

Short Research Article

Broad bean and carob flours, alternative ingredients to amplify sensory notes.

1. Abstract

Objectives: Determine the volatile compounds present in flours obtained from regional fruits and correlate them with sensory descriptors. These legume flours present bioactive compounds that could enhance gluten-free foods by improving sensory and nutritional quality. **Study design:** Cross-sectional experimental. Carob (*Prosopis alba*) flour was obtained from fruits collected from Arraga, Santiago del Estero, Argentina and broad bean (*Vicia faba*) flour, provided by the CAUQUEVA Cooperative in the province of Jujuy, Argentina. These were subjected to the study of volatile composition and sensory profile of aromas. **Place and Duration of the Study:** It was carried out at the Institute of Chemical Sciences and the Institute of Food Science and Technology, National University of Santiago del Estero, Argentina during the year 2019. **Methodology:** Suspensions were made with the flours. Eight trained panelists between the ages of 23 and 60 participated, and worked with the quantitative Descriptive Profile methodology. To determine the volatile compounds in the flours, the manual technique of solid phase microextraction (SPME) and a 100 µm fiber coated with polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA, USA) were used, followed by gas chromatography coupled to mass spectrometry (MEFS-CGMS). **Results:** Acids, esters, ketones, hydrocarbons, terpenes and sulfur compounds were identified. 22 compounds were found in carob flour and 16 in broad bean flour, 12 are common. Broad bean flour aromatic descriptors: fresh bean, bitter, grassy, rancid, yeasty. The ketones would be linked to the smell of grass and fresh beans, the alcohols to the descriptors rancid, bitter and yeast. Carob flour descriptors: toasted, cocoa butter, melon, sweet, spicy, almond. The decanal is related to the smell of melon. The toasty smell is linked to the pyran group of ketones. **Conclusions:** The volatile composition of both flours and the sensory aromatic profile were determined.

Keywords: volatiles, broad bean flour, carob flour, sensory profile

2. Introduction

The smell is one of the first characteristics perceived by the human senses, crucial for the acceptance of food by consumers. The most widely consumed baked goods have traditionally been made with wheat or rye flour, which provide pleasant notes with compounds that come mainly from fermentation, lipid oxidation or Maillard processes. However, it is well known that baked goods made with gluten-free (GF) flours have decreased sensory characteristics concerning traditional wheat counterparts.

Differences in proteins, sugars, lipids, enzymes and antioxidants between the different gluten-free flours/starches could lead to important differences in the volatile profile. Until now, research on the aroma of gluten-free baked goods has focused on understanding the origin of volatile compounds compared to wheat bread, but no sensory data on **broad**

bean and carob flours that could be used in the formulation of GF baked goods were found.

The partial replacement of GF flours by other flours with greater power and aromatic richness —such as alternative cereal flours (teff, millet or sorghum), pseudo-cereals (buckwheat, quinoa or amaranth) or leguminous flours— has a clear impact on the aromatic profile of the bread [1], [2].

In the ecosystem of the Gran Chaco Americano, there is an extraordinary plant biodiversity, with an important production of wild fruits with attractive nutritional qualities [3].

The Food and Agriculture Organization of the United Nations (FAO) recommends promoting the care, production and cultivation of underexploited native plants, to broaden the food base [4].

Despite the beneficial properties of the fruits of native plants, they are still underutilized raw materials. An alternative to overcome this limitation is the transformation of these fruits into flours (F) that can be incorporated into food products and/or fodder for human and/or animal consumption.

From a nutritional point of view, cereals are the main energy providers in the human diet, they are foods widely consumed by the population, but they are not suitable for people with intolerant to gluten, so rice flour is generally used as a base bakery for these individuals.

However, the volatile odorant profile of rice flour is flat and without attractive notes. Recent studies reflect the latent dissatisfaction among celiac consumers regarding the sensory quality of the bread they consume [5], [6].

At present, various authors have focused on the search for flours rich in nutritional compounds of interest such as proteins, fibers, minerals and polyphenols, but free of GF [7], [8], [9], [10], [11], [12], [13], [14] and [15].

Thus, flours composed of cereals and legumes have a double beneficial effect: higher protein content in the mix and a better balance of essential amino acids. The composition of the compound flours affects not only the nutritional quality but also the functional, sensory and phytochemical qualities of the food products made from them.

On the other hand, knowing the profile of volatile odorant components of the flours of these legumes becomes important since it would be useful to incorporate them into GF formulations and design improved foods compared to market counterparts with a different sensory profile, which would expand the food supply to the gluten-intolerant segment of the population.

The sensory profile of baked goods will be strongly influenced by the flour and/or starch used, since the ingredients contain the precursors that will give rise to the volatile compounds responsible for their organoleptic characteristics [16].

3. Materials and methods

The broad bean flour (BF) was provided by the CAUQUEVA Cooperative from Jujuy, Argentina.

The fruits of *Prosopis alba* selected, clean and dry were collected from Arraga, Silípica Department, Santiago del Estero, Argentina.

For the process of obtaining carob flour (CF), the selected and cleaned fruits were dried at 48 ± 2 °C in a forced-air oven (DALVO, DHR/F/I) at a speed of 2 m/s for 340 hours. Subsequently, they were ground for 90 s at 2900 rpm in CROYDON blade mechanical action equipment. The endocarp was separated from the mesocarp and epicarp using an ASTM 8 sieve (2380 μm). The endocarp milling product was sieved through a set of ASTM sieves (35, 80), the fractions used for the different tests were from the fraction that passes the ASTM 35 sieve and is retained on the ASTM 80 sieve (R80) with a particle size between 500 and 177 μm .

Storage conditions were especially careful to avoid the loss of volatiles, so they were vacuum packed (-690 mmHg) in 200 μm bags and stored at refrigerated temperature (4°C).

3.1 Sensory profile of odor in broad bean and carob flour.

To carry out the aroma profile, we worked with 8 trained panelists, between 23 and 60 years old. Before the definitive determinations, training sessions were carried out, following the techniques of the quantitative descriptive analysis (QDA) method developed by Stone [17].

A total of 2.5 hours were organized before the sensory test. During the first 90-minute session, the different flour samples were presented to the panelists. They described the samples individually and then discussed them with the rest of the judges and with the leader of the panel, Norma 20002 [18]. The 8 panelists verbalized their impressions regarding the two samples presented. For the selection of the descriptors, the objective of the study was taken into account and those of similar meaning and those that were used with a frequency of less than 40% were eliminated [19]. After the training in the use of scales, we worked on measuring the intensity of the descriptors on 10 cm scales. Anchored at the ends. Three repetitions were performed.

The resulting data were submitted to the analysis of variance of two factors: sample and evaluators.

3.2 Identification of volatile compounds

For the identification of volatile compounds, the samples were analyzed by applying the manual technique of solid phase micro-extraction (SPME) and a 100 μm fiber coated with polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA, USA), followed by gas chromatography coupled to mass spectrometry (MEFS-CGMS).

For the extraction of volatile compounds, 1 g of flour was placed in a 5 ml vial covered with a PTFE/silicone septum and sealed with aluminum caps (Supelco) for headspace analysis. Before taking the sample, the fiber was conditioned in the CG injector at 250 °C for 3 minutes.

The vial with each of the samples was placed in a bath at a temperature of 60 °C to allow the volatilization of the flour components and their equilibrium with the headspace. The SPME fiber was inserted into the sealed vial by manual penetration of the septum and exposed to the headspace for 30 minutes. After that time, the fiber was inserted into the GC injector and the organic compounds were thermally desorbed (250 °C) for 1 minute.

Chromatographic analyzes were carried out on a Thermo Scientific Focus GC coupled to a DSQII mass detector. The GC was operated in split-less mode. A TR-5MS capillary column (30 m× 0.25 mm× 0.25 μm) (Thermo Fisher Scientific) was used under the following analytical conditions: initial temperature 50°C for 5 min, a temperature ramp of 7°C min⁻¹ until a final temperature of 250°C, which was kept constant for 10 min.

The samples were analyzed in triplicate. The identification of the compounds was carried out using the NIST-08 spectral library (Software Xcalibur 2.0.7, Thermo Fisher Scientific Inc.), the calculation of the retention indices (Kovats indices, KI), data reported in literature (Adams and Sparkman, 2007), and the comparison with commercial standards. Retention indices were calculated using linear interpolation relative to retention times of C7–C25 of n-alkanes and then compared with those commercial standards and data from the literature. The commercial standards used were limonene, dodecane, tridecane, 3-methyltridecane, α-caryophyllene, 2-pentadecanone, pentadecane, hexadecane, heptadecane, octadecane and nonadecane, 3-methyldodecane, decanal. The identification of *t*-muurolene, α-copaene, 5,6-Dihydro-2H-pyran-2-one, 5,6-dihydro-6-propyl-2H-pyran-2-one, and γ-nonalactone is tentative but were reported in literature for Carob flour [20], [21].

4. Results and Discussion

The mechanical damage of the elaboration process contributes to the development of the characteristic reactions of the constituents and the generation of aromas, because its cellular structure is broken and the enzymes come into contact with its precursors and can hydrolyze them.

4.1 Sensory profile of odor in broad bean and carob flour.

A list of 12 odor descriptors for CF and 10 for BF was obtained. Those with the highest frequency of responses issued by the judges were selected and those with a similar meaning were discarded. Figures 1 and 2 present the results for CF and BF respectively.

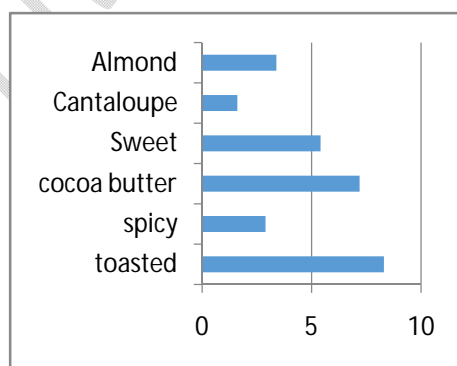


Figure 1: Representation of CF descriptors

It can be seen in the figure that the toasted aroma is the one that is perceived with the greatest intensity, which is attributable to the drying process of the carob fruit prior to grinding.

The smell of grass predominates over the sui generis smell of fresh broad beans. It is noteworthy that, although in a small proportion, a slight rancid odor was detected due to the type of lipids present in beans that are sensitive to oxidation.

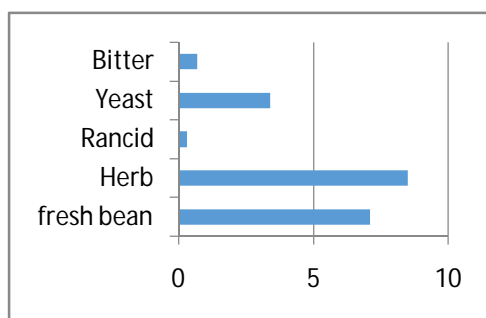


Figure 2: Representation of BF descriptors

4.2 Identification of volatile compounds in bean and carob flours (gluten-free)

Compounds of different chemical families, acids, esters, ketones, hydrocarbons, terpenes and sulfur compounds among others, associated with enzymatic and non-enzymatic reactions and lipid oxidative reactions, were identified. Among the major compounds, 22 compounds were found for CF and 16 compounds in BF, of which 12 are common to the two flours under study.

Among the common compounds are: limonene, dodecane, benzothiazole, tridecane, 3-methyl tridecane, α -caryophyllene, *t*-muurolene, pentadecane, hexadecane, heptadecane, octadecane and nonadecane, these are found in different proportions as shown in Figure 3.

Figure 3 shows that the flours of these legumes under study have a similar qualitative radial representation in their shape, showing the bean flour with a higher concentration in 10 of the 12 common compounds, except for octadecane and tridecane, which in HA is found in greater amount.

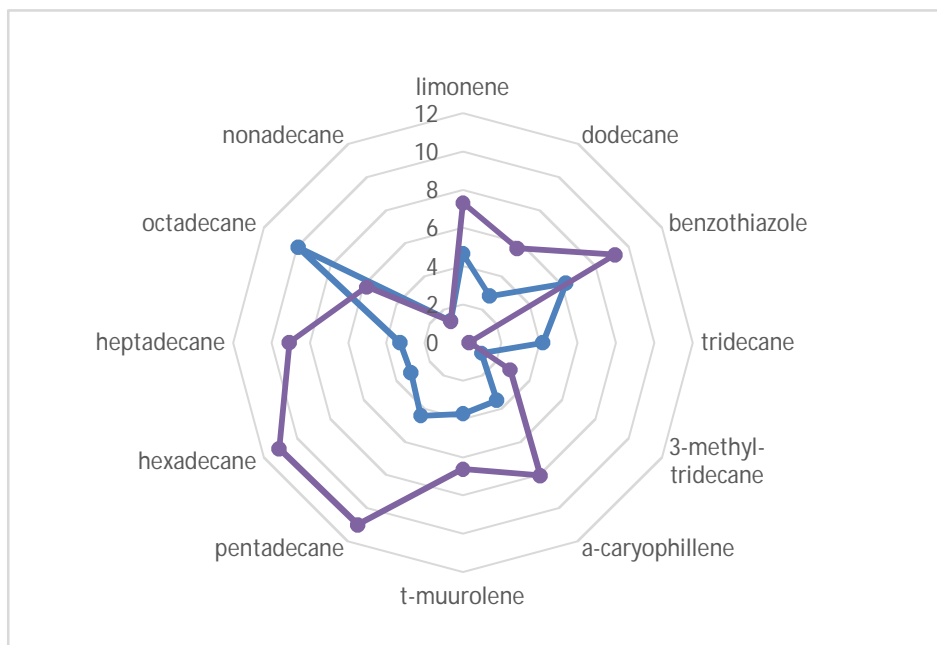


Figure 3. Radial representation of the percentage areas of the BF (—) and CF (—) volatile compound peaks.

BF has 3 compounds that were not found in CF: undecane, gamma nonalactone, and n-Hexyl hexanoate, as shown in Table 1.

Table 1. Exclusive components present in CF and BF.

CF		BF	
Component	%Area	Component	%Area
1,2,4-trimethylbenzene	4,57	undecane	4,28
(2-methoxyethyl)-benzene	5,17	γ -nonalactone	0,48
5,6-dihydro-2H-pyran-2-one	8,28	n-Hexyl hexanoate	10,93
decanal	1,41		
3-methyldodecane	1,55		
α -copaene	2,49		
tetradecane	4,09		

2-pentadecanone	2,14		
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γ -nonalactone is naturally present in many fruits, including pineapple, blackberries, and some melons; and it is also a component of bourbon whiskey [22] and wines aged in oak barrels. γ -nonalactone is widely used in the creation of sweet fragrances and flavors for foods.

N-hexyl hexanoate: odor, herbaceous, fresh. Hexyl hexanoate belongs to the class of organic compounds known as fatty acid esters. Hexyl hexanoate has an odor of apple peel, cut grass, and a fresh taste. This could make hexyl hexanoate a potential biomarker for the consumption of these foods.

Regarding CF, the areas of 6-Propyl-5,6-dihydro-2H-pyran-2-one and 5,6-Dihydro-2H-pyran-2-one stand out according to what is shown in Figure 4.

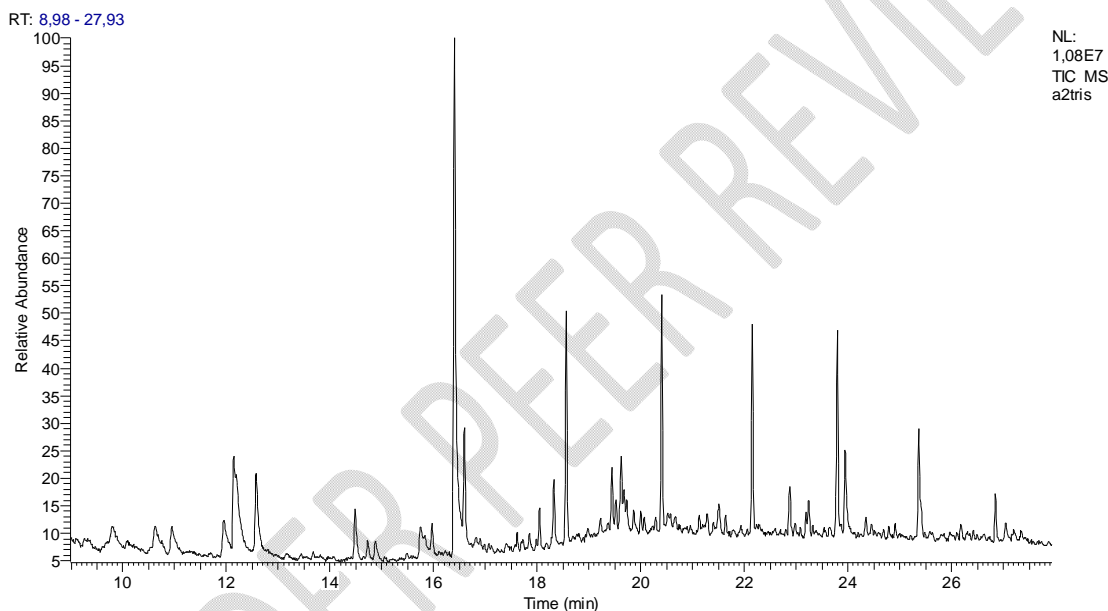


Figure 4. Chromatogram obtained by SPME extraction (100 μ m coated with polydimethylsiloxane (PDMS)) and GC/MS determination on CF.

Table 2: Volatile compounds identified in the chromatogram of Figure 3.

Compound	RT	KI	KIcal	%Area
1,2,4-trimethylbenzene	9,78	1006	1003	4,57
limonene	10,61	1034	1036	4,63
1-bromoheptane	10,93	nc	1049	2,18
(2-methoxyethyl)-benzene	11,94	1083	1089	5,17
5,6-dihydro-2H-pyran-2-one	12,12	1094	1096	8,28
dodecane	14,48	1200	1199	2,80

decanal	14,86	1208	1217	1,41
benzothiazole	15,72	1258	1258	6,20
3-methyldodecane	15,96	1270	1269	1,55
5,6-dihydro-6-Propyl-2H-pyran-2-one	16,39	1290	1290	19,88
tridecane	16,59	1300	1299	4,17
3-methyl-tridecane	18,04	1373	1373	1,12
α -copaene	18,32	1382	1387	2,49
tetradecane	18,56	1400	1399	4,09
α -caryophyllene	19,44	1447	1447	3,49
<i>t</i> -muurolene	19,62	1457	1457	3,71
pentadecane	20,41	1500	1499	4,41
hexadecane	22,15	1600	1599	3,14
heptadecane	23,79	1700	1699	3,30
2-pentadecanone	23,93	1703	1706	2,14
octadecane	25,36	1800	1800	9,94
nonadecane	26,85	1900	1899	1,32

The compound 5, 6-dihydro-6-propyl-2H-pyran-2-one, found among the volatiles present in CF, contributes to an aroma of chocolate and coconut, which is related to what was stated by the trained judges who describe this smell like cocoa butter. In addition, the compounds that present pyrano groups in their structure, due to the magnitude of their odor threshold, probably contribute strongly to the odor of carob flour, linked to the roasted descriptor found by the sensory panelists.

The odor notes attributed to volatile compounds together with other sensory characteristics are interesting properties as a strategy to improve the sensory quality of gluten-free products on the market.

5. Conclusions

Being the aroma one of the most important sensory attributes of food, in this study it was possible to characterize in a preliminary way the volatile composition of these flours and the profile of odorants determined by the panel of trained judges.

The results found would be very useful when considering the formulations of LG products, especially in baked goods, suggesting studies of volatile compounds in these foods after their preparation.

6. References

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