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Nutritional Approach of Carob Pulp Powder "*Ceratonia siliqua* L.'' from Algeria: Potential as Cocoa Substitute in Chocolate Formulations

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ABSTRACT

Background: This study explores the viability of carob pulp flour (CPF) as an alternative to cocoa formulation, focusing on its nutritional attributes and sensory acceptability.

Methods: Physicochemical analysis was conducted to assess the composition of CPF, including its fiber, sugar, mineral, protein and fat content using GC-MS. X-ray fluorescence (XRF) was employed to determine essential mineral concentrations. Three chocolate formulations (F0, F1 and F2) were developed and evaluated.

Result: CPF was found to be rich in fibers (7%) and sugars (79.64%), with notable levels of potassium (61.76%) and calcium (28.18%). However, it contained relatively low levels of protein (1.51%) and fat (0.6%). The predominant fatty acids in CPF were palmitic acid (16.70%) and oleic acid (18.37%). Among the chocolate formulations tested, F2 (73.3g CPF and 10g sugar) emerged as the most preferred by participants across different demographics and age groups. This suggests that CPF-based chocolate, with a balanced flavor profile and moderate sweetness, provides a highly appealing sensory experience.

Key words: Carob based chocolate, Carob pulp flour (CPF), *Ceratonia siliqua*, Cocoa substitute.

INTRODUCTION

The carob tree (*Ceratonia siliqua* L.), a perennial plant from the Fabaceae family, holds significance in the food industry for its diverse chemical constituents, pleasing flavor profile and nutritional advantages. It thrives in Mediterranean climates and is extensively cultivated for its ability to thrive in harsh environments and grow in less fertile soils with low to moderate rainfall (250-500 mm/year) (Theophiloul *et al.,* 2017).

Carob′s fruit is a brown pod, primarily composed of pulp (90%) and a smaller proportion of seeds (10%). Exploring the potential of using carob flour without removing these seeds warrants further investigation. The interest in carob pulp as a food ingredient is growing steadily because of its positive health impacts. Study of Yousef *et al.* (2013) have indicated that carob flour contains (76%) of carbohydrates, (6%) of proteins, (2%) of fats, dietary fibers, along with a range of minerals and vitamins. This chemical composition endows carob with strong antioxidant properties and a variety of therapeutic benefits, including lipid-lowering effects Zunft *et al.,* (2001), cardiovascular protection, anti-cancer activities (Avallone *et al.,* 2002; Corsi *et al.,* 2002), nephroprotective qualities Ahmed *et al.,* (2010) and relief from gastrointestinal issues (Turnbull *et al.,* 2006).

Carob is versatile and finds applications in the textile, paper, food and oil manufactories. Carob powder, produced from roasted carob, is often used as a cocoa substitute due to its chocolate-like flavor and similar sensory attributes (Baumel *et al.,* 2018). Although carob contains fewer bioactive compounds compared to cocoa, it contains higher dietary fiber, which promotes improved digestion and has a greater carbohydrate content. This makes it possible to reduce the amount of added sugar in products incorporating carob. Additionally, carob is a source for producing locust bean gum (LBG), extensively used in various industrial applications like bakery products, noodles, dairy items and edible coatings (Turnbull *et al.,* 2006; Hariri *et al.,* 2023).

The purpose of this study was to determine the chemical constitution and mineral content of Algerian carob flour and to evaluate its influence on the acceptability, texture, aroma and taste of food products. The findings will offer essential insights into the feasibility and potential of

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using carob powder as a substitute to cocoa in the food industry.

MATERIALS AND METHODS

Plant materials

Carob fruits, was harvested from Bissa region, Chlef, Algeria (Fig 1), during August-September 2023, were processed the same year at Hassiba Benbouali University's Biotechnology Laboratory. Seeds were removed and segments were oven-dried (50°C, 48h) and ground into Carob Pulp Flour (CPF). Samples were refrigerated at 4°C until analysis.

Analytical determination

Dry matter content was determined by drying samples in a convection oven at 105°C. Ash content was determined by incinerating samples in a muffle furnace at 550°C for 8 hours (AOAC, 2006). Protein content was determined using the Kjeldahl method, with nitrogen converted to protein using a 6.25 factor Fendri *et al.,* (2013). Crude fiber content was determined according to the method by Pádua *et al.,* (2004). Total sugar content was determined using the phenol sulfuric acid method Dubois *et al.,* (2002) and analyzed with an SS Read 2200 Microplate reader. pH levels were determined using a pH meter (AFNOR, 1970). Lipid content was determined using a modified Soxhlet extraction, where 10g of sample was extracted with 100 mL of diethyl ether/hexane mixture for 3 hours, then the solvent was evaporated and the residue quantified as lipids Mamyrbékova-békro *et al.,* (2009). Fatty acid analysis was performed using GC-MS (Agilent Technologies) with helium carrier gas, identifying components by retention indices and mass spectral library matching (Pieracci *et al.,* 2022; Zakari *et al.,* 2021). Mineral fraction was analyzed by XRF, using 5g samples pressed into 32 mm pellets under 10 tons force. Chocolate preparation followed an artisanal method Lagha-benamrouche *et al.,* (2023), involving roasting carob flour at 50°C, mixing with sugar, oil, cocoa/ carob powder, lecithin and vanilla over 12 hours, resulting in three formulations (Table 1).

Rheological and sensory analysis of chocolate

Chocolate viscosity measured via capillary viscometer Monteiro *et al.,* (2024). Sensory evaluation conducted with participants aged 20-60 using hedonic analysis questionnaire for three formulations (Table 1). Overall, preference rated 1-10; participants identified influential organoleptic characteristics (appearance, color, sweetness, carob aroma, texture, taste) Molu *et al.,* (2021). Questions assessed familiarity with and consumption habits of regular and carob-based chocolate.

Microbiological analysis of chocolate

Microbiological analysis of chocolate was performed to identify and quantify microorganisms per regulatory standards. Details of targeted flora, culture media, conditions and standards are shown in Table 2.

RESULTS AND DISCUSSION

Results of carob pulp flour (CPF) preparation

The obtained (CPF) (Fig 2) revealed distinct characteristics: dark brown color, fine texture providing unique tactile experience and sweet aroma occasionally enhanced by subtle dried fruit notes. These attributes stem from the pulp's richness in dietary fibers and natural sugars, contributing to its specific texture and sensory profile.

Results of physico-chemical characterization and chromatographic analyses

The results of physico-chemical characterization are summarized in (Table 3). The measured pH of carob pulp

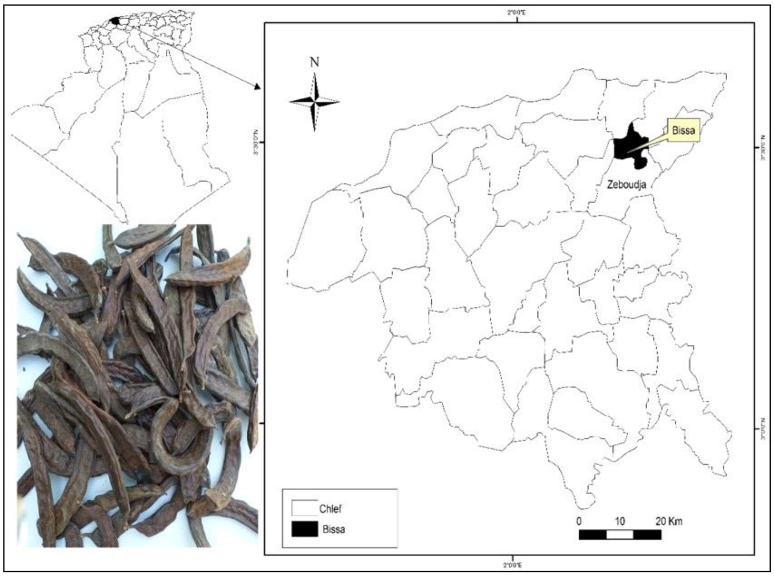

Fig 1: Location of *Ceratonia siliqua* L plant.

flour (CPF) powder is 5.19, closely aligning with the value reported by Yousif *et al.,* (2000) at pH 5.96 and exceeding that reported by Baston (2016) at pH 4.34±0.01.

The moisture content of CPF in this study is 12.45%, higher than that reported by Baston (2016) at 10% and Ozcan *et al.,* (2007) at 6.26%, while Avallone *et al.* (1997) indicated a range of 6% to 10% for moisture content. Avallone *et al.,* (1997) further noted a moisture content range of 8.1% to 8.7%, indicating that moisture variation in carob powder may be influenced by factors such as processing, storage conditions, cultivar variations, geographical location and agricultural practices, as observed by Khlifa *et al.* (2013).

The dry matter content of carob pulp powder in our study is measured at 87.55%, which is slightly higher than the value reported by Albanell *et al.,* (1991) at 87.31%, but lower than the value reported by Salih *et al.* (2020), which is 90.8±0.53%.

The ash percentage in carob pulp powder amounts to 3.3%, falling within the range typically observed in the literature, which generally ranges between 2% and 3.2% (Sigge *et al.,* 2011; Azab 2022) and between 1% and 6% according to Avallone *et al.* (1997).

A previous study report that the fiber content in carob ranges from 4% to 8.5% Karkacier and Artik (1995). However, different research findings show considerable variability in the fiber content of carob powder, with estimates ranging from 2% to 40% (Khlifa *et al.,* 2013; USDA 2016; Basharat *et al.,* 2023). The carob pulp, often regarded as a secondary output in the carob pod processing manufactory, is actually a rich supplier of nutrients. It is abundant with carbohydrates, especially sugars and fiber and contains an array of minerals, amino acids and vitamins, among other valuable components Loullis and Pinakoulaki (2018). Recently, attention has been drawn to the potential health benefits of carob products, particularly focusing on the advantageous effects of dietary fibers. These fibers play a role in the prevention of diabetes, cardiovascular diseases and gastrointestinal disturbances Brassesco *et al.* (2021). Previous research has shown that carob pods have a high sugar amount, with total sugar contents ranging between 52.7% and 62.3% according to Karkacier and Artik (1995) and between 48% and 56% in carob flour, primarily comprising sucrose, glucose and fructose Goulas *et al.,* (2016). Our results indicate that total sugars constitute approximately 79.64±2% of the major constituents of carob pulp powder. Salih *et al.* (2020) recorded a value of 51.5% for total sugars in their study on carob pulp powder, while Baston (2016) reported a value of 58% for CR1 and Ayaz *et al.* (2007) reported that carob pods contain about 88% sugars. In a different study, Youssef *et al.* (2013) noted a slightly lower sugar content at 76%, while Khlifa *et al.* (2013) documented an even lower figure of 45%. Furthermore, Kumazawa *et al.* (2002) and Biner *et al.,* (2007) identified sucrose, glucose and fructose as the principal sugars present in carob pods.

The fat content of the (CPF) is measured at 0.6%, a figure notably lower than the range documented by Azab (2022), who reported variations in carob powder fat content spanning from 2% to 4.4%. Studies, conducted by Papaefstathiou *et al.* (2018) and Oziyci *et al.* (2014), corroborated this finding, affirming a very low fat content in carob pods, typically ranging between 0.21% and 0.23%.

Detailed analyses unveil substantial and distinctive proportions of fats in (CPF), with oleic acid comprising 18.37% and palmitic acid 16.70% (Table 4 and Fig 3). The presence of oleic and palmitic acids in carob flour highlights the nutritional relevance of these fatty acids, which play a significant role in Mediterranean diets. Oleic acid is particularly noted for its heart-protective properties Massaro *et al.,* (1999) and has been demonstrated to decelerate the advancement of adrenoleucodystrophy (ALD), a severe neurodegenerative condition (Rizzo *et al.,* 1986; Simopoulos, 2002). Carob syrups, pulps and pods are known for their exceptionally low fat content, usually falling between 0.2% and 1% Musa Özcan, (2007).

Loullis and Pinakoulaki (2018) report that carob pulp contains a variety of fatty acids, including stearic (C18:0), palmitic (C16:0), linoleic (C18:2n6c, omega-6), α-linolenic (C18:3n6) acids and oleic (C18:1n9c). The presence of fat in carob products often stems from additional ingredients such as sunflower seeds, oils, or sesame seed paste. Carob's low fat content (<1% compared to cocoa's 37-57%) positions it as a recommended alternative in infant food formulations (Rodríguez-Solana *et al*., 2021).

Carob pulp is notably low in protein, with a content of just 1.51%, unlike other parts of the *C. siliqua* fruit, including

Table 1: Composition of the three different formulations of chocolates.

Sample name	Composition
F_0	15 g Cocoa, 35 g Vegetable oil, 45 g Sugar, 1 g Vanilla, 0.4 g Lecithin, 0.3 g Salt
F_1	40 g CPF, 35 g Vegetable oil, 23.3 g Sugar, 1 g Vanilla, 0.4 g Lecithin, 0.3 g Salt
F_2	73.3 g CPF, 15 g Vegetable oil, 10 g Sugar, 1g Vanilla, 0.3 g Salt

Table 2: Microbiological analysis parameters of chocolate.

Flora sought	Culture media	Culture conditions	Seeding	References
Yeasts and molds	PDA	3 days, 25°C	In surface	ISO7954
Enterobacteria	Violet red bile glucose agar	1 day, 37°C	In surface	ISO21528-2
Coliforms	Violet red bile agar (VRBA)	1 day, 37°C	In surface	ISO4832
Total germs	PCA	3 days, 30°C	In depth	ISO4833

its seeds (18.6%) or the combined pulp and seed of the carob pod (4%) Mahtout *et al.* (2018). This modest protein level in carob fruit powder (CPF) is consistent with Azab (2022), who reported protein contents in carob powder ranging from 1.7% to 5.9%.

Under Regulation (EC) No. 1924/2006, unprocessed carob and food items containing carob are not classified as significant protein sources since they do not meet the minimum required percentage of 12%. Nonetheless, incorporating functional ingredients such as carob pod flour can enhance the protein content and quality of food by leveraging its compatible amino acid profile (Arribas *et al.,* 2019; Rodríguez De Marco *et al.,* 2014). The nutritional impact of a food extends beyond protein quantity to encompass the ease of digesting these proteins.

Mineral analysis results by XRF

XRF analysis of carob fruit powder (CPF) revealed that potassium (61.76%) and calcium (28.18%) are the major minerals, aligning with Khlifa *et al.,* (2013), who also found high levels of these elements in their samples. The analysis identified five trace elements: magnesium, copper, zinc, selenium and iron, along with sodium, chlorides and phosphorus (Table 5).

Compared to the pulp alone, the entire fruit (pod) integrates minerals from the seed, providing a rich source of essential elements like potassium (K), phosphorus (P), magnesium (Mg) and calcium (Ca), as well as trace elements such as copper (Cu), iron (Fe), zinc (Zn), boron (B) and manganese (Mn) (Oziyci *et al.,* 2014). The mineral composition of carob pods, influenced by factors like geographic origin, fruit variety, cultivation methods (*e.g.*, fertilizer application) and environmental conditions, varies significantly. These factors collectively determine the levels of minerals essential for both plant and human nutrition

Aspect and organoleptic results of carob chocolate

The initial findings of this evaluation reveal that carob-based chocolate exhibits a solid appearance, with a dark brown color (Fig 4), characteristic chocolate flavor and no foreign odor. The taste is deemed free from defects and no foreign elements were observed upon macroscopic examination.

Additional aspects such as mouthfeel hardness, solubility, flexibility and adhesion level are also important texture properties to consider in the overall evaluation of chocolate (Afoakwa 2010; Pallavi *et al.,* 2018). These elements are essential to ensure a pleasant sensory experience and optimal quality of the final product.

Fig 2: Representative image of carob pulp flour (CPF).

Table 3: Results of physico-chemical analyses of carob pulp flour (CPF).

Parameters	CPF
PH	5.19
Moisture (%)	12.45
Dry matter content (%)	87.55
Ash content (%)	3.3
Fat content (%)	0.6
Electrical conductivity (µS)	2.5
Total sugars (%)	79.64
Crude proteins (%)	1.51
Fibers (%)	7

Table 4: Fatty acids identified by GCMS in the CPF.

TR (min)	%	Identified compounds
14.79	2.55	Decanoicacid (Capric acid)
17.14	1.70	Tridecanoicacid (Tridecylic acid)
19.26	2.03	Hexadecanoicacid (Palmitic acid)
19.76	16.70	n-Hexadecanoicacid (Palmitic acid)
20.92	1.14	Cis-11,14-Octadecadienoic acid
20.97	4.19	Cis-8-Octadecenoic acid
21.48	18.37	Oleicacid (Oleic acid)
23.50	3.69	Hexanedioicacid (Adipic acid)
24.68	1.42	1,2-Benzenedicarboxylic acid
26.25	2.90	1,2-Benzenedicarboxylic acid
26.70	2.04	Hexadeca-2,6,10,14-tetraen-1-ol (2-cis-Geranylgeraniol)
28.93	2.63	Anthiaergosta-5,7,9-trien-3-one (dehydroegosterol)

Based on Fig 5, our results demonstrate that formulation F2 is the most preferred in all sensory aspects, including appearance, color, odor, texture, sweetness and taste. F2 provides a superior sensory experience, optimally meeting consumers′ expectations in terms of quality and taste.

The results of the tasting sessions for the three chocolate formulations (F0, F1 and F2) (Fig 6) reveal distinct sensory preferences based on gender and age. Formulation F2, with the highest percentage of carob pulp flour (CPF) and reduced sugar content, emerged as the favorite across all categories. Men showed a clear preference for F2 (60.8%), followed by F1 (54.83%) and F0 (45.12%). Among women, F2 also dominated with a high score of 68.88%, surpassing F1 (54.16%) and F0 (42.13%). These preferences suggest that the sensory characteristics of formula F2, such as the intensity of CPF and lower sweetness, are particularly appealing to both genders.

Examining age groups, individuals aged 18 to 25 exhibited a slight preference for F2 (50.66%), nearly equal to F1 (49.77%), while those aged 26 to 60 displayed a more pronounced preference for F2 (66.6%) compared to F1 (57.52%) and F0 (54.54%). These variations indicate that taste perceptions evolve with age and adults aged 26 to 60 are more likely to appreciate the taste nuances brought by high CPF and low sugar content. Overall, the data demonstrate that formulation F2 better meets the diverse taste expectations of consumers.

Results of microbiological analysis

Results show absence of spoilage flora (TAMF, yeasts, molds, Enterobacteria, coliforms), meeting quality standards. Low moisture content and hygienic storage inhibit microbial growth (Iacumin *et al*., 2022). CPF-based chocolate maintained microbial safety over 21 days, ensuring product integrity during storage.

Table 5: Mineral Composition of CPF in %, Measured by XRF.

	Mass fraction (%)
Mineral element	Pulp
Mg	0.90
Al	0.08
Si	0.22
P	1.32
S	1.07
Cl	5.59
K	61.76
Ca	28.18
Fe	0.47
Cu	0.14
Zn	0.12
Sr	0.14

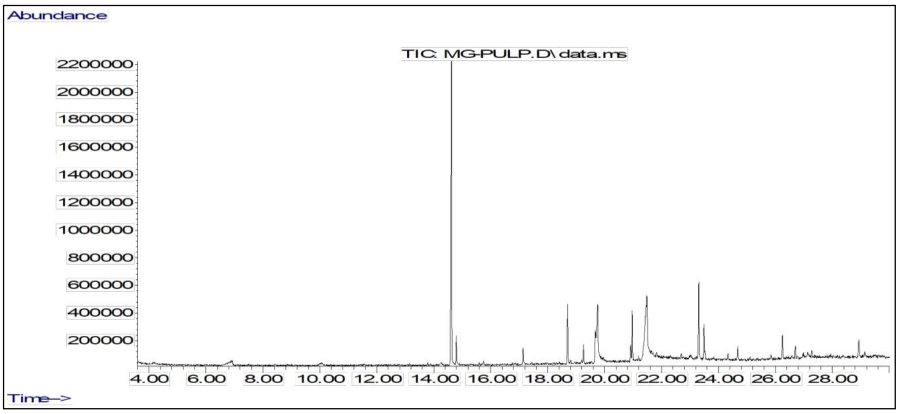

Fig 3: Chromatogram of the fatty acid analysis of CPF by GCMS/HP-5MS column in Scan mode, TIC, Splitless.

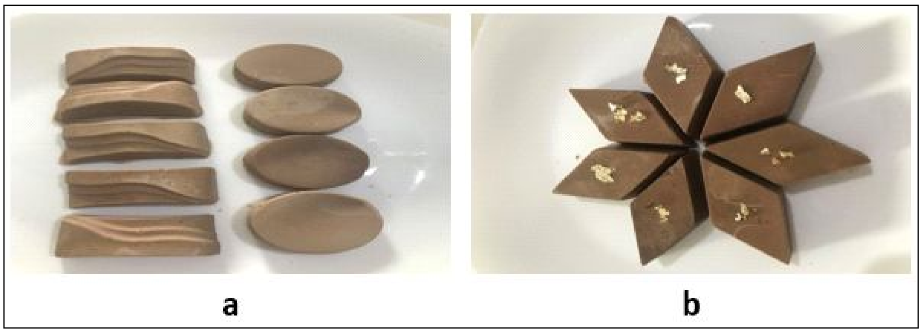

Fig 4: Appearance of carob-based chocolate (a) and cocoa-based chocolate (b).

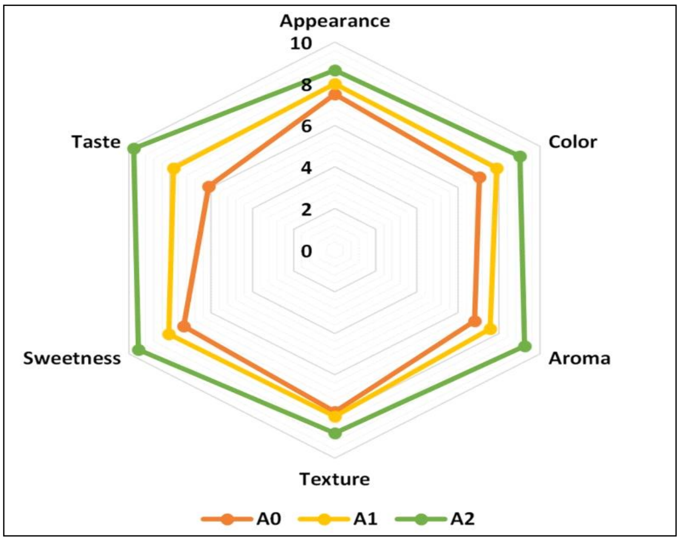

Fig 5: Radar chart of overall appreciation of samples A and B by the subjects.

Fig 6: Radar chart of appreciation of different samples according to gender and age.

CONCLUSION

This study highlights the nutritional potential of carob pulp flour (CPF), emphasizing its richness in fibers, carbohydrates and essential minerals. The fats present, primarily palmitic and oleic acids, have beneficial health properties.

In chocolate formulation trials, the third formulation (F2) with 73.3 g of CPF and 10 g of sugar was the most preferred, showing strong sensory appeal. Carob pulp shows promise as a cocoa substitute, enhancing the nutritional profile of alternatives. Future research should focus on optimizing carob-based products for maximum benefits, establishing carob as a sustainable alternative to cocoa.

Conflict of interest

The authors declare no competing of interests.

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