Development of an antioxidant formula based on peanut by-products and effects on sensory properties and aroma stability of fortified peanut snacks during storage

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Running title: Sensory properties and aroma stability of peanut bars fortified with natural antioxidants

Abstract

Background

An antioxidant formula based on peanut skins and hulls, was developed and characterized for total and single polyphenols, and antioxidant power, considering the contribution provided by each peanut by-product. Then, it was evaluated for its effect on sensory properties and aroma stability of peanut bars over a 100-day period. To this purpose, snacks fortified and not with the natural additive were experimentally produced.

Results

Peanut hulls contributed to a greater extent than skins to boost the content of bioactives and the antioxidnt activity of the antioxidant formula, which was marked by a phenol content of (~807 mg GAE g^{-1}) and a DPPH activity similar to that of butylated hydroxytoluene (respectively, 85.96% and 89.30%).

From a sensory perspective, the incorporation of the formulation in snacks caused only a slightly stronger perception of astringent and bitter notes. Pyrazines, phenol, furan, and pyrrole derivatives outlined the aroma of snacks, being more abundant in fortified than conventional samples. Such volatiles faded over storage with different trends in examined products. For example, the sum of 2,5-dimethylpyrazine, 2-ethylpyrazine and 2,3-dimethylpyrazine was 9.49 and 8.87 ppm at day 15; 5.57 and 7.16 ppm at day 45; 5.03 and 4.65 ppm at day 100, respectively in fortified and conventional snacks; hydroxymethylfurfural decreased constantly over storage in conventional samples, and only after day 45 in fortified bars.

Conclusion

Overall, the antioxidant formulation did not compromise the sensory desirability of peanut snacks and induced a preservative effect on their aroma, especially during the first 15 days of storage.

Keywords: peanut snack; flavor fade; natural additives; peanut by-products; storage.

Introduction

Peanut (*Arachis hypogaea* L.) is one of the most valued oilseed and food crop throughout the world, for both developing and developed markets. According to the last data released by FAO (2018), world peanut production was approximately 45 million metric tons in 2017, with China and India being the leading producers accounting for nearly 60% of the production[1].

Peanut fruit is made of an external curled hull and the nut itself, consisting of the kernel, wrapped in a thin and brownish skin. Hulls and skins are considered as abundant wastes of the peanut processing industry, coming respectively from the shelling and blanching of peanuts which are meant to be transformed in a variety of products. Similarly to other agrowastes[2-4], the management of such by-products has raised environmental and economical issues, especially due to their seasonal and polluting characters[5]. On the other hand, kernels enjoy a widespread popularity, primarily due to several health benefits induced by the consistent fat content (44-56%, of which ~80% unsaturated lipids), vegetable protein (22-30%), fiber (3-8%), and significant levels of micronutrients[6]. Beside the nutritional value, a pleasant aroma, smooth and crisp texture and, not least, practical issues (e.g. high availability and affordability) contribute to an increasingly wider consumer acceptance and market share. The most notorious products include roasted whole peanuts, and derived products, such as peanut butter, oil, sauce, or flour, and salted or sweet peanut bars[6].

Roasting is a key step of the peanut value chain, where important physical and chemical changes lead to the development of unique flavor, color and texture of peanut products. However, such procedure is known to damage the structure of lipid storage cells, to induce the inactivation of antioxidant

enzymes, and the oxidation of other beneficial chemicals[7]. Basically, lipid oxidation occurring after roasting is the primary cause of the "flavor fade" -i.e. the loss of the fresh roasted peanut aroma and taste, accompanied by the concomitant development of unpleasant sensory attributes. Extrinsic variables not properly controlled during storage, such as light, temperature, moisture, and oxygen levels, can speed up this degradation process[8].

At industrial level, the retardation of lipid oxidation is, therefore, mandatory to obtain high-quality peanut products, and usually performed by nitrogen-filled headspaces, vacuum packaging, light barriers or, not least, antioxidant addition. However, oxidation of polyunsaturated fatty acids, still occurs, even under the strict packaging practices, and the safety of synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), is questioned as scientific evidences suggest carcinogenic and toxic effects in animal models over-exposed in terms of concentration and duration to such compounds[9,10,11].

Recent literature has extensively encouraged the safe employment in food preparations of natural additives from a number of vegetable sources[12] or, even better, from by-products generated during the processing of plant-based food[13]. In this respect, around 13.7 million metric tons of hulls and over 0.74 million metric tons of skins are churned out every year from the global peanut processing industry, most of which are treated as waste, and, hence, dumped into the environment or burned[14,15]. However, during the last 20 years, the value of peanut by-products has been optimized, and the effect of their nutritional composition on the product quality in food processing has been widely investigated[5]. In particular, differently from the underexplored hulls, skins have already demonstrated to be a rich source of free monomeric polyphenols, (i.e. phenolic acids, flavonoids, and stilbenes) and, proanthocyanidins (i.e. oligomers and polymers of flavan-3-ols, representing alone ~17% by

weight of skins)[16,17]. Such bioactives would explain the high antioxidant activity of peanut skins, as well as their ability to successfully prevent the lipid oxidation in a variety of foods[16,17].

To the best knowledge of the authors, this is the first work aimed to *i*) develop and characterize a natural formula based on peanut hulls+skins, by evaluating the contribution provided by each by-product, and *iii*) study the sensory properties and aroma stability of peanut bars fortified with such additive over a 100-day storage period.

2. Materials and methods

2.1 Materials and reagents

Antioxidant formula: ethanol (HPLC grade) was purchased from Carlo Erba (Val de Reuil, France); while maltodextrin (dextrose equivalent of DE=19) was supplied by Roquette Lab 2509 (Lille, France).

Polyphenol analysis: Folin–Ciocalteu reagent was from Sigma-Aldrich (Steinheim, Germany). Methanol, acetonitrile and water (LC-MS grade) were provided by Carlo Erba. Formic acid (95-97%) and commercial standards of polyphenols were supplied by Supelco (Bellefonte, USA).

DPPH assay: 2,2-diphenyl-1-picrylhydrazyl（DPPH) and BHT were supplied by Sigma-Aldrich.

GC analysis: n-heptanal was provided by Sigma-Aldrich; whereas *n*-hexane and ethanol (reagent grade) were from J.T. Baker (Deventer, Netherlands).

2.2 Development of the antioxidant formula

Three different formulations, based respectively on peanut skins, peanut hulls, and peanut skins+hulls, were separately prepared in laboratory in an attempt to evaluate the single contribution from each peanut by-product during the development of the natural antioxidant additive.

Around 1 Kg of raw peanut pods (*Arachis hypogaea* L., cv. Runner) was purchased from a local retailer and transported in a polyethylene bag to the laboratory, where they were manually cleaned and shelled. Once hulls were separated, kernels were dry-blanched at 80±10 °C for 25 min, so that the brownish skins were manually removed.

The extraction and microencapsulation procedures were performed accordingly to what recently reported by do Valle Calomeni *et al.*[18]. Depending on the formulation, 1 gr of fine-ground skins, 1 gr of fine-ground hulls and 1 gr of mixed fine-ground skins and hulls (1:1, *w*/*w*) were separately mixed with 10 mL of an 80% ethanol aqueous solution, and stirred at 40 °C for 40 min in the dark. Next, every mixture was centrifuged at 4,000 rpm for 20 min (Awel MF 20-R centrifuge, Awel SAS, France), so that the supernatant was first filtered on Whatman N° 50 paper (Whatman International Ltd., UK), and then concentrated to 20% of the initial volume in a Büchi V700 rotating evaporator operating at 40 °C (BUCHI Labortechnik AG, Switzerland). The three extracts were stored in amber vials at +4 °C until microencapsulation. The spray-drying was carried out by a Büchi Mini B-290 spray-dryer (Büchi Labortechink AG, Switzerland), employing DE maltodextrin as carrier agent, as already reported by Avellone *et al.*[19] The feed consisted of the extract mixed with 30% of maltodextrin (*w*/*w*), and was atomized with a constant inlet temperature of 150 °C, and an outlet temperature of 90 ± 5 °C. The feed pump flow and the nitrogen flow were set at 44 mL min^{-1} and 40 mL min^{-1}, respectively. The spray-dried powders were stored in amber vials at + 4 °C, until analysis. In the development of every formula, the extraction and microencapsulation protocol was replicated three times.

2.3 Production of the peanut bars

Once the natural antioxidant formula based on peanut skins+hulls was developed, it was provided to a local confectionery company, that produced peanut (*Arachis hypogaea* L., cv Runner) bars coated by a syrup solution fortified with the natural formulation (herein referred as fortified samples, $n = 5$), and conventional peanut bars coated with a simple syrup solution (herein referred as conventional samples, $n = 5$). Briefly, shelled and blanched peanuts were dry-roasted at 150 °C for 40 min. Next, they were placed into a stainless steel rotating pan, and 30 g of syrup solution were strained *per* 100 g of roasted product. The syrup consisted of sucrose, glucose+fructose, and water (50/35/15, *w*/*w*/*w*) and, in the case of fortified peanut bars, it was added with 15 % (*w*/*w*) of the spray-dried powder based on skins+hulls described above. During coating, the pan was kept rotating at 30 rpm until the syrup was spread evenly on the product (~5 min). Then, the coated kernels were heated at 150 °C for 20 min to dry off the excess of moisture (final moisture: 1.5-2.0%) and, once cooled at room temperature, they were cut in 5×12 cm bars. Every snack bar was singularly packed within silver-foiled and heat-sealed flow packs, and transported to laboratory in short time.

2.3.1 Storage and sampling

Once in laboratory, packaged peanut bars were stored at ambient temperature (20 ± 2 °C), in a dry (relative humidity: 50-60%) and dark place for 20 days. This preliminary storage was established based on distribution information provided by the producer company. After this time lapse, packages of snacks were opened, so that sensory and aroma analyses could be carried out. In particular, for aroma analyses, peanut bar samples were collected at 0, 15, 45, and 100 days after packaging's opening. These time intervals were defined by the producer as "critical" moments of aroma decay for this type of food. Following each sampling time, packages of snacks were sealed with tape and kept in the same cool, dry and dark place described above.

2.4 Characterization of the spray-dried powder

2.4.1 Total and single polyphenols

For every powder, phenols were extracted from microparticles following the procedure proposed by Robert *et al.*[20]: 200 mg of powder were mixed with 2 mL of a methanol:acetic acid:water solution (50:8:42 *v*/*v*/*v*). The mixture was stirred for 20 min and then centrifuged at 4,000 rpm for 5 min. Finally, the supernatant was filtered consecutively through 0.45 μm and 0.20 μm PTFE filters. Total phenol content was evaluated by the method described by Capillo *et al.*[21]. Briefly, about 1 mL of every sample was mixed with 5 mL of Folin–Ciocalteau reagent and 10 mL of a Na_2CO_3 solution (20%) in a 100-mL flask, and added with distilled water up to the mark. The obtained solution was kept in the dark for 120 min, and subsequently read at 760 nm with an UV–VIS spectrophotometer (UV-2401 PC, Shimadzu, Italy). A five-point calibration curve ranging from 50 to 5000 ppm was constructed using appropriate solutions of gallic acid as external standard. As a result, the total phenol content was calculated as mg of gallic acid equivalents in g of powder (mg GAE g^{-1}). Measurements were conducted in triplicate along with analytical blanks (distilled water).

For the determination of single polyphenols, the filtered methanol:acetic acid:water solutions coming from every formulation, were first properly diluted and then characterized by high performance liquid chromatography coupled to diode-array detection and mass spectrometry (HPLC-DAD-MS). Analyses were conducted by a Shimadzu Prominence UFLC XR system (Shimadzu, Japan), equipped with a CBM-20A controller, a LC-20AD-XR binary pump system, a DGU-20A3R degasser, a SPD-M20 detector, a CTO-20AC column oven and a SIL-20A-XR autosampler. The LC system was interfaced through an electrospray ionization (ESI) source to an LCMS-8040 triple quadrupole mass spectrometer (Shimadzu, Japan). Data collection and handling was performed by LabSolution

software v. 5.53 (Shimadzu, Japan). Chromatographic separations occurred on a Ascentis Express C18 (250 x 4.6 mm I.D. x 2.7 μm d.p., Supelco, USA) and mobile phases were constituted by water/formic acid (99.9:0.1, *v*/*v*) (solvent A) and acetonitrile/formic acid (99.9:0.1, *v*/*v*) (solvent B). The method of analysis was adapted from the protocol proposed by Certo *et al.*[22] and was and consisted of the following gradient program: 0 min, 5% B, 5 min, 5% B, 15 min, 30% B, 40 min, 60% B, 45 min, including also final column washing and re-equilibrating steps. The mobile phase flow rate was 0.5 mL min^{-1}, while the oven temperature and injection volume were, respectively, set at 30 °C and 5.0 μL. The PDA spectra were acquired in the range 190–400 nm, and the chromatograms were extracted operating at wavelengths between 280 nm and 370 nm (time constant: 0.60 s; sample frequency: 1.5625 Hz). It was assured that only ~1/3 of the total flow was directed from the LC system to the ESI-MS by means of a stainless steel splitting device (VICI AG International, Switzerland).

Then, MS acquisition was performed using ESI interface in negative mode, and operating in full-scan (*m/z* 100–800) and selected ion monitoring (SIM) modes according to the following conditions: interval, 1.0 s; scan speed, 715 amu sec^{-1}; nebulizing gas (N_2) flow, 1.5 L min^{-1}; drying gas (N_2) flow, 10 L min^{-1}; ESI temperature, 350°C; heat block, 300°C; DL (desolvation line) temperature, 300°C; DL voltage -34 V; probe voltage, +4.5 kV. Measurements were conducted in triplicate along with analytical blanks (methanol).

The investigated compounds were: *p*-coumaric acid, ferulic acid, gallic acid, chlorogenic acid, caffeic acid, *trans*-resveratrol, (-) -epigallocatechin, (+) -catechin, (-) -epicatechin, (-) -epicatechin-3-*O*-gallate, luteolin, rutin and quercetin. They were selected based on the standard availability, and their peculiar occurrence in peanut by-products[23-25]. An external calibration procedure was conducted for quantification purposes. In particular, five-point calibration curves were constructed in the range 100-

1 mg L^{-1}, by serially diluting a stock solution of each commercial standard (1000 mg L^{-1}) in methanol. Obtained polyphenols concentrations were then corrected by using dilution factors.

2.4.2 DPPH assay

The antioxidant activity of the spray-dried powders coming from peanut skins, peanut hulls and peanut skins+hulls was evaluated by a DPPH free radical-scavenging assay, according to the procedure proposed by Albergamo *et al.*[2] Around 0.5 mg of every powder were mixed with 3 mL of a DPPH methanol solution (0.05 mM). The mixture was kept in the dark at room temperature for 30 min, and read at 515 nm by an UV-2401 PC spectrophotometer. Inhibition percentage of the DPPH• radical was calculated as follows:

$$Inhibition\ (\%) = \frac{Ac(0) - Ac(t)}{Ac(0)} \times 100$$

where $A_c(0)$ is the absorbance of control DPPH solution at t=0 min and $A_c(t)$ is the absorbance after addition of sample at t=30 min. BHT (16.6 mg 100 mL^{-1}) was used as reference antioxidant and tested according the same procedure. Triplicate measurements were conducted for every formulation.

2.5 Characterization of peanut snacks

2.5.1 Sensory analysis

Sensory analysis was carried out in the Food Chemistry laboratory of the Biomorf Department, University of Messina. The panel was composed by eight people (5 males, 3 females, aged between 25 and 55 years) chosen among expert personnel and graduate students. Panelists were trained during specific sessions to acquire the attributes typical notes of peanut flavor lexicon, such as roasted peanuty, raw/beany, sweet caramel, woody/hull/skin, bitter, astringent, burnt[26].

For each attribute, reference samples were utilized, such as standard roasted peanuts, to which an intensity score of 6 was assigned, as anchor. Other reference samples were: raw immature peanuts, peanut hulls and skins, caramelized candies, hardly roasted peanuts, grape seeds. In particular, roasted peanuts were from Cameo (Italy) and caramelized candies were purchased unpackaged in a local candy shop. Grape seeds were manually obtained from fresh fruit, and hardly roasted peanuts were obtained by roasting in laboratory the Cameo peanuts.

The intensity of panelists' perception was rated on a 1-10 scale, using reference foods during training, as anchors. In particular, for an intensity score of 2, sodium carbonate in saltines; score 4, apple in apple sauce; score 8, grape in grape juice; score 10, cinnamon in cinnamon candies. Samples were blind and randomly provided to assessors, who performed each duplicate analysis, with a 10 minutes break in between, during which palates were rinsed with water. Samples were equilibrated at ambient temperature (20 ± 3 °C) before testing and consisted of ~5 g of peanut snacks.

2.5.2 Aroma analysis

Samples underwent HS-SPME-GC-FID/MS analyses and a relative quantification of major and common volatiles occurred exploiting an internal standard.

The SPME apparatus was the same as used in our previous works[3,27]. A stock solution (10 mg Kg^{-1}) of n-heptanal in ethanol was prepared, 500 µg were drawn and added to a 20 mL headspace vial. Peanut bars were crushed in a mortar, and for each extraction 5 g were added to headspace vial along with the internal standard. The SPME fiber was a DVB/Carbon WR/PDMS 80 µm (Agilent Technologies, USA). Headspace presaturation, 20 min at 40 °C; fiber exposure, 40 °C for 60 min; stirring speed, 3000 rpm; desorption time, 5 min.

GC- FID analyses were carried out on a GC-2010 system (Shimadzu, Japan). The apparatus was equipped with a capillary column, namely a Zebron-5ms (Zebron, USA), 30 m × 0.25 mm i. d. × 0.25 µm film thickness; oven temperature program was from 50 °C (1 min) to 250 °C (1 min) at 4 °C min^{-1}, from 250 °C to 300 °C (10 min) at 10 °C min^{-1}. Injection occurred in splitless mode, sampling time was 5 min, split ratio 1:20, temperature 250 °C. Carrier gas (He) linear velocity: 30 cm sec^{-1}. FID: 300 °C, gases H_2 (40 mL min^{-1}), N_2 (80 mL min^{-1}), air (400 mL min^{-1}). Data were handled by means of *GCsolution* software v. 2.32 (Shimadzu, Japan) and each sample was analyzed in duplicate. Semi-quantitative determination of volatile compounds was carried out according to the following equation:

$$C_{\mathrm{VOC}} = \frac{peak\ area\ VOC}{peak\ area\ i.s.} \times C_{\mathrm{i.s.}}$$

where C_{VOC} is the concentration (mg Kg^{-1}) of each volatile compound, and $C_{\mathrm{i.s.}}$ is the concentration of internal standard in the sample (1.0 mg Kg^{-1}).

GC-MS analyses were performed on a GCMS-TQ8030 (Shimadzu, Japan), equipped with the same capillary column described above. Mass spectrometric parameters were as follows: source (EI) 200 °C, interface 230 °C, scan speed 10000 amu sec^{-1}, and scan mass range 35-350 m/z. Data handling was conducted by *GCMSsolution* software. Beside the employment of mass spectral libraries, such as FFNSC 2 (Shimadzu, Japan), Adams 4th edition, Wiley 9, NIST11, single peaks identity was assigned according to Retention Indices, measured in real samples after the SPME extraction and injection of a C8-C18 n-paraffins mixture.

2.6 Statistical analysis

Total and single polyphenols of every microencapsulated extract were expressed as mean ± standard deviation of triplicate samples, each analyzed three times.

With respect to aroma and sensory analyses of peanut bars, since each sample set (either conventional or fortified) was characterized by similar volatile fingerprints and sensorial measurements (relative standard deviation, RSD ≤ 10%), the huge amount of data was expressed as mean ± standard deviation of five samples, each analyzed two times.

Analysis of variance (ANOVA) followed by Tukey's HSD post-hoc test were conducted both for phenols and volatiles to check for any significant difference among antioxidant formulations and fortified/non-fortified peanut snacks, respectively. Also, a two-tailed Student's t-test for unpaired data was carried out for comparing fortified and conventional samples with regard to sensory attributes, and aromas at every sampling time, during the storage. Statistical significance was accepted at $p \leq 0.05$ in all statistical analyses.

3. Results and discussion

3.1 Polyphenols and DPPH activity of the spray-dried powder

Total polyphenol contents and levels of single polyphenols from the three formulations derived from peanut by-products are shown in Table 1. The phenol content of the formulation based on peanut skins (157.29 mg GAE *per* g of powder) was comparable to that of a peanut skin powder (125.67 mg GAE g^{-1}) developed according to the same experimental conditions by do Valle Calomeni and colleagues[18]. However, it was also higher than that of a powder (106.7 mg GAE g^{-1}) formulated by Costanza and coworkers[28], employing different peanut material (Virginia/Runner blend) and a slightly different extraction and microencapsulation procotol. The total phenol content of the hull powder (739.56 mg GAE g^{-1}) was higher ($p < 0.05$) than that of the skin-based powder, but lower when compared to the polyphenol contents of peanut hull extracts. In this respect, Adhikari and

colleagues[29] revealed recently phenol levels ranging from 428.1 to 739.8 μg GAE g^{-1} in different Korean peanut cultivars extracted by a methanol-based procedure.

Finally, the powder based on peanut skins+hulls showed a total phenol content equal to 807.23 mg GAE g^{-1}, significantly higher than the counterparts of the other formulations tested in this study ($p < 0.05$). Overall, such result pointed out that the combination of different peanut by-products in an innovative antioxidant formulation led to a boosted total phenol content, as well as to an unique phenol profile, as highlighted in Table 1.

Concerning single polyphenols, a direct comparison of the actual findings with data from peanut by-product extracts results somehow arduous, due to the limited literature on polyphenols of peanut skins[17,24,25,30] and the absence of studies on the polyphenol profile from peanut hulls. Overall, obtained results confirmed that the powder obtained from the combination of peanut skin and hull extracts represented a precious source of polyphenols. Overall. catechins, such as (-) -epigallocatechin, (+) -catechin, and (-) -epicatechin, were the most abundant compounds (respectively, 160.49, 190.84, and 120.96 μg g^{-1} of powder). They derived from both skins and hulls, although hulls contributed in a significantly higher way than skins ($p < 0.05$). However, coherently with previous literature, catechins confirmed to be one of the most representative compound classes of the polyphenol profile of peanut skin extracts[17,24,25,30]. Through to a lesser extent, also few phenolic acids (e.g. chlorogenic, ferulic and *p*-coumaric acids) from both skins and hulls gave their contribution in the determination of the phenol profile of the final formula. Concerning flavonoids, the skin+hull formulation was marked by quercetin, presumably derived only from peanut skins (respectively, 8.88 and 11.39 μg g^{-1}, $p > 0.05$), and luteolin, most likely come from peanut hulls (respectively, 1439.34 and 1367.19 μg g^{-1}, $p > 0.05$). In particular, luteolin has been already recognized as the major antioxidant and antimicrobial constituent of such by-product[23,31] and was found at comparable or even higher levels in hull extracts

from Chinese (2410 µg g^{-1}) and Korean (1264.6-4485.0 µg g^{-1}) cultivar[32,33]. *Trans*-resveratrol, another chemopreventive agent present in peanut skins at higher levels than kernels[34], was the least abundant phytochemical in both the peanut skins and skins+hulls formulations (respectively, 3.04 and 1.36 µg g^{-1}, $p > 0.05$, Table 1).

The mix of different peanut by-products, each marked by an appealing antioxidant activity (skins: 68.495 and hulls 71.27%, $p < 0.05$, Table 1), provided an antioxidant formulation characterized by an enhanced DPPH activity. This could be due not only to the higher total phenol content, but also to the co-presence of polyphenols peculiar to hulls (i.e. luteolin) or skins (i.e. *trans*-resveratrol) (Table 1). Indeed, the powder resulting from the combination of skins and hulls reached an inhibition value comparable to that of the synthetic antioxidant BHT (respectively, 85.96% and 89.30%, $p > 0.05$, Table 1). Taken together, these experimental evidences strongly encourage the employment of such formula as natural additive in food preparations.

Table 1. Total polyphenol content (mg GAE g^{-1} of powder) and single polyphenols (µg g^{-1} of powder) detected in microencapsulated extracts based on peanut by-products. Results are expressed as mean ± standard deviation of 3 samples, each analyzed three times.

Characterization of the spray-dried powders						
Total polyphenol content (mg GAE g^{-1})						
Peanut skins				157.29±10.74[a]		
Peanut hulls				739.56±18.60[b]		
Peanut skins/hulls				807.23±43.59[c]		
Single polyphenols						
Peak no.	**Analytes**	**λ_{max}** (nm)	**[M-H]$^-$**	**Concentration** (µg g^{-1})		
				Peanut skins	**Peanut hulls**	**Peanut skins+hull**
1	Gallic acid	270	169	nd	nd	nd
2	(-) -epigallocatechin	274	457	40.76±4.45[a]	70.34±7.37[b]	160.49±13.67[c]

3	(+) -catechin	276	289	87.79±7.68[a]	108.00±8.16[b]	190.84±21.25[b]
4	Chlorogenic acid	324	353	7.07±0.27[a]	nd	4.12±0.98[b]
5	Caffeic acid	320	179	nd	nd	nd
6	(-) -epicatechin	278	289	67.18±7.49[a]	100.09±15.33[b]	120.96±15.18[c]
7	*p*-coumaric acid	310	163	57.34±5.89[a]	21.73±3.35[b]	60.17±5.01[c]
8	Ferulic acid	320	193	1.07±0.00[a]	6.53±0.87[b]	3.37±0.61[c]
9	(-) -epicatechin-3-*O*-gallate	278	441	41.03±3.89[a]	nd	33.21±10.09[b]
10	Rutin	360	609	nd	nd	nd
11	*trans*-resveratrol	306	227	3.04±0.05[a]	nd	1.36±0.23[b]
12	Luteolin	337	285	nd	1367.19±367.98[a]	1439.34±202.19[a]
13	Quercetin	354	301	11.39±3.32[a]	nd	8.88±1.91[a]

DPPH assay (%)	
Peanut skins	68.49±0.75[a]
Peanut hulls	71.27±2.35[b]
Peanut skins/hulls	85.96±2.76[c]
BHT (positive control)	89.30±0.95[c]

nd = not detected

a-c = Different superscript letters in the same column (for total polyphenol content and DPPH assay) or row (for single polyphenols) indicate significantly different values ($p \leq 0.05$ by post hoc Tukey's HSD test); same superscript letters in the same column (for total polyphenol content and DPPH assay) or row (for single polyphenols) indicate not significantly different values ($p > 0.05$ by post hoc Tukey's HSD test).

3.2 Peanut bars

3.2.1 Sensory properties

Results from the sensory analysis conducted on peanut bars were shown through the spider diagram of Figure 1. Comparable results were obtained for roasted peanut (6.27 and 6.38, $p > 0.05$) and sweet caramel (7.51 and 8.0, $p > 0.05$) attributes, in both fortified and conventional groups. The raw/beany and burnt notes slightly varied from 1.38 to 1.80 ($p > 0.05$), and from 2.91 to 2.50 ($p > 0.05$), in conventional and fortified samples, respectively (Figure 1). However, the other attributes varied significantly, generally with a higher intensity evidenced in fortified samples. In fact, the woody/hulls/skin note resulted definitely less pronounced in conventional samples (1.9 vs. 3.7, $p \leq 0.05$); while bitter (2.3 vs. 3.6, $p \leq 0.05$) and astringent (2.2 vs. 3.7, $p \leq 0.05$) characters, typically conferred by polyphenols, such as quercetin proanthocyanidins[35,36], were tasted as more intense in

fortified samples (Figure 1). These findings are widely in agreement with the employment of the natural antioxidant formulation based on peanut skins+hulls.

3.2.2 Aroma stability

Figure 2 shows the GC-FID chromatograms of a conventional peanut bar headspace, sampled at four different times after opening the packaging. The volatile fingerprint was quite rich, although the chromatographic space becomes less crowded as time passes. The 23 selected peaks (common to all samples) were significant both for the nature of the matrix under investigation, and for their impact on the quantitative and olfactory aspects. They included pyrazines, phenyl, furan, and pyrrole derivatives (Table 2). The occurrence of such volatiles is widely in agreement with the type of processing undergone by peanuts for the production of snacks[37]. During roasting and caramelization, the latter necessary for sugar coating, Maillard reactions, lipid oxidation and Strecker degradation take place. Sugars breakdown upon heating causes the formation of furan derivatives, such as hydroxymethylfurfural. According to Min and Smouse[38], thermal degradation is responsible also for the occurrence of aldehydes, such as nonanal and nonadienal; whereas Maillard reaction leads to the formation of phenylacetaldehyde, as reported by Pripis-Nicolau and colleagues[39]. Traces of benzaldehyde were determined in all samples: this compound, typically found in almonds, has been negatively correlated with pyrazines in roasted peanuts, and treated as an off-flavor along with other aldehydes[40]. Indeed, findings of the present study confirm that a high presence of pyrazines, such as 2,5-dimethylpyrazine, 2-ethylpyrazine, 2,3-dimethylpyrazine, corresponds to a low amount of benzaldehyde (Table 2). Concerning pyrazines, it has been reported that an abundant fraction of such volatiles in roasted peanuts is correlated with higher content of oleic acid, ensuring not only a typical roasted aroma, but also a longer period of storage[40].

The presence of γ-butyrolactone finds support in a previous report, where various lactones have been listed among peanut aroma compounds[41]. Other typical flavour components deriving from sucrose browning are maltol and ethylpyrrole; whereas vanillin is considered more involved with table browning, namely a fermentation breakdown of sugars[42]. Volatiles such as 2-phenylbutenal and 4-vinylguaiacol are characteristic flavor components of peanut oil[43]; while 2-undecanone, although known as not having an aroma impact, has been already reported in roasted peanuts[44]. On the other hand, 3,4-dimethoxyacetophenone is here reported for the first time as a component of caramelized roasted peanuts; it can be speculated that its formation is strictly associated with the same pathway of vanillin, being the two molecules very similar in structure (Table 2).

Figures 3 and 4 highlight the trend of modifications occurring on the single volatiles, during the storage of and conventional samples and sample fortified with antioxidant formulation based on peanut skins+hulls, respectively. In every case, fingerprints were dominated by the first eluting pyrazines, namely 2,5-dimethylpyrazine, 2-ethylpyrazine, 2,3-dimethylpyrazine, grouped under the denomination "3 pyrazines". This was considered appropriate to overcome troubles with data handling, arising from possible coelutions in the first region of the chromatogram. Overall, Figures 3 and 4 show that a great part of volatiles followed the same decreasing trend and were characterized by a slightly higher concentration in fortified than in conventional samples, at the predefined storage times. However, certain compounds, such as γ-butyrolactone and benzaldehyde, reported very similar contents ($p > 0.05$) during the entire storage time, regardless of the type of peanut bar (Table 2).

When considering pyrazines, some differences can be highlighted: the 3 pyrazines showed a higher concentration in fortified than conventional samples at day 15 (9.49 vs. 8.87 ppm, $p \leq 0.05$), dropping down respectively to 5.57 vs. 7.16 ppm ($p \leq 0.05$) at day 45; finally, at day 100, approximately the same amount is found in both groups (5.03 vs 4.65, $p > 0.05$). A similar trend was observed for 2-

ethyl-3-methylpyrazine and 2-ethyl-3,5-dimethylpyrazine: in fortified and conventional samples, 2-ethyl-3-methylpyrazine was equal to 4.30 and 3.28 ppm ($p \leq 0.05$) at day 15; 1.71 and 2.29 ppm at day 45 ($p \leq 0.05$); 2.15 and 2.16 ppm ($p > 0.05$), at day 100, respectively. In fortified and conventional peanut bars, 2-ethyl-3,5-dimethylpyrazine amounted respectively to 2.08 and 1.24 ppm ($p \leq 0.05$), at day 15; 0.83 vs. 1.02 ppm ($p \leq 0.05$), at day 45; 0.51 and 0.56 ppm ($p > 0.05$), at day 100 (Table 2).

The most evident difference arising from the comparison of fortified and conventional samples during storage, concerns hydroxymethylfurfural, more concentrated in fortified samples immediately upon packaging's opening (day 0). Indeed, in the conventional group, its initial concentration significantly decreased of a 0.25 factor ($p \leq 0.05$) as sampling day increased; conversely, in fortified samples, its reduction was significantly not uniform ($p \leq 0.05$), with a drastic fall from day 45 to day 100 (from 5.67 to 1.73 ppm, $p \leq 0.05$) (Table 2). Individual minor differences could be caught in the remaining cases, such as in nonanal, (2E,4E)-nonadienal, 2-phenyl-2-butenal, (6Z)-nonen-1-yl acetate, vanillin and 3,4-dimethoxyacetophenone.

In Figure 5 are displayed the total amounts of the selected volatiles in conventional and fortified groups, determined in the four sampling dates. It is evident that the volatile fraction is more abundant in fortified samples, especially in day 0 and day 15, where samples added with the natural antioxidant formulation present a surplus of 17% and 23% volatiles compared to conventional peanut bars ($p \leq 0.05$). This discrepancy narrows considerably at day 45 and day 100, as a surplus of 8% ($p \leq 0.05$) and 1.7% ($p > 0.05$) of compounds characterized the fortified snacks.

Table 2. Key volatiles sampled by HS-SPME in peanut snack bar samples on four selected times during storage. Volatile contents (mg Kg^{-1}) are expressed as mean ± SD and are average of 5 samples analyzed in duplicate for each sample set (Conv= conventional samples; Aox= fortified samples).

	Compound	RI[¤]	RI[†]	Day 0		Day 15		Day 45		Day 100	
				Aox	Conv	Aox	Conv	Aox	Conv	Aox	Conv
				Concentration (mg Kg^{-1})							
1	2,5-dimethylpyrazine	908	912	12.76±1.03^{a}	13.54±0.98$^{\alpha}$	10.20±0.96^{b*}	8.27±0.66$^{\beta*}$	7.39±0.63^{c}	6.83±0.53$^{\gamma}$	4.32±0.16^{d}	4.32±0.09$^{\delta}$
2	2-ethylpyrazine	910	914	0.32±0.04^{a*}	0.02±0.00$^{\alpha*}$	0.38±0.04^{a}	0.36±0.03$^{\beta}$	0.21±0.03^{a}	0.14±0.04$^{\gamma}$	0.27±0.03^{a*}	0.13±0.02$^{\gamma*}$
3	2,3-dimethylpyrazine	913	916	0.92±0.05^{a*}	0.16±0.02$^{\alpha*}$	0.57±0.03^{b*}	0.24±0.04$^{\beta*}$	0.48±0.06^{b*}	0.19±0.03$^{\alpha*}$	0.44±0.09^{b*}	0.19±0.02$^{\alpha*}$
4	γ-butyrolactone	938	941	0.07±0.04^{a}	0.04±0.00$^{\alpha}$	0.09±0.03^{a}	0.04±0.02$^{\alpha}$	0.05±0.03^{a}	0.02±0.00$^{\beta}$	0.00±0.01^{b}	0.00±0.00$^{\gamma}$
5	ethylpyrrole	940	941	1.80±0.11^{a*}	1.64±0.05$^{\alpha*}$	1.27±0.01^{b*}	0.92±0.01$^{\beta*}$	0.93±0.03^{c*}	0.61±0.03$^{\gamma*}$	1.02±0.04^{d*}	0.60±0.01$^{\gamma*}$
6	benzaldehyde	959	960	0.09±0.02^{a}	0.07±0.00$^{\alpha}$	0.04±0.00^{b}	0.05±0.01$^{\beta}$	0.01±0.03^{c}	0.03±0.01$^{\gamma}$	0.08±0.00^{a*}	0.02±0.00$^{\gamma*}$
7	2-ethyl-6-methylpyrazine	997	1000	0.61±0.02^{a*}	0.69±0.02$^{\alpha*}$	0.67±0.02^{b*}	0.46±0.01$^{\beta*}$	0.29±0.03^{c}	0.31±0.00$^{\gamma}$	0.20±0.01^{d}	0.20±0.01$^{\delta}$
8	2-ethyl-3-methylpyrazine	999	1001	5.53±0.14^{a}	5.54±0.02$^{\alpha}$	4.30±0.02^{b*}	3.28±0.03$^{\beta*}$	1.71±0.03^{c*}	2.29±0.00$^{\gamma*}$	2.15±0.04^{d}	2.16±0.03$^{\delta}$
9	acetylpyrazine	1020	1023	0.44±0.02^{a*}	0.49±0.01$^{\alpha*}$	0.35±0.01^{b*}	0.39±0.01$^{\beta*}$	0.25±0.03^{c*}	0.31±0.00$^{\gamma*}$	0.04±0.00^{d*}	0.09±0.00$^{\delta*}$
10	phenylacetaldehyde	1042	1045	0.28±0.01^{a*}	0.60±0.01$^{\alpha*}$	0.24±0.01^{b*}	0.44±0.01$^{\beta*}$	0.18±0.03^{c*}	0.30±0.01$^{\gamma*}$	0.05±0.00^{d*}	0.07±0.00$^{\delta*}$
11	acetylpyrrole	1070	1074	0.52±0.01^{a*}	0.29±0.01$^{\alpha*}$	0.44±0.01^{b*}	0.20±0.01$^{\beta*}$	0.26±0.03^{c}	0.17±0.06$^{\beta}$	0.10±0.00^{d}	0.10±0.00$^{\gamma}$
12	2-ethyl-3,5-dimethylpyrazine	1078	1081	2.23±0.08^{a}	2.19±0.01$^{\alpha}$	2.08±0.04^{b*}	1.24±0.02$^{\beta*}$	0.83±0.03^{c*}	1.02±0.01$^{\gamma*}$	0.51±0.01^{d*}	0.56±0.01$^{\delta*}$
13	2-acetyl-3-methylpyrazine	1080	1082	0.69±0.02^{a*}	0.62±0.01$^{\alpha*}$	0.65±0.02^{b*}	0.36±0.01$^{\beta*}$	0.59±0.03^{c*}	0.28±0.01$^{\gamma*}$	0.08±0.00^{d*}	0.09±0.00$^{\delta*}$

14	nonanal	1104	1107	1.24±0.03^{a*}	0.78±0.01$^{\alpha*}$	1.10±0.02^{b*}	0.40±0.01$^{\beta*}$	0.42±0.03^{c*}	0.29±0.01$^{\gamma*}$	0.29±0.01^{d}	0.27±0.01$^{\gamma}$
15	maltol	1106	1108	2.66±0.09^{a*}	2.42±0.02$^{\alpha*}$	1.72±0.04^{b*}	1.61±0.01$^{\beta*}$	1.60±0.03^{c*}	1.10±0.01$^{\gamma*}$	0.21±0.01^{d*}	0.46±0.01$^{\delta*}$
16	(2E,4E)-nonadienal	1215	1218	0.24±0.03^{a}	0.21±0.01$^{\alpha}$	0.29±0.01^{b*}	0.12±0.01$^{\beta*}$	0.13±0.03^{c*}	0.09±0.00$^{\gamma*}$	0.07±0.00^{d*}	0.08±0.00$^{\delta*}$
17	hydroxymethylfurfural	1222	1225	11.12±0.45^{a*}	7.34±0.04$^{\alpha*}$	6.81±0.07^{b*}	5.75±0.01$^{\beta*}$	5.67±0.03^{c*}	3.82±0.11$^{\gamma*}$	1.73±0.01^{d}	1.76±0.03$^{\delta}$
18	2-phenyl-2-butenal	1269	1272	1.18±0.06^{a*}	0.93±0.01$^{\alpha*}$	0.41±0.01^{b*}	0.58±0.01$^{\beta*}$	0.45±0.03^{b}	0.42±0.01$^{\gamma}$	0.31±0.17^{c}	0.35±0.00$^{\delta}$
19	2-undecanone	1290	1294	0.52±0.02^{a}	0.48±0.01$^{\alpha}$	0.38±0.01^{b*}	0.28±0.00$^{\beta*}$	0.29±0.03^{c*}	0.21±0.01$^{\gamma*}$	0.09±0.00^{d}	0.09±0.00$^{\delta}$
20	(6Z)-nonen-1-yl acetate	1301	1304	2.14±0.07^{a*}	1.31±0.01$^{\alpha*}$	1.28±0.02^{b*}	0.68±0.03$^{\beta*}$	1.22±0.03^{c*}	0.59±0.00$^{\gamma*}$	0.42±0.02^{d*}	0.46±0.00$^{\delta*}$
21	4-vinylguaiacol	1306	1309	0.71±0.01^{a*}	0.51±0.02$^{\alpha*}$	0.56±0.01^{b*}	0.35±0.01$^{\beta*}$	0.39±0.03^{c*}	0.32±0.00$^{\gamma*}$	0.10±0.00^{d}	0.11±0.01$^{\delta}$
22	vanillin	1392	1394	0.83±0.01^{a*}	0.04±0.00$^{\alpha*}$	0.24±0.01^{b*}	0.03±0.00$^{\beta*}$	0.45±0.03^{c*}	0.02±0.00$^{\gamma*}$	0.03±0.00^{d}	0.02±0.03$^{\beta,\gamma}$
23	3,4-dimethoxyacetophenone	1565	1568	0.55±0.03^{a*}	0.85±0.01$^{\alpha*}$	0.16±0.00^{b*}	0.49±0.02$^{\beta*}$	0.04±0.03^{c*}	0.31±0.01$^{\gamma*}$	0.02±0.00^{c*}	0.14±0.03$^{\delta*}$

RI¤ = Retention Indices measured against a mixture of C8-C18 n-alkanes on a Zebron-5ms column. **RI†** = Published Retention Indices measured on a 5% diphenyl- stationary phase (source: FFNSC 2 library).

a-d Fortified samples: different superscript letters in the same row indicate significantly different values ($p \leq 0.05$ by post hoc Tukey's HSD test); same superscript letters in the same row indicate not significantly different values ($p > 0.05$ by post hoc Tukey's HSD test).**α-δ** Conventional samples: different superscript letters in the same row indicate significantly different values ($p \leq 0.05$ by post hoc Tukey's HSD test); same superscript letters in the same row indicate not significantly different values ($p > 0.05$ by post hoc Tukey's HSD test); *****significantly different values ($p \leq 0.05$ by Student's t-test) of conventional and fortified samples at each storage time.

4. Conclusions

Due to valuable antioxidant phenols and a high antioxidant activity, the formula derived from a combination of peanut skins and hulls showed a preservative effect on the aroma of fortified peanut snacks during storage, especially during the first 15 days. Additionally, beyond the bitter and astringent notes reasonably more perceived in the fortified bars, panelists emphasized that the employment of such natural additive still provided a good desirability of the product. Overall, the formulation based on bioactives from peanut by-products may represent not only a profitable recycling strategy for the peanut processing industry, but also an appealing alternative for synthetic additives able to retardate the flavor fade of peanut-based products.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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Figure 1. Spider diagram showing a comparison of the sensorial attributes perceived from fortified and conventional samples of peanut bars.

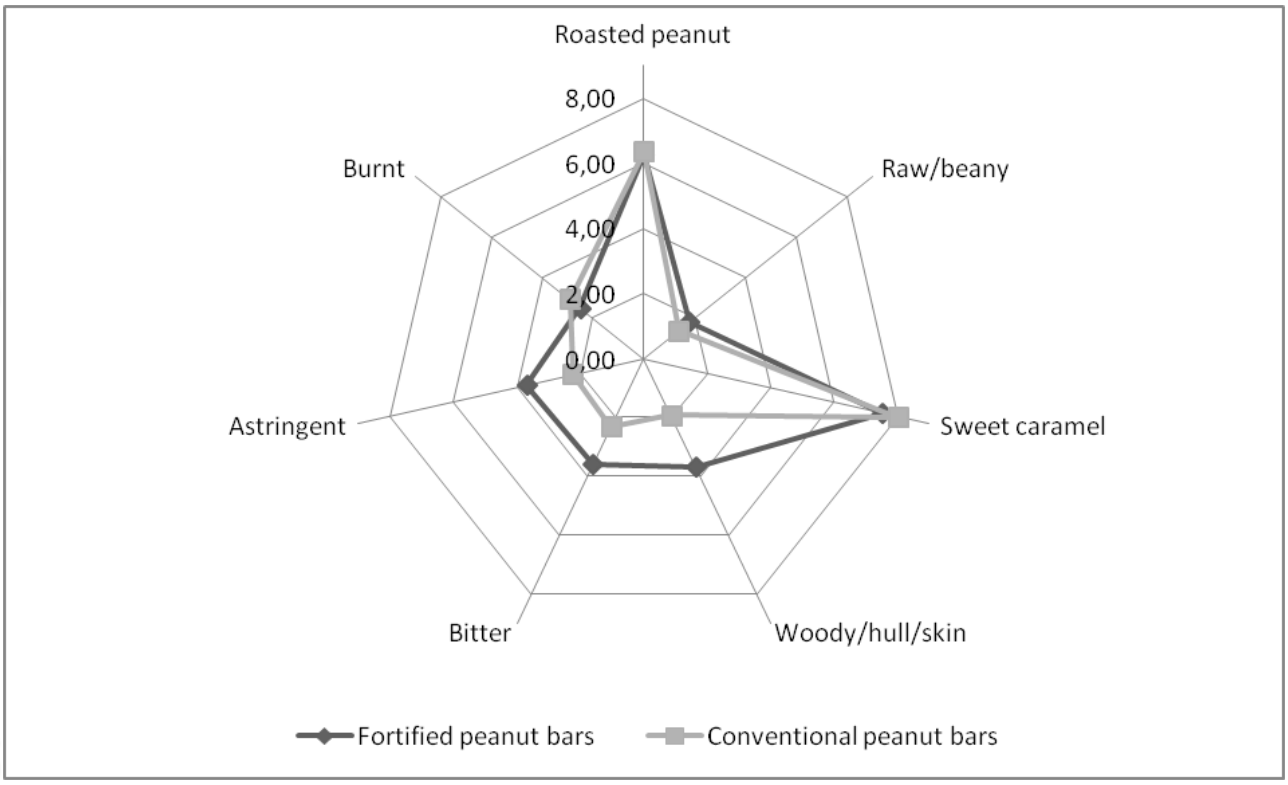


Figure 2. HS-SPME-GC-FID chromatograms of a peanut snack bar sample, extracted in four different times after opening its package. **I** = day 0; **II** = day 15; **III** = day 45; **IV** = day 100.

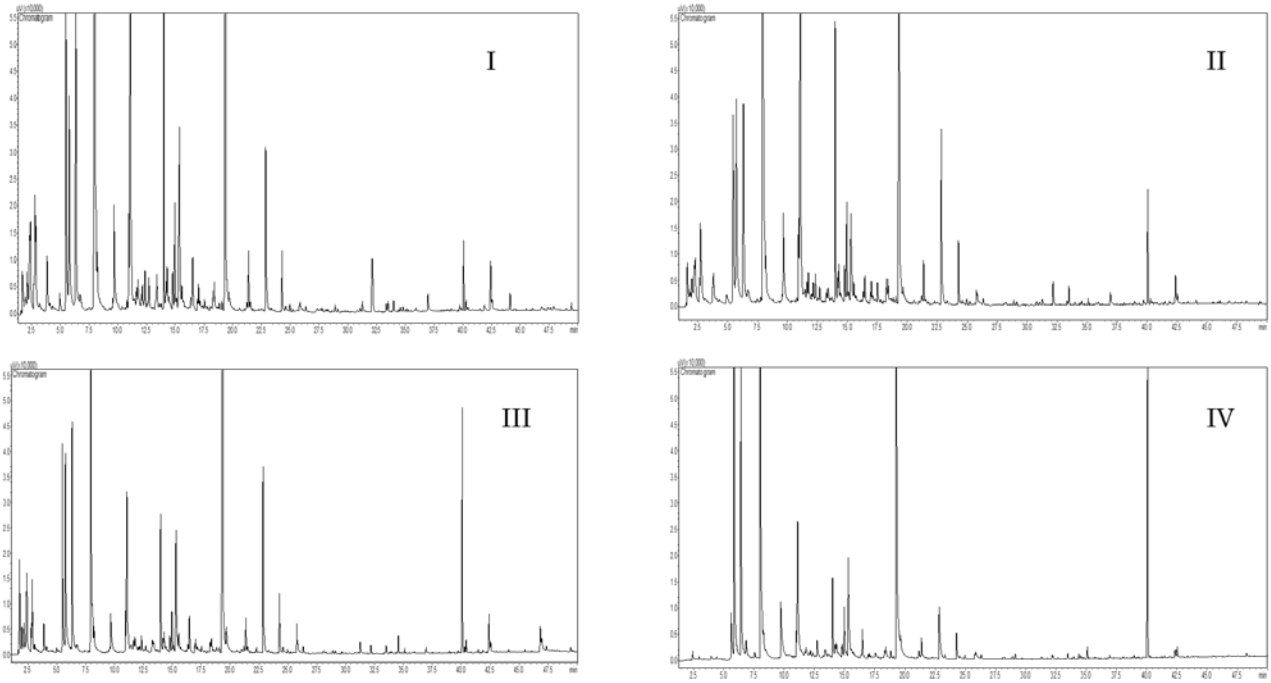
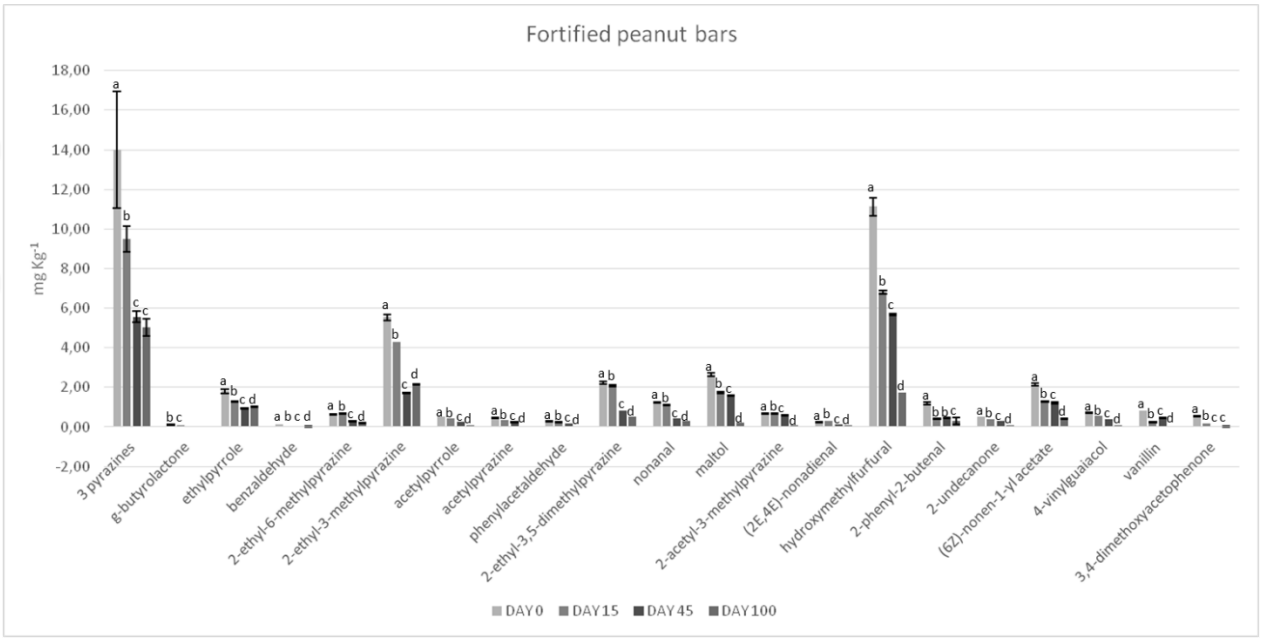
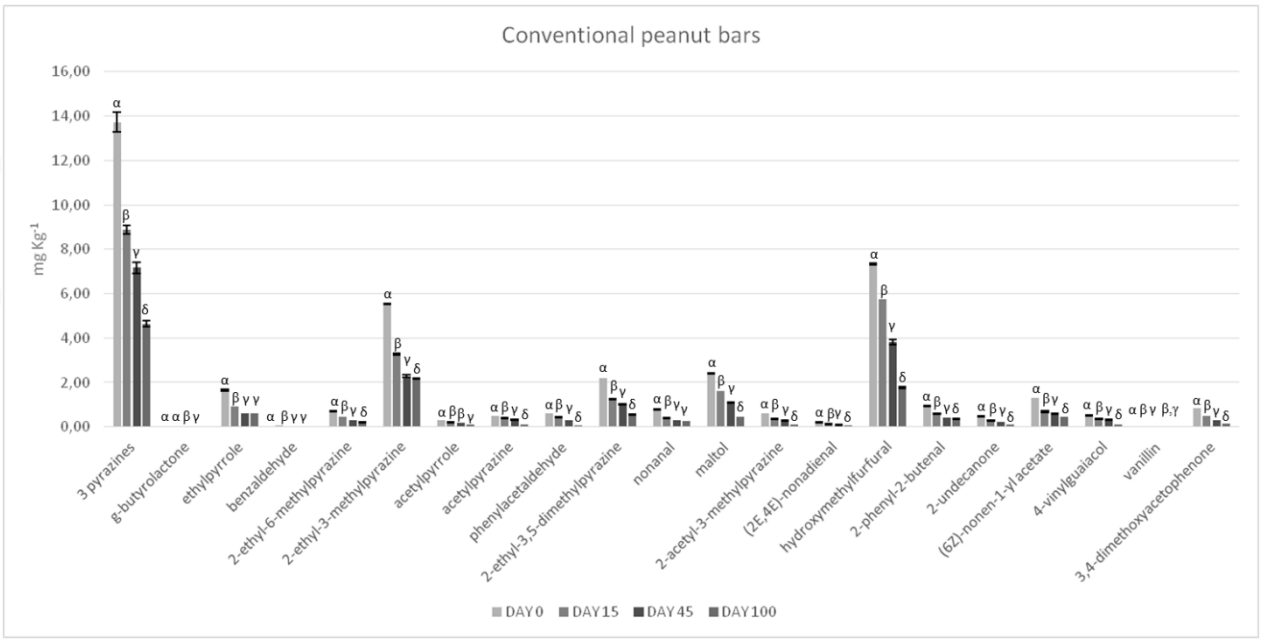


Figure 3. Quantitative (mg Kg^{-1}) changes of significant volatiles occurring during storage in fortified samples (*n = 5*).



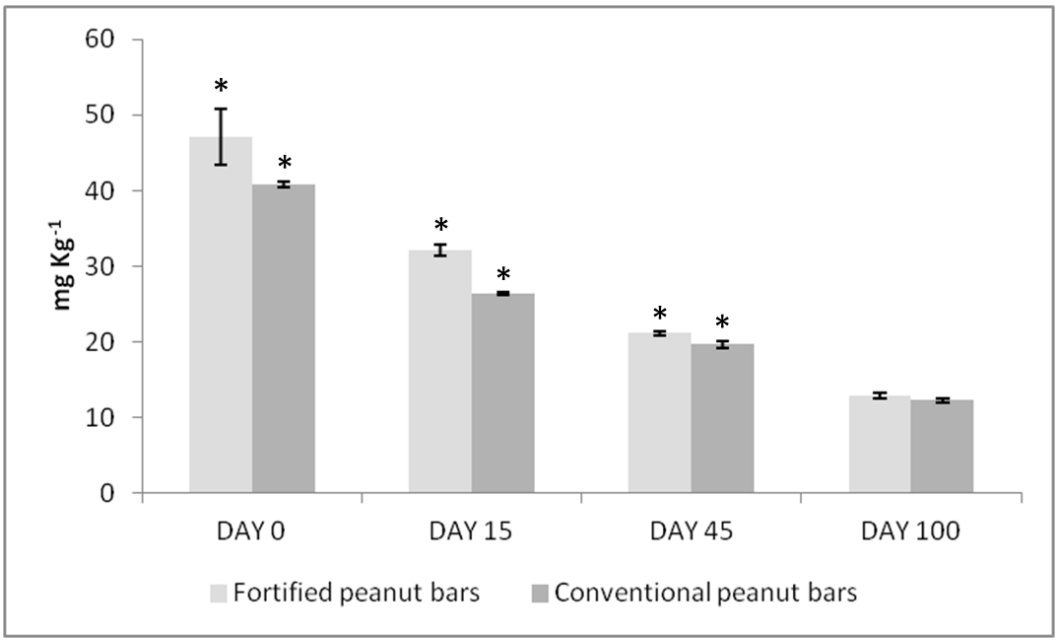
a-d For a given compound, different superscript letters indicate significantly different values ($p \leq 0.05$ by post hoc Tukey's HSD test); same superscript letters indicate not significantly different values ($p > 0.05$ by post hoc Tukey's HSD test).

Figure 4. Quantitative (mg Kg^{-1}) changes of significant volatiles occurring during storage in conventional samples (*n = 5*).



α-δ For each compound, different superscript letters indicate significantly different values ($p \leq 0.05$ by post hoc Tukey's HSD test); same superscript letters indicate not significantly different values ($p > 0.05$ by post hoc Tukey's HSD test).

Figure 5. Changes of the total flavor fraction (mg Kg^{-1}) in conventional (*n = 5*) and fortified samples (*n = 5*), observed during the storage trial.



*significantly different values ($p \leq 0.05$ by Student's t-test)