermal Gravimetric Analyzer (Perkin Elmer™, STA 6000). An amount of approximately 10 mg (± 0.1 mg) was weighed in aluminum oxide crucibles and heated under a pure nitrogen atmosphere from 30 to 900°C at a heating rate of 10°C/min.

Statistical Analyses

Measures of central tendency and dispersion and Student t-tests were calculated using Microsoft Excel™ 2016. In this work, the standard deviation is indicated in the text by a ± sign, unless used to specify instrument precision. Analysis of variance and Duncan's multiple range tests were conducted for multiple comparisons between results averages for chemical analysis of whole bean, peeled bean and cocoa bean shells [16].

Results and Discussion

Moisture content and water activity (a_w) of cocoa beans

Moisture content of cocoa beans was 6.51 ± 0.05% (wet basis) with a range from 6.48 to 6.59% (wet basis). The water activity measured at 25-27°C, averaged 0.617 ± 0.010 with a range of 0.618-0.611.

Relative weight of peeled cocoa beans and shells, and shell thickness

The results regarding the relative weight of peeled cocoa beans and shells are presented in Table 1.

From the results above, the ratio of shells to peeled beans was calculated as 0.1839. Alvarez *et al*. [17] and Lares Amaíz *et al*. [18] reported weight shell values of Venezuelan commercial cocoa beans (no variety specified) of 14.81% and 14.21% respectively. Cocoa bean shell of Venezuelan Criollo fermented cocoa beans from Chuao ranged from 14.29% to 15.50% [19].

Average shell thickness determined was 0.310 ± 0.076 mm with a range of 0.499-0.177 mm and a 95% confidence interval from 0.297-0.323 mm. Cocoa bean shells have little commercial value and can be considered waste material. Its value as feed is limited due to the elevated content of theobromine and caffeine. However, its use in infusions has been reported [20]. Hutagalung and Chang [21] reported that the aminoacid profile of shells compares favorably with palm kernel cake and therefore, it could be utilized as an alternative protein source to substitute grain protein in animal diets. Cocoa beans shells also have relatively high potassium content and may be used to manufacture fertilizers or composts [21]. When used as mulch, the shell contains approximately 2.5% nitrogen, 1% phosphate and 3% potash, as well as a natural gum that is activated when watered, having use for mulch and compost preparation [21]. Its fat content makes it suitable for burning as fuel [1]. From the commercial point of view, the shell percentage should be as low as possible, usually between 10-14%.

Chemical Analyses of beans and shell

The results for the moisture content and water activity of whole and peeled cocoa beans and shells are presented in Table 2.

Table 1. Results obtained for the percent of shell and shell thickness in whole fermented Trinitario cocoa beans with 6.51% average moisture content (wet basis).

Physical property	Mean value	Range	Standard deviation	95% confidence interval
Shell in whole beans (% w/w)	15.5	15.9-15.2	0.37	14.6-16.5
Shell thickness (mm)	0.310	0.499-0.177	0.076	0.297-0.323

Table 2. Moisture content (wet basis) and water activity (aw) of Trinitario cocoa beans grown in Venezuela.

Moisture content (% wet basis)					
Cocoa bean and constituents	Average*	Standard deviation	Range	95% confidence interval	aw (25-27°C)
Whole beans	6.75[a]	0.29	7.09-6.54	6.42-7.08	0.657
Peeled beans	6.22[a]	0.20	6.44-6.07	6.00-6.44	0.684
Shells	17.30[b]	0.50	17.84-16.85	16.73-17.87	0.660

*Different characters in the same column indicate statistically significant differences ($p \leq 0.05$)

There were no significant differences ($p > 0.05$) between the percent moisture content of the peeled beans (6.75 %) and that of the whole beans (6.22%). However, the moisture content of the cocoa bean shells (17.30%) was significantly higher ($p \leq 0.05$) than those of the whole and peeled beans.

A material balance carried out, for the moisture present in the peeled cocoa beans and in cocoa bean shells (dry basis), assuming the percent of shells in the whole beans was that found experimentally presented in Table 1 (15.5%), indicated that the percentage of the total water present in peeled cocoa beans was around 64% of the total bean moisture, while the amount of water in cocoa bean shells resulted in about 36% of the total cocoa bean water present. This fact indicated that about one third of the total water in cocoa beans was located in the shell, in spite of the fact that the shell represents only about one sixth of the weight of the whole bean, being only a small part of the linear dimensions of the bean (2.6 to 4.9%, data not shown). Average thickness of shells was about 0.31 mm. This fact evidenced the higher water adsorption capacity of the cocoa bean shell as compared with that of the peeled bean.

In spite of the fact that cocoa bean shells had higher moisture content (17.30%) than the peeled cocoa bean (6.22%), its water activity (a_w) was similar but slightly lower (0.660) than that of peeled beans (0.684). This evidenced that a large fraction of the water present in the shells should be bound water resulting in lower water activity. The elevated water adsorption capacity of the shell could be explained by the nature of the chemical species formed during the fermentation process in the shell and inside the bean. After beans are removed from the pod, they have their surface covered by a mucilaginous pulp. This pulp contains non-reducing sugars and other nutrients that are utilized by microorganisms such as yeast, lactic acid and acetic acid producing bacteria, and aerobic mesophilic bacteria that proliferate over this pulp in the surface of the beans. Non-reducing sugars are converted by microorganisms to reducing sugars of lower molecular weight, alcohols, lactic acid, acetic acid, and other compounds. Also, protein is hydrolyzed to form peptides and free aminoacids [7]. These changes were confirmed by Afoakwa *et al*. [22] and Lagunes Galvez *et al*. [23], who studied the change in biochemical composition of cocoa beans during fermentation.

The results of other proximal analysis of Trinitario cocoa beans are presented in Table 3 for the whole and peeled beans and shells.

The results for the whole beans are similar to those presented by other authors [3, 4, 17, 18].

The crude fat content was significantly higher ($p \leq 0.05$) in the whole bean (44.23%) than in the peeled bean (42.73%) and both of them significantly higher ($p \leq 0.05$) than that in the shell (6.53%). It has to be pointed out that a smaller but substantial amount of fat was present in the cocoa bean shell.

The statistical analysis showed that crude protein content (10.27%) in the shell was significantly less ($p \leq 0.05$) than in peeled cocoa beans (12.25%) and this in turn, lower than in the whole bean (12.65%). The lower protein content in the shell could be explained by protein degradation and utilization by microorganisms growing in the outer part of beans during fermentation.

The ash content was significantly higher ($p \leq 0.05$) in the shell (6.10%) than in whole beans (3.34%) and peeled beans (2.84%). Also, the ash content in peeled beans was lower than in whole beans. It is known that the shell is a good source of minerals, particularly various phosphates and potash, allowing its use as a light fertilizer [20].

Thermal analysis of cocoa

Thermal analysis of cocoa constituents was carried out by means of DSC and TGA. Figure 1 shows DSC curves for cocoa bean shell, peeled cocoa bean and whole cocoa bean.

In all cases, the figure shows bimodal endothermic events with peaks at 18.9/31.4°C and 18.4/30.4°C for whole and peeled cocoa beans, respectively. On the other hand, shells exhibit the bimodal peaks at 17.8 and 30.4°C.

Table 3. Analyses of Venezuelan Trinitario cocoa beans: crude fat, protein, and ash (wet basis) of whole and peeled cocoa beans and shells.

Crude fat content (% wet basis)				
Cocoa bean and constituents	Average*	Standard deviation	Range	95% confidence interval
Whole beans	44.23[a]	0.30	44.52-43.93	43.89-44.57
Peeled beans	42.73[b]	0.59	43.30-42.12	42.06-43.39
Shells	6.53[c]	0.31	6.87-6.26	6.18-6.88
Crude protein content (% wet basis)				
Cocoa bean and constituents	Average*	Standard deviation	Range	95% confidence interval
Whole beans	12.65[a]	0.22	12.86-12.43	12.41-12.90
Peeled beans	12.25[b]	0.16	12.40-12.08	12.07-12.43
Shells	10.27[c]	0.68	10.95-9.59	9.50-11.04
Ash content (% wet basis)				
Cocoa bean and constituents	Average*	Standard deviation	Range	95% confidence interval
Whole beans	3.34[a]	0.03	3.31-3.37	3.31-3.37
Peeled beans	2.84[b]	0.04	2.88-2.80	2.79-2.88
Shells	6.10[c]	0.07	6.14-6.05	6.05-6.15

*Different characters in the same column indicate statistically significant differences ($p \leq 0.05$)

These endothermic events correspond to the melting of the different stable forms of cocoa butter. As known, cocoa butter can crystallize in six different forms; i.e., it is polymorphic, namely from the unstable form I to the stable form VI, according to the nomenclature used in chocolate industry. These different crystalline forms melt in a relatively small temperature range varying from 16-18°C for form I to 34-36°C for form VI, with the intermediate temperatures values corresponding to the melt of crystalline forms from II to V [24].

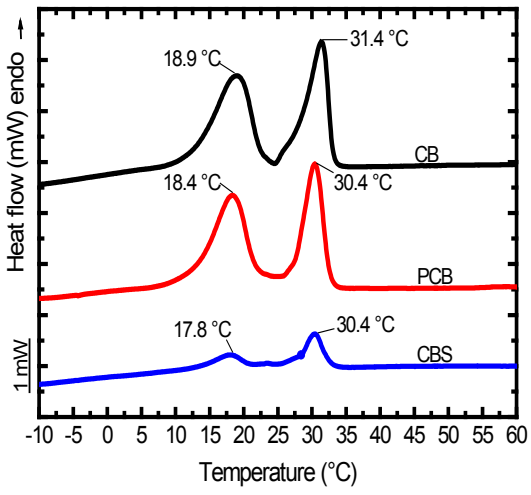
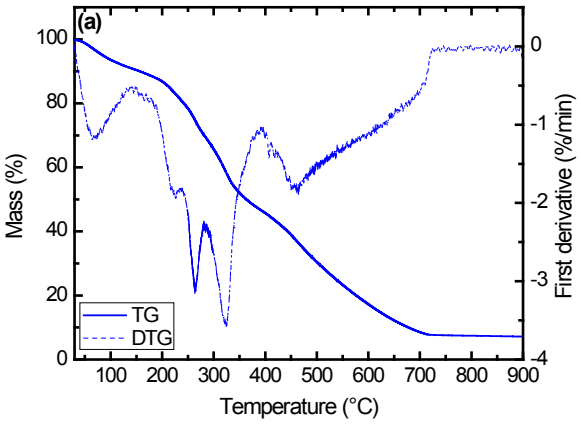


Figure 1. DSC heating scan for cocoa bean shell (CBS), peeled cocoa bean (PCB), and whole cocoa bean (CB).

Figure 1 shows that the crystalline forms present in cocoa constituents correspond to form I and form V, as evidenced by the lower and higher temperature peaks in the three DSC heating scans. The presence of these forms, also named respectively g and b_2, according to Greek letter nomenclature, indicates the coexistence of the less stable crystallites and the more desirable crystalline form in chocolate industry for the final product (V or b_2 form).

Thermal degradation behavior of cocoa constituents was studied by TGA up to 900°C under nitrogen atmosphere. The weight loss percentage due to heating (TG curve) along with its first derivative (DTG curve), are shown in Figure 2.



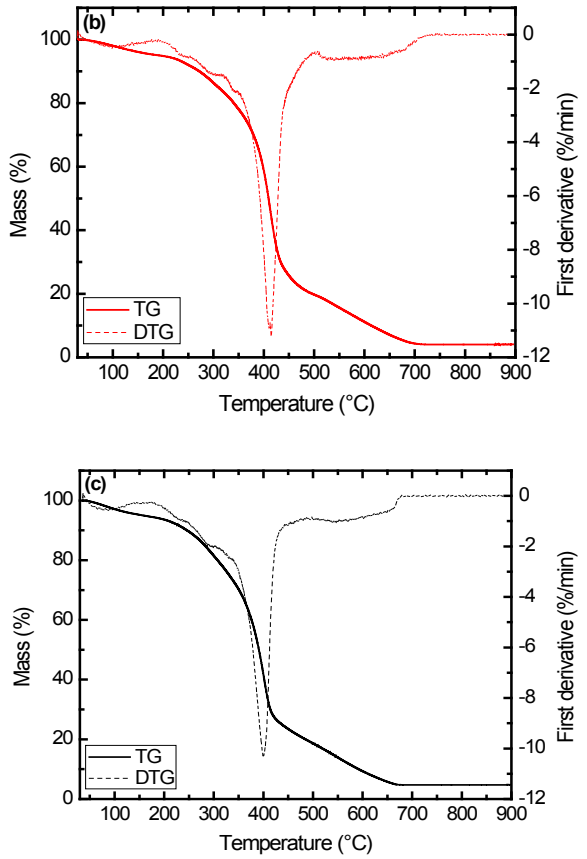


Figure 2. TGA/DTA heating graphs for cocoa bean shell (a), peeled cocoa bean (b), and whole cocoa bean (c)

Figure 2a shows a first mass loss step in a temperature range of 25-160°C, with a peak at ca. 64°C. Evaporation of moisture and water linked with the structure has been associated to shell heating in this temperature range [11]. The corresponding weight loss at the end of this range was 10%. Figure 2a then shows that pyrolysis starts with a shoulder at around 225°C, followed by three peaks at 264, 324 and 464°C. The shoulder has previously been related to the pyrolysis of pectic polysaccharides in the shell [11]. The following two peaks, on the other hand, have been linked to the thermal degradation of high molecular weight macromolecules such hemicellulose and cellulose [2, 11]. The high temperature peak appearing at ca. 464°C and extending to ca. 720°C indicates the thermal degradation of cocoa butter and proteins [10, 11].

The TGA graphs for peeled and whole cocoa beans are shown in Figures 2b and 2c. The figures show similar behavior for both materials, with a first mass loss step in the same temperature range as that of the shell (25-160 °C). This first peak, occurring at ca. 98°C and 88°C for peeled and whole beans, respectively, is related to moisture lost. The moisture content at the end of this temperature range is around 4% for the peeled bean and 6% for the whole bean. Both figures show small step changes between 230-350°C, related to the simultaneous pyrolysis of high molecular weight polysaccharides which are also present in these materials in smaller proportions. A marked peak at ca. 400-415 °C are exhibited by both, peeled and whole beans, evidencing thermal decomposition of fat. Finally a wide mass step change between 500-700 °C is observed in both TGA graphs, linked to protein decomposition and further carbonization. Similar thermogravimetric behavior has been reported for cocoa liquor, consisting of cocoa butter and cocoa powder by Materazzi *et al*. [10].

Figures 2a through 2c also show that the remaining mass at the end of the TGA tests were around 7%, 4%, and 5% of initial weight for shells, peeled and whole beans, respectively. These percentages represent the residues formed by carbonized sample (ashes). It is noteworthy that the residue yield shown in these figures, grade samples in the same fashion as that shown in Table 3 for ashes content determined by standard methods.

Conclusions

The shell moisture was higher than that in the whole and peeled beans. In spite of the fact that the shell had higher moisture content than the peeled bean, its water activity (a_w) was lower, evidencing a higher water binding capacity of the shell. This is probably due to the formation during fermentation of compounds capable of adsorbing water, such as reducing sugars, peptides, free aminoacids, organic acids and minerals.

It was found that crude fat content was higher in whole beans than in peeled beans and significantly larger than that in shells. Crude protein content presented a decreasing order for whole beans, peeled beans and shells. The shell showed an ash content significantly higher than in whole and peeled beans.

Thermal properties of cocoa constituents showed bimodal endothermic events between 18-30°C, indicating the coexistence of crystalline forms I (g) and V (b_2) in these materials. After water evaporation, occurring

up to about 160°C, cocoa constituents decompose over a temperature range of 220-700°C, with a final carbonized residue of less than 10%.

References

[1] Fowler, G. S.: The composition and feeding value of cocoa shells. Armhest, Massachusetts, USA. Massachusetts Agricultural College, MSc thesis, 1914.

[2] Puglia, D., Dominici, F., Badalotti, M., Santulli, C. and Kenny, J. M.: "Tensile, thermal and morphological characterization of cocoa bean shells (CBS)/ polycaprolactone-based composites". Journal of Renewable Materials, Vol. 4, No. 3 (2016) 199-205.

[3] Sandoval, A. J. and Barreiro. J. A.: "Water sorption isotherms of non-fermented cocoa beans (*Theobroma cacao*)". J. Food Eng., Vol. 51, No. 2 (2002) 119-123.

[4] Sandoval, A. J., Barreiro, J. A., Tovar, X. and Angueira, M.: "Sorption characteristics of fermented cocoa powder (*Theobroma cacao*)". Rev. Téc. Ing. Univ. Zulia, Vol. 25, No. 1 (2002) 49-55.

[5] Wood G. A. R. and Lass R. A.: "Cocoa". 4th ed. Blackwell Science Ltd. London, 2001.

[6] Anonymous: Cocoa beans. Venezuelan Comisión for Standardization. Standard COVENIN 1339. Caracas, Venezuela: Ministry of Development, 1978.

[7] Braudeau, J.: Cocoa. Barcelona, Editorial Blume. Spain, 1981.

[8] Afoakwa, E.O., Paterson, A., Fowler, M. and Vieira, J.: "Characterization of melting products in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry". Food Res. Int., Vol. 41, No. 7 (2008) 751-757.

[9] Fernandes, V.A., Müller, A.J. and Sandoval, A.J.: "Thermal, structural and rheological characteristics of dark chocolate with different compositions". J. Food Eng., Vol. 116, No. 1 (2013) 97-108.

[10] Materazzi, S., De Angelis, S., Vecchio, S., Risoluti, R. and Finamore, J.: "Thermogravimetric characterization of dark chocolate". J. Therm. Anal. Calorim., Vol. 116, No. 1 (2014) 93-98.

[11] Du, Y., Jiang, X., Lv, G., Li, X., Chi, Y., Yan, J., Liu, X. and Buekens, A.: "TG-pyrolysis and FTIR analysis of chocolate and biomass waste". J. Therm. Anal. Calorim., Vol. 117, No. 1 (2014) 343-353.

[12] Norma Venezolana Covenin 50:1995. Granos de cacao (2da revisión). Ministerio de Fomento. Caracas, Venezuela.

[13] A.O.A.C.: "Official Methods of Analysis of the Association of Official Analytical Chemists". 16th ed. Arlington, VA, Association of Official Analytical Chemists. USA, 1996.

[14] Visvanathan, R., Palanisamy, P.T., Gothandapani, P.T. and Sreenarayanan, V.V.: "Physical properties of neem nut". J. Agric. Eng. Res., Vol. 63, No. 1 (1996) 19-25.

[15] Bart-Plange, A. and Baryeh, E.A.: "The physical properties of category B cocoa beans". J. Food Eng., Vol. 60, No. 3 (2003) 219-227.

[16] Ott, R.L. and Longnecker, M.: "An introduction to statistical methods and data analysis". Sixth edition. Books /Cole, Beltmont Californnia, USA, 2010.

[17] Alvarez, C., Pérez, E. and Lares, M.C.: "Physical and chemical characterization of fermented, dried and toasted cocoa almonds grown in Cuyagua, Aragua state". Agr. Trop., Vol 57, No. 4 (2007) 249-256.

[18] Lares Amaíz, M. C., Gutierrez, R., Perez, E. and Alvarez, C.: "Effect of roasting process on physical and physicochemical properties, proximate composition and fatty acid profile of the cocoa bean from Miranda state, Venezuela". Rev. Cient. UDO Agríc., Vol. 12, No. 2 (2012) 439-446.

[19] Lares Amaíz, M., Perez Sira, E., Alvarez Fernández, C., Perozo González J. and El Khon, S.: "Physicochemical changes and fatty acids profile of cocoa grown in Chuao, throughout post harvest process". Agr. Trop., Vol. 63, No. 1 (2013) 37-47.

[20] Personal Communication. Ms. Carmen Fernández. *Cacao de Origen*, Hacienda La Trinidad, Caracas, Venezuela (2017).

[21] Hutagalung, R. L. and Chang, C.C.: Utilization of cocoa byproducts as animal feed, in Proceedings of the International Conference on Cocoa and Coconuts, pp. 447–456, Kuala Lumpur, Incorporated Society of Planters, 1978. Cited by Puglia *et al*. (2016).

[22] Afoakwa, E.O., Kongor, J. E., Takrama, J. and Budu, A. S.: "Changes in nib acidification and biochemical composition during fermentation of pulp pre-

conditioned cocoa (Theobroma cacao) beans". Int. Food Res. J., Vol. 20, No. 4 (2013) 1843-1853.

[23] Lagunes Gálvez, S., Loiseau, G., Paredes, J. L., Barel, M. and Guiraud, J. P.: "Study on the microflora and biochemistry of cocoa fermentation in the Dominican Republic". Int. J. Food Microb., Vol. 114, No. 1 (2007) 124-130.

[24] Beckett, S.T.: "The Science of Chocolate". 2nd ed. The Royal Society of Chemistry. Cambridge, UK, 2008.

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