biology and life sciences forum

MDPI

*Proceeding Paper*

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

**Daria Polovnikova, Victoria Evlash, Olena Aksonova and Sergey Gubsky ***

Department of Chemistry, Biochemistry, Microbiology and Hygiene of Nutrition, State Biotechnological University, 61051 Kharkiv, Ukraine

* Correspondence: sergey.m.gubsky@gmail.com

† Presented at the 3rd International Electronic Conference on Foods: Food, Microbiome, and Health—A Celebration of the 10th Anniversary of Foods' Impact on Our Wellbeing, 1–15 October 2022; Available online: https://sciforum.net/event/Foods2022.

**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. However, muffins have low nutritional value. The aim of this study was to develop a 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 the partial replacement of flour in the classic formulation. Physico-chemical and sensory analyses were performed to evaluate muffins with and without defatted milk thistle seed powder. The moisture sorption isotherms of the porous structure were determined by the gravimetric method with a MacBen microbalance over a 0.05–1.0 water activity range, and the data were fitted to Brunauer–Emmet–Teller (BET) and Guggenheim–Anderson–de Boer (GAB) models. It was established that the addition of milk thistle powder reduces baking, increases the drying out of products and the water-holding capacity, and increases the volume and crumb density of muffins. The microstructure of the muffins 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 the BET models varied in the range of 1.63–2.15 mmol/g of the dried sample, showing a slightly decreasing trend for muffins 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 a consumer evaluation indicate that both samples were characterized by the traditional pleasant appearance of the muffin, without visible flaws and with a pleasant taste and a good flour aroma. The result is a muffin with the same texture and sensory characteristics but as a potential functional food.

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

check for updates

**Citation:** Polovnikova, D.; Evlash, V.; Aksonova, O.; Gubsky, S. Muffin Enriched with Bioactive Compounds from Milk Thistle By-Product: Baking and Physico–Chemical Properties and Sensory Characteristics. *Biol. Life Sci. Forum* **2022**, *18*, 49. https://doi.org/10.3390/Foods2022-12930

Academic Editor: Antonio Cilla

Published: 30 September 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

Flour-containing confectionery, in particular, muffins, have increased calories and an unbalanced chemical composition and 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*) is 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 in two diastereoisomeric forms, A and B). Milk thistle is also a rich source of ingredients, including 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 food technologies. At the moment, this trend is not widespread. A more traditional way of using milk thistle is as a hepatoprotective food supplement [2]. However, a study on the effect of the 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 the development of high-quality bakery food technologies [3].

The purpose of this study was to develop the technology of a muffin enriched with bioactive compounds from milk thistle by-product that allows for 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 seed powder (flour) was obtained from special crushed cakes as waste residues of cold-pressed seed oil manufacturing (KhersonAgroYug, Kherson, Ukraine). The ingredients used in this study were obtained from local stores in the city of Kharkiv, Ukraine. All chemical reagents used were of analytical grade.

### *2.2. Samples*

A sample, M1, as a 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. The technological loss consisted of 9.0 g, so the total mass was 100.0 g. The formulation of a milk thistle-enriched muffin (M2) partially replaced (25%) the 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 at 293 K in a range of relative humidity of 0.20–0.95 with the gravimetric method with a MacBen microbalance (helical spring quartz scales).

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

### *2.4. Calculations*

The BET [5] and the GAB [6,7] equations have been successfully applied over the past decade to describe food moisture isotherms, and 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 the water activity; n is the number of adsorbed water molecules; $n_m$ is the capacity of the monolayer; $C_{BET,}$ $C_{GAB}$, and k are system- and equation-dependent adjusted constants. The classical BET multilayer sorption (1) has been 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 is calculated from the moisture adsorption isotherm according to [9] as:

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

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

### *2.5. Statistics Analysis*

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

## 3. Results and Discussions

### *3.1. DMTP Characteristics*

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

### *3.2. Baking Characteristics and Physico-Chemical Properties*

The transformation of dough into a 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, the values for the M1 and M2 samples were 14.8% and 12.0%, respectively. These results indicate a positive effect of adding DMTP to the formulation.

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, the M1 and M2 samples were characterized by the amount of drying at the levels of 10% and 16%, respectively. From these data, it follows that the control sample had the best water-retaining properties.

The densities of the porous structure were 0.59 g/cm$^3$ for M1 and 0.57 g/cm$^3$ 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. The control sample had an acidity equal to 1.8 degrees. The addition of DMTP as a richer source of acid led to an increase in the 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 and the surrounding atmosphere affects the physical or textural characteristics of foods, as well as their 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 isotherms of the muffin samples could be valuable information about their storage stability and for the prediction of their microbiological stability during their shelf life. Adsorption–desorption isotherms of the M1 and M2 samples are presented in Figure 1a,b, respectively.

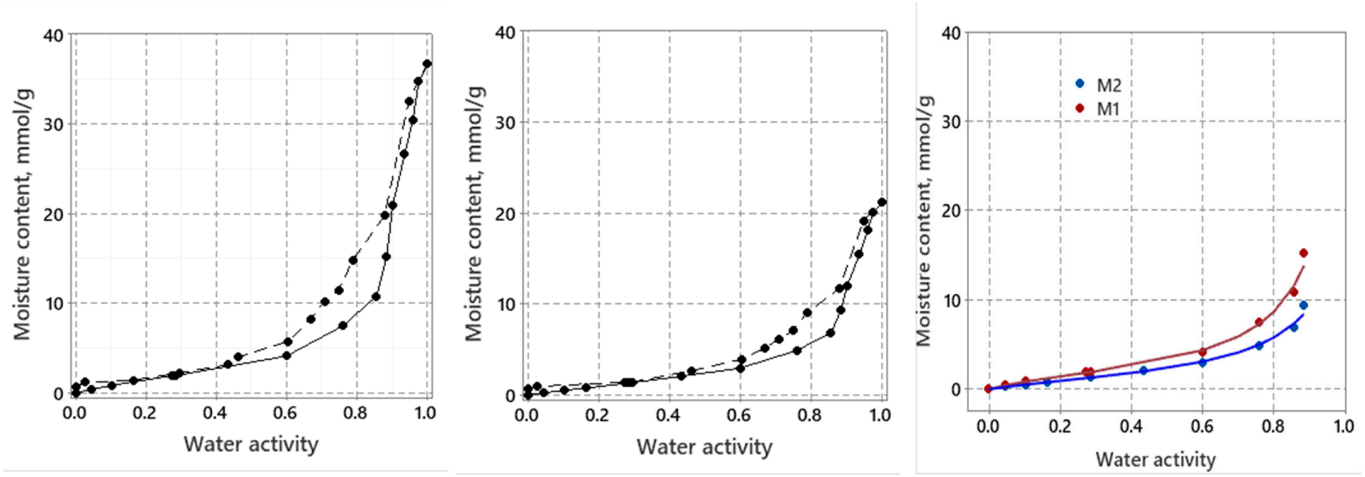


**Figure 1.** Moisture isotherm adsorption (solid line) and desorption (dashed line) of muffins: (**a**) sample M1; (**b**) sample M2; (**c**) fit of the experimental moisture isotherm (dot) of muffins by the GAB equation (solid line).

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 have been 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 between the 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 of 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 represents three zones of water activity. The presence of hysteresis on the curves indicates its 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 are 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 a $a_w$ range of ~0.05–0.30 for Type II [13]. The GAB equation is 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 the sorption isotherms are presented in Table 1, along with the statistical parameters and estimated model coefficients. According to the BET model, the monolayer of the M1 sample had a large sorption capacity, and thus, the $a_s$ of the $S_{BET}$ monolayer was 162 $m^2/g$ versus 123 $m^2/g$ for the M2 sample (Table 1). This correlates well with the data on the sample desiccation. $S_{BET}$ values in the range of 3–5 indicate a weak adsorbent–adsorbate interaction. However, this interaction was slightly higher for the M1 sample.

**Table 1.** Calculated BET and GAB model 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 [13]. Therefore, similar characteristics of the 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 to 20, and the coefficient k is in the range of 0.70–1. 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 of 0.05–0.9 [14]. This fact was confirmed for the studied samples. The GAB model satisfactorily ($p < 0.05$) fit the adsorption behavior of both muffin samples in the water activity range of 0.046–0.884 (Figure 1c).

### *3.4. Sensory Characteristics*

In almost all respects, the developed muffin had the same parameters as the control sample (Table 2). The exception was color. The DMTP muffin had 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 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 sections | |
| Taste and smell | Intrinsic to this variety of muffin without foreign smells and tastes | |

## 4. Conclusions

Thus, as a result of the research, a technology for the production of a muffin with a partial replacement of wheat flour with defatted milk thistle seed flour was developed. The baking characteristics and physico-chemical properties of the samples were investigated. The microstructures of the cakes, as evidenced by the data on the adsorption behavior of the samples, were 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 were slightly higher than those of the developed one. This explains the resulting baking parameters. Both the BET and GAB models made it possible to obtain the comparable microstructural parameters by calculation. However, 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.

**Author Contributions:** Conceptualization, V.E.; methodology, V.E. and S.G.; formal analysis, D.P. and S.G.; investigation, D.P. and S.G.; software, S.G.; writing—original draft preparation, S.G.; writing—review and editing, O.A., V.E. and S.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data presented in this study are available upon request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References


1. Corchete, P. *Silybum marianum* (L.) Gaertn: The Source of Silymarin. In *Bioactive Molecules and Medicinal Plants*; Springer: Berlin/Heidelberg, Germany, 2008; pp. 123–148. [CrossRef]
2. Gligor, F.; Dobrea, C.M.; Cecilia, G. Silymarin Food Suuplements-Oral Solid Dosage Forms. *Sci. Study Res. Chem. Eng. Biotechnol. Food Ind.* **2016**, *17*, 349–354.
3. Apostol, L.; Lorga, S.; Moşoiu, C.; Racovita, R.C.; Niculae, O. The Effects of Partially Defatted Milk Thistle (*Silybum marianum*) Seed Flour on Wheat Flour. *J. Int. Sci. Publ.* **2017**, *5*, 74–84.
4. McLaren, K. XIII—The Development of the CIE 1976 (L* A* B*) Uniform Colour Space and Colour-difference Formula. *J. Soc. Dyers Colour.* **1976**, *92*, 338–341. [CrossRef]
5. Brunauer, S.; Emmett, P.H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60*, 309–319. [CrossRef]
6. Anderson, R.B. Modifications of the Brunauer, Emmett and Teller Equation 1. *J. Am. Chem. Soc.* **1946**, *68*, 686–691. [CrossRef]
7. Guggenheim, E. *Applications of Statistical Mechanics*; Clarendon Press: Oxford, UK, 1966.
8. Majd, M.M.; Kordzadeh-Kermani, V.; Ghalandari, V.; Askari, A.; Sillanpää, A. Adsorption Isotherm Models: A Comprehensive and Systematic Review (2010−2020). *Sci. Total Environ.* **2022**, *812*, 151334. [CrossRef] [PubMed]
9. *ISO 9277:2010*; Determination of the Specific Surface Area of Solids by Gas Adsorption—BET Method. ISO: Geneva, Switzerland, 2010.
10. Ergun, R.; Lietha, R.; Hartel, R.W. Moisture and Shelf Life in Sugar Confections. *Crit. Rev. Food Sci. Nutr.* **2010**, *50*, 162–192. [CrossRef] [PubMed]
11. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [CrossRef]
12. Barbosa-Cánovas, G.V.; Fontana, A.J.; Schmidt, S.J.; Labuza, T.P. (Eds.) *Water Activity in Foods*; Wiley: Hoboken, NJ, USA, 2020. [CrossRef]
13. Timmermann, E.O. Multilayer Sorption Parameters: BET or GAB Values? *Colloids Surf. A Physicochem. Eng. Asp.* **2003**, *220*, 235–260. [CrossRef]
14. Blahovec, J.; Yanniotis, S. Gab Generalized Equation for Sorption Phenomena. *Food Bioprocess Technol.* **2008**, *1*, 82–90. [CrossRef]