DEVELOPMENT OF EGGLESS GLUTEN-FREE MUFFINS WITH IMPROVED CONTENT OF ESSENTIAL ELEMENTS

GLUTEN-FREE MUFFINS IMPROVED IN MINERALS

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Abstract The nutritional adequacy of gluten-free diet has been questioned due to the elimination of wheat, an important vehicle for micronutrient fortification and source of fibre.The current study was carried out to use blends of gluten-free flours as a good source of essential mineral elements for production of muffins designated to patients with celiac disease. Initially the mineral content of the gluten-free flours available on the Bulgarian market was determined by means of AES-ICP. Based on the results the gluten-free flours comparable to the whole grain flour mineral composition were mixed and eggless muffins prepared from rice flour/corn flour/chickpeas/buckwheat/carob bean powder blends. The gluten-free flour mixtures contained magnesium and iron close to the content of these elements in the whole grain flour, exceeded calcium and contained less zinc. Muffin batters and muffins were subjected to basic physical properties tests including batter viscosity and moisture, Texture Profile Analysis (TPA) by TAXT. Plus Texture analyzer, thermal properties were investigated by the method of differential scanning calorimetry (DSC) and sensory analysis was performed to the final products.

Key words**:** physical properties, sensory properties, thermal properties, muffin batter rheology, celiac disease

Introduction

The only way to control the condition of celiac patients is for them to follow a strict diet excluding gluten-containing foods. Such a drastic change in the diet leads to a high risk of deficiency of certain micronutrients (folic acid, some minerals, especially calcium, magnesium, iron and zinc), as well as excess of some macronutrients, especially saturated fatty acids (ZUCCOTTI et al., 2013). A major factor leading to the described deficiency of essential elements is the body's autoimmune response, which reduces the absorption of essential elements due to iron and zinc deficiency (CARUSO et al., 2013). A number of researchers reported that the gluten-free diet could be mineral-

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poor (GOBBETTI et al., 2017). SHEPHERD et al. stated out at least one in ten patients on a gluten-free diet suffered deficiency of essential elements, calcium and magnesium, respectively, in both genders, zinc in men and iron in women (SHEPHERD et al., 2013). ÖHLUND and co-authors evaluated nutrient intake in children undergoing a gluten-free diet and found out they followed the same trends as healthy children, in particular simple sugars and saturated fat higher intake but lower intake of fibers, vitamin D and magnesium (ÖHLUND et al., 2010). There are numerous suggestions in the literature for gluten-free products with increased nutritional value. YALCIN and co-authors offer tarhana based on rice flour combined with chickpea flour to increase nutritional value (YALCIN et al., 2008). Some teams used sorghum combined with rice flour and corn starch, others used different mixtures of sorghum, rice and corn with potato starch for the production of pasta (FERREIRA et al., 2016; RAI et al., 2014). Several authors utilized buckwheat as a source of polyunsaturated fatty acids in bread (COSTANTINI et al., 2014). SHAROBA et al. also investigated the potential to increase the content of essential elements (Ca, Mg, Fe) using mixtures of corn flour and artichoke flour (SHAROBA et al., 2014).

The aim of the present work was to test gluten-free flours, in order to develop eggless muffins enhanced with essential elements targeting their quality parameters.

Materials and Methods

Materials. Based on recent studies and availability the following gluten-free flours were selected and purchased from the Bulgarian market: rice, corn, oat (conventional and organic), millet, buckwheat, quinoa, amaranth, chickpea, carob and chestnut. Whole wheat flour was purchased as a control. The mineral content of the gluten-free flours (data not shown), blends and muffins were determined by means of AES-ICP (Spectroflame MODULA-FTMOA 81A) in terms of Ca, Mg, Fe and Zn.

Mineral composition modeling

The gluten-free flours study indicated (data not shown) the largest difference in elemental composition was at the expense of the magnesium shortage and excess of calcium if compare to the wholegrain flour. An approach was chosen flours with a high magnesium content were added to the basic flour available. Rice and corn flours were selected as basic flours for reasons of price and availability. The selected blends and the contents of the investigated essential elements are presented in Table 1.

The proposed mixtures contain magnesium and iron close to the content of these elements in the wholegrain flour. The calcium content of most mixtures exceeded the control and zinc content was less than the control.

Table 1. Mineral composition of gluten-free flour blends

Samples	Whole flour, %	Corn flour, %	Rice flour, %	Chick pea flour, %	Buck Wheat flour, %	Carob flour, %	Ca, mg/kg	Mg, mg/kg	Fe, mg/kg	Zn, mg/kg
F1	-	45	0	50	0	5	421.00	1254.0	37.50	20.60
F2	-	30	0	65	0	5	476.20	1401.0	41.10	22.85
F3	-	65	0	0	30	5	327.00	1283.0	30.30	18.50
F4	-	55	0	0	40	5	411.45	1456.0	31.10	21.90
F5	-	0	35	60	0	5	476.20	1241.4	45.85	20.73
F6	-	0	10	85	0	5	555.70	1565.4	47.60	25.46
F7	-	0	55	0	40	5	396.60	1282.2	41.25	18.15
F8	-	0	25	70	0	5	508.00	1371.0	46.55	22.62
F9		0	40	0	55	5	438.30	1589.1	41.10	21.44
F10		0	50	0	45	5	460.00	1384.5	40.30	21.05
Control	100	-	-	-	-	-	340.00	1400.0	39.00	29.00

The ten blends were used to produce muffin batters and based on the rheological study four formulations were selected for further experiments designated as F2, F4, F8, F10 and the Control.

Muffin formulations and preparations

Muffin recipe contained the following ingredients: pure granulated white sugar, double-acting baking powder (Dr. Öetker), sunflower oil, white rice flour, corn, chickpea, buckwheat, carob and whole wheat flour (control) all purchased from the local supermarket. Flour blend 41%, sucrose 16%, baking powder 1%, sunflower oil 13% and water 29% were mixed together in a bowl and blended at speed 3 for 10 seconds. Muffin pans were filled with the batter (55-65 g each) and were baked for 20 minutes or until done at 180°C in a preheated oven. Following the five-minute setting period, muffins were removed from the pans, allowed to cool on wire racks for one hour. Afterwards the analyses were performed.

Batter viscosity: The dough viscosity was measured by rotational viscometer HAAKE VT 550 (Germany) in five repetitions. All the measurements were done at 25°C using standard cone-cylinder geometry (10.65 mm diameter and 0.9 mm gap). The flow experiments were conducted under steady-shear conditions with shear rate ranging from 0.0123 to 1000 s^{-1}. The experimental data were evaluated by Herschel–Bulkley equation.

Thermal properties: The starch gelatinization and the water state in the batters and muffins were characterized by means of a Differential Scanning Calorimetry Analysis (DSC 204 F1 Phoenix NETZSCH-Gerätebau GmbH, Germany). The samples (15 mg) were closed hermetically in aluminum pans and cooled down from 20°C to -50°C at cooling rate 5°C min^{-1} and heated to 150°C at a rate 10°C min^{-1}, in two repetitions. The endothermal transitions of free water melting and starch gelatinization were evaluated with the use of instrument's software Proteus Analysis (Netzsch, Germany). The amount of the bound water is calculated as the difference between the total water content and the free water.

Texture analysis: The texture of the muffins was examined by texture analyser (StableMicroSystems TA-XT2Plus) in five repetition. All experiments were done at 25°C in retardation (stress holding in time) and relaxation (strain holding in time) mode using standard cylinder in cylinder (d_1 = 30 mm, d_2 = 25 mm, h = 40 mm, m = 30 g) geometry. 2 kPa compression stress was obtained by 1 mms^{-1} deformation speed and hold for 180 s and after that caused deformation was hold for 180 s. The retardation and relaxation curves were evaluated by generalized Kelvin and Maxwell models respectively.

Sensory evaluation test: 9-point hedonic scale was used to evaluate the overall acceptability of the muffin formulations. Analysis of variance (ANOVA) was used for statistical analysis of data.

Results and discussion

Study on muffin batters and muffins

Quality of the muffins depends mainly on the batters physical properties. The changes in batter viscosity for all the different formulations are represented in the Table 2.

Table 2. Herschel–Bulkley model for muffin batters viscosity

Batters	Yield stress, τ_0, Pa	Consistency index, K_H, Pa. s_H^n	Flow behavior index, n_H	R^2
F2	0.014± 0.002^a	104.566±3.296^b	0.488±0.002^d	0.9971^b
F4	8.042± 0.905^b	99.428±4.245^b	0.417±0.004^a	0.9440^a
F8	0.012± 0.002^a	139.778±2.331^c	0.425±0.005^a	0.9901^b
F10	18.177± 3.878^c	18.177± 3.878^c	0.452±0.008^b	0.9989^b
Control	211.672±30.303^d	374.734±4.685^d	0.470±0.012^c	0.9891^b

Values are mean of duplicate ±SD and means followed by different subscripts in the same column are significantly different at $p=0.05$

Herschel's model showed the highest correlation and described all the batters. According to the flow behavior index of this model (n_H), all the batters appeared to be an elastic-plastic body. According to the other parameters of the model, buckwheat flour caused higher yield stress and that way diminished the viscosity. The effect was less apparent in the presence of corn flour and more noticeable if rice flour was concerned. The combo of rice and chickpea flours demonstrated the highest viscosity hence better performance during baking was expected.

The changes in moisture content and water activity due to gluten free batters blends used was studied via DSC analysis. The percentage of free and bound water was determined by the enthalpy value of the melting peak provided the 100% free water enthalpy value was known (Table 3).

Table 3. Free and bound water in gluten free muffin batters

Batters	ΔH, J/g	Free water, %	Bound water, %
F2	23.89	0.242563	0.757437
F4	31.97	0.324601	0.675399
F8	22.74	0.230886	0.769114
F10	22.27	0.226114	0.773886
Control	26.62	0.270281	0.729719

The amount of bound water was relatively high and varies between 67.5% and 77.4%. The F4 batter exhibited the lowest amount of bound water (67.5%) and F10 the highest (77.4%). As a rule the higher water binding capacity the higher the percentage increase in height due to baking.

During the baking the endothermic phase transition of the starch gelatinization in the dough takes place (Figure 1). The lowest value of the initial gelatinization temperature (76 °C) was reported for F4 sample, e.g. the swelling process began the earliest in here and at the same time it was the largest characterized by the highest enthalpy value - 1.732 J / g (Table 4). It happened most likely due to the relatively low proportion of bound water compared to other batters. The situation was similar with the Control where the higher free water content was apparent and the gelatinization process was quite complete. In the F2, F8 and F10 batters, due to the lower free water content, the gelatinization was hindered and the process shifted to higher temperatures. At the same time, the enthalpies of the endothermic transition appeared to be lower meaning the process was not entirely completed.

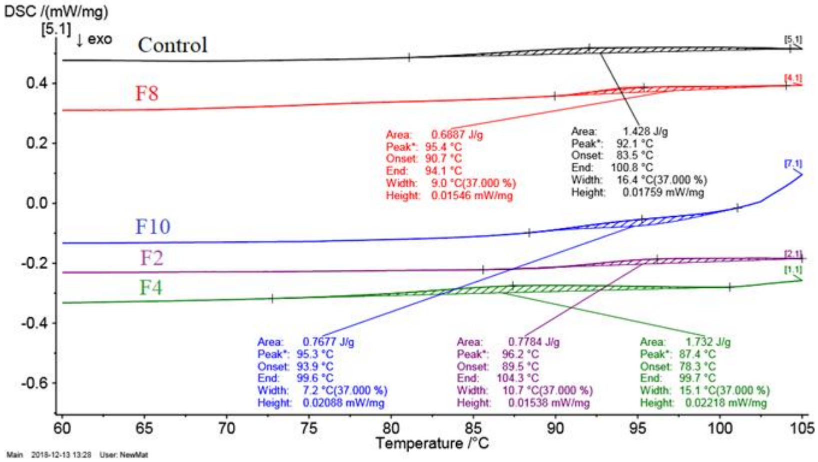

Figure 1. Muffin batters starch gelatinization by DSC

Table 4. Starch gelatinization in muffin batters

Batters	Temp. interval, ΔT, °C	Endothermic pick temp., T_p, °C	Enthalpy, (ΔH), J/g
F2	85 - 105	96.2	0.7784
F4	76 - 101	87.4	1.732
F8	90 - 103	95.4	0.6887
F10	87 - 102	95.3	0.7677
Control	82 - 105	92.1	1.428

Quality of muffins

The loss of weight was due to technological reasons (10% on average, data not shown). The AES-ICP test determined the mineral content of the final products showing insignificant differences of about 1.5 % loss if compare to the initial content in the selected flour blends (Table 5).

Table 5. Mineral content losses in muffin formulations, mg/kg

Formulas	Whole wheat flour, %	Corn, %	Rice, %	Chick peas, %	Buck Wheat %	Carob %	Mg. mg/kg	Ca. mg/kg	Fe. mg/kg	Zn. mg/kg
F2	-	30	0	65	0	5	7.28	22.00	0.65	0.35
F4	-	55	0	0	40	5	6.46	23.00	0.48	0.34
F8	-	0	25	70	0	5	7.92	21.94	0.73	0.34
F10	-	0	50	0	45	5	7.08	21.46	0.64	0.33
Control	100	-	-	-	-	-	5.89	21.98	0.59	0.43

Textural properties of muffins

The texture characteristics of the baked muffins are presented on Table 6. Wholegrain muffins showed relatively high firmness, the lowest cohesiveness (slower relaxation), high gumminess and medium chewiness. The overall texture characteristics of rice flour based muffins were closer to each other if compare to those based on corn flour. The firmness varies between 18.44 N (F2) and 31.38 N (F4). According to the results obtained the buckwheat flour increased the firmness. This effect was more pronounced in corn muffins. These samples exhibited lower springiness and cohesiveness, and the highest gumminess and chewiness. Lower springiness and cohesiveness mean more deformability. The springiness and cohesiveness of muffins varies over a very narrow interval. The gumminess and chewiness were the lowest for the F2 formulation.

Table 6. Texture evaluation of muffins

Formulas	Firmness, N	Springiness, cm	Cohesiveness	Gumminess, N	Chewiness, N.mm
F2	18.44±3.57a	0.93±0.01b	0.80±0.10b	15.00±2.55a	13.93±2.41a
F4	31.38±5.16d	0.90±0.02a	0.76±0.13ab	24.29±4.85c	21.86±3.79c
F8	20.96±2.15ab	0.92±0.02b	0.81±0.10b	17.16±3.23ab	15.90±3.05ab
F10	22.72±2.15b	0.90±0.03a	0.83±0.07b	18.84±2.66b	17.03±2.68ab
Control	27.69±5.02c	0.91±0.02a	0.73±0.10a	20.11±4.02b	18.26±3.63b

Values are mean of duplicate ±SD and means followed by different subscripts in the same column are significantly different at p=0.05

Sensory analysis of muffins

Consumers rated on overall acceptability of each sample four in total and the control using a 9-point hedonic scale with 1=dislike extremely and 9=like extremely. All the samples and the control were rated "like slightly" ($x \geq 6$, $p=0.05$) except F8 sample that had the highest rating on overall acceptability "like moderately", p=0.05.(data not presented)

Conclusion

The selected gluten-free flour blends contained Mg and Fe close to the content of these elements in the whole wheat flour, exceeded the Ca content and contained less Zn. The combination of rice and chickpea flours demonstrated the highest viscosity whether the blend based on corn showed higher plasticity. The process of gelatinization was well pronounced in systems containing more free water (F4). Buckwheat flour (F4 and F10) contributed to a tighter structure with small pores and deeply cracked surface. The combination of corn and chickpea flours (F2) bound the free water and very tight, pore less and furrowed structure was formed. The best structure was achieved with the combination of rice and chickpea flour (F8), with the highest volume and porous structure. F8 batter was characterized by a relatively high value of bound water and the lowest enthalpy of gelatinization. As a result, the structure of the crumb was less elastic and softer. The F8 sample had also the highest rating on overall acceptability “like moderately” by the consumers.

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