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QUALITY ASSESSMENT OF THE TOFFEE WITH SWEETENERS AND DYE FROM WALNUT SEPTUM OR KERNEL'S PELLICLE

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Abstract. Reduction of "bad" carbohydrates in sweets is a complex issue, because carbohydrates provide important sensory, physical and textural properties of food. This research illustrated the possible use of the colorant Brown 7 (0.6...1.0%) in combination with sucralose and isomalt for alerting the functional quality of toffee candies. Sensory and physicochemical properties, microbiological indicators and color parameters were analyzed for four samples of toffee. The combination of sweetener with anti-crystallizer and Brown 7 significantly improves the color of toffees. It was established by HPLC that during thermal processing the Casuarictin from Brown 7 transforms into Ellagic acid. These transformations lead to an increase in the intensity of the brown color in the toffee. The addition of Brown 7 contributes to the decrease of titratable acidity from 0.28 ± 0.08 in the control to 0.21 ± 0.06 degrees of acidity in the sample which contain 1.0% dye. The chromatic parameters L*, a*, b* of the toffee sample with 0.6% Brown 7 content are the closest to the classic toffee parameters. Use of colorant in combination with sweetener illustrates a potential synergy of sensorial properties. This help to increase the intake of natural bioactive compounds and to decrease carbohydrates in sweets, promising health benefits.

Keywords: *Brown 7, CIELab, color, HPLC, pellicle, RGB, sweeteners, toffee candies, walnut.*

Rezumat: Reducerea carbohidraților „răi" din dulciuri este o problemă complexă, deoarece carbohidrații oferă proprietăți senzoriale, fizice și texturale importante ale alimentelor. Această cercetare a ilustrat posibila utilizare a colorantului Brown 7 (0.6...1.0%) în combinație cu sucraloză și izomalt pentru a mări calitatea funcțională a bomboanelor de tip toffee. Proprietățile senzoriale și fizico-chimice, indicatorii microbiologici și parametrii de culoare au fost analizate pentru patru mostre de toffee. Combinația de îndulcitor cu anticristalizant și Brown 7 îmbunătățește semnificativ culoarea produsului. Sa stabilit prin HPLC că în timpul procesării termice, casuarictină din Brown 7 se transformă în acid ellagic. Aceste transformări duc la o creștere a intensității culorii maro din toffee. Adăugarea Brown 7 contribuie la scăderea acidității titrabile de la 0.28 ± 0.08 în proba de control la 0.21 ± 0.06 grade de aciditate în proba cu 1.0% colorant. Parametrii cromatici L*, a*, b* ai probei de caramel cu 0.6% conținut Brown 7 sunt cei mai apropiați de parametrii de caramel clasic. Utilizarea colorantului Brown 7 în combinație cu îndulcitorul ilustrează o potențială sinergie a proprietăților senzoriale. Acest lucru contribuie la creșterea aportului de compuși bioactivi naturali și la scăderea carbohidraților din dulciuri, promițând beneficii pentru sănătate.

Cuvinte-cheie: *Brown 7, CIELab, culoare, HPLC, peliculă, RGB, îndulcitori, bomboane toffee, nucă.*

1. Introduction

The color is the first quality indicator of the food product, to which the consumer draws attention. Sweets, which contain synthetic dyes are beloved by little children, but because of their possible negative effect on health, the question arises of replacing synthetic dyes with natural ones. Among the sources of perspective for obtaining yellow and brown dyes can be mentioned the parts of the walnut Juglans regia L. fruit - septum and kernel's pellicle. In tandem, the Republic of Moldova and Romania annually produce about 1500-3000 tons of septum. The septum contains significant amounts of polyphenols with expressed physiological properties [1], which, in addition to their physiological activity, have the ability to generate deep-brown color.

In the confectionery production, natural colorants are used, which include carotenoids [2], anthocyanins (E163i, the extract of black currants, rosehips, aronia, and the enoch dye produced from the processing of winemaking waste [3]), flavonoids (Brown 7) and chlorophylls (E140m from spirulina, chlorella) etc. Caramel dye E150 is used in various food systems as a substitute for brown synthetic dye and as an antioxidant. FAO/WHO Expert Group on Food Additives divides the caramel color into 4 classes, depending on the preparation method and physical properties. But this dye can be toxic in large quantities [4]. Available studies of other authors [5] support the conclusion that caramel colors are not genotoxic or carcinogens, so, the intake of caramel colors and constituents does not present safety risks. A synthetic brown dye, similar with color of old walnut pellicle is Brown HT or E155 [6]. These dyes are used in the confectionery industry in combination with other color influencing factors [7-10].

A distinctive feature of the toffee is the amorphous or microcrystalline structure obtained from boiled mass of caster sugar, glucose syrup, dairy products [11]. The milk and butter provided in the toffee recipe determine not only its nutritional value, but also the taste, aroma, color and structure of the products. Toffee has recently been highlighted as a potential antioxidant due to its high sugar content [12]. In order to expand the range of fortified products with increased biological value, in the complete absence of synthetic additives in the composition of the recipe, it was proposed to add Lavitol-M antioxidant premix, powder of viburnum berries, schisandra, Amur grape berries and powders from preserved reindeer antlers containing a unique complex of vitamins and minerals [13]. In order to increase the biological value of the drawn toffee, a recipe composition was proposed in which carrot puree and whey were added, which contribute significantly to increasing the content of dietary fiber, carotenes, essential amino acids (lysine, methionine) and minerals [14]. Also known are sugar-based toffee varieties with fillings containing molasses, condensed milk, invert syrup, dehydrated milk fat, vegetable fats, glycerin, strawberry juice, lecithin [15]. When using guava pulp in toffee preparation technology, changes in the chemical composition and sensory properties of toffee during storage at ambient temperature (27 ± 2°C), as well as under refrigerated conditions (5 ± 2°C), for 90 days [16]. A similar study focused on the preparation of toffee with the addition of a mixture of Aonla pulp (Emblica officinalis Gaertn.) and ginger extract, which contains vitamin C, is intensely energizing and has a strong beneficial antioxidant activity in the body. Toffee prepared using an 80:20 g/g mixture (Aonla pulp: ginger extract) was found to be superior to other mixtures in terms of yield, organoleptic properties and nutritional quality during 90 days of storage at different temperatures [17].

The major problem eating toffee is its high sugar content. Great efforts have been made to replace the sugar in toffee with bioactive ingredients. The sugar content in toffee was replaced with jojoba powder at concentrations of 20-100% [18, 19]. Examples of classic technologies and with the replacement of sucrose in confectionery products with various sweeteners are known. A method was proposed for the production of semi-hard toffee with the substitution of sugar with 85.7 - 83.4% isomalt or lactitol, with the addition of powdered milk, melted fat, emulsifier and vanilla flavor. The obtained toffee contained reduced carbohydrates - 15% and a reduced energy value - 260 kcal, due to the absence of sucrose in the recipe [20]. Therefore, the objective of the present work is to select the necessary amount of colorant, the optimal quantities of sweetener and the method of their administration, to expand the range of marketed toffee with dietary and diabetic properties, with a low carbohydrate content. To accomplish this task, sugar was replaced with sucralose and glucose syrup with isomalt - products that serve both as anti-crystallizers and sweeteners. In order to improve the nutritional value and sensorial aspect of the finished product, natural Brown coloring obtained from walnuts was added.

2. Materials and Methods

2.1. Extraction of Brown 7 from walnut fruit pellicle and septum

The walnuts of the “Kogâlniceanu” variety, harvested in 2020-2022, were used. The walnut core was treated with a 1.0% sodium carbonate solution, 15.0% ethanol and 0.02% pectolytic enzyme at a temperature of 18...20 °C, in 5 repetitions. Extracts were united in one and filtered. After filtration, the solution was concentrated at 60-70 °C at a rotary speed of 150-200 rpm. About 150 mL of ethanol were added to the obtained dark-brown (almost black) viscous paste to separate a very viscous mass. This mass was dried under vacuum at 60 – 70 °C and 90-100 mbar. The obtained powder was kept cold (4.0 ± 1.0 °C) [21]. Because the mass part of the pellicle in the kernel is max. 10%, in turn, the content of extractable substances is equal to 10.0%. Respectively, the yield of the dye, recalculated to the walnut kernel, was 1.0 ± 0.2%. The septum was separated from the walnut core and placed in an ultrasonic bath (22 ± 2°C, 37 kHz, 10...15 min*)*. Separation of the dye from the septum in powder form takes place under similar conditions. The dye yield was 4.0 ± 0.2%.

2.2. RGB-analysis method

The determination and digitization of the sample colors in solid dry state is usually performed by the CIELab method [22, 23]. At the same time, determining the exact shade of the color of the samples in the wet state represents some difficulties. This led us to develop our own method, based on the use of the three-bytes Red-Green-Blue (RGB) code, in which the intensity of the respective component is rendered by 1 byte of information [24]. Sample images were processed with the help of the application, which determines the RGB codes of the chosen pixels [25]. To reduce the inevitable color inhomogeneity, the RGB codes were recorded in three equidistant points. The arithmetic mean, calculated for each byte, is only rounded to a whole number, given the fact that the RGB code consists exclusively of whole numbers.

2.3. High-Performance Liquid Chromatography with Photodiode Array (HPLC-PDA)

Analysis of extracts, dyes, and food products were performed on the „Shimadzu LC2030 3D Plus" instrument, using the reverse-phase column C_{18} „Phoenomenex" (150 mm×4.6 mm×5 µm×80 nm) and biphasic gradient elution. **Phase A**: Water / Acetic Acid 0.1%. **Phase B:** MeCN / Acetic acid 0.1 %. The temperature of the samples in the autosampler – 15.0 °C. Constant flow rate 0.5 mL/min. Phase B content in the extremes of the gradient curve from 5 % to 90%, column temperature 25 °C, PDA detection cell temperature of 30 °C [26, 27].

2.4. Toffee-candies producing

Toffee candies were prepared according to the classic method using in the manufacturing recipe: concentrated milk, sugar, glucose syrup, whipped cream and essence [28, 29]. The toffee production method provides for the tempering of glucose syrup to a temperature of 45...50 °C, concentrated milk to 30 °C and fats to 33...36 °C. The classic manufacturing recipe does not contain water. The materials were mixed until a homogeneous mass was obtained. In order to avoid worsening the properties of the mass (excess caramelization of sugars), the heating of the mixture took place gradually: in the first stage, up to a dry substance content of 84.0 ± 0.1 %, and in the second stage boiling of toffee mass up to the temperature of 120 ± 2 °C and dry substance content of 91.0 ± 1 %. When mixture is heated and boiled, various processes of sugars and proteins transformation take place: inversion, monosaccharide decomposition, sugar-amine reactions. There is an increase in reducing substances, change in acidity, color, taste and aroma. This is mainly due to the melanoidin formation reaction [30]. Milk proteins are essential for the color and flavor of toffee masses by the Maillard reaction [31]. Constant stirring of the mixture ensures a distribution of fat throughout the mass, prevents protein coagulation and burning [20], the toffee mass acquires a fuller milky taste and a caramel color. Then, in the toffee mass rapidly cooled to the 60 ± 1 °C, the essence was added and mixed for 4...6 minutes to obtain a homogeneous product [32]. The confectionery masses were molded using a toffee forming unit, then cooled, dried at ambient temperature, packaged in a moisture and grease resistant label and stored at 18 ± 3 °C and ϕ = 75 ± 1 % [11].

2.5. Preparation of toffee for HPLC analysis

The toffee samples of 1.000 ± 0.002g were dissolved in 5mL of distilled water and placed in the 37MHz ultrasound bath at room temperature for 10 minutes. Obtained dispersed samples were filtered through filter paper and then through a 0.22-micron polytetrafluorethylene (PTFE) syringe filter and immediately placed in cooled autosampler.

2.6. Moisture content

Samples were dried at 105 ± 1 °C to obtain constant weight [33, 34].

2.7. Ash content

Ash content was measured by complete combustion of organic substances with the aim of obtaining the residue of mineral substances at a temperature of 550 ± 5 °C.

2.8. Titrable acidity

Dispersed samples of toffee candies were titrated with a 0.1 mol/L potassium hydroxide solution in the presence of phenolphthalein indicator until a pale pink color, which did not disappear for one minute [35].

2.9. Reductants content

The iodometric method, based on the ability of the sugar carbonyl groups to reduce potassium ferrocyanide in alkaline solution, was used [33].

2.10. Fat content

Fats were extracted from weighted toffee probes with hexane as solvent using „VELP Scientifica" fat extraction system.

2.11. Water activity (a_w)

It was measured using "Rotronic Hygro Palm" system [36].

2.12. CIELab color parameters

CIELab color parameters were measured using "Chroma Meter CR-400" [37, 38]. Luminosity (L*), red/green component (a*), yellow/blue component (b*), hue angle (H*) were measured. Total color difference was calculated using Eq. (1) [39]:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

2.13. Microbiological analysis

It was performed in accordance with the "Rules on microbiological criteria for foodstuffs" [40, 41].

2.14. Sensory analysis

It was performed according to [42, 43] by 9 trained evaluators. The individual score was given according to the deviations from the sensory requirements (Table 1) [11].

Table 1

Scoring 5-point scale of the deviation from the official sensory requirements

Points	Description of the evaluation stage
5	No deviation from sensory quality requirements
4	Minimal non-conformities from sensory quality requirements
3	Visible nonconformities from sensory quality requirements
2	Obvious/considerable non-conformities from sensory quality requirements
1	Very obvious/considerable non-conformities from the sensory quality requirements
0	The product cannot be analyzed from a sensory point of view

2.15 Statistical analysis

Confidence intervals were calculated for significance P = 95%, by "2σ-rule", $X = \langle X \rangle \pm 2\sigma$. The statistical analysis of the results was carried out with the application of Microsoft Excel 2017 programs. To exclude results with accidental errors and those with high levels of uncertainty, three parallel measurements were performed.

3. Results and Discussion

3.1. Brown 7 quality and composition

Brown 7 analysis by the RGB-method requires the scanning of more than 3 experimental points sufficient for wet samples or solutions [44], due to the "play of lights and shadows" in the image of powder. In Table 2 are shown RGB data and colors for 7 random points of the image, as well as the "average" of the RGB bytes and color.

Table 2

Detected RGB values and corresponding color for Brown 7 in powder form

Analysed image	R (red)	G (green)	B (blue)	Color
	81	70	57	
	39	30	19	
	67	61	49	
	29	21	12	
	61	51	40	
	34	25	14	
	47	40	30	
	Average values, rounded to closest integer			<Color>
	51	43	32	

3.2. Evaluation of the nutritional and functional characteristics of the toffee candies

Reducing the sugars in foods is a complex issue because sugars contribute to important sensory and physical food properties. Near the 20-50% of sugar can be reduced or replaced by several ingredients without affecting sensory acceptance [45, 46]. Two commonly used sweeteners, sucralose and isomalt have been proposed to replace sugar in toffee masses. The amount of sweetener, sucralose and isomalt, were calculated in relation to the sweetness index of sucrose: sucrose – 100 c.u., sucralose – 600 c.u., isomalt – 50 c.u. The glucose syrup in the recipe was substituted with a quantity of isomalt, resulting from the sweetness of the glucose syrup – 75 c.u. [45].

The control sample without sugar (TSIM) was prepared similarly to the sample with sugar (TZGS), dissolving the sweetener and anti-crystallizer in an amount of water of 35...40% of the mass of the mixture of dry components, without dye. In this case, the masses were obtained with a slightly pronounced color due to the lack of sucrose that contributes to the process of caramelization of the mass. To improve the color of the mass, the Brown 7 from the walnut pellicle was used, in a proportion of 0.6 and 1.0% compared to the amount of sugars, giving birth to TSIB_0.6 and TSIB_1.0. Colorant was added with the essence at the stage of the toffee’s cooling at continuous stirring until a homogeneous mass was obtained. The obtained samples (Figure 1) were analyzed according to sensory, physicochemical, textural and microbiological quality indicators (Table 3).

TZGS TSIM TSIB_0.6 TSIB_1.0

Figure 1. Toffee samples: TZGS – control with sugar and glucose syrup, TSIM – control with sucralose and isomalt, TSIB_0.6 – with sucralose, isomalt and 0.6% Brown 7, TSIB_1.0 – with sucralose, isomalt, 1.0% Brown 7.

Table 3

Physicochemical indicators of toffee samples

Parameters	TZGS	TSIM	TSIB_0.6	TSIB_1.0
Moisture content, %	8.10 ± 0.03	8.50 ± 0.03	8.93 ± 0.03	10.05 ± 0.04
Titratable acidity, degrees	0.32 ± 0.01	0.28 ± 0.08	0.27 ± 0.08	0.21 ± 0.06
Reducing substances, %	19.40 ± 0.17	17.23 ± 0.19	21.02 ± 0.22	20.90 ± 0.20
Ash content, %	0.038 ± 0.003	0.032 ± 0.002	0.036 ± 0.003	0.050 ± 0.004
Fat content, %	7.7 ± 0.1	7.0 ± 0.1	5.9 ± 0.1	6.2 ± 0.1
Water activity (a_w), c. u.	0.608 ± 0.002	0.622 ± 0.002	0.640 ± 0.001	0.732 ± 0.003

Note: TZGS – toffee with sugar and glucose syrup; TSIM – toffee with sucralose and isomalt; TSIB_0.6, TSIB_1.0 – toffee with sucralose, isomalt and 0.6 or 1.0% of Brown 7.

Water content is an important factor for confectionery quality, influencing texture, and is often the limiting parameter during storage that controls shelf life. This parameter can be controlled by the boiling point of toffee masses during manufacturing [47].

The TZGS control sample has a lowest value of 8.10 ± 0.03% due to the presence of sugar in the recipe [48]. At the temperature of 160 °C, the caramelization of the sugars takes place, which begins with the melting of the sugar at high temperatures followed by foaming (boiling). Sucrose is first broken down into glucose and fructose. This is followed by a condensation step, where the individual sugars lose water and react with each other [49, 50].

Table 3 demonstrates that the substitution of sugar in the recipe and the addition of Brown 7 increase the moisture content of the products comparing with the control samples. For TSIM and TSIB_0.6 they constituted 8.50 ± 0.03% and 8.93 ± 0.03%, respectively. In the TSIB_1.0 the value of this quality indicator increased 1.3 times compared to the control sample and was 10.05 ± 0.04%. According to Moldovan Government Decision 204/2007 the mass fraction of moisture in acidulated toffee should be maximum of 9.0%, and for non-acidulated masses up to 10.0%. Only TSIB_1.0 does not correspond the required value. Was reported that due to the presence of non-hygroscopic isomalt in the recipe, there is no absorption of moisture by the product and there is no recrystallization of crystals with the formation of larger ones. It was found that the obtained toffee retains a fine-crystalline consistency for a longer time compared to commercial toffee obtained by traditional sucrose-based technology [20].

In the control sample TZGS the ash content was 0.038 ± 0.003%, while in the control sample with sweeteners, TSIM, it was 0.032 ± 0.002% and increases with the increase in the concentration of Brown 7, ranging from 0.032 ± 0.002% to 0.050 ± 0.004%. The content of reducing substances correspond to the permitted regulated values up to max. 22.0% [11]. The fat content for all products is between 7.7 ± 0.1% and 6.2 ± 0.1%. The acidity correlate with the concentration of Brown 7, showing a decreasing trend, from 0.32 ± 0.01 for TZGS to 0.21 ± 0.06 degrees of acidity for TSIB_1.0. The reduction in titratable acidity may occur due to the basicity of the quinones in Brown 7 [21]. Many sugar-free labeled sweets are high in food acids and have teeth-erosive potential. Applying an in vitro dental erosion test of surface microhardness modification, it was found that 56% of sugar-free sweets (even some with "Tooth friendly" message) contain high concentrations of food acids and low pH [51]. The lower acidity values and higher pH of our experimental samples suggests that they are safety for the teeth.

3.3. Transformation of Brown 7 during the toffee production

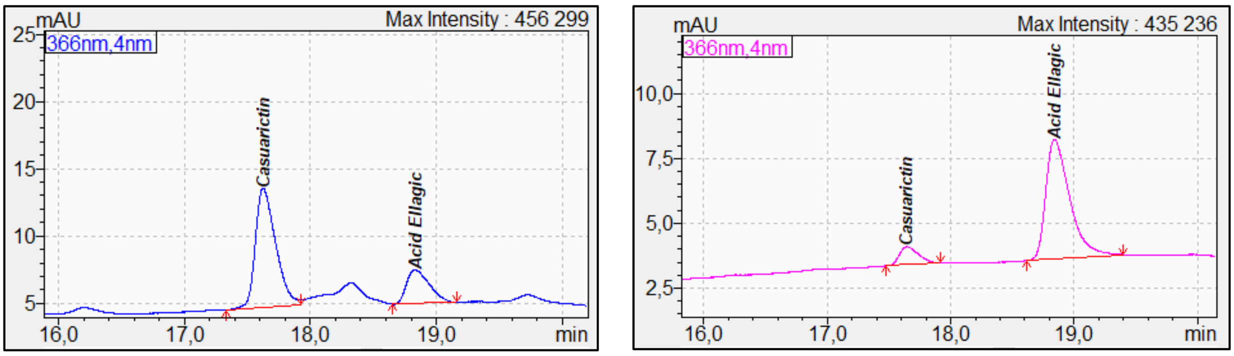
In time of the heat treatment profound changes occur in the composition of carbohydrates, proteins and fats of the toffee [30]. The dark brown color of the toffee mass is due to the formation of melanoidins [52].

Table 4

HPLC data for different systems with Brown 7

Compound	R_T	λ, nm	Area	Area, %	Summ, %
Brown 7 dye from walnut fruit septum					
Catechin	15.175	278	503031	86.770	100
Epicatechin	16.488	278	76696	13.230	
Casuarictin	17.096	366	498754	39.657	100
Ellagic Acid	18.795	366	758899	60.343	
Brown 7 dye from walnut kernel pellicle					
Casuarictin	17.625	366	98562	75.644	100
Ellagic Acid	18.831	366	31735	24.356	
TSIB_**0.6 with Brown 7 from walnut kernel pellicle**					
Casuarictin	17.693	366	3739	15.311	100
Ellagic Acid	18.896	366	20679	84.689	
TSIB_**1.0 with Brown 7 from walnut kernel pellicle**					
Casuarictin	17.645	366	7562	10.906	100
Ellagic Acid	18.841	366	61775	89.094	

From data presented in the Table 4, it follows that during the production of toffee there is an increase in the Ellagic Acid / Casuarictin ratio from 1/3 up to 9/1 (Figure2).



a) b)

Figure 2. Phenols relationship: a) in powdered Brown 7; b) in TSIB_0.6.

This change allows us to propose the mechanism of the transformation of Casuarictin into Ellagic Acid (Figure 3). Both Gallic and Ellagic Acids are converted to brown quinones upon oxidation [53], which enhances the effect of the Brown 7 dye.

Water activity is a critical parameter related to candy stability and the main controlling characteristic of microbial growth in sugar confectionery [31]. Toffee has a water activity between 0.60-0.65 c.u. [54, 55].

Sugar-free samples show increasing aw values, from 0.622 ± 0.002 c.u. (TSIM) to 0.732 ± 0.003 c.u. (TSIB_1.0). It is considered that the sample values do not exceed the range determined for the quality and safety of food for sweets [56].

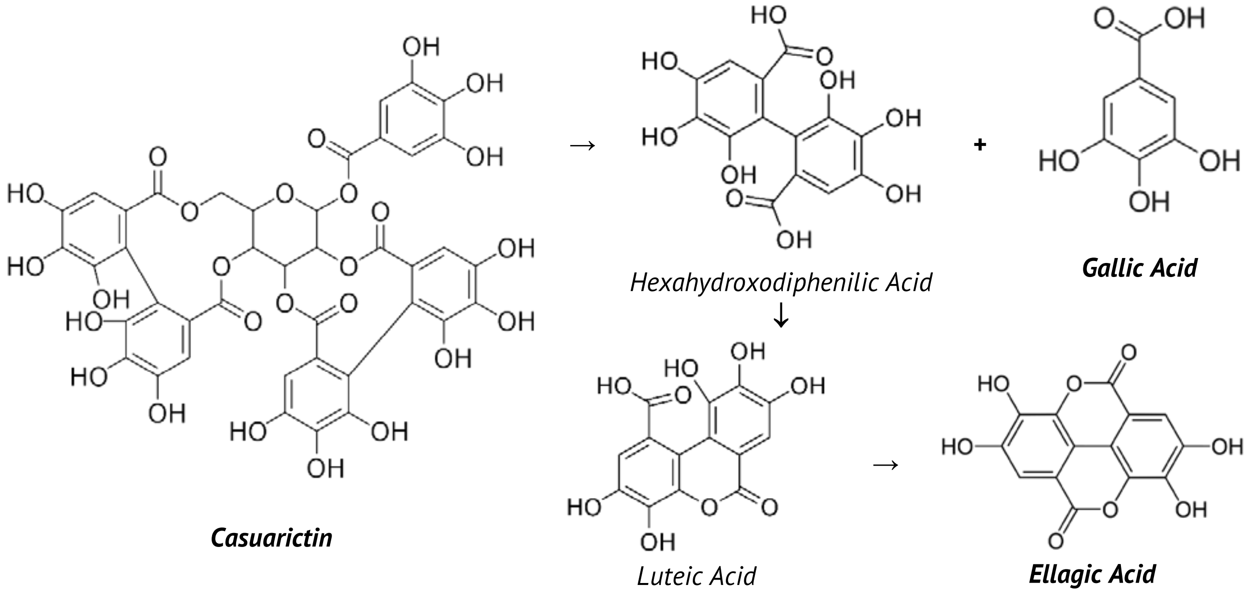


Figure 3. Casuarictin hydrolysis scheme during the toffee heat treatment.

The total number of germs (TNG) in the experimental samples was reduced, with a maximum of 5 ± 1 CFU/g, therefore they are in accordance with the values allowed by the regulations [36]. Was reported an antimicrobial activity of tannins and flavonoids against pathogenic bacteria [57]. This was also confirmed by other authors [58], who indicate that the total content of phenolics and flavonoids inhibited bacterial and fungal growth, reduced cell viability, showed free radical scavenging capacity and inhibited the formation of superoxide anions. Polyphenol content of walnut extract is more than 4000 mg/100 g and 24 compounds from the group of flavonoids, phenolic acids and juglone derivatives were identified [59]. A strong correlation between polyphenol content and antioxidant capacity and cytotoxic activity was observed. In addition, the toffee is processed at temperatures above 93 °C, which proves that the growth and survival of vegetative cells of bacteria, yeasts and molds will be stopped and the samples will be stable during storage.

Toffee rarely suffers microbial spoilage if properly prepared, packaged and stored. The source of microorganisms in toffee products can be taken from the raw materials used in production. Another source of contamination can be air, equipment, workers and improper humidity [60]. Microorganisms that can be identified in toffee masses include *Bacillus spp.* and Clostridium spp. Other microorganisms that can be observed are introduced post-processing.

The most common primary microorganisms associated with the alteration of sugar confectionery products were identified as *Zygosaccharomyces rouxii* and *Brettanomyces bruxellensis* yeasts [61]. Other studies demonstrate detectable mold genera such as *Aspergillus*, *Penicillium*, *Verticillium*, *Rhizopus*, *Mucor* and *Trichothecium*. The authors argue that this could be due to increased humidity and water activity [62, 63]. Controlling moisture content will prevent the spoilage of sugar confectionery products most susceptible to mold growth [64].

CIELab chromatic parameters were analyzed for the toffee samples. The results show that the TZGS control sample is characterized by the highest L* (luminosity) value of 48.22 (Table 5).

Table 5

CIELab chromatic parameters of toffee candies

Toffee sample	Luminosity, L*	Red/Green, a*	Yellow/Blue, b*	Hue angle, H*,°	Total color difference, ΔE*
TZGS	48.2 ± 1.3	8.27 ± 0.42	20.4 ± 1.2	67.9 ± 1.2	6.7 ± 1.3
TSIM	46.8 ± 1.3	3.84 ± 0.60	12.0 ± 1.1	72.2 ± 1.1	6.27 ± 0.17
TSIB_0.6	41.8 ± 1.1	5.07 ± 0.57	12.9 ± 0.9	68.57 ± 0.83	9.2 ± 1.5
TSIB_1.0	34.27 ± 0.88	4.7 ± 1.2	9.2 ± 0.5	52.79 ± 0.82	17.2 ± 1.1

Note: TZGS – toffee with sugar and glucose syrup; TSIM – toffee with sucralose and isomalt; TSIB_0.6, TSIB_1.0 – toffee with sucralose, isomalt and 0.6 or 1.0% of Brown 7.

The hue angle H* of 67.89 °, is in the first trigonometric quadrant, in which the orange hue predominates. With the removal of sugar from the recipe, it is not possible to obtain the caramel color. In the case of the addition of the Brown 7 dye, it was observed that the hue angle remains in the first trigonometric quadrant, but with the addition of a larger amount of dye, the values reduced from 72.20 to 52.79. In the TSIM sample a low color intensity and the presence of the gray shade, presenting a combination of unpleasant colors. The closest to the control sample with TZGS sugar, was the TSIB_0.6 sample, which was characterized by a suitable color, generates chromatic harmony, provides a state of well-being and pleasure.

The sensory analysis, carried out by nine specialists in the field, a clearly defined sweet taste, caramel color and a pleasant smell of sugar characteristic of the product were observed in the sugar-based control sample (figure 4). Addition of Brown 7 significantly led to change in sensory characteristics, especially color and texture. The samples with 0.6% and 1.0% addition (TSIB_0.6 and TSIB_1.0) obtained a darker color with the increase of the amount of Brown 7, having a pleasant and homogeneous shade. The change in color is explained by the content of polyphenols present in the walnut skin, which when homogenized with other components in the recipe and after heat treatment lead to a change in the color of the finished product [65].

The texture of toffee masses [66] is determined by factors such as chemical composition and cooling rate. Milk protein, especially casein, denatures in the heat treatment process, forming a viscoelastic structural network throughout the candy mass, that gives the following textural properties: rigidity, texture and chewability [31].

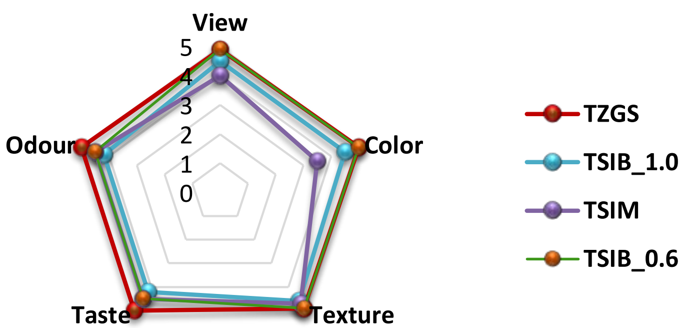


Figure 4. Toffee candies sensorial profiles.

Processing conditions also affect the crystallization of fats [67], thus having an effect on their functional properties. The effects of cooling rate on the macroscopic properties of a network of fat crystals were studied by crystallization of anhydrous milk fat (5 °C/min, Newtonian cooling) or slowly (0.1 °C/min, step cooling). The microstructure was also different between the two treatments. When they crystallized rapidly, the crystallites were numerous and small, while a smaller number of larger crystallites were observed when they crystallized slowly.

The color of a translucent sample will change when the length of the light path through it changes. The path length must be fixed with a fixed white background [68]. The control sample with sugar and glucose syrup (TZGS) scored 4.96 out of 5 points. The control sample with sucralose and isomalt (TSIM) was degraded, accumulating 4.24 points, it was characterized by an opaque color with a gray tint that can be seen entirely by reflected light.

The highest total sensory score was accumulated by TSIB_0.6 (23.8), followed by TSIB_1.0 (22.0), compared to TSIM control sample (21.2). The sample with 0.6% Brown 7 dye shown an optimal combination as it reported the most pleasant color, flavor and texture, similar to the sugar control sample (TZGS). It was also characterized by a soft texture, viscous consistency, with a sweet taste due to the substitution of sugar in the recipe.

4. Conclusions

Extracts and powders from *Juglans regia* are sources of natural dyes of a polyphenolic nature, which, in addition to color, can provide food products with some functional properties.

The possibility of correcting the color of confectionery products with a reduced amount of sugar, by adding the natural brown dye, obtained from the walnut kernel's pellicle or from walnut septum, has been confirmed. The toffee samples were obtained by replacing sugar with sucralose and isomalt, and the addition of the natural dye Brown 7 allowed to obtain the characteristic color of the product obtained by the classic technology (with sugar). The incorporation of the Brown 7 dye in concentrations from 0.6% to 1.0% contributes to the formation of the product with optimal sensory characteristics.

It was confirmed by HPLC, that during thermal processing, the composition of the polyphenols in the natural dye Brown 7 changes, which is expressed by increasing the Ellagic Acid / Casuarictin ratio from 1/3 to 9/1. Since the thermal hydrolytic transformation products of Casuarictin (Gallic, Hexahydroxydiphenylic, Luteic, Ellagic Acids; Glucose) are harmless, the natural dye Brown 7 can be used in sweets, especially in the case when long heat treatments take place in the technological production process.

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