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Valorization of *Cynara cardunculus* L. var. *scolymus* Processing By-Products of Typical Landrace "Carciofo Di Montelupone" from Marche Region (Italy)

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Abstract: Food waste is a growing global problem that originates from a variety of sources, with about 38% of it coming from food processing. In recent years, the European Union has encouraged investigations into by-products for their exploitation in several fields. In this study, the main processing by-products of artichoke (*Cynara cardunculus* L. var. *scolymus*), being leaves, stems, and external bracts, were analyzed. This study aims to valorize the by-product in order to promote its cultivation and help producers to create a new supply chain of this cultivar, typical of the Marche region in Italy, which is subject to the potential risk of genetic erosion. Several bioactive substances were monitored and quantified, including inulin, an important D-fructose polymer widely used for its physical–chemical and functional properties and prebiotic activity. Inulin extraction was optimized through an experimental design in terms of time and temperature. Moreover, the total content of polyphenols, flavonoids, and tannins was investigated in each artichoke by-product, revealing the stems as the richest fraction in all the monitored bioactive compounds.

Keywords: artichoke; food by-products; food waste; inulin; bioactive compounds

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1. Introduction

Globe artichoke (*Cynara cardunculus* var. *scolymus* L. Fiori) is a native plant of the Mediterranean basin; it is an herbaceous perennial plant, and it belongs to the family of Asteraceae [1]. The name derives from Latin—'Cineres', meaning ashes, because it is used as fertilizer—and from Greek—'Skolymos', meaning sharp, because of the spines in the capitula [2]. Worldwide, based on data from the Food and Agriculture Organization (FAO), global artichoke production is about 1,584,513.73 tons per year. Italy is the second largest artichoke producer, with 378,110 tons per year, after Egypt [3]. Artichoke is an important component of the Mediterranean diet, serving as a main ingredient in several traditional dishes.

The immature inflorescence, also known as the capitulum or head, is the edible portion of the plant and is shielded by fleshy leaves (bracts) [4]. The edible part has excellent nutritional quality, being a good source of minerals, such as Fe, K, and Zn; vitamins, in particular, vitamin C; soluble and non-soluble dietary fibers; and bioactive compounds. These nutritional qualities are related to a lot of health benefits, like hepatoprotective, prebiotic, anti-inflammatory, neuroprotective, and hypoglycemic effects [5,6].

During artichoke industrial canning processing, the edible part is separated from other parts and discarded. For the bottom half (receptacle), the edible component to total weight head ratio is 10–18%, and for the core (receptacle and inner bracts), it is around 40% [7]. Therefore, artichoke by-products, including its leaves, stems, and exterior bracts, constitute a significant quantity of waste. It has recently been suggested by several research works that it may be possible to recover bioactive compounds from food industry by-products [8–10].

As vegetable matrices, artichoke by-products can be investigated in terms of the bioactive compound concentrations to be reused in the food and nutraceutical sectors [11]. Among them, polyphenolic compounds, such as 1,5-dicaffeoylquinic acid (also called cynarin), chlorogenic acids, and flavonoid derivatives play key roles [7]. They have a variety of beneficial qualities, such as long-term resistance to cardiovascular illnesses, chemoprotective action, and strong antioxidant and anti-inflammatory effects. The amount of phenolic compounds in a crop depends on several factors, including the cultivar, age, post-harvest conditions, and agronomic practices.

Among the most interesting bioactive metabolites, inulin, a fructan, was found to be present in artichoke roots, stems, and head and in very low quantities in their leaves, as a sugar reserve [12–15]. It is a D-fructose polymer linked by β-(21)fructosyl–fructose bonds, usually with a glucose residue at the end of the chain. Depending on the number of monomers, it can acquire different degrees of polymerization (DP), which affects its physicochemical and functional properties, such as its solubility, glass transition temperature, and gel formation capacity [16,17]. In the food industry, inulin has various applications. Low-DP structures are used as low-calorie sweeteners, while high-DP ones as technological enhancers. Moreover, it is widely used for its prebiotic activity, being able to increase the diversity and richness of microbiota [11,18].

Interest in the application of artichoke by-products is increasing, not only in the food industry, where they are involved in food preparation and functionalization, but also in the pharmaceutical sector, as their bioactive molecules could be used for nutraceutical and food supplement formulations [19].

This study focuses on "carciofo di Montelupone", a typical artichoke landrace belonging to the "Romanesco" variety, which is cultivated in the Marche region and is experiencing a potential risk of genetic erosion [20,21]. Therefore, the promotion of its cultivation is crucial to protect biodiversity, together with helping the producers propose the application of a by-product waste-alternative supply chain. The aim of this research work is the valorization of processing by-products in terms of bioactive compounds with a focus on inulin extraction optimization. To achieve these goals, a water-based inulin extraction procedure was optimized using statistical tools, and total polyphenols, flavonoids, tannins, and radical scavenging activity were quantified in extracts from artichoke stems, leaves, and external bracts extracts.

2. Materials and Methods

2.1. Plant Materials

The globe artichokes and their by-products were provided by Cipriani Marisa farm, based in Montelupone (MC, Marche, Italy), at 270 a.s.l. In this study, organic artichokes of the "Montelupone" landrace were analyzed (Figure 1). The samples were characterized by a capitula weight of about 40–140 g, having a characteristic green color with shades of violet and non-spiny bracts. The entire plant was about 30–60 cm tall with pinnatisect leaves and a total diameter of about 120–160 cm. Fresh samples were manually harvested on 19th of April and then frozen at −20 °C until use.

2.2. Chemical and Reagents

Inulin powder from the chicory roots (*Cichorium intybus*) (90% inulin content, 90% fiber content) was purchased from ACEF (Fiorenzuola D'arda, Italy). Sodium carbonate anhydrous (≥99%, Na_2CO_3, CAS No 497-19-8), resorcinol (≥99%, C_6H_6O, CAS No 108-46-3), Folin-Ciocalteu phenol reagent (FC), 2,2-diphenyl-1-picrylhydrazil (DPPH, $C_{18}H_{12}N_5O_6$, CAS No 1898-66-4), sodium nitrite (≥99%, $NaNO_2$, CAS No 7632-00-0), aluminum chloride (≥99%, $AlCl_3$, CAS No 7446-70-0), sodium hydroxide (≥98%, NaOH, CAS No 1310-73-2), gallic acid (analytical standard, ≥97.5-102.5%, $C_7H_6O_5$, CAS No 149-91-7), rutin (≥94%, $C_{27}H_{30}O_{16}$, CAS No 153-18-4), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (≥97%, Trolox, $C_{14}H_{18}O_4$, CAS No 53188–071), tannic acid ($C_{76}H_{52}O_{46}$, CAS No 1401-55-4) were purchased from Merck (Milan, Italy). Ethanol (96%, C_2H_6O, EtOH, CAS No 64-17-5),

hydrochloric acid (37%, HCl, CAS No 7647-01-0), methanol (99.9%, CH_3OH, CAS No 67-56-1) were purchased from Carlo Erba Reagents Srl (Cornaredo, Milan, Italy).

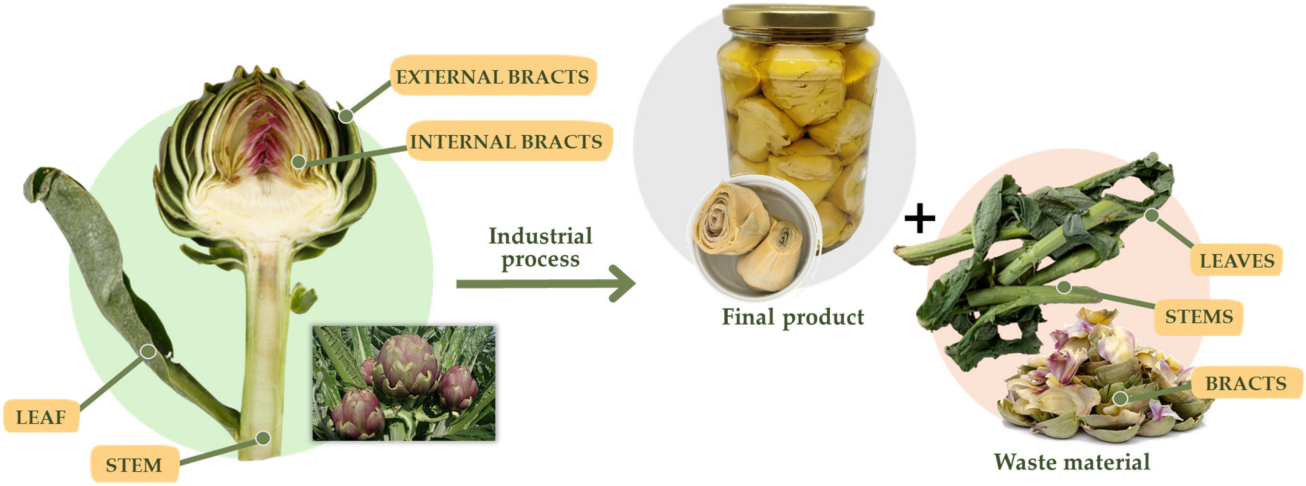

Figure 1. "Carciofo di Montelupone" landrace artichoke fractions and waste material from industrial process.

2.3. Samples Preparation

Globe artichoke and its by-product (*Cynara cardunculus* var. *scolymus*) were sliced and separated in four parts, being leaves, stem, internal bracts, and external bracts. Subsequently, each fraction was frozen in liquid nitrogen and freeze-dried until constant weight using a BUCHI Lyovapor™ L-200 freeze-dryer (Büchi Labortechnik AG, Flawil, Switzerland), then stored separately in hermetic containers until analysis.

2.4. Inulin Extraction and Optimization

To optimize the extraction conditions, several tests were performed on external bracts as they represent the main percentage of the discarded biomass in the process. This step was carried out on a single by-product according to the objective to provide an easily appliable method for the artichoke waste reuse. The optimization for each single artichoke fraction would result in four different methods, with difficulties in possible large-scale applications. A previously conducted optimization process was taken as starting point for the solvent/solid ratio, which was set at 37.4 [22]. To evaluate the temperature and the extraction time, a Design of Experiment (DoE) tool of XLSTAT software (version 2023.1.4.1408) was used in Box–Behnken design mode. The experiments were performed according to the resulting experimental design combining temperature values from 30 °C to 80 °C and extraction times from 10 to 60 min. These ranges were chosen with a view to large-scale applicability as high-temperature extraction longer than 60 min would be energy- and time-consuming. Moreover, the over 80 °C temperature increasing would involve more sophisticated and expensive instruments, since water is the solvent. The concentration of inulin was monitored in triplicate after each repetition. In particular, the inulin extraction was carried out as follows: 1 g of freeze-dried sample was mixed with 37.4 mL of distilled water in a falcon tube, which was placed in a water bath, set at each DoE temperature, under constant stirring. After the experimental time, samples were centrifuged for 10 min at 5000 rpm (IEC CL10 Centrifuge, Thermo Fisher Scientific, Waltham, MA, USA) and filtered with filter paper. Finally, the extracts were frozen and freeze-dried to obtain the dry residue.

2.5. Determination of Inulin Content

Inulin content of different parts of globe artichoke was evaluated through a spectrophotometric method, as described by Perinelli et al. (2023), with little modifications due

to the involvement of a different matrix [17]. In each DoE experiment, the derivatization step was performed using 1 mL of 1:100 water-diluted dry extract mixed with 5 mL of 1 mg/mL resorcinol ethanolic solution and 10 mL of HCl (30%, *v*/*v*); then, water was added to reach a final volume of 20 mL. Subsequently, samples were covered with aluminum foil and kept in the water bath at 80 °C for 30 min under agitation. Finally, the samples were cooled down and the absorbances were analyzed at 480 nm with a spectrophotometer (Agilent technologies, Cary 8454 UV–Vis, Woburn, MA, USA). The method was based on the colorimetric Seliwanoff test. In this reaction, D-fructose, derived from inulin hydrolysis due to the acidic pH, interacts with resorcinol and forms a colored compound. The calibration curve was prepared using inulin reference standard (Merck, Milan, Italy) and the results were expressed in mg of fructose/g of freeze-died matrix. The residual values were calculated according to the formula

$$Residual = Y - Yest \quad (1)$$

with *Y*: obtained result; and *Yest*: software-estimated results. Moreover, the standard residuals were determined as

$$std\ residual = \sqrt{\frac{\sum(Y - Yest)^2}{n - 2}} \quad (2)$$

where *n*: data points in population.

2.6. Phenolic Compound Extract Preparation

Extractions of flavonoids and phenolic compounds were carried out as described by Mustafa et al. (2021) with some modifications [23]. Briefly, 1 g of each ground freeze-dried sample was weighted in a falcon tube and a 70% EtOH solution was added up to a volume of 10 mL and vortexed (argolab mix, Argolab, Arezzo, Italy). The extraction was carried out in an ultrasound water bath (UAE, FALC, Treviglio, Italy) at 59 Khz for 30 min at 25 °C. Samples were then centrifuged at 5000 rpm for 10 min (IEC CL10 Centrifuge, Thermo Fisher Scientific, Waltham, MA, USA) and filtered with filter paper. The extracts were collected and used for spectrophotometric assays. Each artichoke fraction was extracted and analyzed in triplicate.

2.7. Spectrophotometric Assays

2.7.1. Determination of Total Phenolic Content (TPC)

The total content of polyphenols in the extracts was assessed through Folin-Ciocalteu method as described by Mustafa et al. (2021) with some variations [23]. A total of 250 µL of 1:100 diluted extract was mixed with 1.25 mL of 0.1 M Folin-Ciocalteau reagent, and then 3.5 mL of a 7.5% Na_2CO_3 solution was added. Reaction was allowed for 2 h in the dark at room temperature and then the absorbance was measured at 765 nm with a UV-Vis spectrophotometer. The absorbance of samples was compared to a gallic acid calibration curve used as the standard, and the TPC results were expressed as mg of gallic acid equivalents on extract volume (mg GAE/mL).

2.7.2. Determination of Total Flavonoid Content (TFC)

The total flavonoid content was determined through method described by Chileh-Chelh et al. (2024), with some variations [24]. A total of 0.5 mL of 1:10 diluted extract was mixed with 0.15 mL of a 0.5 M $NaNO_2$ and 3.2 mL of a 30% methanol/water solution. After 5 min, 0.15 mL of 0.3 M $AlCl_3$ solution and 1 mL of 1 M NaOH solution were added, and then the mixture was incubated for 30 min in the dark at room temperature. The absorbance was evaluated at 506 nm through the UV-Vis spectrophotometer. The results were calculated by comparing the absorbance value with a calibration curve prepared with rutin solutions and were expressed as mg of rutin equivalents (RT)/mL of extract.

2.7.3. Determination of Total Tannins Content (TTC)

The total tannin content of samples was evaluated through a method described by CI and Indira (2016), slightly modified according to the matrix [25]. A 50 µL extract was mixed with 0.25 mL of 0.1 M Folin-Ciocalteau reagent, 0.5 mL of a 35% sodium carbonate solution, then diluted with water up to 5 mL of volume. The absorbance of the solution was evaluated by spectrophotometer at 725 nm after leaving it for 30 min in the dark at room temperature. Tannic acid was used as reference to build the calibration curve, and the results were expressed as mg of tannic acid equivalents (TAE)/mL of extract.

2.7.4. Radical Scavenging Activity (DPPH)

Radical scavenging activity of samples from globe artichoke was evaluated through DPPH assay, as explained by Rejeb et al. (2020) with some variations [26]. An aliquot of 0.5 mL of each extract, previously diluted 1:100, was mixed with 4.5 mL of a 0.1 mM DPPH methanolic solution. Then, samples were placed for 30 min in the dark at room temperature. After that, DPPH reduction was evaluated using a spectrophotometer set at 517 nm. The percentage of inhibition was calculated. The calibration curve was prepared with Trolox (6-hydroxy-2,5,7,8 tetramethylchromane-2-carboxylic acid) as reference standard.

2.8. Statistical Analysis

The Design of Experiment was examined through XLSTAT software (version 2023.1.4.1408). All experimental results of inulin and spectrophotometric assays were analyzed using one-way analysis of variance (ANOVA) and are reported as triplicate average values and standard deviations. Subsequently, all variables were analyzed using principal component analysis (PCA) to allow for the visualization of their distribution within the corresponding sample group.

3. Results

3.1. Inulin Extraction Optimization Results

The inulin extraction was optimized according to the Box–Behnken design mode using external bracts, with time and temperature as variables. The solvent-to-solid ratio was 37.4 in all experiments, as previously optimized in another research work [22].

The Box–Behnken design was selected because, unlike central composite designs, it has fewer design points; thus, it is less expensive to run with the same number of factors. Moreover, this design can efficiently estimate the first- and second-order coefficients, always having three levels per factor, unlike central composite designs, which can have up to five.

Thus, Box–Behnken designs bear the main advantages of figuring out the potential interactions between parameters, and they are time-saving by reducing the number of experiments.

The surface plot in Figure 2 illustrates the results of the performed DoE experiments. The detailed experimental plan, point-by-point results, and prediction residuals are reported in Table S1.

The plot shows the inulin concentration in each extract prepared according to the different temperatures and the extraction times suggested by the software. High-temperature and long-time experiments resulted in higher inulin concentrations, so higher extraction yields. Accordingly, the best extraction conditions were found at 80 °C and 60 min with 38.98 ± 0.45 mg/g of inulin in freeze-dried (FD) matrix.

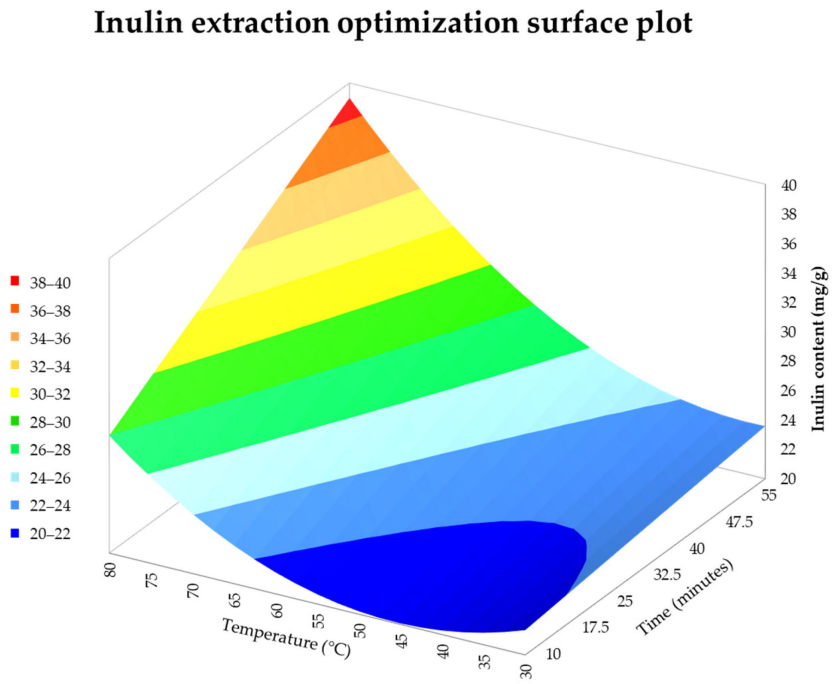

Figure 2. Surface plot resulted from the Design of Experiment to evaluate the best inulin extraction time and temperature. Inulin content is expressed in mg/g of FD matrix.

3.2. Inulin Content of Artichoke By-Products

The optimized extraction procedure was applied to each artichoke fraction, and the inulin content was then evaluated through the Seliwanoff test spectrophotometer method, as previously described. The artichoke fraction water content, calculated during the freeze-drying process, and resulting inulin content are reported in Table 1.

Table 1. Water percentage of artichoke by-product fractions and inulin concentration, expressed in mg/mL of extract. Significant differences ($p < 0.05$) between samples in inulin column are indicated by different letters.

Artichoke Fractions	Water (%)	Inulin (mg/g of FD Matrix)
Leaves	85.71 ± 5.74	4.07 ± 0.23 d
Stems	84.46 ± 3.98	40.96 ± 2.34 b
Internal bracts	83.54 ± 4.97	51.30 ± 1.17 a
External bracts	79.68 ± 4.39	38.98 ± 0.45 c

The water content emerged as similar in each artichoke fraction with external bracts presenting the lowest value (79.68 ± 4.39%), and leaves the highest one (85.71 ± 5.74%). The inulin-richer fraction emerged to be the internal bracts with 51.30 ± 1.17 mg/g of FD matrix. According to the previously described production method, this artichoke fraction cannot be considered aby-product, in fact internal bracts are kept in the final product. Among the by-products, the highest inulin content was found in stems, with values of 40.96 ± 2.34 mg/g of FD matrix, while leaves showed the lowest content with 4.07 ± 0.23 mg/g FD matrix. Statistically significant differences emerged among each analysed artichoke fraction.

3.3. Bioactive Compounds in Artichokes

The total polyphenol, flavonoid, and tannin content along with the antioxidant activity (TPC, TFC, TTC and DPPH assays) of the different artichoke fractions (leaves, stem, internal and external bracts) were evaluated as additional data for the valorization of "carciofo

di Montelupone" landrace. Extracts were obtained through an UAE procedure using EtOH/H_2O 70:30 solution as a solvent. The results of the assays are reported in Table 2.

Table 2. Spectrophotometric assays results of each artichoke fraction. Significant differences ($p < 0.05$) between samples in each column are indicated by different letters.

Artichoke Fractions	TPC (mg GAE/mL)	TFC (mg RT/mL)	TTC (mg TAE/mL)	DPPH (mg TE/mL)
Leaves	63.19 ± 11.30 b	4.22 ± 0.45 c	0.71 ± 0.001 c	8.98 ± 0.54 c
Stem	213.46 ± 9.57 a	23.37 ± 2.98 a	2.52 ± 0.03 a	21.93 ± 0.04 a
Internal bracts	73.15 ± 5.24 b	8.59 ± 0.74 b	1.29 ± 0.03 b	12.64 ± 0.89 b
External bracts	30.29 ± 8.06 c	1.02 ± 0.22 d	0.27 ± 0.03 d	6.67 ± 0.13 d

Noticeably, the highest total contents of polyphenols, flavonoids, tannins, and antioxidant activity were observed in the stem samples. In each experimental result, the highest values of stem samples were statistically significant compared to the other artichoke fractions. The external bracts showed the lowest content of total polyphenols, which is also statistically significant. No differences were reported between leaves and internal bracts with values more than three-times lower than in stems.

In the TFC assay results, the stem samples showed a statistically significant value, which is three-times higher than the internal bract one, 23.37 ± 2.98 mg RT/mL and 8.59 ± 0.74 mg RT/mL, respectively. The lowest values were reported in external bracts and leaves with values, respectively, eight-times and two-times lower than internal bracts, also with significative differences. In total tannin content results, the differences between the artichoke fractions are smaller, even with statistically significant differences among each of the analysed samples. The highest value is once again the stem sample with 2.52 ± 0.03 mg TAE/mL. External bracts showed the lowest data (0.27 ± 0.03 mg TAE/mL). The radical scavenging activity was estimated through the DPPH assay. The results followed the same trend as the other assays with stems extracts in first place with 21.93 ± 0.04 mg TE/mL and external bracts with 6.67 ± 0.13 mg TE/mL as the lower antioxidant fraction. Furthermore, it can be observed that the total contents of tannins, flavonoids, and the radical scavenging activity present an analogous increasing tendency in their values, when considering all the analysed artichoke fractions, from the outer bracts to the stems. Accordingly, the antioxidant activity may interestingly be more related to these two classes then to other secondary metabolites.

The variable projection by means of a principal component analysis (PCA) allowed for a clear view on the distribution of the four by-products groups according to their results in monitored variables. A PCA biplot is illustrated in Figure 3. The high variability percentage (99.38%; 79.68% and 19.70% for F1 and F2, respectively) underlines the reliability of the results, and the sample distribution reflects a good reproducibility of the performed analyses. Among the variables, TPC, DPPH, TTC, and TFC were strongly and positively correlated with each other as they follow the same direction. The inulin content indicator is quite perpendicular to the others, a sign that it is uncorrelated with them. Thus, internal bracts, as the richest inulin fraction, are not the best source of analysed bioactive polyphenols and antioxidants. Moreover, the distribution of leaves samples reflects their low values in each of the monitored variables.

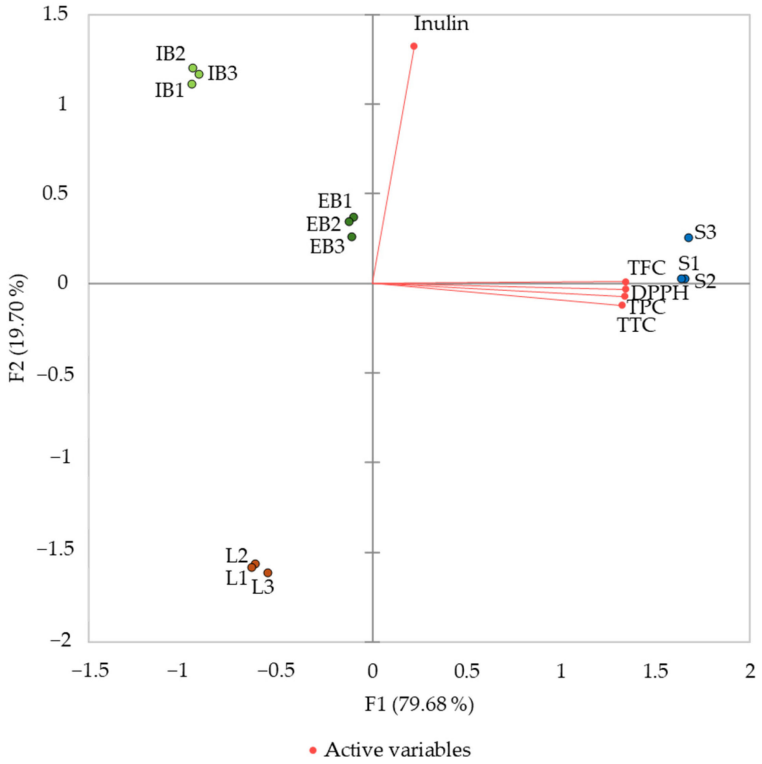

Figure 3. Principal component analysis (PCA) biplot highlighting the distribution of the 5 variables and the distribution of the four groups of samples (S: stems; L: leaves; IB: internal bracts; EB: external bracts, numbers represent the replicates).

4. Discussion

The artichoke production chain uses a low percentage of total artichoke biomass to obtain the commercial product. Nowadays, the valorization and the reuse of by-products is a common focus for researchers. The presence of inulin is a characteristic of plants belonging to the Asteraceae family, as they can store inulin and oligofructans as carbohydrates stock [27]. The inulin recovery was the main aim of this work because of its high concentration in artichokes and its multiple reuses and applications.

The optimized inulin extraction procedure was studied in terms of reproducibility and sustainability. Previous works involved ultrasound-assisted extraction (UAE) and different polar solvent solutions, which emerged to be very highly extractive strategies, but, in this work, with an eye to the applicability, the extraction was tested involving just simple equipment and water as a solvent [12]. Moreover, five different cultivars from three growth sites were analyzed by Castellino et al. (2020), who concluded that plant genetic and pedoclimatic conditions are crucial parameters in artichoke's inulin content [12].

Regarding the performed extraction optimization, the most effective parameters were 80 °C and 60 min, underlining a higher extraction power at high temperature and longer times. This result was quite predictable as inulin is reported to be more soluble in hot water [28]. Also, the extraction time emerged as a crucial parameter; in fact, among the 80 °C tests, the inulin concentration varied from 27.97 ± 1.78 mg/g FD matrix in the 10 min experiments to 38.98 ± 0.45 mg/g FD matrix in the 60 min experiments. The matrix–solvent ratio was 37.4, taken as previously optimized by Redondo-Cuenca et al. (2021), who reported an extraction optimization study on different Spanish varieties of inulin-containing plants, including Spanish globe artichoke (*Cynara cardunculus* L. var. Blanca de Tudela) [22]. In their research, artichoke samples were divided into two parts: edible and non-edible part (by-products), including stems, leaves, and external bracts. The inulin content results in artichoke by-products sample were 4.22 ± 0.01 g/100 g of dry weight, which is in line with data in the present work, considering stems and external

bracts. Moreover, internal bracts, the edible part, represented an inulin-richer fraction in Redondo-Cuenca and colleagues' published data.

In accordance with our results, previous research showed that a higher content of inulin and sugars is present in the aerial part of globe artichoke, so the edible portion constituted by the inner bracts and heart [14]. At the same time, the inulin content in by-products is still significant, except for leaves. The polymerization degree of artichoke inulin was calculated as 37 by Zeaiter et al. (2019), who reported similar results in terms of concentration [29].

A crucial point to be discussed is the relationship between inulin and free ketoses in the extracts. In fact, the content of inulin is affected by the presence of FOS (fructo-oligosaccharides) and other mono- and polysaccharides, which are present in the matrix and are easily extracted by water. The colorimetric Seliwanoff test involves a derivatization step. This step, carried out in strongly acidic conditions, leads to the release of monosaccharides in the solution, where they are derivatized by the resorcinol [29]. This reaction produced a colored compound, which was then detected by the spectrophotometer. Therefore, the results reflect the concentration of monosaccharides in the extracts, which are the monomeric units of inulin. In this vein, further analysis would be useful to characterize inulin, FOS, and free sugars using analytical separation techniques, such as chromatography.

From an applicative standpoint, inulin from artichoke by-products can be used as rheological modifiers in food and non-food formulations. In this regard, previous studies have shown that fibers from artichoke by-products can be used in bakery products such as cake [30] and bread [31], without changing the organoleptic characteristics, when dosed properly [32]. Furthermore, globe artichoke blend with water was used as a fat replacer due to its inulin concentration, in ice cream production, with good results in terms of sensory and nutritional qualities [33]. The rheological characteristics and possible uses as a gelling or emulsion agent are influenced by its DP and molecular weight [11].

The belonging of artichoke phenolic substances to different classes, such as benzoic and cinnamic derivatives, flavonoids, and tannins, was already reported, even if no studies are available on the "carciofo di Montelupone" landrace [34]. It is well known from the scientific literature that genetic, cropping system, treatments, season, and plant fraction have a crucial impact on the phenolic metabolite production. For instance, a recent paper from Palma et al. (2023) underlined that polyphenolic molecules and antioxidant compounds are higher in organic than in conventional cropping [35].

In the present study, bioactive compounds were investigated through spectrophotometric assays. Both the higher TPC values in the stems and the lowest in the outer bracts are in line with previous studies reported in the literature for globe artichokes cultivated in different Italian regions, including Sicily or Campania [36,37]. These results were confirmed using other antioxidant assays such as FRAP (ferric-reducing antioxidant power) [38] Thus, for the specific artichoke landrace, it is further confirmed that not just the edible fractions can be a source of phenolic compounds but also the by-products (leaves, floral stem, and bracts). Moreover, good values of TPC reported for stems, leaves, and internal bracts may be related to the spring harvest of this studied globe artichoke [39]. In leaves, polyphenols were more concentrated in petioles and midribs, as they play an important role in the cell wall structure, providing mechanical and structural support [38].

In the food industry, inulin finds various applications, and phenolic-rich extracts from artichoke bracts and stems were used, for example, in fresh egg pasta formulations. The resulting products, with 10% of artichoke extract, achieved considerable TPC results, both before and after cooking, and also an extended shelf life [40]. Furthermore, artichoke by-product extracts can be used as a natural antioxidant additive, as shown by Claus et al. (2015) [41]. Instead, in another study, 1 mg of artichoke by-product extract was used to functionalize tomato juice, resulting in a great improvement in antioxidant activity without altering the sensory proprieties [42].

5. Conclusions

The main purpose of this research was to valorize artichoke processing by-products. In particular, the common landrace of artichokes from the Italian Marche region, called "carciofo di Montelupone", a variety at risk of genetic erosion, was investigated. The performed experiments allowed for the optimization of inulin extraction and the application to each single artichoke by-product fraction, with very promising results for internal and external bracts. Moreover, polyphenols, tannins, flavonoids, and the antioxidant activity of by-product extracts were monitored, revealing the stems as the richest fraction. The method efficiency, the quantitative bioactive compounds together with the simplicity and the applicability of the proposed solution can pave the way to a more intensive reuse of artichoke waste as inulin and bioactive compound sources. Subsequent studies will involve the identification of bioactive substances and inulin through more accurate analytical techniques, such as chromatography or enzymatic methods. Moreover, for a stronger applicability at the industrial level, the deletion of the freeze-drying step must be investigated to reduce time and costs. Further developments could involve artichoke-derived inulin reuse in food formulations as a technological enhancer, such as in the pastry, bakery, or cream sectors, and/or prebiotics, in particular for local industries in the perspective of food waste management and locally sourced ingredients.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/gastronomy2040010/s1, Table S1: Detailed experimental design, results for each performed experiment, predictions and residuals. The residuals explain the difference between the detected and the expected results in a data-driven prediction model. Inulin content is expressed in mg/g of FD matrix.

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Data Availability Statement: Data will be made available on request.

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References

1. Cappelletti, R.; Mezzetti, B.; Balducci, F.; Diamanti, J.; Capocasa, F. Morphological, nutraceutical and chemical characterization of globe artichoke (*Cynara cardunculus* L. *var. scolymus* (L.) Fiori) landraces typically cultivated in Marche area. In Proceedings of the VIII International Symposium on Artichoke, Cardoon and their Wild Relatives, Viterbo, Italy, 10–13 April 2012; Volume 983, pp. 39–46.
2. De Falco, B.; Incerti, G.; Amato, M.; Lanzotti, V. Artichoke: Botanical, agronomical, phytochemical, and pharmacological overview. *Phytochem. Rev.* **2015**, *14*, 993–1018. [CrossRef]
3. FAOSTAT. Artichokes Production Indices. 2022. Available online: https://www.fao.org/faostat/en/#data/QI (accessed on 16 July 2024).
4. Olas, B. An Overview of the Versatility of the Parts of the Globe Artichoke (*Cynara scolymus* L.), Its By-Products and Dietary Supplements. *Nutrients* **2024**, *16*, 599. [CrossRef] [PubMed]
5. Ayuso, P.; Quizhpe, J.; Rosell, M.d.l.Á.; Peñalver, R.; Nieto, G. Bioactive Compounds, Health Benefits and Food Applications of Artichoke (*Cynara scolymus* L.) and Artichoke By-Products: A Review. *Appl. Sci.* **2024**, *14*, 4940. [CrossRef]
6. Biswas, O.; Kandasamy, P.; Nanda, P.K.; Biswas, S.; Lorenzo, J.M.; Das, A.; Alessandroni, L.; Lamri, M.; Das, A.K.; Gagaoua, M. Phytochemicals as natural additives for quality preservation and improvement of muscle foods: A focus on fish and fish products. *Food Mater. Res.* **2023**, *3*, 5. [CrossRef]

7. Ruiz-Cano, D.; Pérez-Llamas, F.; Frutos, M.J.; Arnao, M.B.; Espinosa, C.; López-Jiménez, J.Á.; Castillo, J.; Zamora, S. Chemical and functional properties of the different by-products of artichoke (*Cynara scolymus* L.) from industrial canning processing. *Food Chem.* **2014**, *160*, 134–140. [CrossRef] [PubMed]
8. Helkar, P.B.; Sahoo, A.K.; Patil, N. Review: Food industry by-products used as a functional food ingredients. *Int. J. Waste Resour.* **2016**, *6*, 1–6.
9. Kowalska, H.; Czajkowska, K.; Cichowska, J.; Lenart, A. What's new in biopotential of fruit and vegetable by-products applied in the food processing industry. *Trends Food Sci. Technol.* **2017**, *67*, 150–159. [CrossRef]
10. Ravindran, R.; Jaiswal, A.K. Exploitation of food industry waste for high-value products. *Trends Biotechnol.* **2016**, *34*, 58–69. [CrossRef]
11. Colombo, R.; Moretto, G.; Pellicorio, V.; Papetti, A. Globe Artichoke (*Cynara scolymus* L.) By-Products in Food Applications: Functional and Biological Properties. *Foods* **2024**, *13*, 1427. [CrossRef]
12. Castellino, M.; Renna, M.; Leoni, B.; Calasso, M.; Difonzo, G.; Santamaria, P.; Gambacorta, G.; Caponio, F.; De Angelis, M.; Paradiso, V.M. Conventional and unconventional recovery of inulin rich extracts for food use from the roots of globe artichoke. *Food Hydrocoll.* **2020**, *107*, 105975. [CrossRef]
13. Garcia-Castello, E.M.; Mayor, L.; Calvo-Ramirez, A.; Ruiz-Melero, R.; Rodriguez-Lopez, A.D. Response surface optimization of inulin and polyphenol extraction from artichoke (*Cynara scolymus* (L.)) solid wastes. *Appl. Sci.* **2022**, *12*, 7957. [CrossRef]
14. Raccuia, S.A.; Melilli, M.G. Seasonal dynamics of biomass, inulin, and water-soluble sugars in roots of *Cynara cardunculus* L. *Field Crops Res.* **2010**, *116*, 147–153. [CrossRef]
15. Zayed, A.; Serag, A.; Farag, M.A. *Cynara cardunculus* L.: Outgoing and potential trends of phytochemical, industrial, nutritive and medicinal merits. *J. Funct. Foods* **2020**, *69*, 103937. [CrossRef]
16. Apolinário, A.C.; de Lima Damasceno, B.P.G.; de Macêdo Beltrão, N.E.; Pessoa, A.; Converti, A.; da Silva, J.A. Inulin-type fructans: A review on different aspects of biochemical and pharmaceutical technology. *Carbohydr. Polym.* **2014**, *101*, 368–378. [CrossRef]
17. Perinelli, D.R.; Santanatoglia, A.; Caprioli, G.; Bonacucina, G.; Vittori, S.; Maggi, F.; Sagratini, G. Inulin Functionalized "Giuncata" Cheese as a Source of Prebiotic Fibers. *Foods* **2023**, *12*, 3499. [CrossRef] [PubMed]
18. Rubel, I.A.; Iraporda, C.; Manrique, G.D.; Genovese, D.B.; Abraham, A.G. Inulin from Jerusalem artichoke (Helianthus tuberosus L.): From its biosynthesis to its application as bioactive ingredient. *Bioact. Carbohydr. Diet. Fibre* **2021**, *26*, 100281. [CrossRef]
19. Ceccarelli, N.; Curadi, M.; Picciarelli, P.; Martelloni, L.; Sbrana, C.; Giovannetti, M. Globe artichoke as a functional food. *Mediterr. J. Nutr. Metab.* **2010**, *3*, 197–201. [CrossRef]
20. Cappelletti, R.; Balducci, F.; Diamanti, J.; Mazzoni, L.; Capocasa, F.; Battino, M.; Mezzetti, B. Agronomic and nutritional quality, and fresh and processing attitude, of globe artichoke (*Cynara cardunculus* L. *var. scolymus*) cultivars and an Italian landrace. *J. Hortic. Sci. Biotechnol.* **2016**, *91*, 634–644. [CrossRef]
21. AMAP, Agenzia per l'Innovazione nel Settore Agroalimentare e della Pesca "Marche Agricoltura Pesca", Regional Repertoire Database, 0.47.Carciofo di Montelupone. Available online: https://www.amap.marche.it/progetti/biodiversita-agraria-delle-marche/banca-dati-repertorio-regionale/sezione-vegetale/specie-erbacee/047-carciofo-di-montelupone (accessed on 12 July 2024).
22. Redondo-Cuenca, A.; Herrera-Vázquez, S.E.; Condezo-Hoyos, L.; Gómez-Ordóñez, E.; Rupérez, P. Inulin extraction from common inulin-containing plant sources. *Ind. Crops Prod.* **2021**, *170*, 113726. [CrossRef]
23. Mustafa, A.M.; Abouelenein, D.; Acquaticci, L.; Alessandroni, L.; Abd-Allah, R.H.; Borsetta, G.; Sagratini, G.; Maggi, F.; Vittori, S.; Caprioli, G. Effect of roasting, boiling, and frying processing on 29 polyphenolics and antioxidant activity in seeds and shells of sweet chestnut (*Castanea sativa* Mill.). *Plants* **2021**, *10*, 2192. [CrossRef]
24. Chileh-Chelh, T.; Carmona-Fernández, M.; Ezzaitouni, M.; Rincón-Cervera, M.Á.; López-Ruiz, R.; Gómez-Mercado, F.; Guil-Guerrero, J.L. Bioactive compounds and bioactivity of the heads of wild artichokes. *Food Biosci.* **2024**, *59*, 104134. [CrossRef]
25. CI, K.C.; Indira, G. Quantitative estimation of total phenolic, flavonoids, tannin and chlorophyll content of leaves of Strobilanthes Kunthiana (Neelakurinji). *J. Med. Plants* **2016**, *4*, 282–286.
26. Rejeb, I.B.; Dhen, N.; Gargouri, M.; Boulila, A. Chemical composition, antioxidant potential and enzymes inhibitory properties of Globe artichoke by-products. *Chem. Biodivers.* **2020**, *17*, e2000073. [CrossRef] [PubMed]
27. Barclay, T.; Ginic-Markovic, M.; Johnston, M.R.; Cooper, P.D.; Petrovsky, N. Analysis of the hydrolysis of inulin using real time 1H NMR spectroscopy. *Carbohydr. Res.* **2012**, *352*, 117–125. [CrossRef] [PubMed]
28. Mensink, M.A.; Frijlink, H.W.; van der Voort Maarschalk, K.; Hinrichs, W.L. Inulin, a flexible oligosaccharide I: Review of its physicochemical characteristics. *Carbohydr. Polym.* **2015**, *130*, 405–419. [CrossRef] [PubMed]
29. Zeaiter, Z.; Regonesi, M.E.; Cavini, S.; Labra, M.; Sello, G.; Di Gennaro, P. Extraction and characterization of inulin-type fructans from artichoke wastes and their effect on the growth of intestinal bacteria associated with health. *BioMed Res. Int.* **2019**, *2019*, 1083952. [CrossRef]
30. Dadalı, C. Artichoke bracts as fat and wheat flour replacer in cake: Optimization of reduced fat and reduced wheat flour cake formulation. *J. Food Meas. Charact.* **2023**, *17*, 98–107. [CrossRef]
31. Boubaker, M.; Omri, A.E.; Blecker, C.; Bouzouita, N. Fibre concentrate from artichoke (*Cynara scolymus* L.) stem by-products: Characterization and application as a bakery product ingredient. *Food Sci. Technol. Int.* **2016**, *22*, 759–768. [CrossRef]
32. Frutos, M.; Guilabert-Antón, L.; Tomás-Bellido, A.; Hernández-Herrero, J. Effect of artichoke (*Cynara scolymus* L.) fiber on textural and sensory qualities of wheat bread. *Food Sci. Technol. Int.* **2008**, *14* (Suppl. S5), 49–55. [CrossRef]

33. Abo El Enien, K.; Abd El Aziz, M.; Nasr, W. Effect of using artichoke as a source of inulin on low calorie ice cream quality. *J. Food Dairy Sci.* **2015**, *6*, 725–734. [CrossRef]
34. Lattanzio, V.; Cicco, N.; Linsalata, V. Antioxidant activities of artichoke phenolics. *Acta Hortic.* **2000**, *681*, 421–428. [CrossRef]
35. Palma, A.; Cossu, M.; Deligios, P.A.; Ledda, L.; Tiloca, M.T.; Sassu, M.M.; D'Aquino, S. Organic versus conventional globe artichoke: Influence of cropping system and harvest date on physiological activity, physicochemical parameters, and bioactive compounds. *Sci. Hortic.* **2023**, *321*, 112304. [CrossRef]
36. Fratianni, F.; Tucci, M.; De Palma, M.; Pepe, R.; Nazzaro, F. Polyphenolic composition in different parts of some cultivars of globe artichoke (*Cynara cardunculus* L. *var. scolymus* (L.) Fiori). *Food Chem.* **2007**, *104*, 1282–1286.
37. Lombardo, S.; Pandino, G.; Mauro, R.; Mauromicale, G. Variation of phenolic content in globe artichoke in relation to biological, technical and environmental factors. *Ital. J. Agron.* **2009**, *4*, 181–190. [CrossRef]
38. Pandino, G.; Lombardo, S.; Mauromicale, G.; Williamson, G. Phenolic acids and flavonoids in leaf and floral stem of cultivated and wild *Cynara cardunculus* L. genotypes. *Food Chem.* **2011**, *126*, 417–422. [CrossRef]
39. Lombardo, S.; Pandino, G.; Mauromicale, G.; Knödler, M.; Carle, R.; Schieber, A. Influence of genotype, harvest time and plant part on polyphenolic composition of globe artichoke [*Cynara cardunculus* L. *var. scolymus* (L.) Fiori]. *Food Chem.* **2010**, *119*, 1175–1181.
40. Pasqualone, A.; Punzi, R.; Trani, A.; Summo, C.; Paradiso, V.M.; Caponio, F.; Gambacorta, G. Enrichment of fresh pasta with antioxidant extracts obtained from artichoke canning by-products by ultrasound-assisted technology and quality characterisation of the end product. *Int. J. Food Sci. Technol.* **2017**, *52*, 2078–2087. [CrossRef]
41. Claus, T.; Maruyama, S.A.; Palombini, S.V.; Montanher, P.F.; Bonafé, E.G.; Junior, O.d.O.S.; Matsushita, M.; Visentainer, J.V. Chemical characterization and use of artichoke parts for protection from oxidative stress in canola oil. *LWT-Food Sci. Technol.* **2015**, *61*, 346–351. [CrossRef]
42. Larrosa, M.; Llorach, R.; Espín, J.C.; Tomás-Barberán, F.A. Increase of antioxidant activity of tomato juice upon functionalisation with vegetable byproduct extracts. *LWT-Food Sci. Technol.* **2002**, *35*, 532–542. [CrossRef]