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Gluten-Free Cookies Enriched with Baobab Flour (*Adansonia digitata* L.) and Buckwheat Flour (*Fagopyrum esculentum*)

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Featured Application: The paper has application potential in the bakery and related industries, considering that the proposed technological solutions can be implemented in the profile units in order to diversify the assortment range of flour products.

Abstract: To provide people with celiac disease with nutrient-rich gluten-free foods, this study aimed to produce cookies based on buckwheat and baobab flours, which were then subjected to nutritional, phytochemical, and sensory analyses. Results demonstrate that baobab flour (BF) and buckwheat flour (BWF) work together to enhance the nutritional properties of the cookies, in that nutrients that BWF is deficient in, BF provides sufficiently, and vice versa. BF is rich in minerals and carbohydrates, while BWF contains comparatively higher fat and protein levels. As for macro- and micro-elements, potassium (K) is the predominant macro-element in BF and BWF, with 13,276.47 ± 174 mg/kg and 1255.35 ± 58.92 mg/kg, respectively. The polyphenol content is higher in BF than BWF, at 629.7 ± 0.35 mg/100 g as opposed to 283.87 ± 0.06 mg/100 g. Similarly, the total flavonoid content and antioxidant activity of BF was greater than that of BWF, while BF exhibited 213.13 ± 0.08 mg/100 g and 86.62 ± 0.04%, in contrast to BWF, which had 125.36 ± 1.12 mg/100 g and 79.72 ± 0.01%, respectively. BF significantly enhanced the phytochemical composition of the cookies, with the richest sample being BBC3 containing 30% baobab. Buckwheat and baobab have the most abundant phenolic compounds of rutin and epicatechin, respectively. About the analysis of sensory attributes of the cookies, the partial substitution of BWF by BF of up to 20% (BWF3) significantly increased the scores for all attributes. Indeed, the appearance (physical aspect of the cookie: whether it is firm or not) and color (influence of baobab addition on cookie coloration) of the cookies were significantly improved with the addition of BF of up to 20%, but above 20% they were less appreciated. Similarly, up to 20% BF, the texture, flavor, and overall acceptability of the cookies were significantly improved. Taste, on the other hand, was not significantly improved, maybe due to the acidic taste provided by the baobab.

Keywords: gluten-free cookies; *Adansonia digitata*; *Fagopyrum esculentum*; celiac disease; individual polyphenols; antioxidant activity; flavonoids

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1. Introduction

Cookies are a beloved baked food around the globe, appreciated for their unique flavor and texture [1]. While wheat flour has been the primary ingredient in commercial cookies, there has been a growing interest in using gluten-free cereals due to the high prevalence of celiac disease [2]. Celiac disease is an auto-immune disorder affecting the small intestine. It is a disease that causes permanent intolerance to gluten ingestion in genetically predisposed individuals, in that gluten ingestion leads to the destruction of enterocyte villi in affected patients [3]. About 1% of the global population is affected by celiac disease, and they must adhere to a strict gluten-free diet, which may lack certain essential nutrients [4]. Gluten is a mixture of proteins that ensures the elasticity of the dough and the maintenance of fermentation gases during the technological process of producing bread. The absence of gluten leads to a flattened product with low volume. For people with celiac disease, gluten ingestion causes an abnormal immune response in the small intestine. This reaction not only destroys gluten, as if it is dangerous to the body, but also attacks the lining of the small intestinal mucosa. Inflammatory substances end up destroying the intestinal villi, which allow the nutrient absorption [5]. Thus, the development of gluten-free products for celiacs has become more challenging, requiring the formulation of products that are not only gluten-free but also nourishing.

Originally hailing from the high-altitude regions of southern China, buckwheat (*Fagopyrum esculentum*) now thrives in Asia, Europe, and America. Despite its name, buckwheat is not a true cereal but rather a pseudocereal. Buckwheat, an ancient crop, is abundant in phytochemicals that are salutary to health. High levels of flavonoids and polyphenols are found in buckwheat, with rutin and quercetin being the primary polyphenol group with antioxidant properties [6,7]. Buckwheat has piqued interest in recent years due to its nutritional and medicinal makeup, providing complex carbohydrates, protein, fiber, vitamins, and minerals. Buckwheat proteins are gluten-free and boast a balanced amino acid composition, which is advantageous to those with celiac disease [8,9]. This behavior of buckwheat proteins was previously demonstrated, also emphasizing that the effect of buckwheat flour consumption by celiac patients did not present any toxic prolamin or toxicity to the patients examined in the study [10]. Wheat proteins possess a deficiency of certain amino acids, such as lysine, while buckwheat flour has an excellent protein quality, including specific amino acids like leucine, lysine, histidine, and valine [11]. Generally speaking, every 100 g of buckwheat flour contains 16.66 g of protein, 3.42 g of fat, 72.19 g of carbohydrates, 0.58 g of fiber, and 1.68 g of ash [12]. When compared to wheat, buckwheat contains higher levels of essential minerals such as zinc (Zn), iron (Fe), magnesium (Mg), and calcium (Ca) [6,7].

Researchers seem to be increasingly interested in including buckwheat in the production of healthier foods such as bread, muffins, pasta, cakes, and many other foods [5,13–17], as its composition can have a positive impact on the health of consumers [13]. Taken together, these studies indicate that buckwheat makes an excellent contribution to improving the nutritional and technical quality of gluten-free baked foods due to its content of proteins, lipids, fibers, and minerals as well as bioactive compounds. Buckwheat is an ideal food ingredient for making a variety of foods in general, and bakery products in particular, due to the gluten-free aspect and its abundance of nutrients and health-promoting phenolic compounds [18].

The baobab (*Adansonia digitata* L.) is a big tree native to arid and semi-arid regions of West Africa. Much of its content is important in improving the livelihoods of people in several African countries [19,20]. The most useful part of the baobab tree is the fruit, which is a source of food for a large rural population. The powder obtained from the pulp can be used as a spice in traditional dishes or dissolved in water or milk to make a drink, known as Gunguliz in Sudan [19,21,22]. Baobab fruit is an excellent source of amino acids as it contains all eight essential amino acids and is also rich in vitamins and minerals [23,24]. According to several studies, its pulp contains calcium, phosphorus, potassium, carbohydrates, fiber, protein, lipids, and vitamin C [23,25–28]. It can provide 54–100% of the recommended dietary intake of vitamin C or H. The value is ten times that of oranges. Dried baobab pulp provides between 3 and 499 mg/100 g of vitamin C. It thus contributes to the European Union's (EU) recommended daily requirement for vitamin C (80 mg/day) [23,29]. Baobab pulp is also rich in phenolic compounds, flavonoids, and organic acids [30–33]. These advantages make baobab pulp an ideal carrier for functional food formulations.

Given the functional properties and health benefits of buckwheat and baobab, this study aimed to prepare cookies based on buckwheat flour and baobab pulp in different proportions and to assess the improvement in nutritional and phytochemical values, as well as the sensory properties of the finished products.

2. Materials and Methods

2.1. Preparation of Composite Flours

The baobab (BF) and buckwheat flours were procured, respectively, from Beninese producers and from the SELGROS supermarket in Romania. Composite buckwheat/baobab flours (3) were produced according to [25]. There were BBF1 (10% baobab flour (BF) and 90% buckwheat flour (BWF)), BBF2 (20% BF and 80% BWF), and BBF3 (30% BF and 70% BWF).

2.2. Cookie Preparation

The cookies were prepared according to Farzana et al., 2022, and Mounjouenpou et al., 2018 [18,34], with some modifications. All ingredients (honey, salt, butter, and egg) used for the formulation of the different cookies, except baobab and buckwheat flour, were acquired from the Profile supermarket, in Timisoara, Romania. Four (4) types of cookies (CC, BBC1, BBC2, and BBC3) were formulated with different levels of substitution of BWF by BF (CC—control cookie with 100% BWF; BBC1—biscuit with 10% BF and 90% BWF; BBC2—biscuit with 20% BF and 80% BWF; and BBC3—biscuit with 30% BF and 70% BWF). The dough was obtained by mixing honey, salt, butter, egg, and flour (Figure 1). It was then rolled up in a biodegradable plastic bag and placed in the fridge. After 6 h in the fridge (at 5 °C), the biodegradable plastic bag was removed, the dough cut into rounds, and placed in the oven at 180 °C for 10 min.

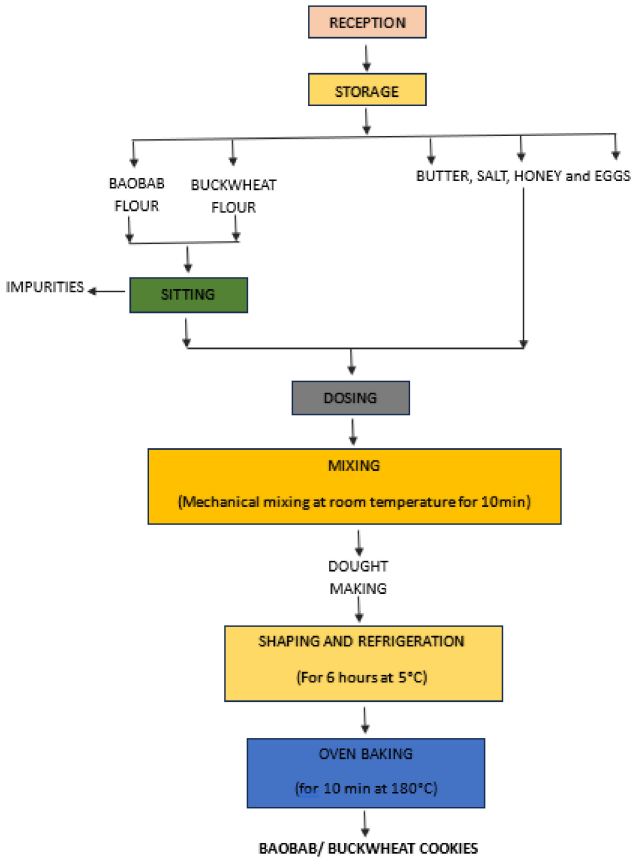

Figure 1. The technological scheme for obtaining cookies.

Table 1 shows the composition of each cookie.

Table 1. Recipe for cookies with composite baobab/buckwheat flour.

Samples	Ingredients					
	Baobab Flour (g)	Buckwheat Flour (g)	Butter (g)	Salt (g)	Honey (g)	Eggs (pcs)
CC	-	340	200	0.5	200	2
BBC1	34	306	200	0.5	200	2
BBC2	68	272	200	0.5	200	2
BBC3	102	238	200	0.5	200	2

Figure 1 shows the technological scheme for obtaining different cookies.

The different types of cookies that resulted from this study are shown in Figure 2.

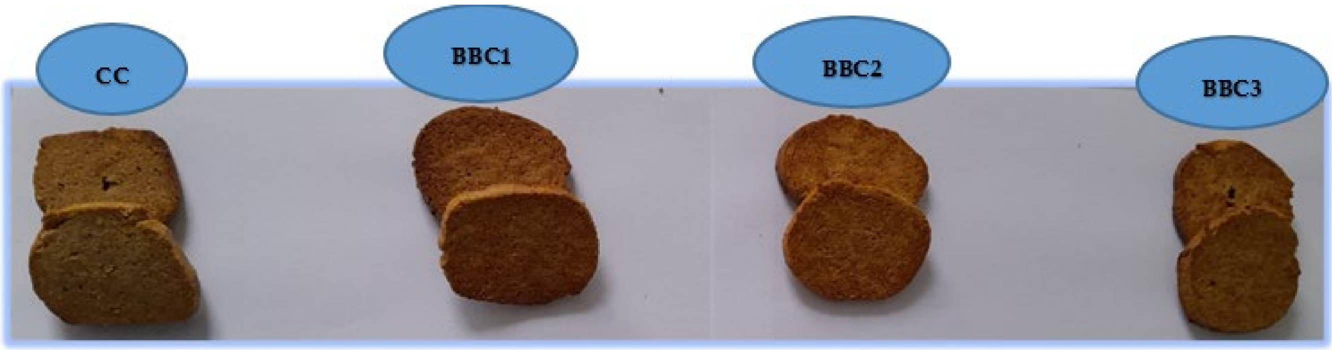

Figure 2. Control cookies and cookies with different proportions of buckwheat/baobab composite flour (CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour).

2.3. Determination of Proximate Composition

The proximate composition of baobab, buckwheat, and composite baobab/buckwheat flours was determined as part of this study. The same approach was carried out for the various cookies obtained. The methods used to achieve this are presented in Table 2.

Table 2. Methods used to determine the proximate composition of the various samples.

Parameters	Methods	Unit
Ash	ISO 2171/2007 [35]	%
Moisture	Standard Methods of the International Association for Cereal Science and Technology (2003) [36]	%
Protein	Standard Methods of the International Association for Cereal Science and Technology (2003) [36]	%
Fat	Association of Official Analytical Chemists [37]	
Carbohydrate	Carbohydrate content was calculated as the difference between 100 and the sum of moisture, ash, protein, and fat content [38]	g/100 g
Energy value	The energy value was obtained by summing 4 times the protein content, 4 times the carbohydrate content, and 9 times the fat content [38]	kcal/100 g

2.4. Macro- and Micro-Elements

The content of macro- and micro-elements in the various samples was obtained in this study using the method applied in the studies of Plustea et al., 2022 [38]. Results were reported in mg/kg.

2.5. Phytochemical Profile

2.5.1. Preparation of Alcoholic Extracts

Extraction was carried out according to the procedure described by [25]. Alcoholic extracts were prepared by dissolving 1 g of each sample in 10 mL of ethanol (70%) in a hermetically sealed plastic container, then filtering after 30 min of stirring.

2.5.2. Evaluation of Total Phenolic Content (TPC)

The TFC (mg gallic acid equivalents (GAE)/100 g) of different flours (baobab, buckwheat, and baobab/buckwheat) and different cookies (control cookies and cookies with composite baobab/buckwheat flour) was determined using the previously prepared extracts. For this purpose, the Folin–Ciocâlteu method described by Danciu et al., 2019 [39], and Obistioiu et al., 2021 [40], was used as a reference. All determinations were performed three times.

2.5.3. Determination of Total Flavonoid Content (TFC)

The TFC (in mg QE/100 g) of the different flours and cookies in this study was determined using quercetin (QE) as the standard solution and according to the method of [41].

2.5.4. Antioxidant Activity (AA)

The AA of the various cookies and flours was determined using a spectrophotometer at an absorbance of 518 min. The method described by [42] with a few modifications was used. AA was obtained in % according to the following formula:

$$AA\ (\%) = (ControlAbsorbance - SampleAbsorbance/ControlAbsorbance) \times 100$$

where ControlAbsorbance refers to the absorbance values of the control and SampleAbsorbance to the absorbance values of the sample.

Note that ethyl alcohol for the control absorbance was used.

2.5.5. Determination of Individual Polyphenols via LC-MS

To determine individual levels of polyphenols, the method described in [39] was utilized with slight adaptations. A Shimadzu chromatograph equipped with SPD-10A UV and LC-MS 2010 detectors was used with two chromatographic columns. Column I was Adsorbosphere UHS C18, 5 µm, lot 007250, while column II was EC 150/2 NU-CLE-ODUR C18 Gravity SB 150 × 2 mm × 5 µm, ref:760618.20, SN E 15110907, lot 38775055.

The following chromatographic conditions were used:

The mobile phase A was composed of water that was acidified with formic acid to a pH of 3. To create the mobile phase B, a combination of acetonitrile that had been acidified with formic acid to a pH of 3 was utilized.

The grading program was as follows: 0.01 to 20 min at 5% B; 20.01 to 50 min at 5 to 40% B; 50 to 55 min at 40 to 95% B; 55 to 60 min at 95% B.

The solvent flow rate was 0.3 mL/min at 20 °C and the wavelength used for the control was 280 to 320 nm. Calibration curves were performed in the range of 20–50 µg/mL. All measurements were performed in triplicate and results were expressed as mg/kg. All measurements were done in triplicate, and the results were expressed in mg/kg.

2.6. Sensory Analysis

The sensory evaluation of the different cookies was carried out in accordance with ISO 6658:2017 [43]. Twenty-one assessors participated in the sensory analysis. Panel members were trained and aged between 19 and 46. The panel comprised 12 females and 9 males.

2.7. Statistical Analysis

Three replicates were performed for each parameter. All results are expressed as mean ± SD. Microsoft Excel 365 was used to analyze differences between mean values using a two-sample *t*-test assuming equal variances. Differences were considered significant if $p < 0.05$.

3. Results and Discussion

3.1. Proximate Composition of Composite Flours and Cookies

The characteristics of the different flours and formulated cookies are presented in Table 3.

Table 3. Proximal composition of buckwheat flour, baobab flour, buckwheat/baobab composite flours and cookies.

Samples	Nutritional Characteristics					
	Moisture (%)	Mineral Content (%)	Proteins (%)	Lipids (%)	Carbohydrates (g/100 g)	Energy Values (kcal/100 g)
			Composite flours			
BWF	10.13 ± 1.15 [a]	1.66 ± 0.01 [a]	12.63 ± 0.02 [a]	3.19 ± 0.07 [a]	72.38 ± 1.09 [a]	368.79 ± 4.87
BF	13.79 ± 0.01 [b]	4.00 ± 0.02 [b]	4.31 ± 0.05 [b]	1.56 ± 0.02 [b]	76.34 ± 0.06 [b]	336.62 ± 0.16
BBF1	9.07 ± 0.06 [c]	1.99 ± 0.02 [c]	11.72 ± 0.03 [c]	2.46 ± 0.02 [c]	74.76 ± 0.09 [c]	368.03 ± 0.20
BBF2	9.23 ± 0.04 [c,d]	2.22 ± 0.19 [d]	11.13 ± 0.02 [d]	2.29 ± 0.04 [d]	75.13 ± 0.24 [c,d]	365.65 ± 0.96
BBF3	9.38 ± 0.03 [d]	2.67 ± 0.01 [e]	9.98 ± 0.03 [e]	2.20 ± 0.02 [d]	75.78 ± 0.01 [d]	362.80 ± 0.12
			Cookies			
CC	10.58 ± 0.28 [a]	1.10 ± 0.20 [a]	8.27 ± 0.03 [a]	22.96 ± 0.04 [a]	57.09 ± 0.13 [a]	468.05 ± 0.67
BBC1	11.58 ± 0.01 [b]	1.31 ± 0.04 [b]	7.67 ± 0.03 [b]	21.53 ± 0.08 [b]	57.91 ± 0.04 [a,b]	456.12 ± 0.56
BBC2	12.05 ± 0.08 [b,c]	1.42 ± 0.04 [c]	7.00 ± 0.03 [c]	20.78 ± 0.08 [c]	58.75 ± 0.10 [b,c]	450.05 ± 0.65
BBC3	12.25 ± 0.12 [c]	1.51 ± 0.03 [d]	6.87 ± 0.10 [c]	20.13 ± 0.07 [d]	59.24 ± 0.05 [c]	445.63 ± 0.55

Table values represent the mean ± standard deviation (SD) of three determinations, and different letters (a–e) in the same column for each sample category represent statistically significant differences ($p < 0.05$) detected using the *t* test. BF—baobab flour; BWF—buckwheat flour; BBF1—10% baobab flour and 90% buckwheat flour; BBF2—20% baobab flour and 80% buckwheat flour; and BBF3—30% baobab flour and 70% buckwheat flour; CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour.

From the analysis of the results in Table 3, it can be seen that BF is richer in minerals, carbohydrates and water than BWF, while BWF is rich in protein and fat. In addition, BWF provides more energy than BF. The baobab and buckwheat flours complement each other, so blending them would give a complete composite flour in terms of nutritional composition. Moisture content was 10.13 ± 1.15% for BWF and 13.79 ± 0.01% for BF. These results are in line with those of [12,44–48]. Composite flour and cookie samples with high proportions of baobab are abundant in terms of moisture. This finding is explained by the high content observed in BF and is similar to those observed by Dossa et al. (2023) [25] and Barakat et al. (2021) [26]. Indeed, in the study by Dossa et al., 2023, from 11.39 ± 0.24% for the flour composed of 10% baobab, moisture content rose to 11.80 ± 0.03% for that with 30% baobab. Similarly, in the study by Barakat et al., 2021, from 11.80 ± 0.35% in the sample with 5% baobab, moisture rose to 11.97 ± 0.42% in the sample with 15% baobab. BF is more than two times richer in mineral substances than BWF (4 ± 0.02% vs. 1.66 ± 0.01%). These results are almost identical to those of Mohajan et al., 2019 [12], and Chopra et al., 2014 [48], who obtained 1.68 ± 0.01% and 1.38 ± 0.01%, respectively, for mineral substances in buckwheat flour. Similar results were also found by Bhinder et al., 2020, where the mineral content for several buckwheat varieties ranged from 1.76 ± 0.26% to 2.80 ± 0.06%. On the other hand, the mineral content obtained in this study for baobab is slightly lower than that obtained by [46], which ranged from 4.9 to 6.4%. This would be due to the variation in Baobab's nutritional values from one region to another [49]. However, other factors such as the species or the method of processing the pulp into flour can also influence nutritional values. For both flours and cookies, the higher the quantity of baobab, the higher the mineral content. From 1.99 ± 0.02% for BBF1, the mineral content rose to 2.67 ± 0.01% for BBF3. In the case of cookies, mineral content increased by 0.41% between CC and BBC3. This increase in mineral content can be explained by the fact that baobab is richer in minerals than buckwheat.

Unlike mineral substances, the protein content of BWF is around four times higher than that of BF. As a result, the protein content of composite flours and cookies decreases as the quantity of BF increases. The same applies to lipid content, which is higher in BWF than in BF. These results are in line with those of [12,25,26,44–47].

Carbohydrate content at BWF was 72.38 ± 1.09 g/100 g. This value is in line with that obtained by [12], which was 72.19 ± 0.09%. It is higher than the BF level (76.34 ± 0.06 g/100 g). This superiority of BF over BWF in carbohydrate content led to an increase in carbohydrate content in samples (flours and cookies) with more BF. From 74.76 ± 0.09 g/100 g for BBF1, it had risen to 75.78 ± 0.01 g/100 g for BBF3, and from 57.09 ± 0.13 g/100 g for CC, it had risen to 59.24 ± 0.05 g/100 g for BBC3.

In terms of energy value, baobab flour and the composite flours provided less than BWF. In addition, the energy value provided by the baobab cookies was lower than that provided by the control cookie. These results suggest that BWF provides a superior source of energy than BF. In the article by [25], between the control sample and the sample containing the highest quantity of baobab (30%), there was a significant decrease in the energy value provided. Similarly, the results of studies by [26,34] show the same observation. This suggests that BF provides less energy in both composite flours and cookies.

A comparison of the nutritional composition of BBC3 with cookies made from 100% wheat flour obtained in the studies by [18,48] shows that BBC3 is richer than cookies made from 100% wheat flour in terms of minerals, lipids, and carbohydrates. It is concluded that BF and BWF contribute to improving the nutritional values of cookies.

3.2. Macro- and Micro-Element Composition of Composite Flours and Cookies

The macro-element and the micro-element contents of buckwheat flour, baobab flour, buckwheat/baobab composite flours, and the resulting cookies are shown in Table 4.

Table 4. Macro- and micro-element content of various samples.

Samples	Macro- and Micro-Element Contents (mg/kg)							
	Fe	Zn	Ni	Cu	K	Mg	Ca	Mn
				Composite flours				
BF	155.14 ± 2.95 [a]	14.90 ± 0.01 [a]	0.598 ± 0.002 [a]	8.04 ± 0.05 [a]	13,276.47 ± 174.00 [a]	1066.73 ± 9.97 [a]	1570.67 ± 29.67 [a]	4.84 ± 0.05 [a]
BWF	57.66 ± 0.16 [b]	17.30 ± 0.11 [b]	0.391 ± 0.01 [b]	4.23 ± 0.02 [b]	1255.35 ± 58.92 [b]	287.82 ± 2.01 [b]	181.55 ± 3.24 [b]	10.65 ± 0.04 [b]
BBF1	71.65 ± 0.12 [c,e]	14.12 ± 0.15 [a,c]	0.412 ± 0.01 [b]	4.46 ± 0.14 [b,c]	1389.57 ± 36.28 [a]	288.83 ± 0.48 [b,c]	586.12 ± 2.62 [c]	10.02 ± 0.12 [b]
BBF2	81.96 ± 0.07 [d]	13.60 ± 0.34 [c]	0.467 ± 0.001 [c]	4.57 ± 0.12 [c]	1640.07 ± 135.16 [c]	322.78 ± 23.95 [c,d]	628.74 ± 10.40 [d]	9.10 ± 0.08 [c]
BBF3	89.03 ± 0.1 [e]	12.30 ± 0.13 [d]	0.516 ± 0.02 [d]	4.88 ± 0.06 [d]	2488.81 ± 435.58 [d]	378.57 ± 9.07 [d]	865.82 ± 9.28 [e]	8.26 ± 0.05 [c]
				Composite cookies				
CC	29.99 ± 0.11 [a]	7.09 ± 0.10 [a]	0.175 ± 0.03 [a]	3.18 ± 0.17 [a]	951.30 ± 64.88 [a]	272.42 ± 1.00 [a]	144.13 ± 12.19 [a]	6.51 ± 0.15 [a]
BBC1	33.02 ± 0.11 [a,b]	6.91 ± 0.09 [a]	0.243 ± 0.01 [b]	3.34 ± 0.14 [a,b]	1192.13 ± 127.20 [b]	275.96 ± 4.55 [a]	442.54 ± 8.15 [b]	6.03 ± 0.22 [a]
BBC2	36.22 ± 0.18 [b,c]	5.72 ± 0.12 [b]	0.347 ± 0.02 [c]	3.55 ± 0.05 [b,c]	1386.30 ± 104.14 [c]	293.20 ± 7.94 [b]	572.73 ± 15.01 [c]	5.16 ± 0.15 [b]
BBC3	39.99 ± 0.03 [c]	5.37 ± 0.08 [b]	0.382 ± 0.01 [c]	3.88 ± 0.04 [c]	2093.07 ± 38.86 [d]	298.72 ± 15.19 [b]	672.97 ± 38.99 [d]	4.67 ± 0.06 [c]

Table values represent the mean ± standard deviation (SD) of three determinations, and different letters (a–e) in the same column for each sample category represent statistically significant differences ($p < 0.05$) detected using the *t* test. BF—baobab flour; BWF—buckwheat flour; BBF1—10% baobab flour and 90% buckwheat flour; BBF2—20% baobab flour and 80% buckwheat flour; and BBF3—30% baobab flour and 70% buckwheat flour; CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour.

Minerals are important for maintaining the body's overall physical and mental health and contribute to the maintenance and development of muscles, nerve cells, teeth, bones, tissues, and blood. They also play a crucial role in maintaining the immune system. Conversely, deficiencies in these minerals can lead to poor growth, bone loss, reduced appetite, hypogonadism, and cognitive impairment [50–53]. These results are similar to those of [6,7], who estimated that buckwheat contains higher amounts of essential minerals compared to wheat. These results are also in line with those of [26] for baobab.

The results also reveal that, apart from zinc (Zn) and manganese (Mn), BF is richer than BWF in all the other minerals studied. Moreover, potassium (K) is the dominant macro-element in both baobab and buckwheat, with 13,276.47 ± 174 mg/kg and 1255.35 ± 58.92 mg/kg, respectively. Several authors, [26,27,47,49] on the one hand and [12,44] on the other, have revealed in their respective studies that potassium (K) is the dominant macro-element in BF and BWF. Furthermore, the value found for potassium is in the range of those obtained by [26,27,47,49], i.e., ranging from 9875 to 2390 mg/kg for BF. Similarly, the results for BWF in this study were in the same range as those obtained by [12,44] (between 1087.8 and 6487 mg/kg). K is also the major macro-element in buckwheat/baobab composite flours and cookies according to Table 4. Also, samples (flours and cookies) with high quantities of baobab flour were the richest in K. This can be explained by the abundance of K in BF compared to BWF (Table 4). It can therefore be deduced that BF would contribute more K to buckwheat gluten-free fortified cookies. All these results were also reported by [25,26,34] in their various studies. A total of 100 g BBC3 would cover up to 6% of an adult's daily K requirement recommended by the World Health Organization (3510 mg/day) [54].

Calcium (Ca) is the most prevalent mineral in the body. Beyond its function in keeping bones strong and stable, calcium takes part in a plethora of metabolic processes that include cell adhesion, blood clotting, cell differentiation and growth, the release of hormones and neurotransmitters, muscle constriction, and glycogen metabolism. It serves as a crucial constituent of teeth and bones [53]. In this study, Ca was higher in BF compared to BWF (1570.67 ± 29.67 mg/kg vs. 181.55 ± 3.24 mg/kg). The Ca content obtained for baobab flour in this study does not fall within the range (between 237.03 and 370 mg/100 g) obtained by other researchers [26,27,45–47,49]. Also, the Ca value obtained in BWF is lower than the range found by [44] (30 and 272 mg/100 g). These differences could be attributed to variations in nutritional values of Baobab and buckwheat from one region to another and from one species to another [44,49]. Aside from differences in regional baobab, cultivars state other reasons might influence the varied mineral content, such as cultivation technologies, harvest period, storage, or conditioning conditions. Calcium content increased with the quantity of BF in the formulation of composite flours and cookies. It increased by 376.90% between BWF and BBF3 and by 366.92% between CC and BBC3. These results show that BF improves Ca availability in composite flours and cookies. The EFSA Scientific Panel [55] suggests a maximum daily calcium consumption of 2500 mg for adults, comprising pregnant and breastfeeding women. So, around 3% (67.29 mg Ca) of daily Ca requirements should be covered by 100 g of BBC3.

According to the results of the present study, like Ca and K, BF is richer in magnesium (Mg) and iron (Fe) than BWF. For Mg, BF and BWF were, respectively, 1066.73 ± 9.97 mg/kg and 287.82 ± 2.01 mg/kg. Fe levels were 155.14 ± 2.95 mg/kg and 57.66 ± 0.16 mg/kg for BF and BWF, respectively. Furthermore, as the proportion of baobab in flour and cookie composition increases, the Mg and Fe content becomes more abundant. These results not only agree with those of [12,25–27,44,47,49] but also allow us to deduce that BWF partial substitution by BF results in composite flours and cookies with significantly higher magnesium (Mg) and iron (Fe) contents. Iron's main function is to transport oxygen from the lungs to the tissues. It is also an important constituent of various enzyme systems such as cytochromes, which are involved in oxidative metabolism [53]. Concerning magnesium, the adequate daily intake was estimated [56] at 350, 300, and 170 to 300 mg, respectively, for men, women, and children. This being said, 100 g of the 30% BF cookie from the present study would provide 29.87 mg of Mg, representing, respectively, over 8.53%, 9.97%, and between 17.57 and 9.97% of the adequate Mg intake for men, women, and children.

About the micro-elements zinc (Zn), copper (Cu), manganese (Mn), and nickel (Ni), BWF is more abundant in Zn and Mn than BF. On the other hand, BF is richer in Cu and Ni than BWF. BF had 8.04 ± 0.05, 0.598 ± 0.002, 14.90 ± 0.01, and 4.84 ± 0.05 mg/kg, respectively, for Cu, Ni, Zn, and Mn. These values are close to those of [26,27,47,49]. BWF values for Cu, Ni, Zn, and Mn were 4.23 ± 0.02, 0.391 ± 0.01, 17.3 ± 0.11, and 10.65 ± 0.04 mg/kg, respectively. These values are also close to those of [12,44]. After the exploitation of these results, it is important to conclude that BF and BWF, each in their case, have contributed in one way or another to improving the nutritional composition of the cookies obtained in this study.

3.3. Phytochemical Profile of Composite Flours and Cookies

The results of phytochemical analyses of the various samples are presented in Table 5.

Table 5. Phytochemical composition of various samples.

Samples	Total Polyphenol Content (mg/100 g)	Total Flavonoid Content (mg/100 g)	Antioxidant Activity, DPPH (%)
		Flours	
BWF	283.87 ± 0.06 ^{a}	125.36 ± 1.12 ^{a}	79.72 ± 0.01 ^{a}
BF	629.7 ± 0.35 ^{b}	213.13 ± 0.08 ^{b}	86.62 ± 0.04 ^{a,b}
BBF1	292.35 ± 0.35 ^{a,c}	181.03 ± 0.12 ^{c}	81.56 ± 0.19 ^{b}
BBF2	311.62 ± 0.78 ^{c,d}	194.94 ± 1.78 ^{d}	83.11 ± 0.02 ^{b}
BBF3	320.12 ± 2.07 ^{d}	209.28 ± 0.85 ^{b}	84.78 ± 0.01 ^{b}
		Cookies	
CC	226.34 ± 0.75 ^{a}	102.96 ± 4.07 ^{a}	76.33 ± 0.07 ^{a}
BBC1	250.06 ± 1.17 ^{b}	135.74 ± 3.10 ^{b}	78.74 ± 0.03 ^{a,b}
BBC2	252.74 ± 0.15 ^{b}	140.44 ± 0.81 ^{b,c}	80.32 ± 0.03 ^{b,c}
BBC3	285 ± 32.82 ^{c}	147.69 ± 2 ^{c}	82.52 ± 0.07 ^{c,d}

Table values represent the mean ± standard deviation (SD) of three determinations, and different letters (a–d) in the same column for each sample category represent statistically significant differences ($p < 0.05$) detected using the *t* test. BF—baobab flour; BWF—buckwheat flour; BBF1—10% baobab flour and 90% buckwheat flour; BBF2—20% baobab flour and 80% buckwheat flour; and BBF3—30% baobab flour and 70% buckwheat flour; CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour.

Polyphenols are secondary metabolites produced by plants through the pentose phosphate, phenylpropanoid, and shikimate pathways. They possess various physiological properties, such as antioxidant, antitumoral, antibacterial, and other activities [57,58]. In this study, the total polyphenol content of BF is more than 2 times higher than that of BWF, i.e., 629.7 ± 0.35 mg/100 g versus 283.87 ± 0.06 mg/100 g. For Baobab, [59] reported a total polyphenol content around 1.25 times lower than in the present study. In contrast, [27] reported a total polyphenol content 1.72 times higher than in the present study. For buckwheat, the results of this study are similar to those of [60], who obtained 2.83 ± 0.73 g/mg. However, they are below those obtained by [17,61], which were 7.25 ± 0.2 mg/g and 33.51 ± 0.52 mg/g, respectively. Analysis of the results also shows that the more BF in the various flours and cookies, the higher the total polyphenol content. Thus, there were 292.35 ± 0.35 mg/100 g, 311.62 ± 0.78 mg/100 g, and 320.12 ± 2.07 mg/100 g for BBF1, BBF2, and BBF3, respectively. For the cookie samples, there were, respectively, 226.34 ± 0 mg/100 g, 250.06 ± 1.17 mg/100 g, 252.74 ± 0.15 mg/100 g, and 285 ± 32.82 mg/100 g for CC, BBC1, BBC2, and BBC3. This observation could be explained by BF's abundance of polyphenols compared to BWF (Table 5). The same observation was made by [26]; i.e., polyphenol content increases with the amount of baobab.

Flavonoids are a collection of polyphenolic compounds located in both flora and human sustenance. They possess impressive antitumor, antioxidant, and microcirculation-enhancing attributes [62]. Buckwheat predominantly comprises flavonoids as the main active components [63]. In this study, the total flavonoid content of baobab flour was around 1.70 times higher than that of buckwheat (213.13 ± 0.08 vs. 125.36 ± 1.12 mg/100 g). Chlopicka et al., 2012 [61], found a lower flavonoid value than in the present study

(153 ± 12 µg/g). In this study, flavonoid content was significantly different between BF and BWF. Furthermore, there is a significant increase in flavonoids as the proportion of BF in the different flours and cookies is higher. An increase of 28.25 mg/100 g was observed between BBF1 and BBF3 and of 44.73 between CC and BBC3. Therefore, BF would be responsible for the abundance of flavonoids in the composite flours and cookies obtained compared to the control samples, thanks to its richness in flavonoids compared to buckwheat (Table 5). Similar results have been obtained by [59].

The antioxidant activity (AA) behaved in the same way as the total flavonoid and polyphenol content. In other words, the AA of BF is higher than that of BWF. BF and BWF obtained 86.62 ± 0.04% and 79.72 ± 0.01%, respectively. Similar results were obtained by [64]. In their study of the antioxidant activity of buckwheat extracts, Sun et al. [64] obtained an AA of 78.6 ± 6.2% for buckwheat flour. On the other hand, Antoniewska et al. [17] obtained a result lower (32.06 ± 0.17%) than the present study and [64]. In both buckwheat/baobab composite flours and cookies, AA increases with the proportion of BF in them. From 81.56 ± 0.19% for BBF1, AA rose to 84.78 ± 0.01% for BBF3, while from 76.33 ± 0.07% for CC, it rose to 82.52 ± 0.07% for BBC3. This was also observed by [26]. They highlighted the increase in antioxidant activity and total polyphenol content with the incorporation of a high percentage of baobab. Studies by Bolang et al., 2023 [65], on the combination of several plant ingredients (porang tubers, moringa leaves, and tempe made from black soybeans) in the formulation of functional cookies also reported improved antioxidant activity. It is interesting to note that consuming antioxidant-rich foods plays an important role in preventing degenerative and non-communicable diseases [66].

Following on from all the data concerning bioactive compounds, it should be emphasized that the substitution of BWF by BF significantly increased the phytochemical properties of buckwheat/baobab composite flours and cookies. Baobab could therefore be an alternative for the formulation of flour products with high antioxidant activity and high polyphenol and flavonoid content, without recourse to chemical additives.

3.4. Individual Polyphenols of Composite Flours and Cookies Determined via LC-MS

The quantification of some phenolic compounds in flours and cookies is shown in Table 6.

Table 6. Quantification of individual polyphenols.

Samples	Epicatechin (mg/kg)	Cafeic Acid (mg/kg)	Rutin (mg/kg)	Rosmarinic Acid (mg/kg)	Resveratrol (mg/kg)	Quercitin (mg/kg)
			Composite flours			
BWF	90.03 ± 0.21 ^{a}	17.57 ± 0.93 ^{a}	246.93 ± 0.75 ^{a}	68.13 ± 0.60 ^{a}	126.30 ± 1.67 ^{a}	15.80 ± 0.44 ^{a}
BF	158.6 ± 0.46 ^{b}	17.67 ± 1.01 ^{a}	nd *	67.93 ± 0.57 ^{a}	141.73 ± 0.57 ^{b}	16.10 ± 0.61 ^{a}
BBF1	106.63 ± 0.21 ^{c}	17.63 ± 0.15 ^{a}	145.80 ± 0.56 ^{b,c}	68.00 ± 0.50 ^{a}	128.50 ± 1.14 ^{a}	15.90 ± 0.10 ^{a}
BBF2	109.23 ± 0.04 ^{c}	17.64 ± 0.15 ^{a}	137.60 ± 0.61 ^{c,d}	68.01 ± 0.61 ^{a}	129.90 ± 0.10 ^{a,c}	15.91 ± 0.08 ^{a}
BBF3	121.18 ± 0.73 ^{d}	17.64 ± 0.14 ^{a}	122.20 ± 0.02 ^{d}	68.00 ± 0.05 ^{a}	132.20 ± 0.02 ^{c}	16.05 ± 0.13 ^{a}
			Cookies			
CC	nd	17.80 ± 0.1 ^{a}	259.57 ± 0.40 ^{a}	68.0 ± 0.53 ^{a}	116.53 ± 0.55 ^{a}	15.90 ± 0.10 ^{a}
BBC1	92.55 ± 0.05 ^{a}	17.75 ± 0.04 ^{a}	151.40 ± 0.18 ^{b}	67.97 ± 0.15 ^{a}	121.31 ± 0.45 ^{b}	15.94 ± 0.19 ^{a}
BBC2	99.79 ± 0.52 ^{b}	17.77 ± 0.04 ^{a}	140.98 ± 0.28 ^{b}	67.83 ± 0.06 ^{a}	124.12 ± 0.64 ^{c}	16.20 ± 0.13 ^{b}
BBC3	108.59 ± 0.62 ^{c}	17.77 ± 0.03 ^{a}	130.47 ± 0.51 ^{b}	67.83 ± 0.12 ^{a}	126.98 ± 0.25 ^{c}	16.26 ± 0.09 ^{b}

Table values represent the mean ± standard deviation (SD) of three determinations, and different letters (a–d) in the same column for each sample category represent statistically significant differences ($p < 0.05$) detected using the t test. BF—baobab flour; BWF—buckwheat flour; BBF1—10% baobab flour and 90% buckwheat flour; BBF2—20% baobab flour and 80% buckwheat flour; and BBF3—30% baobab flour and 70% buckwheat flour; CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour. * nd: not detected.

Phenolic compounds are vital bioactive substances possessing antioxidant, anti-inflammatory, and antimicrobial properties [67]. Buckwheat and baobab are both commendable sources of these compounds [7,59,67]. The various phenolic compounds identified in flours and cookies are presented in Table 6. This table shows that the most abundant phenolic compounds studied (Table 6) in buckwheat and baobab are rutin and epicatechin, respectively. Several previous studies have identified rutin as the most abundant phenolic compound in buckwheat [7,13,68]. Buckwheat is a significant source of rutin in the human diet [68]. Similarly, Balarabe et al. [59] concluded that the most abundant phenolic compound in baobab fruit pulp was epicatechin.

Epicatechin is a type of phenolic compound that is thought to offer potential health benefits in preventing or mitigating cardiovascular disease [69]. In this study, BF was more abundant in epicatechin (158.6 ± 0.46 mg/kg) than BWF (90.03 ± 0.21 mg/kg). As the amount of BF in composite flours and cookies increases, the sample becomes more abundant in epicatechin. This is explained by the fact that BF is more abundant in epicatechin than BWF. This suggests that partial substitution of BWF by BF results in flours and cookies with higher epicatechin content. Apart from epicatechin, BF is also more abundant in resveratrol. BF had a resveratrol composition of 141.73 ± 0.57 mg/kg versus 126.3 ± 1.67 for BWF. Here too, the higher the BF content in the various flour and cookie samples, the more abundant the resveratrol content. From 128.5 ± 1.14 mg/kg for BBF1, resveratrol content rose to 132.2 ± 0.02 mg/kg for BBF3. Also, from 116.53 ± 0.55 mg/kg for CC, its content rose to 124.12 ± 0.64 mg/kg for BBC3. Unlike resveratrol and epicatechin, BF and BWF have virtually identical values for cafeic, rosmarinic, and quercitin. In the case of these compounds, the values did not practically change from one sample to the next. There is therefore no significant difference between the values obtained for these compounds from one sample to another.

Rutin, also known as vitamin P, is a flavonoid glycoside found in citrus fruits. This biologically active molecule can impact a wide range of both non-reproductive and reproductive processes, offering potential therapeutic benefits for various disorders. Among natural antioxidants, rutin is considered to be one of the most potent within its known class [70,71]. In the present study, BWF contained 246.93 ± 0.75 mg/kg rutin. However, BF did not obtain a value. This may be due to the analysis conditions and, above all, the solvent used. As an example, in the work carried out by [59] where they identified and quantified phenolic acids and flavonoids in baobab fruit powder extracts via HPLC using different solvents (µg/g), when they used ethyl acetate as the solvent, they had not been able to determine a value for rutin. On the other hand, when they used acid methanol, they obtained a value of 12.21 ± 0.86 µg/g. In the case of this study, the greater the quantity of BWF in the various flour and cookie samples, the greater the rutin content. This finding is explained by the fact that BWF is a good source of rutin compared to BWF. The same observation was made by [13]. It can therefore be deduced that BWF provides rutin-rich cookies.

There is also an increase in rutin content in cookies compared with flour. Similar results were reported by [13]. They reported a significantly higher rutin content after baking than before. This is explained by the fact that rutin, which was present in bound form before baking, was released during baking [68].

3.5. Sensory Analysis

The acceptability of the different cookies to consumers was determined by a sensory evaluation according to a five-point hedonic scale. The average scores for the various consumer sensory properties: appearance (the physical aspect of the cookie: whether it is firm or not), color (influence of the addition of baobab on the color of the cookie), flavor, texture, aroma, and overall acceptability of the cookies are presented in the figure below.

Partial substitution of BWF by BF of up to 20% significantly increased scores for all attributes (Figure 3). For each of the attributes, BBC2 was the sample with the highest scores across all samples, including the control sample (CC). It scored 4.53 ± 0.51, 4.65 ± 0.49, 4.53 ± 0.51, 4.41 ± 0.71, 4.47 ± 0.72, and 4.41 ± 0.62, respectively, for appearance, color, texture, taste, flavor, and overall acceptability. Having obtained scores between 4.5 and 5 for appearance, color, and texture, BBC2 is very acceptable for these different criteria. On the other hand, it is acceptable for the rest of the criteria, since its scores for these criteria (taste, flavor, and overall acceptability) were between 3.5 and 4.49. Sample BBC3 had the lowest scores among the samples with different proportions of BF (BBC1, BBC2, and BBC3). It should be noted that for some attributes BBC3 scored higher than CC. These were appearance (4.29 ± 0.69 vs. 3.41 ± 1.33), color (4.24 ± 0.66 vs. 4.12 ± 1.36), and texture (3.94 ± 0.75 vs. 3.71 ± 1.31). From all this information, it should be noted that BF improved all the sensory qualities of buckwheat gluten-free cookies by up to 20%. It should also be noted that up to 30% BF continues to improve the appearance, color, and texture of cookies. However, at 30% BF and above, consumers were less and less appreciative of the taste and flavor of the cookies, probably due to the tangy, lemony flavor that baobab brings to the cookies, which was not necessarily to consumers' taste. In conclusion, the limit of acceptability of baobab in cookies is 20%. It was also reported in [34] that replacing 20% BF in the cookie improved sensory qualities. A comparison of the acceptable limit level of BF substitution in bakery products from several studies [25,26,34], including the present study, allows us to say that Baobab is more suitable for cookie production than cake and bread production from a sensory point of view. Indeed, the substitution limit for BFs was 10% in bread [25] and 15% in cakes [26] but can be as high as 20% for cookies (Figure 3; [34]).

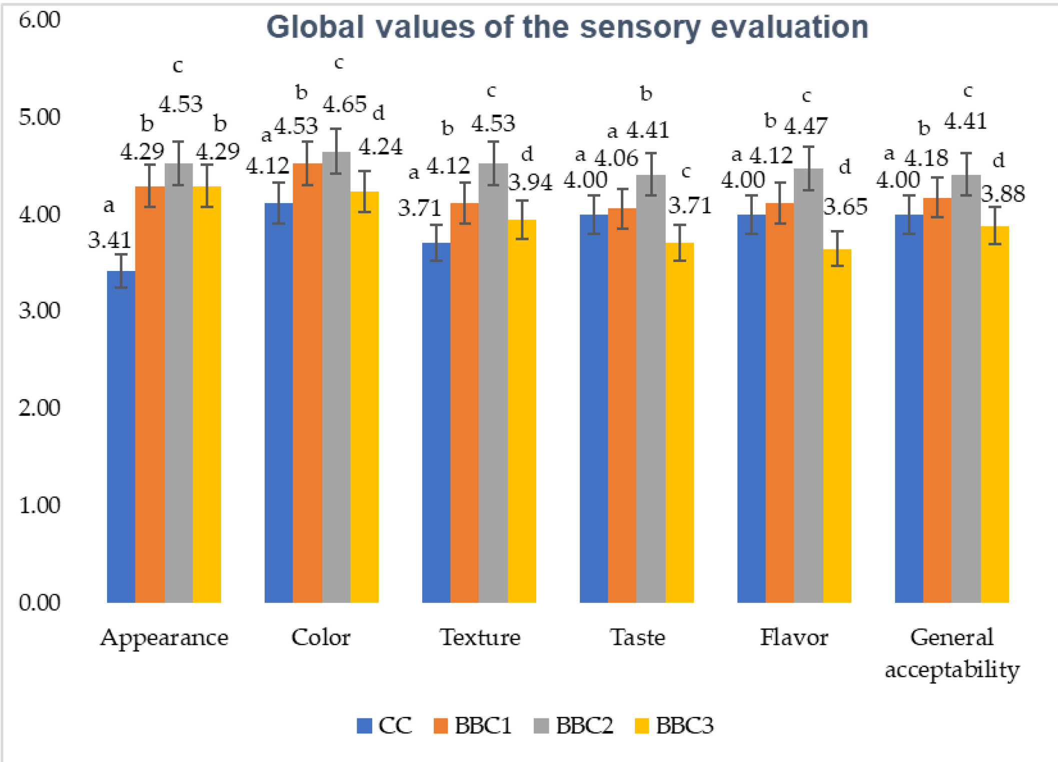

Figure 3. Overall sensory-evaluation values (consumer acceptance). Column values represent the mean of three determinations ± standard deviation (SD). Within each characteristic category, statistically significant differences ($p < 0.05$) are indicated by different letters (a–d) in the columns. CC—control cookie with 100% buckwheat flour; BBC1—cookie with 10% baobab flour and 90% buckwheat flour; BBC2—cookie with 20% baobab flour and 80% buckwheat flour; and BBC3—cookie with 30% baobab flour and 70% buckwheat flour.

4. Conclusions

The first objective of the study was to formulate functional, gluten-free cookies using a composite flour made up of baobab and buckwheat. In addition, the study investigated the nutritional, phytochemical, and sensory attributes of baobab flour in cookie production. The analyses conducted during the study revealed that the combination of baobab and buckwheat can effectively enhance bakery products, particularly cookies. The mineral and carbohydrate composition of cookies was enhanced by baobab, while buckwheat had a significant impact on their protein and lipid composition. In the same vein, the partial substitution of buckwheat flour for baobab flour resulted in composite flours and cookies with a high content of micro- and macro-elements. Rutin and epicatechin were found to be the most abundant phenolic compounds in buckwheat and baobab, respectively. It is worth noting that replacing BWF with BF significantly improved the phytochemical properties of buckwheat/baobab composite flours and cookies. This could make baobab a viable alternative to chemical additives for producing bakery products with high antioxidant activity and high levels of polyphenols and flavonoids. The study also found that substituting baobab improved cookie acceptability by up to 20%. However, when substituted at levels above 30%, although certain nutritional and phytochemical values increased, the resulting cookies were less well liked from an organoleptic perspective. This may be due to baobab's acidic taste, which hurt the cookie's taste. Therefore, the acceptable limit for baobab in cookies is 20%, regardless of appearance, color, taste, texture, flavor, or overall acceptance of the cookies. This formulation results in cookies with an impressive nutrient content and attractive physical-chemical characteristics, which are also highly appreciated by consumers and do not adversely affect their nutritional and technological properties. Therefore, it is concluded that the optimal recipe for producing cookies with higher nutritional quality and suitable sensory characteristics, utilizing baobab/buckwheat composite flours, is 20% baobab and 80% buckwheat. Consequently, the formulation and use of these functional foods can improve the nutritional well-being of consumers.

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