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Proceeding Paper

Muffin Enriched with Bioactive Compounds from Milk Thistle by-Product: Baking and Physico–Chemical Properties, and Sensory Characteristics †

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Abstract: Muffins are sweet, high-calorie baked products with a typical porous structure and high volume which confer a spongy texture. Because of this texture and good taste, these products are highly valued by consumers. But muffins have low nutritional value. The aim of this study was to develop the technology of muffins as a functional product with hepatoprotective activity using defatted milk thistle powder (DMTP). The incorporation of this dietary supplement was carried out by partial replacement of flour in the classic formulation. Physico-chemical and sensory analysis were performed to evaluate muffins either with or without defatted milk thistle seeds powder. The moisture sorption isotherms of porous structure were determined by the gravimetric method with a microbalance MacBen over 0.05–1.0 water activity range, and the data fitted to Brunauer-Emmet-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models. It has been established that the addition of milk thistle powder reduces baking, increases the drying out of products and increases the water-holding capacity, as well as increasing the volume of muffins and crumbs density. The microstructure of the muffin was examined using a moisture sorption isotherm. The moisture sorption isotherms of muffin samples presented a sigmoid shape and belong to type II of classification. The hysteresis loops of the samples are almost the same, which indicates similar structural data. The capacity of the monolayer according to BET models varied in the range 1.63–2.15 mmol/g of dried sample, showing a slight decreasing trend for muffin with DMTP. The GAB model accurately fits the adsorption isotherms in the water activity range from 0.05 to 0.88. The sensory results from consumer evaluation indicated that both samples are characterized by the traditional pleasant appearance of the muffin, without visible flaws, pleasant taste, and a good flour aroma. The result is a muffin with the same texture and sensory characteristics, but with a potential functional food.

Keywords: muffin; milk thistle; moisture adsorption isotherm; baking; monolayer; sensory characteristics; specific surface area

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1. Introduction

Flour-containing confectionery, in particular, muffins, have increased calories and an unbalanced chemical composition, contain a significant amount of easily digestible carbohydrates represented by starch and sucrose, which characterizes them as products with a lack of usefulness for human health. At the same time, the practical daily and systematic use of them by the population actualizes the task of correcting their ingredient composition in the direction of reducing the energy value and increasing the nutritional value due to the incorporation of bioactive substances.

Milk thistle (*Silybum marianum L., Gaertn*), known as a medicinal plant that has physiological effects on liver function and provides protection against certain liver diseases [1]. Its beneficial properties are due to the presence of silymarin, an isomeric mixture of the flavonolignans silydianin, silychristin, silybin and isosilybin (the last three are present present in two diastereoisomeric forms, A and B). Milk thistle is also a rich source of ingredients, such as amino acids, fatty acids, minerals, and phytochemicals. This fact is important for the possibility of using this plant as a potential fortifying agent in the development of functional foods technologies. At the moment, this trend is not widespread. A more traditional way of using milk thistle as a hepatoprotective food supplement [2]. However, a study on the effect of partial replacement (5–15%) of wheat flour with defatted milk thistle seed flour on the rheological properties of dough confirmed the good technological prospects of such a replacement for development of high quality bakery foods technologies [3].

The purpose of this study is to develop of technology of a muffin enriched with bioactive compounds from milk thistle by-product that allows expanding the assortment of flour-containing functional food with the potential to prevent liver diseases.

2. Materials and Methods

2.1. Materials

Defatted milk thistle seeds powder (flour) was obtained from special crushed cake as waste residues of cold-pressed seeds oil manufacture (KhersonAgroYug, Kherson, Ukraine). The ingredients used in this study obtained from local stores in city Kharkiv, Ukraine. All chemical reagents used were analytical grade.

2.2. Samples

A sample M1 as control muffin was manufactured according to the following formulation: wheat flour, 50.0 g; sugar, 10.0 g; margarine, 8.0 g; egg 14.0 g; milk, 24.0 g; ammonium acid carbonate, 3.0; and technological loss consisted of 9.0 g, so, total mass was 100.0 g. The formulation of milk thistle-enriched muffin (M2) was partial replacement (25%) of wheat flour with DMTP (12.5 g). The choice of this amount was based on the recommended daily dose of the supplement for primary prevention purposes.

2.3. Methods

Water vapor adsorption/desorption isotherms were obtained using were measured at 293 K in a range of relative humidity of 0.20–0.95 with the gravimetric method with a microbalance MacBen (helical spring quartz scales).

The color measurement of DMTP was carried out using an UV-2600i spectrophotometer with ISR-2600Plus Integrating Sphere (Shimadzu Inc., Kyoto, Japan) for relative diffuse reflectance measurements in wavelength range 380–780 nm with the eight degrees angle of incidence to the sample. Color parameters L* (whiteness (100) or blackness (0)), a* (indicates red or green) and b* (indicates yellow or blue) in CIE L* a* b* color system [4] determined using Waves software (Broadcom Inc., San Jose, CA, USA).

2.4. Calculations

The BET [5] and the GAB [4,5] equations have been successfully applied over the past decade to describe food moisture isotherms, which are usually written as follows:

$$n = n_m \cdot C_{BET} \cdot a_w/[(1 - a_w)(1+(C - 1)a_w)], \quad (1)$$

$$n = n_m \cdot C_{GAB} \cdot k \cdot a_w/[(1 - k \cdot a_w)(1-k \cdot a_w + C_{GAB} \cdot k \cdot a_w)] \quad (2)$$

where a_w is water activity; n is number of adsorbed water molecules; n_m is capacity of monolayer; C_{BET}, C_{GAB} and k are a system and equation dependent adjusted constants. The classical BET multilayer sorption (1) is used to calculate monolayer values in very different physicochemical fields [8]. One of the main applications of the BET equation is the estimation of the specific surface area of the a_s monolayer of porous adsorbents, which was calculated from the moisture adsorption isotherm according to [9] as:

$$a_s = n_m \sigma L, \quad (3)$$

where σ is the cross-sectional areas in filled monolayer of water molecules adsorbed on solid surfaces; L is Avogadro number.

2.5. Statistics Analysis

All experiments were conducted at least in duplicate, and the corresponding results were statistically analyzed by Minitab v. 19 software (Minitab, LLC., State College, PA, USA). The significant differences between means were evaluated by using one way ANOVA, and a Turkey's multiple range tests was applied for the multiple comparisons among experimental means ($p < 0.05$).

3. Results and Discussions

3.1. DMTP Characteristics

The defatted milk thistle seeds are a by-product produced by oil as a hepatoprotective dietary supplement. It is a fine powder 80–82% of its fractional makeup consists of particles with size about 50 μm. In CIE L* a* b* color space has the following color's parameters: L* = 62.7484, a* = 3.3138, b* = 21.9569. DMTP is odorless, characterized by a slight bitter aftertaste, without a specific oily aftertaste. Some compounds of the proximate composition of milk thistle seeds flour is as follows: water content (6.9 wt%), crude proteins (30.15 wt%), fiber (22.36 wt%), fat (8.29 wt%).

3.2. Baking Characteristics and Physico-Chemical Properties

The transformation of the dough into the finished product is accompanied by the process of weight loss and is characterized by the difference in percentage between the masses of the dough before baking and the finished hot product. According to the results obtained, this value for samples M1 and M2 is 14.8% and 12.0%, respectively. The result indicates a positive effect of adding DMTP to the formulation.

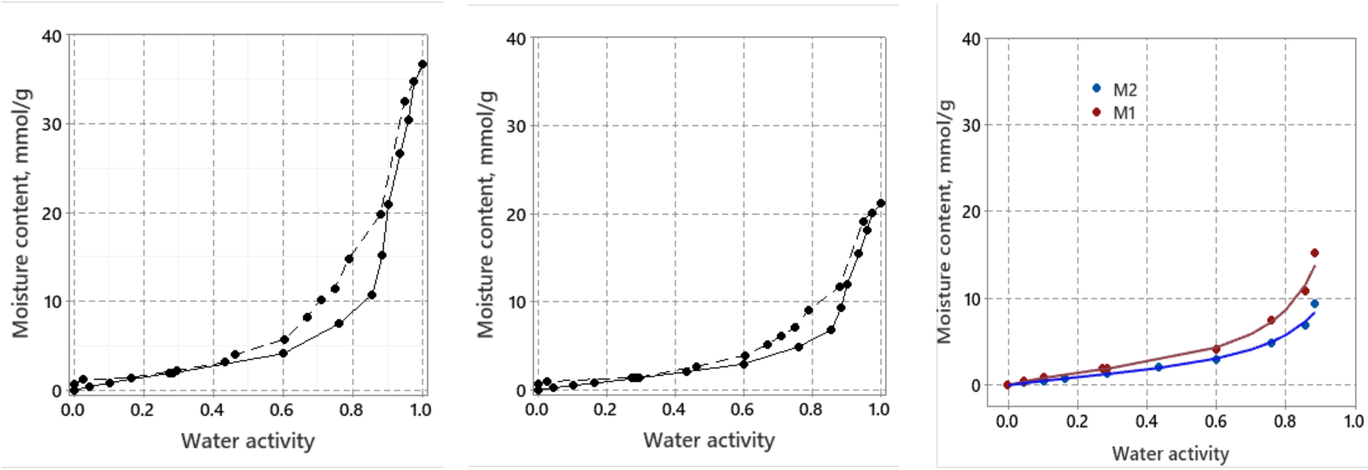
Studies of the drying process of muffins during their storage for 8 days in standard packaging was determined as the difference between the masses of hot and cooled bread for a certain period of time in percent. According to the results of the study, samples M1 and M2 are characterized by the amount of drying at the level of 10% and 16%, respectively. From these data it follows that the control sample has the best water-retaining properties.

The densities of the porous structure are 0.59 g/cm3 for M1 and 0.57 g/cm3 for M2, which corresponds to the normative documentation.

The acidity, as an indicator of the qualitative and quantitative acidic composition affects the course of the most important technological processes and the taste of finished products Control sample has the acidity equals 1.8 degrees. Addition of DMTP as a richer source of acids leads to the increase of bread acidity to 2.2 degrees.

3.3. Moisture Sorption Behavior

One of the most important chemical components of any foodstuffs is water. The nature of the interaction of water with the components of the food**s** and the surrounding atmosphere affects the physical or textural characteristics of foods, as well as theirs stability and shelf life [10]. In general, for a correct description of the water status in foods, it is necessary to know both the water content and the water activity. This possibility is provided by the analysis of sorption isotherms, which reflects the dependence of the moisture content from the activity of water. The moisture sorption isotherm of muffin samples could be valuable information on its storage stability as well as prediction of microbiological stability during the shelf life. Adsorption-desorption isotherms of samples M1 and M2 are presented in Figure 1a,b, respectively.



(**a**) (**b**) (**c**)

Figure 1. Moisture isotherm adsorption (solid line) and desorption (dashed line) of muffins: (**a**) for sample M1; (**b**) for sample M2; (**c**) fit of the experimental moisture isotherm (dot) of muffins by the GAB equation (solid line).

Moisture sorption isotherms of both samples have a sigmoid shape, which is typical for the phenomenon of multilayer adsorption with hysteresis. According to the classification of physical sorption isotherms in the IUPAC Technical Report [11], these curves are type II isotherms. Such isotherms are observed for non-porous or macro porous materials with unlimited monolayer-multilayer adsorption up to high values of water activity. The curves are characterized by the presence of an ill-defined point B (the start point of the middle almost linear section of the isotherm, which usually corresponds to the end of the monolayer). This indicates a significant overlap of monolayer adsorption and the beginning of multilayer adsorption [11]. All curves are characterized by the presence of hysteresis loops, which, according to the classification of hysteresis loops according to the IUPAC classification, corresponds to type H3. The adsorption curves of the samples coincide in shape, which indicates the similarity of the adsorption structures.

According to classical concepts [12], the adsorption of mesoporous solids with capillary-condensation hysteresis is three zones of water activity. The presence of hysteresis on the curves indicates the presence in the system, in addition to the process of physical adsorption and capillary phenomena, the process of swelling of the corresponding components and chemisorption processes. The latter is indicated by the residual amount of water at the level of 1.0–2.0% of the amount adsorbed. A detailed analysis of adsorption isotherms suggests that the largest amount of water from the total is in a hygroscopic state.

The classical BET equation is used to calculate monolayer values in very different physicochemical fields. The range of linearity of the BET plot is always restricted to a limited part of the isotherm, often within the a_w range of ~0.05–0.30 for Type II [13]. The GAB equation has very popular in the field of food technology. The reason for this is that the range of water activity covered by this isotherm is much wider than the range of the BET equation. The coefficients of the BET and GAB sorption models were calculated from the sorption data. The regression analysis results for sorption isotherm are presented in Table 1 along with statistical parameters and estimated model coefficients. According to the BET model, the monolayer of sample M1 has a large sorption capacity and thus a_s of the S_{BET} monolayer 162 m^2/g versus 123 m^2/g for sample M2 (Table 1). This correlates well with the data on sample desiccation. S_{BET} values in the range of 3–5 indicate a weak adsorbent-adsorbate interaction. But this interaction is slightly higher for sample M1.

Table 1. Calculated BET and GAB models parameters for muffins.

Sample	BET Models Parameters				GAB Models Parameters			
	n_m, mmol/g	C_{BET}	R^2	a_s, m^2/g	n_m, mmol/g	C_{GAB}	k	R^2
M1	2.15 ± 0.18	4.83 ± 0.42	0.9969	162	2.08 ± 0.25	5.37 ± 0.23	0.967 ± 0.012	0.9768
M2	1.63 ± 0.16	3.45 ± 0.25	0.9968	123	1.70 ± 0.19	3.63 ± 0.34	0.917 ± 0.020	0.9780

In general, it should be noted that the BET and GAB isotherms are closely related, since they follow from the same statistical model [14]. Therefore, similar characteristics of moisture adsorption in the monolayer were obtained. The C_{GAB} coefficient represents the water primary layer binding strength for various systems and varies from 1–20, and the coefficient k in the range 0.70 to 1. The C_{GAB} and k obtained for both samples meet these requirements (Table 1). The standard GAB equation (2) was fitted to the experimental data in the a_w range 0.05–0.9 [15]. This fact is confirmed for the studied samples. The GAB model satisfactorily ($p < 0.05$) fits the adsorption behavior of both muffin samples in the water activity range from 0.046–0.884 (Figure 1c).

3.4. Sensory Characteristics

In almost all respects, the developed muffin has the same parameters as the control sample. The exception is color. The DMTP muffin has a non-uniform taupe color that is not typical for muffins in this recipe. It should be noted that from the point of view of the consumer, this color also cannot be considered as a successful and stimulating purchase. Therefore, as a possible color correction option, the addition of another natural ingredient as a colorant should be considered. For example, adding a small amount of cocoa powder will give the finished product a pleasant brownish color and chocolate flavor.

Table 2. Sensory characteristics of muffins.

Indicator	M1	M2
Color	Light yellow	Gray-brown
Form	Correct, according to the form in the formulation data	
Surface	The surface without the presence of cracks and tears	
Appearance	A well-baked muffin with good porous structure in section	
Taste and smell	Intrinsic to this variety of muffin without the foreign smell and taste	

4. Conclusions

Thus, as a result of the research, a technology for the production of muffin with a partial replacement of wheat flour with defatted milk thistle seeds flour was developed. The baking characteristics and physic-chemical properties of the samples were investigated. The microstructures of cakes, as evidenced by the data on the adsorption behavior of the samples, are identical. At the same time, according to the calculations performed using the BET model, the capacity and specific surface of the monolayer of the control muffin sample are slightly higher than those of the developed one. This explains the resulting baking parameters. Both used BET and GAB models make it possible to obtain comparable microstructural parameters by calculation. But the GAB model has a better descriptive capability of the adsorption process in a wider range of water activity. The sensory characteristics of the developed muffin are satisfactory.

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