

## Bioactive compounds, volatile, and texture profile of muffins after partial substitution of butter and milk

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### Abstract

The aim of the present work was to determine the optimal level for partial substitution of butter and milk with pistachio paste and rose water. The quantity of pistachio paste added to the muffins was 6, 9, and 12%, while the quantity of rose water was 5% for all the samples, except for control sample. A significant increase in protein (6.52 - 8.01%), total phenols (13.19 - 18.54 mg GAE/100 g), and antioxidant capacity (10.83 - 16.69% RSA) was observed, as well as a decrease in fat (13.06 - 11.98%). The concentrations of individual sugars namely sucrose, glucose, and fructose were not significantly influenced by the added pistachio paste. The volatile compounds which were predominant in the analysed samples were benzaldehyde, D-limonene, 1,3-dioxolane, 4-methyl-2-phenyl-,  $\beta$ -myrcene,  $\alpha$ -pinene,  $\beta$ -linalool, phenylethyl alcohol, and  $\beta$ -citronellol. Regarding the textural profile, the muffin samples added with pistachio paste and rose water were not significantly influenced ( $p > 0.05$ ).

### Keywords

muffins,  
pistachio,  
rose water,  
quality characteristics,  
sensory properties

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## Introduction

Muffins are a popular bakery product due to their convenient easy-to-eat form and long shelf-life (Sindhuja *et al.*, 2005). Muffins are a ready-to-eat snack foods (Sathiya Mala *et al.*, 2018) appreciated among consumers for their sensory attributes such as soft texture, pleasant taste, reliable cost, and availability in various versions (Mildner-Szkudlarz *et al.*, 2016). However, muffins have low dietary fibre content and high sugar and fat (Cho and Kim, 2014). Muffins are traditionally made from wheat flour (which is deficient in amino acids, *i.e.*, lysine, tryptophan, and some minerals) (Zouari *et al.*, 2016), sugar, oil, eggs, and milk as the main ingredients.

Muffins are the most commonly consumed snacks despite the growing awareness of the influence of food intake on people's health; in spite of nutritionists' recommendations to limit the consumption of sugar and fat. They are often consumed for breakfast, and alternatively, they can be served with tea or other meals (Rosales-Soto *et al.*, 2012). Muffins' composition can be easily adapted to meet the special needs of consumers (Zouari *et al.*, 2016). In response

to the growing consumer interest in healthy diet, food industry is increasingly focusing on designing an innovative health-promoting foods. Muffins are often used as matrices for introducing nutrients such as proteins and antioxidants (Mildner-Szkudlarz *et al.*, 2016), fibres (Heo *et al.*, 2019),  $\beta$ -carotene (Sathiya Mala *et al.*, 2018), fruits, nuts, herbs, spices (Sudha *et al.*, 2007), and linseed (Santiago *et al.*, 2018).

Muffin batter is a complex mixture of fat-in-liquid phase (oil/egg/sugar/water) in combination with dry ingredients (flour/leavening) which produces a porous structure with high volume (Matos *et al.*, 2014). In the present work, muffins were selected as the vehicle for fortification with pistachio paste and rose water. Pistachio nut (*Pistacia vera* L.) is nutritious and popular around the world (Venkatachalam and Sathe, 2006). Pistachio is cultivated in the Middle East, United States, and Mediterranean countries. The nutritional composition of pistachio includes fat, protein, carbohydrate, ash, and moisture with values of 45, 20, 28, 3, and 5%, respectively (w/w). The predominant fatty acid of pistachio oil is oleic acid (69.6%), followed by linoleic acid (15.4%), and palmitic acid (9.9%)

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(Venkatachalam and Sathe, 2006). Recent publications have shown beneficial effects of pistachio consumption on the risk factors of cardiovascular diseases, lipid parameters, endothelial functions, inflammations, and oxidative status (Sari *et al.*, 2010). When compared with other nuts, pistachios are very rich in phytosterols, potassium, vitamin B<sub>6</sub>, carotenoids, tocopherols (USDA, 2019), chlorophyll a, chlorophyll b, lutein, and anthocyanins (Bellomo and Fallico, 2007), and have been ranked among 50 foods containing the highest antioxidants (USDA, 2019). Pistachio seed is particularly appreciated for its flavour and emerald-green colour (Bellomo and Fallico, 2007).

Damask rose (*Rosa damascena* Mill.) is an important aromatic plant used in the commercial production of rose oil, rose water, and in perfume industry. It is a small plant with pleasant aroma and light pink flowers which blossom during spring (Haghighi and Tabrizi, 2013). The major components of rose water volatiles are phenyl ethyl alcohol, geraniol, and citronellol (Verma *et al.*, 2011). Rose water is a liquid preparation obtained by hydrodistillation of fresh rose flower petals (Agarwal *et al.*, 2005), and used as an additive for food flavouring, components in some cosmetic and medical preparations, and as perfume (Loghmani-Khouzani *et al.*, 2007).

The objective of the present work was to determine the optimal level of partial substitution of butter and milk with pistachio paste and rose water. Additionally, in order to prove the added value, the nutritional values, bioactive compounds, textural properties, flavour profile, and consumers' acceptance of the formulated muffins were also assessed.

## Materials and methods

### Muffin ingredients and preparation

The following raw materials and ingredients used in the preparation of muffins were purchased from local supermarket and bio food store in Cluj-Napoca, Romania: type 000 white flour, crystal type white sugar, multifloral honey, M size eggs, baking powder, cow's milk (1.5% fat), butter (65% fat), pistachio paste (obtained from 99% pistachio), and rose water. Muffins were produced in the pilot station of Faculty of Food Science and Technology, University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Romania.

The muffins were prepared according to Table 1. The amount of pistachio paste added was 6, 9, and 12%, and the quantity of rose water was 5% for all samples, except for control. Before use, the eggs were disinfected with 2% chlorine solution for 5 - 10 min, rinsed with water for 5 to 6 min, and whisked before mixed together with the other ingredients. The butter, pistachio paste, sugar, honey, milk, rose water, and baking powder were mixed with a mixer (6.9 L, Artisan, Empire Red - KitchenAid) for 3 min at speed number 3, and later, whisked egg was added, and mixed with the mixer for 2 min. Finally, the wheat flour were mixed, and the final dough/batter was obtained and poured into moulds, and baked (Zanolli, Italy) at 180°C for 20 - 25 min. The muffins were cooled for 1 h to avoid condensation build-up.

### Determination of physical properties

The mass was determined by weighing samples using a Shimadzu analytical balance. The upper diameter, lower diameter, and height of the samples were measured with callipers.

Table 1. Composition of muffin samples added with pistachio paste and rose water.

Ingredient	CS	S1	S2	S3
Wheat flour (g)	100	100	100	100
Egg (medium size)	1	1	1	1
Sugar (g)	50	50	50	50
Honey (g)	6.5	6.5	6.5	6.5
Butter (g)	44	38	35	32
Pistachio paste (g)	0	6	9	12
Milk (mL)	50	45	45	45
Rose water (mL)	0	5	5	5
Baking powder (g)	2.5	2.5	2.5	2.5

CS = control sample, muffins without the addition of pistachio paste; S1 = muffins with 6% pistachio paste; S2 = muffins with 9% pistachio paste; and S3 = muffins with 12% pistachio paste.

### Determination of chemical compositions

Chemical compositions (moisture, ash, and proteins) were determined according to STAS 91-2007 (RENAR, 2007). Nitrogen (N) content was determined using the Kjeldhal method, and crude protein was calculated by using 5.7 as N conversion factor for proteins of vegetable products, according to ISO 1871-2002 (ISO, 2002). Fat content was determined using the Soxhlet method according to ISO 6492:2001 (ISO, 2001), while acidity was determined using the ethyl alcohol method (67%, v/v) according to STAS 90/1988 (RENAR, 1988). Total carbohydrates were determined by subtracting content of moisture, protein, lipid, and ash (Eq. 1; Barros *et al.*, 2008):

$$\text{Total carbohydrates (g/100 g)} = 100 - [\text{moisture (g/100 g)} + \text{protein (g/100 g)} + \text{lipids (g/100 g)} + \text{ash (g/100 g)}] \quad (\text{Eq. 1})$$

Energy was determined from the content of protein, carbohydrate, and lipid using energy factors (Eq. 2; Barros *et al.*, 2007):

$$\text{Energy value (kcal/100 g)} = 4 \times (\text{g protein} + \text{g carbohydrate}) + 9 \times \text{g lipid} \quad (\text{Eq. 2})$$

### Determination of total phenolic content

In order to obtain the extract for determination of total phenolics and antioxidant activity, 1 g of sample was extracted with 20 mL of methanol using an ultrasonication bath for 10 min, and centrifuged at 4,000 rpm for 10 min. The extract was collected and stored at -18°C for further analysis. The total phenolic content was determined by the Folin-Ciocalteu method (Singleton *et al.*, 1999). Briefly, 0.1 mL of the extract was mixed with 6 mL of distilled water and 0.5 mL of Folin-Ciocalteu reagent. After 4 min, 1.5 mL of Na<sub>2</sub>CO<sub>3</sub> solution (7.5%) was added, and the sample was diluted to a final volume of 10 mL with distilled water. After incubation for 120 min at room temperature, the absorbance was read at 750 nm using a Shimadzu UV-1700 PharmaSpec spectrophotometer against a blank (sample replaced with methanol). The calibration curve was constructed using different concentrations of gallic acid standard ( $R^2 = 0.9936$ ), and the results were expressed as mg GAE/100 g fresh weigh.

### Determination of 2,2-diphenylpicrylhydrazil radical scavenging capacity (DPPH)

The DPPH scavenging activity assay was performed according to the method reported by Brand-Williams *et al.* (1995). Briefly, 3.9 mL of

methanolic DPPH (0.025 g/L) solution was allowed to react in darkness for 30 min with 10 µL of sample and 90 µL of distilled water. The absorbance was measured at 515 nm against methanol. The antioxidant activity was calculated using Eq. 3:

$$\% \text{ DPPH scavenging activity} = [(A_d - A_s) / A_d] \times 100 \quad (\text{Eq. 3})$$

where,  $A_d$  = absorbance of DPPH solution, and  $A_s$  = absorbance of the sample.

### Determination of individual sugars by HPLC

#### Materials

Acetonitrile (HPLC purity) was purchased from Merck (Darmstadt, Germany). The glucose, fructose, and sucrose standards were purchased from Sigma Aldrich (Milwaukee, USA). The ultrapure water used was Millipore water (18.2 MΩ•cm; Milli-Q Ultrapure water purification system, Millipore, USA). Ethanol (p.a.) was purchased from Nordic (Cluj-Napoca, Romania).

#### Sample preparation

Standard stock solutions (10 mg/mL) for each sugar were prepared by dissolving the solid in Millipore water. Working standard solutions were prepared by appropriate dilution of stock solutions in water.

The extraction of sugars from the muffin samples was carried out in Millipore water. Known amounts of samples were well milled, then extraction solvent was added, and the whole mixture was transferred to the rated flask, and brought to the mark. The mixture was ultrasonicated for 15 min and then centrifuged for 20 min at 4,000 rpm. The supernatant was then filtered through a 0.45 µm membrane filter, and injected into HPLC.

#### Instrument

The analyses were performed on a Jasco 980 HPLC chromatograph (Tokyo, Japan) equipped with HPLC pump (Model PU-980), ternary gradient unit (Model LG-980-02), column thermostat (Model CO-2060 Plus), UV-Vis detector (Model UV-975), refractive index detector (Model RI-2031 Plus), and an injection valve equipped with 20 µL sample loop (Rheodyne, USA). Samples were injected manually with a Hamilton Rheodyne (50 mL) syringe. The HPLC system was controlled, and the experimental data were analysed with the ChromPass software.

#### HPLC-RI method

Separation was performed on a CARBOsep

COREGel 87C (300 × 7.8 mm) column (Transgenomic, USA) with CARBOSep 87C guard column and CARBOSep 87C guard cartridge at 70°C column temperature. The mobile phase was ultra-pure Millipore water. The flow rate was 0.5 mL/min, and the injector volume was 20 µL. All analyses were performed in triplicate. The HPLC-RI method developed by Filip *et al.* (2016) was improved and optimised to identify and quantify the carbohydrates in muffin samples.

#### *Extraction and identification of volatile compounds*

The separation of the volatile compounds was achieved using a Shimadzu GC-MS QP-2010 (Shimadzu Scientific Instruments, Kyoto, Japan) model gas chromatograph-mass spectrometer equipped with a CombiPAL AOC-5000 autosampler (CTC Analytics, Zwingen, Switzerland) and ZB-5ms capillary column of 30 m × 0.25 mm (i.d.) and 0.25 µm film thickness (Phenomenex, USA). Muffin samples were placed in a headspace sealed vial, and incubated at 60°C for 20 min under continuous agitation, and for 15 min in the case of rose water and pistachio powder samples. The volatiles accumulated in the headspace of the vial were initially adsorbed into the Tenax trap (ITEX-2TRAPTXTA, (G23)-Siliconert 2000, Tenax ta 80/100 mesh, Switzerland) and then thermally desorbed into the GC-MS injector using an appropriate split ratio. The trap was afterwards flush-heated with N<sub>2</sub>. The program for the column oven temperature was 35°C (maintained for 5 min), raised to 155°C at 5°C/min, and then to 260°C at 10°C/min (hold for 5 min). The carrier gas was helium at a constant flow of 1 mL/min and the injector, ion source, and interface temperatures were set at 250°C. The MS detector was used in electron impact ionisation (EI) mode in a scan range of 35 - 400 *m/z*. The separated volatile compounds were tentatively identified by comparing the obtained mass spectra with those from NIST27 and NIST147 mass spectra libraries, and verified by comparison with retention indices drawn from www.pherobase.com and www.flavornet.org (for columns with a similar stationary phase to ZB-5ms), considering a minimum similarity of 85%. This technique offers a qualitative assessment of volatile profile of the samples, thus for each identified compound, the results were expressed as a fraction of its integrated ion area from the total ion chromatograms (TIC) area (100%) (Fărcaş *et al.*, 2015).

#### *Texture analysis*

Texture analysis was performed using the

Brookfield equipment with the following conditions: target value = 40% of the deformation, maximum test load = 5 g; test speed = 1 mm/s; geometry used = TA11/1000 Brookfield Kit samples (standard AOAC); cylindrical shape = diameter of 25.4 mm; transparent acrylic = weight of 21 g and 35 mm in height; waiting time between compression ramps = 5 s; and sample dimensions = 2.5 × 2.5 × 2.5 cm middle crumb. The specific texture parameters were computed by Texture Pro CT V1.6 software (Vlaic *et al.*, 2019).

#### *Acceptability test performed on the 9-point hedonic test*

Sensory evaluation of muffins was performed by means of the hedonic test according to ISO 13299:2016 (ISO, 2016). Briefly, the samples were sliced (thickness of slices was of about 1.5 cm), encoded, and served to the instructed consumers. The samples were analysed for 4 h after they were removed from the oven. Sensory characteristics of the samples were evaluated by a panel of 45 trained assessors (31 female and 14 male assessors), aged between 21 and 58. The degree of pleasure for different types of muffins was rated based on a 9-point hedonistic scale (1 being “extreme dislike” and 9 being “greatly like”). Overall exterior appearance of muffins such as aspect in section, smell acceptability, colour, taste, smell, appearance, and general appreciation were among the sensory attributes that were evaluated. Water was used to rinse the palate before and after each test.

#### *Statistical analysis*

The results of three independent assays (performed with replicates each) were expressed as mean value ± SD; for each parameter, Tukey's comparison tests was performed at a 95% confidence level.

## **Results and discussion**

#### *Analysis of pistachio paste*

The pistachio paste used in the process of producing fortified muffins was subjected to physicochemical analysis. Pistachio products have been rarely studied, with previous studies focusing more on raw, or roast pistachio. In the present work, it was found that pistachio paste contained very small amount of water (0.97 ± 0.04%) and total amount of minerals (2.95 ± 0.10%). The amounts of individual minerals have been reported by D'Evoli *et al.* (2015) where the amount of fat (54.55 ± 0.80%), protein (21.97 ± 0.36%), and bioactive compounds

(total phenols  $72.09 \pm 0.33$  mg GAE/100 g and DPPH inhibition  $82.47 \pm 1.57\%$  RSA) varied depending on the variety and region where the pistachio plants were grown. The values reported in the present work are in line with previous studies (Bellomo and Fallico, 2007; D'Evoli *et al.*, 2015). It is of utmost importance to note that the total amount of polyphenols reached up to 72.09 mg GAE/100 g, and the antioxidant capacity up to 82.47% RSA. The carbohydrate content was very low ( $19.58 \pm 0.50\%$ ), while the amount of lipids was very high ( $54.55 \pm 0.80\%$ ). Pistachio oil is characterised by a high proportion of unsaturated fatty acids, but with a wide variability in oleic and linoleic acid contents. Pistachio oil is an interesting source of phytosterols, tocopherol, and natural antioxidants (Catalán *et al.*, 2016).

#### Analysis of muffin samples

##### Physicochemical characteristics of muffins with pistachio and rose water

The physicochemical characteristics of muffin samples are shown in Table 2. To highlight the advantages of fortifying muffins with pistachio paste and rose water, they are compared with control sample (muffin samples without any additions).

Muffin heights were between 37.20 and 38.79 mm, while upper diameters (56.47 - 58.22 mm) were bigger than lower ones (51.32 - 53.39 mm), and the weight was between 29.84 - 30.36 g, a direct consequence of conical shaped paper moulds. There was no statistically significant influence of the

addition of the pistachio paste on the physical properties (upper diameter, lower diameter, height, and weight). This is similar to that reported by Miranda-Villa *et al.* (2018).

Pistachio paste muffins showed higher moisture contents than the control, but not statistically significant. The higher the pistachio content, the higher the moisture content; owing to the water-holding capacity of the dietary fibre, as previously noted by Kim *et al.* (2012) for the fibres of *Opuntia humifusa*. Meanwhile, ash increased from 0.89 - 1.19%. According to the results obtained by Heo *et al.* (2019) and Zin *et al.* (2014), the inorganic components in food are related to the ash content. Therefore, pistachio paste was considered to have capability to improve the mineral contents of muffins.

As expected, the amount of protein increased from 6.52 to 8.01% with the addition of the pistachio paste, which is a protein-rich source (21.97%). With the addition of a protein-rich supplement, it is but normal for this percentage to increase such as muffins with cricket powder (Pauter *et al.*, 2018) and muffins with squash seed dietary fibre. Although pistachio paste is a rich source of fat (54.55%), the total amount of fat decreased from 13.06 to 11.98%, due to the replacement of butter (65% fat) with pistachio paste, which has a lower fat content than butter.

The total amount of carbohydrates and energy value was calculated according to the aforementioned parameters, and both showed a

Table 2. Physicochemical characteristics and energy values of muffin samples added with pistachio paste and rose water.

Sample	CS	S1	S2	S3
Upper diameter (mm)	$58.22 \pm 0.28^a$	$58.06 \pm 0.37^a$	$57.62 \pm 0.85^a$	$56.47 \pm 0.74^a$
Lower diameter (mm)	$53.39 \pm 0.37^a$	$52.9 \pm 0.28^{ab}$	$51.74 \pm 0.74^{ab}$	$51.32 \pm 0.33^b$
Height (mm)	$38.79 \pm 0.22^a$	$38.68 \pm 0.57^a$	$37.80 \pm 0.35^a$	$37.20 \pm 0.40^a$
Weight (g)	$29.84 \pm 0.39^a$	$30.34 \pm 0.31^a$	$30.69 \pm 0.08^a$	$30.36 \pm 0.59^a$
Moisture (%)	$24.55 \pm 0.43^a$	$24.59 \pm 0.25^a$	$24.66 \pm 0.47^a$	$24.73 \pm 0.25^a$
Ash (%)	$0.89 \pm 0.14^a$	$0.94 \pm 0.06^a$	$1.08 \pm 0.04^a$	$1.19 \pm 0.05^a$
Protein (%)	$6.52 \pm 0.44^b$	$6.93 \pm 0.27^{ab}$	$7.50 \pm 0.41^{ab}$	$8.01 \pm 0.26^a$
Fat (%)	$13.06 \pm 0.28^a$	$12.83 \pm 0.20^{ab}$	$12.22 \pm 0.16^{bc}$	$11.98 \pm 0.15^c$
Total carbohydrate (g/100 g)	$54.88 \pm 0.41^a$	$54.72 \pm 0.78^a$	$54.66 \pm 1.08^a$	$54.11 \pm 0.71^a$
Energy value (kcal/100 g)	$363.10 \pm 0.91^a$	$362.07 \pm 0.25^a$	$358.60 \pm 1.29^b$	$356.22 \pm 0.47^b$
Total phenol (mg GAE/100 g)	$13.19 \pm 0.18^c$	$16.60 \pm 0.39^b$	$17.53 \pm 0.58^{ab}$	$18.54 \pm 0.33^a$
DPPH inhibition (% RSA)	$10.83 \pm 0.27^d$	$12.31 \pm 0.35^c$	$14.54 \pm 0.29^b$	$16.69 \pm 0.21^a$

CS = control sample, muffins without the addition of pistachio paste; S1 = muffins with 6% pistachio paste; S2 = muffins with 9% pistachio paste; and S3 = muffins with 12% pistachio paste. Values are mean  $\pm$  SD. Means with similar lowercase superscripts letters within a row are not significantly different ( $p > 0.05$ ).

decrease with the addition of pistachio paste and rose water (54.88 - 54.11 g/100 g for carbohydrates and 363.10 - 356.22 kcal for energy value, respectively). These results are close to those reported by Heo *et al.* (2019), but with a lower energy value than that reported by Pauter *et al.* (2018).

The amounts of polyphenols has increased in a statistically significant manner ( $p < 0.05$ ) from 13.19 - 18.54 mg GAE/100 g. The muffins' antioxidant capacity has also increased from 10.83 - 16.69%. These increases are justified by the properties of pistachio paste. The same increases were also reported for muffins with buckwheat flakes

and amaranth (Antoniewska *et al.*, 2018), black rice (Croitoru *et al.*, 2018), and *Prosopis alba* (Sciannaro *et al.*, 2018).

#### Analysis of individual sugars by HPLC method

For individual sugar analysis, the sucrose, glucose, and fructose contents were analysed. Representative chromatograms for sugar standards and muffin samples are presented in Figure 1.

With the addition of pistachio paste in the muffins, a slight decrease in sucrose (1.425 to 1.352 g/100 g) and glucose (0.318 to 0.307 g/100 g) contents were noticed, and the variation of the

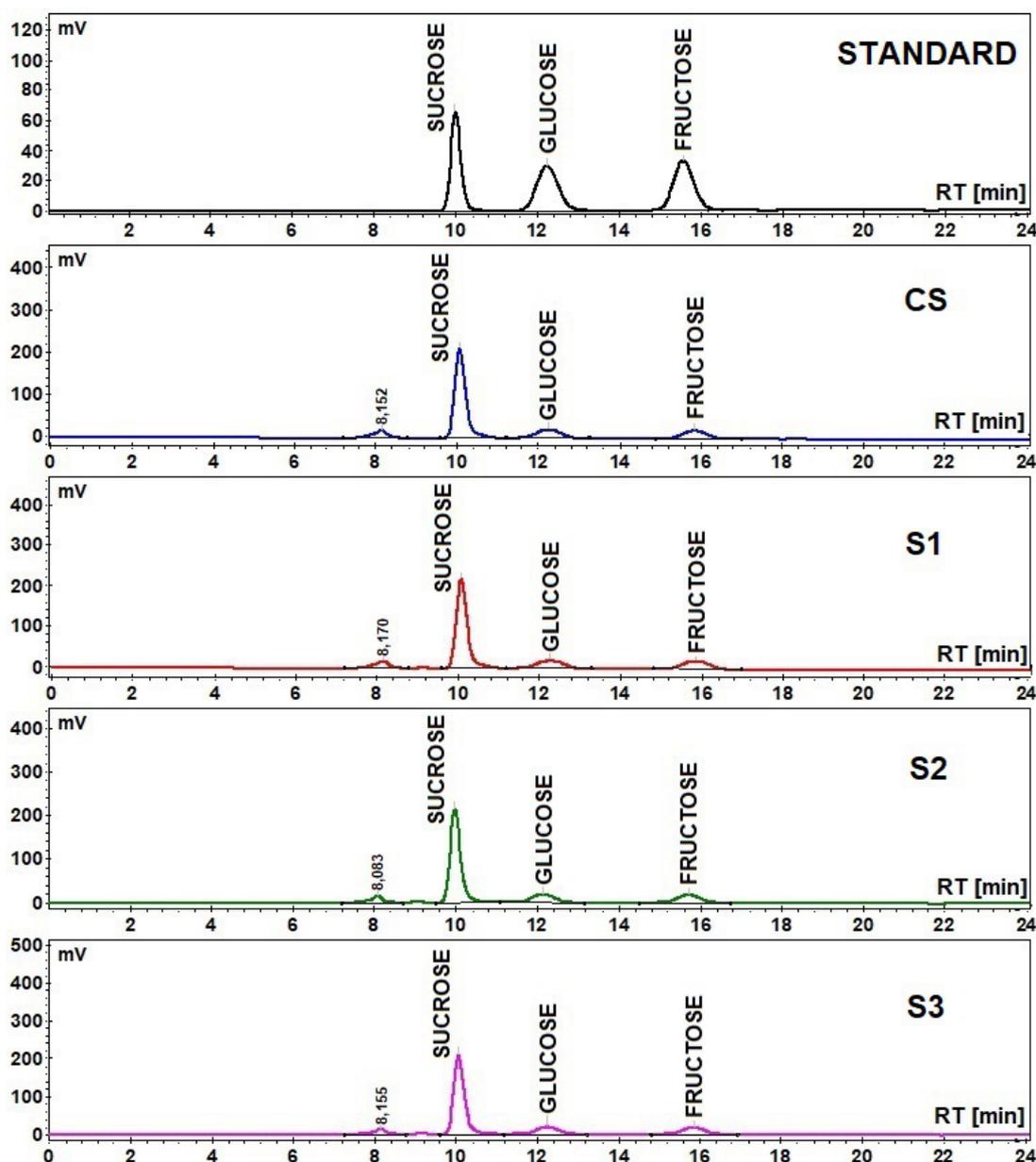


Figure 1. HPLC-RI chromatograms of the standard sugars (sucrose, glucose, and fructose) and muffin samples namely CS = control sample, muffins without the addition of pistachio paste; S1 = muffins with 6% pistachio paste; S2 = muffins with 9% pistachio paste; and S3 = muffins with 12% pistachio paste.

Table 3. Texture profile analysis of muffin samples added with pistachio paste and rose water.

Sample	CS	S1	S2	S3
Hardness cycle 1 (g)	515.00 ± 67.00 <sup>a</sup>	555.00 ± 273.00 <sup>a</sup>	680.00 ± 162 <sup>a</sup>	556.00 ± 57.00 <sup>a</sup>
Sample height (mm)	24.96 ± 1.01 <sup>a</sup>	24.92 ± 1.12 <sup>a</sup>	25.48 ± 0.77 <sup>a</sup>	25.58 ± 0.42 <sup>a</sup>
Hardness work cycle 1 (mJ)	32.60 ± 5.80 <sup>a</sup>	31.90 ± 11.50 <sup>a</sup>	39.40 ± 8.00 <sup>a</sup>	35.60 ± 4.80 <sup>a</sup>
Recoverable work cycle 1 (mJ)	7.00 ± 1.70 <sup>a</sup>	7.10 ± 3.50 <sup>a</sup>	9.20 ± 2.60 <sup>a</sup>	7.70 ± 1.10 <sup>a</sup>
Total work cycle 1 (mJ)	39.70 ± 7.50 <sup>a</sup>	39.00 ± 15.00 <sup>a</sup>	48.50 ± 10.50 <sup>a</sup>	43.30 ± 5.90 <sup>a</sup>
Peak stress (dyn/cm <sup>2</sup> )	80754.50 ± 10522.50 <sup>a</sup>	87004.6 ± 42813.2 <sup>a</sup>	106748.60 ± 25408.30 <sup>a</sup>	87240.00 ± 8969.80 <sup>a</sup>
Resilience	0.22 ± 0.10 <sup>a</sup>	0.22 ± 0.03 <sup>a</sup>	0.23 ± 0.02 <sup>a</sup>	0.21 ± 0.01 <sup>a</sup>
Hardness cycle 2 (g)	417.00 ± 44.00 <sup>a</sup>	459.00 ± 247.00 <sup>a</sup>	554.00 ± 140.00 <sup>a</sup>	429.00 ± 27.00 <sup>a</sup>
Hardness work cycle 2 (mJ)	14.10 ± 3.00 <sup>a</sup>	14.40 ± 7.30 <sup>a</sup>	17.60 ± 4.90 <sup>a</sup>	14.90 ± 1.90 <sup>a</sup>
Cohesiveness	0.43 ± 0.02 <sup>a</sup>	0.44 ± 0.06 <sup>a</sup>	0.44 ± 0.04 <sup>a</sup>	0.42 ± 0.03 <sup>a</sup>
Recoverable work 2 (mJ)	5.00 ± 1.10 <sup>a</sup>	5.10 ± 2.90 <sup>a</sup>	6.60 ± 1.90 <sup>a</sup>	5.10 ± 0.60 <sup>a</sup>
Total work cycle 2 (mJ)	19.10 ± 4.10 <sup>a</sup>	19.60 ± 10.20 <sup>a</sup>	24.10 ± 6.70 <sup>a</sup>	20.00 ± 2.50 <sup>a</sup>
Springiness (mm)	8.59 ± 0.29 <sup>a</sup>	8.52 ± 0.24 <sup>a</sup>	8.72 ± 0.10 <sup>a</sup>	8.76 ± 0.16 <sup>a</sup>
Springiness index	0.87 ± 0.02 <sup>a</sup>	0.86 ± 0.01 <sup>a</sup>	0.86 ± 0.02 <sup>a</sup>	0.86 ± 0.02 <sup>a</sup>
Gumminess (g)	223.00 ± 36.00 <sup>a</sup>	253.00 ± 162.00 <sup>a</sup>	304.00 ± 95.00 <sup>a</sup>	232.00 ± 23.00 <sup>a</sup>
Chewiness (mJ)	18.80 ± 3.70 <sup>a</sup>	21.00 ± 12.90 <sup>a</sup>	26.00 ± 8.10 <sup>a</sup>	20.00 ± 2.30 <sup>a</sup>
Chewiness index (g)	193.00 ± 32.00 <sup>a</sup>	217.00 ± 140.00 <sup>a</sup>	263.00 ± 86.00 <sup>a</sup>	199.00 ± 21.00 <sup>a</sup>
Corrected cohesiveness	0.35 ± 0.02 <sup>a</sup>	0.36 ± 0.05 <sup>a</sup>	0.36 ± 0.04 <sup>a</sup>	0.35 ± 0.02 <sup>a</sup>
Corrected gumminess (g)	184.00 ± 31.00 <sup>a</sup>	210.00 ± 135.00 <sup>a</sup>	248.00 ± 81.00 <sup>a</sup>	193.00 ± 22.00 <sup>a</sup>
Corrected chewiness (mJ)	15.60 ± 31.00 <sup>a</sup>	17.40 ± 10.80 <sup>a</sup>	21.30 ± 6.90 <sup>a</sup>	16.60 ± 2.10 <sup>a</sup>

CS = control sample, muffins without the addition of pistachio paste; S1 = muffins with 6% pistachio paste; S2 = muffins with 9% pistachio paste; and S3 = muffins with 12% pistachio paste. Values are mean ± SD. Means with similar lowercase superscripts letters within a row are not significantly different ( $p > 0.05$ ).

Table 4. Mean relative concentration (% from total peak areas) of volatile compounds as analysed by HS-ITEX/GC-MS technique.

<b>Volatile compound</b>	<b>CS</b>	<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>Pistachio paste</b>	<b>Rose water</b>
Butanal, 3-methyl-	18.88 ± 0.45	12.94 ± 0.98	16.17 ± 0.50	13.02 ± 1.08	3.51 ± 0.52	-
Butanal, 2-methyl-	6.49 ± 0.24	4.05 ± 0.24	5.35 ± 0.24	3.83 ± 0.16	1.00 ± 0.02	-
Acetic acid	3.47 ± 0.39	1.37 ± 0.09	0.81 ± 0.15	1.07 ± 0.08	-	-
2-Propanol, 1-methoxy-	-	11.8 ± 0.26	-	11.93 ± 1.10	-	-
2,3-Pentanedione	5.06 ± 0.46	5.2 ± 0.16	2.61 ± 0.39	4.46 ± 0.41	-	-
2-Propanone, 1-hydroxy-	-	2.83 ± 0.19	-	-	-	-
Ethane, 1,1-diethoxy-	-	-	-	-	2.61 ± 0.28	-
1H-Pyrrole, 1-methyl-	-	-	-	-	9.08 ± 0.28	-
Disulphide, dimethyl	2.45 ± 0.16	2.48 ± 0.33	2.22 ± 0.28	2.27 ± 0.18	-	-
1-Butanol, 2-methyl-	-	-	-	-	3.33 ± 0.39	-
Propylene glycol	-	-	-	-	3.88 ± 0.15	-
Propanoic acid, 2-methyl-, ethyl ester	1.85 ± 0.11	1.53 ± 0.31	1.30 ± 0.41	0.59 ± 0.11	-	-
Toluene	4.28 ± 0.24	3.27 ± 0.22	2.72 ± 0.18	2.35 ± 0.32	-	-
Hexanal	2.51 ± 0.21	1.59 ± 0.39	2.22 ± 0.29	2.06 ± 0.15	0.36 ± 0.15	-
Furfural	-	5.03 ± 0.15	3.42 ± 0.35	4.82 ± 0.69	-	-
2-Furanmethanol	-	5.22 ± 0.25	1.99 ± 0.29	1.00 ± 0.07	-	-
2-Heptanone	5.52 ± 0.22	3.17 ± 0.16	3.70 ± 0.26	3.42 ± 0.43	-	-
Heptanal	0.59 ± 0.05	-	-	-	-	-
α-Pinene	0.83 ± 0.07	1.12 ± 0.09	2.59 ± 0.50	3.32 ± 0.42	9.39 ± 0.38	-
Benzaldehyde	4.34 ± 0.29	5.61 ± 0.38	10.80 ± 0.45	10.75 ± 0.89	57.46 ± 1.73	0.16 ± 0.04
5-Hepten-2-one, 6-methyl-	-	-	-	-	-	2.28 ± 0.28

Phenol	3.87 ± 0.15	1.99 ± 0.24	3.33 ± 0.33	1.8 ± 0.25	-	1.82 ± 0.19
β-Pinene	-	-	-	-	0.16 ± 0.04	-
β-Myrcene	-	-	1.05 ± 0.24	0.64 ± 0.12	0.32 ± 0.09	-
p-Cymene	-	-	0.57 ± 0.19	0.27 ± 0.12	-	-
3-Carene	-	-	-	-	0.30 ± 0.09	-
D-Limonene	1.21 ± 0.14	1.16 ± 0.16	5.73 ± 0.35	3.84 ± 0.42	4.48 ± 0.48	0.13 ± 0.02
Benzyl Alcohol	-	-	-	-	-	0.25 ± 0.05
Acetophenone	7.51 ± 0.32	5.21 ± 0.16	5.75 ± 0.36	4.05 ± 0.43	-	0.12 ± 0.01
2-Nonanone	1.26 ± 0.09	0.90 ± 0.12	1.05 ± 0.08	0.77 ± 0.19	-	-
1-Octanol	-	-	-	-	-	0.36 ± 0.09
β-Linalool	-	0.41 ± 0.09	0.96 ± 0.07	0.66 ± 0.26	-	6.67 ± 0.45
Maltol	-	0.44 ± 0.09	0.16 ± 0.08	-	-	-
Phenylethyl alcohol	-	4.13 ± 0.11	4.76 ± 0.28	3.26 ± 0.32	-	47.99 ± 0.25
2H-Pyran, tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-	-	-	-	-	-	0.10 ± 0.01
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	0.24 ± 0.07	1.18 ± 0.22	0.80 ± 0.19	1.32 ± 0.28	-	1.28 ± 0.09
Terpinolene	-	-	-	-	0.74 ± 0.26	-
Benzoic acid	26.4 ± 1.07	14.33 ± 0.14	16.16 ± 0.41	14.52 ± 0.60	0.61 ± 0.12	0.31 ± 0.08
1-Octanol, 2,7-dimethyl-	-	-	-	-	-	0.14 ± 0.01
α-Terpineol	-	-	-	-	-	2.52 ± 0.06
γ-Terpineol	-	-	-	-	-	0.24 ± 0.03
α-Citronellol	-	-	-	-	-	0.73 ± 0.05
β-Citronellol	-	-	1.84 ± 0.15	1.26 ± 0.12	1.32 ± 0.12	26.87 ± 0.35

<i>cis</i> -Geraniol	-	-	-	-	-	-	-	-	2.56 ± 0.32
Acetic acid, 2-phenylethyl ester	-	-	-	-	-	-	-	-	0.31 ± 0.04
Nonanoic acid	-	-	-	-	-	-	-	-	0.15 ± 0.04
Ethanol, 2-ethoxy-1,2-diphenyl-	-	-	-	-	-	-	-	1.71 ± 0.12	-
1,3-Dioxolane, 4-methyl-2-phenyl-	-	-	0.66 ± 0.07	0.72 ± 0.155	-	-	-	1.06 ± 0.09	-
2-Decanone	0.35 ± 0.08	0.38 ± 0.12	-	-	-	-	-	-	-
1-Undecanol	-	0.26 ± 0.04	-	-	-	-	-	-	-
Eugenol methyl ether	-	-	-	-	-	-	-	-	0.11 ± 0.01
1-Dodecanol	-	-	-	-	-	-	-	-	0.09 ± 0.01
Isoeugenol methyl ether	-	-	-	-	-	-	-	-	4.55 ± 0.45
1,6,10-Dodecatrien-3-ol, 3,7,11-trimethyl-	-	-	-	-	-	-	-	-	0.09 ± 0.01
Diethyl phthalate	0.71 ± 0.09	0.54 ± 0.32	0.05 ± 0.01	0.32 ± 0.056	-	-	-	-	-
Benzophenone	1.11 ± 0.09	0.69 ± 0.14	0.79 ± 0.14	0.53 ± 0.169	-	-	-	-	-
Vinyl benzoate	1.07 ± 0.05	-	-	0.88 ± 0.12	-	-	-	-	-
Octanoic acid, decyl ester	-	-	-	-	-	-	-	-	0.15 ± 0.02
n.i.	-	1.15 ± 0.09	-	0.26 ± 0.04	-	-	-	-	-

CS = control sample, muffins without the addition of pistachio paste; S1 = muffins with 6% pistachio paste; S2 = muffins with 9% pistachio paste; S3 = muffins with 12% pistachio paste. Values are mean ± SD. n.i. = not identified.

fructose content between 0.286 and 0.297 g/100 g was also noticed (Table 3). As compared to other studies on individual sugar contents (Sonmezdag *et al.*, 2019), the amount of sucrose reached up to 22 g/100 g, and glucose and fructose up to 6 g/100 g for gluten-free muffins with *Prosopis alba* flour. Therefore, muffins formulated in the present work had a lower content of sucrose, glucose, and fructose.

#### *ITEX/GC-MS profile of volatile compounds*

A total of 33 compounds were identified in the analysed muffin samples (Table 4), 17 compounds in the pistachio paste sample, and 25 compounds in the rose water sample.

The major compound in the pistachio paste was benzaldehyde which gives the characteristic aroma of pistachio and almonds. The level of the benzaldehyde in the muffin samples increased with the increase of added pistachio paste. The same pattern was also noticed for  $\alpha$ -pinene, another characteristic compound of pistachio paste which imparts a pine-like flavour.

The main volatile compounds identified in the rose water were phenylethyl alcohol (47.99%) and  $\beta$ -citronellol (26.87%). These compounds contributed to a sweet (honey-like) and floral (rose and lilac) notes to the aroma profile of the samples. They were identified only in the muffin samples with added rose water and not in the control sample. Nevertheless, due to their high volatility when added in the muffins, these compounds may be lost during baking process, but some amounts are still retrieved in the final products, imparting their specific aroma.

#### *Texture profile analyses*

The texture (hardness, height, resilience, cohesiveness, springiness, gumminess, and chewiness) of muffins with pistachio paste and rose water was evaluated (Table 3). Textural characteristics are of a prime importance since they can affect consumer acceptance of products (Shevkani and Singh, 2014). The control sample showed the lowest value of hardness regardless of the cycle (515 g for cycle 1 and 417 g for cycle 2), and increased insignificantly ( $p > 0.05$ ) with the addition of pistachio paste and rose water, up to 680 g and 554 g, respectively. Heo *et al.* (2019) reported similar results in muffins with dietary fibre from kimchi. The cohesiveness values did not change significantly, corroborating the findings of Marchetti *et al.* (2018), in which the muffins were supplemented with pecan nut flour. The springiness and resilience of the muffins with pistachio paste showed a slight decrease, which is comparable to the results obtained

by Heo *et al.* (2019). The muffins also showed slight decrease in cohesiveness values (a factor associated with increased hardness), while the fluctuating values for chewiness were statistically insignificant (Table 3).

#### *Sensory analysis*

Health-promoting properties and high nutritional value must be accompanied by sensory attractiveness (Sun-Waterhouse and Wadhwa, 2013) to create a viable product. In the present work, sensory features namely exterior appearance, appearance in the section, colour core, taste, smell, and general acceptance scored of over 7 ("I like moderately") and 8 ("I really like"). The mean sensory scores for the exterior look dropped from 7.95 in CS to 7.82 in P3. The scores for appearance in the section were reported similarly. These minor decreases were statistically insignificant ( $p > 0.05$ ). The colour core of the muffins dropped from 8.24 in CS to 7.41 in P3 due to consumers' lack of preference to an unusual colour of the muffins. These results are in agreement with those reported by Kaur and Kaur (2018) who observed that the colour score of muffins decreased with the increase in flaxseed content. For taste, the rating score increased from 7.40 in CS to 7.68 in P3. This could be due to the taste of pistachio and rose water. The odour of muffin samples showed minor and statistically insignificant decrease ( $p > 0.05$ ) from 8.42 in CS to 8.30 in P3. Even though four out of five characteristics showed minor decrease and statistically insignificant ( $p > 0.05$ ), the general acceptance of muffin samples showed an increase from 7.48 to 7.85. It was noted that taste had a major influence on consumers' perception. Thus, the most appreciated sample, in terms of general acceptance, was P3 with 12% pistachio paste.

#### **Conclusions**

The present work demonstrated that partial replacement of butter and milk with pistachio paste and rose water in the muffins improved both their nutritional and physico-chemical features, as well as the sensory characteristics of the end product. Pistachio paste was proven to be a rich source of protein, fat, and total phenols with high antioxidant capacity, whereas rose water was proven to have flavour enhancement properties. Since the bakery products made from refined flour were low in vitamins, minerals, and dietary fibres, pistachio paste incorporation could enhance the nutritive value of muffins. Further, physico-chemical features such as upper and lower diameters, height, weight, moisture,

ash, total carbohydrates, and energy value were not significantly influenced ( $p > 0.05$ ). In contrast, an increase in the protein contents, total phenols, and DPPH inhibition, alongside with a decrease in fat were noticed. The concentrations of individual sugars namely sucrose, glucose, and fructose were not significantly influenced by the added pistachio paste. The volatile compounds which were predominant in the analysed samples were benzaldehyde, D-limonene, 1,3-dioxolane, 4-methyl-2-phenyl-,  $\beta$ -myrcene,  $\alpha$ -pinene,  $\beta$ -linalool, phenylethyl alcohol, and  $\beta$ -citronellol. Regarding the textural profile, the muffin samples added with pistachio paste and rose water were not significantly influenced ( $p > 0.05$ ). Based on consumers' preference analysis, the sample with the highest amount of pistachio paste was the preferred one. Thus, the sample with the highest content of pistachio paste (P3) was recommended due to its sensory features and bioactive compounds.

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