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Identification of Phenolics and Structural Compounds of Different Agro-Industrial By-Products

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Abstract: This study provides a comprehensive analysis of the composition of onion peels, tomato peels, and pistachio green hulls, with a focus on their structural and bioactive compounds. Onion peels, regardless of cultivar, were found to be rich in quercetin and its derivatives, along with other flavonoids and pectin. Tomato peels emerged as a notable source of naringenin (0.52 mg/g in ethanol extract) and rutin (0.24 mg/g in water extract) and showed an unexpectedly high lignin content, comprising nearly 50% of their structural components. Pistachio green hulls demonstrated a high extractive content (63.4 g/100 g), 73% of which were water-soluble. Protocatechuic acid, rutin, and quercetin derivatives were the dominant phenolic compounds in the water extract, while luteolin was most abundant in the ethanol extract. Regarding structural composition, tomato peels and pistachio green hulls shared similarities, exhibiting a high lignin content (53.4% and 33.8%, respectively) and uronic acids (10–15%). In contrast, onion peels were characterized by high levels of glucans (around 38%) and galacturonic acid (33%). The insights from this study pave the way for the design of sustainable and efficient extraction processes, enabling the sequential recovery of valuable bioactive compounds and promoting the valorization of these agro-industrial by-products. Additionally, onion and tomato peels were evaluated as sources of pectin using two extraction methods: conventional acid water extraction and subcritical water extraction. The results revealed significant differences in the pectin composition (53–68% galacturonic acid) and degree of esterification (79–92%) compared to commercial pectin (72.8% galacturonic acid and 68% esterification), highlighting the influence of the raw material and extraction method on the final properties of pectin.

Keywords: onion; tomato; pistachio; antioxidants; polyphenols; pectin

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1. Introduction

The agro-food industry generates vast quantities of by-products and waste, many of which contain valuable compounds with potential applications in various sectors, including food, pharmaceuticals, and cosmetics. Within the framework of a circular economy, there is growing interest in revalorizing these by-products to reduce waste and promote sustainable resource utilization. Two main approaches can be followed for the valorization of agro-industrial waste [1]: whole-stream utilization (after a pretreatment, if necessary, the raw material is directly used for energy generation) and component-oriented utilization, in which the original agro-waste is fractionated in a different manner to recover specific compounds, from high-value to lower-value components (Figure 1). A comprehensive characterization of agro-industrial waste is essential for developing this biocascade process,

as it allows the identification of key bioactive compounds and structural components that can be extracted. Additionally, the selection of raw materials should prioritize locally produced by-products, which can be processed in centralized biorefineries. These facilities can convert waste into valuable products and contribute to rural and regional development in areas where the waste is generated. This approach reduces the reliance on external resources and goods within the global value chain [2].

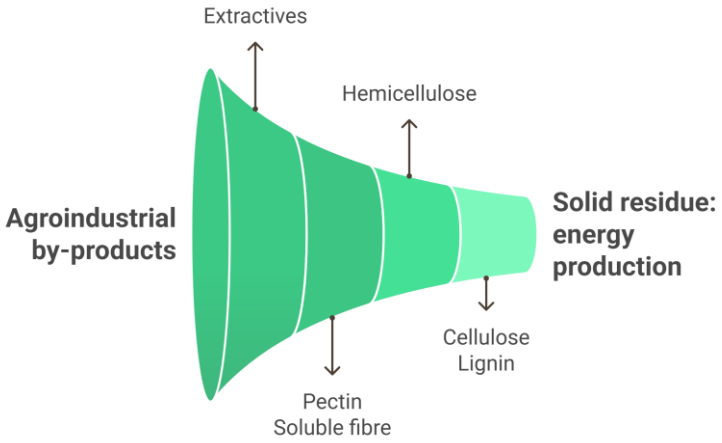

Figure 1. Biocascade approach for the complete valorization of agro-industrial wastes.

Among the numerous by-products of the agro-food sector, onion peels and tomato pomace stand out due to their large production volumes and high concentrations of bioactive compounds. Onion (*Allium cepa*) is widely cultivated worldwide, with onion peels—comprising the dry outer layers—representing a significant by-product. These peels are generated not only by the processing industry but also from agricultural fields and household consumption. In the European Union alone, approximately 0.6 Mt of onion peel waste (OPW) is produced annually [3], out of a total onion production of 6.26 Mt [4]. Spain accounts for nearly 20% of the EU's onion production, second only to the Netherlands, which contributes 24%. OPW is a rich source of valuable bioactive compounds, including flavonoids, phenolic acids, and pectins, which can account for up to 30% of its dry weight, as noted by Benito-Román et al. [5]. These compounds have significant potential for applications in the food, pharmaceutical, and cosmetic industries. However, most onion peels are discarded as waste because they are unsuitable for animal feeding due to the presence of sulfur compounds, leading to environmental challenges and the loss of valuable resources. In recent years, growing interest has emerged in valorizing OPW to enhance sustainability and resource efficiency. This trend is driven by the increasing demand for pectin-derived compounds (PDCs) as functional additives in the pharmaceutical and food sectors. Meeting this demand requires exploring new sources of PDC and developing eco-friendly extraction methods. Tomato (*Solanum lycopersicum*) is another widely consumed vegetable, both fresh and processed into products such as paste, juice, sauce, and ketchup [6]. Processing these products generates a by-product known as tomato pomace, primarily consisting of skins and seeds [7,8]. The annual production of tomato pomace ranges from 5% to 13% of the initial tomato weight, amounting to 0.6–2 Mt of organic waste. In 2022, Italy accounted for 40% of the EU's tomato harvest, followed by Spain (24%) and Portugal (9%), contributing to a total EU production of 15 Mt, according to FAOSTAT. Tomatoes are rich in lycopene, phenolics, organic acids, and vitamins, making tomato pomace a valuable resource [8]. However, the improper disposal of this by-product poses environmental challenges due to its high water content and nutrient richness, which lead to spoilage. The efficient utilization of tomato pomace through biorefineries could transform waste into valuable products such as lycopene, dietary fibres, and tomato seed oil. This approach reduces waste and promotes

resource efficiency within the tomato industry, providing a more sustainable alternative to its current underutilization in animal feeding.

In addition to onion peels and tomato pomace, pistachio green hulls (PGHs) have been included in this study due to the recent significant growth in pistachio cultivation and the associated environmental concerns. Pistachio (*Pistacia vera*) production reached approximately 1.027 Mt globally in 2022 (FAOSTAT). The by-products of pistachio processing include pistachio green hulls (PGHs), leaves, clusters, remaining kernels, and hard woody shells [9]. Among these, PGH represents the largest portion of pistachio industry waste, accounting for 34–45% of the total [10]. Despite its high volume, PGH is typically discarded as waste [11], posing significant environmental risks due to its accumulation in agricultural and food-processing settings. While PGH is occasionally used as animal feed, its high content of phenolic compounds and tannins can lead to gastrointestinal issues by interfering with the absorption of carbohydrates, proteins, and minerals [12,13]. Additionally, PGH contains over 70% water, making it highly susceptible to microbial contamination and fermentation. As a result, drying processes are required to reduce its moisture content and ensure safe handling. PGH is particularly rich in phenolic compounds, including gallic acid, rutin, and luteolin, which confer antioxidant, antimutagenic, cytoprotective, antitumor, and anticancer properties [10]. This highlights its potential as a valuable resource for recovering high-value bioactive compounds, offering opportunities to enhance its economic value and reduce environmental impacts.

All three agro-industrial by-products—onion peels, tomato pomace, and pistachio green hulls—have been identified as rich sources of bioactive compounds, including polyphenols, flavonoids, carotenoids, dietary fiber, and essential minerals. They have also been recognized as potential sources of pectin, which could help meet the growing demand for this biopolymer, estimated at 40,000 tons per year with an annual growth rate of approximately 5% [8].

Despite their high potential, these by-products face a common challenge: limited valorization through the recovery of their valuable bioactive compounds. Studies in the literature often focus on recovering a single component. In contrast, the aim of this work is to identify the phenolic and structural compounds present in various agro-industrial by-products, providing detailed compositional knowledge as a foundation for developing a multi-stage biocascade process. This process sequentially extracts different families of compounds, starting with easily accessible non-structural components. By maximizing the recovery and utilization of these valuable compounds, this approach seeks to promote sustainable practices and enhance resource efficiency across industries, aligning with the principles of the circular economy.

2. Materials and Methods

2.1. Raw Materials and Chemicals

Onion (*Allium cepa*) peel wastes (OPWs) used in this work corresponded to the cultivars (cv.) 'Horcal' and 'Red', and were provided by a local company dedicated to the blood sausage production. OPWs were manually sorted in order to separate the outermost peels, which contain the highest levels of flavonoids and have no culinary value. Tomato pomace was kindly provided by the company Vega del Ebro S.L., dedicated to the tomato processing. Pistachio green hulls (PGHs) were obtained from Santiago del Arroyo (Valladolid, Spain). Prior to the chemical analysis carried to determine their composition, all the raw materials were milled using a SM100 mill (Retsch GmbH, Haan, Germany), equipped with a 0.5 mm sieve.

Glucose (Glu, 99.5%), galactose (Gal, 99%), arabinose (Ara, 99%), rhamnose (Rha, 99%), xylose (Xyl, 99%), and sacarose (99%) were supplied by Sigma-Aldrich (Burlington, MA, USA).

Phenolic compounds used in this work were provided by Extrasynthese (Lyon, France), (QC4′ (≥99%), QC3,4′ (≥98%), and isorhamnetin (≥99%)); Sigma-Aldrich (USA) (QC (≥95%), QC3′ (≥98%), protocatechuic acid (≥98%), p-cumaric acid (≥98%), kaempferol (≥97%), myricetin (≥98%), chlorogenic acid (>95%), luteolin (>97%), rutin (>95%), naringenin (≥95%), and naringin (>90%)) and Honeywell Fluka (Charlotte, NC, USA), company that supplied p-hydroxybenzoic acid (≥98%) and glucuronic acid (GluA, >98%). D-galacturonic acid monohydrate (GalA, purity >97%) was obtained from Alfa Aesar (ThermoFischer GmbH, Kandel, Germany); and sulphuric acid used for the sample hydrolysis was 96% purity and was provided by Labbox Labware (Barcelona, Spain), whereas the one used for the HPLC mobile-phase preparation was 96% Suprapur provided by Merck KGaA (Darmstadt, Germany). All chemicals were used without further purification.

2.2. Extractive Determination and Characterization

The initial stage of biomass characterization involved determining extractives. As defined by the NREL Technical Report NREL/TP-510-42619, extractives comprise all non-structural materials that may interfere with subsequent analyses aimed at determining the structural components of the biomass. The procedure was carried out in two steps. In the first step, water was used as the solvent to extract water-soluble materials, such as inorganic compounds, non-structural sugars, and nitrogenous substances. This extraction was performed over 24 h at 60 °C, with a solvent-to-solid ratio of 20:1. After the extraction period, the suspension was filtered, and the liquid phase was analyzed according to the protocol. The solid residue was then dried and prepared for the second extraction step using ethanol. In the second step, ethanol served as the solvent to extract additional components, including chlorophyll, waxes, and minor compounds such as polyphenols. This extraction was also conducted over 24 h at 60 °C, maintaining the same solvent-to-solid ratio of 20:1. After ethanol extraction, the mixture was filtered, the liquid phase was analyzed, and the solid residue was dried for further characterization of the biomass's structural components, as described in Section 2.3.

The extractives were characterized by identifying free carbohydrates in both monomeric and oligomeric forms (after acid hydrolysis) and phenolic compounds, as detailed in Sections 2.2.1 and 2.2.2, respectively.

2.2.1. Carbohydrates Identification

For the carbohydrates identification, the HPLC model 1260 Infinity II (Agilent Technologies, Santa Clara, CA, USA) equipped with a Biorad Aminex HPX-87 H column (300 × 7.8 mm, Bio-Rad Laboratories Inc., Hercules, CA, USA) coupled with a guard column Micro-Guards Cation H^+ (Bio-Rad Laboratories Inc., CA, USA), with a variable wavelength detector (VWD, model G7114A, Agilent Technologies, CA, USA) and a refractive index detector (RID, model G7162A, Agilent Technologies, CA, USA), using 0.005 M sulfuric acid as mobile phase (0.6 mL/min), was used. The column and detectors were maintained at 40 °C and the total running time was 67 min per injection. Samples were filtrated through a 0.22 µm-pore-size syringe filter (Scharlab, Barcelona, Spain).

For the analysis of free carbohydrates, the liquid sample was filtered and directly injected into the HPLC system as described in the previous paragraph. For carbohydrates in oligomeric form, the sample was subjected to acid hydrolysis (121 °C for 1 h, following the addition of 174 mL of 72% sulfuric acid). After hydrolysis, the resulting liquid was injected into the HPLC system for monomer quantification.

2.2.2. Total Organic Carbon (TOC) and Total Nitrogen (TN) Quantification

TOC was determined using the Shimadzu TOC-V CSN Analyzer (Shimadzu Co., Kyoto, Japan). TOC was calculated as the difference between total carbon (TC) and in-

organic carbon (IC). The standard for the TC determination was potassium hydrogen phthalate ($C_8H_5KO_4$), in a concentration range from 0 ppm to 1000 ppm. For inorganic carbon (IC) determination, a solution of sodium hydrogen carbonate ($NaHCO_3$) up to 200 ppm was used as standard. Results were expressed as g of TOC/100 g of raw material.

TN was determined using the same equipment; the standard was a solution of potassium nitrate (KNO_3) in a concentration up to 200 ppm. Results were expressed as g of TN/100 g of raw material. From this value, using a nitrogen factor of 6.25, it was calculated the protein content in the water extractive (expressed as g of protein/100 g of raw material).

2.2.3. Phenolic Compound Identification

Each sample was characterized by High-Performance Liquid Chromatography using a Diode Array Detector (HPLC-DAD, Agilent 1100, CA, USA) with a Kinetex® Biphenyl column (250 × 4.6 mm, particle size 5 µm, and pore size 100 Å) supplied by Phenomenex (Torrance, CA, USA). The mobile phase consisted of (A) ammonium acetate 5 mM with acetic acid (1%, *v*/*v*) in water and (B) ammonium acetate 5 mM with acetic acid (1%, *v*/*v*) in acetonitrile. A detailed description of the method is presented in Benito-Román et al. [14].

2.3. Structural Component Determination and Characterization

The determination of biomass structural components was conducted according to the NREL protocol NREL/TP-510-42618. As outlined by NREL, structural carbohydrates are bound within the biomass matrix, while non-structural carbohydrates can be removed through extraction or washing steps. These non-structural carbohydrates were previously removed, as described in Section 2.2. In summary, the NREL protocol employs a two-step acid hydrolysis process to break down the biomass into its monomeric components, which are soluble in the hydrolysis liquid and can be quantified via high-performance liquid chromatography (HPLC), as detailed in Section 2.2.1. The protocol also provides procedures for determining lignin content—both soluble lignin, measured using UV–Vis spectroscopy, and insoluble lignin, determined gravimetrically—as well as ash content.

The elemental analysis (C, H, N, and S) of the solid samples (raw material and exhausted solid residue after the extraction) was also carried out using the FLASH 2000 elemental analyzer (Thermo Fisher Scientific, San Jose, CA, USA). The oxygen content in the samples was determined by difference, considering the ash content of the sample.

2.4. Pectin Isolation and Characterization

In this study, pectin was isolated from selected raw materials using two different extraction techniques: a conventional acidified water extraction and an alternative subcritical water method. In the first method, 10 g of raw material were mixed with 100 mL of water (pH 2, adjusted with HCl) and heated at 90 °C for 1.5 h. The solid residue was then separated from the liquid phase by filtration. To precipitate the dissolved pectin, the filtrate was mixed with an equal volume of 80% ethanol (*v*/*v*). In the alternative procedure, 15 g of raw material were processed in a subcritical water reactor, as described by Benito-Román et al. [5], using 150 mL of water. The mixture was heated to 125 °C and stirred for 180 min. After extraction, the solid–liquid mixture was separated by centrifugation (4500 rpm, 4 °C, and 10 min), and the pectin in the supernatant was precipitated by adding ethanol, as in the conventional method. In both procedures, the precipitated pectin was separated from the ethanol–water mixture by filtration using cheesecloth. The solid was then dried at 35 °C under vacuum. Once dried, the pectin was ground into a fine

powder and stored at 4 °C until further analysis. The pectin extraction yield was calculated using Equation (1):

$$Pectin\ yield\ (\%) = \frac{Pectin\ Isolated\ (\mathrm{g})}{Raw\ Material\ (\mathrm{g})} \times 100 \quad (1)$$

2.4.1. Pectin Composition

The determination of neutral sugars and uronic acids was performed using the HPLC system described in Section 2.2.1. For this analysis, an aqueous pectin solution (1 mg/mL) was prepared and subjected to hydrolysis. Specifically, 5 mL of the pectin solution were transferred to a 15 mL test tube, followed by the addition of 0.174 mL of H_2SO_4 (72%, v/v). The sample was then heated at 121 °C for 1 h. After hydrolysis, $CaCO_3$ was used to neutralize the sample. Based on the compositional results for GalA and neutral sugars, the relative proportions of the HG and RG-I domains were estimated using Equations (2) and (3), proposed by M'sakni et al. [15]:

$$HG\ (\%, mol) = GalA - Rha \quad (2)$$

$$RG - I\ (\%, \mathrm{mol}) = (GalA - HG) + Rha + Gal + Ara \quad (3)$$

2.4.2. Pectin Molecular Weight

The weight-average molecular weights (MWs) and polydispersity of the samples were determined employing high-pressure size exclusion chromatography coupled to refraction index detector (HPSEC-RID). The 1260 HPLC system (Agilent Technologies, CA, USA) consisted of a PL Aquagel guard column linked in series with PL Aquagel-OH 30, PL Aquagel-OH 40 columns from Agilent Technologies (300 mm × 7.5 mm, particle size 8 µm). Characterization of pectin from OSW and subcritical water hydrolysates was performed at 40 °C. Then, 10 µL of each sample were eluted in isocratic mode with 0.01 M NH_4Ac, at a flow rate of 0.7 mL/min. In addition, a pullulan standard set (0.342–400 kDa) provided by PSS Polymer Standards Service GmbH (Mainz, Germany) was used for calibration and data were analyzed with Agilent OpenLab Data Analysis 2.5 software. Standards and samples were filtered through 0.22 µm syringe filters.

2.4.3. Degree of Esterification of Pectin

The degree of esterification of the isolated pectins was determined using a titration method. In summary, 0.2 g of pectin were dissolved in 200 mL of water. This solution was then titrated with 0.1 M NaOH using phenolphthalein as the indicator, and the volume consumed was recorded as V1. Afterwards, saponification of pectin was initiated by adding 10 mL of 0.1 M NaOH under vigorous stirring. When the reaction was completed, 10 mL of 0.1 M HCl was added, and the excess HCl was neutralized with 0.1 M NaOH; the volume consumed was recorded as V2.

2.5. Statistical Analysis

All the statistical calculations were carried out using Statgraphics 19-X64. The significance of the differences was determined based on an analysis of the variance with the Fisher's least significant difference (LSD) procedure at p-value ≤ 0.05.

3. Results and Discussion

The tomato pomace provided by the industry was a heterogeneous mixture consisting of peels and seeds. Since the primary component of interest in this work was the peels, the seeds and stems were manually separated prior to moisture content determination.

The peels comprised 77% of the total weight, while seeds accounted for 19%, and stems constituted the remaining 4%. The moisture content of the isolated tomato peels (TPs) was determined to be 73.3 ± 1.2%, a notably high value that increases the risk of rapid spoilage. To mitigate this, the raw material (after seed and stem removal) was thoroughly dried at a mild temperature (50 °C for 24 h) prior to characterization, resulting in a final moisture content of 6.5 ± 0.4%. For the other raw materials, onion peel waste (OPW) sourced from the industry was analyzed. The Horcal variety exhibited a moisture content of 11.2 ± 0.4%, while the Red variety had a higher moisture level of 16.1 ± 0.5%. Pistachio green hulls (PGHs), which had been partially dried in the field, showed a moisture content of 6.8 ± 0.2% upon receipt in the laboratory. In light of these moisture content measurements, all raw materials were subsequently characterized, with all results expressed on a dry matter basis.

3.1. Extractive Quantification and Identification

Extractives are defined as any material in a biomass sample that is soluble in either water or ethanol during exhaustive extraction. These extractives include non-structural components that may interfere with a downstream biomass analysis. As shown in Table 1, significant differences were observed among the raw materials analyzed in this study.

Table 1. Extractives content in the raw materials studied in this work.

	Raw Material			
Extractives (g/100 g Raw Material)	**Tomato Peels**	**Onion Peels ('Horcal')**	**Onion Peels ('Red')**	**Pistachio Green Hulls**
Water soluble	12.1 ± 0.3 ^{c}	6.6 ± 0.3 ^{a}	8.9 ± 0.2 ^{b}	46.3 ± 1.3 ^{d}
Ethanol soluble	4.0 ± 0.1 ^{b}	1.8 ± 0.4 ^{a}	2.0 ± 0.1 ^{a}	17.0 ± 0.9 ^{c}
Total	16.1 ± 0.4 ^{c}	8.4 ± 0.7 ^{a}	10.9 ± 0.3 ^{b}	63.4 ± 2.2 ^{d}

Different letters indicate statistically significant differences at a 95% confidence level, according to the LSD test.

The highest extractive content was found in PGHs, with 63.4 ± 1.1 g per 100 g of raw material, of which 73% were water-soluble. Tomato peels followed, with an extractive content of 16.1 ± 0.4 g per 100 g of raw material, of which 75% were water-soluble. Onion peels displayed a similar trend, with approximately 80% of the total extractives being water-soluble. However, the total extractive content in onion peels was lower, at 8.4 ± 0.7 g and 11.1 ± 0.3 g per 100 g of raw material for the Horcal and Red varieties, respectively. The subsequent sections will provide a detailed analysis of the composition of both water-soluble and ethanol-soluble extractives.

3.1.1. Non-Structural Carbohydrates in Water Extractives

Water extractives primarily consist of sugars, which may be present in either free or oligomeric forms, as detailed in Table 2. Significant differences in the composition of free monosaccharides are observed depending on the raw material analyzed. In tomato peels, xylose is the most abundant monosaccharide, followed by GluA and glucose. The high xylose content in tomato peels can be attributed to the presence of hemicelluloses, a major component of dietary fiber in plant cell walls. Tomato peels are particularly rich in hemicelluloses, alongside pectins and other polysaccharides [16]. Mannose, galactose, xylose, arabinose, and glucose have been identified as the most abundant sugars in tomato peels [17]. This composition influences their industrial potential, as xylose can be fermented into bioethanol or converted into xylitol, a low-calorie sweetener. Additionally, the functional properties of tomato peel fiber (e.g., water retention and viscosity) make it valuable in food applications as a thickener and stabilizer. PGHs are characterized by a high content

of xylose, GluA, and glucose, which constitute the main water extractives. Similarly, onion peels exhibit a comparable monosaccharide profile, with glucose and xylose being the predominant free sugars, regardless of the cultivar considered. Tomato peels and PGHs contain significant amounts of proteins (2.1 and 3.9 g/100 of raw material, respectively, calculated from the TN value and a nitrogen factor of 6.25), whereas onion peels present significantly lower values.

Table 2. Water extractive content in the raw materials studied in this work (ND, not detected).

		Raw Material			
Extractives (g/100 g Raw Material)		**Tomato Peels**	**Onion Peels ('Horcal')**	**Onion Peels ('Red')**	**Pistachio Green Hulls**
Total Organic Carbon (TOC)		5.2 ± 0.2^{b}	2.7 ± 0.3^{a}	2.3 ± 0.3^{a}	17.1 ± 0.9^{c}
Total Nitrogen (TN)		0.33 ± 0.02^{b}	0.075 ± 0.006^{a}	0.053 ± 0.004^{a}	0.63 ± 0.05^{c}
Free	Sacarose	0.06 ± 0.01^{a}	0.06 ± 0.02^{a}	ND	0.21 ± 0.02^{b}
	Glucose	0.61 ± 0.02^{a}	0.69 ± 0.03^{a}	1.22 ± 0.06^{b}	2.02 ± 0.04^{c}
	Xylose	2.86 ± 0.03^{b}	0.49 ± 0.02^{a}	0.64 ± 0.06^{a}	6.5 ± 0.3^{c}
	Arabinose	ND	ND	ND	ND
	GalA	0.27 ± 0.02^{b}	0.13 ± 0.01^{a}	ND	ND
	GluA	0.73 ± 0.02^{c}	0.07 ± 0.01^{a}	0.31 ± 0.02^{b}	4.5 ± 0.6^{d}
Oligomeric	Glucose	0.28 ± 0.03^{b}	0.25 ± 0.03^{b}	0.17 ± 0.02^{a}	0.38 ± 0.04^{c}
	Xylose	ND	ND	ND	0.51 ± 0.0^{a}
	Galactose	0.42 ± 0.03^{b}	$0.34 \pm 0.04^{a,b}$	0.31 ± 0.03^{a}	ND
	Arabinose	0.07 ± 0.01^{b}	0.07 ± 0.02^{b}	0.02 ± 0.00^{a}	0.29 ± 0.01^{c}
	Rhamnose	0.05 ± 0.01^{a}	0.12 ± 0.01^{b}	0.02 ± 0.00^{a}	ND
	GalA	1.96 ± 0.06^{c}	1.79 ± 0.13^{c}	0.84 ± 0.04^{b}	0.11 ± 0.01^{a}

Different letters indicate statistically significant differences at a 95% confidence level, according to the LSD test.

Regarding the oligomeric composition, galacturonic acid (GalA) was the most abundant in both tomato peels and onion cultivars. This finding, along with the presence of rhamnose, suggests the presence of pectin in the water extractive profile of these two raw materials. The detection of other sugars, such as galactose, further supports this observation, as galactose is typically found in the side chains attached to the GalA backbone in pectin. In contrast, the most abundant oligosaccharides in pistachio green hulls were glucose and xylose. The oligosaccharide profile of PGH, dominated by xylose and glucose, is in agreement with the results published by [18] and differs from tomato peels due to variations in the cell wall structure and polysaccharide content. PGH polysaccharides exhibit high water and oil retention, which makes them suitable for food industry applications such as emulsifiers and stabilizers. Furthermore, their composition supports their use in bioethanol production and as potential prebiotics [19], promoting gut health.

3.1.2. Phenolic Compounds Present in the Extractives

As polar compounds, phenolic compounds are readily soluble in polar solvents, including water and alcohol-based organic solvents [9]. The individual phenolics identified in both water (Table 3) and ethanol (Table 4) extractives is described next.

The water-soluble extractives were further characterized by analyzing the individual phenolic compounds present in the extracts. The results are shown in Table 3. Notably, a significant number of phenolic compounds were detected. In tomato peels, the most abundant phenolic was the flavonoid rutin, followed by p-hydroxybenzoic acid, chlorogenic acid, and other minor flavonoids. Onion peels exhibited high concentrations of protocatechuic acid, which is typically highly water-soluble with a solubility at 25 °C of 29.4 ± 0.98 g/L, along with QC4′ and QC3,4′, flavonoids that generally display greater

water solubility compared to QC or QC3′ [14]. In PGHs, protocatechuic acid and rutin were also present in considerable amounts, contrasting with the other raw materials. The recovery of these high-value compounds using water as a solvent at mild temperatures highlights the potential of these raw materials as a source of various flavonoids.

Table 3. Individual phenolics identification present in the water extractives, expressed in mg of individual phenolic per g of raw material in dry basis (ND, not detected).

	Raw Material			
Phenolic (mg/g Raw Material)	**Tomato Peels**	**Onion Peels ('Horcal')**	**Onion Peels ('Red')**	**Pistachio Green Hulls**
Protocatechuic Ac.	ND	1.19 ± 0.04 ^{a}	2.98 ± 0.18 ^{b}	3.19 ± 0.17 ^{b}
p-Cumaric Ac.	ND	ND	ND	0.006 ± 0.001
p-Hydroxybenzoic Ac.	0.067 ± 0.003	ND	ND	ND
Chlorogenic Ac.	0.027 ± 0.001 ^{a}	ND	ND	0.113 ± 0.009 ^{b}
QC	0.016 ± 0.001 ^{a}	0.060 ± 0.003 ^{b}	0.63 ± 0.07 ^{d}	0.29 ± 0.02 ^{c}
QC-4′	ND	0.097 ± 0.002 ^{b}	0.098 ± 0.008 ^{b}	0.042 ± 0.005 ^{a}
QC3,4′	ND	0.086 ± 0.009 ^{b}	0.025 ± 0.004 ^{a}	ND
QC3	ND	0.110 ± 0.008 ^{c}	0.011 ± 0.001 ^{a}	0.86 ± 0.03 ^{b}
Rutin	0.24 ± 0.01 ^{b}	0.032 ± 0.001 ^{a}	ND	1.11 ± 0.19 ^{c}
Myricetin	0.021 ± 0.005 ^{b}	0.012 ± 0.001 ^{a}	ND	0.021 ± 0.001 ^{b}
Luteolin	ND	ND	ND	0.21 ± 0.02
Kaempferol	ND	0.013 ± 0.002 ^{a}	0.039 ± 0.005 ^{b}	0.018 ± 0.001 ^{a}
Naringenin	0.027 ± 0.003	ND	ND	ND
Isorhamnetin	ND	0.003 ± 0.000 ^{a}	0.024 ± 0.006 ^{b}	ND

Different letters indicate statistically significant differences at a 95% confidence level, according to the LSD test.

Table 4. Individual phenolics identification present in the ethanol extractives, expressed in mg of individual phenolic per 100 g of raw material in dry basis (ND, not detected).

	Raw Material			
Phenolic (mg/g Raw Material)	**Tomato Peels**	**Onion Peels ('Horcal')**	**Onion Peels ('Red')**	**Pistachio Green Hulls**
Protocatechuic Ac.	ND	0.22 ± 0.02 ^{a}	0.22 ± 0.01 ^{a}	0.93 ± 0.09 ^{b}
p-Cumaric Ac.	0.023 ± 0.002 ^{a}	0.02 ± 0.00 ^{a}	ND	0.077 ± 0.005 ^{b}
QC	0.007 ± 0.001 ^{a}	1.31 ± 0.14 ^{b}	2.89 ± 0.18 ^{c}	0.97 ± 0.3 ^{b}
QC-4′	ND	0.89 ± 0.05 ^{c}	0.36 ± 0.03 ^{b}	0.058 ± 0.004 ^{a}
QC3,4′	ND	0.027 ± 0.002	ND	ND
QC3	ND	0.021 ± 0.003	ND	ND
Rutin	ND	ND	ND	0.54 ± 0.03
Myricetin	ND	ND	ND	0.094 ± 0.002
Luteolin	0.027 ± 0.004 ^{a}	0.049 ± 0.004 ^{b}	ND	1.34 ± 0.05 ^{c}
Kaempferol	0.028 ± 0.002 ^{a}	0.068 ± 0.003 ^{b}	0.12 ± 0.01 ^{c}	0.25 ± 0.01 ^{d}
Naringenin	0.52 ± 0.3	ND	ND	ND
Isorhamnetin	ND	0.028 ± 0.002 ^{a}	0.071 ± 0.002 ^{b}	ND

Different letters indicate statistically significant differences at a 95% confidence level, according to the LSD test.

The ethanol-soluble extractive profiles for each of the raw materials are presented in Table 4. As expected, the most abundant phenolic compound detected in onion peels, regardless of the cultivar, was quercetin (QC), followed by QC4′. This observation aligns with previous findings reported by other authors who identified QC, QC4′, and QC3,4′ as the major flavonoids in onion [20], while other compounds, such as kaempferol and isorhamnetin derivatives, were reported as minor flavonols. In general, the extraction of flavonoids in the literature is carried out using mixtures of ethanol and water. Benito-

Román et al. [21] demonstrated that an ethanol/water mixture (70/30, *v*/*v*) provided the best results, as further increases in the ethanol content reduced the total amount of quercetin and its derivatives extracted, and pure water showed poor performance. These results are in agreement with Khalili et al. [22], who studied the effect of the solvent on total flavonoid extraction and reported higher yields when using organic solvents (such as ethanol and methanol, which provided equivalent results) compared to using water.

Furthermore, naringenin was identified as the predominant flavonoid in tomato peels, highlighting the potential of this material as a valuable source of naringenin for early-stage valorization processes aimed at flavonoid recovery. The presence of naringenin and quercetin has also been confirmed by previous studies, such as Perea-Domínguez et al. [23], who reported these flavonoids in the bound form. In addition to naringenin and quercetin, these authors detected smaller amounts of kaempferol and rutin, with rutin concentrations being nearly 200 times lower than those of naringenin. Regarding phenolic compounds, our study identified p-coumaric and caffeic acids as the most abundant. A comparison of our results with those reported in the literature reveals significant discrepancies. For example, Szabo et al. [24] analyzed the composition of ten different tomato peel varieties and found substantial variation. Their extraction, performed using an ethanol/water mixture (80%), identified naringenin chalcone as the most abundant flavonoid, followed by rutin (6.4–51 mg/100 g of raw material). Naringenin was also detected in a variable range of 4.6–12.1 mg/100 g. These two compounds have been consistently reported as the most abundant flavonoids in earlier works, such as that by Navarro-González et al. [17], with similar ranges (10.71–41.01 mg/100 g for quercetin-3-rutinoside, and 7.94–28.76 mg/100 g for naringenin). Navarro-González et al. [17] also noted the presence of rutin derivatives and chlorogenic acid. Other studies, such as Souza da Costa et al. [16], employed a methanol:water:formic acid solvent (79:20:1, *v*/*v*/*v*) to extract phenolic compounds from tomato pomace fractions. Their findings indicated a total phenolic content ranging from 518.32 to 949.46 mg/kg of sample, with 85.5% of these being flavonoids and 14.5% phenolic acids. In tomato peels, naringenin was again the most abundant flavonoid, at 557 mg/kg, while quercetin and kaempferol concentrations were 14.6 mg/kg and 1.68 mg/kg, respectively, in line with our observations. Additionally, they reported the presence of caffeic acid (21.26 mg/kg), p-coumaric acid (27.17 mg/kg), hydroxybenzoic acid (32.1 mg/kg), and protocatechuic acid (6.65 mg/kg). When comparing their results with ours, the total concentration of extractives from water and ethanol fractions (Tables 3 and 4) are quite similar. Finally, Martínez-Inda et al. [25] employed a solvent mixture of ethanol (96:4, *v*/*v*) at 40 °C, reporting chlorogenic acid (0.13 mg/g extract), protocatechuic acid (0.085 mg/g), gallic acid (0.057 mg/g), and caffeic acid (0.04 mg/g), with an extraction yield of approximately 30% (g of extract per 100 g of dry, milled waste). The wide variation in the reported compositions among studies can likely be attributed to genetic factors, cultivation conditions, or differences in processing techniques such as the solvent used. In fact, the study by Maged et al. [26] investigated the effect of the solvent used on the extraction yield of phenolics and flavonoids. It was observed that water allows for the extraction of significant amounts of these compounds. In the case of tomato peels, these authors reported that the greatest solubility was observed when acetone (5.03 mg phenolics/100 g of dry mater) was used, followed by water (3.04 mg phenolics/100 g of dry mater) and methanol (2.91 mg phenolics/100 g of dry mater).

In the case of PGH, luteolin was found to be the predominant flavonoid, followed by protocatechuic acid, quercetin (QC), and rutin (QC-3-rutinoside). The high concentration of these flavonoids underscores the potential of PGH to be valorized through the extraction of compounds with a high antioxidant activity. These results are consistent with previous findings published by other authors, who have reported that gallic acid,

quercetin-3-O-rutinoside, cyanidin-3-O-galactoside, quercetin-O-hexoside, protocatechuic acid, galloylshikimic acids, phloroglucinol, theogallin, galloyl-O-hexoside, catechin, or pyrogallol are the most abundant [27–31]. The revision of the scientific literature revealed that the phenolic compounds profile of PGH is varied due to the difference in the cultivar, soil condition, climate, degree of fruit ripeness, and the solvent used for the extraction. In this sense, both organic solvents (such as ethanol or methanol), together with water, have been used in the literature, providing excellent results. In the case of using water as solvent, in the study by Seifzadeh et al. [30], after a characterization of the extract by UHPLC/MS, these authors could identify 34 compounds, including the most abundant galloylshikimic acids, gallic acid, theogallin, galloyl-O-hexoside, quercetin-O-hexoside and pyrogallol. Noorolahi et al. [29] provided a complete identification of the phenolic compounds obtained after an aqueous extraction: these authors reported that the predominant phenolic acid compounds were quercetin-O-hexoside (1.363 μg/g of extract) and galloyl-O-hexoside-O-quercetin (0.560 μg/g of extract). On contrary, the concentration of luteolin was only 0.024 μg/g of extract. The work of Berreca et al. [27] demonstrated that solvent selection plays a critical role in the extraction of phenolic compounds. Methanol, in particular, yielded the highest extraction efficiency among all phenolics. Selecting an appropriate extraction method is essential in order to avoid an inaccurate quantification of the components. The preparation method and choice of solvent significantly influence the extractability of functional compounds.

As demonstrated, different flavonoids can be found in the selected raw materials. Each flavonoid possesses specific functional properties that make it suitable for particular applications. Quercetin is more effective as an antioxidant, making it valuable for food preservation and cosmetics. Luteolin is known for its potent antioxidant and anti-inflammatory properties [32], which make it valuable for use in skincare products and as a functional ingredient in food. Naringenin, on the other hand, is a flavonoid with notable anti-inflammatory, antimicrobial, and potential anticancer properties [33], making it particularly useful for the pharmaceutical and food industries, especially in the development of functional foods and nutraceuticals. The extraction technique also plays a role in the selective recovery of flavonoids: depending on the solvents and conditions used, certain flavonoids may be extracted in higher concentrations, affecting the extract's functional properties and its potential use in various applications. Variations in flavonoid profiles directly influence the properties of the extracts, such as the solubility, stability, color, and taste. These characteristics are crucial for determining the suitability of the extracts for different industrial processes, including those in the food, cosmetics, and pharmaceutical industries.

Given the composition of both water and ethanol extractives, the use of an ethanol/water mixture can help to maximize the recovery of flavonoids. A common strategy to maximize the extraction of flavonoids is the use of ethanol/water mixtures, taking advantage of the properties of both solvents: water swells the plant matrix and helps to increase the polarity of the medium, promoting the extraction of organic compounds that are soluble in either ethanol or water [34].

3.2. Structural Component Quantification and Identification

As an initial step in characterizing the structural composition of the selected biomasses, an elemental analysis was conducted, with the results presented in Table 5. All biomasses exhibited a low nitrogen content, suggesting that these raw materials are not suitable as protein sources. Among them, tomato peels showed the highest nitrogen content, which may explain their current use in animal feed. The composition of both onion peel samples was quite similar, displaying a lower carbon content and higher oxygen levels com-

pared to tomato peels. Pistachio green hulls (PGHs) had intermediate values between the two other biomasses, as reflected by the Higher Heating Value (HHV) and Lower Heating Value (LHV) calculations, based on the equations presented by Uzoagba et al. [35]. The LHV is, by definition, the HHV minus the heat of vaporization of the water content in the sample. Tomato peels had the highest HHV, indicating their potential as a fuel source after extractive recovery. In contrast, onion peels exhibited an HHV nearly 50% lower than that of tomato peels, suggesting that, after extractive recovery, this biomass may be more suitable for isolating structural components, such as pectin. For PGHs, the further determination of the structural components is necessary in order to guide decisions regarding its optimal valorisation pathway.

Table 5. Composition of the different raw materials used in this work, expressed in g/100 g of raw material in extractive-free basis.

	Raw Material			
Component (g/100 g Raw Material)	**Tomato Peels**	**Onion Peels ('Horcal')**	**Onion Peels ('Red')**	**Pistachio Green Hulls**
Ash	2.6 ± 0.2 ^{a}	7.9 ± 0.6 ^{b}	7.8 ± 0.4 ^{b}	9.6 ± 0.3 ^{c}
Lignin (Sol.)	5.0 ± 0.6 ^{a}	10.4 ± 0.2 ^{b}	10.2 ± 0.1 ^{b}	10.9 ± 0.2 ^{b}
Lignin (Ins.)	48.4 ± 1.4 ^{c}	3.6 ± 0.1 ^{a}	4.6 ± 0.2 ^{a}	22.9 ± 0.5 ^{b}
Protein	10.7 ± 1.3 ^{b}	3.0 ± 0.1 ^{a}	2.1 ± 0.2 ^{a}	9.2 ± 0.5 ^{b}
Glucan	16.0 ± 1.3 ^{a}	37.5 ± 2.2 ^{b}	38.4 ± 1.7 ^{b}	16.6 ± 1.2 ^{a}
Arabian	0.74 ± 0.09 ^{b}	0.32 ± 0.02 ^{a}	0.38 ± 0.02 ^{a}	4.1 ± 0.2 ^{b}
Xylan	1.57 ± 0.23 ^{a}	1.69 ± 0.15 ^{a}	1.67 ± 0.18 ^{a}	10.9 ± 0.8 ^{b}
Galactan	2.8 ± 0.3 ^{a}	3.0 ± 0.4 ^{a}	3.1 ± 0.3 ^{a}	ND
Rhamnose	0.18 ± 0.02 ^{a}	0.47 ± 0.06 ^{b}	0.37 ± 0.05 ^{b}	0.41 ± 0.04 ^{b}
Galacturonan	9.6 ± 0.08 ^{a}	32.7 ± 1.4 ^{b}	33.2 ± 1.8 ^{b}	9.9 ± 0.4 ^{a}
Glucuronan	0.91 ± 0.05 ^{b}	0.31 ± 0.04 ^{a}	0.29 ± 0.03 ^{a}	5.48 ± 0.17 ^{c}
C (%)	53.2 ± 0.9 ^{c}	35.6 ± 0.4 ^{a}	35.9 ± 0.3 ^{a}	44.4 ± 0.5 ^{b}
H (%)	7.6 ± 0.1 ^{b}	5.2 ± 0.2 ^{a}	5.3 ± 0.1 ^{a}	6.0 ± 0.3 ^{a}
N (%)	1.7 ± 0.2 ^{b}	0.5 ± 0.0 ^{a}	0.3 ± 0.0 ^{a}	0.4 ± 0.0 ^{a}
O (%)	34.9 ± 0.9 ^{a}	50.8 ± 0.4 ^{c}	50.6 ± 0.5 ^{c}	38.5 ± 0.6 ^{b}
HHV (MJ/Kg)	23.4 ± 0.4 ^{c}	12.7 ± 0.3 ^{a}	12.9 ± 0.2 ^{a}	18.1 ± 0.3 ^{b}
LHV (MJ/Kg)	21.3 ± 0.3 ^{c}	10.9 ± 0.3 ^{a}	11.0 ± 0.2 ^{a}	16.3 ± 0.2 ^{b}

Different letters indicate statistically significant differences at a 95% confidence level, according to the LSD test.

The individual identification of the structural components of the raw materials considered in this work is presented in Table 5. Significant differences were observed among the raw materials (tomato peels, onion peels, and pistachio green hulls), but no statistically significant differences were found between the two onion cultivars considered in this work. In both cultivars under consideration, pectin (32.7 ± 1.4% for the Horcal cultivar and 33.2 ± 1.8% for the Red cultivar), along with cellulose (approximately 38% for both cultivars) and lignin (making up approximately 70% of the total soluble fraction) were the primary structural components present in the raw material. A minor presence of proteins (2–3%) was also noted, which is consistent with the results reported by Suutarinen et al. [36], who found a protein content of 1.9%. In both cultivars considered in this study, the lignin content was significantly higher than other results reported in the literature. For instance, Choi et al. [37] reported that Klason lignin was 9.4 ± 0.1%. The complexity and variability in the lignin determination methods could explain the differences among the results reported in the literature.

The composition of tomato peels, as shown in Table 5, reveals a notably high lignin content, with total lignin accounting for 53.4 ± 2.0% of the raw material, 91% of which is

insoluble. Tomato peels also contain significant amounts of glucans, proteins, and pectin (galacturonan), each at approximately 10%, as summarized in Table 5. This is consistent with previous studies reporting high levels of dietary fiber in tomato peels. Dietary fiber is a complex mixture of hydrophilic compounds, such as soluble and insoluble polysaccharides, along with non-swellable compounds like cutins, suberins, and lignins. Therefore, the lignin content is likely included in the total fiber reported by other authors. For example, Kaur et al. [6] reported a crude fiber content of 71.3%, along with 14.3% protein, 1.28% ash, and 3.5% carbohydrates. Other authors have reported ranges of 6.69–10% moisture, 10–10.7% crude protein, 1.7–3.96% crude fat, 1.13–5.6% ash, 46.1–55.9% crude fiber, and 26.7% carbohydrates. Other studies, such as that by Lu et al. [8], reported wide ranges of composition: proteins at 5.7–20%, fibers 29.9–65.5%, carbohydrates 1.1–8.6%, ash 2.6–25.6%, and moisture up to 10%. Navarro-González et al. [17] found that tomato peels contained 13.3% of crude protein (13.3%), lipid (6%), and ash (3%). The total dietary fiber was high at 84.2%, with 71.8% being insoluble and the remaining 14.4% soluble. These authors performed a more complete analysis of the dietary fiber, finding out that the main sugars in tomato peels were mannose (38.56%), galactose (16.17%), xylose (15.38%), arabinose (15.16%), and glucose (14.64%), indicating hemicelluloses as the predominant polysaccharides.

PGHs exhibited a distinct composition compared to onion and tomato peels, with significant amounts of lignin, ash, and glucans, as well as a notable presence of uronic acids. Toghiani et al. [38] reported 11.4% ash and 13.3% crude protein in PGH, while Hassan et al. [11] found it to be an excellent source of carbohydrates (80.64 $\pm$ 0.98%), including glucose, galactose, rhamnose, arabinose, xylose, mannose, and GalA. They also reported 6.32 $\pm$ 0.26% ash, 1.80 $\pm$ 0.28% protein, and small amounts of fats (0.04 $\pm$ 0.005%). Other studies, such as Hamed et al. [39], identified 39.70% carbohydrates, 14.74% ash, 11.23% protein, and 20.41% fat in PGH. Özbek et al. [40] reported a moisture content of 70.81 $\pm$ 0.77% (wb), along with 11.40 $\pm$ 0.41% ash, 8.54 $\pm$ 0.37% protein, and 9.50 $\pm$ 0.16% non-polar extract on a dry basis.

3.3. Pectin Obtained from Onion and Tomato Peels

Once the composition of the different agro-industrial wastes was completed, pectin extraction from tomato peels and onion peels (cv. 'Horcal') was carried out using two distinct methods: a conventional acidified water technique (pH 2, adjusted with HCl) and a subcritical water extraction method at 125 °C for 180 min. Given the high content of extractives in PGHs, the proposed primary use for this raw material is as a source of phenolics. The yield and compositional results of these extractions are presented in Table 6, where they are compared to those of a commercial citrus pectin.

It was generally observed that subcritical water (SubW) extraction provided higher pectin yields compared to the conventional acid extraction method. This highlights SubW's ability to enhance hydrolysis reactions and facilitate the release of structural components such as pectin. Regardless of the extraction method, tomato peels yielded more pectin than onion peels. In comparison to commercial citrus pectin, the pectins extracted from agro-industrial waste exhibited a lower GalA content in all cases, although notable differences in structural domains were observed. Pectins obtained through the conventional procedure displayed a relatively low presence of the RG-I domain, even lower than that in commercial pectin, suggesting that the branched regions were hydrolyzed during extraction. This finding is supported by the Rha/GalA ratio, which reflects the contribution of the RG-I domain. According to Yang et al. [41], when the Rha/GalA molar ratio falls between 0.05 and 1, RG-I is considered a major component of the pectin. As shown in Table 6, pectins obtained via SubW extraction had a Rha/GalA ratio greater than 0.05, indicating a

significant presence of the RG-I domain. Additionally, the ratio of (Gal + Ara)/Rha, also presented in Table 6, helps assess whether the RG-I domain is highly branched. Pectins extracted by SubW exhibited higher values for this ratio, suggesting that the RG-I domain is more branched compared to pectins from acid extraction. Significant differences in molecular weight distribution were observed based on both the source of pectin and the extraction technique employed, as shown in Figure 2. Commercial citrus pectin displayed a monomodal distribution, which was similarly observed for pectin extracted conventionally from OPW. However, pectin from tomato peels differed, showing the presence of low-molecular-weight fractions. For pectins obtained via subcritical water extraction, the main peak in the distribution shifted toward lower-molecular-weight families. In all cases, tomato peel pectins exhibited lower molecular weights compared to those from OPW, as reported in Table 6.

Table 6. Composition of pectin extracted from OSW following a conventional extraction procedure and SubW treatment.

	Raw Material				
Component	**Citrus Commercial (Conventional)**	**Tomato Peels (Conventional)**	**Onion Peels (Conventional)**	**Tomato Peels (SubW)**	**Onion Peels (SubW)**
Yield (%)	-	4.3 ± 0.1	3.4 ± 0.2	6.3 ± 0.2	4.9 ± 0.1
GluA (%)	1.1 ± 0.1	2.6 ± 0.3	1.6 ± 0.2	1.8 ± 0.3	0.98 ± 0.14
GalA (%)	72.8 ± 0.19	58.3 ± 0.9	53.2 ± 0.2	56.8 ± 0.8	68.6 ± 0.5
Ara (%)	1.3 ± 0.1	1.71 ± 0.03	1.58 ± 0.06	1.8 ± 0.2	0.95 ± 0.06
Gal (%)	8.8 ± 0.5	5.08 ± 0.12	6.91 ± 0.07	15.1 ± 0.6	7.13 ± 0.15
Rha (%)	2.8 ± 0.2	1.98 ± 0.05	0.65 ± 0.06	3.3 ± 0.2	2.99 ± 0.02
Xyl (%)	2.1 ± 0.1	1.18 ± 0.03	1.61 ± 0.02	3.5 ± 0.6	1.66 ± 0.04
HG (mol, %)	73.4 ± 1.8	74.2 ± 2.8	74.3 ± 1.1	61.3 ± 3.1	70.3 ± 2.6
RG-I (mol, %)	18.9 ± 1.5	15.9 ± 0.6	13.9 ± 0.4	28.6 ± 1.8	22.3 ± 0.8
Rha/GalA	0.046 ± 0.005	0.041 ± 0.003	0.014 ± 0.002	0.071 ± 0.009	0.062 ± 0.002
(Gal + Ara)/Rha	3.6 ± 0.11	3.3 ± 0.23	10.8 ± 0.11	4.77 ± 0.67	2.8 ± 0.47
UA:NS	4.3 ± 0.4	5.1 ± 0.4	4.8 ± 0.1	2.1 ± 0.2	3.8 ± 0.5
DE (%)	67.8 ± 0.8	92.0 ± 2.6	88.9 ± 2.1	85.4 ± 2.9	79.1 ± 1.9
Mw (kDa)	437 ± 10	168 ± 8	353 ± 12	102 ± 5	137 ± 18

Morales-Contreras et al. [42] reported that pectins extracted via the conventional method from tomato husks had a degree of esterification (DE) ranging from 63% to 91%, with molecular weights between 542 and 699 kDa, and galactose as the predominant neutral sugar. Similarly, Grassino et al. [43] reported high extraction yields (up to 32%) and degrees of esterification (up to 82.4%) for pectins isolated from tomato peels. Sengar et al. [44] extracted pectin from tomato peels using different techniques (based on ultrasounds or microwave) with acid water as the solvent (pH 1.5 using HCl). These authors reported that the extraction procedure significantly affected the extraction yield (in the range 9–25%), and the degree of esterification (59.8–73.3%), as well as the pectin composition. With regard to onion peels, Şen et al. [45] studied the effect of the solvent (water, different acids, and their mixtures) and the extraction method (hot temperature or pulsed ultrasound-assisted), concluding the severe effect of each of them. The conventional acid water (HCl) extraction had an extraction yield of 10.6% and the pectin had a degree of esterification of 48% with a GalA content of 55%, a value quite similar to that reported in our work. Unfortunately, to the best of the author's knowledge, there are no published studies on characterization in terms of the degree of esterification of the pectin extracted from either tomato peels or onion peels using subcritical water with which to compare the results.

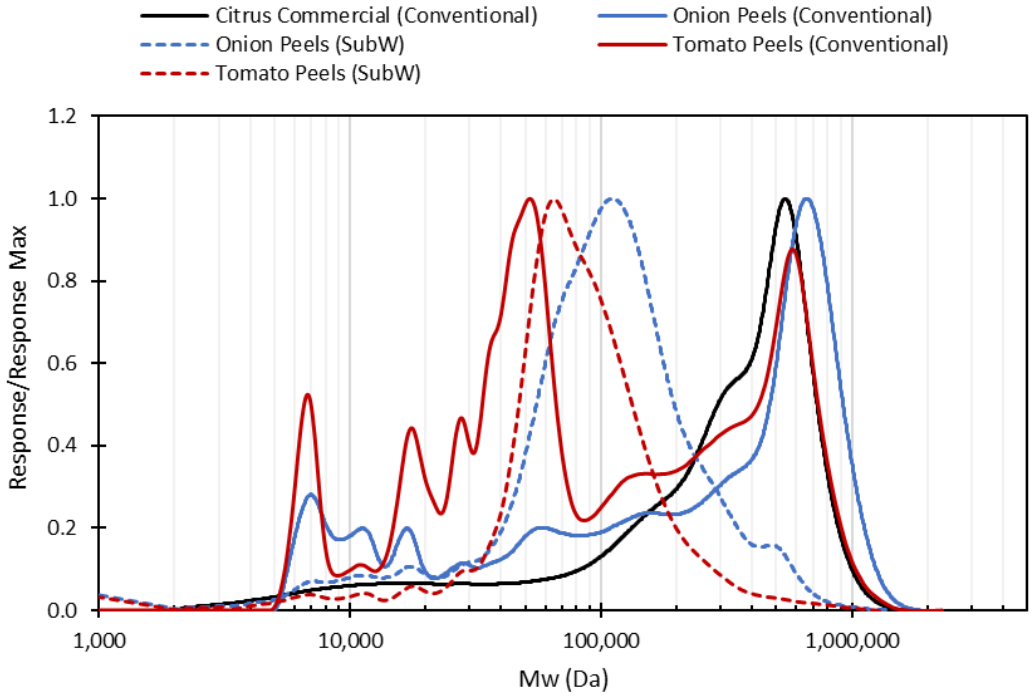

Figure 2. GPC profiles of pectins obtained from different raw materials using different extraction techniques.

4. Conclusions

In this study, the composition of three agro-industrial by-products—onion peels, tomato peels, and pistachio green hulls (PGHs)—was investigated through the characterization of their water and ethanol extractives, as well as their structural components. The results revealed that all three by-products contained significant amounts of phenolic compounds and flavonoids. Notable differences were observed in the ethanol-extracted phenolics: quercetin and its derivatives were most abundant in onion peels (approximately 2.25 mg/g of raw material), naringenin was the predominant flavonoid in tomato peels, and PGHs exhibited a diverse range of phenolics, including protocatechuic acid, luteolin, and kaempferol. The most common water-soluble phenolic across all raw materials was protocatechuic acid. These variations in phenolic profiles suggest different potential industrial applications for each by-product. In terms of structural composition, tomato peels and PGHs shared similarities, exhibiting a high lignin content (53.4% and 33.8%, respectively) and uronic acids (10–15%). In contrast, onion peels were characterized by high levels of glucans (around 38%) and galacturonic acid (33%). This detailed compositional knowledge provides valuable insights for identifying potential compounds and developing targeted valorization strategies to maximize the recovery of valuable components in a biocascade process, which allows the sequential extraction of valuable compounds.

An example of this approach is the recovery of pectin. After recovering the water and ethanol-soluble extractives from the three raw materials, pectin was extracted in the second stage of the biocascade process using two different procedures: conventional acid extraction and subcritical water extraction. The results revealed that the final properties of the pectin depended on both the raw material and the processing strategy used for isolation. These findings highlight the potential of pectin from agro-industrial by-products as an alternative to commercial pectin, opening up new possibilities for its use in various applications.

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resources, J.M.B. and M.T.S.; data curation, Ó.B.-R. and R.M.; writing—original draft preparation, Ó.B.-R.; writing—review and editing, R.M., J.M.B. and M.T.S.; project administration, Ó.B.-R. and M.T.S.; funding acquisition, Ó.B.-R., R.M. and M.T.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

ND	Not detected
QC	Quercetin
QC4′	Quercetin 4-glucoside
QC3	Quercetin 3-glucoside
QC3,4′	Quercetin 3,4′-diglucoside
DE	Degree of esterification
UA:NS	Uronic acid:neutral sugars ratio

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