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Enrichment of Gluten-free Cakes with Grape Molasses and Bioactive Rich Ingredients

Hacer Levent[1*]
https://orcid.org/0000-0002-7321-5577

Abdulvahit Sayaslan[2]
https://orcid.org/0000-0001-7161-1552

Saliha Yeşil[2]
https://orcid.org/0000-0003-1806-7097

[1]Karamanoğlu Mehmetbey University, Department of Nutrition and Dietetics, Karaman, Turkey; [2]Karamanoğlu Mehmetbey University, Department of Food Engineering, Karaman, Turkey.

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*Correspondence: hacerlevent@hotmail.com; Tel.: +90-338-2262131(H.L.).

HIGHLIGHTS

- The use of grape molasses and other additives reduced the cake brightness.
- Enriched cake samples had higher ash and crude protein content than control samples.
- All additives increased the total phenolic content and antioxidant activity ($p<0.05$) of cake samples.
- Pomegranate seed and flaxseed improved the Ca, P and K contents of control cakes.

Abstract: In this study, the sugar used in the gluten-free cake was substituted with 75% grape molasses. In addition, the gluten-free flour mixture used in the cake formulation was prepared as a combination of rice flour (75%), chickpea flour (15%)and carrot flour (10%). This mixture was replaced separately with 5% grape seed, pomegranate seed, flaxseed, poppy seed and turmeric to improve the nutritional composition of gluten-free cakes. Supplemented cakes contained higher ash, crude protein, total phenolic content and antioxidant activity values than gluten-free control sample. Cake samples containing pomegranate seed and flaxseed had higher contents of Ca, P and K than control cakes. In addition, flaxseed and poppy seed containing cakes were found richer in terms of Mn and Mg than control. Utilization of grape molasses together with grape seed, pomegranate seed, flaxseed, poppy seed and turmeric in formulation caused a reduction in volume index of cake samples. The hardness values of the gluten-free cakes were generally higher than that of the control. Cakes containing flaxseed and poppy seed scored higher in sensory analysis than other substituted samples. Based on these results, the use of grape molasses with flaxseed and poppy seed can be recommended for the production of gluten-free cakes with acceptable sensory properties and high total phenolic content and antioxidant activity.

Keywords:gluten-free; molasses; grape; pomegranate; poppy; flaxseed.

INTRODUCTION

Celiac disease (CD) is triggered by the ingestion of gluten in genetically sensitive individuals [1]. CD is characterized by damage of the small intestinal mucosa and results in malabsorption in the small intestine. The alcohol-soluble gliadin fraction of wheat gluten and similar proteins in other grains are responsible for environmental factors of spontaneous mucosal damage[2]. These prolamins are very important not only for CD, but also for non-coeliac gluten sensitivity, gluten ataxia and dermatitis herpetiformis [3].

Celiac patients can have typical gastrointestinal symptoms such as diarrhea, bloating, flatulence, steatorrhea, weight loss, abdominal pain, as well as non-gastrointestinal abnormalities such as anemia, liver function tests, bone disease, and skin disturbances. In addition, many people with celiac disease may have no symptoms at all [4].

The global prevalence of CD is 1.4% according to serological test results, and 0.7% according to biopsy results [5]. The only effective treatment for individuals with these diseases is to completely remove gluten from their diet throughout their life [3]. But some common packaged gluten-free foods have more fat and carbohydrates and less protein, iron and folate compared to regular products [6]. Also, commercially available gluten-free products are poorer in unsaturated fatty acids compared to their gluten-containing counterparts [7]. For that reason, following a gluten-free diet by people with CD causes some macro and micro nutrient deficiencies, as well as to excess saturated fat and carbohydrate intakes [8]. Furthermore, the lack of product range, limited availability, insufficient knowledge of the gluten-free diet and high product price are some of the other problems faced by celiac patients [9]. As a result, most patients are at risk for nutritional deficiency problems such as osteoporosis, anemia and growth retardation [8].

Chickpea is an important legume product in human nutrition due to its carbohydrate, protein, dietary fiber, vitamin and mineral content.Chickpeas contain significant amounts of all essential amino acids except sulfur-containing amino acids, which can be supplemented by cereals [10-11]. Carrots are rich in carbohydrates and minerals (Ca, Fe, P and Mg) and bioactive compounds such as carotenoids and dietary fibers. It is rich in natural antioxidants which have anticancer activity [12]. Molasses, one of Turkey's traditional products, is mainly produced from grape. Since it contains organic acids, mineral substances and partially vitamins, the importance of molasses in nutrition is much more than granulated sugar [13-14]. Iron in grape molasses can be absorbed easily and 35% of the daily iron need can be met by molasses that can be taken daily [15]. Grape seed, one of the waste materials of the wine industry, is valuable components due to its dietary fiber (40%), protein (11%), oil (16%), complex phenols (7%) including tannins and mineral salts contents[16]. The seeds are also rich source of monomeric phenolic compounds such as procyanidins and catechins which have antiviral and antimutagenic effects [16-17]. Flaxseed is a functional food ingredient with many health benefits. It contains α-linolenic acid (ALA), dietary fiber and lignans, and these functional ingredients reduce the risks of cardiovascular diseases and hormone-dependent cancer types [18-19].

Pomegranate seeds, a by-product of the industrial processing of pomegranate, contain valuable oils with nutritional and medicinal properties [20]. Poppy seeds are an important industrial product grown for pharmaceutical and food applications since ancient times.Poppy seeds have a 45-50% oil content and seed oils have a desirable fatty acid composition with 73% linoleic, 13% oleic and 10% palmitic acid as the main fatty acids.In addition, poppy seeds contain carbohydrates, protein and bioactive compounds such as phenolics [21-22]. Turmeric is widely used in India, China, and South East Asia as a spice, coloring agent and food preservative.Curcumin is the main bioactive component of turmeric and it has been shown to have a wide range of biological activities such as antiinflammatory, antioxidant, anticarcinogenic, antimutagenic, antifertility, antidiabetic, hypotensive and hypocholesteremic effects [23].

Cake is a popular product that is consumed by people of all ages due to its unique taste, soft texture, ease of consumption and wide variety. It is a cereal product with a high production amount after bread and biscuit [24]. In this study, the gluten-free cake mixture was reformulated with rice flour, chickpea flour and carrots. Studies on the use of grape molasses in gluten-free cakes and enrichment with bioactive rich ingredients are very few. Therefore, the aim of this study is to improve the gluten-free cake formulation with grape molasses and bioactive rich substances and to evaluate the physical, chemical and sensory quality of the cakes.

MATERIAL AND METHODS

Materials

Rice flour, carrot, chickpea, sugar, shortening, grape molasses, egg, milk powder, salt, baking powder, ethyl vanillin, grape seed, flaxseed, poppy seed and turmeric were obtained from local markets in Karaman, Turkey. Grape seed, flaxseed, poppy seed, and pomegranate seed were ground in a coffee grinder (<500 µm) prior to cake production. Fresh carrot was dried in the oven (KD-200, Ankara, Turkey) below 10% moisture content. Then dried carrot was ground in a hammer mill (POLYMIX, Kinematica AG, Switzerland) and sieved to obtain final powder size <350 µm. Chickpeas were ground into flour with the same laboratory hammer mill. Guar gum was obtained from Tunçkaya Inc., Istanbul, Turkey. DATEM (diacetyl tartaric acid esters of monoglycerides) was kindly provided by Aspek Kimya, Istanbul, Turkey.

Preparation of cake samples

In the study, two control cake samples were produced. First control cake is prepared with wheat flour, and second control cake is prepared with gluten-free flour mix instead of wheat flour. Gluten-free flour mixture consists of rice flour (75%), chickpea flour (15%) and carrot flour (10%). For prepation of supplemented cake samples, gluten-free flour mixture was replaced by 5% with grape seed, pomegranate seed, flaxseed, poppy seed and turmeric, separately. Also, the sugar in the gluten-free cake samples was replaced by 75% grape molasses. The details of cake formulations are given in Table 1. A single application ratio was used to compare the effects of additives and this ratio was determined by preliminary trials. Firstly, shortening and sugar are whipped in the mixer (Kitchen Aid, Artisan, USA) until it turns into white cream. After the egg is added, mixing continues for 5 more min. The remaining ingredients are then added and mixed for 1 min to obtain a homogeneous cake batter. Baking of the cakes was carried out in the oven (Bosch HGD52D12T, Istanbul, Turkey) at 170 °C for 30 min. After baking, the cakes were demoulded and allowed to cool for 30 min. Then, the cake samples were stored in sealed bags until analysis.

Table 1. Experimental design for gluten-free cake production

Ingredients (g)	Control (WF)	Control (GF)	SC1	SC2	SC3	SC4	SC5
Wheat flour	100	-	-	-	-	-	-
Gluten-free flour mix (75% RF:15%CHF:10%CF)	-	100	95	95	95	95	95
Shortening	150	150	150	150	150	150	150
Fine granulating sucrose	150	150	37.5	37.5	37.5	37.5	37.5
Grape molasses	-	-	112.5	112.5	112.5	112.5	112.5
Skimmed milk powder	10	10	10	10	10	10	10
Whole egg	150	150	150	150	150	150	150
Salt	1	1	1	1	1	1	1
Baking powder	9	9	9	9	9	9	9
DATEM	1	1	1	1	1	1	1
Ethyl vanillin	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Grape seed	-	-	5	-	-	-	-
Pomegranate seed	-	-	-	5	-	-	-
Flaxseed	-	-	-		5	-	-
Poppy seed	-	-	-	-	-	5	-
Turmeric	-	-	-	-	-	-	5

WF: Wheat flour; GF: Gluten-free;RF:Rice flour; CHF:Chickpea flour; CF:Carrot flour; SC:Supplemented cake; DATEM: Diacetyl tartaric acid esters of monoglycerides

Cake batter and cake analyses

Specific gravity of cake batters was measured by dividing the weight of the batter in a container of known volume by the weight of the distilled water in the same container. Cake batter mixed with distilled water at a ratio of 1 (batter):10 (distilled water) and the pH of the mixture was measured by a pH meter (WTW pH 315, Weilheim, Germany) calibrated with buffer solutions of pH 4.0 and 10.0.

Cake properties

The volume, symmetry index and uniformity index determination tests were performed using AACC Method (10-91). The crust and crumb color of the cake samples were measured with Hunter Lab Color Quest II Minolta CR-400 (Minolta Camera, Co., Ltd., Osaka Japan). L*(brightness), a*(red-green) and b*(yellow-blue) values were determined on the day of baking. The hardness of the cake slices was measured using a TA-XT2 Texture Analyzer (Texture Tech. Corp., England, U.K.) with an aluminum P36 / R cylindrical probe at room temperature. The instrument setting were as follows: Trigger force 0.049 N, distance 5 mm, the pretest, test, and posttest speeds were 1.0 mm/s, 2.0 mm/s and 10 mm/s, respectively.

Chemical analysis

Raw materials and cake samples were analyzed for moisture, ash, crude protein and crude fat contents using standard AACC procedures [25]. Ca, P, K, Fe, Mn, Mg, Zn and Cu elements were determined by ICP-OES (inductively coupled plasma optical emission spectrometry) (Agilent 720, Agilent Technologies, Santa Clara, CA, USA) [26].

Total phenolic content (TPC) was determined with the Folin-Ciocalteu reagent using gallic acid as standard [27]. The powdered cake samples (1 g) were extracted for 2 h with 10 mL of 80% aqueous methanol (1/10; w/v) at room temperature. Then samples were centrifuged at 2600 *g* for 15 min. For total phenol assay, 0.1 mL of supernatant, 0.9 mL distilled water, 1 mL Folin-ciocalteu reagent (90%, v/v) and 2 mL sodium carbonate solution (10%, w/v) were mixed. The mixture was kept in the dark for 60 min at room temperature. Using a spectrophotometer (Shimadzu UV-1800, Shimadzu Inc., Kyoto, Japan) at 765 nm, absorbance of the mixture was measured and total phenolic content was expresses as gallic acid equivalent (GAE).

DPPH scavenging activity (%), was measured following a previous method [27] with small modification. For the preparation of the sample extracts, the method of total phenolic content analysis was used. To prepare the DPPH (2,2-diphenyl-l-picrylhydrazyl) radical solution, 10 mg DPPH was dissolved in 25 ml 80% methanol. Exactly, 100 µL of 80% methanol extract was mixed with 250 µL of DPPH solution and 2 mL of 80% methanol. The mixture was shaken vigorously and kept for 20 min in the dark at room temperature. A mixture of 250 µL of methanol DPPH solution and 2.1 mL of 80% methanol was used as blank. Using a spectrophotometer (Shimadzu UV-1800, Shimadzu Inc., Kyoto, Japan) at 517 nm, the decrease in absorbance (%) of the resulting solution was monitored for 20 min.

Trolox equivalent antioxidant capacity (TEAC) was also measured against 2,2 azinobis-3-ethylbenzothiazolin-6-sulfonic acid ($ABTS^+$) radical using spectrophotometric assay [28]. For the assay, $ABTS^+$ solution (7 mM) containing 2.45 mM potassium persulfate was prepared and the mixture was kept in the dark for 12-16 h at room temperature. To prepare the $ABTS^+$ working solution, the stock radical solution was diluted with PBS (Phosphate buffered saline) to an absorbance of 0.70 ± 0.02 at 734 nm. Sample extract (10, 20 and 30 µL) was reacted with 1mL of $ABTS^+$ working solution. Absorbance inhibition percentages were calculated using absorbance values at the beginning and at the end of 6 min. The same procedure was carried out for the standard Trolox concentrations (5, 10, 15 and 20 µM). The TEAC value was calculated using the curve slopes of the sample and the standard. The results are reported as mM Trolox/100g.

Sensory evaluation

Sensory analyzes were performed by 26 healthy non-smoking panelists between the ages of 23-48. To avoid any bias, the coded cake samples were presented to the panelists at room temperatures in a random order. Panelists were asked to clean their mouths with purified drinking water between tests to minimize any residual effect. The cake samples were evaluated in terms of appearance, texture, taste-odor, mouthfeel and overall acceptability using a scale 1-9 where (1) extreme dislike and (9)- extreme liked. All samples were compared with control.

Statistical analysis

All measurements were performed in triplicate. The data was processed using a statistical analyses software JMP 5.0.1 (SAS Institute Inc., Cary, NC, USA). Results were reported as the mean ± standard deviation. Differences in samples were tested for statistical significance at the p=0.05 level.

RESULTS AND DISCUSSION

Some properties of the batter and cake samples are presented in Table 2. Batter specific gravity and pH ranged from 0.86 to 0.92 g/cm^3 and 6.83 to 7.06, respectively. Baking loss (%) values of gluten-free cake samples ranged between 10.54 and 14.03. The highest volume index and symmetry index value was determined in the control sample (WF). Pomegranate seed, flaxseed, poppy seed and turmeric decreased to volume index from 139 to 122-112 mm. Volume index is higly correlated with volume and in general the fortification caused a decrease in the volume index values in the cake samples.In this study, sugar was replaced by 75% grape molasses. In addition to the additives, the use of grape molasses in cake formulation was also effective in reducing the volume. Sugar content has been reported to correlate positively with volumetric expansion in gluten-free cakes using baking powders [29]. Similarly, [30] reported a decrease in volume of cakes with the replacement of pekmez with crystal sugar. Also, this reduction may be due to the presence of fibers in ingredients that may have collapsed the carbon dioxide gas bubbles during cooking and led to a reduction in volume [31]. [32] used flaxseed powder in muffin formulation (10-40%) and reported that the cake volumes (cc) decreased from 150 to 145 with the use of raw flaxseed powder. [33] reported that the use of grape seed flour over 5% decreased the bread volume and increased bread hardness and porosity.

Table 2. Some properties of batters and cake samples

	Batter specific gravity (g/cm^3)	**Batter pH**	**Baking loss (%)**	**Volume Index(mm)**	**Symmetry index (mm)**	**Uniformity index (mm)**
Control (WF)	0.86±0.04^a	6.89±0.07^{ab}	10.54±0.74^a	164±1.41^a	13.0±1.27^a	-5.0±0.71^c
Control (GF)	0.92±0.01^a	7.06±0.03^a	12.67±1.40^a	139±4.24^b	8.0±1.13^{bc}	0.0±0.14^{ab}
GM+GS	0.90±0.07^a	6.93±0.04^{ab}	13.02±0.51^a	136±0.71^b	5.0±0.85^c	1.0±0.14^a
GM+ PMS	0.92±0.07^a	6.83±0.03^b	14.03±1.77^a	121±2.83^{cd}	4.6±0.31^c	1.0±0.57^a
GM+FS	0.91±0.01^a	6.90±0.01^{ab}	11.72±0.88^a	118±2.12^{cd}	11.0±0.58^{ab}	-5.0±0.28^c
GM+PS	0.90±0.01^a	6.88±0.06^{ab}	12.10±0.30^a	112±0.71^d	8.0±1.02^{bc}	0.0±0.14^{ab}
GM+T	0.92±0.03^a	6.90±0.07^{ab}	13.11±0.72^a	122±2.26^c	7.2±0.64^c	-1.0±0.35^b

Mean values represented by different letters are statistically different from each other ($p < 0.05$). Values are the average of triplicate measurements on the duplicate samples. WF: Wheat flour. GF:Gluten-free; GM: Grape molasses; GS: Grape seed; PMS: Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric

High symmetry index value indicates that cakes rise mainly in the middle part [34]. Grape seed, pomegranate seed, and turmeric reduced the symmetry index value compared to the gluten-free control sample, but this decrease was insignificant.Except for the flaxseed enriched samples, the symmetry index values of the gluten-free cakes were not different from the gluten-free control samples.The uniformity index is desirable to be close to zero for good quality cakes [35]. It was found that the unuformity index values of the cakes were in the range of -5.0-1.0 mm. The uniformity index was found to be zero in cakes enriched with poppy seed and gluten-free control sample.

Table 3 shows the crust and crumb color values of cake samples. The color of a baked product comes from the color of ingredients and their interactions [36].In addition, the Maillard reaction between sugar and amino acids and the caramelization process of sugars are responsible for the crust color of the cake [37]. The crust L * value of the gluten-free cake samples varied between 32.03 and 43.43, and the crust L * values of the enriched samples were found to be lower than the gluten-free control sample.The highest crust L * and crust b * values were determined in grape seed enriched samples after the gluten-free control sample. It was also observed that the cake samples prepared with pomegranate seed and turmeric had the highest crust a * value.The differences between the crust colors in the cake samples may have resulted from the natural color characteristics of the raw materials, different protein amounts and amino acid compositions. When the crumb color values of the gluten-free cakes were evaluated, it was observed that the lowest L* value (44.43) was in the samples prepared with turmeric. All supplemantations reduced the crumb L* and increased the crumb a* and b* values compared to the gluten-free control samples. [38] observed similar results reporting lower L* and higher a* for uncooked and cooked noodle samples prepared with grape, pomegranate and rosehip seed flours than control samples. [39] used turmeric in bread formulation (2-8%) and reported that crumb color and b values increased with the use of turmeric. In a study by [40], as the grape seed flour ratio increased, the colour of the cookies became darker. Similarly, breads containing flaxseed flour revealed a darker crumb than the control bread, which was attributed to the original dark color of flaxseed flour [41].

Table 3. Color analysis results of gluten-free cake samples

	CRUST			CRUMB		
	L*	**a***	**b***	**L***	**a***	**b***
Control (WF)	38.53±0.38^{c}	15.43±0.13^{b}	30.31±0.23^{c}	67.75±0.47^{b}	-1.82±0.10^{d}	23.26±0.20^{e}
Control (GF)	59.47±0.47^{a}	13.20±0.17^{d}	39.92±0.31^{a}	73.87±0.23^{a}	0.03±0.07^{c}	25.94±0.14^{d}
GM+GS	43.43±0.48^{b}	15.73±0.16^{b}	32.11±0.14^{b}	49.25±0.22^{cd}	7.68±0.16^{a}	27.21±0.16^{c}
GM+ PMS	38.67±0.21^{c}	17.17±0.10^{a}	28.78±0.33^{de}	49.08±0.38^{d}	6.99±0.14^{a}	29.89±0.23^{b}
GM+FS	32.03±0.30^{d}	14.83±0.13^{c}	27.87±0.18^{e}	49.09±0.41^{cd}	7.01±0.27^{a}	29.53±0.31^{b}
GM+PS	39.02±0.57^{c}	14.35±0.07^{c}	29.35±0.21^{cd}	50.42±0.34^{c}	5.68±0.18^{b}	27.01±0.17^{c}
GM+T	33.35±0.16^{d}	17.26±0.11^{a}	22.44±0.35^{f}	44.43±0.21^{e}	5.24±0.23^{b}	45.81±0.24^{a}

Mean values represented by different letters are statistically different from each other (p <0.05). Values are the average of triplicate measurements on the duplicate samples. WF: Wheat flour. GF:Gluten-free; GM: Grape molasses; GS: Grape seed; PMS: Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric

The results of chemical analysis of cake samples are presented in Table 4. Moisture and ash content of gluten-free cake samples ranged from 24.84 to 28.72% and 1.66 to 2.15%, respectively. All supplementations significantly increased ash and crude protein content compared to gluten-free control cake samples.The crude fat contents of the cakes prepared with flaxseed (24.71%) and poppy seed (24.84%) were found to be higher than those prepared with grape seed (22.90%) and turmeric (23.04%). The high crude fat and protein content of flaxseed and poppy seed were noteworthy as raw materials, and these results may have an impact on the fat and protein content of final product (data not shown). Flaxseed has been reported to have a high content of fat (40%), protein (20%) and dietary fiber (30%) [42]. [43] reported that poppy seed have high protein, fat and Ca, P and K contents. [32] reported that addition of raw and roasted flaxseed powder (10-40%) into the muffin increased the ash, fat and protein content of the samples.

Table 4. Chemical analysis results of gluten-free cake samples

	Moisture (%)	**Ash (%)***	**Crude protein (%)***	**Crude fat (%)***	**TFM (mg GAE/kg)***	**DPPH (%)***	**$TEAC_{ABTS}$ (mM /100g)***
Control (WF)	21.22±0.59^{c}	1.81±0.01^{b}	7.96±0.08^{d}	21.84±0.48^{c}	158.15±4.45^{d}	15.45±0.59^{d}	42.50±9.76^{d}
Control (GF)	25.20±0.85^{b}	1.66±0.03^{b}	8.31±0.06^{d}	22.12±0.31^{bc}	167.82±10.32^{d}	16.20±0.25^{d}	57.12±10.07^{d}
GM+GS	26.12±0.31^{b}	2.11±0.06^{a}	8.81±0.11^{c}	22.90±0.55^{bc}	1058.21±7.34^{b}	40.32±0.92^{b}	732.00±8.06^{b}
GM+PMS	26.30±0.28^{b}	2.14±0.01^{a}	9.12±0.07^{abc}	23.42±0.17^{ab}	843.85±13.22^{c}	35.68±0.79^{c}	620.71±9.52^{c}
GM+FS	25.44±0.45^{b}	2.07±0.00^{a}	9.28±0.10^{ab}	24.71±0.3^{a}	1074.62±6.11^{b}	40.85±1.23^{b}	726.10±10.60^{b}
GM+PS	28.72±0.68^{a}	2.08±0.10^{a}	9.55±0.08^{a}	24.84±0.48^{a}	866.92±7.95^{c}	37.90±0.64^{bc}	640.28±13.40^{c}
GM+T	24.84±0.37^{b}	2.15±0.11^{a}	8.95±0.20^{bc}	23.04±0.21^{bc}	1120.56±9.56^{a}	45.56±0.41^{a}	993.42±9.73^{a}

* Results are on dry weight basis; Mean values represented by different letters are statistically different from each other (p <0.05). TFM: Total phenolic content; GAE: Gallic acit equivalents;TEAC:Trolox equivalent antioxidant capacity. Values are the average of triplicate measurements on the duplicate samples. WF: Wheat flour. GF:Gluten-free; GM: Grape molasses; GS: Grape seed; PMS: Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric

Total phenolic content of gluten-free cake samples changed between 167.82 and 1120.56 mg GAE/kg. All supplementations increased the total phenolic content significanlty (p<0.05) compared to control samples, the highest value was obtained with turmeric. As in the total phenolic analysis, grape seed, pomegranate seed, flaxseed, poppy seed and turmeric significantly increased the antioxidant activity of the control cake samples. It is reported that grape and grape products are rich in phenolic compounds, particularly flovonoids which have anticarcinogenic, antimicrobial, anti-inflammatory, antiatherogenic and antioxidant activities [44]. Cake samples containing turmeric revealed the highest antioxidant activity value (DPPH, 45.56% and $TEAC_{ABTS}$, 993.42 mM/100 g) among the cake samples.

In another study by [45], it was reported that the use of turmeric and mahaleb (5 and 7.5%) increased the total phenolic and antioxidant activity values of cracker samples. [40] reported that the use of grape seed flour in the formulation (5, 7.5, and 10%) increased the total phenolic content and antioxidant activity values of the control cookie samples.

Mineral contents of cake samples are reported in Table 5. The Ca, P and K contents of the gluten-free control sample were higher than the control sample prepared with wheat flour. The use of chickpea flour and carrot flour in gluten-free control sample formulation improved the overall mineral matter compared to the control sample prepared with wheat flour. Ca, P, K, Fe, Mn, Mg, Zn and Cu contents (mg/100g) of gluten-free control samples increased from 57.86 to 60.35-92.30 (Ca), 275.10 to 285.67-329.67 (P), 155.42 to 168.42-202.70 (K), 0.92 to 0.98-1.36 (Fe), 0.87 to 0.89-1.28 (Mn), 15.63 to 21.68-42.63 (Mg), 0.64 to 0.77-0.96 (Zn) and 0.12 to 0.17-0.30 (Cu), respectively. An increase was determined in all mineral contents, but no significant difference was determined between Fe, Zn and Cu contents of cake samples. [46] used grape seed, blueberry and poppy seed in cookie formulation (5%) and reported that the all fortification agents increased Mg and Ca contents significantly ($p<0.05$). [47] reported that poppy seed is rich in Ca, P, K, Mg and Mn contents.

The lowest hardness value of gluten-free cakes was determined in the control sample. The use of grape seed, pomegranate seed, flaxseed, poppy seed and turmeric in the gluten-free cake formulation caused an increase in the hardness values, while no significant difference was found between the hardness values of the enriched samples (Figure 1). [39] reported an increase in hardness with the addition of turmeric (2-8%) to bread formulation. Similarly, [48] reported that the crumb hardness of white bread increased with the use of ground flaxseed (15%) in the formulation. The increase in crumb hardness is attributed to the lower loaf volume and denser texture. Similarly, [33] reported increased bread hardness with the use of grape seed flour over 5%.

The use of grape seed, pomegranate seed, poppy seed, flaxseed, and turmeric in addition to grape molasses in cake samples resulted in lower appearance, texture, mouthfeel and overall acceptability scores compared to the gluten-free control sample (Figure 2). Cake samples prepared with poppy seed and grape seed scored equivalent to the gluten-free control sample in terms of taste-odor. In the cake samples, grape seed, pomegranate seed and turmeric decreased the mouthfeel scores more than the flaxseed and poppy seed compared to the control sample. Cakes containing poppy seed and flaxseed received the highest overall acceptability scores after the control sample. [49] used ground flaxseed flour in bread and reported that bread sample prepared with 15% flaxseed flour was the most similar to control. In addition, flaxseed breads at other ratios were also found acceptable. Similar results regarding that flaxseed did not have a negative effect on sensory properties were reported by [41]. [33] used grape seed flour in the bread formulation (0-10%) and reported that breads prepared with 5% grape seed flour had acceptable physical and sensory properties.

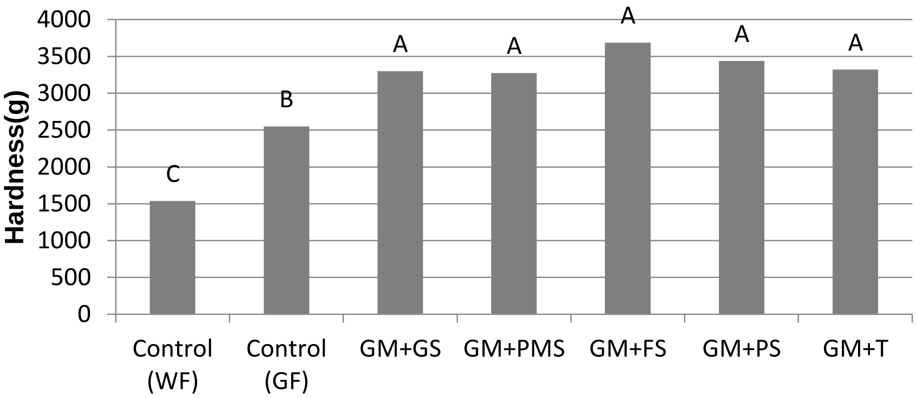

Figure 1. Hardness values of gluten-free cake samples (WF: Wheat flour. GF:Gluten-free; GM: Grape molasses; GS: Grape seed; PMS: Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric)

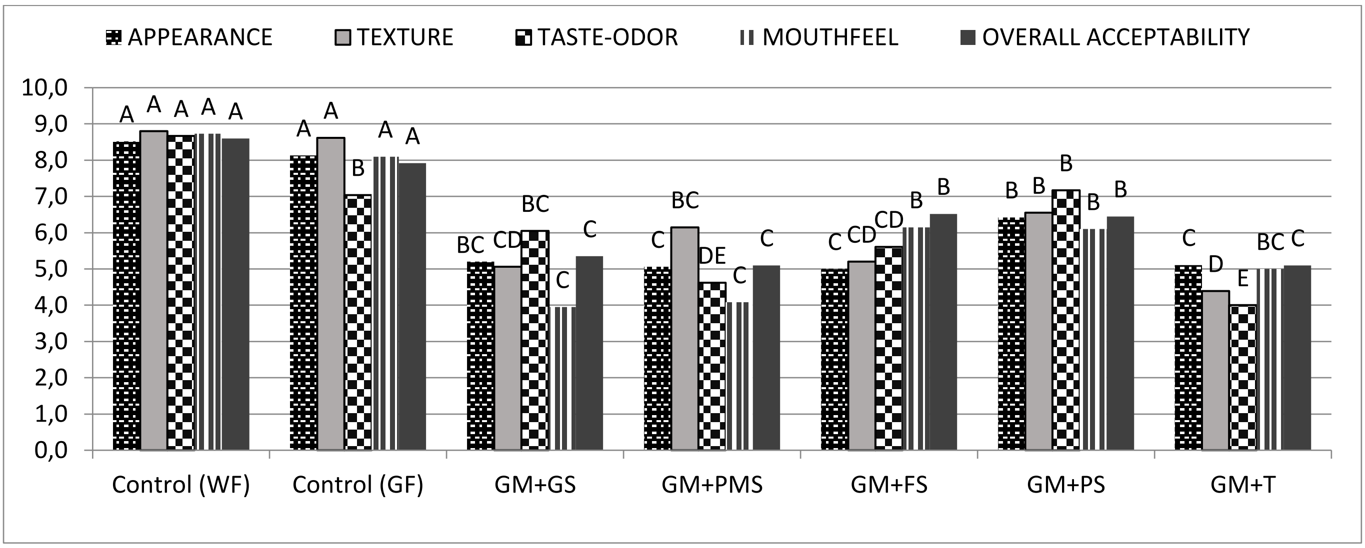

Figure 2. Sensory analysis results of gluten-free cake samples (WF: Wheat flour. GF:Gluten-free; GM:Grape molasses; GS:Grape seed; PMS:Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric)

Table 5. Mineral contents of gluten-free cake samples (mg/100g)*

	Ca	P	K	Fe	Mn	Mg	Zn	Cu
Control (WF)	34.75±0.72^{d}	241.00±6.36^{d}	118.20±4.48^{c}	0.47±0.16^{a}	0.32±0.10^{b}	8.56±1.64^{d}	0.57±0.08^{a}	0.10±0.08^{a}
Control (GF)	57.86±1.40^{c}	275.10±7.17^{c}	155.42±7.24^{b}	0.92±0.24^{a}	0.87±0.24^{ab}	15.63±2.87^{cd}	0.64±0.03^{a}	0.12±0.14^{a}
GM+GS	92.30±3.21^{a}	293.20±3.82^{bc}	176.13±5.37^{ab}	0.98±0.25^{a}	0.89±0.17^{ab}	21.68±2.57^{bc}	0.77±0.08^{a}	0.18±0.10^{a}
GM+ PMS	77.86±2.06^{b}	310.63±7.40^{ab}	202.70±14.28^{a}	1.07±0.16^{a}	0.93±0.18^{ab}	24.50±3.90^{bc}	0.82±0.11^{a}	0.30±0.13^{a}
GM+FS	79.96±4.47^{ab}	321.85±10.25^{a}	191.36±6.31^{a}	1.36±0.23^{a}	1.09±0.20^{a}	42.63±1.46^{a}	0.96±0.13^{a}	0.27±0.08^{a}
GM+PS	91.28±3.05^{a}	329.67±7.17^{a}	183.09±7.76^{ab}	1.22±0.28^{a}	1.28±0.10^{a}	28.63±4.00^{a}	0.93±0.17^{a}	0.20±0.11^{a}
GM+T	60.35±5.26^{c}	285.67±6.58^{bc}	168.42±12.02^{ab}	1.31±0.31^{a}	0.94±0.14^{ab}	25.67±2.93^{bc}	0.78±0.10^{a}	0.17±0.03^{a}

* Results are on dry weight basis; Mean values represented by different letters are statistically different from each other ($p < 0.05$). Values are the average of triplicate measurements on the duplicate samples. WF: Wheat flour. GF:Gluten-free; GM: Grape molasses; GS: Grape seed; PMS: Pomegranate seed; FS:Flaxseed; PS:Poppy seed; T:Turmeric

CONCLUSION

In this study, the sugar used in the gluten-free cake formulation was replaced with 75% grape molasses. In addition, the effects of replacing gluten-free cake mix with 5% grape seed, pomegranate seed, flaxseed, poppy seed and turmeric on the quality of cakes were investigated. In the cake samples, the use of grape molasses together with grape seed, pomegranate seed, flaxseed, poppy seed and turmeric decreased the crust and crumb L* values, while increasing the a * and b * values compared to the gluten-free control samples. In general, the volume index values decreased with the use of additives. All additives significantly increased the ash and crude protein content of the cake samples, while flaxseed and poppy seed also caused significant increases in crude fat content compared to the gluten-free control samples. Grape seed, pomegranate seed, flaxseed, poppy seed and turmeric significantly increased total phenolic content and antioxidant activity of cake samples compared to the gluten-free control sample. Grape seed, pomegranate seed, flaxseed and poppy seed increased Ca, while flaxseed and poppy seeds increased P and Mg contents of the cake samples. In addition to grape molasses, all additives in the formulation caused an increase in hardness values compared to the gluten-free control sample. Cakes containing poppy seed and flaxseed scored the highest overall acceptability scores among enriched samples after gluten-free control sample.Further studies could investigate the use of higher levels of flaxseed and poppy seed and lower levels of turmeric in gluten-free cake production.

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