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Hydrothermal treatment of avocado peel waste for the simultaneous recovery of oligosaccharides and antioxidant phenolics

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HIGHLIGHTS

- Avocado peel (AP) valorization was assessed via friendly environmental technology.
- AP was tested as a source of bioactive oligosaccharides (OS) for the first time.
- Autohydrolysis liquor presented 14.3 g OS/100 g AP and antioxidant compounds.
- AP at optimal conditions was characterized by UHPLC-TOF MS FTIR and TGA.

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ABSTRACT

Avocado industrial processing generates huge quantities of residues that are currently wasted without any valuable commercial application. This work deals with autohydrolysis of Avocado peel (AP) for the concomitant recovery of oligosaccharides and polyphenolics. Temperature of 150 °C allowed the highest recovery of oligosaccharides (14.3 g oligosaccharides/100 g AP) and high recovery of antioxidant phenolics (3.48 g gallic acid equivalents/100 g AP and 10.80 g Trolox equivalents/100 g AP measured with $ABTS^{\bullet+}$ assay). The liquor obtained at this temperature was characterized by TGA and FTIR to study its thermal stability and functional groups. UHPLC-TOF MS analysis of an ethyl acetate extract of AP liquor enabled the tentative identification of 43 compounds, belonging to various metabolite families, including flavonoids, phenolic acids, organic acids, lignans and fatty acids. These findings demonstrated that autohydrolysis of AP is a suitable technology to obtain bioactive agents with potential uses in food and cosmetic industries.

1. Introduction

The industrial processing of vegetables and fruits causes a great amount of agri-food wastes which disposal represents a big economic impact and causes serious environmental problems (Araújo et al., 2018; Del Castillo-Llamosas et al., 2021; Mora-Sandí et al., 2021; Rico et al., 2020). These residues are usually disposed or underused, despite their extremely interesting composition with a wide range of bioactivities. The extraction of high added-value compounds from agri-food residues could reduce the negative environmental issues provoked by its improper management, while enhancing the economic profitability of the food industry (Del Castillo-Llamosas et al., 2021; Figueroa et al., 2018). Moreover, the use of the by-products from agri-food sector as a feedstock for the manufacture of innovative commodities and biocompounds would allow the implementation of a sustainable circular bioeconomy following the "zero waste model" stated by Agenda 2030 (Del Castillo-Llamosas et al., 2021; Gullón et al., 2020).

In this framework, avocado (*Persea americana*), a fruit native to Central America and Mexico, is consumed worldwide as a fresh or processed fruit (Araújo et al., 2018; Del Castillo-Llamosas et al., 2021; Figueroa et al., 2018). Avocado is recognized as a very valuable fruit due to its organoleptic properties and nutritional profile, which comprises components such as vitamins (B1, B2, C, D and E), monounsaturated fatty acids, polyphenols, proteins, dietary fiber or sterols among others. Moreover, avocado is related to certain health-protective features such as antioxidant, anti-obesity, hypoglycemic, antihypertensive,

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antimicrobial and hepatic (Araújo et al., 2021; Araújo et al., 2018; Filannino et al., 2020). These evidences have led to a significant increase in its consumption and production in recent years all over the world (Araújo et al., 2018). For example, the consumption in USA raised from 1 kg per capita in 2000 to 3.64 kg in 2018 (Shirvanimoghaddam et al., 2020). In fact, close to one million hectares are employed currently worldwide for the cultivation of avocado, yielding about 7.2 million tons in 2019. Globally, Mexico is the main manufacturer, and its avocado production has increased by 2.5 times from 2000 to 2019, yielding about 2.3 million tons in the latter year (FAO, 2018). In particular, Spain is the main manufacturer of avocado in the European Union, generating about 98,000 tons (2019), which represents 95% of avocado production in Europe (FAO, 2018).

Avocado industrial processing (for obtaining products like guacamole, avocado pulp and oil) generates huge quantities of seeds and peels that are currently wasted without any valuable commercial application (Araújo et al., 2021; Araújo et al., 2020; Del Castillo-Llamosas et al., 2021; Figueroa et al., 2018). Nevertheless, these byproducts are a remarkable source of extractable phytochemicals with many human health benefits, which could be used for the formulation of functional foods or cosmetic products (Del Castillo-Llamosas et al., 2021). Therefore, the exploitation of this kind of food wastes allows meeting the growing demand of modern society over the "natural food products" while, at the same time, provides environmental benefits and adds value to the avocado industry (Araújo et al., 2020; Gullón et al., 2020).

In the last decade, this scenario has encouraged the development of green technologies to achieve an efficient recovery of biomolecules from agri-food wastes. In this sense, several technologies have been proposed for the recovery of valuable components (mainly phenolics and polysaccharides) from agro-industrial by-products, including microwave-assisted extraction (Araújo et al., 2020; Araújo et al., 2020; Figueroa et al., 2021) pressurized liquid extraction (Figueroa et al., 2018), ultrasound assisted-extraction (Del Castillo-Llamosas et al., 2021); *inter alia*.

Specifically, avocado seeds and peels have been studied as source of bioactive compounds with antioxidant capacity via microwave assisted extraction with acetone and ethanol (Araújo et al., 2021), 2020a). Similarly, microwave assisted extraction with ethanol was applied for the recovery and characterization of phenolic compounds of avocado peel (Figueroa et al., 2021). Organic solvents are widely employed for the extraction of bioactive molecules, however, these solvents entail some limitations due to their volatility, risk of degradation of thermolabile compounds or long extraction times (Del Castillo-Llamosas et al., 2021).

In the last years, the hydrothermal extraction (autohydrolysis) has gained interest owing to being an easy, eco-friendly, safe technique that employs water as an only reagent. This green technology enables the selective solubilization of hemicelluloses and pectic polymers in the reaction liquors, yielding a solid phase enriched in cellulose and lignin that can be used to produce various biobased products in a biorefinery framework (Rico et al., 2020). Hydrothermal processing has been successfully employed for the recovery of antioxidants and oligosaccharides from chestnut shells (Gullón et al., 2018), or purple corn cobs (Gullón et al., 2020). However, to the best of our knowledge, the simultaneous extraction of oligosaccharides and antioxidants compounds from AP via hydrothermal processing has not been tackled so far.

The aim of this work was to assess the suitability of the autohydrolysis treatment of avocado peels to obtain an extract rich in oligosaccharides and antioxidant compounds. The temperature of the hydrothermal treatment was varied to maximize the concentration of oligosaccharides in the liquor, but also looking for compatible conditions for the simultaneous recovery of antioxidant phenolics. Moreover, the liquor obtained under optimal autohydrolysis conditions was characterized by TGA, FTIR, and LC-MS for more in-detailed knowledge about its thermal stability, functional groups, and phenolic compounds profile.

2. Materials and methods

2.1. Materials

Avocado peels (AP) from Hass variety were provided from a local restaurant in Ourense (NW Spain). The avocado peels were then washed with tap water to remove the remaining pulp attached to the peel, placed on a tray and dried at 50 °C for 24 h in drying oven (JP Selecta Theroven), reaching a proximate final moisture of 6%. After that, the dried samples were milled and sieved to achieve a particle size smaller than 0.5 mm using a Polymix PX-MFC 90D. Finally, the ground AP was stored in sealed plastic bags at − 20 °C until use.

The reagents employed in this study (namely 2,2′-azino-di(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tri(2-pyridyl)-Striazine) (TPTZ), 6-hydroxy-2,5,7,8-etramethylcrhoman-2-carboxylic acid (Trolox), acetic acid, acetone, arabinose, ethanol, Folin-Ciocalteu reagent, furfural, gallic acid, glucose, hydrochloric acid, hydroxymethylfurfural, iron (III) chloride hexahydrate, methanol, potassium persulfate, rutin, sodium acetate 3-hydrate, sodium carbonate, and xylose)were purchased from Sigma-Aldrich (Barcelona, Spain).

2.2. Analysis of raw material

Milled AP was subjected to moisture (TAPPI T 264 om-88 method), ethanol extractives (ISO 638:1978 method), and ash determination (T 244 om-93 method). The hemicellulosic, glucan and lignin content of the AP without extractives were determined using quantitative acid hydrolysis (TAPPI T 249 cm-09). The solid fraction recovered by filtration from quantitative acid hydrolysis was gravimetrically quantified after oven-drying and denoted as Klason lignin. The liquid phase was employed for the determination of monosaccharides (glucose, xylose and arabinose), acetic acid and galacturonic acid using an Agilent 1200 series HPLC instrument (Agilent, Germany) with the following characteristics: refractive index detector (at 40 °C), Aminex HPX-87H column (Transgenomic Inc., at 50 °C), mobile phase, 3 mM H_2SO_4 mobile phase at 0.6 mL/min. The ethanol extractives were also analyzed by HPLC to determine its chemical composition. All analyses were performed in three replicates.

2.3. Hydrothermal treatment of avocado peels

AP and distilled water were combined at a liquid/solid ratio (LSR) of 8 kg/kg (oven dry basis) in a 100 mL stainless steel reactor (model 4848 from Parr Instruments, Moline, IL, USA). The LSR was selected based on preliminary studies (data not shown) and other related research (Gullón et al., 2018; Dávila et al., 2016). The treatment was carried out in the range of temperatures of 140–180 °C under non-isothermal conditions (a single experiment was carried out for each temperature). The studied temperatures were also selected based on autohydrolysis studies of raw materials similar to avocado peels, such as melon or lemon peels (Rico et al., 2020; Gómez et al., 2013). The severity (S_0) was calculated to indicate the harshness of the hydrothermal treatment (Lavoie et al., 2010) and with the aim of comparing our results with previously published studies, using the following equation:

$$S_0 = \log R_0 = \log(R_{0HEATING} + R_{0COOLING}) = \log\left(\left[\int_0^{tMAX} \exp\bullet\left(\frac{T(t) - T_{REF}}{\omega}\right)\bullet dt\right] + \left[\int_{tMAX}^{tF} \exp\bullet\left(\frac{T'(t) - T_{REF}}{\omega}\right)\bullet dt\right]\right) \quad (1)$$

where R_0 represents the severity factor, t_{MAX} stands for the time (min) necessary for achieving the aimed temperature (T_{MAX}, °C), t_F represents the time (min) of cooling, T(t) and T'(t) (°C) are the temperature profiles during the heating and cooling steps, respectively, ω represents the empiric parameter related to activation energy and T_{REF} represents the temperature of reference (common values: ω = 14.75 K and T_{REF} = 100 °C).

Once the target temperature is reached, the reactor was cooled down to 60 °C by internal refrigeration, and the resulting slurry was filtered, obtaining separated solid and liquid fractions. The solid residues were then washed with water (to remove the liquid remaining from the autohydrolysis liquor) and dried at room temperature and the liquid phases were stored at 4 °C until further analysis.

2.4. Analysis of avocado peels solids after autohydrolysis treatment

The spent solids from hydrothermal processing were weighed and subjected to moisture analyses to calculate the solubilization of the raw material. The chemical composition of these solids was determined following the same methodology employed for the raw material (section 2.2).

2.5. Chemical characterization of the avocado peels autohydrolysis liquors

An aliquot of the liquor was subjected to filtration via 0.45 μm cellulose acetate membrane, and directly analyzed by HPLC for monomeric sugars (glucose, xylose, arabinose), acetic acid, hydroxymethylfurfural (HMF) and furfural (F) employing the method described previously (section 2.2). The oligomer content was determined by enzymatic posthydrolysis using two enzyme mixtures: cellulase (Celluclast 1.5 L) and endopolygalacturonase (Viscozyme L from *Aspergillus aculeatus*). The conditions employed were: temperature of 37 °C, pH 5, cellulase loading of 5 FPU/g liquor and endopolygalacturonase loading of 45 U/g liquor, for 40 h (Gómez et al., 2013; Martínez et al., 2010). The increase in the concentration of each sugar after enzymatic posthydrolysis with respect to the autohydrolysis liquor allowed to calculate the oligomer and acetyl groups (AcO) content. Oligomers were expressed as monosaccharide equivalents.

The non-volatile compounds (NVC) were determined by oven-drying of an aliquot of the liquors at 105 °C for 24 h. All determinations were made in triplicate.

2.6. Determination of total phenolic content (TPC) and total flavonoid content (TFC)

The TPC of autohydrolysis liquors was measured according to the Folin-Ciocalteau method (Singleton and Rossi, 1965) and the results were recorded in g of gallic acid equivalents (GAE)/100 g AP. The TFC was quantified employing the protocol reported by (Blasa et al., 2006) and the results were stated in g rutin equivalents (RE)/100 g dried AP. Both measurements were performed in triplicate. All spectrophotometric measurements were carried out on a Shimadzu UV-1800 (Shimadzu Europa GmbH, Duisburg, Germany).

2.7. Antioxidant activity

Antioxidant activity was measured using three complementary assays: DPPH$^{\bullet}$ (α,α-diphenyl-β-picrylhydrazyl), ABTS$^{\bullet+}$ (2,2-azino-bis-3-ethylbenzothiazoline-6-sulphonic acid) and FRAP (ferric reducing antioxidant power), following the methods described previously by Gullón et al. (2017). Trolox was used as reference standard, expressing the results as g Trolox/100 g dried AP as mean of three replicates.

2.8. Chemical and structural characterization of the solubilized compounds from avocado peels

In order to achieve in-depth comprehension of the chemical and structural features of the solubilized bioactive compounds at the optimal hydrothermal treatment, the liquor was freeze-dried and subjected to different analysis comprising FTIR, TGA and UHPLC-TOF MS.

2.8.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis of the optimized extract was carried out on a Nicolet 6700 Spectrometer. In total, 8 scans were joined in transmission mode employing a resolution of 4 cm^{-1}. The spectrum range was set at 4000–400 cm^{-1}.

2.8.2. Thermogravimetric analysis (TGA)

The thermal stability of the extract from AP was evaluated by thermogravimetric analysis (TGA) using a Mettler Toledo TGA/DSC1 thermobalance (Mettler-Toledo, Columbus, OH, USA). Between 2 and 4 mg of lyophilized liquor was analyzed using a 20 mL/min nitrogen flow with a heating rate at 10 °C/min increasing from 25 to 600 °C.

2.8.3. Identification of major phenolic compounds using UHPLC-TOF MS

The tentative identification of phenolic compounds present in the liquor acquired at optimal extraction conditions was performed by liquid chromatography coupled with trapped ion mobility spectrometry and TOF high resolution mass spectrometry (LC-TOF MS). The extract was dissolved in deionized water and the resulting solution was subjected to a single stage extraction with ethyl acetate using a liquor:solvent ratio of 1:3 (v/v), with constant stirring for 15 min at room temperature. The organic phase was separated by decantation and stored for successive analysis. Sample (5 μL) was injected into a Kinetex C18 column (2.1 mm × 100.0 mm, 2.6 μm) (Phenomenex) and LC separation were carried out on an Elute UHPLC (Bruker Daltonics). The mobile phases were: 0.1% aqueous formic acid (solvent A) and 0.1% formic acid in methanol (solvent B) at a flow rate of 0.25 mL/min. The linear gradient was: 5% solvent B over 0.4 min, from 5% to 35% solvent B over 0.1 min, 35% to 100% solvent B over 6.5 min, 100 % solvent B over 1 min, 100% to 5% solvent B over 0.1 min and then isocratically 5% solvent B for 2.9 min. Samples were ionized using an ESI source in negative ion mode, with the typical operating conditions of 4000 V capillary voltage, 500 V end plate offset, 2.5 bar nebulizer pressure, 6.0 L/min dry gas, 200 °C dry heater. Identification of metabolites was based on the accurate mass data, isotopic pattern matching (mSigma value) and retention time (when the standard was available). High score was considered when the three criteria were met: < 0.5 mDa differences between measured and theoretical mass (based on chemical formula); mSigma values < 50; < 0.2 min differences between authentic standard and analyte retention times. Medium score was considered when only the criteria of *m/z* data and mSigma values were met.

2.9. Statistical analysis

Statistical analysis was performed using SPSS for Windows version 23.0 (IBM SPSS, Chicago, IL). Significant differences among the results

were analyzed by one-way analysis of variance (ANOVA) followed by Tukey's test considering a significance level of $p < 0.05$.

3. Results and discussion

3.1. Chemical composition of avocado peels

The chemical constituents of AP depend on the cultivar and growing conditions (Araújo et al., 2018). The main component was the lignin (41.91%) with a similar value to that reported by García-Vargas et al. (2021) for this same by-product. In this context, the lignin percentage of AP is significantly higher compared to other related feedstocks such as melon, pineapple and mango peels, which present a lignin content of 19.9, 10.4% and 6.4%, respectively (Banerjee et al., 2019; Rico et al., 2020; Torres-León et al., 2018).

The glucan content (19.43%) was analogous to that reported by García-Vargas et al. (2021) for AP. This result was also in the range of that found for pineapple peels (20.90%, (Banerjee et al., 2019)) and slightly lower than those for melon peels (24.54%, (Rico et al., 2020)). Hemicelluloses (comprising xylan, acetyl groups and arabinan, as well as galacturonic acid, which content is closely related to the presence of pectin in this type of feedstock) represented 26.51%. This content was much higher than that determined in the study of García-Vargas et al. (2021) who reported a content of this heteropolysaccharide around 1.9 times lower.

Another interesting fraction were the extractives which accounted for 8.01% of the avocado peels and contained mostly monomeric sugars and organic acids (Gullón et al., 2008). Ash content was 2.81%. These data were also in range of that found in the aforementioned study by García-Vargas et al. (2021).

Taking into account the composition of the avocado peel, the recovery of valuable compounds by green extraction technologies may be a profitable strategy to decrease the environmental impact of the food chain and to provide added value to this waste.

3.2. Evaluation of hydrothermal processing of avocado peels

Based on the composition of the AP, hydrothermal processing was proposed as a suitable treatment for obtaining pectic-oligosaccharides and antioxidant compounds from this feedstock (see Fig. 1).

3.2.1. Effect of the temperature of hydrothermal processing on the solubilization of avocado peels and the composition of processed solids

Hydrothermal treatment causes the partial hydrolysis and decomposition of the pectin and hemicelluloses as well as phenolic compounds, yielding a solid enriched in glucan and lignin (del Río et al., 2020; Gullón et al., 2018; Martínez et al., 2009; Rico et al., 2020). Fig. 2 shows the substrate solubilization and the chemical composition of the solid phase after hydrothermal processing in the range of temperatures 140–180 °C, which correspond to S_0 values between 1.61 and 2.79. As expected, the percentage of solubilization of AP raised with the temperature, from 23.2% at the lowest temperature and reaching a maximum value of 29.4% at the harsher conditions. Similar results regarding the limited substrate solubilization were determined by Rico et al. (2020) during the hydrothermal treatment of melon peels at 165 °C (36.46%). However, the solubilization values acquired during this work were substantially lower than those found for other fruit by-products. For example, autohydrolysis of lemon and orange peels resulted in solubilization close to 50% and larger than 60%, respectively, under similar operational conditions used in this work (Gómez et al., 2013; Martínez et al., 2010). In this sense, the higher presence of the acid insoluble residue in AP seemed to limit the solubilization during autohydrolysis.

The spent solid was mainly composed of glucan and lignin (which are less susceptible to the autohydrolysis treatment than the other fractions) and became more enriched in these components with the temperature. A maximum of 24.4% of glucan and 52.8% of lignin were reached at 180 °C. This content represented 88% and 89% of the initial values of glucan and lignin in the feedstock. These results are in agreement with those reported for the hydrothermal processing of other substrates rich in pectin. For instance, when melon peels were treated at 140 °C, the percentages of glucan and lignin recoveries were 93% and close to 100%, respectively (Rico et al., 2020). In the case of lemon peels, the glucan recovery accounted for 80% and the lignin recovery was higher than 90% (Gómez et al., 2013).

It should be noted that operating at 180 °C, the combined contribution of glucan and lignin accounted for 77.2% of the treated solid. Hence, a subsequent fractionation of this processed solid to obtain glucan and lignin separately is key for an integrated valorization of avocado peels following a biorefinery approach which is the base of the circular economy (Del Castillo-Llamosas et al., 2021).

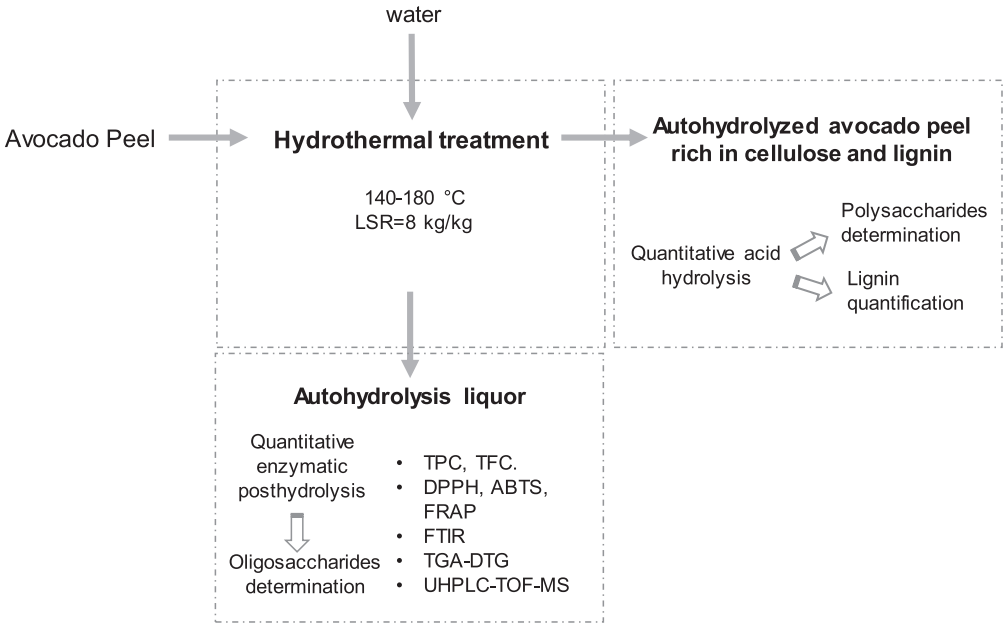

Fig. 1. Main scheme of the processing and analyses carried out in this work.

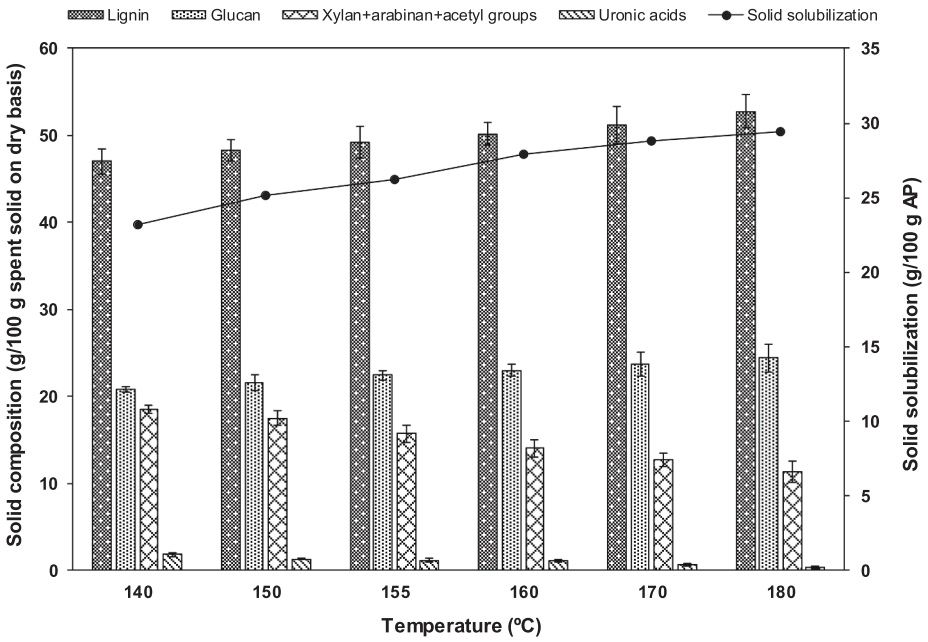

Fig. 2. Avocado peels solubilization and chemical composition of the solid after autohydrolysis under non-isothermal conditions.

3.2.2. Effect of the temperature of hydrothermal processing on the composition of autohydrolysis liquors of avocado peels

The reactions involved in the hydrothermal treatment, including the hydrolytic breakdown of hemicellulose and pectin into oligomers, the release of monomers and the generation of degradation compounds, has been widely studied for several feedstocks (Dávila et al., 2016; Gullón et al., 2018; Rico et al., 2020).

Regarding the hemicelluloses, its solubilization was relatively scant (see Fig. 2), with a maximum value of 69% regarding the initial content of hemicelluloses at the most severe condition of 180 °C ($S_0 = 2.79$), whereas the condition conducive to maximum recovery of oligosaccharides (150 °C, $S_0 = 1.69$) accounted about 47% of solubilization regarding the initial content of hemicelluloses. These values of solubilization were intimately related to the nature of the biomass employed, besides the severity of the treatment. In this context, Branco et al. (2015) reached even lower values of solubilization for hemicelluloses (accounted as xylan, arabinan and acetyl groups) after the autohydrolysis of *Annona cherimola* Mill seeds. Specifically, $S_0 = 2.83$ allowed the release of 26% of the initial content of hemicelluloses, whereas higher severities (S_0 of 3.60–4.70) enabled to solubilize up to 74–100% of the hemicellulosic fraction, respectively. Conversely, Martínez et al. (2010) achieved higher release of hemicelluloses (accounted as galactan, arabinan and galacturonan) when processing orange peel wastes with non-isothermal autohydrolysis at similar ($S_0 = 2.75$) or higher severities ($S_0 = 3.64$), reaching 83% and 95% of solubilization regarding the initial content of hemicelluloses, respectively.

In this sense, the liquid phases obtained after autohydrolysis AP were mainly constituted by oligosaccharides and also contained antioxidant compounds. Fig. 3 displays the mass fraction of Non-volatile compounds (NVC) and the profile of the composition of oligosaccharides (measured

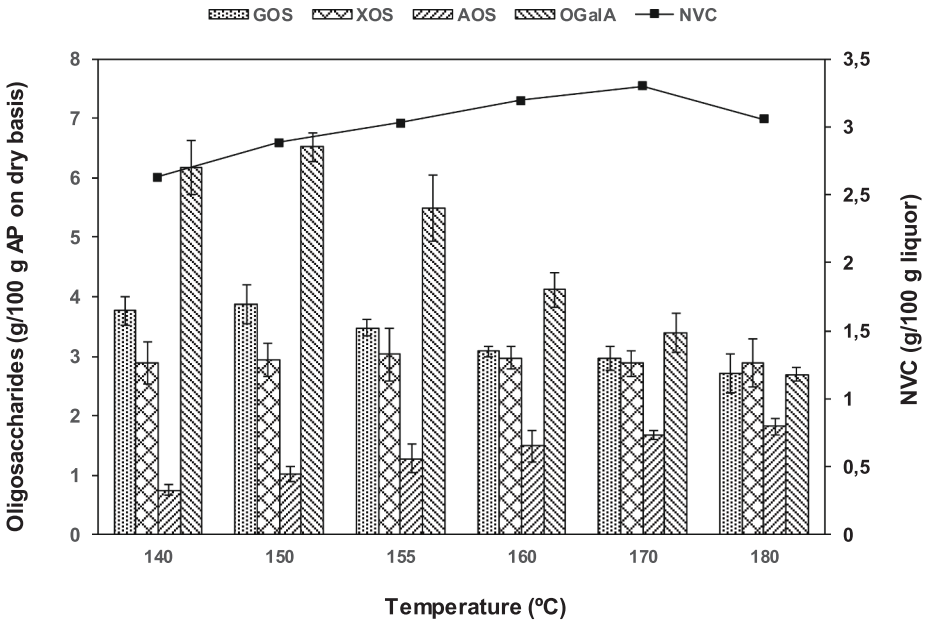

Fig. 3. Effect of hydrothermal treatment temperature on the NVC content and the composition of reaction liquors.

as monosaccharide equivalents) in the liquor as a function of the autohydrolysis temperature. The NVC increased first with temperature to reach a maximum content (3.29 g/100 g liquor) at 170 °C ($S_0 = 2.53$), and above this temperature decreased to 3.06 g/100 g liquor at 180 °C ($S_0 = 2.79$). Operating with sugar beet pulp and lemon peels, and under closely related conditions, Martínez et al. (2009a) and Gómez et al. (2013) reported NVC content in the range found in the present study. These authors also observed a decrease in NVC content in the most severe conditions evaluated. This behavior can be attributed to the decomposition reactions, which would lead to the formation of a variety of undesirable compounds (such as furans or organic acids), as reported by other authors (Martínez et al., 2009; Rico et al., 2020).

As it can be seen in Fig. 3, oligogalacturonides (OGalA) were the major component of liquors, with a maximum content of 6.51 g/100 g AP at 150 °C ($S_0 = 1.90$), which corresponded to 84.4% conversion of the initial galacturonan. This conversion yield compared favorably with those reported for other related feedstock in similar operational conditions. For instance, the maximum galacturonan solubilization from melon peels was 80.02% at 150 °C (Rico et al., 2020) and from lemon peels was 79.32% at 160 °C (Gómez et al., 2013). However, in other studies dealing with the autohydrolysis of sugar beet pulp and orange peels, it led to significantly lower galacturonan conversion yields than that obtained in this work (56.7% at 160 °C and 62.5% at 155 °C, respectively) (Martínez et al., 2009; Martínez et al., 2010). It is important to note that despite the high conversion obtained for this fraction, the minor presence of galacturonan in AP implies the significant lower content of OGalA in the autohydrolysis liquors if compared to other feedstocks such as sugar beet pulp (12.06 g/100 g raw material; (Martínez et al., 2009)); pomegranate (13.58 g/100 g raw material; (Talekar et al., 2018)) and pomelo peels (15.04 g/100 g raw material; (Liew et al., 2018)).

Other oligosaccharides detected at lower concentrations in the autohydrolysis liquors were glucooligosaccharides (GOS), xylooligosaccharides (XOS) and arabinosyl groups linked to oligomers (AOS). Under the conditions that gave rise to a higher production of OGalA (150 °C), 3.9, 2.9 and 1.0 g/100 g AP of GOS, XOS and AOS were obtained, respectively. These results were close to the ones reported by Rico et al. (2020) for melon peels treated at 165 °C.

Temperatures above 150 °C promoted a reduction in oligomers formation (up to 1.4 times lower at 180 °C), as a result of hydrolysis and decomposition reactions. At the highest temperatures tested (180 °C) the average concentration of total monosaccharides achieved a maximum concentration below 1 g/L (data not shown). In addition, degradation products (acetic acid, HMF and furfural) were detected at very low concentrations, with a total amount lower than 0.8 g/L. These values were notably lower than some of the studies cited previously, which is a benefit in the following purification to obtain food-grade oligosaccharides.

It is important to underline that the experiment carried out at 150 °C allowed to obtain the maximum concentration of total oligosaccharides (17.3 g/L), whereas the overall concentration of monosaccharides accounted for 0.5 g/L. Under these conditions, the oligosaccharides to monosaccharide mass ratio was close to 34.6, which is more favorable than the value of 16 determined for orange peel (Martínez et al., 2010).

In this study, the results indicated that the galacturonan fraction exhibited the highest susceptibility to hydrolysis reactions compared to the other structural polymers, which require more severe treatment conditions. This behavior has also been observed in other raw materials rich in galacturonan such as lemon and orange peels and sugar beet pulp, which presented a greater OGalA solubilization at temperatures around 150 and 160 °C (Gómez et al., 2013; Martínez et al., 2009; 2010).

3.2.3. *Effect of the temperature of hydrothermal processing on the phenolic compounds and antioxidant activity*

Another aspect assessed in this research was the antioxidant potential of the autohydrolysis liquors from avocado peels. Table 1 displays the profile of the liquid phases from the autohydrolysis in terms of phenolic compounds and antioxidant activities.

The highest content of phenolics was obtained for the autohydrolysis temperature of 170 °C (Table 1) with a value of 4.06 g GAE/100 g AP. Interestingly, this value was only 17% higher than that obtained at 150 °C (the optimal temperature for the extraction of oligosaccharides). Compared to other technologies used to extract antioxidant phenolics from avocado peel, the maximal phenolic content was higher than that reported by Suleria et al. (2020) using 70% ethanol for 12 h at 4 °C (1.88 g/100 g), but lower than the values using Soxhlet extraction (10.73 g GAE/100 g; (Páramos et al., 2020)) or ultrasound assisted extraction (6.35 g GAE/100 g; (Daiuto et al., 2014)). The trend observed here, a gradual increase with temperature to reach a maximum phenolic content, and then a slight decrease, probably due to degradation reactions, was previously observed in other hydrothermal treatments. As for instance, Gullón et al. (2018) performed the autohydrolysis of chestnut shell and the results exhibited a maximum value of TPC at 180 °C (3.9 g GAE/100 g chestnut shell), that decreased 1.8 times at 220 °C. The phenolic content obtained in the current work compared favorably with the values of earlier works on hydrothermal treatments of different residual streams from food industry, such as chestnut shells (Gullón et al., 2018) or purple corn cobs (Gullón et al., 2020).

Regarding the total content of flavonoids, the maximum value (7.05 g RE/100 g) was also at 170 °C, but not significantly different for the value obtained at 155 °C. Interestingly, the values obtained here are much higher than that reported for avocado extracts (0.124 g quercetin equivalents/100 g; (Suleria et al., 2020)) and for other extracts obtained from fruit peels such as pomegranate peel (3.6–5.4 g RE/100 g; (Derakhshan et al., 2018)) or citrus peel (3.3–4.9 g RE/100 g; (Wang et al., 2008)). Likewise, the total flavonoid content was substantially higher (in the range of 1.8–6.8 times higher) than those determined for other autohydrolysis liquors from residues from food industry, such as chestnut shell (4.0 g RE/100 g; (Gullón et al., 2018)), or purple corn cob (1.35 g RE/100 g; (Gullón et al., 2020)).

Three complementary methods were employed to evaluate the antioxidant activity of the autohydrolysis liquors, since no single antioxidant assay method can provide a complete picture of the antioxidant capacity of complex mixtures such as natural products (Ozgen et al., 2006). $ABTS^{\bullet+}$ and FRAP activities were maximal for the autohydrolysis liquors obtained at 170 °C. In the case of $DPPH^{\bullet}$ assay, the maximum value was reached for the 155 °C extract, but not significantly different from that at 170 °C. In a previous work, the Soxhlet extract from avocado peels showed similar values of antioxidant activity both

Table 1
Effect of temperature on the Total phenolic content (TPC), Total flavonoid content (TFC) and antioxidant activity (measured by the $DPPH^{\bullet}$, $ABTS^{\bullet+}$ and FRAP) in the Avocado peels (AP) autohydrolysis liquors. The bold numbers indicate the highest value of each of the parameters evaluated.

T (°C)	TPC (g GAE/100 g dry AP)	TFC (g RE/100 g dry AP)	$DPPH^{\bullet}$ (g TE/100 g dry AP)	$ABTS^{\bullet+}$ (g TE/100 g dry AP)	FRAP (g TE/100 g dry AP)
140	3.13 ± 0.03^{a}	$6.23 \pm 0.01^{a,b}$	4.32 ± 0.10^{a}	10.14 ± 0.07^{a}	3.44 ± 0.04^{a}
150	3.48 ± 0.02^{b}	$6.37 \pm 008^{b,c}$	4.78 ± 0.01^{b}	10.80 ± 0.25^{a}	$3.89 \pm 0.04^{b,c}$
155	3.73 ± 0.01^{c}	7.00 ± 0.04^{d}	**5.39 ± 0.04^{c}**	11.84 ± 0.47^{a}	$3.95 \pm 0.05^{b,c}$
160	3.73 ± 0.04^{c}	6.60 ± 0.03^{c}	$5.12 \pm 0.04^{b,c}$	11.92 ± 0.20^{a}	3.76 ± 0.04^{b}
170	**4.06 ± 0.01^{e}**	**7.05 ± 0.02^{d}**	4.89 ± 0.05^{b}	**12.00 ± 0.19^{a}**	**4.27 ± 0.03^{d}**
180	3.90 ± 0.04^{d}	6.13 ± 0.01^{a}	$4.74 \pm 0.03^{a,b}$	11.49 ± 0.69^{a}	$4.07 \pm 0.02^{c,d}$

with ABTS$^{\bullet+}$ and DPPH$^{\bullet}$ assays (≈ 28 g TE/100 g; (Páramos et al., 2020)). However, in the present work, differences were observed among methods, which reflected the variability in the chemical composition of avocados, influenced by the genetic context but also various external factors such as climate, processing, cultivation, etc. (Páramos et al., 2020). The highest antioxidant activity was determined with ABTS$^{\bullet+}$ assay (12.00 g TE/100 g at 170 °C), whereas FRAP assay led to lower value of Trolox equivalents (4.24 g TE/100 g at 170 °C), reflecting the difference in the ability of the antioxidant compounds present in the extracts to reduce the free radicals and ferric iron. These values, and particularly the antioxidant activity determined with DPPH$^{\bullet}$ assay, were much higher than those measured in autohydrolysis liquors from purple corn cob (0.422 g TE/100 g; (Gullón et al., 2020)) or melon peels (0.3 g TE/100 g water insoluble solid; (Rico et al., 2020)).

3.3. Characterization of the solubilized compounds from avocado peels

From a practical perspective, the manufacture of a liquor containing high amounts of both antioxidant phenolics and oligosaccharides is important to join the benefits of both fractions. In this context, although the temperature of 170 °C led to a higher TPC and TFC (4.06 and 7.05 g/100 g AP, respectively), these values were only 14 and 10% higher, respectively, compared to those of the liquor obtained at 150 °C. Additionally, regarding the oligosaccharides, 14.3 g /100 g AP were obtained at 150 °C whereas at 170 °C the amount was reduced by 24%. In this sense, 150 °C was the compromise temperature selected for the optimal extraction of oligosaccharides and antioxidant compounds.

In order to evaluate the potential applications of the extracted biomolecules under optimal autohydrolysis conditions (150 °C, $S_0 = 1.90$), this extract was analyzed by FTIR, TGA and UHPLC-TOF-MS to determine the chemical composition and thermal behavior of the biocompounds present in such extract.

3.3.1. FTIR-analysis

Infrared spectroscopy was applied to identify the type of functional groups existent in avocado peel extract. The first peak observed presents a wavelength of 3296 cm^{-1} and is attributed to the O–H stretching vibrations of hydroxyl groups as a consequence of hydrogen bonding in pectin (Raji et al., 2017) while the peak at 2922 cm^{-1} is ascribed to the stretching vibrations of C—H bonds of the carbohydrates that constitute the pectin. The patterns between 1800 and 400 cm^{-1} corresponds to the fingerprint of the sample. The bands located at 1739 cm^{-1} and 1599 cm^{-1} are attributed, respectively, to carbonyl functional groups (C = O) and asymmetric free carboxyl groups (−COO−) and corroborate the presence of pectin with methyl esterification (Dávila et al., 2019; Rico et al., 2020). The signal observed at 1410 cm^{-1} could correspond to acetyl group absorption band and the peak showed at 1238 cm^{-1} may be assigned to C-O stretching vibrations (Dávila et al., 2019; Gullón et al., 2018). One weaker band is situated at 1320–1330 cm^{-1} and is related to the COO^{-} functional group of pectin (Muthukumaran et al., 2017). The signal presented at 1142 cm^{-1} confirm the presence of arabinosyl side chains and the maximum band is located at 1014 cm^{-1} and it is attributed to C-O stretching assigned to C-OH group or C–C stretching in the carbohydrate structure (Dávila et al., 2019; Gullón et al., 2018).

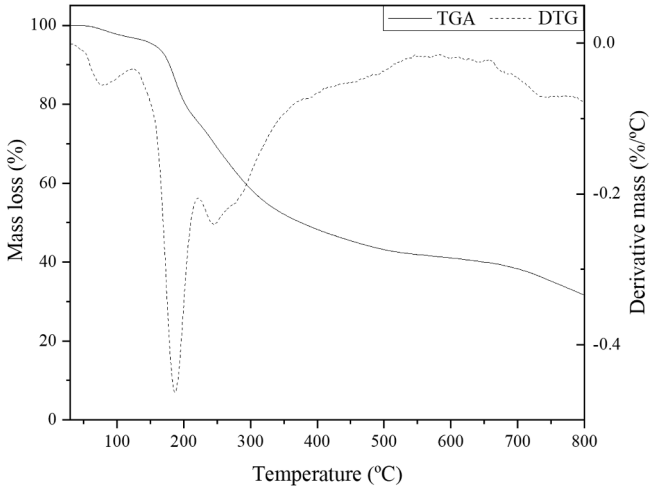

Fig. 4. Thermogravimetric curve (TGA) and first Derivative curve (DTG) of the autohydrolysis liquor obtained at 150 °C.

3.3.2. Thermal stability

The knowledge of the thermal stability of the different biomolecules present in an extract is a key property, since these extracts could be incorporated into the formulation of foods that involve heat treatments. TGA and DTG curves were plotted up to 800 °C in Fig. 4. Thermal decomposition trend is related to the individual contribution of avocado components, including cellulose, hemicellulose and lignin, mainly. These curves, like those of the rest of agro-industrial waste, follow the typical thermal decomposition profile of vegetal biomass (Monje et al., 2021).

A total of three mass loss stages were detected. The first one is known as water evaporation and a small fraction of weight associated to moisture and very light volatile compound was lost (~4.53 %) from room temperature to 150 °C. A weaker DTG peak at 73 °C corroborate the water evaporation process (Ankona et al., 2021; Bhaumik et al., 2014).

The most intense stage of mass loss (~54,42%) was identified between 150 °C to about 600 °C. This high percentage of mass loss is owing to the decomposition of hemicellulose, cellulose and lignin. It is important to note that the thermal decomposition intervals of different compounds sometimes overlap: 150–350 °C hemicellulose, 280–400 °C cellulose and 250–500 °C lignin. Consequently, the curve obtained in each stage can be considered as a combination of the decomposition of several compounds simultaneously (Monje et al., 2021). In the analysis of the derivative curve for this stage (DTG), two clearly distinguished peaks were observed at a temperature of 193 °C and 240 °C that could be attributed to hemicellulose and cellulose, respectively, based on previous reports (Gullón et al., 2018). The degradation of lignin may be related to a widely peak at a temperature of 447 °C (Monje et al., 2021).

Finally, the last thermal degradation stage occurred between 600 and 800 °C and is attributed to the decomposition of the remaining residue into gaseous compounds, including CO, CO_2, CH_4, CH_3COOH or HCOOH among others. Above 800 °C, 30.98% of the sample mass persists as a char without being degraded, which is a similar percentage to previous reports (Dávila et al., 2016). This residue may be attributed to inorganic matter present in the liquor (Dávila et al., 2019; Gullón et al., 2018).

3.3.3. Tentative identification of bioactive compounds by UHPLC-TOF-MS analysis

As far as the authors know, this is the first tentative identification of antioxidant compounds extracted by hydrothermal processing from avocado peels. UHPLC-TOF MS analysis of the ethyl acetate extract of the liquor allowed the tentative identification of 43 compounds (Table 2), which were determined based on the accurate mass data, mSigma value and retention time (when the standard was available). They fitted in various metabolite families, that included flavonoids, phenolic acids, organic acids, lignans and fatty acids. According to the peak areas, the more abundant family was that appearing in the less hydrophilic segment of the chromatographic profile. The presence of non-polar compounds such as palmitic acid and hydroxy derivatives of octadecenoic acid is in agreement with the information reported by Figueroa et al. (2018).

Hydroxy fatty acids present interesting physiological effects, such as anti-inflammatory and immunomodulatory activities (Filannino et al.,

Table 2
Tentative identification of bioactive compounds in AP extracts.

Compound	Class/subclass*	Formula	RT (min)	ΔRT [min]	*m/z* meas.	Delta (mDa)	mSigma	Area
High score (based on m/z, retention time and mSigma)								
Gallic acid	PA/HB	$C_7H_6O_5$	2.11	−0.19	169.0142	−0.03	2.4	1,606,463
Neochlorogenic acid	PA/HC	$C_{16}H_{18}O_9$	2.20	−0.15	353.0881	0.29	19.5	157,185
Procyanidin dimer B	FL/Flavonol oligomer	$C_{30}H_{26}O_{12}$	2.38	−0.05	577.1349	−0.27	32.2	3,489,454
Catechin	FL/flavonol	$C_{15}H_{14}O_6$	2.43	−0.02	289.0719	0.18	6.8	2,892,361
Epigallocatechin	FL/flavonol	$C_{15}H_{14}O_7$	2.45	0.08	305.0670	0.29	9.4	51,382
Chlorogenic acid/caffeoylquinic acid	PA/HC	$C_{16}H_{18}O_9$	2.52	−0.05	353.0879	0.09	48.1	73,607
Epicatechin	FL/flavonol	$C_{15}H_{14}O_6$	2.57	−0.03	289.0719	0.17	2.4	1,713,456
Taxifolin	FL/flavanol	$C_{15}H_{12}O_7$	3.08	−0.02	303.0511	0.05	11.6	136,382
p-Coumaric acid	PA/HC	$C_9H_8O_3$	3.16	−0.02	163.0400	−0.10	5.5	291,391
Ferulic acid	PA/HC	$C_{10}H_{10}O_4$	3.24	−0.03	193.0505	−0.08	4.3	615,185
Quercetin-hexose	FL/flavonol	$C_{21}H_{20}O_{12}$	3.40	−0.11	463.0883	0.07	3.2	902,277
Quercetin	FL/flavonol	$C_{15}H_{10}O_7$	4.31	−0.03	301.0357	0.33	2.5	473,163
Kaempferol	FL/flavonol	$C_{15}H_{10}O_6$	4.84	−0.03	285.0406	0.15	1.6	322,437
Isorhamnetin	FL/flavonol	$C_{16}H_{12}O_7$	4.96	−0.03	315.0514	0.39	11.4	176,191
Medium score (based on m/z and mSigma)								
Syringic acid	PA/HB	$C_9H_{10}O_5$	1.62		197.0457	0.18	14.8	63,636
Succinic acid	Organic acid	$C_4H_6O_4$	1.70		117.0194	0.03	2.6	272,563
Syringic acid	PA/HB	$C_9H_{10}O_5$	2.11		197.0456	0.00	0.4	269,503
Vanillic acid	PA/HB	$C_8H_8O_4$	2.16		167.0350	−0.01	2.6	963,629
Dihydrocaffeic acid/Ethyl protocatechuate	PA/HC or PA/HB	$C_9H_{10}O_4$	2.17		181.0506	−0.07	5.9	154,051
Vanillin	Phenolic aldehyde	$C_8H_8O_3$	2.18		151.0400	−0.02	8.6	167,039
Gentisic acid/Protocatechuic acid	PA/HB	$C_7H_6O_4$	2.19		153.0193	−0.05	1.9	17,361,380
Caffeic acid	PA/HC	$C_9H_8O_4$	2.20		179.0349	−0.06	36.7	75,343
Quinic acid	Organic acid	$C_7H_{12}O_6$	2.20		191.0556	−0.49	28.0	20,379
4-hydroxybenzoic acid	PA/HB	$C_7H_6O_3$	2.26		137.0244	−0.01	1.5	4,395,045
Syringic acid	PA/HB	$C_9H_{10}O_5$	2.50		197.0454	−0.18	1.2	149,360
Quinic acid	Organic acid	$C_7H_{12}O_6$	2.53		191.0563	0.22	17.6	15,052
Vanillin	Phenolic aldehyde	$C_8H_8O_3$	2.67		151.0399	−0.16	8.6	45,974
Vanillic acid	PA/HB	$C_8H_8O_4$	2.67		167.0350	0.03	9.4	229,071
Caffeic acid	PA/HC	$C_9H_8O_4$	2.67		179.0349	−0.04	4.2	860,718
Benzoic acid	PA/HB	$C_7H_6O_2$	2.79		121.0295	0.05	1.8	2,394,144
Quercetin-dihexose	FL/flavonol	$C_{27}H_{30}O_{17}$	2.81		625.1409	−0.17	14.9	133,317
Dihydrocaffeic acid/Ethyl protocatechuate	PA/HC or PA/HB	$C_9H_{10}O_4$	2.84		181.0506	−0.05	11.6	24,640
Syringic acid	PA/HB	$C_9H_{10}O_5$	2.86		197.0456	0.08	20.4	35,795
Vanillin	Phenolic aldehyde	$C_8H_8O_3$	2.93		151.0400	−0.02	7.5	109,538
Nudiposide	Lignan	$C_{27}H_{36}O_{12}$	2.97		551.2133	−0.10	4.1	1,741,576
Cinchonain	Flavonolignan	$C_{24}H_{20}O_9$	3.02		451.1037	0.24	40.9	96,526
Quercetin-O-arabinosyl-glucoside	FL/flavonol	$C_{26}H_{28}O_{16}$	3.05		595.1303	−0.20	11.5	581,333
Dihydrocaffeic acid/Ethyl protocatechuate	PA/HC or PA/HB	$C_9H_{10}O_4$	3.09		181.0506	−0.05	7.2	39,146
Kaempferol-dihexose/ Rutin/ Multinoside A	FL/flavonol	$C_{27}H_{30}O_{16}$	3.11		609.1463	0.19	23.1	130,034
(±)-Naringenin	FL/flavanone	$C_{15}H_{12}O_5$	3.23		271.0608	−0.38	40.6	13,598
Dihydrocaffeic acid/Ethyl Protocatechuate	PA/HC or PA/HB	$C_9H_{10}O_4$	3.30		181.0504	−0.21	6.8	28,035
Quercetin glucuronide	FL/flavonol	$C_{21}H_{18}O_{13}$	3.39		477.0675	0.05	20.2	79,850
Luteolin 7-O-(2́-O-pentosyl)hexoside	FL/flavone	$C_{26}H_{28}O_{15}$	3.40		579.1355	−0.09	20.7	293,268
Kaempferol-dihexose/ Rutin/ Multinoside A	FL/flavanol	$C_{27}H_{30}O_{16}$	3.59		609.1461	−0.04	2.3	782,610
(±)-Naringenin	FL/flavanone	$C_{15}H_{12}O_5$	3.59		271.0612	0.03	15.0	37,687
4-hydroxybenzoic acid	PA/HB	$C_7H_6O_3$	3.69		137.0244	−0.05	1.3	539,728
Kaempferol-hexose	FL/flavanol	$C_{21}H_{20}O_{11}$	3.71		447.0933	0.06	5.9	484,999
Luteolin 7-O-(2́-O-pentosyl)hexoside	FL/flavone	$C_{26}H_{28}O_{15}$	3.74		579.1355	−0.07	3.4	399,504
Nudiposide	Lignan	$C_{27}H_{36}O_{12}$	3.79		551.2134	−0.04	4.0	3,948,831
Isorhamnetin-hexose	FL/flavanol	$C_{22}H_{22}O_{12}$	3.82		477.1039	0.04	24.9	65,500
Kaempferol O-glucosyl-rhamnoside	FL/flavanol	$C_{27}H_{30}O_{15}$	3.95		593.1512	0.05	15.6	312,898
(±)-Naringenin	FL/flavanone	$C_{15}H_{12}O_5$	4.32		271.0615	0.34	12.8	43,062
Trihydroxyoctadecenoic acid	fatty acid	$C_{18}H_{34}O_5$	5.44		329.2335	0.12	9.2	13,230,177
Trihydroxyoctadecenoic acid	fatty acid	$C_{18}H_{34}O_5$	5.79		329.2336	0.24	11.2	7,427,580
Hydroxy-oxo-octadecenoic acid	fatty acid	$C_{18}H_{32}O_4$	6.28		311.2229	0.12	8.2	1,313,073
Hydroxy-oxo-octadecenoic acid	fatty acid	$C_{18}H_{32}O_4$	6.48		311.2230	0.23	31.1	1,441,098
Dihydroxy-octadecenoic acid	fatty acid	$C_{18}H_{34}O_4$	6.59		313.2386	0.12	4.5	515,764
Hydroxy-octadecadienoic acid	fatty acid	$C_{18}H_{32}O_3$	7.06		295.2281	0.28	4.4	1,128,073
Palmitic acid	fatty acid	$C_{16}H_{32}O_2$	8.22		255.2329	−0.07	8.7	16,764,869

*Abbreviations: PA: phenolic acid; HB: hydroxybenzoic acid; HC: hydroxycinnamic acid; FL: flavanoids

2020). The second most representative family of compounds, according to the peak areas, was phenolic acids, and particularly, the hydroxybenzoic acid subclass. Protocatechuic acid or gentisic acid (both display the same precursor ion) showed the highest signals. According to literature, both compounds can occur in avocado fruit, however protocatechuic acid is more common and more abundant (Hurtado-Fernández et al., 2013). Protocatechuic acid was found to be potent antioxidant, antibacterial, anticancer, antihyperlipidemic, antidiabetic, and anti-inflammatory (Kakkar and Bais, 2014). Other hydroxybenzoic acids with high peak areas were gallic acid, 4-hydroxybenzoic acid, benzoic acid, syringic acid and vanillic acid. Among the hydroxycinnamic acids present in the extract, the most abundant according to the peak areas were caffeic acid and ferulic acid.

Flavonoids from different subclasses were tentatively identified. The highest peak area was observed for procyanidin dimer, followed by catechin and epicatechin. Compounds belonging to flavonol, flavone and flavanone subclasses were identified: naringenin, quercetin, kaempferol, luteolin and their glucosides derivatives. The beneficial

effects of flavonoid consumption on health have been demonstrated in recent studies (de Araújo et al., 2021).

The presence of the lignan nudiposide is in accordance with previous studies in avocado peel (Figueroa et al., 2018). Other families of compounds such as organic acids (succinic and quinic), the phenolic aldehyde vanillin and the flavolignan cinchonain were tentatively identified.

4. Conclusions

The hydrothermal treatment of avocado peel effectively solubilized oligosaccharides and antioxidant phenolics. Treatment at 150 °C enabled the maximum recovery of total oligosaccharides, being OGalA the main component. Conversely, 170 °C treatment produced the highest total phenolic and total flavonoid content, and the highest antioxidant activities. The FTIR spectra showed numerous bands of oligosaccharides, and the thermogravimetric curve followed the typical thermal decomposition profile of vegetal biomass. UHPLC-TOF MS allowed to identify fatty acids, phenolic acids, flavonoids, organic acids and lignans. The findings obtained here demonstrated the great potential of AP as an economical source of bioactive agents with potential uses in food and cosmetic industries.

E-supplementary data of this work can be found in online version of the paper

CRediT authorship contribution statement

Alexandra Del Castillo-Llamosas: Investigation, Visualization, Writing – review & editing. **Beatriz Rodríguez-Martínez:** Visualization, Writing – review & editing. **Pablo G. del Río:** Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Visualization, Writing – review & editing. **Gemma Eibes:** Funding acquisition, Investigation, Validation, Visualization, Writing – review & editing. **Gil Garrote:** Visualization, Writing – review & editing. **Beatriz Gullón:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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