# Wood processing industry by-products as a source of natural bioactive compounds

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**ABSTRACT**

The chemical composition of three by-products from a fibreboards manufacture green industrial process, which only employs wood and water, was deeply evaluated. The by-products analyzed imply different steps of the industrial process and different types of wood: chips from pine, walnut and cherry tree, and chestnut- and oak- screw waters and concentrates. For all of them, total polyphenols content (TPC), and antioxidant activity (AA) have been evaluated, showing significant differences.

To characterize the most volatile compounds, an environmentally-friendly technique, solid-phase microextraction (SPME) has been employed. Besides, aqueous and generally recognized as safe (GRAS) organic extracts derived from the by-products have been prepared, and their chromatographic fingerprint was obtained by gas chromatography-mass spectrometry (GC-MS), and liquid chromatography-tandem mass spectrometry (LC-MS/MS) to identify the main extractable organic wood components.

Significant differences were observed for the studied by-products. Up to 30 and 32 different compounds were successfully identified in the screw waters, and concentrates by-products, respectively; including terpenes, sesquiterpenes, or polyphenols among others. Regarding the derived by-products extracts, up to 30 compounds were identified in the chips, highlighting the presence of 13 polyphenols in the cherry tree chips. On the other hand, 6 and 8 compounds were identified in the screw water ethanolic, and ethyl lactate-based extracts, respectively, whereas more than 20 compounds with interesting properties were found in the concentrate extracts.

This work contributes to improve the knowledge about the chemical composition of several wood industry by-products, which could be exploited to obtain natural extracts with added value for their reuse in the food, cosmetic or pharmaceutical industry.

**KEYWORDS:** wood industry by-products; waste reutilization; bioactive compounds; analytical characterization; SPME-GC-MS; LC-MS/MS.

## 1. Introduction

Worldwide, the wood industry generates a large number and a broad type of waste products. Among the different wood industry types, the related with the production of high-density fibreboards (HDF) usually employs chemical additives during the manufacture procedure, therefore, the generated by-products can be toxic and their safely reuse implies a high cost [1]. However, there is an alternative to manufacture green fibreboards based on the use of wood, from sustainable woods, and water as green raw materials. This environmentally-friendly procedure is based on the self-adhesion of the wood fibres without the need to add chemical additives. In this way, lignin, which is naturally present in wood, acts as a natural glue, preventing the emission of the toxic formaldehyde [2, 3] and obtaining ecological and biodegradable high-density fibreboards which can be re-exploited after its useful life, producing energy as a natural heat source. This green manufacture procedure also converts the different by-products generated during the green fibreboards manufacture into a highly attractive source of bioactive compounds that are originally present in the wood employed as raw material. These green by-products could be employed to obtain natural extracts with added value which could be reused in the pharmaceutical, cosmetic or alimentary industry, reducing the environmental impact of the industrial activity and obtaining, in parallel, an economical profit.

In this work, three different by-products from different steps of the industrial process have been studied. Besides, different types of wood were considered. Wooden chips from pine (*Pinus pinaster*), walnut (*Juglans regia*) and cherry tree (*Prunus avium*), coming from the first industrial step, were selected. Besides, screw waters, derived from the chips (chestnut, *Castanea sativa*, and oak, *Quercus robur*) washing, and the main industrial by-product, called concentrate, that remains after a condensation and evaporation step of the screw waters, were also investigated. Although several authors reported the characterization of wood industry by-products, most of them are focused in a specific wood type [4-6], or in the study of a unique by-product [6-8]. Therefore, there is a lack of studies regarding the complete chemical characterization of fibreboards manufacture by-products.

Depending on the structural characteristics of the studied by-products, different extraction and analysis techniques were proposed. The first approach consisted on the obtaining of the volatile composition for the screw waters and concentrates employing an environmentally friendly technique, the solid-phase microextraction (SPME). This

extraction technique can be used *in-situ*, does not require the use of organic solvents, the sample can be directly analyzed without pre-treatment, and allows the extraction and concentration of the extracted analytes in a single step. Besides, aqueous and green organic extracts, prepared in ethanol and ethyl lactate, were directly analyzed by gas chromatography-mass spectrometry (GC-MS) and by liquid chromatography-tandem mass spectrometry (LC-MS), for an exhaustive study and characterization of their chemical composition; in order to explore their potential for future reutilization in the cosmetic, food or pharmaceutical industry.

## 2. Experimental

### 2.1. Reagents and materials

Water and methanol both MS grade were supplied by Scharlab (Barcelona, Spain), ethanol (EtOH) absolute (>99.8%) was provided by VWR (Leicestershire, England), ethyl lactate was supplied by Fluka Analytical (Steinheim, Germany), and formic acid (>99%) by Merck (Darmstadt, Germany). Folin-Ciocalteu phenol reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), and gallic acid (99%) were obtained from Sigma-Aldrich (Steinheim, Germany). Sodium carbonate ($Na_2CO_3$) was provided by Panreac (Barcelona, Spain), and sodium sulfate anhydrous ($Na_2SO_4$) was provided by Carlo Erba Reagents (France). Commercial 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre housed in manual SPME holders was obtained from Supelco (Bellefonte, PA, USA). The fibre was conditioned as recommended by the manufacturer (270 ºC for 30 minutes), inserting it in the GC injector with carrier gas flow. The studied polyphenols, their CAS number, suppliers and MS/MS transitions employed for their identification are summarized in Table S1.

### 2.2. Studied by-products

The three different studied by-products, chips, screw waters, and the concentrates were provided by the wood board industry Betanzos HB (Betanzos, Galicia, NW Spain), specialized in the elaboration of high density fiberboards employing a green industrial procedure based on high-pressure pressing employing water without chemicals additives. Figure 1 partially summarizes the industrial procedure, showing the origin of the three studied by-products. The chromatographic techniques employed for their characterization are also shown.

Three different wood chips from pine tree, cherry tree, and walnut, were directly collected after the chipping procedure and kept in a container protected from light until their analysis. Screw waters and concentrates from chestnut and oak tree were collected in 2.5 L plastic bottles, and they were also kept at room temperature and protected from light until their analysis.

### 2.3. Solid-liquid and liquid-liquid extraction

To obtain the different wood chips extracts (pine tree, walnut and cherry tree), a green solid-liquid extraction was performed. Figure 2a summarizes the procedure. Seventy grams of the corresponding chips were mixed with 300 mL of water and kept under magnetic stirring. Two different temperatures were employed to perform the extraction: 25 ºC, and 80 ºC for 168 hours (a week), and 14 hours, respectively. After the corresponding extraction time, the aqueous extracts were filtered by gravity flow, and directly analyzed by SPME-GC-MS and LC-MS/MS.

For the obtaining of the chestnut- and oak- screw waters and concentrates derived-extracts, the extraction efficiency of two different solvents were tested: ethanol and ethyl lactate. Both were selected for their demonstrated extraction effectiveness of bioactive compounds from different wood industrial wastes and plants [9]. Besides, they are considered environmentally friendly and GRAS solvents (Generally Recognized As Safe) and, as such, safe agents according to the European Food Safety Authority (EFSA). Their use in food products is allowed by both the United States Food and Drug Administration (FDA) and the European Union, being a suitable option for the reutilization of the obtained extracts in the food industry. Figure 2b represents the experimental procedure. Twenty-five mL of the different screw waters and concentrates were mixed with 25 mL of the correspondent solvent (ethanol or ethyl lactate) into a Falcon 50 mL conical centrifuge tube and the mixture was centrifuged at 3500 rpm for 10 minutes employing an Ortoalresa Digicen 21centrifuge (Madrid, Spain). Afterwards, the organic supernatant was filtered by gravity flow, 1 mL was transferred to a 1.8 mL glass-vial, and $Na_2SO_4$ was added to remove possible aqueous content. Finally, the dried extract was filtered through 0.22 μm PTFE filters, and directly analyzed by GC-MS. It is important to note that the extraction procedure produced a homogeneous precipitate of the wood fibers which is easy to handle and isolate, and it can be also reused in the manufacturing process.

## 2.4. Solid-phase microextraction procedure

Aliquots of 10 mL of the corresponding (pine tree, walnut and cherry tree) chip aqueous extracts, and chestnut- and oak- organic screw waters and concentrate extracts were placed in a 22 mL glass vial. See Figure 2a for the chip aqueous extracts. The vials were sealed with aluminium caps furnished with PTFE-faced septa and immersed into a water bath maintained at 100 ºC under magnetic stirring. After 5 min of thermostating, the PDMS/DVB fibre was introduced into the vial and exposed to the headspace over the sample for 30 minutes. Afterwards, the fibre was retracted into the needle of the holder syringe, thermally desorbed in the GC injector for 5 min at 270 ºC and then GC-MS analysis was carried out.

## 2.5. Total polyphenols contents and antioxidant activity procedures

The total polyphenols content (TPC) of the raw wood by-products and the derived extracts were determined according to the Folin-Ciocalteu (FC) colorimetric method described by Singleton and Rossi [10]. The TPC was quantified employing a calibration curve prepared with gallic acid standards solutions ranging from 3 to 20 mg $L^{-1}$ ($R^2$=0.9970) and expressed as mg of gallic acid equivalents in the liquid extract (mg GAE $L^{-1}$). The antioxidant activity (AA) was determined employing a modified method of Brand-Williams et al. [11] The AA was calculated employing a calibration curve prepared with Trolox ranging from 0.1-1 mM ($R^2$=0.9994). The DPPH scavenging activity is expressed as mM Trolox equivalents in the liquid extract (mM TRE $L^{-1}$). In both cases, a Shimazdu UVmini-1240 Spectrophotometer (Japan) was employed to measure the absorbances.

## 2.6. GC-MS analysis

The GC-MS analysis was performed using an Agilent 7890A coupled to an Agilent 5975C inert mass spectra detector (MSD) with triple-axis detector and an Agilent 7693 autosampler from Agilent Technologies (Palo Alto, CA, USA). A ZB-Semivolatiles (30m × 0.25 mm i.d., 0.25 µm film thickness) column obtained from Phenomenex (Torrance, CA, USA) was employed. The oven temperature was set at 60 ºC (held 1 min) to 290 ºC at 5 ºC $min^{-1}$ (held 1 min). Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL $min^{-1}$. The total run time was 48 min. The sample volume was 1 µL when direct injection was performed (organic extracts analysis). The injector temperature was 270 ºC. The mass spectrometer detector (MSD) was operated in the electron impact (EI) ionization positive mode (+ 70 eV), and the temperatures of the

transfer line and the ion source were set at 290 ºC and 150 ºC, respectively. For an exhaustive characterization of the concentrate organic extracts, a polar DBWAX column (50 m × 0.20 mm i.d., 0.20 µm film thickness) obtained from Agilent Technologies was also employed. In this case, the oven ramp was programmed from 50 ºC (1 min) to 240 ºC at 8 ºC $min^{-1}$ (held 25.25 min), at a constant flow of 0.6 mL $min^{-1}$. The total run time was 50 min. In this case, the injector temperature was kept at 240 ºC, and the transfer line at 230 ºC.

In all cases, Full Scan (FS) acquisition mode was employed, monitoring mass/charge (*m/z)* fragments between 25-700. The tentative identification of the compounds was performed by comparison (match > 80%) between the obtained experimental MS spectral and the provided by the commercial spectral library database (NIST).

### 2.7. LC-MS/MS analysis

The identification of the polyphenols in the aqueous chips extracts was performed by LC-MS/MS. A Thermo Scientific (San José, CA, USA) instrument based on a TSQ Quantum Ultra TM triple quadrupole mass spectrometer equipped with a HESI-II (heated electrospray ionization), and an Accela Open autosampler with a 20 µL loop was employed. The chromatographic separation was achieved on a Kinetex C18 column (100 × 2.1 mm, 2.6µm, 100 Å), obtained from Phenomenex. The temperature of the column was set at 30 ºC. The mobile phase consisted on water (A) and methanol (B), both with 0.1% formic acid. The eluted gradient started with 5% of B (held 5 min), it was increased to 90% of B in 11 minutes and kept constant for 3 minutes. Finally, initial conditions were reached in 9 minutes. The injection volume was 10 µL and the mobile phase flow-rate was 0.2 mL $min^{-1}$. The total run for each injection was 25 minutes. The mass spectrometer and the HESI source were working simultaneously in the positive and negative mode, monitoring two or three MS/MS transitions for each compound. MS/MS transitions for the identified polyphenols are summarized in Table S1.

## 3. Results and discussion

### 3.1. Wood chips

Wood chips are one of the first by-products derived from the wood processing industry (see Figure 1). Several studies reported the presence of volatile organic and antioxidant compounds in wood chips extracts. However, most of them are focused in the study of oak wood, which is the main raw material employed for the wine and other alcoholic

beverages aged. Besides, in most cases the extraction of the wood chips is long-time consumption, with several experimental steps, and is performed employing toxic organic solvents such as dichloromethane [6-8].

In this case, three different species of trees were evaluated: pine tree, cherry tree, and walnut. To characterize the volatile and bioactive compounds present in the chips, the efficiency of an environmentally friendly solid-liquid extraction procedure, employing water at two different temperatures, 25 ºC and 80 ºC has been tested (the procedure is detailed in Section 2.3). Several parameters such as pH, density, TPC and AA for the obtained extracts were evaluated, and the results are summarized in Table 1.

The chromatographic profile for the three different wooden chips aqueous extracts was obtained by SPME-GC-MS. The procedure is described in Section 2.4. Figure 3a shows the obtained chromatogram for each wood specie, after performing the solid-liquid extraction at the two studied temperatures. As can be seen, the chromatographic profile was clearly different for the three evaluated wood species. However, no significant differences regarding the composition of the extracts were observed between performing the chips extraction at 25 ºC or 80 ºC, although the abundance of the peaks was clearly higher when the extraction was performed at 80ºC. For that reason, Figure 3b shows the detailed chromatographic profile for each chip aqueous extract obtained at 80 ºC. Chromatographic peaks were tentatively identified by comparing their mass spectra with those included in the NIST database commercial library (match > 80%). The SPME-GC-MS analysis of the aqueous chip extracts revealed the presence of 17 different compounds that are summarized in Table 2. Eleven out of the 17 identified compounds were found in the pine tree chips extract, whereas 6 and 5 were identified in the walnut, and cherry tree chip extracts, respectively. Highlights the abundance of α-terpineol (peak 2) in the pine tree chip extract. This compound is a well-known monoterpene, usually employed as perfuming agent in cosmetics and as flavoring in the food and beverages industry. Several biological properties of α-terpineol include its antioxidant and antitumoral activity, as well as cardiovascular and antihypertensive effects. Regarding the most abundant detected compounds in the cherry tree and walnut chip extracts, respectively, trans-benzylideneacetone (peak 3) is employed as flavoring agent in food and perfumes, and 1,2,3-trimethoxy-5-allylbenzene (peak 7), also known as elemicin is a phenylpropene with a high antibacterial activity [12, 13].

The three different chips extracts were also directly analyzed by LC-MS/MS analysis to identify the presence of polyphenols. In this case, an unequivocal identification of the

compounds was possible using commercially available standards of polyphenols, and working in SRM mode, monitoring two or three MS/MS transitions per compound (see Table S1). Results are summarized in Table 3. As can be seen, up to 13 different polyphenols were detected in the extracts, being all of them found in the cherry tree chips extract, whereas on the other hand, 8 and 7 of such polyphenols were found in the walnut, and pine tree chips extract, respectively. The presence of polyphenols, compounds which possess a high radical scavenging activity, provides an additional value to the extracts due to the demonstrated beneficial properties of them (antioxidants, anti-inflammatory, antimicrobial...). Three of them, 2,4,6-trihydroxybenzoic acid, procyanidine A2 and orientin, were only identified in the cherry tree chips aqueous extract. To the best of our knowledge, this is the first time that the presence of these 3 polyphenols is reported in cherry trees [14]. Figure 4 shows a SRM reconstructed chromatogram for the cherry tree chips extract.

It is important to note that, although TPC and AA values for the aqueous chips extracts were clearly lower than those obtained for the other studied by-products (see Table 1); the possibility to obtain environmentally friendly chip extracts employing only water without the addition of organic solvents and chemical additives, could favor the reuse of them as flavor agents in the cosmetic or in the alimentary industry, revalorizing the potential of this primary wood industry by-product.

### 3.2. Screw waters

Basic physico-chemical parameters, and TPC and AA values were obtained for chestnut and oak screw waters, and they are summarized in Table 1.

Both screw waters were also directly analyzed by SPME-GC-MS (the procedure was previously described in Section 2.4). Figure 5a shows the overlapped chromatograms for both screw waters. As can be seen, the chromatographic profile was similar for both, although the abundance of the identified compounds was clearly higher in the oak screw water (red chromatogram). Figure 5b shows the individual chromatogram for each screw water, and the identified compounds are summarized in Table 4. As can be seen, up to 30 different organic compounds were identified in the screw waters, being the most abundant ones the sesquiterpenes γ- and β-eudesmol (peaks 18 and 20), and hinesol (peak 19), especially in the oak screw water. Several studies reported the beneficial properties of these compounds, that are considered as antitumoral, antioxidants and antimicrobials [15]. Other identified compounds with interesting properties in both screw waters were

oxygenated monoterpenes (eucalyptol (peak 2), β-linalool (peak 3), α-terpineol (peak 4)) and sesquiterpenes (globulol (peak 16), and fatty acids such as myristic acid (peak 22), palmitoleic acid (peak 25), hexadecanoic acid (peak 26), linoleic acid (peak 27), and oleic acid (peak 28).

Chestnut and oak screw water organic extracts, in ethanol and ethyl lactate, were also obtained (see Section 2.3), and directly analyzed by GC-MS analysis. Figure 6a and Figure 6b show the obtained chromatograms for the ethanolic and ethyl lactate-based extracts, respectively, for the chestnut and oak screw waters. Here, the chromatographic profile was completely different depending on the extraction solvent employed, but similar for both types of screw waters. The identified compounds are summarized in Table 5. Six organic compounds were found in the ethanolic extract (peaks 1-6), whereas 8 different compounds (peaks 7-14) were identified in the ethyl lactate-based extract. Highlights the presence of two acids: acetic acid (peak 1) in the ethanolic extracts and lactic acid (peak 12) in the ethyl lactate extracts for both types of screw waters. The presence of these compounds is usually associated with the wood carbohydrates and lipids degradation. Other identified compounds, also associated with sugars degradation, were furfuryl alcohol (peak 3) and pyranone (peak 4), which have been reported in oak wood extracts [7]. Besides, monoterpene alcohols such as linalol (peak 2), was found only in the ethanolic chestnut screw water extract, and geraniol (peak 11) in ethyl lactate-based screw waters extracts.

### 3.3. Concentrates

The density, pH, TPC and AA values for the chestnut and oak concentrates have been evaluated and they are summarized in Table 1. In view of the high AA and TPC values compared with the other studied by-products, both concentrate samples were analyzed by SPME-GC-MS and also their derived organic extracts, in ethanol and ethyl lactate were directly analyzed by GC-MS employing two different chromatographic columns, a polar, and a non-polar column for their exhaustive characterization.

Figure 7a shows the chromatographic profile obtained by SPME-GC-MS for the chestnut (black), and oak (red) concentrates. Up to 32 different organic compounds were identified in both concentrates, summarized in Table 6. It has been observed the presence of furanic aldehydes and ketones coming from the thermic degradation of celluloses and hemicelluloses, such as 5-methylfurfural (peak 1), and 5-(hydroxymethyl)furfural (peak 3), 5-butyl-4-methyldihydro-2H(3H)-furanone (peak 7), 2,3,4-trimethoxydibenzofuran

(peak 14) or 2,4'-dihydroxy-3'-methoxyacetophenone (peak 15). Several compounds related with the thermal decomposition of lignin, such as syringol (peak 8), its derivatives phenolic aldehydes syringaldehyde (peak 20) and vanillin (peak 9) have been also identified in both concentrates, and their presence have been reported in oak wood extracts [6-8].

Although a high number of organic compounds with interesting properties have been identified in the chestnut and oak concentrates, the direct use of these wood manufacture by-products is complex due to their high viscosity (see Figure 1 and Table 1), and high density. Therefore, organic extracts in ethanol and ethyl lactate were obtained, and deeply characterized by GC-MS employing both non-polar and polar chromatographic column. Since the obtained results were similar for both concentrate extracts, only results for chestnut concentrate derived extracts are shown. Figure 7b and Figure 7c shows the overlapped chromatogram for the chestnut concentrate extracts (ethanolic in black, ethyl lactate in blue) obtained in the non-polar, and polar chromatographic column, respectively. The identified compounds are also summarized in Table 6.

Several compounds identified in the organic extracts have been also previously identified in the concentrate raw material, such as 5-methyl furfural (peak 1), syringol (peak 8), vanillin (peak 9), antiarol (peak 17), and syringaldehyde (peak 20). Besides, several syringol and vanillin derivatives such as acetosyringone (peak 41), syringic acid (peak 42), and homosyringic acid (peak 43) and methyl vanillyl ketone (peak 37) have been also identified in both ethanolic and ethyl lactate-based concentrates extracts. The presence of these compounds has been reported in oak and chestnut wood extracts [6-8, 16].

On the other hand, the use of a polar chromatographic column allowed the identification of several acids which were not identified employing the non-polar column, such as acetic acid (peak 45), formic acid (peak 47) or lactic acid (peak 50). Besides, 4 compounds derived from sugars degradation, furfural (peak 46), α-furfuryl alcohol (peak 48), 2(5H)-furanone (peak 49), and pyranone (peak 51) could be successfully identified employing the polar column. The presence of these compounds have been reported in different wood extracts, and some of them have been described as responsible of the 'toasted' and 'honeyed' organoleptic characteristics, positively valued in wood-aged alcoholic beverages [7, 16].

## 4. Conclusions

This work contributes to the bioactive profiling of three wooden industry by-products, such as wood chips, screw waters and concentrates obtained from different types of wood. A high number of volatile and semi-volatile organic compounds from different chemical nature have been identified in the studied by-products, and in their derived aqueous, ethanolic and ethyl lactate extracts. Highlights the presence of terpenes, sesquiterpenes, omega-3 fatty acids, and precursors of fragrance synthesis. Most of the identified compounds present antioxidant, antimicrobial, antifungal and interesting organoleptic properties, demonstrated that these industrial wastes could be an interesting option for their reuse in the food, pharmaceutical and/or cosmetic industry, reducing the environmental impact of the wood industry activity and obtaining, in parallel, an economical profit.

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## Figure captions

**Figure 1.** Schematic representation of the industrial wood fibreboards manufacture procedure, showing the origin of the studied by-products and the chromatographic techniques employed for their characterization.

**Figure 2.** Experimental procedure for obtaining **a)** aqueous wood chips extracts; **b)** screw water and concentrate organic extracts.

**Figure 3.** Cherry tree, walnut and pine tree aqueous extracts: SPME-GC-MS analysis **a)** comparison between the studied extraction temperatures; **b)** identified compounds.

**Figure 4.** Cherry tree chips aqueous extract: SRM reconstructed chromatogram obtained by LC-MS/MS analysis.

**Figure 5.** Chestnut and oak screw water: SPME-GC-MS analysis **a)** overlapped chromatograms; **b)** identified compounds.

**Figure 6.** Chestnut and oak screw organic extracts (GC-MS analysis) prepared in **a)** ethanol; **b)** ethyl lactate. *Differences between retention time are due to the different solvents employed.

**Figure 7.** Chestnut and oak concentrates: **a)** SPME-GC-MS analysis; **b)** organic extracts: GC-MS analysis (non-polar column); **c)** organic extracts: GC-MS analysis (polar column).

**FIGURES**

**Figure 1**

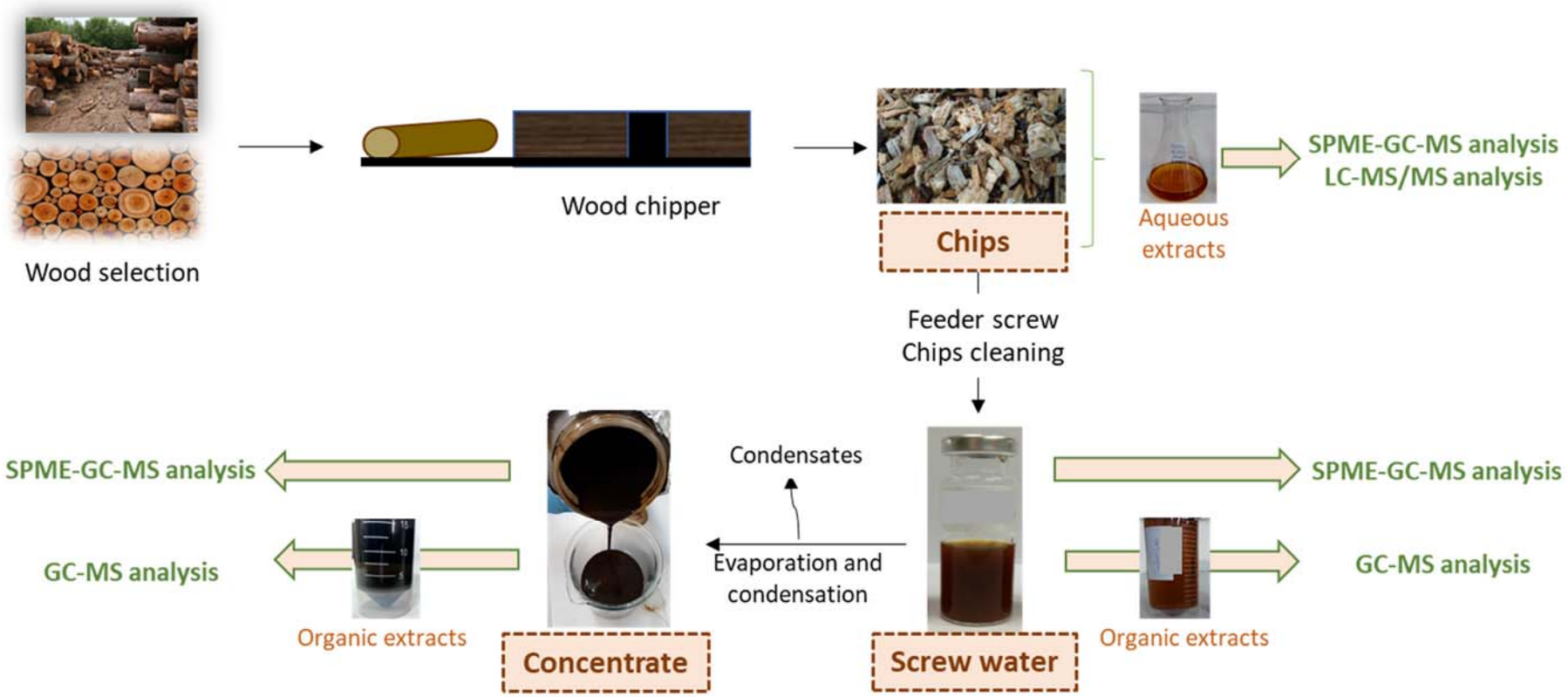


**Figure 2**

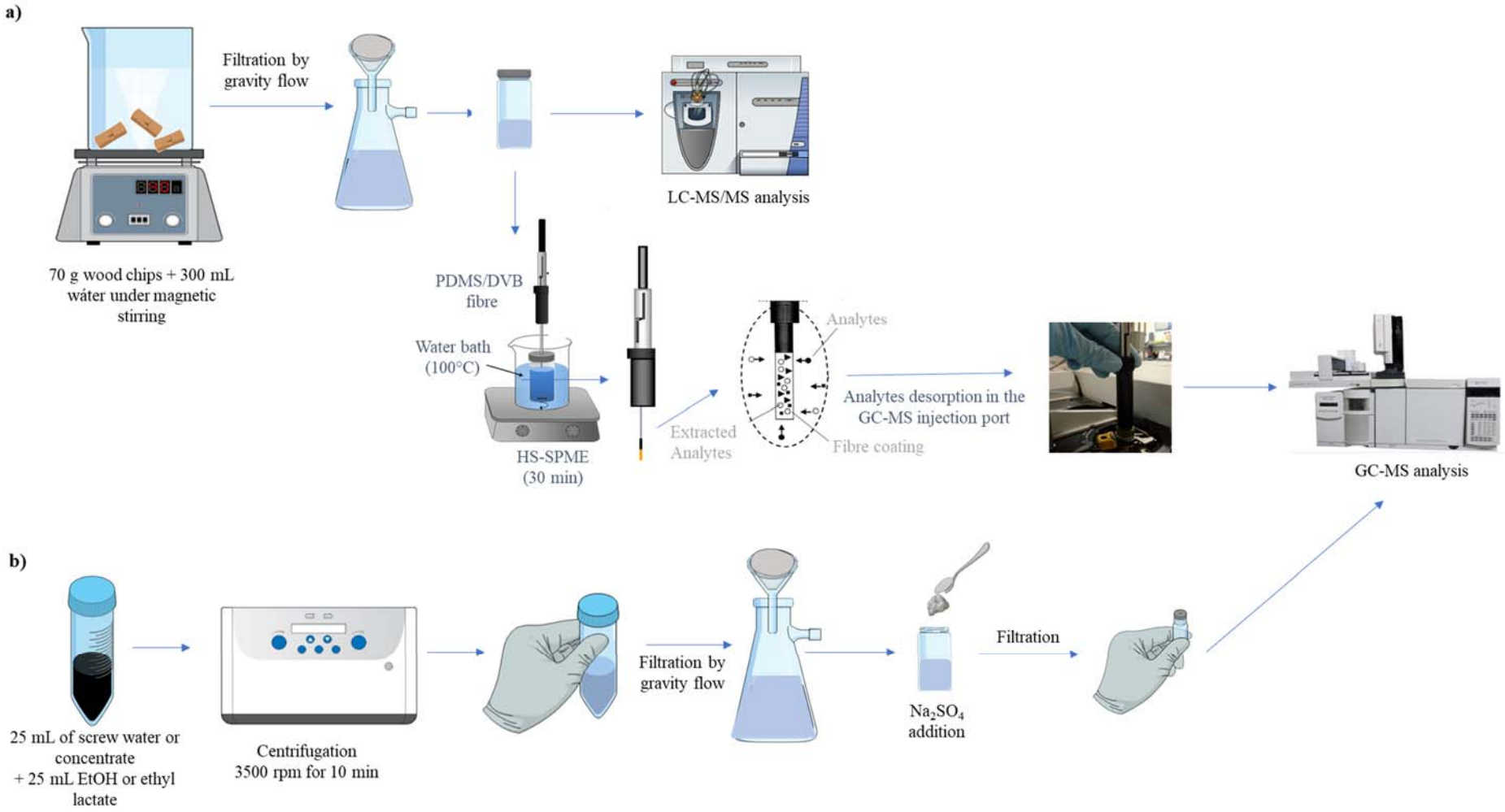
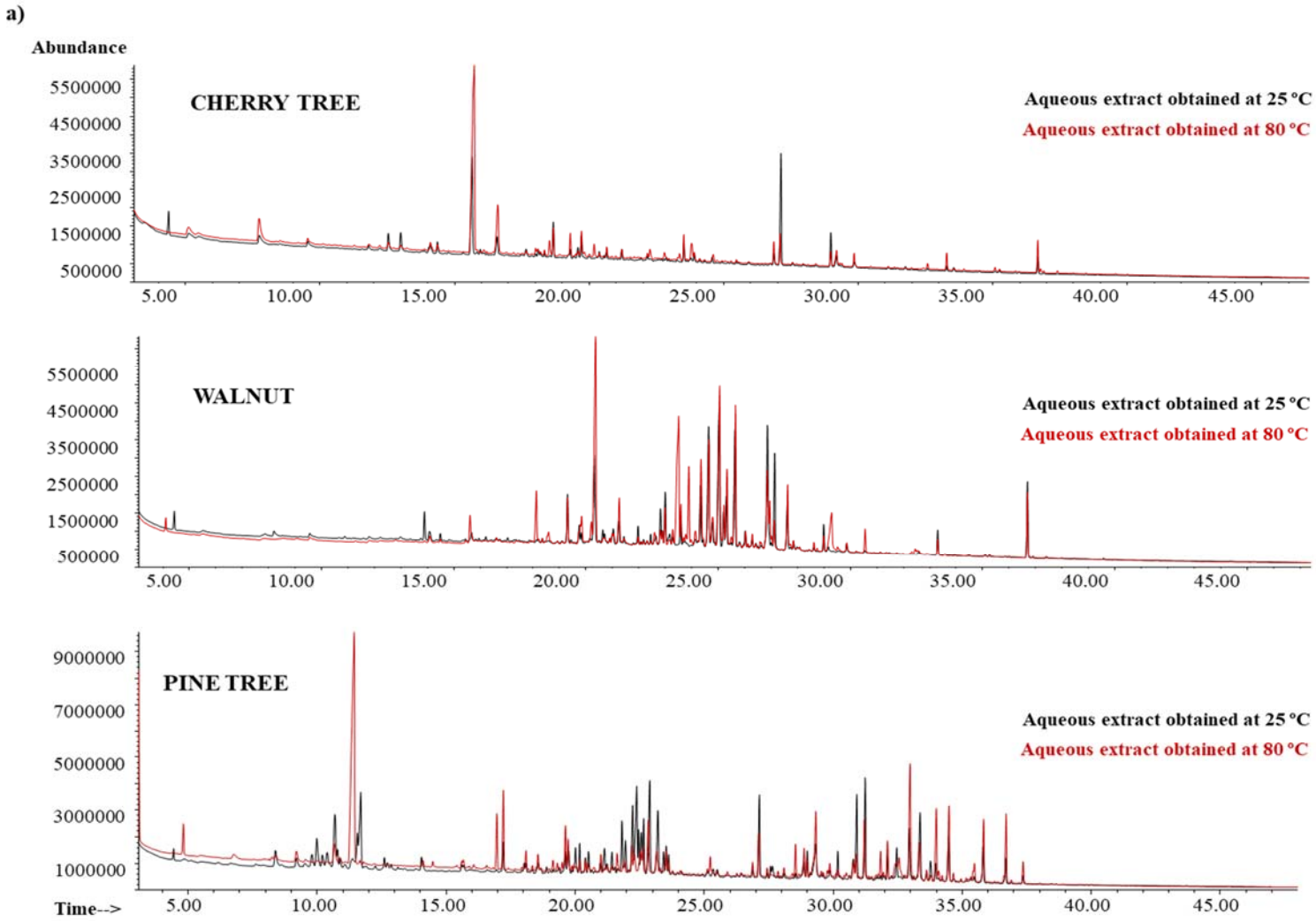

a)
Filtration by gravity flow
LC-MS/MS analysis
70 g wood chips + 300 mL water under magnetic stirring
PDMS/DVB fibre
Water bath (100°C)
HS-SPME (30 min)
Extracted Analytes
Analytes
Fibre coating
Analytes desorption in the GC-MS injection port
GC-MS analysis
b)
25 mL of screw water or concentrate + 25 mL EtOH or ethyl lactate
Centrifugation 3500 rpm for 10 min
Filtration by gravity flow
$Na_2SO_4$ addition
Filtration

**Figure 3**


a)
Abundance
CHERRY TREE
Aqueous extract obtained at 25 °C
Aqueous extract obtained at 80 °C
5500000
4500000
3500000
2500000
1500000
500000
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
WALNUT
Aqueous extract obtained at 25 °C
Aqueous extract obtained at 80 °C
PINE TREE
Aqueous extract obtained at 25 °C
Aqueous extract obtained at 80 °C
9000000
7000000
5000000
3000000
1000000
Time-->

b)

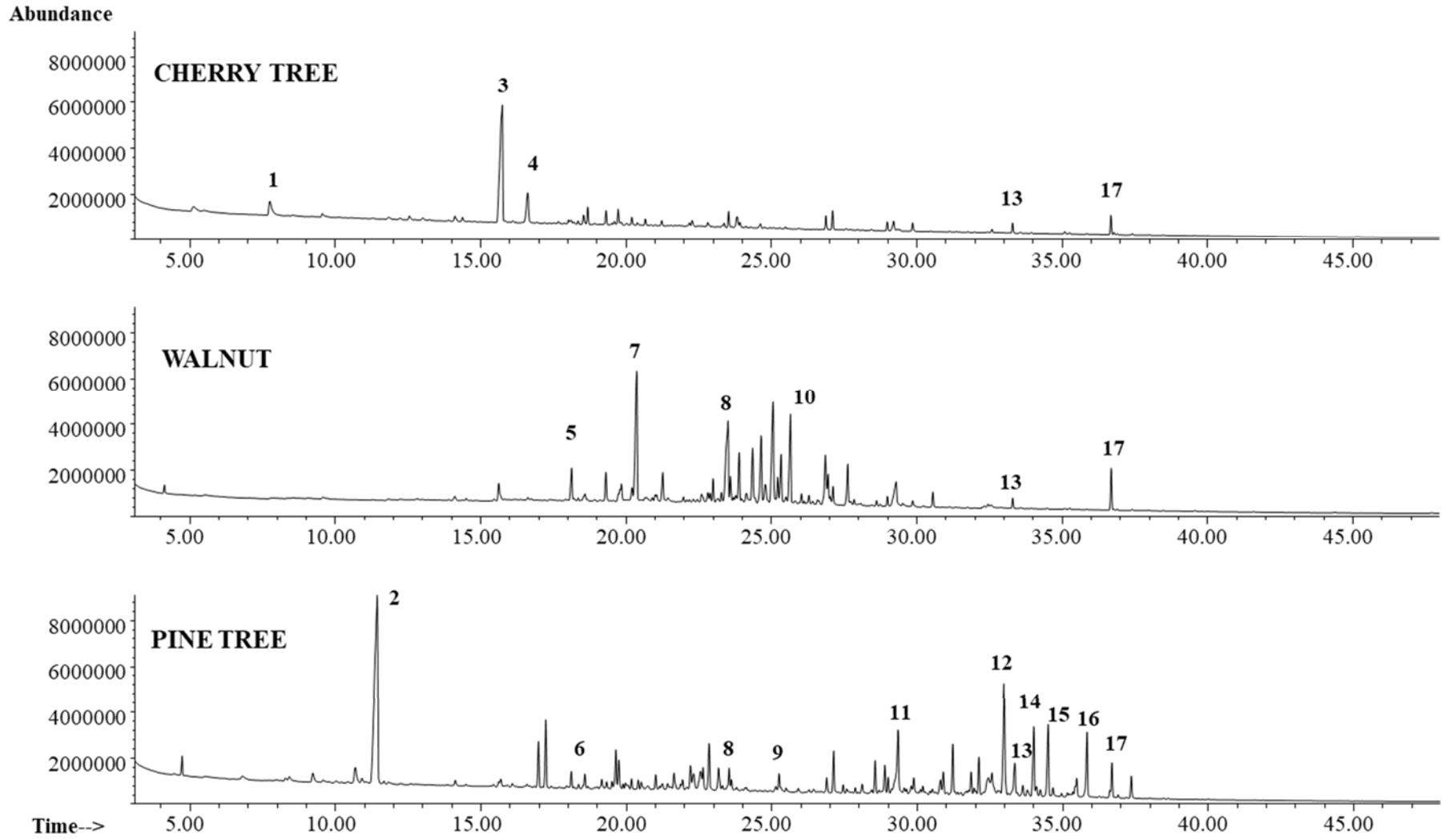

Abundance
CHERRY TREE
WALNUT
PINE TREE
Time-->
8000000
6000000
4000000
2000000
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

**Figure 4**

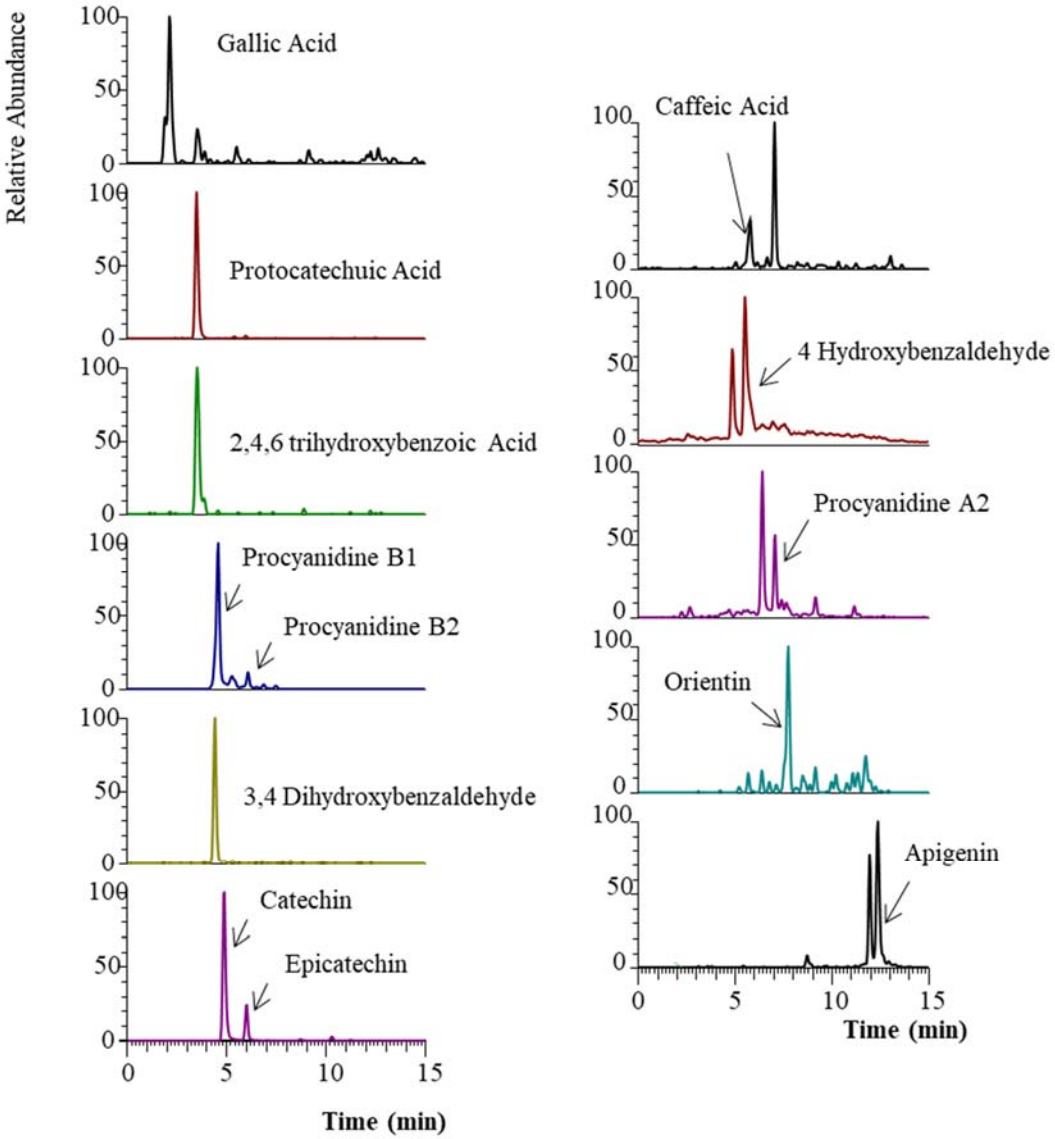

Relative Abundance
Gallic Acid
Protocatechuic Acid
2,4,6 trihydroxybenzoic Acid
Procyanidine B1
Procyanidine B2
3,4 Dihydroxybenzaldehyde
Catechin
Epicatechin
Caffeic Acid
4 Hydroxybenzaldehyde
Procyanidine A2
Orientin
Apigenin
100
50
0
0
5
10
15
Time (min)

**Figure 5**

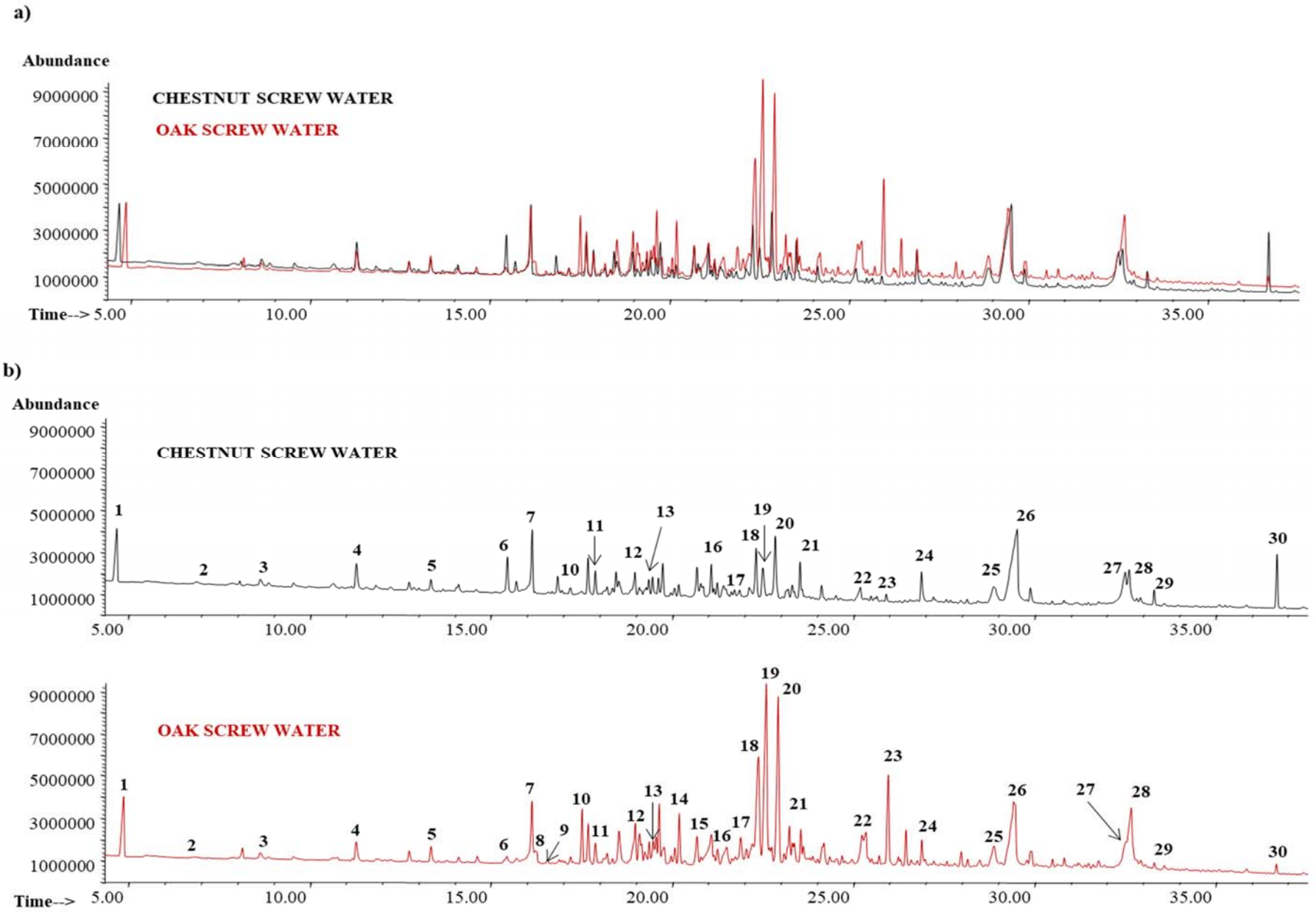
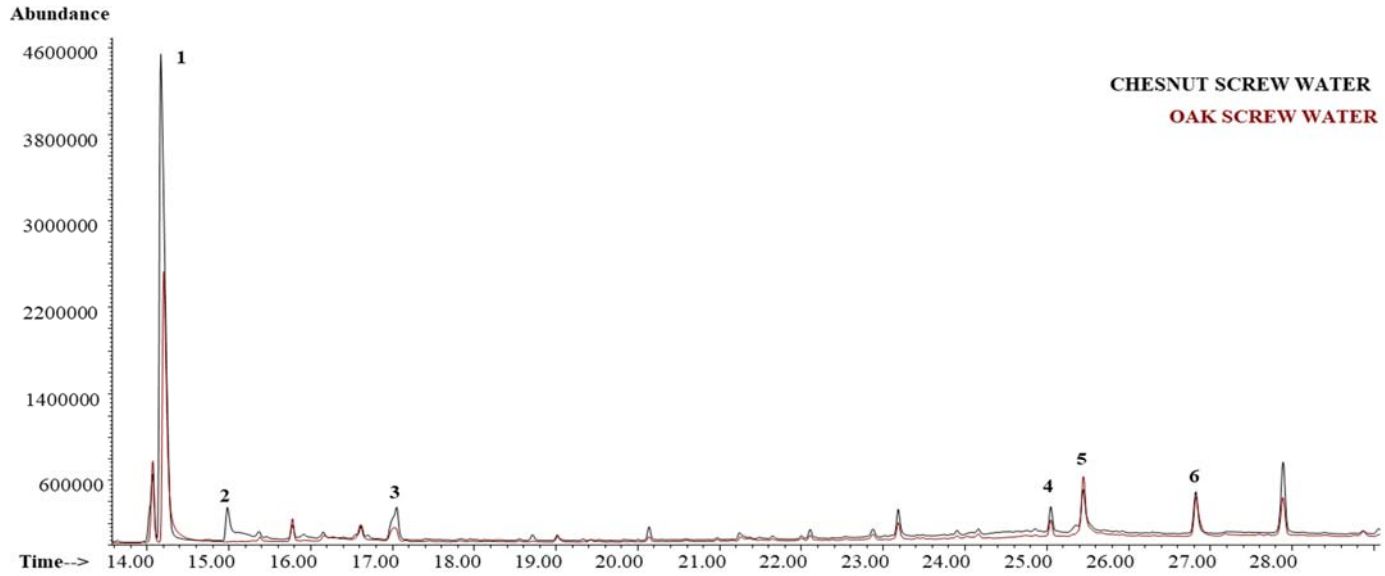

a)
Abundance
CHESTNUT SCREW WATER
OAK SCREW WATER
9000000
7000000
5000000
3000000
1000000
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
b)
Abundance
CHESTNUT SCREW WATER
OAK SCREW WATER
Time-->

**Figure 6**

a)


Abundance
4600000
3800000
3000000
2200000
1400000
600000
1
2
3
4
5
6
CHESNUT SCREW WATER
OAK SCREW WATER
Time-->
14.00
15.00
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
27.00
28.00

b)

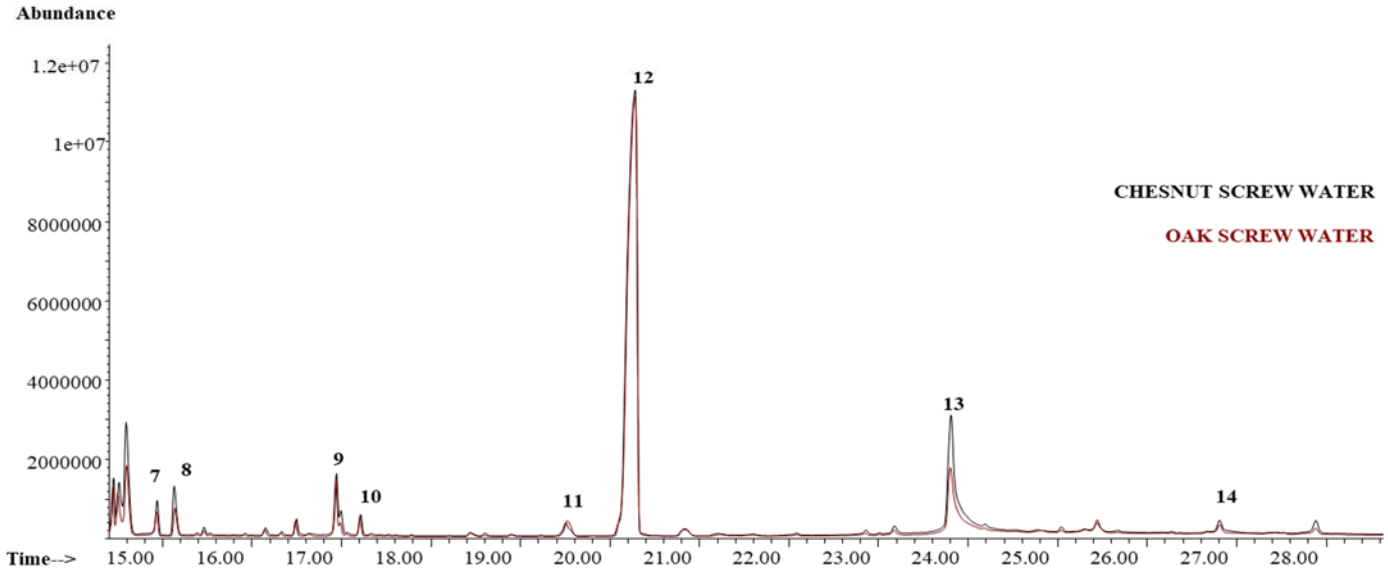

Abundance
1.2e+07
1e+07
8000000
6000000
4000000
2000000
7
8
9
10
11
12
13
14
CHESNUT SCREW WATER
OAK SCREW WATER
Time-->
15.00
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
27.00
28.00

**Figure 7**

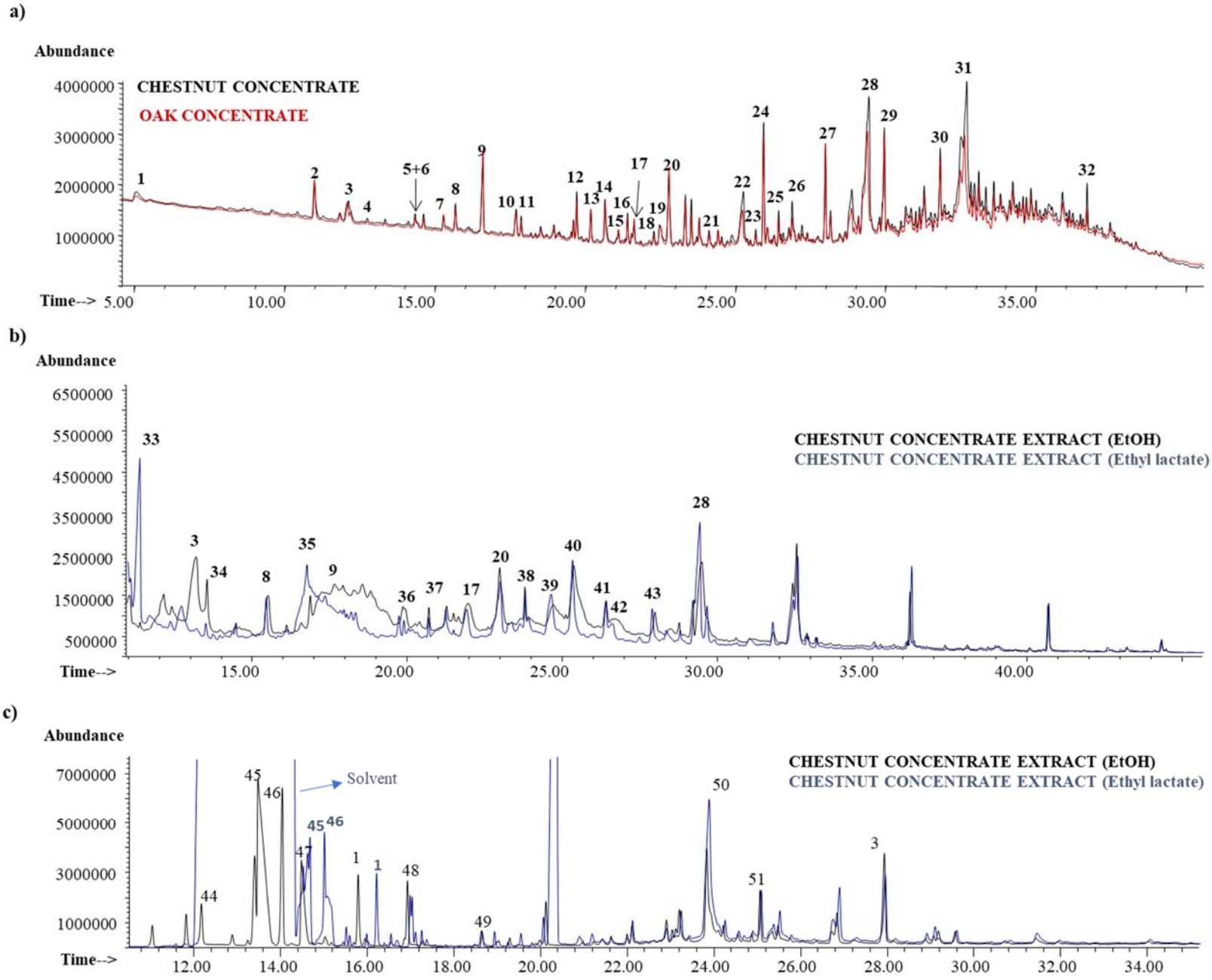

a)
Abundance
CHESTNUT CONCENTRATE
OAK CONCENTRATE
Time-->
b)
Abundance
CHESTNUT CONCENTRATE EXTRACT (EtOH)
CHESTNUT CONCENTRATE EXTRACT (Ethyl lactate)
Time-->
c)
Abundance
CHESTNUT CONCENTRATE EXTRACT (EtOH)
CHESTNUT CONCENTRATE EXTRACT (Ethyl lactate)
Solvent
Time-->

**Table 1.** Basic physicochemical parameters, total polyphenols content (TPC), and antioxidant activity (AA) for the studied wood by-products.

| By-product | | | Density (g $mL^{-1}$) | pH | TPC (mg GAE $L^{-1}$) | AA (mM TRE $L^{-1}$) |
|---|---|---|---|---|---|---|
| Chips | Water extract, 25 ºC | Pine Tree | 0.9962 | 4.20 | 378 ± 3 | 2.43 ± 0.03 |
| | | Cherry Tree | 0.9942 | 6.13 | 164 ± 3 | 0.81 ± 0.01 |
| | | Walnut | 0.9907 | 6.77 | 160 ± 1 | 0.46 ± 0.03 |
| | Water extract, 80 ºC | Pine Tree | 0.9721 | 3.76 | 638 ± 3 | 5.47 ± 0.04 |
| | | Cherry Tree | 0.9947 | 4.78 | 536 ± 2 | 2.98 ± 0.06 |
| | | Walnut | 0.9812 | 4.75 | 496 ± 1 | 2.08 ± 0.02 |
| Screw water | Raw material | Chestnut | 0.885 | 3.45 | 9895 ± 95 | 40.4 ± 0.4 |
| | | Oak | 0.991 | 3.57 | 8800 ± 252 | 41.7 ± 0.8 |
| | Ethyl lactate extract | Chestnut | 1.0035 | 3.85 | 3653 ± 60 | 32.0 ± 0.2 |
| | | Oak | 1.0244 | 4.02 | 2765 ± 78 | 21.0 ± 0.3 |
| | Ethanolic extract | Chestnut | 0.9224 | 4.22 | 3553 ± 63 | 27.0 ± 0.1 |
| | | Oak | 0.9324 | 4.35 | 2650 ± 27 | 18.0 ± 0.3 |
| Concentrate | Raw material | Chestnut | 1.1574 | 3.60 | 53633 ± 1586 | 279 ± 20 |
| | | Oak | 1.1840 | 3.48 | 40260 ± 2313 | 223 ± 14 |
| | Ethyl lactate extract | Chestnut | 1.0544 | 4.45 | 31938 ± 1281 | 214 ± 3 |
| | | Oak | 1.0351 | 4.15 | 31768 ± 464 | 187 ± 2 |
| | Ethanolic extract | Chestnut | 0.9462 | 4.79 | 25582 ± 167 | 161 ± 3 |
| | | Oak | 0.9438 | 4.46 | 25905 ± 779 | 163 ± 6 |

**Table 2.** Identified compounds by SPME-GC-MS analysis in the wooden chips aqueous extracts (solid-liquid extraction at 80 ºC for 16 hours).

| Number | Compound | CAS | Ret time (min) | Cherry tree | Walnut | Pine tree |
|---|---|---|---|---|---|---|
| 1 | Camphol | 507-70-0 | 10.72 | X | | |
| 2 | α-Terpineol | 98-55-5 | 11.35 | | | X |
| 3 | trans-Benzylidenacetone | 1896-62-4 | 15.71 | X | X | |
| 4 | Acetoacetophenone | 93-91-4 | 16.72 | X | | |
| 5 | Pentyl-α-pyrone | 27593-23-3 | 18.11 | | X | |
| 6 | Humulene | 6753-98-6 | 18.12 | | | X |
| 7 | 1,2,3-Trimethoxy-5-allylbenzene | 487-11-6 | 20.35 | | X | |
| 8 | 4-hexyl-2,5-dihydrofuran-3-acetic acid | 39212-21-0 | 23.50 | | | X |
| 9 | Benzyl benzoate | 120-51-4 | 25.26 | | | X |
| 10 | Curzerene | 17910-09-7 | 25.30 | | X | |
| 11 | n-Hexadecanoic acid | 57-10-3 | 29.31 | | | X |
| 12 | Pimaral | 472-39-9 | 32.96 | | | X |
| 13 | Butyl palmitate | 111-06-8 | 33.30 | X | X | X |
| 14 | Pimara-7,15-dien-3-one | 7715-48-2 | 34.03 | | | X |
| 15 | Sclarene | 511-02-4 | 34.50 | | | X |
| 16 | Methyl dehydroabietate | 1235-74-1 | 35.80 | | | X |
| 17 | Isobutyl stearate | 646-13-9 | 36.70 | X | X | X |

**Table 3.** Identified polyphenols in the different wooden chips aqueous extracts (solid-liquid extraction at 80 ºC for 16 hours). LC-MS/MS analysis.

| Polyphenols | Cherry tree | Walnut | Pine tree |
|---|---|---|---|
| Gallic acid | XX | XX | XX |
| Protocatechuic acid | XX | XX | XX |
| 2,4,6 Trihydroxybenzoic acid | XX | | |
| Procyanidine B1 | XX | XX | XX |
| 3,4 Dihydroxybenzaldehyde | XX | XX | XX |
| Catechin | XX | | XX |
| Procyanidine B2 | X | X | |
| Caffeic acid | X | XX | |
| 4 Hydroxybenzaldehyde | XX | XX | XX |
| Epicatechin | XX | XX | |
| Procyanidine A2 | XX | | |
| Orientin | X | | |
| Apigenin | XX | | XX |

**Table 4.** Identified compounds in the chestnut and oak screw waters. SPME-GC-MS analysis.

| Number | Compound | CAS | Ret. time (min) | Chestnut | Oak |
|---|---|---|---|---|---|
| 1 | Methoxy-phenyloxime | 222866* | 4.65 | X | X |
| 2 | Eucalyptol | 470-82-6 | 6.89 | X | X |
| 3 | β-Linalool | 78-70-6 | 8.64 | X | X |
| 4 | α-Terpineol | 98-55-5 | 11.31 | X | X |
| 5 | 1-decanol | 112-30-1 | 13.10 | X | X |
| 6 | Eugenol | 97-53-0 | 15.46 | X | X |
| 7 | Geranyl acetate | 105-87-3 | 16.12 | X | X |
| 8 | n-Decanoic acid | 334-48-5 | 16.23 | X | |
| 9 | Decanoic acid, ethyl ester | 110-38-3 | 16.53 | X | |
| 10 | 2,6-Di-tert-butylphenol | 128-39-2 | 17.51 | X | X |
| 11 | cis-Isoeugenol | 5912-86-7 | 17.90 | X | X |
| 12 | Geraniol butyrate | 106-29-6 | 19.36 | X | X |
| 13 | δ-Cadinene | 483-76-1 | 19.60 | X | X |
| 14 | α-Calacorene | 21391-99-1 | 20.18 | | X |
| 15 | Dodecanoic acid | 143-07-7 | 21.08 | X | |
| 16 | Globulol | 51371-47-2 | 21.26 | X | X |
| 17 | Methoxyeugenol | 6627-88-9 | 21.42 | X | X |
| 18 | γ-Eudesmol | 1209-71-8 | 22.32 | X | X |
| 19 | Hinesol | 23811-08-7 | 22.51 | X | X |
| 20 | β-Eudesmol | 473-15-4 | 22.83 | X | X |
| 21 | Isopropyl-1,6-dimethylnaphthalene | 483-78-3 | 23.20 | X | X |
| 22 | Myristic acid | 544-63-8 | 25.10 | X | X |
| 23 | Diethylene glycol monododecyl ether | 3055-93-4 | 25.60 | X | X |
| 24 | 5-hydroxycalamenene | 55012-72-1 | 25.90 | X | X |
| 25 | Palmitoleic acid | 373-49-9 | 28.88 | X | X |
| 26 | n-Hexadecanoic acid | 57-10-3 | 29.47 | X | X |
| 27 | Linoleic acid | 60-33-3 | 32.50 | X | X |
| 28 | Oleic acid | 112-80-1 | 32.60 | X | X |
| 29 | Hexadecanoic acid, butyl ester | 111-06-8 | 33.30 | | X |
| 30 | Isobutyl stearate | 646-13-9 | 36.68 | X | X |

* NIST number

**Table 5.** Identified compounds in the screw water organic extracts. GC-MS analysis.

| Number | Compound | CAS | Ret. Time (min) | EtOH extracts | | Ethyl lactate extracts | |
|---|---|---|---|---|---|---|---|
| | | | | Chestnut | Oak | Chestnut | Oak |
| 1 | Acetic acid | 7785-70-8 | 14.46 | X | X | | |
| 2 | Linalol | 123-35-3 | 15.07 | X | | | |
| 3 | Furfuryl alcohol | 470-82-6 | 17.54 | X | X | | |
| 4 | Pyranone | 673-84-7 | 25.05 | X | X | | |
| 5 | Glycerin | 78-70-6 | 25.52 | X | X | | |
| 6 | 3-Pyridol | 7216-56-0 | 26.82 | X | X | | |
| 7 | Formic acid | 64-18-6 | 15.15 | | | X | X |
| 8 | 2,3-Butanediol | 24347-58-8 | 15.54 | | | X | X |
| 9 | Diethyl fumarate | 623-91-6 | 16.94 | | | X | X |
| 10 | Ethyl succinate | 123-25-1 | 17.22 | | | X | X |
| 11 | Geraniol | 106-24-1 | 19.50 | | | X | X |
| 12 | Lactic acid | 50-21-5 | 20.19 | | | X | X |
| 13 | L-Lactic acid | 79-33-4 | 23.81 | | | X | X |
| 14 | 3-Pyridinol | 109-00-2 | 26.90 | | | X | X |

**Table 6.** Identified compounds in the chestnut and oak concentrates. SPME-GC-MS analysis.

| Number | Compound | CAS | Concentrate | | Chestnut concentrate extracts | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | EtOH | Ethyl Lactate | EtOH | Ethyl Lactate |
| | | | Chestnut | Oak | Non-polar column | | Polar column | |
| 1 | 5-Methyl furfural | 620-02-0 | X | X | | | X | X |
| 2 | 1-(2-Butoxyethoxy)ethanol | 54446-78-5 | X | X | | | | |
| 3 | 5-(Hydroxymethyl)furfural | 67-47-0 | X | X | X | X | X | X |
| 4 | cis-Geraniol | 106-25-2 | X | X | | | | |
| 5 | 2-Methoxy-4-vinylphenol | 7786-61-0 | X | X | | | | |
| 6 | 1,8-Terpin | 80-53-5 | X | X | | | | |
| 7 | 5-Butyl-4-methyldihydro-2(3H)-furanone | 39212-23-2 | X | X | | | | |
| 8 | Syringol | 91-10-1 | X | X | X | X | | |
| 9 | Vanillin | 121-33-5 | X | X | X | | | |
| 10 | Phenol, 4-methoxy-3-(methoxymethyl)- | 59907-65-2 | X | X | | | | |
| 11 | Isoeugenol | 97-54-1 | X | X | | | | |
| 12 | (+)-δ-Cadinene | 483-76-1 | X | X | | | | |
| 13 | Mellein | 1200-93-7 | X | X | | | | |
| 14 | 2,3,4-Trimethoxydibenzofuran | 88256-11-5 | X | X | | | | |
| 15 | 2,4'-Dihydroxy-3'-Methoxyacetophenone | 18256-48-9 | X | X | | | | |
| 16 | Methoxyeugenol | 6627-88-9 | X | X | | | | |
| 17 | Antiarol | 642-71-7 | X | X | X | X | | |
| 18 | γ-Eudesmol | 1209-71-8 | X | X | | | | |
| 19 | Homovanillic acid | 306-08-1 | X | X | | | | |
| 20 | Syringaldehyde | 134-96-3 | X | X | X | X | | |
| 21 | 3-Methoxy-4-hydroxycinnamaldehyde | 458-36-6 | X | X | | | | |
| 22 | Myristic acid | 544-63-8 | X | X | | | | |
| 23 | Diethylene glycol monododecyl ether | 3055-93-4 | X | X | | | | |
| 24 | 1,4-Di-tert-butylbenzene | 1012-72-2 | X | X | | | | |
| 25 | Hexadecane, 2,6,10,14-tetramethyl- | 638-36-8 | X | X | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 26 | Pentadecanoic acid | 1002-84-2 | | X | | | | |
| 27 | Nonadecane | 629-92-5 | X | X | | | | |
| 28 | n-Hexadecanoic acid | 57-10-3 | X | X | X | X | | |
| 29 | Eicosane | 112-95-8 | X | X | | | | |
| 30 | Heneicosane | 629-94-7 | X | X | | | | |
| 31 | Oleic Acid | 112-80-1 | X | X | | | | |
| 32 | n-Butyl stearate | 123-95-5 | X | X | | | | |
| 33 | 2-(Methoxymethoxy)propanoic acid | 81327-29-9 | | | | X | | |
| 34 | 2-Acetylresorcinol | 699-83-2 | | | X | X | | |
| 35 | Pyrogallic acid | 87-66-1 | | | | X | | |
| 36 | 3,4-Dihydro-6-hydroxycoumarin | 2669-94-5 | | | X | X | | |
| 37 | Methyl vanillyl ketone | 2503-46-0 | | | X | X | | |
| 38 | Methoxyeugenol | 6627-88-9 | | | | | | |
| 39 | 3-(4-Hydroxy-3-methoxyphenyl)propionic acid | 1135-23-5 | | | X | X | | |
| 40 | Desaspidinol | 437-72-9 | | | X | X | | |
| 41 | Acetosyringone | 2478-38-8 | | | X | X | | |
| 42 | Syringic acid | 530-57-4 | | | X | X | | |
| 43 | Homosyringic acid | 4385-56-2 | | | X | X | | |
| 44 | Acetone alcohol | 67-64-1 | | | | | X | |
| 45 | Acetic acid | 64-19-7 | | | | | X | X |
| 46 | Furfural | 98-01-1 | | | | | X | X |
| 47 | Formic acid | 64-18-6 | | | | | X | |
| 48 | α-Furfuryl alcohol | 98-00-0 | | | | | X | X |
| 49 | 2(5H)-Furanone | 497-23-4 | | | | | X | X |
| 50 | L-Lactic acid | 79-33-4 | | | | | X | X |
| 51 | Pyranone | 156511* | | | | | X | X |

* NIST number

# Supplementary material

# Wood processing industry by-products as a source of natural bioactive compounds

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**Table S1.** Retention time and MS/MS transitions for the identified polyphenols in the aqueous chips extracts.

| Polyphenols[a] | CAS | Retention time (min) | MS/MS transitions (Collision energy, eV)[b] |
|---|---|---|---|
| Gallic acid | 149-91-7 | 2.03 | 169.02 → 125.04 (17)<br>169.02 → 153.1 (15) |
| Protocatechuic acid | 99-50-3 | 3.30 | 152.98 → 109.04 (17)<br>152.98 → 91.04 (28)<br>152.98 → 108.03 (26) |
| 2,4,6-trihydroxybenzoic acid | 487-70-7 | 3.34 | 168.98 → 150.99 (17)<br>168.98 → 83.02 (23)<br>168.98 → 107.02 (22) |
| Procyanidine B1 | 20315-25-7 | 4.33 | 577.03 → 407.07 (26)<br>577.03 → 288.93 (25)<br>577.03 → 424.97 (26) |
| Procyanidine B2 | 29106-49-8 | 5.18 | 577.03 → 407.07 (26)<br>577.03 → 288.93 (25)<br>577.03 → 424.97 (26) |
| 3,4-dihydroxybenzaldehyde | 139-85-5 | 4.47 | 137.07 → 136.11 (21)<br>137.07 → 91.09 (24)<br>137.07 → 92.13 (25) |
| Catechin | 225937-10-0 | 4.55 | 289.00 → 245.02 (17)<br>289.00 → 203.11 (22) |
| Epicatechin | 490-46-0 | 5.72 | 289.00 → 245.02 (17)<br>289.00 → 203.11 (22) |
| Caffeic acid | 331-39-5 | 5.52 | 178.98 → 135.03 (19)<br>178.98 → 134.01 (28) |
| 4-hydroxybenzaldehyde | 123-08-0 | 5.64 | 122.97 → 95.04 (13)<br>122.97 → 51.1 (36)<br>122.97 → 77.96 (20) |

| | | | |
|---|---|---|---|
| Procyanidine A2 | 41743-41-3 | 6.95 | 577.09 → 287.02 (32)<br>577.09 → 136.99 (62) |
| Orientin | 28608-75-5 | 7.69 | 577.09 → 425.08 (13)<br>447.16 → 327.14 (23)<br>447.16 → 357.16 (22) |
| Apigenin | 520-36-5 | 12.42 | 269.09 → 117.12 (37)<br>269.09 → 149.12 (26)<br>269.09 → 151.062 (26) |

[a] All polyphenols standardards were supplied by Sigma-Aldrich. [b] Underlined values: Quantification MS/MS transitions