Reaserch article
Food Eng. Prog. 2024;28(4):296-301
pISSN: 1226-4768, eISSN: 2288-1247
https://doi.org/10.13050/foodengprog.2024.28.4.296

산업식품공학
Food Engineering Progress

Steady shear flow behavior of commercial dark chocolates at different temperatures

Jun Ho Lee*

Department of Food Engineering, Daegu University, Gyeongsan 38453, Korea

Abstract

The objective of this study was to determine the rheological properties of commercial dark chocolates with high cocoa content (86%, 95%, and 100%) at different temperatures (25℃, 35℃, and 45℃). The pH values ranged from 6.14 to 6.47, the soluble solids content ranged from 0.64 to 1.34 (°Brix), and the moisture content ranged from 1.29% to 1.66% (wb). No significant differences were observed between the samples with 86% and 95% cocoa content in terms of all color coordinate values (p>0.05). However, samples with 100% cocoa content exhibited significantly higher coordinate values for L*, a*, and b* (p<0.05). The molten chocolate was found to exhibit non-Newtonian fluid behavior, following the Herschel-Bulkley model, with flow behavior index (n) values ranging from 0.83 to 0.89, indicating pseudoplastic behavior. The yield limit (σ_y) decreased as the cocoa content increased at the same temperature, and decreased as the temperature increased within the same sample. An Arrhenius-type relationship was used to correlate the consistency coefficient (K) to temperature. The activation energy (E_a) values exhibited a positive correlation with cocoa content, ranging from 32.54 to 39.64 kJ/mol.

Keywords: Commercial dark chocolates, Non-Newtonian, Herschel-Bulkley model, Activation energy

Introduction

The global demand for chocolate is increasing, and its appeal is growing due to its physiological and health-enhancing effects (Katz et al., 2011; Montagna et al., 2019). These health benefits of chocolate are mainly attributed to the antioxidant properties of flavonoids found in cocoa (Faccinetto-Beltran et al., 2021). Molten chocolate is a suspension of particles of sugar, cocoa solids, and/or milk powder in which cocoa butter, mixed with other fats, serves as the continuous phase (Rhom et al., 2018; Vasquez et al., 2019). This concentrated suspension is a crucial ingredient in the food processing industry for the production of various products, including ice cream and bakery items. The flow characteristics of this suspension play a significant role in subsequent processing stages, as they greatly influence the final texture and appearance.

The rheological properties of these products are influenced by a number of processing techniques, including refining, conching, and tempering. These properties are dependent on several process parameters, including time and temperature, particle size distribution, and the amount of fat present in the product (Afoakwa et al., 2009; Faccinetto-Beltran et al., 2021). Previous studies have demonstrated that the apparent viscosity of dark chocolate increases with higher sugar content and lower fat solids content (Fernandes et al., 2013; Vasquez et al., 2019). Furthermore, it has been observed that molten chocolate displays a shear-thinning behavior, characterized by a yield stress and a plastic viscosity (Fernandes et al., 2013; Rohm et al., 2018; Quispe-Chambilla et al., 2022). It was also demonstrated that the rheological properties were affected by the intensity of grinding and could be targeted (Rohm et al., 2018). Quispe-Chambilla et al. (2022) found that the partial addition of

Received: Apr 17, 2024 / Revised: Jun 09, 2024 / Accepted: Jun 25, 2024
Corresponding author: Jun Ho Lee, Department of Food Engineering, Daegu University, Gyeongsan 38453, Korea
E-mail: leejun@daegu.ac.kr

food ingredients, such as peanut paste and Sacha Inchi, significantly impacted the rheological and functional properties of dark chocolate. Velciov et al. (2021) reported on the proximate composition of dark chocolate containing 40%-80% cocoa mass.

Although the qualitative influence of fat content on chocolate rheology is well established in the literature (Glicerina et al., 2016; Vasquez et al., 2019), there is a paucity of comparative studies among commercially available dark chocolates to evaluate their rheological characteristics on cocoa mass content. These flow characteristics have a significant impact on product yields, production facility efficiency, transportation during the manufacturing process, and consumer preferences. Consequently, the evaluation of rheological properties is of paramount importance in practical applications concerning handling and quality control, as well as for engineering calculations. The objective of this study was to systematically investigate the rheological properties of dark chocolates, in order to establish a relationship between cocoa mass content and its temperature dependency.

Materials and Methods

Materials

Commercial dark chocolate samples containing 86% and 95% cocoa mass (Meiji Co., Ltd., Tokyo, Japan) and a cocoa mass sample (ECC NV, Malle, Belgium) were procured from a local market. The samples were designated as 86CM, 95CM, and 100CM, respectively, according to the concentration of cocoa mass in the sample. The samples were stored in a chiller at approximately 4℃ and liquefied at 40℃ prior to each analysis.

Physicochemical characterization

A 5 g sample was mixed with 45 mL of distilled water and homogenized for 1 min. The mixture was left at room temperature for 1 h to allow for separation of the solid and liquid phases. The pH of the resulting liquid was measured using a pH meter (pH/Ion 510, Oakton Instruments, Vernon Hills, IL, USA). The color determination of the samples on a petri dish was conducted using a Chromameter (CM-600d, Minolta Co., Osaka, Japan) set for CIELAB color space. Total soluble solids (TSS) were measured using a refractometer (PR-301, Atago Co., Tokyo, Japan). Moisture content was obtained by drying a specific amount (5 g) of the sample to a constant weight at 105°C in an oven (FOL-2, Jeio Tech Co., Ltd., Daejeon, Korea), and the results were reported on a wet basis. Five measurements were taken for each sample.

Rheological characterization

Steady shear rheological measurements were conducted using a rotational rheometer (RV1, Thermo Fisher Scientific Inc., Karlsruhe, Germany) at 25℃, 35℃, and 45℃. The sample temperature was controlled using a temperature-controlled recirculating water bath (RW-0525G, Jeio Tech Co., Ltd., Daejeon, Korea). Prior to the measurements, the rheometer was first zero-adjusted. The tube was filled with approximately 40 mL of the sample. The rotor and sample tube were attached to the rheometer for experimentation. Twelve shear rates, ranging from 1 to 50 s^{-1} were selected, and the measuring time was 120 s. The experiments were replicated three times, and the mean values were compared.

Modeling of rheological model

The shear rate rheological properties of chocolate samples can be described by the Herschel-Bulkley model, which is commonly used to explain the flow behavior of various food products (Alsalman & Ramaswamy, 2021; Ramirez-Brewer et al., 2023). This model can be used to demonstrate the shear rate dependency of the properties.

$$\sigma = \sigma_y + K\dot{\gamma}^n$$

where, σ is the shear stress (Pa), σ_y is the yield stress (Pa), K is the consistency coefficient (Pa · s^n), $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the flow behavior index (dimensionless).

The shear stress and shear rate data for chocolates at different temperatures were fitted with various linear regression equations using the RheoWin Job Manager software. The regression equations with the highest coefficient of determination were selected. The adequacy of the derived Herschel-Bulkley equations in predicting the shear stress values at different temperatures was further evaluated using the mean relative percentage error (MRPE), as outlined in Quispe-Chambilla et al. (2022).

$$\mathrm{MRPE} = \frac{1}{\mathrm{N}}\sum_{i=1}^{N}\frac{(\sigma_{\exp})_i - (\sigma_{\mathrm{pre}})_i}{(\sigma_{\exp})_i} \times 100$$

where, N is the number of experiments, $\sigma_{\exp}$ is the measured σ from experiments and σ_{pre} is the calculated σ.

Temperature dependency of rheological property

The viscosity parameter of samples can be related to temperature using an Arrhenius-type equation, as demonstrated by Diamante & Liu (2016) and Choi & Lee (2017).

$$K = K_0 \exp(E_a/R \cdot T)$$

where, K is the consistency coefficient ($P_a \cdot s^n$), K_0 is the pre-exponential constant ($P_a \cdot s^n$), E_a is the activation energy (J/mol), R is the universal gas constant (8.314 J/mol · K), and T is the absolute temperature (K).

Statistical analysis

The mean and standard deviation were used to express the collected data (n=5). The results were analyzed using one-way analysis of variance (ANOVA) with general linear models (GLM) in Statistical Analysis System ver. 9.4 software (SAS/STAT, Cary, NC, USA). Duncan's multiple range test was used to compare means, and significance was defined at the 5% level.

Results and Discussion

Sample characterization

Table 1 presents the key characteristics of the chocolate samples used in this study. The pH values of the samples ranged from 6.14 to 6.47 and were influenced by the cocoa mass content ($p<0.05$). The pH of 100CM was relatively low compared to other chocolates due to the absence of added sugar and the presence of only cocoa solids. Lee (2023) reported similar pH values ranging from 6.10 to 6.55, depending on the addition of wheat sprout powder. The chocolate samples' soluble solids content ranged from 0.64 to 1.34 and was significantly affected by the amount of cocoa mass ($p<0.05$). The soluble solids content of the 86CM samples was found to be higher than that of the 100CM samples, which can be attributed to the additional sugars and other ingredients present in the formulation. The moisture content of the samples ranged from 1.29 to 1.66%, which is comparable to the range of 1.22–1.39% reported for dark chocolates by Velciov et al. (2021).

The L* coordinate values of the various chocolate samples exhibited a range of 16.71 to 30.37. The lightness values were found to be significantly higher in the 100CM samples that did not contain any added ingredients, such as sugar, soy lecithin, and sucrose fatty acids, in the formulation ($p<0.05$). Although no significant differences were found between the 86CM and 95CM samples ($p>0.05$), the 100CM samples were darker. The values for coordinates a* and b* ranged from 2.43 to 6.34 and 1.17 to 10.72, respectively, and showed a pattern similar to that of the lightness values. Puchol-Miquel et al. (2021) reported a similar range (13.2–14.7) in the lightness values of chocolates made from reconstituted cocoa liquor and high cocoa content.

Rheological characterization

Fig. 1 displays the shear stress and shear rate behavior of 86CM,

Table 1. Characterization of commercial dark chocolate and cocoa mass samples used in this study

Sample code	Nutritional information (per 100 g solid)[1)]						Physicochemical properties					
	Carbohydrates (g)	Sugars (g)	Proteins (g)	Fat (g)	Salt (g)	Energy (kcal)	pH	Soluble solids content (°Brix)	Moisture content (wb, %)	Color L*	Color a*	Color b*
86CM[2)]	36	20	14	46	0	580	6.31±0.02[b,5)]	1.34±0.11[a]	1.29±0.10[a]	17.37±0.86[b]	2.64±0.21[b]	1.37±0.17[b]
95CM[3)]	28	12	14	52	0	620	6.47±0.03[a]	1.04±0.09[c]	1.62±0.22[a]	16.71±0.48[b]	2.43±0.07[b]	1.17±0.03[b]
100CM[4)]	5.5	0.3	12	54	0.02	598	6.14±0.03[c]	0.64±0.09[c]	1.66±0.38[a]	30.37±1.23[a]	6.34±0.36[a]	10.72±0.50[a]

[1)] The information provided by the respective food labelling.
[2)] 86CM, dark chocolate samples containing 86% cocoa mass.
[3)] 95CM, dark chocolate samples containing 95% cocoa mass.
[4)] 100CM, cocoa mass only.
[5)] Values represent mean±SD (n=5).
[a–c] Means with the different letters within a property (column) are significantly different ($p<0.05$) by Duncan's multiple range test.

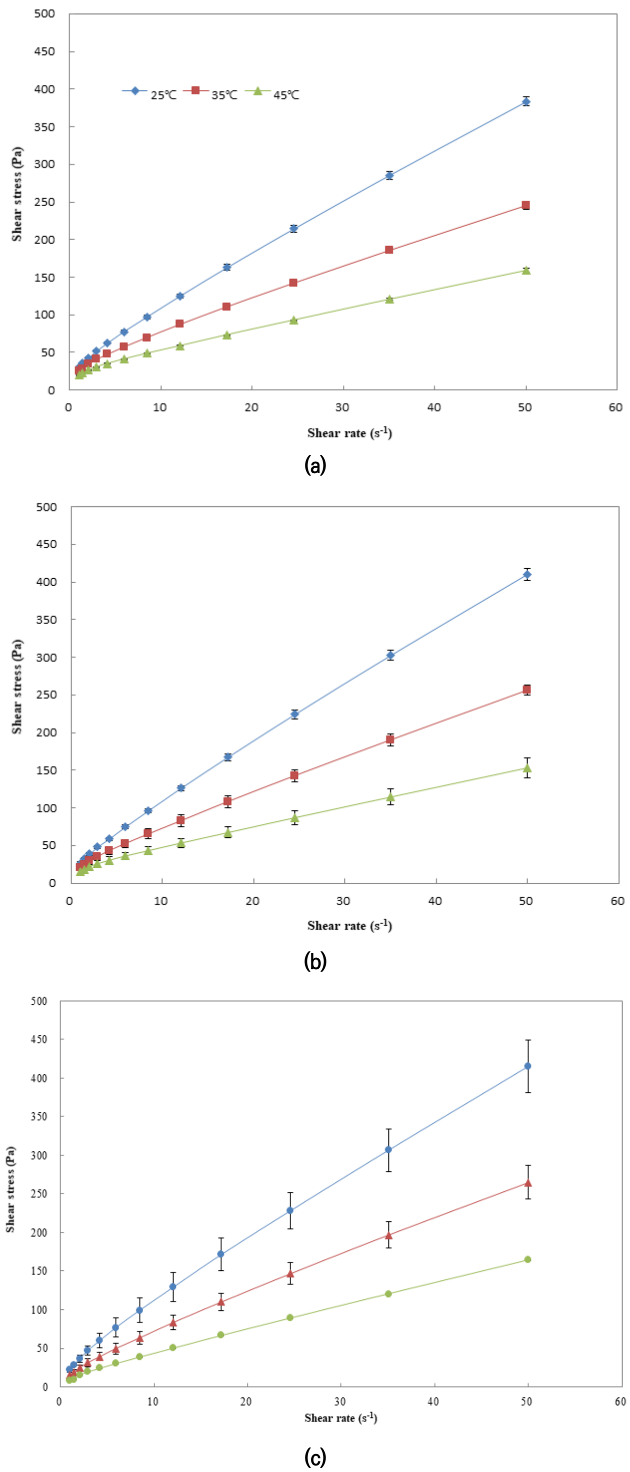

Fig. 1. Rheograms of shear stress vs. shear rate for (a) chocolates with 86% cocoa mass, and (b) chocolates with 95% cocoa mass, and (c) cocoa mass samples at different temperatures.

95CM, and 100CM samples at temperatures of 25℃, 35℃, and 45℃. The results demonstrate that the shear stress increases rapidly with increasing shear rate at the studied temperatures, indicating shear-thinning behavior due to shear stress. Previous studies on chocolate samples have also demonstrated non-Newtonian fluid behavior of the pseudoplastic type (Vasquez et al., 2019; Quispe-Chambilla et al., 2022).

Table 2 presents the model constants obtained by fitting the Herschel-Bulkley model to experimental viscosity values as a function of shear rate within a shear rate range of 1–50 s^{-1} and the considered temperature range. The mean relative percentage error (MRPE) was calculated for experimental and predicted shear stresses in order to evaluate the equation’s goodness of fit. The MRPE values for the 86CM, 95CM, and 100CM samples were found to be in the range of 1.25–2.89, 0.87–3.45, and 2.21–4.97, respectively. All MRPE values were less than 10%, which is considered acceptable and suitable for most engineering purposes (Diamante & Liu, 2016; Pardeshi et al., 2009). The fitted model was confirmed to be adequate as all R^2 values were higher than 0.99. All samples exhibited an expected pseudoplastic behavior with an initial resistance to flow (yield stress) and plastic viscosity. The mean n values were found to range between 0.83 and 0.89, which is consistent with the characteristics of a non-Newtonian fluid (Glicerina et al., 2016).

The yield stress values were observed to be significantly lower in 100CM samples compared to 86CM and 95CM samples at the same temperature (p<0.05). However, there was no significant difference was found between the 86CM and 95CM samples at the same temperature (p>0.05). Nevertheless, the yield stress values exhibited a tendency to decrease as the concentration of cocoa mass increased in the chocolate samples. This indicates that the samples with a higher concentration of cocoa mass require less energy to initiate fluid flow. This is consistent with the findings of Vasquez et al. (2019), where sample A (73% cocoa) underwent a solid-liquid transition at approximately 10 Pa, while sample D (41% cocoa) did so at approximately 500 Pa. This suggests that the stress required to overcome the initial interaction forces between fat and solid particles in chocolate matrices increases with decreasing fat content (Fernandes et al., 2013).

The consistency coefficient (K) is also used to characterize the flow properties of chocolate. A higher K value indicates a thicker, more viscous consistency. There were no significant differences in K values among samples at the same temperature (p>0.05), but

Table 2. Rheological parameters of the Herschel-Bulkley model and activation energy from the Arrhenius equation

Sample code	Rheological parameter						Temperature dependency		
	T (℃)	σ_y (Pa)	K (Pa · s^n)	n	R^2	MRPE	K_0	E_a (kJ/mol)	R^2
86CM	25	20.34±0.25[a,1)]	11.95±0.68[ab]	0.87±0.01[a]	1.0000	1.25	0.0000247	32.54	0.9763
	35	18.02±0.64[ab]	8.71±0.22[bcd]	0.83±0.00[a]	0.9999	1.92			
	45	16.60±0.54[abc]	5.22±0.42[cd]	0.84±0.02[a]	0.9996	2.89			
95CM	25	15.71±1.17[abc]	11.93±0.40[ab]	0.89±0.00[a]	1.0000	0.87	0.0000051	36.38	0.9973
	35	14.38±2.43[bcd]	7.72±1.21[cd]	0.88±0.04[a]	0.9999	2.14			
	45	12.77±3.46[cd]	4.74±0.28[d]	0.86±0.00[a]	0.9996	3.45			
100CM	25	10.42±3.16[de]	14.25±4.70[a]	0.86±0.06[a]	1.0000	2.51	0.0000017	39.64	0.9943
	35	7.55±2.37[ef]	9.05±1.09[bc]	0.86±0.01[a]	0.9999	2.21			
	45	4.93±0.34[f]	5.21±0.04[cd]	0.87±0.00[a]	0.9997	4.97			

[1)]Values represent mean±SD (n=3).
[a-f]Means with the different letters within a parameter (column) are significantly different (p<0.05) by Duncan's multiple range test.

decreased with increasing temperature within the sample. Changes in plastic viscosity are closely linked to the surface area of particles in contact with cocoa butter (Mongia & Ziegler, 2000) and the interaction between cocoa particles and cocoa fat (Do et al., 2007). Further research is required to clarify the effect of cocoa mass on K in these commercial samples, particularly in terms of particle size and distribution, which can significantly affect the rheological properties of chocolate samples.

Temperature dependency of the consistency coefficient

The effect of temperature on chocolate rheology during steady shear was examined using an Arrhenius-type relationship. The pre-exponential constant (K_0) and the activation energy (E_a) were determined from the slope and intercept of the Arrhenius regression, showing a good fit with R^2>0.98 (Table 2). As previously stated, K decreases as temperature increases, in accordance with the typical trend of viscosity decreasing with temperature. The study found that the 100CM samples, which had the highest cocoa level, were the most temperature-sensitive. These samples exhibited a larger decrease in viscosity with increasing temperature due to their high activation energy of 39.64 kJ/mol. The 95CM samples had a slightly higher activation energy of 36.38 kJ/mol compared to the 86CM samples (32.54 kJ/mol). In a similar vein, Quispe-Chambilla et al. (2022) observed that dark chocolates with partial substitution of peanuts and Sacha Inchi exhibited activation energies in a comparable order of magnitude. Furthermore, Vasquez et al. (2019) also reported that the activation energy decreased with decreasing cocoa content of chocolate samples.

Conclusion

The study confirmed that dark commercial chocolates with varying amounts of cocoa mass at different temperatures (25℃, 35℃, and 45℃) exhibited non-Newtonian fluid behavior, as predicted by the Herschel-Bulkley model. The model was successfully used to construct the flow curves for the molten chocolate samples. The rheology of chocolate is significantly influenced by both cocoa mass content and temperature. The yield stress values decreased as the concentration of cocoa mass increased at the same temperature, and also with increasing temperature within the sample. No significant differences were found in the consistency coefficient due to cocoa mass content (p>0.05), but the consistency coefficient decreased with increasing temperature. The flow behavior index was not affected by any processing parameters, such as cocoa mass content and temperature (p>0.05). An Arrhenius-type relationship was used to relate the consistency coefficient temperature. The samples with the highest cocoa mass content exhibited the greatest temperature sensitivity, with an activation energy of 39.64 kJ/mol. The activation energy decreased as the cocoa content of the chocolate samples decreased.

ORCID

Jun Ho Lee https://orcid.org/0000-0002-8718-4791

Conflict of interests

No potential conflict of interest relevant to this article was reported.

Acknowledgements

This research was supported by Daegu University Research Grant, 2020.

Data availability

Upon reasonable request, the datasets of this study can be available from the corresponding author.

Authorship contribution statement

The article is prepared by a single author.

Ethics approval

Not applicable.

References

Afoakwa EO, Paterson A, Fowler M, Vieira J. 2009. Microstructure and mechanical properties related to particle size distribution and composition in dark chocolate. Int. J. Food Sci. Technol. 44: 111-119.

Alsalman FB, Ramaswamy HS. 2021. Changes in carbohydrate quality of high-pressure treated aqueous aquafaba. Food Hydrocol. 113: 106417.

Choi JE, Lee JH. 2017. Non-Newtonian characteristics of gochujang and chogochujang at different temperatures. Prev. Nutr. Food Sci. 22: 62-66.

Diamante LM, Liu H. 2016. Rheological properties of green and gold kiwifruit purees at different temperatures. J. Food Chem. Nanotechnol. 2: 50-56.

Do TA, Hargreaves J, Wolf B, Hort J, Mitchell J. 2007. Impact of particle size distribution on rheological and textural properties of chocolate models with reduced fat content. J. Food Sci. 72: E541-E552.

Faccinetto-Beltran P, Gomez-Fernandez AR, Santacruz A, Jacobo-Velazquez DA. 2021. Chocolate as carrier to deliver bioactive ingredients: current advances and future perspectives. Foods 10: 2065.

Fernandes VA, Muller AJ, Sandoval AJ. 2013. Thermal, structural and rheological characteristics of dark chocolate with different compositions. J. Food Eng. 116: 97-108.

Glicerina V, Balestra F, Rosa MD, Romani S. 2016. Microstructural and rheological characteristics of dark, milk and white chocolate: a comparative study. J. Food Eng. 169: 165-171.

Katz DL, Doughty K, Ali A. 2011. Cocoa and chocolate in human health and disease. Antioxid. Redox Signal. 15: 2779-2811.

Lee, WG. 2023. Quality characteristics and antioxidant activities of white ganache chocolate added with wheat sprout powder. Culin. Sci. Hopital. Res. 29: 40-48.

Mongia G, Ziegler GG. 2000. The role of particle size distribution of suspended solids in defining flow properties of milk chocolate. Int. J. Food Prop. 3: 137-147.

Montagna MT, Diella G, Triggiano F, Caponio GR, De Giglio O, Caggiano G, Di Ciaula F, Portincasa P. 2019. Chocolate, "food of the gods": history, science, and human health. Int. J. Environ. Res. Public Health 16: 4960.

Pardeshi IL, Arora S, Borker PA. 2009. Thin-layer drying of green peas and selection of a suitable thin-layer drying model. Drying Technol. 27: 288-295.

Puchol-Miquel M, Palomares C, Barat JM, Perez-Esteve E. 2021. Formulation and physico-chemical and sensory characterization of chocolate made from reconstituted cocoa liquor and high cocoa content. LWT-Food Sci. Technol. 137: 110492.

Quispe-Chambilla L, Pumacahua-Ramos A, Choque-Quispe D, Curro-Perez F, Carrion-Sanchez HM, Peralta-Guevara DE, Masco-Arriola ML, Palomino-Rincon H, Ligarda- Samanez CA. 2022. Rheological and functional properties of dark chocolate with partial substitution of peanets and Sachi Inchi. Foods. 11: 1142.

Ramirez-Brewer D, Quintana SE, Garcia-Zapateiro LA. 2023. Effect of microwave treatment on technological, physicochemical, rheological and microstructural properties of mango (*Mangifera indica*) kernel starch variety Tommy and Sugar. LWT-Food Sci. Technol. 187: 115311.

Rohm H, Bohme B, Skorka J. 2018. The impact of grinding intensity on particle properties and rheology of dark chocolate. LWT-Food Sci. Technol. 92: 564-568.

Vasquez C, Henriquez G, Lopez JV, Penott-Chang EK, Sandoval AJ, Muller AJ. 2019. The effect of composition on the rheological behavior of commercial chocolates. LWT-Food Sci. Technol. 111: 744-750.

Velciov AB, Rivis A, Lalescu D, Popescu GS, Cozma A, Kiss AA, Gherman AM, Anghel IM, Simescu RE, Rada M. 2021. Determination of some nutritional parameters of dark chocolate. J. Agroalim. Proc. Technol. 27: 271-276.