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Review

Carob Pulp: A Nutritional and Functional By-Product Worldwide Spread in the Formulation of Different Food Products and Beverages. A Review

Raquel Rodríguez-Solana [1,2,*], Anabela Romano [2] and José Manuel Moreno-Rojas [1,*]

[1] "Alameda del Obispo" Centre, Department of Food Science and Health, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA), Avdenida Menéndez Pidal s/n, 14004 Córdoba, Spain
[2] Campus de Gambelas, MED—Mediterranean Institute for Agriculture, Environment and Development, Faculdade de Ciências e Tecnologia, Universidade do Algarve, Ed. 8, 8005-139 Faro, Portugal; aromano@ualg.pt
* Correspondence: raquel.rodriguez.solana@juntadeandalucia.es (R.R.-S.); josem.moreno.rojas@juntadeandalucia.es (J.M.M.-R.); Tel.: +34-671-532-749 (R.R.-S.)

Abstract: Carob (*Ceratonia siliqua* L.) pod is a characteristic fruit from the Mediterranean regions. It is composed by seeds, the valuable part due to the extraction of locust bean gum, and the pulp, considered a by-product of the fruit processing industry. Carob pulp is a mixture of macro- and micronutrients, such as carbohydrates, vitamins and minerals, and secondary metabolites with functional properties. In the last few years, numerous studies on the chemical and biological characteristics of the pulp have been performed to encourage its commercial use. Its potential applications as a nutraceutical ingredient in many recipes for food and beverage elaborations have been extensively evaluated. Another aspect highlighted in this work is the use of alternative processes or conditions to mitigate furanic production, recognized for its toxicity. Furthermore, carob pulp's similar sensorial, chemical and biological properties to cocoa, the absence of the stimulating alkaloids theobromine and caffeine, as well as its low-fat content, make it a healthier potential substitute for cocoa. This paper reviews the nutritional and functional values of carob pulp-based products in order to provide information on the proclaimed health-promoting properties of this interesting by-product.

Keywords: carob pulp; functional food; nutritional composition; bioactive compounds; furanic compounds

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1. Introduction

Carob tree (*Ceratonia siliqua* L.) (Fabaceae) is one of the most useful trees in the Mediterranean basin and other Mediterranean-like regions, because of its economic and environmental implications. This species presents interesting agroecological features, such as resistance to drought and salinity, adaptation to poor soils, and minimal cultural requirements, and as such it has been introduced successfully into these areas with scarce agronomic resources [1].

The fruit of this species, also known as the carob pod, is composed of seeds (kernels) and pulp. For the different applications of the fruit, the first step is carob pod deseeding or kibbling, whereby the seeds are separated from the pulp (Figure 1).

The seed consists of germ, endosperm and husk. Because the germ and the endosperm are each used in different (food and/or non-food) applications, it is also necessary to separate the different fractions of the seed. Due to the hardness of the husk, there are several possible treatments to achieve high-quality seed part separation, usually involving a chemical treatment (e.g., sulfuric acid) [2]. Once the endosperm is separated, the food additive locust bean gum (E-410, also called carubin) is obtained from the grinding of this part of the seed. In the case of pulp processing, it can be kibbled to various grades (pieces/kibbles, and flour/powder) for animal feed. Moreover, the pulp can be roasted

to improve its organoleptic characteristics, obtaining, when together with other food ingredients, a taste very similar to cocoa [3]. After this, it is common to include grinding and sieving steps to obtain carob flour, a product often used in different food preparations for human consumption.

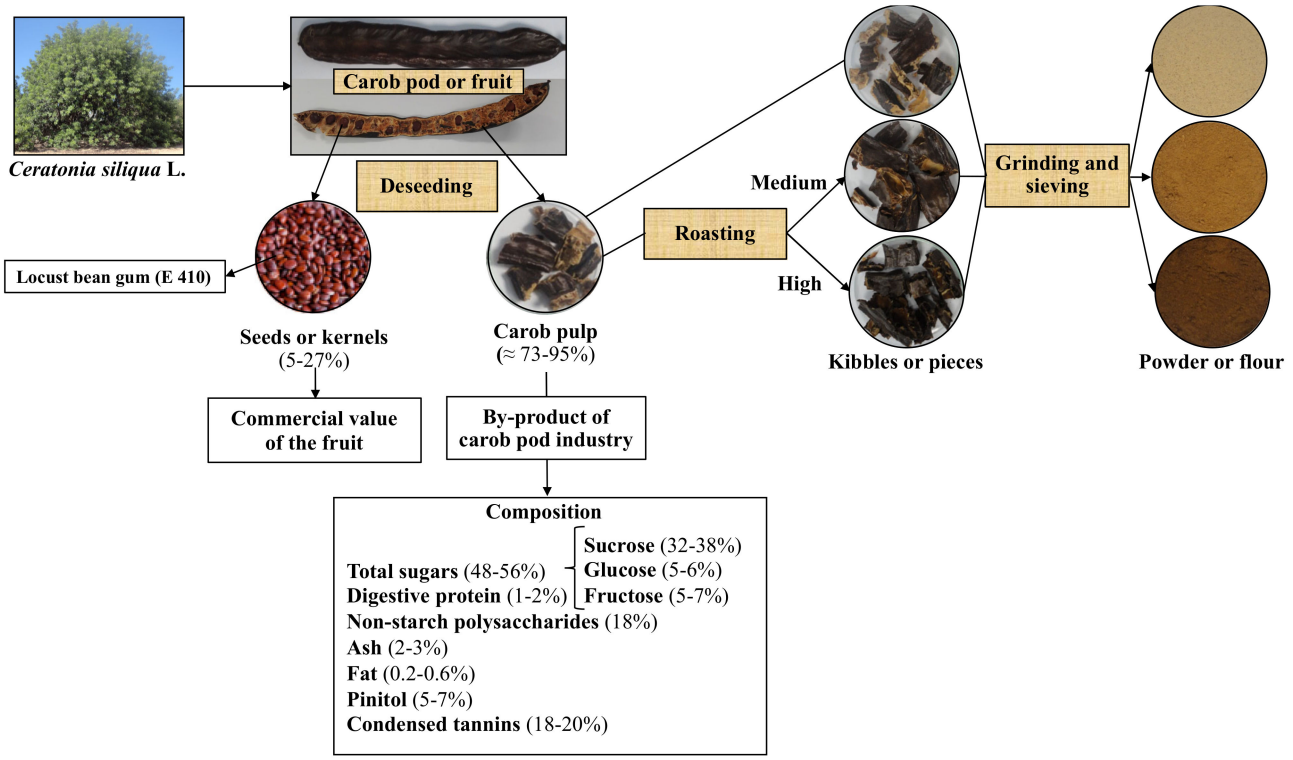

Figure 1. Main chemical constituents of carob pulp and its processing steps.

Among the different carob products (husk, endosperm, germ and pulp), the economic importance of carob pod comes from the industrial utilization of locust bean gum. This additive is employed in a wide range of products in the food and non-food industries as a thickener and stabilizer. On the other hand, the pulp is considered a by-product of the carob pod industry, and represents an important source of nutrients, such as carbohydrates (mainly sugars and fiber), minerals, amino acids, and vitamins, among other components [4] (Figure 1). Due to these characteristics, carob pulp has, over the years, been used as a cheap source for animal nutrition and also for humans in times of famine [1]. In addition, other components with great importance in carob pulp are the secondary metabolites, such as phenolic acids, flavonoids, tannins, etc., which have functional properties and provide health benefits (antioxidant, anti-inflammatory or anti-aging properties, etc.) to the human body. Compounds derived from Maillard and caramelization reactions generated during the roasting process, such as Maillard reaction products (MRPs) or melanoidins, and their intermediaries, e.g., the furanics, 5-hydroxymethyl furfural (HMF), furfural, furan, and acrylamide, may be present. These compounds are involved/associated with the sensory properties of carob pulp products, and are the intermediaries that are considered harmful to human health [5].

Furthermore, carob pulp has similar nutritional, functional and organoleptic properties to cocoa, with the advantage of being a theobromine- and caffeine-free food with low fat content [6]. For all the aforementioned issues, in recent years there has been an upswing in the study of food products using carob pulp as a promising new ingredient. Carob pulp flour, or the syrup made from the concentrated water extracted from kibbles or carob flour, are used in the elaboration of multiple products such as drinks (infusions, kvass,

hydro-alcoholic macerates, liqueurs and carob-based milk beverages), baked goods (bread, biscuits, muffins, and cakes), snacks, pasta, and yogurt (Table 1).

Table 1 shows the origin of the raw material used in some carob products, the elaboration steps, and the nutritional and functional properties. The method of pulp preparation and processing during the elaboration of the different food products is of utmost importance, as will be explained in detail later. Another important aspect is the fact that when the whole pod is used for carob food production, the contribution of the chemical compounds present in the seed might also modify the final composition of the carob product.

The composition and nutritional quality of carob products are affected mainly by the carob genotype/variety, the harvesting period, the growing conditions, the climatological conditions (e.g., sun and water availability), the soil, and the overall microclimate. In the same way, the postharvest conditions (e.g., storage and distribution of the food chain) and the food processing approach should not be underestimated [7]. As such, and in order to study and evaluate the nutritional and functional properties of the resulting food products, many factors have been assessed, such as the carob's origin, its variety, and the carob fruit ripening stage (harvesting time) [8,9]. In addition, one of the key points assessed in these studies was the use of different processing stages, to see the influence of this on the chemical and sensory characteristics and biological activities of the carob products. The grinding of the carob to reduce its particle size and the roasting degree are of utmost importance. The particle size—kibbles or flour—influences the extraction duration and the composition of the final extract [10]. The thermal treatment used to improve the quality of food in terms of flavor, wettability, and digestibility has major effects on the functional properties of the food products. As a result of this processing step, the formation of new compounds from different reactions, such as Maillard, caramelization and thermal degradation, or the release of other compounds from complex structures, all take place [11]. Thus, certain chemicals, such as phenolics, Maillard and caramelization intermediates (e.g., furanic compounds), and final products (e.g., volatile compounds, and brown pigments called melanoidins), as well as the functional properties such as the antioxidant capacity, increased with increasing roasting temperature [8,9]. Therefore, the carob pulp processing method greatly affects the final composition of the carob products.

All these factors might explain why studies carried out with traditional products that are commercialized by small local markets or producers present great variability in chemical composition, suggesting a lack of standardization in the manufacturing process [7]. This fact will be discussed in detail later.

2. Nutritional Parameters of Carob Products

The intake of balanced products helps to prevent health problems arising from inadequate eating habits. For that reason, nowadays, the demand for nutritious and safe products is growing globally, which is becoming a major concern to consumers [12–14]. Among the different components ingested in the diet, appropriate amounts of macronutrients, such as carbohydrates (mainly sugars), fats (lipids), proteins, and micronutrients such as vitamins and minerals, are essential to the processes that support life.

In this section, the nutritional compositions of different food products that use carob pulp as a novel natural ingredient will be explained in detail (short summary in Figure 2).

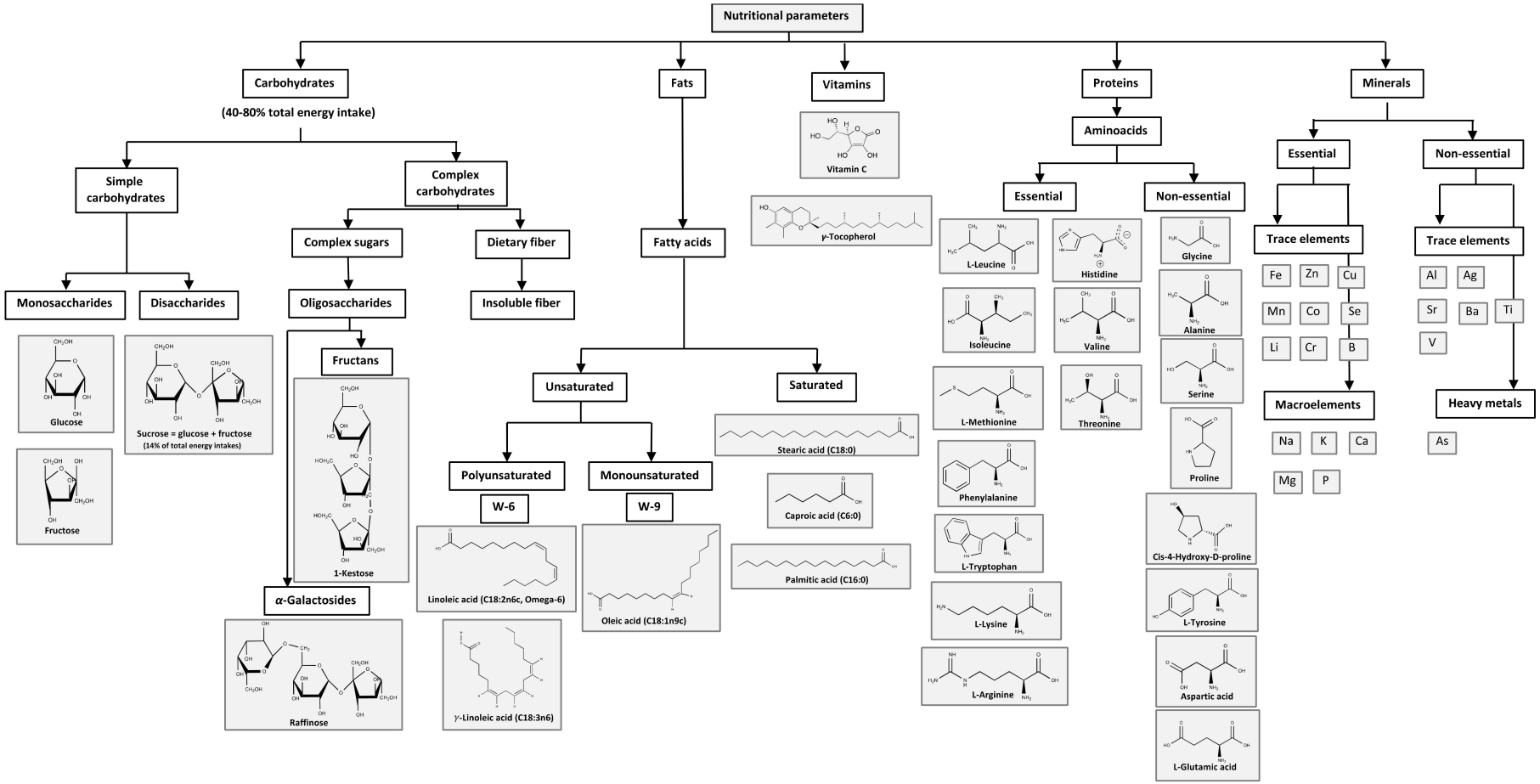

Figure 2. Nutritional parameters, carbohydrates, fats (fatty acids), proteins (amino acids), vitamins, and minerals observed in carob products, coming from the carob pulp or produced during the different steps of carob product processing.

Table 1. Origin of the carob pulp, and the elaboration process of carob products (syrups, creams, baked goods, pasta, dairy products and beverages). Nutritional and functional characteristics studied in the different works.

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Syrups and creams				
Commercial syrups (Malatya, Turkey)	-	Invert sugars. Glucose. Sucrose. Total lipids. Minerals: Na; K; Ca; Fe; Mn; Ni; Zn; Cu; Se (FAAS and flame photometry); P (vanadium phosphomolybdate colorimetric method).	HMF (UV absorbance at 284 nm). TPC (F-C). AC: DPPH	[15]
Commercial syrups (local markets, Kayseri, Turkey)	Carob fruit syrups were subjected to different storage times (0, 45 and 90 days) and temperatures (25, 35, 45 °C)		HMF (C_{18} column; HPLC-DAD).	[16]
Commercial syrups (Uşak, Turkey)	-		Phenolic profile: Gallic acid, gentisic acid, vanillic acid, luteolin (Green capillary electrophoresis method)	[17]
Commercial syrups (Atışeri Co., Antalya, Turkey)		Total carbohydrate content. Glucose. Fructose. Sucrose.	TPC (F-C). AC (DPPH).	[18]
Commercial syrups (local markets, Antalya, Turkey)	-	Total sugars. Inverted sugars. Sucrose. Protein. Minerals: K, Mg, Ca, Na, Fe, Cu, Zn, Mn (AAS); P (vanadium phosphomolybdate method, spectrophotometry at 430 nm).	TPC (F-C). HMF (nucleosil C_{18} column HPLC-UV-Vis).	[19]
Commercial syrups (obtained from Nutrinova)	-		Phenolic profile. Gallic acid, catechin, caffeic acid, coumaric acid, ferulic acid, myricetin-desoxyhexoside, quercetin-desoxyhexoside, cinnamic acid (column and guard column 3 µm C_{18}; 280 nm; HPLC-DAD-ESI-MSn). TPC (F-C). Condensed tannins (catechins and proanthocyanidins) (vanillin method at 500 nm). AC (DPPH).	[20]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob syrups (local markets, Turkey)	Mixtures of starch (from corn or wheat), carob syrups (0, 1, 5, 10, 20, 30%), and water (100, 99, 95, 90, 80 and 70%) and holding temperature (90, 92, 95 and 98 °C)	Sugars: glucose, fructose, sucrose (HPLC-RI; LC-NH_2 column)		[21]
Carob fruits (Antalya, Turkey)	Mined carob fruits + hot water (1:5, *w/w*) (60 °C, 8 h) to obtain a carob juice (21 °Bx) using the reverse osmosis method. Then, juice with levansucrase was incubated (35 °C, 6 h). Finally, carob juice was concentrated (65 °C, 4 h) until 65 °Bx.		FOS: 6-Kestose (NH_2-column, HPLC-RID). HMF (C_{18} column, HPLC-DAD).	[22]
Homemade (HCS) (Bekalta, Monastir region, Tunisia) and commercial (CCS) (Tunisia) carob fruit syrups	Carob fruits (washed, sun-dried (homemade) or oven-dried (commercial) and milled) were extracted with water and filtered. Finally, the filtrate was concentrated.	Soluble sugars. Reducing sugars. Sucrose (difference between soluble and reducing sugars). Proteins. Lipids. Minerals: K, Na, Mg, Ca, Fe, Zn, Cu, Mn (by AAS); P (colorimetrically by molybdo-vanadate method). Fatty acid profile (%): oleic acid, palmitic acid, linoleic acid, stearic acid, caproic acid (GC-MS).	TPC (F-C). AC: TAA (phosphomolybdenum assay). DPPH. FRAP. Antibacterial (*Listeria monocytogenes*, *Staphylococcus aureus*, *Escherichia coli*, *Salmonella enterica*, *Pseudomonas aeruginosa*, *Micrococcus luteus*, *Klebsiella pneumoniae*, *Enterococcus faecalis*, *Salmonella typhimurium*, and *Enterobacter* sp.) potential (agar diffusion method). BI (absorbance at 420 nm). HMF.	[23]
Carob fruits (local market, Sfax, Tunisia)	Washed, sun-dried and fragmented carob fruits were mixed with boiling water (ratio 1/4 g/mL; 30 min). Then, the juice (J; 6 °C) was filtered and concentrated (60, 70 and 80 °Bx)	Reducing sugars. Proteins.	TPC (F-C). AC (DPPH).	[24]
Carob fruit syrup (Semas Company Ltd. Ankara, Turkey)	Washed carob fruits (3–5 cm) were extracted via the reverse osmosis (50–55 °C) method. Filtrate (15–20 °Bx) was evaporated (65 °C) until approx. 68–72 °Bx.		HMF (red color at 550 nm; UV-Vis spectrophotometry).	[25]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob fruits harvested from Bulgaria (B) (Plovdiv region) and Turkey (T) (Mersin province)	Simulating commercial preparation: Carob fruits were deseeded and dried (40 °C, 1 day). Pulp:water (1:2) was extracted (55 h at 22 °C) and the resulting juice was concentrated under vacuum (45 °C, 30 min). Domestically produced: idem procedure, but the juice was concentrated by heating in a pot (3 h at 65 °C).	Total carbohydrate content. Reducing sugars. Glucose. Fructose. Sucrose. 1-Kestose (TLC; HPLC-RID, Pb^{2+} guard column, sugar SP0810, column)		[26]
"Tilliria" carob fruits (Avdimou, Limassol district, Cyprus)	Carob fruit flour was mixed with water (24 h). The filtrate was concentrated (100 °C) until it reached 67 °Bx (carob syrup).		In vitro simulated digestion: salivary, gastric and duodenal steps. TPC (F-C). Phenolic profile (phenolic acids: gallic acid, caffeic acid, and syringic acid; flavonols: myricetin, quercetin and rutin; flavon-3-ols: catechin, epigallocatechin gallate) (HPLC–multi-fluorescence detector). AC: DPPH and FRAP methods.	[27]
Syrups (local carob-processing plants, Antalya, Turkey)	Pieced, deseeded and roasted carob fruits were boiled (2 h) in water (1:2; *w/v*). The supernatant was evaporated up to 65 °Bx.	Total sugars. Crude fiber. Protein content. Energy. Minerals: Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ag, Na, Ni, P, Sr, Ti, Va, Zn (ICP-AES).	HMF (spectrophotometric method (284 and 336 nm) after clarifying samples with Carrez reagents (I and II) and the addition of sodium bisulphate).	[28]
Carob fruits (local market, Sfax, Tunisia)	*Carob syrups* (CS): carob fragments:water (1:4 p/v) were boiled (30 min). The juice was filtered and then concentrated (60, 70 and 80 °Bx). *Commercial sesame paste* (tahin) (Confiserie factory from Sfax, Tunisia): milled, hulled and roasted white sesame seeds. *Syrup/paste blend preparation* (SPB): Syrup/sesame paste (Tahin) (30, 40 and 50%, *w/w*) blends were homogenized.	Protein. Fat. Soluble sugar.	TPC (F-C).	[29]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Commercial samples (Cyprus)	*Carob creams*: A (pure carob syrup juice 53%, vegetable fat, glucose, milk powder, lecithin). Traditional A (traditional product: 50% carob syrup and 50% tahini). *Carob syrups*: Milled carob fruits were boiled with water. Supernatant continued boiling for approx. four hours.	Carbohydrates. Sugars (column: NH_2; HPLC-RID). Dietary fibers. Fat content. Proteins. Energy value. Minerals: K; Na; Ca; Mg; P; Cu; Fe; Mn; Zn (ICP-OES).	Caffeine and theobromine: <LOD (HPLC-PDA, 273 nm).	[7]
Carob flour (CF) (GKM Food Additives Ltd., Mersin, Turkey)	*Spreadable cream:* Commercial chocolate spreads (control). Different amounts of carob flour (CF) and hydrogenated palm oil (HPO) (42:38; 40:40; 38:42; 36:44; 34:46; 32:48), milk powder, soybean flour, lecithin and hazelnut puree were homogenized. CF38 was the spread cream optimized and selected for chemical analysis. It presented closer instrumental spreadability values to the control sample, and a higher sensory score.	Minerals: Ca; Mg; Fe; P; K; Zn; Na (ICP-MS).	TPC (F-C). HMF (defatted sample was extracted with water, then supernatant was mixed with Carrez I and Carrez II reagents and stirred. The diluted and filtered supernatant was injected into HPLC-UV (C_{18} column)).	[30]
-	*Spreadable cream*: Grinded roasted sunflower kernel (control), carob or cocoa, sugar, palm oil and lecithin were mixed (2 h) to obtain the spreadable creams.	Protein. Fat content.	TPC (F-C). AC (DPPH method).	[31]
Carob fruit flour (Incom A.S. Co., Mersin, Turkey).	*Wafer cream:* Oil was mixed with sugar. Then, milk powder, lecithin, cocoa/carob pod/chicory root flour (proportions 20:0:0; 0:20:0; 10:0:10; 0:10:10; 0:0:20; 3/33:3/33:3/33; 3/33:13/33/3/33; 6/67:6/67:6/67; 10:10:0; 3/33:3/33:13/33) were added and mixed.	Total sugars. Reducing sugars. Total fat.	Caffeine (UV-VIS spectrometry, 276.5 nm). AC (DPPH method).	[32]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
-	*Cupcakes*: sugar, salt, whole fresh egg, vanilla essence and milk were mixed and homogenized; then, wheat flour and/or pumpkin seed flour in different proportions was added and mixed. Finally, baking powder was added and manually mixed. Margarine was placed in paper forms and dough was oven baked (40 min, 180 °C). The cupcakes were filled with carob filling (milk, sugar, carob flour and margarine).	Proteins. Lipids. Carbohydrates. Energy value.		[33]
		Baked goods		
Carob flour (Bio Planet, Italy)	*Muffin*: Soy bean powder, white sugar, eggs, water, sesame oil, flax seeds powder, wheat flour, cocoa or carob flour, baking powder and sodium bicarbonate were mixed and homogenized. The dough was placed into muffin cups and baked in an oven (25 min, 180 °C).		AC: ABTS; DPPH. Isoflavones: daidzin, glycitin, genistin, daidzein, genistein (column (C_{18}) and guard column (RP-18); 254 nm; HPLC-PDA).	[34]
Commercial carob pulp flour (Register-SP, Brazil)	*Cookie:* Whole wheat flour, brown sugar, cinnamon powder, baking soda, baking powder and cocoa flour (control) or different proportions of carob pulp flour (24, 12 or 6 g) were homogenized. Then, egg and oil were added and mixed. The dough was molded and baked (180 °C, 10 min).	Energy content. Carbohydrates. Proteins. Total fats. Saturated fats. Dietary fibers. Sodium.		[35]
Carob fruit flour (Aswan Governorate, Egypt)	*Biscuit:* Sugar powder and margarine were creamed. Then, water with sodium chloride, sodium carbonate, and ammonium bicarbonate were added and mixed. Baking powder was added to the wheat flour/carob pulp flour (different proportions: 100:0 (control); 90:10 (CF10); 80:20 (CF20)) and was mixed. The dough was sheeted (3 mm), cut into round shapes and oven baked (180 °C for 6 min).	Protein. Crude fat. Crude fiber. Carbohydrates. Caloric value. Minerals: Zn, Fe, Cu, Mn (AAS); Na, K (flame photometry); Ca (titration), Se, P, S.	Phenolic profile: gallic acid; pyrogallol; protocatechuic acid; vanillic acid; chlorogenic acid; catechol; caffein; catechin; ferulic acid; salicylic acid; coumarin; benzoic acid; caffeic acid (HPLC-UV, 280 nm).	[36]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob fruits (local market, Giza, Egypt)	*Biscuit:* The dough of rice biscuits (control) or biscuits wherein the rice flour was replaced with deseeded carob flour (0.45 mm) (20, 25, 30, 35 and 40%) was prepared according to the formula: powdered sugar and shortening agent were creamed (2 min at high speed). Then, egg and vanillin were added and mixed (5 min). Baking powder was added to the flour and mixed (2 min at low speed). Then, the dough was sheeted (thickness 3 mm), and cut into round shape (45 mm diameter). Finally, the biscuits were baked (170 °C, 12 min).	Protein. Crude fiber. Crude fat. Total carbohydrate. Minerals: Na, K, Mg, Mn, Zn, Ca, Fe.	TPC (F-C). AC: DPPH.	[37]
Carob (Carob House®) flours (specialized store, Santa Maria, RS, Brazil)	*Cake:* Eggs, salt-free margarine, and sugar were mixed. Then, milk, soy flour, banana flour, cocoa flour/carob flour (proportions: 100:0 (control); 75:25; 50:50; 25:75; 0:100) and baking powder were added. Finally, the dough was baked (200 °C, 35 min).	Carbohydrates. Total dietary fibers. Protein. Lipids. Calorific value.		[14]
Carob fruit (Adín Alimentaria, Valencia, Spain)	*Bread*: Flour mixtures (100% wheat (control), 8% (w:w) carob by-product or seaweed flour), dried baker's yeast, salt and tap water were mixed. The doughs were fermented (38 °C, 90 min), and then baked (180 °C, 40 min).	Protein. Fat. Carbohydrate content.	TPC (F-C). AC. DPPH; ORAC; FRAP; TEAC.	[38]
Carob fruit (Konya, Turkey)	*Tarhana:* Wheat/carob fruit flour (in CF 3, 5, and 8% ratios), yogurt, tomato paste, chopped onions, paprika, table salt and baker's yeast were blended, fermented (3 days) and finally dried at room temperature (RT). Then, samples were ground, sieved (1 mm) and stored.	Carbohydrates as sugars (dry matter loss; %). Protein content. Minerals: Ca; Mg; K; P; Zn; Cu (ICP-MS).		[39]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob flour (CF) (Atışeri Ltd., Mersin, Turkey)	*Tarhana:* Blended onions, tomato paste, dry red pepper and dry mint were blended. Then, wheat flour, CF (0, 5, 10, 15, 20%), salt, yogurt, tap water and baker's yeast were added to the mixture. The dough was fermented (4 days, at 30 °C). Then, the mixture was dried (48 h at 50 °C) and ground (particle size <1 mm).	Total dietary fiber. Raw fiber. Fat. Protein. In vitro protein digestibility (IVPD). Amino acid profile: alanine, glycine, valine, leucine, isoleucine, threonine, serine, proline, arginine, tryptophan, aspartic acid, methionine, cis-4-hydroxy-D-proline, glutamic acid, phenylalanine, lysine, histidine, tyrosine; ∑protein (UFLC). Fatty acid profile: C15:0; C16:0; C16:1; C17:0; C18:0; C18:1n9c; C18:2n6c omega-6; C18:3n6; C20:0; C20:1n9c; C6:0; C8:0; C10:0; C12:0; C14:0; C14:1; ∑total fat (GC). Minerals: Ca, K, Cu (ICP-OES).	TPC (F-C). AC.	[40]
		Snack		
Commercial origin (Greece)	*Snack:* Consists of 35 g roasted carob flour, 32 g carob syrup, 23 g ground hazelnuts, 10 g soft vegetable fat (homogenizing agent).	Energy content; Total carbohydrates; Sugars. Starch. Dietary fiber. Soluble fiber. Protein. Fat. Saturated fat. Polyunsaturated fat. Monounsaturated fat. Trans fatty acids. Glycemic index (GI) (glucose as reference food); GI (white bread as reference food).		[41]
Negreta and Roja carob fruits (Armengol Hermanos, Tarragona, Spain)	*Snacks (rice, bean and carob fruit flours):* White rice (50–80%), bean (20 or 40%), and whole carob fruit (5 or 10%) flours were extruded (25 kg/h; 125 °C; 900 (20% bean)/950 (40% bean) rpm; water addition (kg/h): 2.5 (0% carob), 3.0 (5% carob), and 3.2 (10% carob)).	Sugars. Sucrose. Galactinol. Raffinose. Ciceritol. Stachyose. Total α-galactosides (HPLC-RID; column NH_2). Individual inositol phosphates: IP3; IP4; IP5; IP6; Total inositol phosphates (HPLC-RID, PRP-1 column).	Anthocyanins (520 nm). Flavonols (360 nm). Tartaric esters (320 nm). TPC (280 nm). AC (ORAC).	[42]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Negreta and Roja carob fruits (Armengol Hermanos, Tarragona, Spain)	*Snacks (rice, pea and carob flours blends):* White rice (*Oryza sativa* var. Montsianell; 80–50%), pea seed (*Pisum sativum* var. Cartouche, 20 or 40%), and whole carob fruit (0, 5 or 10%) flours were extruded (25 kg/h; 125 °C; 900 (20% pea)/950 (40% pea) rpm; water addition (kg/h): 2.5 (0% carob), 3.0 (5% carob), and 3.2 (10% carob)). All the formulations included salt and calcium carbonate to help texturization and enhance flavor.	Protein content. Soluble protein. Fat content. Total carbohydrates. In vitro protein digestibility (multienzymatic system (peptidase, trypsin and chymotrypsin) and casein as control). Total starch. Resistant starch. Amylose. Amylopectin (concanavalin A precipitation procedure). Total dietary fiber. Soluble dietary fiber. Insoluble dietary fiber.		[43]
Negreta and Roja carob fruits (Armengol Hermanos, Tarragona, Spain)	*Snacks (rice, pea and carob flours blends):* White rice (80–50%), bean (20 or 40%), and whole carob fruit (0, 5 or 10%) flours were extruded (25 kg/h; 125 °C; 900 (20% bean)/950 (40% bean) rpm; water addition (kg/h): 2.5 (0% carob), 3.0 (5% carob), and 3.2 (10% carob)).	Protein content. Soluble protein. Lipid contents. Total carbohydrates. In vitro protein digestibility (multienzymatic system, peptidase, trypsin and chymotrypsin, and casein as control). Total starch. Resistant starch. Amylose. Amylopectin. Total dietary fiber (TDF). Soluble dietary fiber (SDF). Insoluble dietary fiber (IDF).		[12]
Negreta and Roja carob fruits (Armengol Hermanos, Tarragona, Spain)	*Carob fruit, pea and rice blends*: White rice (Oryza sativa var. Montsianell; 70–55%), pea seed (Pisum sativum var. Cartouche, 20 or 40%), and whole carob fruit (0, 5 or 10%) flours were extruded (25 kg/h; 125 °C; 900 (20% pea)/950 (40% pea) rpm; water addition (kg/h): 2.5 (0% carob), 3.0 (5% carob), and 3.2 (10% carob)). All the formulations included salt and calcium carbonate to help texturization and enhance flavor.	Sucrose. Galactinol. Raffinose. Ciceritol. Stachyose. Verbascose. Total α-galactosides (HPLC-RID; NH_2 column). Inositol phosphates: IP3; IP4; IP5; IP6; Total inositol phosphates (HPLC and PRP-1 column).	Anthocyanins. Flavonols. Tartaric esters. TPC. AC (ORAC).	[44]
		Pasta		
Carob fruit flour (Bio Planet S.A., Leszno, Poland)	Durum wheat semolina/carob flours (0%, 1–5% *w/w*) and distilled water (flour: water, 2.5:1, *w/w*) were mixed. The dough was formed, cut and dried. Dried pasta was boiled in water (360 s for control and at 430 s for fortified pasta).	GI.	TPC (F-C). AC: ABTS; FRAP.	[45]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Commercial carob fiber (CF, extract from carob kibble) (Carob General Application, Valencia, Spain)	Wheat flour with CF flour of 1, 2, 3, 4, and 5 g/100 g was mixed with water up to a moisture content of 30 g/100 g. Finally, the dough was formed, cut and dried until a moisture of 11 g/100 g (wb).		In vitro digestion (salivary, gastric and intestinal digestions). TPC (F-C). AC: ABTS. FRAP. Chelating power (CHEL). Ability to inhibit lipoxygenase (LOX).	[46]
Carob fruits (Armengol Hermanos, Tarragona, Spain)	*Fettuccine-shape pasta*: Different white rice (0–100%; *Oryza sativa* L. var. Montsianell)/dry bean (0–100%; *Phaseolus vulgaris* L. var. Almonga)/whole carob fruit (0–10%) formulas were mixed with hot water (42–72% for the lower and higher bean amount, respectively) (5 min). Hydrated flours were kneaded (constant speed, 15 min), prepared by conventional cold (30–40 °C) extrusion of the dough in a pasta extruder, and formed into a fettucine shape (20 cm length). The formed pasta was predried (room temperaure, 30 min) and dried (70 °C, 2 h). Fresh commercial pasta (control) was dried (same procedure as experimental pasta). Pasta cooking method: pasta was boiled in water (2 L per 100 g proportion containing 0.70% *w/v* of sodium chloride) for an optimal cooking time (method 60–55), then cooled and frozen (−20 °C).	Total protein content. Soluble protein. Fat. Total carbohydrates. Total dietary fiber. Soluble dietary fiber. Insoluble dietary fiber.		[47]
		Dairy products		
Commercial carob syrups (Merter Helva San. ve Tic. A.S., Istanbul, Turkey)	*Yogurt:* Concentrated raw milk (14% total solids) was pasteurized (90 °C, 5 min). Then, grape/mulberry/carob syrup (6, 10 and 14% *v/v*) was added. Finally, each mixture was inoculated (5% *v/v* of yogurt culture), placed into plastic cups and incubated (42 °C) until reaching pH 4.7.	Mineral: Cu; Fe; Zn; Mn; K (AAS). Volatile fatty acids.		[48]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob flour (Carob House, Brazil)	*Yogurt:* Skimmed hydrolyzed/non-hydrolyzed milk was heated (90 °C, 15 min) and cooled (45 °C). Then milk was inoculated with starter culture (0.02% (*w/v*), *Streptococcus salivarius* ssp. *Thermophilus* and *Lactobacillus delbrueckii* ssp. *Bulgaricus)*. Finally, it was mixed with sugar and vanilla with/without carob and fermented (42 °C) until pH 4.6 was reached.	Fat. Protein. Total fibers. Sugars: Lactose. Glucose. Galactose (deproteinization of samples; HPLC-RID, C-610H column).		[49]
Carobs collected naturally (Tazmalt, North of Algeria)	*Kefir:* Fermentation (*Lb. plantarum* and *Lb. rhamnosus*, *Lactoccocus lactis*, *L. cremoris*, and *Leuconostoc cremoris*) of pasteurized milk. Carob flours (pulp (washed, deseeded, milled and sieved) or fruit) (1.5 g; 3%, *w/v*) were added to the kefir samples and incubated (RT, overnight).		AC by ORAC.	[50]
Khishebeh Sela'ata (KS), Jnoubi (JN), Baladi Ikleem el Kharoob (BIK), Makdissi Jnoub (MJ), Akkari (AK) and Sandali Makdissi (SM) carob fruits (different regions from Lebanon)	*Carob-based milk beverage (CBM):* Roasted (150 °C, 60 min) and unroasted kibbled, deseeded and milled (0.5 mm) fruits from each variety were mixed with Splenda no-calorie sweetener, and reconstituted (with water) fat-free powdered milk (0% fat), carrageenan gum and soy lecithin. The mixture was heated (75 °C, 2 min). Then, it was cooled and strained. Finally, vanilla extract was added.		TPC (F–C). TAA: ABTS.	[8]
		Beverages		
Carob fruits (local farm, Ajloun, Jordan)	*Juice*: Carob fruits were washed, deseeded and cut into pieces (particle size 0.5–1 cm) or milled (flour). Carob pulp (pieces or flour):water (1:2) was stirred (43 °C, 160 min). The juice (supernatant) was pasteurized (63 °C, 30 min), and refrigerated at 4 °C.		TPC. TFC. Total tannins. AC (DPPH).	[51]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Carob fruits (Beni Mellal region (Ait Oum Elbakht and Dir Elkssiba), Morocco)	*Moroccan traditional drink:* Deseeded and washed carob pulp pieces (particle size of 0.5–1.0 cm) were heated (80 °C, 45 min) in water (carob pulp:water ratio 1:3). Then, the mixture was boiled under vacuum (15 min). The filtrated aqueous extract was pasteurized (63 °C, 30 min).		TPC (F-C). TFC (aluminium chloride method). Condensed tannins (Folin Denis method).	[52]
Carob fruits (Synbio; Warsaw, Poland)	*Kvass:* Roasted (130 °C) and milled carob, rye malt extract, sucrose, citric acid and distilled water were mixed and boiled (5 min). The cooled mixture was filtered and inoculated with dried starter (lactose, *Saccharomyces cerevisiae*, *Streptococus thermophilus*, *Lactobacillus delbrueckii* ssp. *bulgaricus*, *Lactobacillus acidophilus* and *Bifidobacterium lactis*). Sample was fermented (27 °C, 4 h; 34 °C, 4 h) and cooled to obtain the product.		TPC (F-C). TAA: ABTS. Phenolic profile (gallic acid, 4-hydroxybenzoic acid, syringic acid, quercetin and myricetin derivatives), HMF and Furfural (HPLC-UV-visible; C_{18} column). Probiotic potential (*Saccharomyces boulardii* and *Lactobacillus plantarum*).	[53]
Carob fruits (local producer, island of Vis, Dalmatia, Croatia)	*Liquor/macerate*: Pieced, unroasted carob fruits and hydroalcoholic base (30, 50, and 70% *v/v* of ethanol) in 1:5 and 1:10 proportions were macerated (12 weeks, room temperature, exposed to sunlight/darkness). Samples were manual shaken daily.	Total sugars: sucrose, glucose, and fructose (Carrez reagents were added to macerates for precipitation of proteins. Supernatants were used for HPLC-RID analysis; ion exchange column and guard column C-610H).	TPC (F-C). AC (FRAP).	[54]
AIDA, Galhosa and Mulata carob fruits (germplasm repository, DRAP Algarve, Tavira, Portugal) Commercial carob flour (Industrial Farense LDA, Faro, Portugal)	*Liquor/macerate:* AIDA, Galhosa and Mulata roasted (120 °C or 150 °C) and unroasted carob kibbles or flour were mixed with fig distillate (45% *v/v*) in a proportion of 5% (*w/v*). Both raw materials were kept in contact for 1 or 3 weeks, in the dark and at room temperature. Samples were shaken daily and finally filtered and stored.		Phenolics: gallic acid. Furanics: furfural; HMF (HPLC-PDA and a Kromasil 100 A pore size C_{18} column). TPC (F-C). AC: TEAC; FRAP. BI (spectrophotometry method).	[9]

Table 1. *Cont.*

Raw Material Origin	Sample Processing//Elaboration Process	Nutritional Parameters Analyzed	Functional Composition and Non-Desirable Compounds Determined	Ref.
Commercial roasted plurivarietal carob pulp flour (Industrial Farense Lda, Faro, Portugal)	*Liqueur:* Carob pulp and fig spirit (45% *v/v*) or soft water were mixed (proportion of 5% *w/v*) to obtain macerates, (aqueous and hydroalcoholic) infusions and distillates. Then, syrup was added to filtered macerate/infusion/distillate (1:2 proportion) to obtain the different final liqueurs (22.5% *v/v*).		Liqueurs were subjected to a simulated gastrointestinal digestion process. Phenolic: gallic acid. Furanics: furfural and HMF (HPLC-PDA; 100 A pore size C_{18} column). TPC (F-C). TFC (aluminium chloride method). AC: TEAC and ORAC. Enzyme inhibitory capacities: acetylcholinesterase; tyrosinase; α-amylase; α-glucosidase.	[55]
	Liqueur: Commercial carob pulp liqueurs (Algarve region, Portugal)	Minerals: Cu, Ca, Mg, Na, K, Fe, Zn, Mn, P, Cd, Pb (MP-AES)		[56]
Pieces of carob fruit (local herbal shop, Dokki, Egypt)	*Infusion:* Washed berry (*Sambucus nigra* L.) leaves; roasted carob fruit; doum (*Hyphaene thebaica*) fruit or mixtures were dried (40 °C, 6 h) and milled (0.8–1.0 mm). Exactly weighted portions were packed in tea bags.		TPC (F-C). AC (DPPH). Antibacterial (*Bacillus subtilis* and *Bacillus megaterium; Escherichia coli*, *Staphylococcus aureus* and *Enterococcus faecalis*) and antifungal (yeast *Debaryomyces hansenii*, *Zygosaccharo ycesrouxii*, *Rhodotorula rubra*, *Candida shehatae*, *Candida tropicalis*) activities: carob tea infusions and their mixture inhibited the growth of all tested bacterial and fungal strains (disc diffusion method).	[57]

* Syrup, molasses or pekmez; $ Fruit, pod or bean: pulp + seeds. Flour or powder. HMF: 5-hydroxymethyl furfural; FOS: Fructooligosaccharide; BI: Browning index; TPC: total phenolic content; F-C: Folin–Ciocalteau; TFC: total flavonoid content; TAA: total antioxidant activity; AC: antioxidant capacity; DPPH: 1,1-diphenyl-2-picrylhydrazyl; FRAP: ferric ion-reducing antioxidant power; ORAC: oxygen radical absorbance capacity; ABTS: 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid; TEAC: Trolox equivalent antioxidant capacity. Analytical techniques—TLC: thin layer chromatography; UFLC: ultra-fast liquid chromatography; HPLC: high-performance liquid chromatography; PDA: photodiode array; RI: refractive index; AAS: atomic absorption spectrophotometry; FAAS: flame atomic absorption spectrometry; ICP-OES: inductively coupled plasma with optical emission spectrometry; ICP-AES: inductively coupled plasma atomic emission spectrometry; ICP-MS: inductively coupled plasma atomic emission spectrometry; MP-AES: microwave plasma atomic emission spectrometry; GC: gas chromatography.

2.1. Carbohydrate Composition

Carbohydrates are the single most important source of food energy in the world [58]. Depending on their chemical structure, these compounds are traditionally classified as simple (sugars) or complex (polysaccharides such as starch and dietary fibers) [59]. Due to its satiating power, diets rich in carbohydrates, such as dietary fiber, may reduce an individual's propensity to obesity by preventing overconsumption of energy, and may also provide some protection against various non-communicable or chronic human diseases and conditions [58]. In addition, simple carbohydrates, known as sugars, have other roles, such as acting as sweeteners to make food more palatable, increasing the viscosity, enhancing flavor, adding texture and color, inhibiting protein coagulation, and assisting in food preservation [60]. Fruits such as carob are important sources of carbohydrates; however, other ingredients used in carob food products, such as whole wheat flour, rice, cereals, and vegetables, have great influence on the content of carbohydrate [61]. The importance of these ingredients, especially carob pulp, for the carbohydrate contents of food products will be discussed below.

Total carbohydrate content (TCC). Total carbohydrate content is a mixture of fructose, glucose, sucrose, glycerol glucoside and starch [62]. Due to its importance from a nutritional point of view, this parameter has been widely studied in carob products.

High value ranges (46.66–71.5% g/100 g DW) were found in carob syrups and creams (Table 1), and these were elaborated almost exclusively with carob pulp, an ingredient with high sugar content [7,26].

Previous studies on the production of fermented carob products (e.g., tarhana, cookies, cakes, snacks, etc.) showed a reduction in carbohydrate content when different raw materials (wheat, rice or cocoa flours) were replaced with carob pulp flour as the sweetening, gluten-free or functional ingredient [14,35,37]. According to Lar et al. [39], this was because the partial substitution produced a dry matter (carbohydrate) loss, especially in the form of sugars, after dough fermentation. In other cases, in general, no significant differences were found in the final composition when carob was used in snacks with high a percentage of pea [12,43], in fettuccine pasta when carob fruit was added in the formulation of rice and bean blends [47], or in bread when carob or seaweed (8%) was replaced by wheat flour [38]. This was probably due to the low percentage of carob pulp used in the formulation, and because the rest of the raw materials used in the formulation had high percentages of carbohydrates.

Glycemic index (GI). This index is used to classify the carbohydrate content in foods and to evaluate how these compounds affect blood glucose levels. The amount of carbohydrates, the nature of the meal, previous meals, and recent physical activity or bodyweight changes in the subject are factors influencing the glycemic response to a meal [63]. To determine this parameter, the blood glucose response to 50 g available carbohydrate in a test food is compared with that to a reference food (either glucose or white bread, given a value of 100). High GI values (>70) mean a rapid, sharp rise in blood glucose concentrations, whereas low GI values (<55) cause a slower and more sustained release of glucose into the blood. Therefore, diets rich in low-GI carbohydrates are associated with a reduced risk of chronic diseases.

Comparing the GI (on the glucose scale) of a carob snack (40) versus a chocolate cookie (78), Papakonstantinou et al. [41] found better results for the first. According to these results, the carob snack led to greater satiety, and decreased the overall energy intake during the meal, therefore also decreasing the post-meal glycemic response, contributing to body weight and glycemic control.

On the other hand, in the case of fortifying durum wheat pasta with carob flour, the estimated GI values increased from 72.2 (control pasta) to 94.4 (at the highest carob flour substitution level, 5% *w/w*) [45]. That is, carob pasta permitted higher carbohydrate digestion compared to the control pasta. The modification of certain factors associated with methods of pasta processing, and the chemical composition of pasta with this functional ingredient (e.g., the arrangement of components in the pasta structure, the encapsulation

of starch granules in a protein network and dietary fiber, the presence of polyphenols, etc.) may lead to changes in the susceptibility of starch to amylosis, the starch digestibility, and the glycemic index [64,65]. Thus, this type of fortified product is a good source of rapidly digestible carbohydrates. This high estimated GI seems appropriate for people with higher energy requirements (an active lifestyle), and generally should not be recommended for people predisposed to obesity, diabetes, and cardiovascular diseases [66].

2.1.1. Simple Carbohydrates or Sugars

Simple carbohydrates or sugars, consisting of one (monosaccharides) or two (disaccharides) sugar units, play a central role in metabolism as sources of energy. These compounds provide calories but very few or no nutrients [67].

Nowadays, the food industry looks for ingredients containing natural sugars, among other nutritional and functional compounds, avoiding the excessive use of added sugars linked to negative health outcomes (body weight increase, type II diabetes, and cardiovascular disease [68]). In this sense, carob pulp is a very useful industrial ingredient in food preparation, because sugars are naturally present. Thus, in addition to providing the necessary daily dose of sugars, this ingredient also provides fiber, vitamins, minerals, and antioxidants, among other healthy substances.

Total sugar content (TSC). The high presence of sugars in carob pulp implies that foods made exclusively or mainly with this ingredient will have a high sugar content. This is the case for syrups, wherein the content (between 50 and 63.88%) was found to be similar in different homemade and commercial samples from Tunisia [23], Cyprus [7], and Turkey [19,28].

The addition of carob syrups (TSC 33%) to sesame paste (TSC 1.17%) (ratio 1:1) for the elaboration of carob creams significantly increased the sugar content in the formulated blend (TSC approx. 10%) [29]. However, the value was lower than expected, probably due to the formation of a stable emulsion between the sugar and fat molecules present in the blend. Higher levels were found in commercial creams (35.2 and 43.04%) [7] and in wafer creams, where the replacement of cocoa with carob fruit flour significantly increased the sugar content from 45.01% to 54.61% [32].

In the elaboration of liqueurs (solid to liquid ratio, 1:5), macerates presented a similar range (96–107 g/L) of total sugars regardless of the alcoholic strength and its exposure to sunlight. The lowest contents were found in macerates with the lowest carob quantities (ratio 1:10) and highest alcohol strength, probably due to the higher solubility of the polar sugar molecules in water (in higher quantities at lower alcohol strength) [54].

Invert sugars. The use of invert sugars is very common in the elaboration of beverages, baked goods, and syrups, among others. This equimolar mixture of two simple sugars (glucose and fructose) is commonly used to retard the crystallization of sugar and to retain moisture, and when freshness in the final product is desired [69]. Furthermore, this is one of the factors, along with pH and temperature, that greatly influences the quality and storage capabilities of syrups. Thus, in this carob product, invert sugars were found at high concentrations (17.05 g/100 g) [19].

Reducing sugars. These compounds encompass monosaccharides; hexoses (such as glucose, fructose and galactose) and pentoses (such as xylose and arabinose); and disaccharides, maltose and lactose [70]. They are important for the flavor of heat-treated carob products, as they react with amino acids via the Maillard reaction to provide many important flavor compounds, including furanics [71].

During juice concentration to prepare carob syrups, the content of reducing sugars is significantly decreased [24]. This fact is mainly due to the involvement of proteins and reducing sugars in non-enzymatic browning reactions, which occur during juice boiling as a result of either caramelization or Maillard reactions. In addition to the degree of concentration, the production technique used also affects the contents of these compounds. According to Fidan et al. [26], carob syrup elaborated via the conventional procedure was the richest source of reducing sugars, and the differences observed during the vacuum

procedure (lower content) may be due to differences in the heating treatment and storage conditions. Hence, the production conditions of carob syrups were shown to be favorable for the occurrence of non-enzymatic reactions during juice concentration (thermal processing or boiling, acidic pH, and presence of proteins and reducing sugars). To avoid the non-enzymatic reactions and preserve the juice quality, athermal concentration, such as cryoconcentration and osmotic evaporation, may be favorable options for concentrating fruit juices at low temperatures and maintaining their physico-chemical, biochemical, nutritional, and sensorial characteristics [24].

Sugar profile. The chemical analysis (thin-layer and HPLC-RID) of carob pulp syrups from Turkey and Bulgaria obtained via vacuum and conventional processing showed that these samples were characterized by the presence of the monosaccharides glucose and fructose, and the disaccharide sucrose [26]. As mentioned before, the natural presence of these main reducing sugars in syrups could diminish their crystallization and provide a good source of rapid energy, since they pass easily into the blood without digestion [72]. Sucrose was the main sugar in carob syrups, and the concentration was higher in Turkish samples regardless of the elaboration method used (vacuum or traditional method) [19,23,26]. Moreover, the glucose and fructose contents in Turkish carob syrups prepared via the conventional procedure contained more than three times the sugar concentration of Bulgarian syrups. According to Papaefstathiou et al. [7], carob syrups are differentiated from other commercial carob products mainly by their glucose content, which is significantly higher due to the mixing of carob syrup and honey.

In the same vein, the most abundant sugars extracted from carob pulp into the alcoholic base for the elaboration of liqueurs were sucrose (≈75%), glucose (≈15%), and fructose (≈10%) [54]. In extruded snacks elaborated with different quantities of carob (5 and 10%), the sucrose content was between 1.72 and 3.23 times higher than in the commercial samples without carob (values between 9.44 and 14.46 mg/100 g) [44]. These results confirm again that the highest amount of sucrose was in products elaborated with carob pulp.

2.1.2. Complex Carbohydrates: Oligosaccharides and Polysaccharides

Complex carbohydrates are made up of more than three sugar units strung together into a long chain. They comprise oligosaccharides (3–10 sugar units) and polysaccharides (>10 sugar units) (starch; glycogen and non-starch polysaccharides (dietary fibers)). The complex structure of these compounds makes its break-up more complicated and therefore provides a steadier supply of energy for the body [73].

Oligosaccharides (prebiotics), dietary fiber molecules. Oligosaccharides are compounds whose monosaccharide units are joined by glycosidic linkages. These include galacto-oligosaccharides, fructo-oligosaccharides, and mannan-oligosaccharides, which resist pancreatic and small intestinal digestion, and are soluble in 80% ethanol [74].

Galacto-oligosaccharides. From a physiological perspective, sugars of the raffinose family oligosaccharides (RFOs) or α-galactosides are considered as an antinutrient because of the flatulence activity associated with their consumption. Humans cannot digest these compounds due to the lack of α-galactosidase enzymes in our digestive system. However, some of them are readily fermented by intestinal microbes in the small intestine, and others escape fermentation in the small intestine and enter the large intestine, where they may exert a prebiotic effect, increasing the bifidobacterial population in the human colon, stimulating the immune system, and reducing diarrhea or constipation [75]. Moreover, the colonic flora can ferment these sugars, producing a mixture of short-chain fatty acids that reduces glycemic symptoms and cholesterol once assimilated into the intestine [76]. Among these compounds, raffinose, stachyose and verbascose are present abundantly in legumes [74].

Among the different galactosides (raffinose, stachyose, verbascose) and the cyclitol ciceritol (a pinitol digalactoside) observed in snacks elaborated with pea, rice and carob, raffinose is the only one to have been identified from carob fruit [44], and has been pre-

viously found in carob pulp [77]. Despite peas being a better source of α-galactosides (71.45 mg/100 g) compared to the carob pod (5.96 mg/100 g), the quantity of these compounds significantly increased when the carob content was raised from 5 to 10% in the snacks formulation. Furthermore, the increase in the total amount of α-galactosides after extrusion can be explained by the alteration (increasing of the porosity) in the food matrix structure, improving the diffusion of the solvent, and thus the release of carbohydrates linked to other macromolecules.

Fructo-oligosaccharides (FOS) or fructans. These compounds are carbohydrates that are composed mainly of fructose with varying degrees of polymerization. They are classified as inulins or levans [74,78]. Inulins (β(2–1)-linked fructans) are present in several fruits and vegetables, such as 1-kestose. Levans (β(2–6)-linked fructans) are synthesized by some bacteria and fungi that secrete levansucrase, e.g., 6-kestose [79].

Turkish carob pods and syrups are a source of prebiotics because of the presence of 1-kestose. The levels (g/100 g DW) of this prebiotic compound were found to be 0.5 in carob pods, and 0.3/0.2 in carob syrups prepared by vacuum/conventional procedures. However, no inulin or other FOS were found [26]. Since at the end of syrup storage the amount of 1-kestose is reduced (around 30%), Taştan et al. [22] studied the production of 6-kestose using the *Zymomonas mobilis* levansucrase enzyme. The addition of this enzyme resulted in the conversion of sucrose, and the released fructose units were further converted into kestose. This procedure was performed to stabilize the FOS content in concrete 6-kestose during storage (up to 4 months at room temperature). Therefore, increased amounts of prebiotic FOS were found in the derived carob syrups in relation to the traditional product.

Starch. Starch is a carbohydrate composed of two polysaccharides, amylose and amylopectin, consisting of many glucose units joined together by glycosidic bonds [80]. It is the most common constituent of human diet, wherein it provides the major share of energy required for the sustenance of life. According to Arribas et al. [12,43], carob pulp has no starch content; thus, the increase in carob content in the formulation of snacks elaborated with pea and rice with high starch values (35.09% and 76.24%, respectively) resulted in a reduction in starch levels in the samples.

Dietary fiber (DF). DF is generally defined as the macromolecules present in the diet that resist digestion by human endogenous enzymes. It is essentially composed of non-starch polysaccharides, resistant oligosaccharides (FOS, galacto-oligosaccharides), analogous carbohydrates (e.g., indigestible dextrins, synthesized carbohydrate compounds), lignin, and other plant substances associated with the non-starch polysaccharide and lignin complex (e.g., waxes, phytates, tannins, saponines) [81]. It is used as an important moderator of digestion in the small bowel and as a major substrate for fermentation in the colon, where the non-starch polysaccharides are metabolized into short-chain fatty acids (whose absorption provides some energy).

Based on its chemical, physical and functional properties, fiber can be classified as soluble or insoluble. Soluble dietary fiber (SDF) dissolves in water after it has been consumed, forming a gel-like material that slows down digestion, making an individual feel full for longer. It also functions to lower blood cholesterol, which helps to protect against heart disease. Insoluble dietary fiber (IDF) is found in the rough, fibrous structures of plants (outer coverings, seeds, and strings). It is insoluble in water, passing through the gastrointestinal tract relatively intact and providing roughage or bulk to the diet, which promotes normal elimination and prevents obstipation. It may also reduce the risk of diverticular disease and some forms of cancer, such as colon cancer [82,83]. Despite the aforementioned benefits, according to EFSA, per capita dietary fiber intake is below the recommended consumption (25 g/day), and therefore, it is of great importance to include in the diet new ingredients, such as carob pulp, that may help reach this objective [84,85].

Products containing less than 3 g of edible fiber per 100 g are not considered sources of dietary fiber, while contents higher than 6 g/100 g indicate a high fiber content [7,86]. In general, although carob pulp presents a high DF (9.69–37.32%), this content is mostly in the form of insoluble fiber [7,28]. Thus, carob syrups and spread creams usually present

values that do not satisfy the "source of DF" claim. These products are elaborated with the concentrated water-soluble part of carob pulp, while the insoluble fraction (composed of substances such as IDF) is discarded. That said, in the literature, we have also found examples of syrups in which the minimum DF values (3.34%) are reached [28].

In the elaboration of tarhana supplemented with carob flour, the increase observed (from 5.2 to 13.5% DF) was low in comparison with the initial quantity found in the raw material (carob flour, total DF content of 35.2%), probably because of the small amount of carob pulp used in the formulation (5 or 20%) [40]. In the case of gluten-free bread (GFB) containing 15% carob flour, the amount of DF (6.10 g/100 g bread) found was higher than in typical wheat bread, and in this case the bread can be considered a fiber-enriched product [87]. Moreover, an increase in fiber content can be found when cocoa and rice flours in cookies [35,37], or soy and banana flours in cakes [14], are replaced by carob flour.

Again, according to Arribas et al. [12], the inclusion of carob in the formulation of non-extruded blends (snacks) increased the total dietary fiber (TDF), mainly as an insoluble dietary fiber (IDF). In processed snacks (after extrusion), reductions in the TDF (10–39%) and IDF (19–95%) contents were observed. This may be because the heat and moisture levels used during extrusion can solubilize and degrade pectic substances, leading to a decrease in dietary fiber. Moreover, the soluble fraction (SDF) increased after extrusion, the SDF values being higher in carob-free formulations, since carob fruit provides mainly IDF [43]. This SDF could be attributable to the formation of complex compounds, such as polysaccharide–proteins, or the increase in the in vitro protein digestibility, which both are measured as soluble fiber [82,88–91]. According to the United States Department of Agriculture food pattern recommendations [92], one serving of an extruded blend with 5–10% carob fruit supplies (on average) 13.3% of the recommended intake of dietary fiber; thus, these products reach the requirements to be considered "high in fiber" foods.

In the elaboration of fettuccine pasta, the carob fruit added in the formulations of rice and bean blends significantly increased the contents of total and insoluble dietary fiber. An increase was also observed in cooked pasta (with or without carob), because in this process, soluble components such as sugars, oligosaccharides and starch, and other water-soluble and insoluble compounds of the fibers, leached to the water, thus increasing the fiber fraction in terms of dry matter [47].

The addition of carob flour (with total DF values of 43%) to yogurts elaborated with hydrolyzed and non-hydrolyzed milk allowed a significant increase in total DF, thus increasing the fiber consumption [49,93].

Therefore, according to the literature, the incorporation of carob pulp in most of the food formulations allows these products to be considered fiber-enriched products.

2.2. Lipids or Fats

Lipids are one of the most important components of natural foods that include triglycerides (TGs, commonly called fats), phospholipids (inositols), and sterols. The TGs present in food consist of fatty acids (FA saturated or unsaturated) bounded to glycerol molecules [94]. In general, fats play a central role in transporting fat-soluble vitamins (A, E, D, K), and provide essential fatty acids and energy for the body. It is considered important for a healthy diet that monounsaturated fats predominate over polyunsaturated (omega-3, omega-6 FAs) and saturated forms, as is the case in foods from the "Mediterranean diet" [95]. These healthy unsaturated fats may protect against cardiovascular disease by providing more membrane fluidity than the more solid saturated fats. However, the excessive consumption of saturated fatty acids promotes visceral fat storage, which has been associated with the development of cardiovascular disease and with certain types of cancer [96,97]. Therefore, dietary fat restriction as a preventive strategy for these chronic diseases must be considered. Recommendations based on total fat intake range between 20% and 35% of total energy, and saturated fat intake should constitute less than 10% of total energy for individuals over the age of 2 years [98].

Carob pulp/pods and carob syrups contain a very low fat content (values 0.2–1%) [6,28]. However, the percentage of fat is higher—between 0.11% and 40.13%—in other carob products because of the additional ingredients, such as butter, cream, whole milk, egg yolk and vegetable oils, in their formulation. According to the health and nutrition claims of EC Regulation 1924/2006, products containing less than 3 g of fat per 100 g are considered low-fat products. This is the case for the carob syrup, bread, snacks and yogurt studied [86].

In light of the above, cakes showed lower fat contents when the quantity of carob increased or when cocoa was replaced with carob [14,99]. Among creams elaborated with different ingredients (sunflower kernels, carob, cocoa and chicory root), those with carob or chicory + carob pod presented lower fat contents [31,32].

In carob creams, the fat content was lower than expected, and this could be explained by the formation of a compact network, wherein the oil droplets in the sesame paste (fat) were retained by long chains of sugar syrups [29,100]. In snacks, the main factor affecting the lipid composition was the extrusion process, which reduced the lipid content via the formation of complex structures among lipids, starch (amylose) and proteins [43,82,89,101]. Despite this, the addition of carob in extruded and non-extruded blends gave rise to no significant differences in fat content [12,43]. However, at the maximum pea content, the increase in carob flour (from 5 to 10%) in extruded blends increased the contents of inositol phosphates IP3 and IP6 [44].

According to the individual fatty acid content found in tarhana samples, the compounds that can be derived from carob pulp, such as the palmitic (C16:0), stearic (C18:0), oleic (C18:1n9c), linoleic (C18:2n6c, omega-6) and γ-linolenic (C18:3n6) acids, showed small differences among supplemented and control samples.

Therefore, according to the results obtained in the different works on carob products, the fat content is mainly derived from the other ingredients used in the formulations, such as oil, sesame paste or sunflower kernels, among others. In addition, its promotion for use in infant food products as a cocoa substitute is encouraged due to its low fat percentage (>1% vs 37–57%) [6].

2.3. Proteins

Proteins are complex chain-like structures made of amino acids (AA). According to nutritional requirements, AAs are divided into essential (phenylalanine, valine, tryptophan, threonine, isoleucine, methionine, histidine, leucine and lysine) and non-essential (alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, proline, serine, tyrosine, selenocysteine). The dispensable AAs can be excluded from a diet, as the human body is capable of synthesizing them using the essential AAs.

Carob pulp presents low protein contents (3%), while other components of the *C. siliqua* plant, such as the seeds (18.6%), or the whole fruit of the carob pod (pulp + seed: 4%), present higher values [102]. In this sense, the protein contents found in carob products probably derive from sources such as eggs, milk and legumes, among others.

Therefore, due to the low protein content of the carob pulp, it is not surprising that the substitution of high-protein ingredients, such as sesame paste or sunflower kernels (with 25.35 and 20–25%, respectively), with carob pulp or carob syrups in cream formulations causes a protein reduction in the final product [29,31]. Additionally, in the elaboration of cookies, the replacement of cocoa [35] or rice [37] flours with carob flour results in a decrease in protein content.

In the elaboration of carob syrup (whose main ingredients are carob pulp and water), the conditions of the heat treatment process for juice concentration favored the non-enzymatic browning reaction (Maillard reaction) [24,103]. Thus, the raw material (carob pulp) contains a higher protein content than the product (carob syrup) [7,23,24,28]. In the case of snack elaboration, the extrusion process slightly increased the total protein content in samples elaborated with 20% pea and 5 or 10% carob flour, but reduced (between 61 and 86%) the amount of soluble protein. In this type of food, the main protein (total and soluble) source is pea (soluble protein 15.09 g/100 g DM), as compared to rice (0.65 g/100 g DM)

and carob flours (0.10 g/100 g DM). The reduction in protein solubility (higher in formulations with 10% carob fruit flours) during extrusion might be caused by the combined effect of the aggregation of legume proteins (hydrophobic interactions, hydrogen bonds and disulphide bonds) and/or Maillard-type protein–sugar complex formations [12]. However, the Maillard reaction should have little effect on protein damage due to the mild conditions maintained during extrusion (≤120–130 °C and <15% moisture) [7,23,24,28].

On the other hand, using soy flour as the main source of protein in soy-based cakes means that small additions of functional ingredients, such as carob and cocoa flours, do not manifest significant variations in the final protein contents of the cakes [14]. In the same way, the low contents of carob (3–8% [39] and 5–20% [40]) used in the formulation of tarhana could explain why the protein content did not show significant differences when the carob quantity was increased.

However, according to Racolta et al. [31], roasted sunflower cream (control, 10.56%) presented lower values than carob (11.41%) and cocoa (12.48%) prototypes. Similarly, gluten-free breads (GFB) containing carob flour (15% [87]; 8% [38]) presented a higher protein content (8 g/100 g bread and 11%, respectively) compared to a typical wheat bread. These values, which are within the ranges of those derived from commercial GFBs found in the Spanish market (0.91–15.05 g/100 g), certify carob's use as an ingredient for celiacs, with a complementary nutritional value [104].

In bean and rice GF fettuccine pasta, fortification with 10% carob fruit slightly increased the total and soluble protein contents. After the cooking process, the pasta also showed an increase in total protein due to the loss of soluble solids (change in relative composition of samples). However, during this cooking step, the soluble protein content decreased as a consequence of leaching into the water or the denaturation/aggregation of legume proteins, reducing the solubility and extractability of these compounds [47].

Although the fortification of food products with functional ingredients, such as carob pod flour, can improve the protein content and quality due to the complementation of the amino acid profile [12,65], among the 17 different amino acids identified in carob pulp, supplementation with this by-product in tarhana food only increased the content of arginine [40]. This may be explained by the greater fermentation loss of tarhana containing carob flour with high fermentable sugar contents [39].

The nutritional quality of a food product is dependent not only on the quantity of proteins, but also on their digestibility. A food product with high nutritional quality is one with high protein digestibility [105]. The addition of carob pulp can affect the arrangement of components in the pasta's structure and modify the integrity of the protein network. Thus, fortified durum wheat pasta with 1–5% carob flour showed lower protein digestibility (5–9%) than the control [45]. This decreased digestibility may be associated with the different contents and susceptibilities to hydrolysis of the compounds derived from the functional supplement, compared to the conventional pasta components. Additionally, the limited in vitro bioaccessibility of available starch and protein may be a consequence of interactions between protein/starch, which form indigestible complexes and/or inhibit the activity of digestive enzymes [106,107].

However, in the elaboration of tarhana, the addition of carob flour did not have a significant effect on in vitro protein digestibility (values between 80.1 and 81.1) compared to the control sample (81.2). Similarly, no significant differences in protein digestibility were found among non-extruded carob snacks. However, the extrusion process increased significantly the in vitro digestibility of blends [12,43], and the variables of the process (the feed ratio and the temperature) had a maximal effect (protein denaturation and the inactivation of thermolabile antinutritional factors, such as protease inhibitors or lectins, of legumes). Moreover, cooking mechanical shear forces play an important role in disrupting the protein bodies and thus improving protein digestibility [82,108].

As a general conclusion, raw carob and carob-containing products are not considered sources of proteins since the minimum percentage should be 12% [86].

2.4. Energy

The main macronutrients—carbohydrates, proteins and fats—are sources of energy [109]. However, the energy content of a food is much more related to fat than to protein and carbohydrate contents, and this is because fat is the slowest-releasing source of energy, but the most energy-efficient [110].

Previous works have studied the differences between the energy contribution, in kcal/100 g, of raw materials and carob products. Papaefstathiou et al. [7] found similar energy contents in both carob pods (values approx. 280) and syrups (approx. 270/290). Conversely, Özcan et al. [28] observed that the energy value of carob syrup (approx. 250) was lower than that of raw materials (carob fruit/flour, approx. 400), probably due to the loss, degradation, or reaction of compounds associated with the energy content during processing.

On the other hand, carob creams presented values higher than carob syrups, and this may be because the carob cream is made with sesame paste, which is characterized by high lipid and protein contents, components that are important sources of energy [7].

The replacement of cocoa (control) with different amounts of carob in baked goods (cookies and cakes) caused a reduction in food energy due to the lower lipid and higher fiber contents present in carob [14,35].

Finally, according to Arribas et al. [12], snacks elaborated with carob flour, pea and rice can contribute to around 30% of the total energy intake (FAO/WHO).

2.5. Minerals

Minerals are naturally occurring inorganic substances that are essential to the body's proper functioning [61]. From a nutritional point of view, around 25 minerals (essential elements such as sodium (Na), chloride (Cl), potassium (K), calcium (Ca), phosphorus (P), magnesium (Mg), sulfur (S), iron (Fe), zinc (Zn), iodine (I), selenium (Se), copper (Cu), manganese (Mn), fluoride (F), chromium (Cr), molybdenum (Mo), among others) play an important role in human physiology (e.g., rigid bone formation, transmission of nerve impulses, metabolic reactions, maintenance of colloidal system, and regulation of acid–base equilibrium), and their deficiency in the diet can result in diseases such as rickets and anemia [111]. In addition, the mineral composition of foods is important because of the implications of their organoleptic characteristics, and their nutritional/toxicological implications for human health [30,56,112]. In general, the mineral composition of carob products is derived from the carob pods (seed + pulp) or carob pulp and other materials (e.g., water, alcoholic base, wheat flour, salt, etc.) used in their production, but can also be added during the preparation process of carob products [23,30,56]. The use of the whole fruit (pod) as compared to the pulp includes the minerals from the seed, which is a great source of macronutrients such as P, K, Ca and Mg, and the micronutrients Fe, Cu, Mn, Zn and B [113]. In turn, the minerals derivable from carob pods depend on factors such as fruit variety, geographical origin, cultural practices (e.g., fertilizer addition) and the environmental conditions, which can affect the contents of essential and non-essential minerals [85,86].

Studies on the mineral composition of carob syrups have concluded that, according to the daily reference intakes established in the EC Regulations No. 1924/2006 and 1169/2011, these carob products are a source of essential elements [7,19,23,28,86]. K was the macroelement found at a greater quantity in all samples, followed by Ca, P, Mg and Na. These products presented smaller quantities of the trace elements Cu, Fe, Mn, and Zn [114]. Furthermore, Özcan et al. [28] found other elements such as aluminium (Al), arsenic (As), boron (B), barium (Ba), cobalt (Co), chromium (Cr), lithium (Li), silver (Ag), strontium (Sr), titanium (Ti) and vanadium (V).

Based on the results obtained by Tetik et al. [19], carob syrup presented levels of P, Zn, and Mn that met the nutrient reference values of daily (DI) or adequate intake(AI), as per the Codex Alimentarius, and exceed by two times the value of K, Mg, Ca, and Fe; however, although the value of Na was less than the recommended AI, this element may be widely

incorporated into the diet through different foods and drinks that are consumed frequently during the day.

Comparing the mineral composition, no significant differences were found among samples of Tunisian homemade and commercial carob syrups [23]. On the other hand, among carob products (syrup and flours from fruit and pulp), carob syrup possessed the lowest contents of B, Cr, Cu, Mg, V, P, Ni, Fe, Ca, Ba, and Al, while its Co values were not statistically significant. Finally, low quantities of unusual elements (Ag and Ti) were observed in all quality samples (fruit, pulp and syrup). These probably appeared as contaminants from the different metal utensils used in the preparation of these products [28].

Several minerals were identified and quantified in carob spread creams, with slight modifications regarding the composition of the syrup, and in decreasing order these were: K > P > Ca > Na > Mg > Fe > Zn [30]. This specific mineral composition, that is responsible for healthier growth and prevention of diseases, suggests that the formulated spreads are a promising source of minerals essential for the human metabolism.

Previous works studied the difference between the tarhana elaborated via the traditional recipe (control) and tarhana with different carob fruit flour supplementations (3–8%, [39]; 5–20%, [40]), and clear differences were found in the contents of K, Ca, [39,40], Zn [39] and Cu [40].

Based on the current recommended dietary allowances (RDAs) for some minerals and accepted food labeling regulations, Lar et al. [39] stated that 100 g of tarhana flour provided 32.3% of the K, 9.7% of the Ca and 8% of the Zn [115,116]. Carob flour may be considered to have a high amount of Ca and, based on Dietary Reference Intakes Reports [117], it is a source of K, Cu, Mn, Cr and Se.

Yogurt can be a good source of minerals (especially zinc) for people with lactose intolerance [118]. Yogurt fortified with increasing quantities of carob syrups (6, 10 and 14%) showed significantly higher concentrations of Cu, Fe, Zn, Mn and K, because of the higher quantity present in syrups in relation to milk [48]. However, compared with other fruit syrups, in general, yogurts prepared with grape or mulberry syrups presented higher mineral contents than those prepared with carob syrups.

In the elaboration of biscuits, the study of Youssef et al. [36] revealed that 10 and 20% incorporations of carob pod flour in wheat flour biscuits (control) increased the contents of K, Ca, and Cu. The Se value increased in biscuits elaborated with 10% carob pod flour, and decreased in those with 20%. Finally, it seems that the supplementation of biscuits with carob pod reduced the contents of Mn, Zn, Fe, Na, S and P. According to Ibrahim et al. [37], different specific minerals were increased in rice biscuits following the incorporation of carob flour (CF) into the formulation at different concentrations: Zn (20% CF), Mn (30% CF), Na (35% CF), and K, Fe, and Ca (40% CF).

The mineral content (Na, K, Ca, Mg, P, Cu, Fe, Zn, Mn, Cd and Pb) of commercial carob pulp liqueurs from the south of Portugal was significantly influenced by the different manufacturing processes and the raw materials used (mainly fruits and water) [56]. However, in relation to other types of studied liqueurs (fig and almond), carob liqueurs had the highest mineral concentrations. The authors suggested that although the concentrations of macroelements (mainly Na, K, Mg and Ca) are commonly related to the water used in liqueur production, the high concentrations found suggest that other factors, such as the methods of production (such as the addition of acidity regulators) and particularly the varieties of carob fruits used, had greater influence on the concentrations of these elements [112,119,120]. On the other hand, the low concentrations of trace elements (Cu, Fe, Zn and Mn) in the liqueurs produced in the different locations (western or eastern) of the Algarve (Portugal) suggest good processing practices. Furthermore, although these minerals are present at low quantities in carob pulp, the differences in the liqueur production process (such as the processing of carobs or steps in liqueur production) may make them more accessible during the extraction step.

Regarding the non-essential elements, no trace of Cd was present in the analyzed samples and only two liqueurs contained low concentrations of Pb, probably derived from

the maintenance of the distillation equipment or from polluted water being employed in the dilution step. The results of the non-essential elements highlight the good manufacturing practice of the traditional producers.

2.6. Vitamins

Vitamins are essential dietary components for bodily processes such as normal tissue growth, maintenance, and function. In addition, their intake is important because they either cannot be produced by the body at all, or they cannot be produced in sufficient quantities to sustain health [121].

In recent years, researchers have paid particular attention to the biologically active ingredients, such as vitamin C (ascorbic acid), in food and tea infusions due to their positive effects on human health. The vitamin C in carob pod syrup was shown to be present at 0.07 g/L [122]. Additionally, infusions elaborated with ingredients such as fruit flours from doum and carob, and berry leaves, displayed interesting concentrations of vitamin C, with values of 7.8, 9.5 and 11.05 mg/100 mL, respectively. Furthermore, the mixtures of these ingredients presented intermediate values in relation to the individual ingredients—9.45 mg/100 mL in infusions of berry leaves + carob fruit + doum fruit, and 10.28 mg/100 g for the berry leaves + carob fruit tea infusion [57].

Tocopherols are constituents of vitamin E that appear in several active forms, with α-tocopherol (E307) possessing the highest biological activity and γ-tocopherol (E308) as the most abundant in vegetables. The stability and the sensibility of this fat-soluble vitamin (vitamin E) depend on the food matrix composition, the extrusion processing conditions, and also the thermal processing (lipid degradation), since it is classified as the major lipid-soluble antioxidant that protects lipids and membranes from oxidative damage in vitro and in vivo. Thus, high temperature and moisture values reduce the α-tocopherol and γ-tocopherol contents, respectively. Thus, the γ-tocopherol content in carob fruit (51.0 µg/100 g DW) was higher than that in extruded gluten-free formulations with proportions of bean, rice and carob of 40/55/5 and 40/50/10, with concentrations of 7.4 and 20 µg/100 g DW, respectively. Although α-tocopherol (29 µg/100 g DW) was present in carob fruits, it disappeared in the processed samples [123].

In general, the labels of commercial local carob products include their ingredients, but they have no reference to their nutritional value. In most cases, this is explained by the fact that they are produced by small family companies with limited personnel and resources to perform nutritional composition analyses. Thus, in the absence of research and development departments, products are frequently empirically produced. However, after the transitional period of the EU Regulation EU No 1169/2011 [114], nutritional labeling has become mandatory.

3. Bioactive Compounds and Functional Properties

Phytochemicals, such as phenolics, among others, are bioactive plant compounds endowed with disease-preventive properties, including antioxidative, anti-inflammatory, antitumor, and antimicrobial activities [124]. Thus, these phytochemicals contribute positive functional properties to a wide range of plant-based foodstuffs [44,57]. Antioxidants are a group of particular interest because they play an important role in reducing the risk of free radicals associated with several clinical conditions and degenerative diseases. Overall, antioxidants can be classified as enzymatic (primary and secondary enzymes) and non-enzymatic systems. This last group will be discussed throughout the review, and include flavonoids (anthocyanins, flavanones, flavonols, flavones, isoflavonoids, and flavanones), phenolic acids (hydroxycinnamic acids and hydroxybenzoic acids), vitamins (A, C and E), and minerals (Cu, Zn, Se, Mn), among others [125]. They are exogenous providers of protection that are derived through the diet, and can be subclassified as nutrients and non-nutrients [126]. The nutrients include vitamin A (retinol) obtained from its precursor β-carotene, vitamin C (ascorbic acid), vitamin E (α-tocopherol), lycopene, and carotenoids (carotenes and xanthophyll) naturally present in fruits and vegetables and

with demonstrated beneficial properties against the main degenerative diseases, including cancer, cardiovascular disease, etc. The non-nutrients, which are good antioxidant agents, include the secondary metabolites in plants, such as the (poly)phenolic compounds and coumarins, which can provide many health-promoting benefits, including antioxidant, antimicrobial, anticancer, anti-inflammatory and antiallergic actions [127]. Because of the complexity of the antioxidant defense system, the optimal benefit of antioxidant supplementation will only be obtained from a mixture of these substances (nutrient and non-nutrient antioxidants), while high levels of a single antioxidant may even be disadvantageous [125,128]. For this reason, a high dietary intake of a diversity of fruits and vegetables is recommended [128].

These bioactive compounds are highly sensitive to different factors, such as environmental conditions, the production process, and storage, and also present a limited bioavailability that is modified by the changes caused by the severe gastrointestinal conditions [129]. Thus, the bioactivities identified in different carob products and the influence of different factors that affect their stability will be discussed below.

3.1. Phenolic Content

Phenolic compounds are a broad group of compounds derived from the secondary metabolism of plants, and play an important role in the defense against plant pathogens and abiotic stresses [130]. These compounds possess an aromatic ring bearing one or more hydroxyl groups, and their structures may range from that of a simple phenolic molecule to that of a complex high-molecular-weight polymer [131]. Their bioactivity (antioxidant capacity, enzyme inhibitory properties, etc.) depends on their chemical structure, in particular the number and positions of the hydroxyl groups, and the nature of substitutions on the aromatic rings [132].

Techniques such as spectrophotometry via Folin–Ciocalteu colorimetric assay (to evaluate the total phenolic content (TPC)) and liquid chromatography (for the determination of individual phenolic compounds) are the most common methods used on food products. However, the Folin–Ciocalteu method presents some inconveniences. The reagent is not completely selective, and can measure the total reducing capacity of other components (some nitrogen-containing compounds, vitamins and inorganic compounds) present in the sample, thus providing an overestimated result [40,133]. Despite this, the method continues to be frequently used due to its rapid procedure for screening and comparison, and its provision of a good estimate of the TPC in foods.

Carob pulp is an excellent source of bioactive compounds such as phenolics (gallic acid, gallotannins, etc.) [4,55,134], and has been increasingly used as a raw material in different products. For carob product elaboration, in general, the raw material is subjected to processing, such as heating at high temperatures. Although the application of high temperatures can inactivate microorganisms, it decreases antinutritional factors, increases the digestibility of foods, and modifies the bioavailability of the phenolics; furthermore, thermal processing may have negative effects on these bioactive compounds, as well as on their bioactivity [135]. In most of the foods that will be addressed later, heating plays an important role, with great influence on the final composition of the food products.

Total phenolic (TPC), anthocyanins (TA) and flavonols (TF) contents. Carob syrups were found to be a good source of phenolic compounds [24], and small differences in their phenolic content may be due to differences in the variety and origin of the raw material, as well as in the production technique [17]. It has been demonstrated that the values of TPC in the carob pod [19] or carob juice [26] are higher than in the concentrated syrups. This indicates that various steps of the processing, and the prolonged heat treatments applied during the carob syrup production, may cause degrading reactions in these compounds (destruction of polyphenols structure) [19]. Comparing different raw materials (grape, date, apricot, mulberry and carob) in the elaboration of syrups, we found that the TPC content (mg GAE/100 g) of carob (205) was in the third position after apricot (243) and date (225) [15]. However, these values are well below those found by Tounsi et al. [23] in

carob syrups (in the range of 1600), corroborating that other factors (e.g., carob origin, etc.) may affect their content.

In the elaboration of tarhana and pasta, the supplementation of both products with carob pulp increased significantly the values of TPC [40,45,46]. Although the effects of oxygen, water, and the heat treatment during pasta processing and cooking induce the oxidation of some sensitive phenolic antioxidants, cooking leads to the release of some bound phenolics from the food matrix [136–138]. Other factors that may affect the potential activity of fortified products are interactions between the food matrix components and bioactive compounds (phenolics), and/or among the bioactive compounds themselves, e.g., phenolic–phenolic interactions [106,107,139]. This type of interaction could explain the low values found by these authors in terms of the potential bioactivity (experimental TPC) of the studied pasta products in relation to the theoretical/predicted values [106,107,140].

In the same way, several works showed increases in the content of phenolics after the addition of carob pulp flour in cream recipes [29,30]. Furthermore, comparing raw materials in cream elaboration, Racolta et al. [31] found that the cocoa prototype displayed the highest content of polyphenols (929 mg GAE/100 g), followed by the carob prototype (844 mg GAE/100 g), and, as expected, the control (sunflower kernel) sample had the lowest value (749.80 mg GAE/100 g).

The observed increase in TPC and TA in bean- and rice-based snacks fortified with 5 or 10% carob fruit flour could be related to the extrusion step, which releases some non-available phenolics bound to the cell wall (dietary fibers of the carob pod) and thus increases their extractability [38,44]. Compared to the commercial sample without carob, the extruded formulations with carob flour presented approx. 1.5-fold higher amounts of TPC, and around 1.6 times more anthocyanins.

Comparing raw materials such as carob by-products and seaweeds in the elaboration of functional breads, Rico et al. [38] found that the bread containing carob pod showed significantly higher TPC values. The increase was especially significant in those breads containing carob peel, germ and pod, wherein the values were almost five times higher than the values observed in the control wheat flour bread.

In the case of beverages, we studied the use of different fruits (berry leaves, carob and doum) in the preparation of infusions [57]. The authors found that blended infusions containing carob showed higher TPC compared to individual plant infusions. In a traditional Moroccan carob drink, different values of TPC and TFC were found according to the area of elaboration within the Beni Mellal region. The results were higher compared with the results for other fruits' (apple, orange, grapefruit, pineapple, plum, grapes and prickly pear) juices in the literature [52]. On the other hand, the TPC content found in kvass beverages elaborated with roasted carob flour as an alternative to the use of rye malt extract was higher in the sample elaborated with 100% carob, and the result did not change after the fermentation process [53]. Regarding the elaboration of carob-based milk (CBM) beverages prepared with carob flour (4% *w/w*), factors such as the variety, roasting, and their interaction had significant effects on total phenolics [8]. In general, the CBM beverages prepared using roasted carob presented significantly higher amounts of TPC, because roasting induced the breakdown of the cellular structures, which could allow the release of phenolics, tannins and Maillard reaction products (MRPs). According to this study, the values of TPC per 250 mL cup of CBM beverages were higher than in other kinds of beverages known for their high phenolic contents, such as coffee, tea and wine.

The phenolic contents of carob hydro-alcoholic macerates may be derived from intrinsic parameters such as the variety of carob used, and may be increased by the different treatments used during the manufacturing process of the beverage. Thus, Rodríguez-Solana et al. [55] found that the TPC content was strongly influenced by the carob variety (the Portuguese Galhosa, Mulata and AIDA) used. Particle size (kibble or flour) and roasting degree (unroasted, 120 °C and 150 °C) also presented a significant influence on the phenolic content, while the maceration period (1 or 3 weeks) was statistically non-significant. The general tendency found was that the higher the carob roasting degree, the

greater the values of TPC in liquors. According to these authors, the results could also be explained by the formation of MRPs with a phenolic-type structure during the roasting process, because this type of compound is also detected by Folin–Ciocalteu reagent, thus its value may be overestimated [141]. For these reasons, it is important to be discriminative regarding the reaction techniques used for the quantification of this type of compound, it being better to focus on techniques such as liquid chromatography for identifying and quantifying the individual phenolic profile.

Hanousek et al. [54] studied different maceration parameters affecting the TPC, and found the highest values in macerates elaborated with the lowest strength of alcohol (50 and 30% *v/v*) and the highest proportion of carob flour (1:5 solid/liquid ratio), and in those exposed to darkness. The strength of alcohol proved to be the most important parameter in phenolic extraction because changes in ethanol concentration modify the physical properties of the solvent and may influence the extraction of these compounds. Furthermore, as mentioned before, the particle size and its structure also influence the efficiency of compound extraction and the duration of the maceration. The use of dry and larger-sized chopped carob pods, and longer extraction times, were necessary to obtain macerates with the highest TPC. Another important factor influencing phenolic instability and susceptibility to degradation was the exposition to sunlight. It should be highlighted that sunlight exposition, frequently used in liqueur production, should be avoided due to the sensitivity and degradation of phenolic compounds. Furthermore, to avoid such degradation, the authors advise the use of colored bottles, which provide some protection from UV and visible light radiation.

The TPC of different carob products was assessed after in vitro digestion. In digested carob pulp products (carob flour, carob syrup, carob fiber and carob extract), the value decreased from 18% to 57% compared to initial contents, with a great impact on the food matrix. The acidic conditions of gastric digestion may release phenolic compounds, mainly phenolic acids, from the food matrix (e.g., cell wall), or increase the reactivity of phenolic compounds towards the Folin–Ciocalteu reagent, while on the contrary, flavonols and flavon-3-ols may be decreased under gastric conditions. On the other hand, intestinal digestion was shown to be mainly responsible for the reduction of compounds [27].

In carob pasta, the TPC was significantly higher, increasing with the percentage of functional supplement added and after simulated digestion, with values increasing from 12.2 to 12.9 mg GAE/g DM, indicating higher bioaccessibility after this process.

In liqueurs elaborated with techniques such as percolation, maceration, aqueous or hydro-alcoholic infusions and distillation [55], the TPC values after the gastric and intestinal phases were significantly higher in comparison to the initial liqueur, regardless of the extraction method used. The increase in TPC under gastric conditions (acidic medium) could be caused by the release of phenolic compounds from the matrix or the increased reactivity of phenolic compounds towards Folin–Ciocalteu reagent [27]. Regarding the content of flavonoids (TFC) (mg quercetin equivalents (QE)/L), hydro-alcoholic infusion (65), maceration (57) and percolation (50) presented significantly higher values, followed by aqueous infusion (31) and finally distillation (4). For all of these, the TFC increased significantly after the gastric and intestinal digestions, presenting in the latter the highest value. After the intestinal step, flavonoids bound to sugar residues may be released into the extractant medium. Additionally, the mixture of sugar and soluble fiber in the medium could be responsible for the protective effect on the recovery and enhancement of the flavonoids' bioaccessibility. The statistically significant high correlations found between TFC and TPC (0.615) suggest that the contents in flavonoids have a great influence on the variation of TPC in the samples.

Phenolic profile. Many factors involved in sample preparation, including the types of solvent and extraction process [20], may influence the qualitative and quantitative identification of the compounds in carob products examined by different techniques, such as liquid chromatographic coupled to ultraviolet absorbance detection (HPLC-UV) and/or

mass spectrometry (HPLC-MS, HPLC-UV-ESI/MS, etc.) [20,27], or using the green, simple, fast and effective technique of capillary electrophoresis (CE-DAD) [17].

Gallic acid (GA) was the major phenolic compound identified in carob products (Figure 3). According to Papagiannopoulos et al. [20], the extraction process might lead to the release of this compound by the hydrolysis of tannins, and to a lesser extent the formation of more stable galloyl esters, resulting in an overestimation of GA. This makes the comparison of both qualitative and quantitative data from different sources derived using a variety of extraction methods more complicated. It was found that in syrups, the preparation of roasted carob flours or the sugar concentration step of the carob juice had a large impact on the GA content, and the hydrolyzable tannins contents were lowered by the hydrolyzation processes [20].

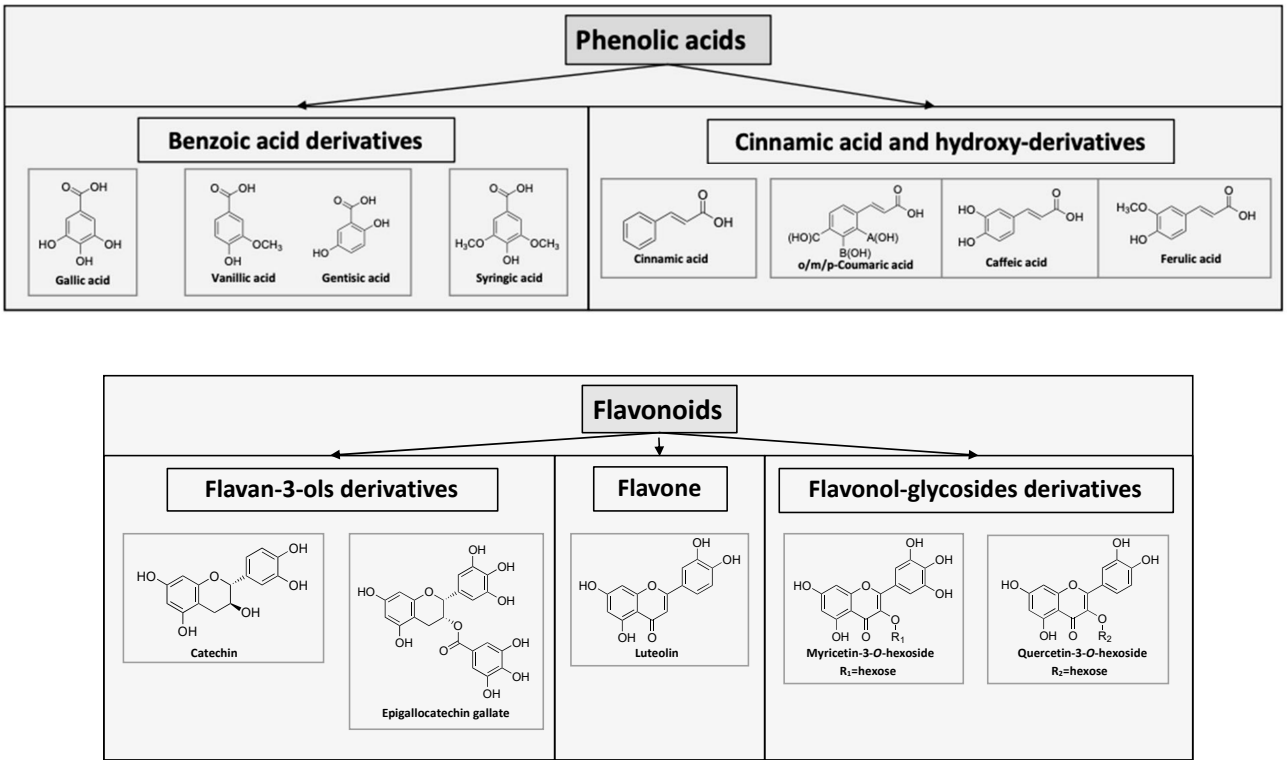

Figure 3. Main phenolic compounds found in carob products.

In carob liquors or macerates, GA was also present at greater amounts, and the concentration was influenced by the cultivar or processes that took place during beverage production [9]. In a later work, comparing different techniques of liqueur elaboration (percolation, maceration, aqueous or hydro-alcoholic infusions and distillation), GA was extracted at higher quantities via hydro-alcoholic infusion and maceration methods, followed by percolation and aqueous infusion [55]. The short contact time between solvent and solute used in the percolation procedure, or the use of a single solvent cycle passing through the carob flour, was insufficient to extract greater amounts of this compound. In the case of aqueous infusion, water (even at elevated temperatures) was a poor solvent for extracting GA. As for the distillation technique, only compounds with certain volatility are extracted, and therefore it is to be expected that GA was not present.

In the kvass beverage elaborated with different quantities of roasted carob flour and/or rye malt extract, the higher the carob content, the higher the GA concentration [53]. Furthermore, this compound was present in higher quantities than the quercetin and myricetin derivatives identified in samples containing carob.

Caffeic and syringic acids, and catechin, were found in higher quantities in carob syrup than in other carob products (carob flour, carob fiber and carob extract) [27]. Other compounds

such as cinnamic acid, coumaric and ferulic acids (hydroxycinnamic acids); condensed tannins; syringic, gentisic and vanillic acids (derivatives of benzoic acid); luteolin (flavone); epigallocatechin gallate (galloyl ester of flavan-3-ol) [27]; and quercetin (quercetin-desoxyhexoside and quercetin-3-o-rutinoside or rutin) and myricetin (myricetin-desoxyhexoside) derivatives (flavonol-glycosides) were identified in different syrups [17,20,27].

Among the different isoflavones (daidzin, glycitin, genistin, dadidzein and genistein) studied in muffins, genistein was the only one that differentiated muffins elaborated with carob as compared to cocoa [34]. The thermal processing carried out on samples only allowed us to determine the simple structures of these molecules, without the glycoside. Although the main source of isoflavones in the muffins was soybean, carob may significantly influence the genistein content. For that reason, the carob muffins were characterized by higher genistein contents in dry matter. This compound is a promising, potent drug in the prophylaxis and treatment of breast and prostate cancer, postmenopausal bone loss and osteoporosis, cardiovascular disorders in postmenopausal type 2 diabetic patients, and menopausal symptoms [142].

These compounds presented alterations in their content during gastrointestinal digestion. According to Goulas and Hadjisolomou [27], the initial GA concentration of carob syrup (3368 μg/g) slightly decreased after oral digestion, and significantly increased after the gastric step due to the acidic conditions, which may release GA from the food matrix or favor the release of GA bound to other structures present in the food matrix (hydrolysis of gallotannins) [143,144]. Finally, a dramatic decrease was observed after intestinal digestion due to the instability of this compound under intestinal conditions [144,145].

The gastric hydrolytic process only favored the increase in GA in the liqueur obtained by aqueous infusion [55]. After intestinal digestion, appreciable alterations in the structure and physicochemical properties of the bioactive compounds, and/or different interactions resulting in oxidation, the precipitation of phenolics (e.g., tannins) with enzymes present in the digestive mixture, and interactions with other components such as polysaccharides, may occur. The different performances can be associated with the food matrix present in the different carob liqueurs. In this sense, GA was almost entirely degraded in liqueurs made via percolation and aqueous infusion, probably because this compound may be more susceptible to degradation in these less complex liqueur matrices. On the other hand, no significant differences and a slightly significant reduction were found after intestinal digestion in the hydro-alcoholic infusion and maceration liqueurs, respectively. The higher contents of sugars and soluble fiber present in the matrices of the liqueurs elaborated via hydro-alcoholic infusion and maceration could act as a protective barrier to GA degradation [145].

A significant reduction in the mentioned hydroxycinnamic acids was also observed during the in vitro digestion of carob products (syrup and extracts) [27]. The intestinal digestion step induced the highest losses of caffeic acid. In relation to syringic acid, this compound was strongly affected by the food matrix. In carob syrup, the gastric conditions caused significant decreases in its content, reaching at least half of its initial amount in the final digestion fraction. Carob syrup showed a slight decrease in catechin content after the gastric step, followed by a substantial drop (50–60%) after intestinal digestion. In general, simple catechins are more stable than derived gallocatechins [146]. Finally, rutin presented a gradual content reduction, with the lowest values reached at the end of the digestion.

3.2. Antioxidant Capacity

Nowadays, there is great interest in the contents of natural antioxidants (e.g., phenolics, vitamins (mainly E and C), and carotenoids) present in plant-based foods from a human health perspective [27]. The antioxidant capacity (AC) of a plant extract such as carob product is of particular interest because of the beneficial physiological activity it has in human cells, helping to prevent the oxidative stress caused by free radicals and oxygen, and aiding the prevention of diseases such as inflammatory, cardiovascular, cancer, atherosclerosis, and aging-related disorders [147]. In addition, these natural antioxidants

can replace the synthetic antioxidants used in foodstuffs, which can be harmful components due to their toxicity and carcinogenic effects [148].

In order to evaluate the AC of natural products, it is crucial to perform more than one in vitro antioxidant test with different mechanisms concerning the various oxidation reactions taking place in food products [23]. Hydrogen atom transfer (HAT)-based (e.g., oxygen radical absorption capacity (ORAC)), single electron transfer (SET)-based (ferric ion-reducing antioxidant power (FRAP) and cupric ion reducing antioxidant capacity (CUPRAC)) and mixed (HAT and SET)-mode (2,2-azino-bis-3-ethylbenzthiazoline-6-sulfonic acid radical ($ABTS^{\cdot+}$)-scavenging assay, or Trolox equivalent antioxidant capacity (TEAC) and 1,1-diphenyl-2picrylhydrazyl (DPPH) free radical-scavenging capacity) assays are widely used for measuring the total AC of a compound or mixture [55,57,149]. Although these chemical methods have a questionable ability to predict in vivo activity, they are still widely used for the evaluation of the AC of different carob-based products, as is discussed below [55].

The chemical composition analysis of carob products revealed the presence of different bioactive compounds, such as non-enzymatic browning products and polyphenols, among others, which justify the evaluation of their functional properties, namely, their antioxidant capacities [23]. For that reason, the incorporation of carob pulp/pod flour or carob syrups in several food formulations, such as in yogurt, pasta, alcoholic base, baked goods, etc., has been studied in many works to improve their antioxidant properties, as will be seen in detail below.

In general, the high AC observed in carob syrups does not depend on syrup concentration or on its origin (industrial or homemade), probably because traditional processing is also used at the industrial scale [18,20,23,24]. This AC could be mainly attributed to the high content of phenolic compounds present naturally in syrups; however, other antioxidant compounds, such as peptides, organic acids, or the intermediates (e.g., HMF) and products (melanoidins) of non-enzymatic browning reactions (caramelization and Maillard reactions) naturally produced during thermal processing and storage by the interaction between available reducing sugars and amino acids, can also contribute to the AC [23,150,151]. Compared with other fruit syrups (grape, date, apricot and mulberry), carob samples presented the highest ability to scavenging DPPH radicals, and this may be mainly due to the hydrogen-donating ability of polyphenols present in syrups [15]. Accordingly, the studied carob syrups with high AC could be either directly consumed to take advantage of their potential health benefits, or they could be used in the food industry to prevent lipid oxidation in food systems, thereby improving their oxidative stability and prolonging their shelf life [24].

The use of carob flour as an ingredient in the preparation of different carob products also caused an increase in their AC. The substitution of sugar with carob flour (8%) in the formulation of spread creams (with sunflower as a base) gave rise to values closer to those of the cocoa prototype [31]. The AC increase was also observed in snacks elaborated with rice and bean, and in those including 5 or 10% carob fruit flour [42,44], or when cocoa flour was replaced with carob fruit and chicory root in the elaboration of wafer creams, with variations according to the storage time (mainly after the 30th and 60th days) [32]. In snack samples, no significant differences were found between extruded and non-extruded formulations, probably because the AC value is mainly conditioned by the types and amounts of antioxidant compounds in the sample [152]. Moreover, positive correlations were found between anthocyanins and tartaric esters, although the increase in AC (ORAC) after extrusion might also be attributable to the existence of other food components, e.g., proteins, aromatic compounds, or the creation of Maillard reaction products [44,153,154].

In the elaboration of baked goods, the addition of carob by-products for the development of functional bread in comparison with seaweeds or wheat flour (control) [38], or the substitution of cocoa (control sample) with carob in muffins [34], in general contributed to an increase in AC. The low correlations between TPC and AC values, due to the low quantities of functional ingredients added in the bread elaboration, suggest that the most

probable contributors to AC (ORAC) are the non-phenolic components present in other bread ingredients, such as ascorbic acid (vitamin C), α-tocopherol (vitamin E), β-carotene, and fatty acids [38]. On the other hand, in carob and cocoa flour muffins, the antiradical properties (ABTS and DPPH) could be influenced by factors such as the roasting, the cultivars used, and the geographical regions [34]. The reducing non-phenolic substances (e.g., melanoidins) produced during the Maillard reaction in cocoa and carob processing might be responsible for the increased antiradical effects.

Among the factors involved in the AC of pasta are the types and levels of functional supplements (positive correlation between AC and the increase in percentage of carob flour added in pasta formulation), and the pasta processing and cooking methods (the water-soluble antioxidant can leach into the cooking water) [45,46,65,137,138].

Herken and Aydin [40] observed an increase in the AC of tarhana with carob flour supplementation, and the high correlations found between TPC and AC values indicate the high contribution of these compounds to the antioxidant effect.

Infusions with mixtures of berry leaves, carob fruits, and doum fruits exhibited a strong ability to quench DPPH radicals, as follows: berry–carob–doum > berry–carob > berry–doum > carob–doum [57]. These infusions are rich in polyphenolic compounds, which possess various bioactivities [155]. In the kvass beverage elaborated with roasted carob flour and/or rye malt extract, the sample with 100% carob showed the highest capacity to quench ABTS radicals, and in this concrete case, this capacity was significantly increased after the fermentation step [53].

A significant effect of carob variety on TAA levels was observed in the elaboration of carob-based milk beverages (CBM) [8]. However, this TAA was also significantly affected by carob roasting (in general, the higher the roasting degree, the higher the TAA values), and variety × treatment interaction.

In the elaboration of carob macerations to prepare carob liqueurs, different factors such as carob variety, particle size, time of maceration, carob roasting degree, the interactions of variety–roasting degree and particle size–roasting degree [55], exposure to sunlight, and alcoholic strength [54] had the greatest influence on the AC contents.

In general, liquors prepared with the highest roasting degree (150 °C) and the smallest particle size (flour) presented the highest AC (TEAC) results [55]. However, in varietal AIDA liquors, the sample prepared with unroasted flour presented the highest AC value. The high correlations found between AC and phenolic content (GA) or browning index (indicator of the non-enzymatic browning reaction products) confirm the direct influence of these compounds on AC. Hanousek et al. [54] found higher AC (FRAP) values in carob macerates elaborated with the highest carob proportion (1:5 solid/liquid ratio), medium alcoholic strength (50% *v/v*), and in the darkness.

In carob liqueurs elaborated via different techniques (maceration, percolation, infusion and mixture with essential oil), the high correlations found between the AC (as assessed by ORAC and TEAC assays) and the TPC indicated the influence of this kind of compound on AC [55].

Another process that can affect the high AC of the carob syrups is the passage through the digestion step. Previous works have studied the effect of in vitro digestion on AC via DPPH and FRAP assays in different carob products (carob flour, carob syrup, carob fiber and carob extract) [27]. Both antioxidant assays demonstrated a reduction in AC at the end of digestion—between 30% and 50% for DPPH values and between 20% and 50% for FRAP values—as this digestion process caused significant losses of the phenolics that were the main antioxidants in carob pulp. During the digestive process, the AC increased significantly after gastric digestion; however, it decreased after the intestinal step. Some phenolic compounds related to AC may be transformed into different structural forms with other chemical properties due to their sensitivity to alkaline pH [156].

Furthermore, in pasta fortified with carob at a 5 g/100 g blend, the in vitro digestion process helped to release the antioxidative compounds, increasing the bioaccessibility of

the antioxidant compounds and thus the AC. Although the TPC increased after digestion, the total AC may depend also on other bioactive compounds [157].

In liqueurs, after the gastric and intestinal phases, the values of TEAC and ORAC were significantly higher in comparison to the initial values, regardless of the technique (maceration, percolation, infusion or mixture with essential oil) used [55]. The higher AC of the digested samples may be due to the biotransformation, by hydrolyzation, of polyphenolic compounds, in mild alkaline conditions and using digestive enzymes (pepsin and pancreatin). Additionally, the different processing steps of liqueur production contributed to such biotransformation, and therefore, to the increase in AC values. The extraction of flavonoids from the complex structures after digestion could also explain the high ORAC values, since a high correlation between both parameters was observed. ORAC values may also be related to the number of hydroxyl groups present in the A and B rings of flavonoids [158,159]. Finally, the significantly high correlations found between HMF contents and TEAC, and between TFC and ORAC, suggest that these compounds contribute the most to the variation in the AC of the samples.

3.3. Antimicrobial Activities and Prebiotic and Probiotic Effects

Antibacterial and antifungal activities. The presence of different bioactive compounds in carob products, including volatile components, polyphenols and non-enzymatic browning products, justifies the evaluation of the antibacterial and antifungal activities in samples.

Syrup products from homemade and commercial origin inhibited the growth of the bacteria Listeria monocytogenes, Staphylococcus aureus, Escherichia coli, Salmonella enterica, Pseudomonas aeruginosa, Micrococcus luteus, Klebsiella pneumoniae, Enterococcus faecalis, Salmonella typhimurium and Enterobacter sp., known as opportunistic human and animal pathogens and/or for causing food contamination and quality deterioration [23]. The strongest antibacterial activity of the studied syrups was recorded against L. monocytogenes, M. luteus and P. aeruginosa, with inhibition zones more important than those of Gentamicin. The samples also had an inhibitory effect against S. aureus, which is well-known for its resistance to some phytochemical compounds and for the production of several types of enterotoxins that cause gastroenteritis [160].

These inhibitions were attributed to the polyphenolic constituents and other bioactive compounds, such as compounds from non-enzymatic browning reactions (melanoidins and HMF) and volatile components (palmitic acid and terpenes). The bacteriostatic and/or bactericidal action of phenolics could be explained by their ability to adsorb onto cell membranes and to disrupt their permeability barrier, through their interaction with enzymes and effectors or the deprivation of substrates and metal ions. Other bioactive compounds formed during syrup processing—the products/intermediaries of non-enzymatic browning reactions (melanoidins and HMF)—were found to exert an antibacterial effect by binding essential metals or precipitating proteins [151,161].

Additionally, important growth inhibition against eight different bacterial strains, *Staphylococcus aureus*, *S. epidermidis*, *Bacillus cereus*, *B. subtilis*, *S. faecalis*, *P. aeruginosa*, *E. coli* and *Salmonella* sp., was observed in carob syrups [162]. The authors attributed this strong antimicrobial activity to the presence of a high content of polyphenols in the carob syrup extract, mainly GA and epigallocatechin gallate.

Hussein et al. [57] observed that berry leaves, carob or doum fruit infusions and their mixtures were generally more effective against pathogenic bacteria (*E. coli, S. aureus*, *Enterococcus feacalis*, *Bacillus subtilis* and *B. megaterium*) than yeast (*Debaryomyces hansenii*, *Zygosaccharo mycesrouxii*, *Rhodotorula rubra*, *Candida shehatae* and *Candida tropicalis*), with the highest antimicrobial activities against food spoilage as well as food pathogenic microorganisms in infusions elaborated with mixtures (berry leaves, carob and doum fruits) of plants. The largest inhibition zones of bacteria were obtained against *E. coli* (7.0 mm), *S. aureus* (4.7 mm) and *B. megaterium* (4.0 mm), while in yeasts they were against *R. rubra* (5.0 mm), followed by *Z. mycesrouxii* (3.4 mm), and *D. hansenii* (3.0 mm). Thus, the mixture infusion, with synergistic antimicrobial effects, could be incorporated into various food products as

a natural antimicrobial additive. These authors explained that among the antimicrobial compounds, phenolic compounds and alkaloids are very important components [163,164].

Prebiotic and probiotic effects. On the other hand, some beneficial bacteria, such as the lactic acid bacteria, have been important in food for centuries. These beneficial microorganisms play an important role in the food industry for their significant contribution to the flavor, aroma, texture, sensory characteristics, therapeutic properties and nutritional value of food products [165].

Due to the possible prebiotic effects of products such as kefir [50], and yogurt ice cream [166] supplemented with carob, lactic bacterial growth was studied in those samples. In kefir production, the bacterial (*Lactobacillus lantarum*, *Lb. rhamnosus*, *Lactoccocus lactis*, *L. cremoris* and *Leuconostoc cremoris*) count increased during the first week of storage of kefir supplemented with carob (pod, seed, pulp and crude pulp mucilage), thus stimulating bacterial growth similar to inulin (a prebiotic fiber) and suggesting similar prebiotic activity. However, such prebiotic effects decreased with prolonged storage (from 14 to 28 days) for pod and seed supplementation and for inulin.

Contrary to yogurt ice cream processing, such as freezing and the incorporation of air during production that reduce the bacterial (*L. acidophilus* and *Bifidobacterium* BB-12) count due to the freeze-injuring of cells leading to their death, or oxygen toxicity affecting the growth of anaerobic bacteria, carob and whey supplementation at the maximum concentration (1%) produced the highest quantity of viable probiotic bacteria. This was due to the improvement of the survival of *L. acidophilus* and *Bifidobacterium* BB-12 because of the possible prebiotic effects and antioxidant capacity of both raw materials [166].

In the kvass beverage elaborated with different quantities of roasted carob flour and/or rye malt extract, and enriched with *Saccharomyces boulardii* and *Lactobacillus plantarum*, we evaluated the probiotic potential [53]. The results showed that the quantity of *L. plantarum* significantly dropped in the second week of storage in all products (values from approx. 10 log cfu/mL to approx. 0–3 log cfu/mL); however, the survival of the bacterium was improved by the recipe with a higher content of carob flour. The rapid reduction may be due to the presence in the medium of Maillard reaction products (melanoidins), present in roasted carob and rye malt, with known bacteriostatic and bactericidal properties. In the case of *S. boulardii*, although its quantity decreased in the first week of storage in all samples (from approx. 9.5 log cfu/mL to 8–8.5 log cfu/mL), over longer periods, non-significant changes were observed regardless of the recipe used. This indicates the better suitability of this microorganism for the production of probiotic beverages containing both carob flour and rye malt extract.

3.4. Enzyme Inhibitory Capacities

Tyrosinase and acetylcholinesterase (AchE) inhibitors are chemical agents capable of reducing the activity of enzymes related to neurodegenerative (Parkinson's and Alzheimer's, respectively) diseases. On the other hand, the inhibition of α-glucosidase (located in the mucosal brush border of the small intestine) and α-amylase (a salivary or pancreatic enzyme) is known as one of the most effective therapeutic methods against diabetes mellitus (type 2 diabetes).

To evaluate the effect of carob liqueurs in the fight against these enzymes, Rodríguez Solana et al. [55] studied the influence of different techniques of elaboration. Their results showed that all carob liqueurs studied presented inhibitory capacities against the enzymes studied. The highest inhibition percentages were obtained for α-glucosidase and tyrosinase, followed by AchE, and finally α-amylase. The inhibitions of tyrosinase observed in liqueurs were associated with the concentrations of GA, and this was corroborated by the correlations between both parameters. However, no strong correlations were found between α-amylase, α-glucosidase and AchE inhibitory capacities and the compounds identified in the study. Despite this, the AC (which leads to the alleviation of the oxidative stress produced by chronic hyperglycemia in diabetes, thus preventing or reversing diabetic complications) observed in the samples, and the strong ability to inhibit the activity of

α-glucosidase, together with a low inhibitory effect against α-amylase, are considered ideal conditions for the management of postprandial hyperglycemia with minimal side effects.

Depending on the enzyme, different patterns were observed before and after the digestion of samples. Despite the initial differences found in samples, after the gastrointestinal digestion, similar inhibitory capacities were found for all carob liqueurs regardless of the extraction method used in their elaboration. Digested liqueurs caused the potent and low inhibition of α-glucosidase and α-amylase, respectively, and the moderate inhibition of tyrosinase and acetylcholinesterase enzymes.

4. Undesirable Compounds

In human health terms, undesirable compounds from food may be naturally present, such as the stimulants caffeine and theobromine, or may be formed during the processing of raw materials into food products, such as the furanic compounds formed during carob baking. Although their complete elimination is unlikely, in the case of furanics, due to their recognized negative impact on human health, food manufacturers have sought to limit their presence using new mitigation strategies that can be progressively implemented, thus minimizing their impact [167].

4.1. Caffeine and Theobromine

Caffeine and theobromine are naturally occurring purine alkaloids (methylxanthine alkaloids), which act as stimulants to the central nervous system. Both compounds are closely related alkaloids; indeed, theobromine (3,7-dimethyl xanthine) can be readily converted into caffeine (1,3,7-trimethyl xanthine) by methylation with methyl sulfate. While caffeine is the chief alkaloidal constituent of different parts of plants, such as coffee beans, tea and mate leaves, theobromine is the principal alkaloid of cocoa beans [168]. A variety of adverse health effects have been attributed to their consumption, including behavior abnormalities, hypertension, and hypercholesterolemia, though inconsistently. Existing data suggest that caffeine intake begins early in life, and that children are susceptible to caffeine and theobromine toxicity because their detoxifying mechanisms are not fully developed [169].

Different kinds of plants, foods and drinks contain caffeine and/or theobromine, and these are consumed daily by the population [32,170]. As it does not contain (or contains in traces amounts) caffeine or theobromine, the potential use of carob as a healthy alternative to coffee and cocoa is currently being promoted in different food products, such as infusions, syrups, and creams, among others [4,7,32,171].

4.2. Furanic Compounds and Melanoidins

Furanic compounds (5-hydroxymethyl furfural (HMF) and furfural) and melanoidins are intermediate and end-products, respectively, that are formed as a result of the degradation of carbohydrates during the excessive thermal processing of acidic foods and/or preservation processes, in two ways [19]: (a) the Maillard reaction (non-enzymatic browning reaction) of a free amino group, such as an amino acid, amines, peptides, proteins, or ammonia, with a carbonyl compound [172–174], and (b) the direct dehydration of sugars (especially the hexoses in HMF formation and the pentoses in fufural) under acidic conditions during heat the treatments of the foods [175], even at low temperatures [176]. As the end-products of these reactions (Maillard and caramelization reactions), their melanoidins contents are commonly estimated by the browning index (BI; spectrophotometric absorption measured at 420 nm), while the intermediary compounds are commonly determined through chromatographic analysis.

It has been noted that furanics and melanoidins have a variety of harmful effects, including mutagenicity, carcinogenicity, and cytotoxicity [177]. For that reason, these compounds have been widely used as an indicator of quality loss.

HMF, mainly produced during the thermal process of juice concentration or syrup pasteurization, is used as one of the main quality indexes for fruit juices and syrups [16].

In these processes, the initial formation of HMF during juice concentration is due to the presence of free fructose, and it further increases during storage due to the degradation of sucrose [22]. Concentrations found in syrups differ in the literature, indicating that the juices were exposed to different boiling temperatures during concentration. Furthermore, the initial concentration of HMF significantly increased after the long thermal processing or storage of syrups [15,16,19,25], with temperature, time, and the interaction of temperature and time being the factors that significantly affect HMF formation in syrup storage [16]. In addition to the composition (especially protein, and type and content of sugar) of the fruits, factors such as the pH [178], the water activity [179], the phenolic compounds, and the presence of minerals such as Na^+, K^+, Cu^{2+}, Ca^{2+}, Zn^{2+}, and Fe^{3+} in the environment may increase or decrease the rate of HMF formation. The phenolic compounds with antioxidant properties found in carob can inhibit the carbohydrate oxidation occurring in this Maillard reaction, reducing furanic formation [180,181]. On the other hand, the presence of cations may cause glucose molecules to decompose more rapidly during heating, increasing the rate of HMF formation [182]. Regarding the pH, the higher values in the carob syrup versus other fruit syrups (mulberry and black mulberry) can explain the higher HMF concentrations obtained. However, the concentrations found in syrups indicate that they are good-quality samples (values < 75 ppm), according to the Turkish Standard Institute [183].

Regarding the type of sugar, fructose is about 40 times more reactive than glucose as a precursor of HMF [176,184]. Taştan et al. [22] found a way to reduce the production of HMF, via the levansucrase enzymatic elimination of reducing sugars. First, sucrose was hydrolyzed by levansucrase to release glucose and fructose. Then, the transfructosylation activity of levansucrase converted the fructosyl units to fructooligosacaride. Therefore, although the amount of total glucose increased, the amount of HMF decreased due to the conversion of fructose to 6-ketose. Thus, differences in HMF content between levansucrase-treated and non-treated samples differed after storage for 3–4 months, increasing significantly in the non-treated samples (from ~17 to ~19–20.58 mg/kg). According to Tounsi et al. [24], to avoid the non-enzymatic reactions and preserve the juice quality, cryoconcentration and osmotic evaporation (athermal concentration) could be used for concentrating fruit juices, maintaining their chemical and biological characteristics.

Comparing the HMF results from carob spreads or creams (3.96 ppm) and syrups (21.32 ppm), the first presented lower values. Both products presented values below that of processed honey, which is considered as a similar product (40 ppm, Codex Standard). Thus, this demonstrates that the consumption of carob spread (cream) compared to syrups allows one to limit the daily intake of HMF [30].

In macerates and liqueurs, furanic compounds are formed during the thermal processing of carob pulp (furfural and HMF), or during the fired pot-still distillation process of figs to produce the fig spirit (furfural) used as the alcohol-base in liqueur elaboration [9,55]. The roasting temperature of carob was the factor that most affected the furanic composition of liqueurs. Additionally, carob variety, maceration period, and the interactions of roasting temperature–variety and variety–maceration time, influenced this composition. In general, the increase (from 1 to 3 weeks) in the maceration period favors the reduction in the furanic content, probably due to polymerization, or the further degradations of furfural to formic acid and HMF to formic and levulinic acids [55].

On the other hand, although during the storage of carob syrups good correlations were found between the parameters associated with the roasting process, BI and HMF, [25], the non-significant correlations found between these parameters in liqueurs may be due to the fact that these intermediaries can produce other final products (aldols and free polymers), or react with amino acids to produce aldimines or ketimines. In this sense, it is reasonable that a direct link was not found among reactants and intermediary (F and HMF) and final products (melanoidins, BI) [9].

The liqueur extraction methods influence the concentrations of the furanics, before and after the digestion process [55]. The highest HMF contents were found in liqueurs

elaborated by maceration, hydro-alcoholic infusion, percolation and aqueous infusion, in that order. These techniques are all based on direct contact between solvent and solute during the soaking of both raw materials. Only trace amounts were extracted using the distillation technique (volatilization of compounds).

During gastrointestinal digestion, the HMF concentration of liqueurs elaborated with different techniques only differed significantly after the intestinal phase, with recoveries of 59.52% (percolation), 72.18% (maceration), 84.73% (hydro-alcoholic infusion) and 89.64% (aqueous infusion). This reduction could be explained by the high reactivity of HMF with the amino and sulfhydryl groups present in amino acids derived from protein hydrolysis during gastric digestion, and with the subsequent formation of Michael adducts and Schiff bases [185].

The concentrations of furfural (mainly present in the fig spirit) found in liqueurs at the end of the digestion process showed no significant differences among the infusions, maceration and percolation methods, since the same spirit volume was used in these extraction processes. The highest concentrations found in the samples obtained by distillation may be related to the degradation of sugars produced during the distillation of the fig spirit with carob pulp flour.

Finally, in kvass beverage elaborated with carob flour, only HMF was found, and the concentration increased with the addition of rye malt extract. Thus, the F content found in samples containing both ingredients was incorporated with the rye malt extract, indicating the presence of pentoses and hexoses-type compounds in this raw material [53].

5. Conclusions

The modern diet and lifestyle are associated with an increased risk of severe diseases (e.g., obesity, diabetes, and cardiovascular diseases). Functional foods, related to the mitigation of the aforementioned risks to human health, represent one of the most interesting areas of research and innovation in the food industry, and their presence in the market is growing. In this sense, carob products (e.g., syrups, beverages such as liqueurs and tea, pasta, bread, snacks, tahini, yogurt, etc.) appear to fulfill the modern health criteria of consumers (i.e., nutritional value, gluten-free, etc.), present adequate sensory characteristics (such as natural chocolate-like sweetness), and they can also be consumed by individuals allergic to cocoa compounds (caffeine- and theobromine-free). Thus, carob pulp may be considered as a valuable additive containing nutritive and bioactive compounds that can be used in food products as a healthier and cheaper cocoa alternative. This replacement represents a technological solution in the elaboration of innovative, functional and healthier sweet products, with less fat and added sugars and increased fiber content. For all these characteristics, and because of the growing demand for functional foods and the rising costs of cocoa, this by-product of the carob seed industry is considered as a potential future ingredient in cocoa-based formulations, and as a nutraceutical ingredient in gluten-free preparations. In addition, the cultivation of *Ceratonia siliqua* L. trees in regions with a Mediterranean climate, with scarce agronomic resources, will result in the preservation and recovery of natural resources from rural areas, enhancing their economic activity through the industrial exploitation of the whole fruit.

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References

1. Battle, I.; Tous, J. *Carob Tree. Ceratonia siliqua L. Promoting the Conservation and Use of Underutilized and Neglected Crops. 17*; Institute of Plant Genetics and Crop Plant Research, International Plant Genetic Resources Institute: Rome, Italy, 1997; pp. 7–8.
2. Dakia, P.A.; Wathelet, B.; Paquot, M. Isolation and chemical evaluation of carob (*Ceratonia siliqua* L.) seed germ. *Food Chem.* **2007**, *102*, 1368–1374. [CrossRef]
3. Cantalejo, M.J. Effects of roasting temperature on the aroma components of carob (*Ceratonia siliqua* L.). *J. Agric. Food Chem.* **1997**, *45*, 1345–1350. [CrossRef]
4. Goulas, V.; Stylos, E.; Chatziathanasiadou, M.; Mavromoustakos, T.; Tzakos, A. functional components of carob fruit: Linking the chemical and biological space. *Int. J. Mol. Sci.* **2016**, *17*, 1875. [CrossRef]
5. Gunel, Z.; Tontul, İ.; Dincer, C.; Topuz, A.; Sahin-Nadeem, H. Influence of microwave, the combined microwave/hot air and only hot air roasting on the formation of heat-induced contaminants of carob powders. *Food Addit. Contam. Part A* **2018**, *35*, 2332–2339. [CrossRef]
6. Loullis, A.; Pinakoulaki, E. Carob as cocoa substitute: A review on composition, health benefits and food applications. *Eur. Food Res. Technol.* **2018**, *244*, 959–977. [CrossRef]
7. Papaefstathiou, E.; Agapiou, A.; Giannopoulos, S.; Kokkinofta, R. Nutritional characterization of carobs and traditional carob products. *Food Sci. Nutr.* **2018**, *6*, 2151–2161. [CrossRef] [PubMed]
8. Srour, N.; Daroub, H.; Toufeili, I.; Olabi, A. Developing a carob-based milk beverage using different varieties of carob pods and two roasting treatments and assessing their effect on quality characteristics: Effect of roasting on a carob-based milk beverage. *J. Sci. Food Agric.* **2016**, *96*, 3047–3057. [CrossRef] [PubMed]
9. Rodríguez-Solana, R.; Salgado, J.M.; Pérez-Santín, E.; Romano, A. Effect of carob variety and roasting on the antioxidant capacity, and the phenolic and furanic contents of carob liquors. *J. Sci. Food Agric.* **2019**, *99*, 2697–2707. [CrossRef]
10. Mulet, A.; Fernández-Salguero, J.; García-Pérez, J.V.; Bon, J. Mechanistic modeling to address process analysis: Kibbles of carob (*Ceratonia siliqua*, L.) pod extraction. *J. Food Eng.* **2016**, *176*, 71–76. [CrossRef]
11. Van Rijs, P.; Fogliano, V. Roasting carob flour decreases the capacity to bind glycoconjugates of bile acids. *Food Funct.* **2020**, *11*, 5924–5932. [CrossRef]
12. Arribas, C.; Cabellos, B.; Cuadrado, C.; Guillamón, E.; Pedrosa, M.M. Extrusion effect on proximate composition, starch and dietary fibre of ready-to-eat products based on rice fortified with carob fruit and bean. *LWT* **2019**, *111*, 387–393. [CrossRef]
13. Gutkoski, L.C.; de Almeida Bonamigo, J.M.; de Freitas Teixeira, D.M.; Pedó, I. Desenvolvimento de barras de cereais à base de aveia com alto teor de fibra alimentar. *Ciênc. Tecnol. Aliment.* **2007**, *27*, 355–363. [CrossRef]
14. Rosa, C.S.; Tessele, K.; Prestes, R.C.; Silveira, M.; Franco, F. Effect of substituting of cocoa powder for carob flour in cakes made with soy and banana flours. *Int. Food Res. J.* **2015**, *22*, 2111–2118.
15. Alıyazıcıoglu, R.; Kolaylı, S.; Kara, M.; Yıldız, O.; Sarıkaya, A.O.; Cengız, S.; Er, F. Determination of chemical, physical and biological characteristics of some pekmez (molasses) from Turkey. *Asian J. Chem.* **2009**, *21*, 2215–2223.
16. Toker, O.S.; Dogan, M.; Ersöz, N.B.; Yilmaz, M.T. Optimization of the content of 5-hydroxymethylfurfural (HMF) formed in some molasses types: HPLC-DAD analysis to determine effect of different storage time and temperature levels. *Ind. Crops Prod.* **2013**, *50*, 137–144. [CrossRef]
17. Şanlı, S.; Güneşer, O.; Kılıçarslan, S.; Şanlı, N. Screening of eighteen polyphenolic compounds in different carob pekmez by green capillary electrophoresis method. *SN Appl. Sci.* **2020**, *2*, 576–589. [CrossRef]
18. Akkaya, Z.; Schröder, J.; Tavman, S.; Kumcuoglu, S.; Schuchmann, H.P.; Gaukel, V. Effects of spray drying on physical properties, total phenolic content and antioxidant Activity of carob molasses. *Int. J. Food Eng.* **2012**, *8*, 20. [CrossRef]
19. Tetik, N.; Turhan, İ.; Karhan, M.; Öziyci, H.R. Characterization of, and 5-hydroxymethylfurfural concentration in carob pekmez. *GIDA J. Food* **2010**, *35*, 417–422.
20. Papagiannopoulos, M.; Wollseifen, H.R.; Mellenthin, A.; Haber, B.; Galensa, R. Identification and quantification of polyphenols in carob fruits (*Ceratonia siliqua* L.) and derived products by HPLC-UV-ESI/MS^n. *J. Agric. Food Chem.* **2004**, *52*, 3784–3791. [CrossRef]
21. Gökşen, G.; Ekiz, H.I. Pasting and gel texture properties of starch-molasses combinations. *Food Sci. Technol.* **2019**, *39*, 93–102. [CrossRef]
22. Taştan, Ö.; Sözgen, G.; Baysal, T.; Kaplan Türköz, B. Production of prebiotic 6-kestose using *Zymomonas mobilis* levansucrase in carob molasses and its effect on 5-HMF levels during storage. *Food Chem.* **2019**, *297*, 124897. [CrossRef]
23. Tounsi, L.; Ghazala, I.; Kechaou, N. Physicochemical and phytochemical properties of Tunisian carob molasses. *Food Meas.* **2020**, *14*, 20–30. [CrossRef]
24. Tounsi, L.; Karra, S.; Kechaou, H.; Kechaou, N. Processing, physico-chemical and functional properties of carob molasses and powders. *Food Meas.* **2017**, *11*, 1440–1448. [CrossRef]
25. Özhan, B.; Karadeniz, F.; Erge, H.S. Effect of storage on nonenzymatic browning reactions in carob pekmez: Effect of storage on nonenzymatic browning. *Int. J. Food Sci. Technol.* **2010**, *45*, 751–757. [CrossRef]

26. Fidan, H.; Petkova, N.; Sapoundzhieva, T.; Abanoz, E.I. Carbohydrate content in Bulgarian and Turkish carob pods and their products. *CBU Int. Conf. Proc.* **2016**, *4*, 796–802. [CrossRef]
27. Goulas, V.; Hadjisolomou, A. Dynamic changes in targeted phenolic compounds and antioxidant potency of carob fruit (*Ceratonia siliqua* L.) products during in vitro digestion. *LWT* **2019**, *101*, 269–275. [CrossRef]
28. Musa Özcan, M.; Arslan, D.; Gökçalik, H. Some compositional properties and mineral contents of carob (*Ceratonia siliqua*) fruit, flour and syrup. *Int. J. Food Sci. Nutr.* **2007**, *58*, 652–658. [CrossRef]
29. Tounsi, L.; Kchaou, H.; Chaker, F.; Bredai, S.; Kechaou, N. Effect of adding carob molasses on physical and nutritional quality parameters of sesame paste. *J. Food Sci. Technol.* **2019**, *56*, 1502–1509. [CrossRef]
30. Aydın, S.; Özdemir, Y. Development and characterization of carob flour based functional spread for increasing use as nutritious snack for children. *J. Food Qual.* **2017**, *2017*, 5028150. [CrossRef]
31. Racolta, E.; Muste, S.; Muresan, A.E.; Muresan, C.C.; Bota, M.M.; Muresan, V. Characterization of confectionery spreadable creams based on roasted sunflower kernels and cocoa or carob powder. *Bull. Univ. Agric. Sci. Vet. Med. Cluj Napoca Food Sci. Technol.* **2014**, *71*, 62–67. [CrossRef]
32. Habibzadeh, D.; Seyedain Ardabili, S.M. Evaluation of physicochemical, rheological and sensory properties of wafer cream by replacing cocoa powder with carob pod and chicory root powders. *Int. Food Res. J.* **2019**, *26*, 1059–1068.
33. Batista, J.E.R.; Braga, L.P.; de Oliveira, R.C.; Silva, E.P.; Damiani, C. Partial replacement of wheat flour by pumpkin seed flour in the production of cupcakes filled with carob. *Food Sci. Technol.* **2018**, *38*, 250–254. [CrossRef]
34. Pawłowska, K.; Kuligowski, M.; Jasińska-Kuligowska, I.; Kidoń, M.; Siger, A.; Rudzińska, M.; Nowak, J. Effect of replacing cocoa powder by carob powder in the muffins on sensory and physicochemical properties. *Plant Foods Hum. Nutr.* **2018**, *73*, 196–202. [CrossRef] [PubMed]
35. Farias, J.N.; do Nascimento, F.P.B.; Salvador, A.A.; da Silva, A.A.N.; dos Anjos Tamasia, G.; Rossetti, F.X.; de Brito Bello, S.R.; Vicentini, M.S. Desenvolvimento de biscoitos integrais à base de farinha de alfarroba como uma alternativa para substituição do cacau em pó. *Int. J. Nutr.* **2019**, *12*, 41–47. [CrossRef]
36. Youssef, M.K.E.; Ali, H.M.; El-Manfaloty, M.M. Nutritional assessment of wheat biscuits and fortified wheat biscuits with carob pod powder (*Ceratonia siliqua* L.). *Food Public Health* **2013**, *3*, 336–340.
37. Ibrahim, O.S.; Mohammed, A.T.; Abd-Elsattar, H.H. Quality characteristics of rice biscuits sweetened with carob powder. *Middle East J. Appl. Sci.* **2015**, *5*, 1082–1090.
38. Rico, D.; Alonso de Linaje, A.; Herrero, A.; Asensio-Vegas, C.; Miranda, J.; Martínez-Villaluenga, C.; de Luis, D.A.; Martin-Diana, A.B. Carob by-products and seaweeds for the development of functional bread. *J. Food Process. Preserv.* **2018**, *42*, 13700. [CrossRef]
39. Çağ Lar, A.; Erol, N.; Elgün, M.S. Effect of carob flour substitution on chemical and functional properties of tarhana: Utilization of carob flour in tarhana. *J. Food Process. Preserv.* **2013**, *37*, 670–675. [CrossRef]
40. Herken, E.; Aydin, N. Use of carob flour in the production of tarhana. *Pol. J. Food Nutr. Sci.* **2015**, *65*, 167–174. [CrossRef]
41. Papakonstantinou, E.; Orfanakos, N.; Farajian, P.; Kapetanakou, A.E.; Makariti, I.P.; Grivokostopoulos, N.; Ha, M.A.; Skandamis, P.N. Short-term effects of a low glycemic index carob-containing snack on energy intake, satiety, and glycemic response in normal-weight, healthy adults: Results from two randomized trials. *Nutrition* **2017**, *42*, 12–19. [CrossRef]
42. Arribas, C.; Cabellos, B.; Cuadrado, C.; Guillamón, E.; Pedrosa, M.M. Bioactive compounds, antioxidant activity, and sensory analysis of rice-based extruded snacks-like fortified with bean and carob fruit flours. *Foods* **2019**, *8*, 381. [CrossRef]
43. Arribas, C.; Cabellos, B.; Sánches, C.; Cuadrado, C.; Guillamón, E.; Pedrosa, M.M. The impact of extrusion on the nutritional composition, dietary fiber and in vitro digestibility of gluten-free snacks based on rice, pea and carob flour blends. *Food Funct.* **2017**, *8*, 3654–3663. [CrossRef]
44. Arribas, C.; Cabellos, B.; Cuadrado, C.; Guillamón, E.; Pedrosa, M.M. The effect of extrusion on the bioactive compounds and antioxidant capacity of novel gluten-free expanded products based on carob fruit, pea and rice blends. *Innov. Food Sci. Emerg. Technol.* **2019**, *52*, 100–107. [CrossRef]
45. Sęczyk, Ł.; Świeca, M.; Gawlik-Dziki, U. Effect of carob (*Ceratonia Siliqua* L.) flour on the antioxidant potential, nutritional quality, and sensory characteristics of fortified durum wheat pasta. *Food Chem.* **2016**, *194*, 637–642. [CrossRef] [PubMed]
46. Biernacka, B.; Dziki, D.; Gawlik-Dziki, U.; Różyło, R.; Siastała, M. Physical, sensorial, and antioxidant properties of common wheat pasta enriched with carob fiber. *LWT* **2017**, *77*, 186–192. [CrossRef]
47. Arribas, C.; Cabellos, B.; Guillamón, E.; Pedrosa, M.M. Cooking and sensorial quality, nutritional composition and functional properties of cold-extruded rice/white bean gluten-free fettuccine fortified with whole carob fruit flour. *Food Funct.* **2020**, *11*, 7913–7924. [CrossRef] [PubMed]
48. Karaca, O.B.; Saydam, I.B.; Güven, M. Physicochemical, mineral and sensory properties of set-type yoghurts produced by addition of grape, mulberry and carob molasses (*Pekmez*) at different ratios. *Int. J. Dairy Technol.* **2012**, *65*, 111–117. [CrossRef]
49. Moreira, T.C.; Transfeld da Silva, Á.; Fagundes, C.; Ferreira, S.M.R.; Cândido, L.M.B.; Passos, M.; Krüger, C.C.H. Elaboration of yogurt with reduced level of lactose added of carob (*Ceratonia siliqua* L.). *LWT* **2017**, *76*, 326–329. [CrossRef]
50. Mahtout, R.; Zaidi, F.; Ould Saadi, L.; Boudjou, S.; Oomah, B.D.; Hosseinian, F. Carob (*Ceratonia siliqua* L.)(pod, pulp, seed) flours and pulp mucilage affect kefir quality and antioxidant capacity during storage. *Int. J. Eng. Technol.* **2016**, *2*, 168–180.
51. Rababah, T.M.; Al-u'datt, M.; Ereifej, K.; Almajwal, A.; Al-Mahasneh, M.; Brewer, S.; Alsheyab, F.; Yang, W. Chemical, functional and sensory properties of carob juice: Properties of carob juice. *J. Food Qual.* **2013**, *36*, 238–244. [CrossRef]

52. Elfazazi, K.; Harrak, H.; Achchoub, M.; Benbati, M. Physicochemical criteria, bioactive compounds and sensory quality of Moroccan traditional carob drink. *Mater. Today Proc.* **2020**, *27*, 3249–3253. [CrossRef]
53. Polanowska, K.; Varghese, R.; Kuligowski, M.; Majcher, M. Carob kibbles as an alternative raw material for production of kvass with probiotic potential. *J. Sci. Food Agric.* **2021**, 1–11. [CrossRef]
54. Hanousek Čiča, K.; Mrvčić, J.; Srečec, S.; Filipan, K.; Blažić, M.; Stanzer, D. Physicochemical and aromatic characterization of carob macerates produced by different maceration conditions. *Food Sci. Nutr.* **2020**, *8*, 942–954. [CrossRef]
55. Rodríguez-Solana, R.; Coelho, N.; Santos-Rufo, A.; Gonçalves, S.; Pérez-Santín, E.; Romano, A. The influence of in vitro gastrointestinal digestion on the chemical composition and antioxidant and enzyme inhibitory capacities of carob liqueurs obtained with different elaboration techniques. *Antioxidants* **2019**, *8*, 563. [CrossRef] [PubMed]
56. Rodríguez-Solana, R.; Carlier, J.D.; Costa, M.C.; Romano, A. Multi-element characterisation of carob, fig and almond liqueurs by MP-AES. *J. Inst. Brew.* **2018**, *124*, 300–309. [CrossRef]
57. Hussein, A.; Shedeed, N.; Abdel-Kalek, H.; El-Din, M.H.A. Antioxidative, antibacterial and antifungal activities of tea infusions from berry leaves, carob and doum. *Pol. J. Food Nutr. Sci.* **2011**, *61*, 201–209. [CrossRef]
58. Wolever, T. Carbohydrates and health—The FAO/WHO consultation. *Aust. J. Nutr. Diet.* **2001**, *58*, S3–S8.
59. Cho, S.S.; Prosky, L. Complex carbohydrates: Definition and analysis. In *Complex Carbohydrates in Foods*; Cho, S.S., Prosky, L., Dreher, M., Eds.; Marcel Dekker: New York, NY, USA, 1999; pp. 121–133, ISBN 0-8247-0187-9.
60. O'Sullivan, M. Nutritional optimization- reduced-sugar products and challenges. In *Salt, Fat and Sugar Reduction: Sensory Approaches for Nutritional Reformulation of Foods and Beverages*, 1st ed.; Woodhead Publishing: Cambridge, UK, 2020; pp. 29–61, ISBN 978-0-12-819741-7.
61. Bonewit-West, K.; Hunt, S. *Today's Medical Assistant-E-Book: Clinical & Administrative Procedures*, 4th ed.; Elsevier Health Sciences: Maryland Heights, MO, USA, 2019; ISBN 978-0-323-31127-4.
62. Van der Meulen-Muisers, J.J.; van Oeveren, J.C.; van der Plas, L.H.; van Tuyl, J.M. Postharvest flower development in asiatic hybrid lilies as related to tepal carbohydrate status. *Postharvest Biol. Technol.* **2001**, *21*, 201–211. [CrossRef]
63. Lunn, J.; Buttriss, J.L. Carbohydrates and dietary fibre. *Nutr. Bull.* **2007**, *32*, 21–64. [CrossRef]
64. Petitot, M.; Barron, C.; Morel, M.-H.; Micard, V. Impact of legume flour addition on pasta structure: Consequences on its in vitro starch digestibility. *Food Biophys.* **2010**, *5*, 284–299. [CrossRef]
65. Rodríguez De Marco, E.; Steffolani, M.E.; Martínez, C.S.; León, A.E. Effects of spirulina biomass on the technological and nutritional quality of bread wheat pasta. *LWT* **2014**, *58*, 102–108. [CrossRef]
66. Giuberti, G.; Gallo, A.; Cerioli, C.; Fortunati, P.; Masoero, F. Cooking quality and starch digestibility of gluten free pasta using new bean flour. *Food Chem.* **2015**, *175*, 43–49. [CrossRef]
67. Feil, R.; Lunn, J.E. Quantification of soluble sugars and sugar alcohols by LC-MS/MS. In *Plant Metabolomics. Methods in Molecular Biology*; António, C., Ed.; Human Press: New York, NY, USA, 2018; Volume 1778, pp. 87–100, ISBN 978-1-4939-7818-2.
68. Dietary Guidelines Advisory Committee. *Scientific Report of the 2015 Dietary Guidelines Advisory Committee: Advisory Report to the Secretary of Health and Human Services and Secretary of Agriculture*; U.S. Department of Agriculture, Agricultural Research Service: Washington, DC, USA, 2015.
69. Naknean, P.; Maneyam, R.; Kam-onsri, A. Effect of different osmotic agents on the physical, chemical and sensory properties of osmo-dried cantaloupe. *Chiang Mai J. Sci.* **2013**, *40*, 427–439.
70. Joslyn, M. Carbohydrates: Reducing Sugars. In *Methods in Food Analysis: Applied to Plant Products*; Academic Press: New York, NY, USA, 1950; pp. 405–436.
71. Mottram, D.S. Flavor Compounds Formed during the Maillard Reaction. In *Thermally Generated Flavors. Maillard, Microwave, and Extrusion Processes*; ACS Symposium Series; American Chemical Society: Washington, DC, USA, 1993; Volume 543, p. 104, ISBN 978-0-8412-2742-2.
72. Abbès, F.; Bouaziz, M.A.; Blecker, C.; Masmoudi, M.; Attia, H.; Besbes, S. Date syrup: Effect of hydrolytic enzymes (pectinase/cellulase) on physico-chemical characteristics, sensory and functional properties. *LWT* **2011**, *44*, 1827–1834. [CrossRef]
73. Mougios, V. *Exercise Biochemistry*, 2nd ed.; Human Kinetics Publishers: Champaign, IL, USA, 2006; pp. 95–100, ISBN 9781492572695.
74. National Research Council (NRC). *Nutrient Requirements of Swine*, 11th ed.; National Academy Press: Washington, DC, USA, 2012.
75. Tosh, S.M.; Yada, S. Dietary fibres in pulse seeds and fractions: Characterization, functional attributes, and applications. *Food Res. Int.* **2010**, *43*, 450–460. [CrossRef]
76. Lajolo, F.M.; Genovese, M.I.; Pryme, I.F.; Dale, T.M. Beneficial (antiproliferative) effects of different substances. In *Recent Advances of Research in Antinutritional Factors in Legume Seeds and Oilseeds, Proceedings of the Fourth International Workshop on Antinutritional Factors in Legume Seeds and Oilseeds, Toledo, Spain, 8–10 March 2004*; Muzquiz, M., Hill, G.D., Pedrosa, M.M., Burbano, C., Eds.; EAAP Publication: Toledo, Spain, 2004; pp. 123–137, ISBN 978-90-76998-39-8.
77. Jambi, H.A. Effect of roasting at 180°C for 30 min on the sugars content of carob powder. *Life Sci. J.* **2015**, *12*, 21–24.
78. Benkeblia, N. Fructooligosaccharides and fructans analysis in plants and food crops. *J. Chromatogr. A* **2013**, *1313*, 54–61. [CrossRef] [PubMed]
79. Arruda, H.S.; Pereira, G.A.; Almeida, M.E.F.; Neri-Numa, I.A.; Sancho, R.A.S.; Molina, G.; Pastore, G.M. Current knowledge and future perspectives of oligosaccharides research. In *Frontiers in Natural Product Chemistry*; Bentham Science Publishers: Dubai, UAE, 2017; Volume 3, pp. 91–175, ISBN 978-1-68108-535-7.

80. Bettelheim, F.A.; Brown, W.H.; Campbell, M.K.; Farrell, S.O.; Torres, O.J. Carbohydrates. In *Introduction to General, Organic, and Biochemistry*, 11th ed.; Kiselica, S., Woods, E., Mastroianni, K., Weber, L., VanCamp, S., Eds.; Cengage Learning: Boston, MA, USA, 2016; pp. 529–559, ISBN 1-133-10508-4.
81. Praznik, W.; Loeppert, R.; Viernstein, H.; Haslberger, A.G.; Unger, F.M. Dietary fiber and prebiotics. In *Polysaccharides: Bioactivity and Biotechnology*; Ramawat, K.G., Merillon, J.M., Eds.; Springer International Publishing: Cham, Switzerland, 2015; pp. 1–30.
82. Singh, S.; Gamlath, S.; Wakeling, L. Nutritional aspects of food extrusion: A review. *Int. J. Food Sci. Technol.* **2007**, *42*, 916–929. [CrossRef]
83. Mann, J.; Cummings, J.H.; Englyst, H.N.; Key, T.; Liu, S.; Riccardi, G.; Summerbell, C.; Uauy, R.; van Dam, R.M.; Venn, B.; et al. FAO/WHO Scientific update on carbohydrates in human nutrition: Conclusions. *Eur. J. Clin. Nutr.* **2007**, *61*, S132–S137. [CrossRef] [PubMed]
84. Zunft, H.J.F.; Lüder, W.; Harde, A.; Haber, B.; Graubaum, H.J.; Koebnick, C.; Grünwald, J. Carob pulp preparation rich in insoluble fibre lowers total and LDL cholesterol in hypercholesterolemic patients. *Eur. J. Nutr.* **2003**, *42*, 235–242. [CrossRef] [PubMed]
85. EFSA (European Food Safety Authority). Dietary Reference Values and Dietary Guidelines. Available online: https://www.efsa.europa.eu/en/topics/topic/dietary-reference-values-and-dietary-guidelines (accessed on 15 November 2020).
86. Regulation (EC) No. 1924/2006 of the European Parliament and of the Council of 20 December 2006 on Nutrition and Health Claims Made on Foods. 2006. Available online: http://eur-lex.europa.eu/LexUriServ/site/en/oj/2007/l_012/l_01220070118en00030018.pdf (accessed on 10 December 2020).
87. Tsatsaragkou, K.; Yiannopoulos, S.; Kontogiorgi, A.; Poulli, E.; Krokida, M.; Mandala, I. Mathematical approach of structural and textural properties of gluten free bread enriched with carob flour. *J. Cereal Sci.* **2012**, *56*, 603–609. [CrossRef]
88. Martín-Cabrejas, M.A.; Jaime, L.; Karanja, C.; Downie, A.J.; Parker, M.L.; Lopez-Andreu, F.J.; Maina, G.; Esteban, R.M.; Smith, A.C.; Waldron, K.W. Modifications to physicochemical and nutritional properties of hard-to-cook beans (*Phaseolus Vulgaris* L.) by extrusion cooking. *J. Agric. Food Chem.* **1999**, *47*, 1174–1182. [CrossRef] [PubMed]
89. Camire, M.E. Extrusion cooking. In *The Nutrition Handbook for Food Processors*; Henry, C.J.K., Chapman, C., Eds.; CRC Press: Boca Raton, FL, USA, 2002; pp. 314–330.
90. de Almeida Costa, G.E.; da Silva Queiroz-Monici, K.; Pissini Machado Reis, S.M.; de Oliveira, A.C. Chemical composition, dietary fibre and resistant starch contents of raw and cooked pea, common bean, chickpea and lentil legumes. *Food Chem.* **2006**, *94*, 327–330. [CrossRef]
91. Pedrosa, M.M.; Cuadrado, C.; Burbano, C.; Muzquiz, M.; Cabellos, B.; Olmedilla-Alonso, B.; Asensio-Vegas, C. Effects of industrial canning on the proximate composition, bioactive compounds contents and nutritional profile of two Spanish common dry beans (*Phaseolus vulgaris* L.). *Food Chem.* **2015**, *166*, 68–75. [CrossRef]
92. McGuire, S.; U.S. Department of Agriculture; U.S. Department of Health and Human Services. *Dietary Guidelines for Americans*, 7th ed.; Goverment Printing Office: Washington, DC, USA, 2011.
93. Milek dos Santos, L.; Tomzack Tulio, L.; Fuganti Campos, L.; Ramos Dorneles, M.; Carneiro Hecke Krüger, C. Glycemic response to carob (*Ceratonia siliqua* L.) in healthy subjects and with the in vitro hydrolysis index. *Nutr. Hosp.* **2015**, *31*, 482–487.
94. Stephenson, A.L.; Dennis, J.S.; Howe, C.J.; Scott, S.A.; Smith, A.G. Influence of nitrogen-limitation regime on the production by *Chlorella vulgaris* of lipids for biodiesel feedstocks. *Biofuels* **2010**, *1*, 47–58. [CrossRef]
95. De Lorgeril, M.; Salen, P. New insights into the health effects of dietary saturated and omega-6 and omega-3 polyunsaturated fatty acids. *BMC Med.* **2012**, *10*, 50. [CrossRef]
96. Britton, K.A.; Massaro, J.M.; Murabito, J.M.; Kreger, B.E.; Hoffmann, U.; Fox, C.S. Body fat distribution, incident cardiovascular disease, cancer, and all-cause mortality. *J. Am. Coll. Cardiol.* **2013**, *62*, 921–925. [CrossRef]
97. Rosqvist, F.; Iggman, D.; Kullberg, J.; Cedernaes, J.; Johansson, H.E.; Larsson, A.; Johansson, L.; Ahlström, H.; Arner, P.; Dahlman, I.; et al. Overfeeding polyunsaturated and saturated fat causes distinct effects on liver and visceral fat accumulation in humans. *Diabetes* **2014**, *63*, 2356–2368. [CrossRef]
98. FAO. *Fats and Fatty Acids in Human Nutrition. Report of an Expert Consultation*; 10–14 November 2008, Geneva; Food and Agriculture Organization of the United Nations: Rome, Italy, 2010; ISBN 978-92-5-106733-8.
99. Medeiros, M.L.; da S. Lannes, S.C. Avaliação química de substitutos de cacau e estudo sensorial de achocolatados formulados. *Ciênc. Tecnol. Aliment.* **2009**, *29*, 247–253. [CrossRef]
100. Gögüs, F.; Maskan, M. Drying of olive pomace by a combined microwave-fan assited convection pven. *Food Nahr.* **2001**, *45*, 129–132. [CrossRef]
101. De Pilli, T.; Derossi, A.; Talja, R.A.; Jouppila, K.; Severini, C. Study of starch-lipid complexes in model system and real food produced using extrusion-cooking technology. *Innov. Food Sci. Emerg. Technol.* **2011**, *12*, 610–616. [CrossRef]
102. Mahtout, R.; Ortiz-Martínez, V.; Salar-García, M.; Gracia, I.; Hernández-Fernández, F.; Pérez de los Ríos, A.; Zaidia, F.; Sanchez-Segado, S.; Lozano-Blanco, L. Algerian carob tree products: A comprehensive valorization analysis and future prospects. *Sustainability* **2018**, *10*, 90. [CrossRef]
103. Sengül, M.; Fatih Ertugay, M.; Sengül, M.; Yüksel, Y. Rheological characteristics of carob pekmez. *Int. J. Food Prop.* **2007**, *10*, 39–46. [CrossRef]
104. Matos Segura, M.E.; Rosell, C.M. Chemical composition and starch digestibility of different gluten-free breads. *Plant Foods Hum. Nutr.* **2011**, *66*, 224–230. [CrossRef] [PubMed]

105. World Health Organization (WHO). *Diet, Nutrition and the Prevention of Chronic Diseases Report of the Joint WHO/FAO Expert Consultation*; WHO Technical Report Series; World Health Organization (WHO): Geneva, Switzerland, 2003. Available online: http://apps.who.int/iris/bitstream/handle/10665/42665/WHO_TRS_916.pdf;jsessionid=8891602BEADAA580C14581DBBA8EEAC6?sequence=1 (accessed on 30 December 2020).
106. Świeca, M.; Sęczyk, Ł.; Gawlik-Dziki, U.; Dziki, D. Bread enriched with quinoa leaves—The influence of protein–phenolics interactions on the nutritional and antioxidant quality. *Food Chem.* **2014**, *162*, 54–62. [CrossRef] [PubMed]
107. Świeca, M.; Gawlik-Dziki, U.; Dziki, D.; Baraniak, B.; Czyż, J. The influence of protein–flavonoid interactions on protein digestibility in vitro and the antioxidant quality of breads enriched with onion skin. *Food Chem.* **2013**, *141*, 451–458. [CrossRef]
108. Patil, S.; Brennan, M.; Mason, S.; Brennan, C. The effects of fortification of legumes and extrusion on the protein digestibility of wheat based snack. *Foods* **2016**, *5*, 26. [CrossRef] [PubMed]
109. Driskell, J.A.; Wolinsky, I. *Sports Nutrition: Energy Metabolism and Exercise*; CRC Press: Boca Raton, FL, USA, 2007; pp. 84–85, ISBN 978-0-8493-7950-5.
110. Folorunso, A.A.; Ayetigbo, G.F.; Afolabi, W.A.O. Evaluation of nutritional and sensory quality of complementary food from selected spices, soy and maize blends. *Eur. J. Nutr. Food Saf.* **2018**, *8*, 291–299. [CrossRef]
111. Soetan, K.O.; Olaiya, C.O.; Oyewole, O.E. The importance of mineral elements for humans, domestic animals and plants: A review. *Afr. J. Food Sci.* **2010**, *45*, 200–222.
112. Rodríguez-Solana, R.; Salgado, J.M.; Domínguez, J.M.; Cortés, S. Assessment of minerals in aged grape marc distillates by FAAS/FAES and ICP-MS. Characterization and safety evaluation. *Food Control* **2014**, *35*, 49–55. [CrossRef]
113. Oziyci, H.R.; Tetik, N.; Turhan, I.; Yatmaz, E.; Ucgun, K.; Akgul, H.; Gubbuk, H.; Karhan, M. Mineral composition of pods and seeds of wild and grafted carob (*Ceratonia siliqua* L.) fruits. *Sci. Hortic.* **2014**, *167*, 149–152. [CrossRef]
114. Regulation (EU) No 1169/2011 of the European Parliament and the Council, of 25 October 2011 on the provision of food information to consumers, amending regulations (EC) No 1924/2006 and (EC) No 1925/2006 of the European Parliament and of the Council, and repealing Commission Directive 87/250/EEC, Council Directive 90/496/EEC, Commission Directive 1999/10/EC, Directive 2000/13/EC of the European Parliament and of the Council, Commission Directives 2002/67/EC and 2008/5/EC and Commission Regulation (EC) N0 608/2004. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R1169&from=EN (accessed on 20 November 2020).
115. The Ministry of Health of Turkey and the General Directorate of Primary Health Care. *Dietary Guidelines for Turkey. Recommended Safe Level of Intake of Energy and Nutrients for Turkey*, 4th ed.; General Directorate of Primary Healthcare Press: Ankara, Turkey, 2006.
116. Turkish Food Codex. Communiqué on Rules for General Labelling and Nutritional Labelling of Foodstuffs 2002/58. Available online: http://www.kkgm.gov.tr/TFC/2002-58.html#26057 (accessed on 15 September 2020).
117. Anonymous. Dietary Reference Intakes Reports National Academy of Sciences. Institute of Medicine. Food and Nutrition Board. 2012. Available online: http://fnic.nal.usda.gov/dietary-guidance/dietary-referenceintakes/dri-tables (accessed on 23 October 2020).
118. De la Fuente, M.A.; Montes, F.; Guerrero, G.; Juárez, M. Total and soluble contents of calcium, magnesium, phosphorus and zinc in yoghurts. *Food Chem.* **2003**, *80*, 573–578. [CrossRef]
119. Śliwińska, M.; Wiśniewska, P.; Dymerski, T.; Wardencki, W.; Namieśnik, J. The flavour of fruit spirits and fruit liqueurs: A review: The flavour of fruit spirits and fruit liqueurs. *Flavour Fragr. J.* **2015**, *30*, 197–207. [CrossRef]
120. Harju, K.; Ronkainen, P. Metals in finnish liqueurs. *Z. Lebensm Unters Forch* **1984**, *178*, 393–396. [CrossRef] [PubMed]
121. Dempsey, D.T.; Mullen, J.L.; Rombeau, J.L.; Crosby, L.O.; Oberlander, J.L.; KNox, L.S.; Melnik, G. Treatment effects of parenteral vitamins in total parenteral nutrition patients. *J. Parenter. Enteral Nutr.* **1987**, *11*, 229–237. [CrossRef]
122. Djilali, B.; Ahmed, H.; Yerou Karima, O.; Zouaoui, B.; Fatima, S.; Hadjari, M. Kinetic of batch production of lactic acid from carob pods syrup. *Bull. Pharm. Res.* **2017**, *7*, 1–6.
123. Arribas, C.; Pereira, E.; Barros, L.; Alves, M.J.; Calhelha, R.C.; Guillamón, E.; Pedrosa, M.M.; Ferreira, I.C.F.R. Healthy novel gluten-free formulations based on beans, carob fruit and rice: Extrusion effect on organic acids, tocopherols, phenolic compounds and bioactivity. *Food Chem.* **2019**, *292*, 304–313. [CrossRef] [PubMed]
124. Thakur, M.; Singh, K.; Khedkar, R. Phytochemicals: Extraction process, safety assessment, toxicological evaluations and regulatory issues. In *Functional and Preservative Properties of Phytochemicals*; Prakash., B., Ed.; Academic Press: Cambridge, MA, USA, 2020; pp. 341–356, ISBN 978-0-12-818593-3.
125. Babando Aliyu, A.; Ilemona Achika, J.; Adesina Adewuyi, J.; Gangas, P.; Ibrahim, H.; Ojo Oyewale, A. Antioxidants from Nigerian medicinal plants: What are the evidence. In *Lipid Peroxidation Research*; Ahmed Mansour, M., Ed.; IntechOpen: Rijeka, Croatia, 2020; pp. 43–64, ISBN 978-1-83968-547-7.
126. Goñi, I.; Hernández-Galiot, A. Intake of nutrient and non-nutrient dietary antioxidants. Contribution of macromolecular antioxidant polyphenols in an elderly Mediterranean population. *Nutrients* **2019**, *11*, 2165. [CrossRef]
127. Assadpour, E.; Jafari, S.M. Advances in spray-drying encapsulation of food bioactive ingredients: From microcapsules to nanocapsules. *Annu. Rev. Food Sci. Technol.* **2019**, *10*, 103–131. [CrossRef]
128. Dreosti, I.E. Bioactive ingredients: Antioxidants and polyphenols in tea. *Nutr. Rev.* **1996**, *54*, S51–S58. [CrossRef] [PubMed]
129. Nooshkam, M.; Varidi, M. Maillard conjugate-based delivery systems for the encapsulation, protection, and controlled release of nutraceuticals and food bioactive ingredients: A review. *Food Hydrocoll.* **2020**, *100*, 105389. [CrossRef]

130. San Miguel-Chávez, R. Phenolic antioxidant capacity: A review of the state of the art. In *Phenolic Compounds—Biological Activity*; Soto-Hernndez, M., Palma-Tenango, M., Garcia-Mateos, M.d.R., Eds.; InTech: Rijeka, Croatia, 2017; pp. 59–74, ISBN 978-953-51-2959-2.
131. Balasundram, N.; Sundram, K.; Samman, S. Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses. *Food Chem.* **2006**, *99*, 191–203. [CrossRef]
132. Lawal, U.; Leong, S.W.; Shaari, K.; Ismail, I.S.; Khatib, A.; Abas, F. α-Glucosidase inhibitory and antioxidant activities of different *Ipomoea aquatica* cultivars and LC-MS/MS profiling of the active cultivar: α-glucosidase inhibitory activity of *Ipomoea aquatica* cultivars. *J. Food Biochem.* **2017**, *41*, e12303. [CrossRef]
133. Everette, J.D.; Bryant, Q.M.; Green, A.M.; Abbey, Y.A.; Wangila, G.W.; Walker, R.B. Thorough study of reactivity of various compound classes toward the Folin−Ciocalteu reagent. *J. Agric. Food Chem.* **2010**, *58*, 8139–8144. [CrossRef]
134. Nasar-Abbas, S.M.; e-Huma, Z.; Vu, T.-H.; Khan, M.K.; Esbenshade, H.; Jayasena, V. Carob kibble: A bioactive-rich food ingredient. *Compr. Rev. Food Sci. Food Saf.* **2016**, *15*, 63–72. [CrossRef]
135. Minatel, I.O.; Borges, C.V.; Ferreira, M.I.; Gomez, H.A.G.; Chen, C.Y.O.; Lima, G.P.P. Phenolic compounds: Functional properties, impact of processing and bioavailability. In *Phenolic Compounds—Biological Activity*; Soto-Hernndez, M., Palma-Tenango, M., Garcia-Mateos, M.d.R., Eds.; InTech: Rijeka, Croatia, 2017; pp. 1–24, ISBN 978-953-51-2959-2.
136. Fares, C.; Platani, C.; Baiano, A.; Menga, V. Effect of processing and cooking on phenolic acid profile and antioxidant capacity of durum wheat pasta enriched with debranning fractions of wheat. *Food Chem.* **2010**, *119*, 1023–1029. [CrossRef]
137. Khan, I.; Yousif, A.; Johnson, S.K.; Gamlath, S. Effect of sorghum flour addition on resistant starch content, phenolic profile and antioxidant capacity of durum wheat pasta. *Food Res. Int.* **2013**, *54*, 578–586. [CrossRef]
138. Prabhasankar, P.; Ganesan, P.; Bhaskar, N.; Hirose, A.; Stephen, N.; Gowda, L.R.; Hosokawa, M.; Miyashita, K. Edible Japanese seaweed, wakame (*Undaria Pinnatifida*) as an ingredient in pasta: Chemical, functional and structural evaluation. *Food Chem.* **2009**, *115*, 501–508. [CrossRef]
139. Gawlik-Dziki, U. Changes in the antioxidant activities of vegetables as a consequence of interactions between active compounds. *J. Funct. Foods* **2012**, *4*, 872–882. [CrossRef]
140. Sęczyk, L.; Świeca, M.; Gawlik-Dziki, U. Changes of antioxidant potential of pasta fortified with Parsley (*Petroselinum crispum* Mill.) leaves in the light of protein-phenolics interactions. *Acta Sci. Pol. Technol. Aliment.* **2015**, *14*, 29–36. [CrossRef]
141. Şahin, H.; Topuz, A.; Pischetsrieder, M.; Özdemir, F. Effect of roasting process on phenolic, antioxidant and browning properties of carob powder. *Eur. Food Res. Technol.* **2009**, *230*, 155–161. [CrossRef]
142. Shehata, E.M.M.; Elnaggar, Y.S.R.; Galal, S.; Abdallah, O.Y. Self-emulsifying phospholipid pre-concentrates (SEPPs) for improved oral delivery of the anti-cancer genistein: Development, appraisal and ex-vivo intestinal permeation. *Int. J. Pharm.* **2016**, *511*, 745–756. [CrossRef]
143. Mandalari, G.; Bisignano, C.; Filocamo, A.; Chessa, S.; Sarò, M.; Torre, G.; Faulks, R.M.; Dugo, P. Bioaccessibility of pistachio polyphenols, xanthophylls, and tocopherols during simulated human digestion. *Nutrition* **2013**, *29*, 338–344. [CrossRef] [PubMed]
144. Ydjedd, S.; Bouriche, S.; López-Nicolás, R.; Sánchez-Moya, T.; Frontela-Saseta, C.; Ros-Berruezo, G.; Rezgui, F.; Louaileche, H.; Kati, D.-E. Effect of in vitro gastrointestinal digestion on encapsulated and nonencapsulated phenolic compounds of carob (*Ceratonia siliqua* L.) pulp extracts and their antioxidant capacity. *J. Agric. Food Chem.* **2017**, *65*, 827–835. [CrossRef] [PubMed]
145. Ortega, N.; Macià, A.; Romero, M.-P.; Reguant, J.; Motilva, M.-J. Matrix Composition effect on the digestibility of carob flour phenols by an in-vitro digestion model. *Food Chem.* **2011**, *124*, 65–71. [CrossRef]
146. Neilson, A.P.; Hopf, A.S.; Cooper, B.R.; Pereira, M.A.; Bomser, J.A.; Ferruzzi, M.G. Catechin degradation with concurrent formation of homo- and heterocatechin dimers during in vitro digestion. *J. Agric. Food Chem.* **2007**, *55*, 8941–8949. [CrossRef]
147. Hyun, T.K.; Ra, J.H.; Han, S.H.; Kim, J.S. Antioxidant, antimicrobial, and antidiabetic activities of crowberry fruits. *Indian J. Pharm. Sci.* **2018**, *80*, 489–495. [CrossRef]
148. Amarowicz, R.; Barl, B.; Pegg, R.B. Potential natural antioxidant from Saskatchewan indigenous plants. *J. Food Lipids* **1999**, *6*, 317–329. [CrossRef]
149. Gülçin, İ. Antioxidant activity of food constituents: An overview. *Arch. Toxicol.* **2012**, *86*, 345–391. [CrossRef] [PubMed]
150. Abbès, F.; Kchaou, W.; Blecker, C.; Ongena, M.; Lognay, G.; Attia, H.; Besbes, S. Effect of processing conditions on phenolic compounds and antioxidant properties of date syrup. *Ind. Crops Prod.* **2013**, *44*, 634–642. [CrossRef]
151. Wang, B.S.; Chang, L.W.; Kang, Z.C.; Chu, H.L.; Tai, H.M.; Huang, M.H. Inhibitory effects of molasses on mutation and nitric oxide production. *Food Chem.* **2011**, *126*, 1102–1107. [CrossRef]
152. Oomah, B.D.; Cardador-Martínez, A.; Loarca-Piña, G. Phenolics and antioxidative activities in common beans (*Phaseolus vulgaris* L.): Phenolics and antioxidative activities in common beans. *J. Sci. Food Agric.* **2005**, *85*, 935–942. [CrossRef]
153. Anton, A.A.; Gary Fulcher, R.; Arntfield, S.D. Physical and nutritional impact of fortification of corn starch-based extruded snacks with common bean (*Phaseolus vulgaris* L.) flour: Effects of bean addition and extrusion cooking. *Food Chem.* **2009**, *113*, 989–996. [CrossRef]
154. Delgado-Licon, E.; Ayala, A.L.M.; Rocha-Guzman, N.E.; Gallegos-Infante, J.A.; Atienzo-Lazos, M.; Drzewiecki, J.; Martínez-Sánchez, C.E.; Gorinstein, S. Influence of extrusion on the bioactive compounds and the antioxidant capacity of the bean/corn mixtures. *Int. J. Food Sci. Nutr.* **2009**, *60*, 522–532. [CrossRef]
155. Zhang, H.; Tsao, R. Dietary polyphenols, oxidative stress and antioxidant and anti-inflammatory effects. *Curr. Opin. Food Sci.* **2016**, *8*, 33–42. [CrossRef]

156. Bermudez-Soto, M.; Tomás-Barberan, F.; Garcia-Conesa, M. Stability of polyphenols in chokeberry (*Aronia melanocarpa*) subjected to in vitro gastric and pancreatic digestion. *Food Chem.* **2007**, *102*, 865–874. [CrossRef]
157. Jakobek, L. Interactions of polyphenols with carbohydrates, lipids and proteins. *Food Chem.* **2015**, *175*, 556–567. [CrossRef]
158. Lee, Y.J.; Kim, D.B.; Lee, J.; Cho, J.H.; Kim, B.; Choi, H.S.; Lee, B.Y.; Lee, O.H. Antioxidant activity and anti-adipogenic effects of wild herbs mainly cultivated in Korea. *Molecules* **2013**, *18*, 12937–12950. [CrossRef]
159. Cao, G.; Sofic, E.; Prior, R.L. Antioxidant and prooxidant behavior of flavonoids: Structure-activity relationships. *Free Radic. Biol. Med.* **1997**, *22*, 749–760. [CrossRef]
160. Halpin-Dohnalek, M.I.; Marth, E.H. *Staphylococcus aureus*: Production of extracellular compounds and behavior in foods—A review. *J. Food Prot.* **1989**, *52*, 267–282. [CrossRef] [PubMed]
161. Rufián-Henares, J.A.; Morales, F.J. Functional properties of melanoidins: In vitro antioxidant, antimicrobial and antihypertensive activities. *Food Res. Int.* **2007**, *40*, 995–1002. [CrossRef]
162. Dhaouadi, K.; Belkhir, M.; Akinocho, I.; Raboudi, F.; Pamies, D.; Barrajón, E.; Estevan, C.; Fattouch, S. Sucrose supplementation during traditional carob syrup processing affected its chemical characteristics and biological activities. *LWT* **2014**, *57*, 1–8. [CrossRef]
163. Fernández, M.A.; García, M.D.; Sáenz, M.T. Antibacterial activity of the phenolic acids fractions of *Scrophularia frutescens* and *Scrophularia sambucifolia*. *J. Ethnopharmacol.* **1996**, *53*, 11–14. [CrossRef]
164. Ríos, J.L.; Recio, M.C. Medicinal plants and antimicrobial activity. *J. Ethnopharmacol.* **2005**, *100*, 80–84. [CrossRef] [PubMed]
165. Huertas, R.A.P. Bacterias ácido lácticas: Papel funcional en los alimentos. *Biotecnol. Sect. Agropecu. Agroind.* **2010**, *8*, 93–105.
166. Guler-Akin, M.B.; Goncu, B.; Serdar Akin, M. Some properties of probiotic yoghurt ice cream supplemented with carob extract and whey powder. *Adv. Microbiol.* **2016**, *6*, 1010–1020. [CrossRef]
167. Cauvain, S.P.; Clark, R.H. *Baking Technology and Nutrition: Towards a Healthier World*; John Wiley & Sons Ltd.: Oxford, UK, 2019.
168. United States Tariff Commission. *Summaries of Tariff Information. Chemicals, Oils and Paints. Part 1. Non-Coal-Tar Acids, Alcohols, Resins, and Medicinals and Miscellaneous Chemicals*; U.S. Government Printing Office: Washington, DC, USA, 1948; Volume 1, p. 193.
169. Ahuja, J.K.C.; Betty, P.P. Caffeine and theobromine intakes of children: Results from CSFII 1994-96, 1998. *Fam. Econ. Nutr. Rev.* **2001**, *13*, 47–52.
170. Butt, M.S.; Sultan, M.T. Coffee and its consumption: Benefits and risks. *Crit. Rev. Food Sci. Nutr.* **2011**, *51*, 363–373. [CrossRef]
171. Khlifa, M.; Bahloul, A.; Kitane, S. Determination of chemical composition of carob pod (*Ceratonia siliqua* L.) and its morphological study. *J. Mater. Environ. Sci.* **2013**, *4*, 348–353.
172. Tontul, I.; Topuz, A. Effects of different drying methods on the physicochemical properties of pomegranate leather (pestil). *LWT* **2017**, *80*, 294–303. [CrossRef]
173. Anese, M.; Suman, M. Mitigation strategies of furan and 5-hydroxymethylfurfural in food. *Food Res. Int.* **2013**, *51*, 257–264. [CrossRef]
174. Ames, J.M. The maillard reaction. In *Biochemistry of Food Proteins*; Springer: Boston, MA, USA, 1992; pp. 99–153.
175. Kroh, L.W. Caramelisation in food and beverages. *Food Chem.* **1994**, *51*, 373–379. [CrossRef]
176. Nagy, S.; Lee, H.; Rouseff, R.L.; Lin, J.C.C. Nonenzymic browning of commercially canned and bottled grapefruit juice. *J. Agric. Food Chem.* **1990**, *38*, 343–346. [CrossRef]
177. Capuano, E.; Fogliano, V. Acrylamide and 5-hydroxymethylfurfural (HMF): A review on metabolism, toxicity, occurrence in food and mitigation strategies. *LWT* **2011**, *44*, 793–810. [CrossRef]
178. Oral, R.A.; Dogan, M.; Sarioglu, K.; Toker, Ö.S. 5-Hydroxymethyl furfural formation and reaction kinetics of different pekmez samples: Effect of temperature and storage. *Int. J. Food Eng.* **2012**, *8*, 4. [CrossRef]
179. Gökmen, V.; Açar, Ö.Ç.; Serpen, A.; Morales, F.J. Effect of leavening agents and sugars on the formation of hydroxymethylfurfural in cookies during baking. *Eur. Food Res. Technol.* **2008**, *226*, 1031–1037. [CrossRef]
180. Napolitano, A.; Morales, F.; Sacchi, R.; Fogliano, V. Relationship between virgin olive oil phenolic compounds and acrylamide formation in fried crisps. *J. Agric. Food Chem.* **2008**, *56*, 2034–2040. [CrossRef] [PubMed]
181. Capuano, E.; Ferrigno, A.; Acampa, I.; Serpen, A.; Açar, Ö.Ç.; Gökmen, V.; Fogliano, V. Effect of flour type on Maillard reaction and acrylamide formation during toasting of bread crisp model systems and mitigation strategies. *Food Res. Int.* **2009**, *42*, 1295–1302. [CrossRef]
182. Gökmen, V.; Şenyuva, H.Z. Effects of some cations on the formation of acrylamide and furfurals in glucose–asparagine model system. *Eur. Food Res. Technol.* **2007**, *225*, 815–820. [CrossRef]
183. Anonymous. *Mulberry Pekmez*; Turkish Standard Institute: Ankara, Turkey, 1996.
184. Kuster, B.F.M. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch Stärke* **1990**, *42*, 314–321. [CrossRef]
185. Hamzalıoğlu, A.; Gökmen, V. 5-Hydroxymethylfurfural accumulation plays a critical role on acrylamide formation in coffee during roasting as confirmed by multiresponse kinetic modelling. *Food Chem.* **2020**, *318*, 126467. [CrossRef] [PubMed]