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Abstract:

Tannins are phenolic compounds with considerable abundance in nature. They have attracted significant attention lately owing to their huge variety of potential applications. Accordingly, the tannin-related activity in terms of research has undergone a great boost, especially as green feedstock for materials in several fields. Nevertheless, the extraction process remains as the main bottleneck for their valorization, due to their heterogeneous nature. In the present review, a comprehensive study of the main types of tannins extraction techniques was carried out based on the works from the last 20 years. The literature review was carried through analysis of an initial sample of works followed by snowballing process, obtaining the main extraction parameters of each method. Thereby, the different tannins extraction methods were assessed and their major strengths and weaknesses elucidated. Moreover, a direct comparison between the different techniques was done, leading to the main prospectives for the efficient and clean tannins extraction and production.

Keywords: tannin, polyphenols, novel extraction techniques, green production

Abbreviations: GA-gallic acid, HHDP-hexahydroxyphenic acid, EA-ellagic acid, SLE-Solid-liquid extraction, HWE-hot water extraction, SFE-supercritical fluid extraction, PWE-pressurized water extraction, MAE-microwave assisted extraction, UAE-ultrasound assisted extraction.

Highlights:

- The great potential of tannins is hindered by their extraction process
- A literature review was carried out assessing the main tannins extraction methods
- Novel extraction techniques represented a greener option for tannins production
- Combination of novel techniques is an interesting option for industrial scale up

1. INTRODUCTION

Tannins are the most abundant components extracted from biomass, after cellulose, hemicelluloses and lignin (Arbenz and Avérous, 2016). Besides, they represent the second most extensive source of phenolic compounds after lignins (Laurichesse and Avérous, 2014).

Among the vegetal kingdom, tannins are extensively well distributed in both terrestrial and aquatic environments (Barbehenn and Peter Constabel, 2011). Terrestrial tannins, can be found in tropical, arid and semi-arid areas but also in other regions, like Atlantic or Mediterranean ones (Balogun et al., 1998; Jackson et al., 1996). They are present in high concentrations in several species such as *Schinopsis balansae* (quebracho wood), *Acacia mearnsii* (black mimosa bark), *Pinus radiata* and *Pinus nigra* (pine species), *Quercus spp* (oak bark.) and *Castanea sativa* (chestnut wood). They are also found in considerable amounts in various seeds (cocoa, guarana, kola, areca) and leaves (hamamelis, green tea) (Bele et al., 2010; Lochab et al., 2014). They are visibly present too in everyday life products like tea or wine (Mattivi et al., 2009). On the other hand, in aquatic environments tannins occur in smaller extent and prominently in non-vascular plants such as algae (Kirke et al., 2017).

Tannins major features are derived from their phenolic nature. For instance, their antioxidant capacity is linked to the phenolic rings present in their structure, which can act as electron scavenger to trap ions and radicals. Owing to this antioxidant nature, tannins are widely utilized in different areas such as the pharmaceutical, medical or food industry (Chen et al., 2016; Ismail et al., 2016; Park et al., 2014). Tannins phenolic character makes them a potential source of products in the chemical industry as well, as substituent in phenolic resins for several applications (Chupin et al., 2015; Jahanshaei et al., 2012; Ramires and Frollini, 2012).

This abundance in nature and variety of applications have encouraged a growing tendency in the tannins-related research in the last 20 years (figure 1).

Accordingly, they are considered an attractive family of compounds in terms of potential applications and environmental friendliness. However, one important aspect of tannins is their heterogeneous nature which makes impossible to settle a universal method for their extraction (Hagerman, 1988). The yield, purity and composition of the extracts rely normally on several parameters such as the vegetal source, technique employed, extraction time, temperature etc. (Bacelo et al., 2016). Thereby the extraction of tannins from vegetable residues is a process, which constitutes a crucial keypoint for their reuse, valorization and their sustainable production (Bacelo et al., 2017).

In the literature there have already been efforts towards the analysis of the phenolic compounds extraction from plants by different methods (Khoddami et al., 2013; Xu et al., 2017). However, plants polyphenols include a vast range of compound such as flavonoids, phenolic acids, tannins, stilbenes and lignans. For this reason, these works usually lack of specificity concerning the results given. This review was focus only on the extraction of tannins and therefore the results

were provided in terms of specific tannin amounts or tannin equivalents. Moreover, the discussion and evaluation of the different methods presented is exclusively oriented to the tannins cleaner production.

This study aims to describe the evolution of the existing methods for tannin extraction through a comprehensive critical literature review. A detailed comparison between the different techniques was carried out. The main strengths and weaknesses of each methodology are presented, providing a better understanding in the matter and the future lines for the tannins cleaner and more efficient manufacture.

The work structure is divided in several parts. After the introduction, section 2 is presented covering a brief state of the art on the field of tannins related to the tannin extraction. Then section 3, describes the methodology employed for carrying out this research. Section 4 displays the main results related to tannins extraction by the different methods, an in-depth comparison between them and a full discussion of the major advantages and disadvantages of each one. The study is concluded with the main outcomes and future perspectives.

2. BACKGROUND

2.1. Tannin definition

The "tannin" definition has its origin in the primary function of this group of compounds i.e. tanning. The tanning process has been important along history since it allowed the protection of animal skins turning them into leather by means of plant extracts. The first species reported for tanning leather was oak, which was actually designated with the name "tann" among the Celts (Arapitsas, 2012; Frutos et al., 2004).

One of the first tannins definitions was given by A. Seguin in 1796, who described them as substances in vegetable extracts used for converting animal skins into stable leather (Bele et al., 2010). Nevertheless, it was not until the early 1960s that a more accurate definition of tannin was introduced by Swain and Bate-Smith in 1962. They defined tannins as "*naturally occurring water soluble polyphenolic compounds having a molecular weight between 500 and 3000, capable of precipitating alkaloids as well as gelatin and other proteins from aqueous solutions*"(Bate-Smith and Swain, 1962). This definition is the one most frequently found and cited within the literature

2.2. Tannin classification

The categorization of tannins based on their structural aspects and chemical characteristics is the most extended, since it offers a proper framework for further study. Traditionally, tannins were divided into two major classes namely condensed and hydrolysable tannins. However, currently two other types are also considered i.e. complex tannins and phlorotannins.

Chemically, condensed tannins are defined as polymeric flavonoids (Hagerman, 2002). However, they can appear as oligomers as well, when they are composed of two to ten monomeric units

(Haslam, 2007). In the form of polymeric flavonoids they have limited to no solubility in water, whereas in oligomeric form they are water soluble (Bennick, 2002). Within the flavonoids group, condensed tannins are considered as flavanols, since they are composed of flavan-3-ol moieties (figure 2) (Dai and Mumper, 2010).

The flavan-3-ols units can display different structures depending on the type of *A* and *B* rings present. *A* ring can appear as a phloroglucinol or resorcinol moieties (McGraw, 1989), whereas *B* ring can be arranged as a catechol or pyrogallol units. These combinations lead to the formation of several monomers of condensed tannins (table 1).

The compounds showed in table 1 are the precursors of various types of condensed tannins. In this sense, the condensed tannins whose structure is exclusively composed of (epi)catechins are designated as procyanidins. These are the most abundant type present in plants (Hümmer and Schreier, 2008). On the other part, those tannins mainly formed by (epi)fisetinidol, (epi)robinetinidol and (epi)gallocatechin units, are labelled as profisetinidin, prorobinetidin and prodelphindin respectively.

Hydrolysable tannins are heteropolymers composed of polyphenolic acids and their derivatives, esterified to a polyol (Frutos et al., 2004). This polyol, generally a carbohydrate, forms a central core to which several polyphenolic acid units are attached via ester bonds (figure 3).

Gallic acid (GA) is the most basic block attached to the core of the monomeric units (Hernes and Hedges, 2004). Gallic acid moieties can yield other derivatives such as hexahydroxydiphenic acid units (HHDP), via oxidative coupling of two or more molecules (Hartzfeld et al., 2002). In turn, the HHDP units can spontaneously lactonize to ellagic acid (EA) moieties upon hydrolysis (Landete, 2011). In figure 4, the transformation between the different polyphenolic acids, which can be present in hydrolysable tannins structure are showed.

The distinctive property of hydrolysable tannins is their ability of being fractionated hydrolytically into their basic components. This is due to their ester bonds, which are susceptible to break via hydrolysis under acidic and basic conditions. Thererby, they are usually classified into two main subcategories i.e. gallotanins and ellagitannins.

- <u>*Gallotannins*</u>: they represent the simplest kind of hydrolysable tannins and consist of galloyl or digalloyl units linked to a polyol core and therefore they have the ability to yield gallic acid from the hydrolysis reaction.
- <u>*Ellagitannins*</u>: this kind of tannins are characterized by having one to several HHDP units attached to a polyol core. Upon hydrolysis, ellagitannins are able to produce HHDP free units, which spontaneously turn into the dilactone (ellagic acid).

Another type of tannins out of the traditional tannin classification is complex tannins. This kind is characterized by the present of monomeric units of hydrolysable and condensed tannins (Hatano et al., 1991). They are composed of a gallotannin or ellagitannin moiety and a flavan-3-ol building

block connected through a carbon-carbon linkage. This type represents a minoritary group within the tannins family. A typical example of this kind of compounds is accutisim A (figure 5).

The other type of tannins discovered in the recent years is phlorotannins. This group is prominently found in brown algae and is composed of phloroglucinol units (1,3,5-trihydroxybenzene). The research carried out lately on this group of tannins, has led to the structural elucidation of more than 150 compounds with a large range of molar masses between 126-625000 g·mol-1 (Glombitza and Pauli, 2003; Lopes et al., 2012; Sathya et al., 2017).

Structurally phlorotannins form dehydro-oligomers and polymers of phloroglucinol moieties linked via aryl-aryl (C-C) and diaryl ether bonds (C-O) (Koivikko et al., 2008).

Considering the previous information, it is clear tannins can display a variety of structures resulting in diverse chemical compositions. This aspect, which discussed in the next point, is of considerable importance, since it can have a direct impact over the extraction efficiency.

2.3. Tannins abundance and occurrence in nature

In nature, tannin content depends on several aspects such as the plant part and species considered. Within the same species, the tannin content is reported to vary between the different parts with special abundance in barks, leaves, seeds, roots and rhizomes (Bele et al., 2010). In addition, their content can also vary with seasonal and environmental factors e.g. water availability, temperature, light intensity and soil quality (Frutos et al., 2004). These points have a relevant importance, since they can influence the results of the different extraction methods. In the literature, there are several works assessing the effect of different species and plant parts on the tannin extraction results (Geoffroy et al., 2017; Tabaraki et al., 2013). In this sense, it was reported by Cheng et al. (2012) that the variety of the grape employed significantly influenced the amount of tannins quantified in the extracts (Cheng et al., 2012). They found that the extracts of the variety *Pinot Noir* presented higher amount of tannins (gallic acid equivalents) than *Pinot Meunier*. This was attributed to the different viticultural practices and environmental conditions. Moreover, the amount of tannins was higher in the seeds compared to skin and pomace. In another work, tannins from different spices were extracted via microwave and ultrasound and significant differences regarded. Again, the variety of spice was confirmed to have a major role. Thus, the extraction for *Crocus sativus* resulted in a tannin amount thirty times higher than that of *Coriandrum sativum* (Gallo et al., 2010). Besides, the spices were reported to provide higher tannin amounts in the extracts by means of microwave assisted extraction than ultrasound.

Regarding tannin chemical composition, species have a direct influence as well. It has been reported that different plants species display diverse physico-chemical properties, derived from the distinct types of tannins present (Mangan, 1988). In the previous section, it was discussed that the different type of tannins can lead to various chemical compositions, based on their structure. Thus depending on the species, diverse types of tannins could be extracted and therefore the tannin composition of the extracts would be different. A research carried out by Bianchi et al.

(2015), proved that the tannin composition of the extracts from different wood barks species extracted under the same conditions showed several divergences (Bianchi et al., 2015). Thereby, a predominant amount of prodefinidins was determined in Silver fir, whereas a higher amount of procyanidins was found for European Larch. They reported too, that the tannins composition of these species substantially differ from those of tropical species such as Mimosa and Quebracho. This divergences were also displayed on another work on tannin extraction from the seeds of different varieties of grapes (Mattivi et al., 2009). The results showed significant variations between the major tannin monomers present in the different grape species.

3. METHODS AND RESEARCH DESIGN

In this section, the different steps followed for carrying out the bibliographic review are showed, including the search, selection and analysis of articles and limitations.

In the preparation of this review, two bibliographic databases were selected: Scopus and Web of science (all databases). Scopus is reported to cover more than 21500 journals from social, life, health and physical sciences (Elsevier, 2016) whereas Web of science includes over 12000 different journals from science, arts and humanities (Thomson Reuters, 2013). For this reason, these two directories were chosen since they are said to comprise the major part of the articles related to the topic of tannins cleaner production. The selection of the published works was refine by selecting different subjects of interest. A previous search based on the topics of tannin definition, classification and distribution in nature was carried out to provide some background on the field (section 2). Then, the main search linked to the major topic of this work i.e. extraction of tannins was performed. First, general information was seeked about each technique to introduce the main principles of the extraction methods. Afterwards, the results from each method (main extraction parameters) were searched, aiming the comparison between the different techniques and the assessment of their major strengths and weaknesses (section 4).

3.1. Choice of search terms and selection of articles

Regarding the major topic, a general bibliographic search was firstly made by using the search string [tannin AND extraction]. This search produced approximately 4500 hits, from which the main methods of tannin extraction and production were obtained. The selection of the different methods was based on the search of keywords in the articles titles and abstracts (e.g. *ultrasound assisted extraction, solvent extraction, pressurized water extraction*). Then, a narrower search (based on these terms) was done focusing specifically on each extraction technique and giving a considerable smaller number of hits. The parameters employed for this search are presented in table 2. All the hits given in this table, were scanned by their titles, abstracts and keywords. Then the most relevant articles were imported to the Mendeley© reference management system. From this sample, the articles were sorted into eight different categories:

1) Conventional tannins extraction with organic solvents
2) Tannins extraction with hot water
3) Tannins extraction with ionic liquids
4) Tannins extraction with supercritical fluids
5) Tannins extraction with pressurized hot water or subcritical water
6) Tannins extraction assisted by microwave
7) Tannins extraction assisted by ultrasound
8) Comparison of tannins extraction with several extraction methods

The articles that did not belong to any category or that were duplicated in a previous category were removed. To this sample of selected and categorized articles, a semi structured snowballing approach followed (Wohlin and Claes, 2014). Thus, it was possible to add to our sample works that were not found in the previous search and categorization (figure 6).

3.2. Method of analysis and limitations of research

The final sample of articles was analysed by thoroughly examine their content (specially the results and discussion section). Thus, bibliometric information about the main extraction parameters was gathered and summarized for each article. These parameters include the plant species extracted, conditions of extraction (temperature, pressure and times), solvents involved, extraction yields and tannin content of the extract. The data collected was analysed to discuss the main results and tendencies and to compare the divergences between the extraction methods.

Regarding the limitations of the review, it was decided to focus mainly on peer-reviewed articles written in English. The period of time selected was comprising the last 20 years of research on the field (between 1997-2018).

4. RESULTS AND DISCUSSION

Within this section, the main parameters of the tannin extraction methods are presented and examined. A comprehensive comparison between the different techniques is intended as well.

4.1. Extraction parameters for each extraction process

Here the conditions used and the yields obtained for each extraction procedure are presented according to the sample of papers selected from the literature. The aim is the identification of the strengths and weaknesses of each method and the influence of the different parameters over the process.

4.1.1. Solid-liquid extraction (SLE)

This section is devoted to the extraction of tannins exclusively based on the contact between a solvent and a solid matter, without any further assisting mechanism. During this kind of extraction, the solvent penetrates into the cell wall of the feedstock containing the tannins. Then, they are dissolved and taken out in the form of extracts (Mailoa et al., 2013). This is the simplest

and most traditional method employed for tannins extraction. Within this part, several types of solvents are studied namely organic solvents, aqueous solutions, water and ionic liquids.

Concerning the use of organic solvents and their aqueous solutions, the extraction is commonly carried out by means of a soxhlet apparatus whose experimental extraction procedure has been described in several works (Jensen, 2007; Luque de Castro and Priego-Capote, 2010). However, other techniques are also employed and reported in the literature such as infusion or maceration. The extraction with water can be carried out under reflux or through simple maceration in flasks or vessels. At the industrial scale it is generally performed on wood barks by percolation or open diffusion (Ciesla, 1998; Myers, 1998).

The extraction with ionic liquids is an alternative based on the substitution of the traditional solvents with these new liquids, which are known for having unusual combination of properties such as negligible vapour pressure, high thermal stability and dissolution of a broad range of compounds present in plants (Olivier-Bourbigou et al., 2010).

In table 3 is presented a sample of works from the literature devoted to solid-liquid extraction with the previously commented solvents. In regards to these results, it is seen that a considerable percentage of recovery of extracts is achieved by this method. The content of tannins in the extracts is reported to be high as well and can reach even to yields of 96% (grams of reactive tannins per gram of extract) (Vázquez et al., 2001). However, the results presented are influenced by several parameters. Within these parameters, the nature of the solvent employed for the extraction is regarded to be of significant importance. It is reported that the extraction yields increase with the solvent polarity (Markom et al., 2007). Accordingly, high extraction yields are generally obtained using water or methanol as solvent whereas poor extraction efficiencies are achieved with hexane (Widyawati et al., 2014).The employment of water is normally preferred, especially at the industrial scale owing to environmental reasons. Nevertheless, the solution of tannins in water generally leads to acidic pHs (Vieira et al., 2011). Under these conditions, the formation of insoluble precipitates due to tannin self-condensation reactions is promoted, limiting the extraction efficiency (Sealy-Fisher and Pizzi, 1992). The addition of certain amounts of NaOH% is proposed as an alternative to overcome this problem, since it is capable of improving the extraction yields (Chupin et al., 2013). Similarly, the use of salts like sodium carbonate (Na_2CO_3) and sodium bisulfite ($NaHSO_3$) is able to increment the extraction efficiency and to lower the high viscosity of the extracts derived from the tannin self-condensation reactions (Panamgama, 2007). In both cases, the increment of extraction yields is related to the alteration of the pH. Alkaline pH values are reported to increase the percentage of extracts, owing to the partial break of pyran rings in phlobaphenes (tannin-derived compounds). It has been presented in a recent work, that even the change of pH from neutral to slightly alkaline values can lead to higher extraction yields (Lochab et al., 2014). Moreover, a relationship between the base concentrations and the extraction yields is observed. The use of higher percentages of these

components is proved to reach higher extraction yields compared to lower concentrations (Antwi-Boasiako and Animapauh, 2012; Inoue et al., 1998). Nevertheless, the increment of the concentrations can provide a lower tannin content in the extracts due to the raise of undesirable non-tannin components (Ping et al., 2011). For this reason, the indiscriminate increase of the alkaline compounds and salts concentrations is not desirable. Different works were found underlining the importance of employing moderate amount of these compounds (Aires et al., 2016; Vieira et al., 2011).

Regarding the tannin content in the extracts, methanol and ethanol provide the best results (do Prado et al., 2014; Widyawati et al., 2014). For instance, it is stated in a work about anthocyanidins extraction from *Phyllantus niruri*, that methanol and ethanol are more suitable for performing the extraction compared to water (Kaur and Kaur, 2016). This is due to the fact that these organic solvents have more similar characteristics to anthocyanidins.

The use of aqueous solutions of organic solvents has proved its efficiency as well, providing both considerable extraction yields and levels of tannins in the extracts (Vijayalaxmi et al., 2015; Widyawati et al., 2014). Besides, they present the advantage of being able to regulate the polarity of the solvent by adjusting the ratio of both components.

Compared to already mentioned solvents, ionic liquids represent a novel type still under development for tannins extraction. Despite this fact, they have already proved to achieve comparable or even better results than water (Chowdhury et al., 2010). Among this type of solvents, the imidazolium-based ionic liquids are said to be preferred and their concentrations have a direct influence on the results. It is reported that the increase of this parameter provides higher tannins extracted until certain point where not further improvement is regarded (Z. Liu et al., 2016; Lu et al., 2012). For this reason, the concentration of the ionic liquid is normally optimized. Another relevant factor in the tannins extraction with these solvents, is the alkyl chain length of the cation linked to the ionic liquid. It is presented that the increase of the alkyl chain length decrease the surface tension and increment the hydrophobic nature and viscosity (Ćurko et al., 2017). Thus, the ionic liquid can have a stronger interaction with the tannins extracting higher amounts. Above butyl chains, this effect is reported to be the opposite. Consequently, the alkyl chain length of the cations is also further optimized within the different studies.

Apart from the solvents nature, other parameters are regarded to have a major influence over the results namely temperature of extraction, time of extraction and solid to liquid ratio.

Concerning the time of extraction, it is seen that the increment of this parameter provides a higher content of tannins extracted as presented in some of the works from literature (Baldosano et al., 2015; Chowdhury et al., 2010). This is due to the longer times the solute and the solvent are in contact, which favours the mass transfer between both components. Nevertheless, the increase of the extraction times beyond certain values is not desirable. It was discussed by Tan et al. (2013) that the amount of tannins extracted above 4.5h was dramatically decreasing towards a minimum

(Tan et al., 2013). This was explained by the fact that an equilibrium was reached between the tannins concentration in the plant matrix and the solvent (Fick's law of diffusion), resulting in the slowdown of the extraction. Besides, at longer times the possibility of tannins degradation owing to the extraction conditions is enhanced.

The temperature of extraction is observed to increase the extraction yields as displayed in the results from table 3 (Kemppainen et al., 2014; Vázquez et al., 2001). This enhancement is due to the increase of the mass transfer coefficient at higher temperatures (Huang et al., 2016). Moreover the increment of the temperature results in the improvement of the solute solubility and diffusion coefficient and also decreases of solvent viscosity, which promotes the extraction (Al-Farsi and Lee, 2008). This parameter is normally regulated and optimized, since high temperatures can also lead to lower amount of tannins in the extracts as showed by Ramos et al. (2013) (Ramos et al., 2013). This was attributed to the denaturation of these compounds owing to the harsh conditions employed. The use of too high temperatures can also result in solvent evaporation. For this reason, in this kind of extraction the temperature is normally set up at the solvent boiling point.

Regarding ratio solid-liquid, it is showed that the decrease of this parameter provides higher extraction yields, since higher amounts of solvent are employed (Politi et al., 2011). Nevertheless, at low solid-liquid ratios, the differences between the extraction efficiencies are normally minimized and therefore this parameter is generally optimized at certain value.

To conclude, it can be remarked that the main general advantages of this method are its simplicity, efficiency and low cost. In the case of the extraction with hot water, it should be highlighted as well the fact that it can be successfully transferred to the industry, especially the extraction from wood barks (Amaral-Labat et al., 2013; Kemppainen et al., 2014). On the other hand, the major drawbacks of this method are the long times needed for the extraction, which can range from several hours to even several days, and the great amount of solvent normally employed. These disadvantages could be minimized by the use of ionic liquids, which display special properties favorable to the extraction (Hernández-Fernández et al., 2015). Nevertheless, the high prices of this novel solvents and the difficulty to recover the solute from the ionic liquid are still hindering their utilization.

4.1.2. Supercritical fluid extraction (SFE)

In this part, the extraction of tannins by using supercritical fluids is presented. The principle of this method is based on the concept of critical point, which is defined as the highest temperature and pressure at which a pure substance can exist in a vapour-liquid equilibrium (Ajila et al., 2011). Above this point a fluid shares properties between a gas and a liquid, such as the typical weight of liquids with the penetration power of gases (Azmir et al., 2013). The works found in the literature related to this technique are presented in table 4. In regards to the presented results, various common characteristics are identified. The most widely employed solvent among all the works is carbon dioxide (CO_2). This is due to its desirable properties such as non toxicity, non-

flammability, non-corrosive nature, availability and low critical temperature and pressure (31°C and 7.28 MPa) (Palmer and Ting, 1995; Talmaciu et al., 2016). The range of pressures and temperatures used within the different works for this fluid is between 10-65.5MPa for the former parameter and between 40-88ºC for the later.

Concerning the extraction yields and tannins extracted, the parameter with the greatest influence is the utilization of a co-solvent. Thus, poor extraction yields are achieved using supercritical CO_2 alone whereas considerable enhancements are reported after the addition of a co-solvent (Cavalcanti et al., 2012; Conde et al., 2013). This is due to the non-polar nature of CO_2 as solvent and the polar nature of most of tannin compounds. The addition of co-solvents of polar nature such as ethanol, methanol or aqueous mixtures help ameliorating the solvating power of CO_2 towards tannins and improves the extraction yields. The pressure employed also presents a major role in the extraction efficiency and amount of tannins extracted. It is observed that the increment of the pressure promotes the extraction of tannins (do Prado et al., 2014). The reason for that is that at higher pressures the fluid density is increased, decreasing the distance between the molecules and therefore improving the interactions fluid-matrix (Maran et al., 2015).

Regarding the temperature of extraction, low values are said to be preferred. This parameter do not show though a crucial influence over the process, since most of the works do not report big differences in terms of extraction yields and amount of tannins extracted. However, it has been presented that higher temperatures can lead to lower amounts of tannins in the extracts (Luengthanaphol et al., 2004).

The main advantages concerning this extraction method are the utilization of mild temperatures and a nontoxic solvent (CO_2) which can be easily removed and can avoid further oxidation reactions by creating an oxygen free environment. On the other side, one of the main drawbacks are the high investment costs, due to the high pressures needed for the extraction process (Perrut†, 2000). The other main problem concerning CO_2 is its non polar nature, which reduces the extraction power towards tannins (low solubility of polar compounds). Consequently, the addition of co-solvents such as methanol, ethanol, acetone or water, becomes an essential requirement

4.1.3. Pressurized water extraction (PWE)

This extraction method is based on the use of water as solvent at high pressures and temperatures, generally at subcritical conditions i.e. between its atmospheric boiling point (100°C, 0.1 MPa) and its critical point (374°C, 22.1 MPa). Within this range water is maintained in the liquid state but properties such as the polarity, viscosity, surface tension and disassociation constant are considerably lowered compared to water at ambient conditions (Liang and Fan, 2013). The reduction of these parameters enhances the mass transfer of the tannins from the feedstock matrix (Vergara-Salinas et al., 2013). Besides, under these conditions the ability to extract different types of compounds from this family is improved (Rangsriwong et al., 2009). The main difference with traditional solid-liquid extraction using hot water, is that pressurized water extraction utilizes

temperatures above the boiling point and pressures above the atmospheric to maintain water in liquid state.

The results related to this extraction method are presented in table 5. It is observed in most of the works, that the extraction was carried out at subcritical conditions (0.1-22 MPa, 100-374ºC). Nevertheless, in some works pressures above the critical point are reported as well, to improve the results. A significant characteristic of this method is the reduction of the extraction times needed (5-60 minutes). Despite the short extraction times, high extraction yields are reported even up to ≈70% (Erşan et al., 2018). Furthermore, by adjusting the pressure and temperature of the solvent, its polarity can be modulated and a wide variety of tannins in significant amounts can be extracted depending on the source. For this reason, both variables present a significant influence in the extraction process.

The temperature plays a major role and its increment leads to higher extraction yields (Sousa et al., 2016). This effect is attributed to the fact that at higher temperatures the solvent is more easily diffused into the plant matrix. Moreover at higher temperatures the solute vapour pressure is incremented and it is easier for the solute to free itself from the matrix (Markom et al., 2010a). However, the employment of too severe temperatures was proved to have a negative effect, particularly on the tannin content of the extracts (García-Marino et al., 2006; Rangsriwong et al., 2009). This is associated to the possible degradation and denaturation of the different polyphenolic compounds at harsh temperatures (Vergara-Salinas et al., 2013).

Concerning the pressure, the influence on the water properties is little as far as it stays as a liquid (Plaza and Turner, 2015). For this reason, its effect on the results of extraction is normally lower. Despite this fact, the increase of this parameter can result in slightly higher extraction yields and tannin content in the extracts until certain pressure values (Aliakbariana et al., 2012). Above these pressure values the solvent solubility is not further improve and accordingly the extraction yields remain or even slightly decrease as well as the amount of tannin extracted (Markom et al., 2010a).

The main advantages of this method are the reduced handling time and solvent consumption and the no utilisation of toxic organic solvents. Another advantage is the possibility to extract selectively tannins of different polarities by the modification of the temperature, pressure or co-solvent. On the other hand, the major disadvantages are related to the high temperatures and pressures used (reduction of the extraction selectivity and possible degradation of the analytes) and the expensive equipment required (solvent transporting pump, a pressure vessel and system controller, and a collection device for the extract needed).

4.1.4. Microwave assisted extraction (MAE)

This method is based on the combination of the traditional solvents employed for tannins extraction and the fast heating in the microwave field. In some cases, the extraction process is ameliorated because both the solvent and the sample can be rapidly heated by direct interaction with electromagnetic radiation (depending on their dielectric characteristics). Another possibility

is the heating of one of the components by interaction with the other, previously heated by the microwave irradiation. The effect of heating on the solvent increases its solubility, whereas on the material it improves porosity allowing an easier penetration of the solvent (Routray and Orsat, 2012). Thereby, in either case the extraction of tannins from the cell wall of the feedstock is eased. Within this section, a sample of papers focused on the tannins extraction assisted by microwave is displayed (table 6). From the previous results, it is remarked the short times needed for extraction (1-20 minutes), which achieved a significant level of tannin extraction. Regarding the solvent employed, the volume used for the extraction has a direct impact on the amount of tannins extracted. Normally a larger amount of solvent is supposed to achieve a higher quantity of tannins extracted, according to the principle of equilibrium between solvents and materials. In a work by Wang et al., 2010 (Wang et al., 2010), it was found that the increase of the solvent volume led to the enhancement of the tannins extracted until certain point (ratio 1:30) and then decreased. This was attributed to the relatively large amount of solvent employed, which resulted in a dilution of the amount of the tannins in the extracts (Guo et al., 2001; Xiao et al., 2008). The nature of the solvent also plays a major role on the extraction as was already mentioned in section 4.1.1 Accordingly, the increase of the polarity of the solvent leads to higher amounts of tannins extracted (Pan et al., 2010). The effect of the microwave power was discussed in several works as well (Naima et al., 2015; Švarc-Gajić et al., 2013). It is proved that the increase of the power leads to higher amounts of tannins extracted. This is due to the enhancement of the solvent penetration into the matrix and the faster energy transfer to the solvent and material. However, above high values of microwave irradiation, the amount of tannins extracted is observed to decrease. Normally, this fact is due to the thermal degradation of the tannins, which results in a lower content of these compounds in the extracts (Dahmoune et al., 2015). It has been showed as well that too high microwave power can provide excess of energy to the solvent and material. This superfluous energy can generate abnormal molecular interaction, which affect the extraction yields of tannins (Jin et al., 2010). Consequently, this parameter is normally optimized in the majority of the works to achieve the highest amount of tannins recovered.

The main advantages of this method are the employment of considerably short extraction times, and lower amount of solvents compared to traditional solid-liquid extraction. Another advantage is the agitation provided by the microwave irradiation, which can ameliorate the mass transfer phenomenon (Jain et al., 2013). The main disadvantages are the great costs of the equipment needed (specially at larger scale) and the possibility of thermal degradation of the feedstocks and tannins, especially those with high number of hydroxyl groups (Xu et al., 2017).

4.1.5. Ultrasound assisted extraction (UAE)

The extraction of tannins by this technique is based on the formation, growth and collapse of micro bubbles inside a liquid phase submitted to ultrasonic cavitation (Chemat et al., 2011). The bubbles are induced by sound waves, with frequencies above 20 kHz, which cause mechanical

vibrations into the plant matrix. These mechanical vibrations, can rupture cell wall tissues ameliorating the penetration of the solvent into the matrix and achieving higher amounts of tannins extracted (Ali et al., 2018).

In this section, a sample of works related to the extraction of tannins assisted by ultrasound, is discussed (table 7). Within the works presented, the influence of several parameters on tannin extraction efficiency is observed. Again, the solvent employed has a prominent effect and therefore the use of more polar solvents leads to the improvement of the extraction yields. Nonetheless, it was reported that ethanol and methanol presented a higher selectivity to the polyphenolic compounds, providing higher amounts of tannins in the extracts (Dhanani et al., 2013; Tabaraki et al., 2013). Regarding the extraction times, not high values are needed to achieve good extraction yields (below 1hour). The increment of this parameter can lead to higher extraction yields and amount of tannin in the extract (Ivanovic et al., 2014). However, when the extraction time is incremented above relatively high values, the extraction efficiency tends to decrease. A first work by Dalzell and Kerven, (1998) showed that sonication after 30 minutes decreased the tannins extraction efficiency from Leucaena spp. This result was attributed to the possible degradation of the proanthocyanidins due to the increased temperature of the water bath, provided by the prolonged sonication time (Dalzell and Kerven, 1998). In another work, the decrease of the tannins extracted at high extraction times was associated to the prolonged interval of sonication and the possible degradation of the tannins as well but also to the lower concentration gradient of the solvent (Annegowda et al., 2012). A similar tendency is observed for the sonication power. Hence, the increase of this parameter provides higher amounts of tannins extracted until certain point and then began to decrease (Agarwal et al., 2018; Chavan and Singhal, 2013). This is due to the chemical decomposition of tannins extracted. Taking the previous phenomena into consideration, a further optimization of the conditions was carried out in most of the works presented.

The major advantages of this technique are the short extraction times employed and the fact that it is a simple and inexpensive extraction method (Khoddami et al., 2013). On the contrary, the main drawbacks are the lack of uniformity in the intensity of ultrasounds (maximum peak observed in the vicinity of radiating surface and decreasing with the distance to the source) and the reduction of the power with the time (Routray and Orsat, 2012).

4.2. Comparison of extraction methods

In this section, a sample of works devoted to the analysis and assessment of various extraction methods for tannins extraction is presented. A comprehensive and direct comparison between the different techniques is provided as well (table 8). In the majority of the studies, the most traditional tannin extraction method namely solid-liquid extraction, was contrasted with other modern techniques.

Considerable differences are regarded between SLE and SFE, especially when no co-solvent was used (Reátegui et al., 2014). SLE can achieve a higher amount of tannins extracted owing to the more polar nature of the solvent and the longer times employed. It is regarded though, that the addition of a more polar co-solvent or the use of simultaneous sonication highly ameliorates the results of SFE. Thereby, the amounts of tannins extracted are comparable to those of SLE but employing lower times. Concerning PWE, it is reported that the amount of tannins extracted compared to that of traditional method SLE is enhanced owing to the increased solvating power of water under subcritical conditions (Rangsriwong et al., 2009). Moreover, the extraction times are considerably lowered.

Other recent techniques such as MAE and UAE have been also compared to SLE within the literature (Aspé and Fernández, 2011; Belwal et al., 2017; Ghadage et al., 2017). Superior performance is displayed by MAE and UAE in terms of higher extraction yields and amount of tannins recovered. This is due to the acting mechanisms of both methods, which ameliorates the penetration power of the solvent and extraction efficiency of the tannins from the plant matrix. Furthermore, the extraction times can be dramatically decreased by more than a 95% in some of the cases and the amount of solvent used lowered. The use of ionic liquids also provides a great improvement in the extraction of tannins compared to the performance of conventional organic solvents in SLE (Ribeiro et al., 2013)

Within the presented results, a comparison between the modern tannin extraction techniques is observed as well. For example, it was presented that the SFE was able to obtained similar extraction yields to that of UAE. Nevertheless, it was reported to recovered substantially lower amounts of tannins (Pereira et al., 2017, 2016).

In regards to the results presented in table 8, MAE, UAE and PWE are the techniques with the best future perspectives for tannin extraction. Some works were found providing a further comparison between them and the conventional extraction methods (Veličković et al., 2017). In terms of extraction yields, PWE was able to achieve the highest values, followed by MAE and UAE. Nonetheless, concerning the amount of tannins extracted no considerable differences were observed. The main advantage of PWE compared to MAE and UAE, was the use water as solvent instead of organic compounds. MAE was able to provide the shortest extraction times (as seen in several works) compared to UAE and PWE (1-5 min for MAE in contrast to 15-30 min for UAE and PWE). Additionally, MAE and UAE can generally perform the extraction at lower pressure compared to PWE, which requires the use of subcritical conditions.

The combination of several of these modern techniques is also reported to provide synergistic effects and improved results (Lu et al., 2012). For example, the utilization of simultaneous microwave and ultrasound assisted extraction (UMAE) is proved to provide better results than these methods alone. Moreover, the substitution of the conventional organic solvents by ionic

liquid, shows highly ameliorated results and leads to a promising environmentally friendly option for tannins extraction.

4.2.1 Technical and costs comparison

The major economic and operational considerations in the different extraction methods are generally derived from the amount and nature of solvent employed, the extraction conditions, the recovery of the tannin extracts from the solvent and the equipment required for the process. Regarding these costs and technical characteristics, several differences can be observed.

The industrial production of tannins at the moment, is generally performed using traditional solid-liquid extraction. In this regard, water as solvent is preferred in contrast to the organic solvents, owing to the lower emissions of VOC and costs (Lochab et al., 2014). However, there is current a tendency towards the switch of traditional tannin extraction methods by other more environmentally friendly. This is due to the long extraction times and the high amount of solvent required, which has to be evaporated afterwards, resulting in elevated energy costs (Selvamuthukumaran and Shi, 2017).

Consequently, in the majority of the works presented in this study it is showed that the modern extraction techniques are more favourable for future implementation in the industry.

The implementation in larger scale of PWE for tannin extraction was assessed based on a study of the main economic factors by Veggi et al. (2011) (Veggi et al., 2011). Here, it was found that although the addition of a co-solvent can lead to an increment of the manufacturing costs (distillation step for the solvent), in the end the global manufacturing costs were lower owing to the improvement in the recovery of tannins. In addition to that, they reported for the process (design to run 7920h/year) manufacturing costs of 983$/Kg for the global yields. In contrast to that technique, Ravber et al (2015) carried out another research with a preliminary economic evaluation of the PWE for tannins extraction from larch wood (Ravber et al., 2015). After optimization of the process ($V_{extrator}$=350L and T=300ºC, process run 8016h/year), they presented operating costs of 223$/Kg, achieving an extraction yield of 21.60%. This can provide a more environmentally friendly and cheaper option compared to conventional solid-liquid extraction.

Regarding MAE, moderate global capital costs and good performance at atmospheric conditions are reported as well as lower energy demands compared to traditional extraction method (Bouaoudia-Madi et al., 2017). In addition to that, MAE can be highly improved by the use of ionic liquids as solvent. Liu et al. (2016) pointed out the considerable lower energy requirements compared to conventional SLE (0.13 kWh MAE in contrast to 1.54kWh SLE) (Z. Liu et al., 2016). The employment of MAE has been also promoted in other the works from the literature. For instance, Belwal et al. (2017) presented the need of scaling up the MAE process from the laboratory scale to the industry to harness the potential of tannins (Belwal et al., 2017). In comparison to MAE, UAE has been presented as an alternative as well. In fact, Diouf et al. (2009) found that the energy requirements for UAE were slightly lower than MAE for the same amount

of material extracted (0.94kWh and 1.51kWh respectively) (Diouf et al., 2009). The UAE is also reported to save time, energy and costs compared to conventional SLE. Nevertheless, parameters should be optimized as excessive sonication can increase energy and operational costs (Agarwal et al., 2018).

5. Conclusions

After performing the literature review it was clear the interest on the topic of tannins extraction, taking into account the significant number of works found. Besides, a clear evolution was observed from the traditional extraction method towards the most novel methodologies. The modern tannin extraction methods show a similar or even better performance compared to the most traditional one, in terms of extraction yields and amount of tannins extracted. They also display several advantages concerning the environmental impact such as the reduction of the extraction times and amount of solvent needed, leading to a lower energy consumption. Despite these facts, the truth is that the current industrial tannin production still remains old-fashioned, since it is majorly carried out by solid-liquid extraction using large amounts of water. It has been clearly stated from the works presented here, that lately several efforts are being made towards modern ways of extract tannins. Nevertheless, they usually remain in the laboratory scale. For this reason, an inflection point has to be reached in the short-term to switch from this old-fashioned industrial tannin production system to a state-of-the-art one. With this aim, works should be carried in the following years specially focus on the scale up and the economic analysis of the process of tannins extraction.

Finally, it should be added as well that this change in the tannins extraction methods, not only can lead to a cleaner and more effective production but also can promote and spread tannins utilization in several fields of the industry. This is of major importance since they represent a renewable feedstock with numerous applications.

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LIST OF FIGURES:

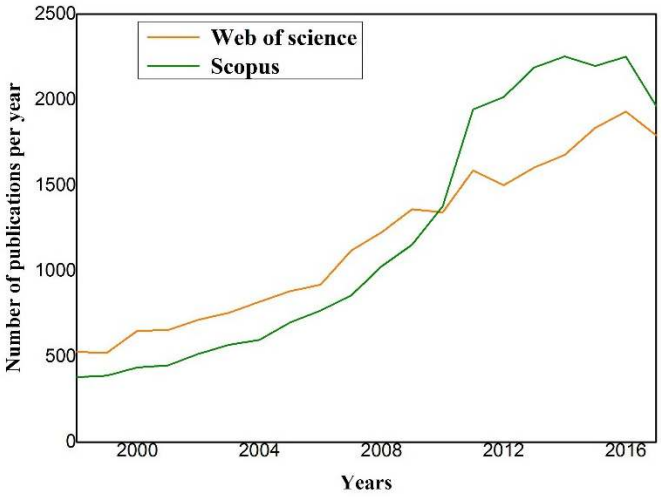


Figure 1. Number of tannins-related publications per year in the period 1998-2017 indexed in Web-of-Science and Scopus.

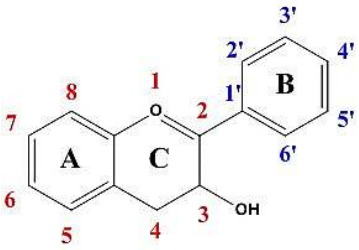


Figure 2. Structure of Flavan-3-ol and its nomenclature

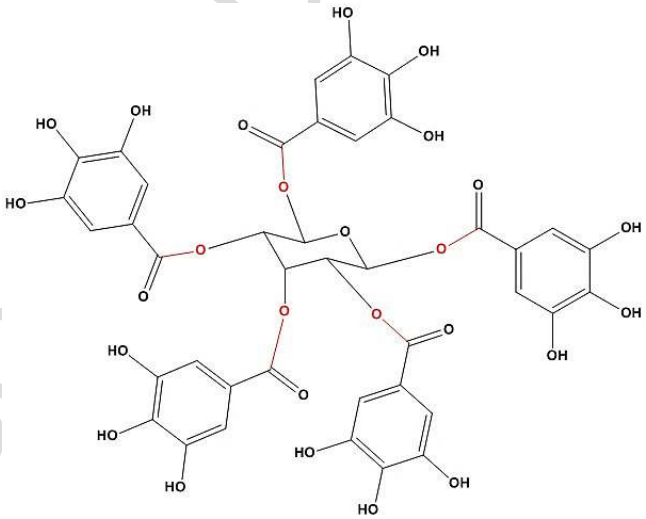


Figure 3. Example of a hydrolysable tannin unit and the linkages present (e.g. pentagalloyl glucose structure linked via ester bonds).

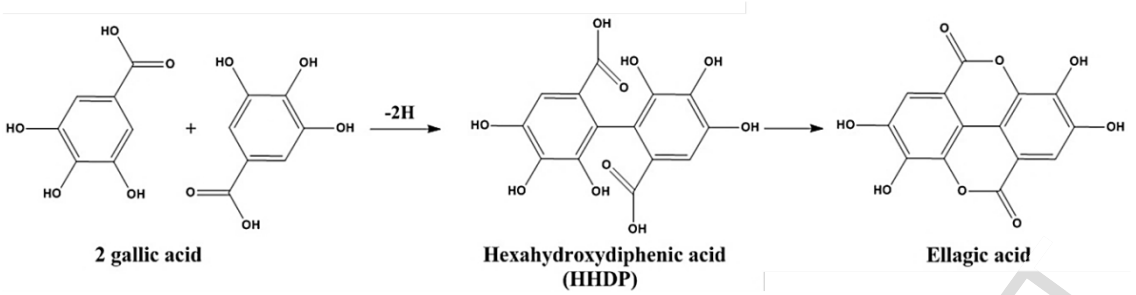


Figure 4. Transformation between the main polyphenolic acids and derivatives present in the structure of hydrolysable tannins

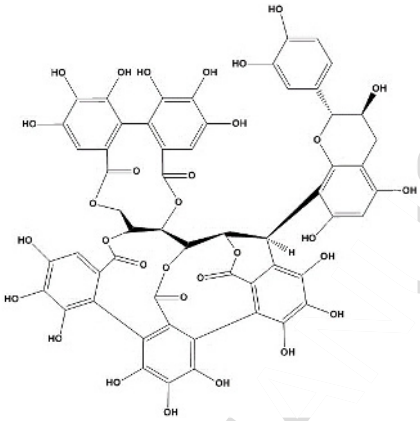


Figure 5. Acutissimin A typical complex tannins group.

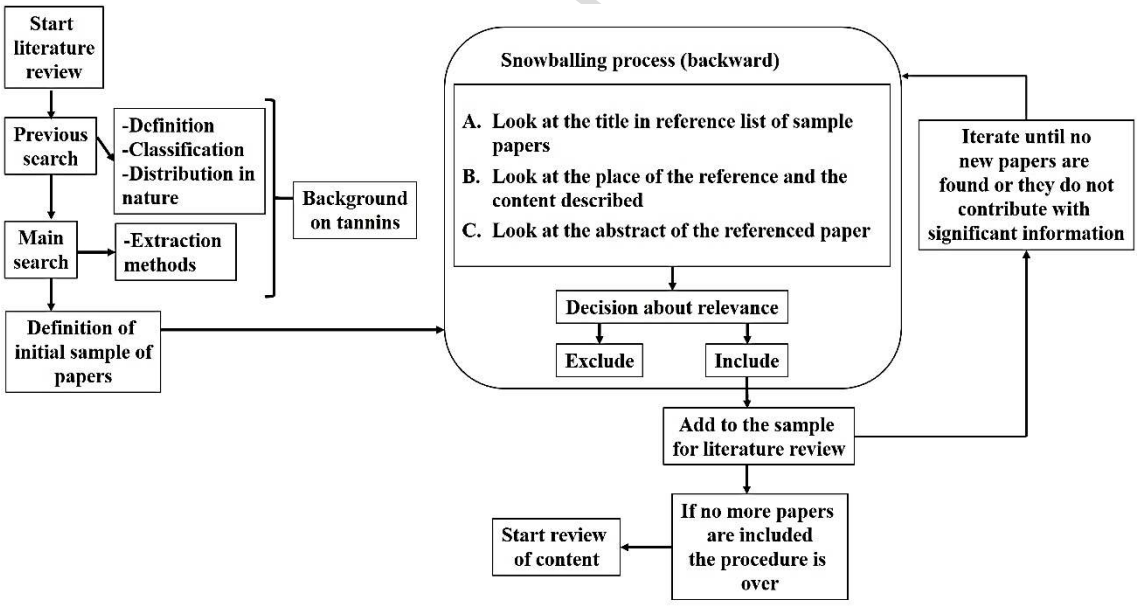


Figure 6. Literature review process

LIST OF TABLES:

Table 1. Structures of the most common flavan-3-ol monomers of condensed tannins

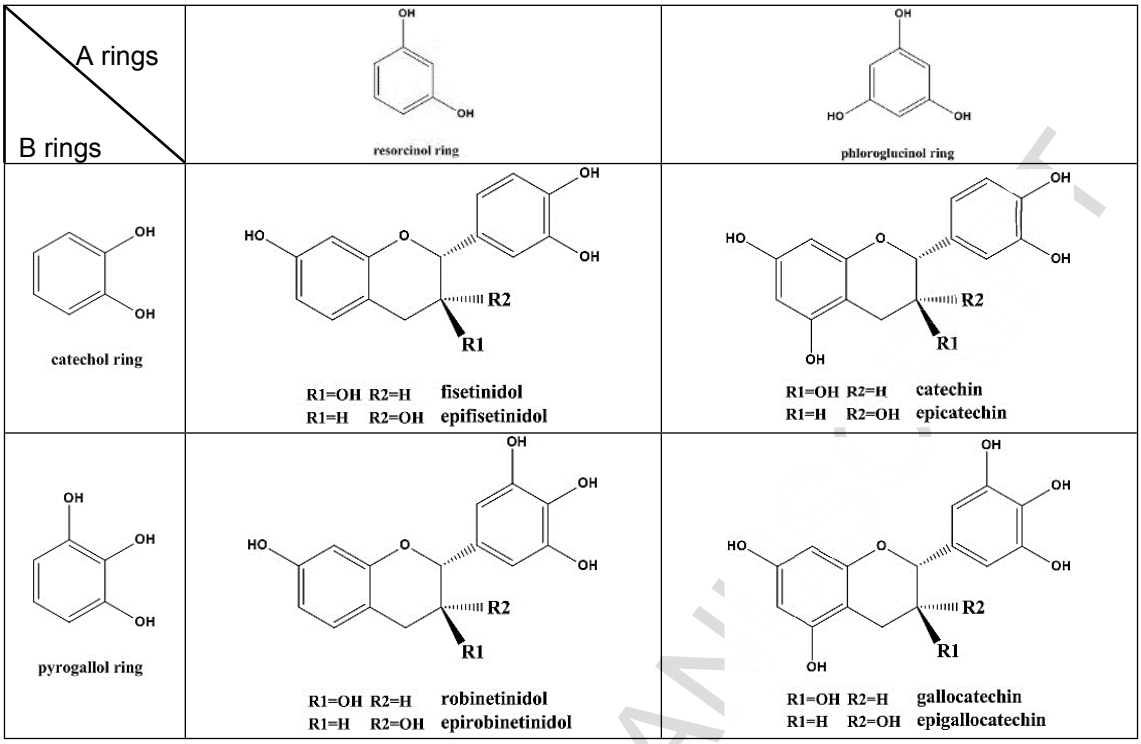


Table 2. Strings and number of results obtained for the individual search of each tannin extraction method

SEARCH STRINGS	NUMBER OF RESULTS	
	SCOPUS	WEB OF SCIENCE
[organic solvent extraction AND tannin]	117	111
[hot water extraction AND tannin]	73	80
[ionic liquid extraction AND tannin]	9	12
[supercritical fluid extraction AND tannin]	31	46
[pressurized water extraction AND tannin]	13	17
[subcritical water extraction AND tannin]	7	11
[microwave assisted extraction AND tannin]	35	48
[ultrasound assisted extraction AND tannin]	36	50

Table 3. Results related to the tannins solid-liquid extraction with different solvents

Species	Plant part	Solvent	Extraction conditions	Extraction Yield (% w/w)[a]	Tannin content (mg/g_{DE}[b])	References
Pinus radiata	Bark	Water	1:20, 2h 100ºC	19.60	887.00[c]	(Inoue et al., 1998)
		Water+ 1% NaOH		30.50	828.00[c]	
Pinus pinaster	Bark	Water + 2.5% NaOH	1:10, 0.5h 70ºC	16.5	965.00[c]	(Vázquez et al., 2001)
		Water + 5% NaOH		18.9	875.00[c]	
		Water + 2.5% NaOH	1:10, 0.5h 90ºC	23.20	963.00[c]	
		Water + 5% NaOH		25.00	812.00[c]	
Mangifera indica	Peels	Acetone (80%)	1:20, 3h	---	1.4[d]	(Berardini et al., 2004)
	Pulp				0.2[d]	
	Kernel				15.5[d]	
Acacia mearnsii	Bark	Ethanol	1:10, 24h	---	237.00[e]	(Pansera et al., 2004)
Phyllanthus niruri	Stem and aerial parts	Water	1:30, 3h b.p[g]	26.2	215.90[f]	(Markom et al., 2007)
		Ethanol (50%)		22.50	149.00[f]	
		Ethanol (70%)		20.80	91.10[f]	
Acacia catechu	Whole plant	N,N-dimethylammonium N',N'-dimethylcarbamate (DIMCARB) (15%)	1:5, 25ºC 1h	30	---	(Chowdhury et al., 2010)
			1:5, 25ºC 2h	60	---	
			1:5, 25ºC 16h	85	61.50[f]	
		Water	1:10, 70ºC 16h	64	28.60[f]	
Pinus radiata	Bark	Acetone (70%)	1:10, 1-6h	12.00	62.10[h]	(Aspé and Fernández, 2011)
Vitis vinifera	Pomace	Water + 10% NaOH	1:8, 2h 120ºC	45.20	550.00[c]	(Ping et al., 2011)
		Water + 20% NaOH		71.10	490.00[c]	
		Water + 30% NaOH		88.40	390.00[c]	
Endopleura uchi	Bark	Water	1:20	9.70	226.60[d]	(Politi et al., 2011)
			1:10	8.85	260.60[d]	
			1:5	8.53	120.80[d]	
Pinus ocarpa	Bark	Water	1:15, 2h b.p.	24.84	655.60[c]	(Vieira et al., 2011)
		Water + 1% Na_2CO_3		30.94	857.20[c]	
		Water + 5% Na_2CO_3		35.74	890.70[c]	
		Water + 1% $NaHSO_3$		19.86	846.40[c]	
		Water + 5% $NaHSO_3$		26.70	722.80[c]	
T.tetraptera	Bark	Water	1:5, 6h b.p.	14.02	884.49[c]	(Antwi-Boasiako and Animapauh, 2012)
		Water + 1% NaOH		75.29	374.60[c]	
Galla chinensis	Whole plant	1-butyl-3-methylimidazole bromide [C4mim]Br 0.5M	1:15, 1min UMAE[d]: Microwave 400W Ultrasound 50W	---	380.00[d]	(Lu et al., 2012)
		1-butyl-3-methylimidazole bromide [C4mim]Br 1.5M			555.00[d]	

		1-butyl-3-methylimidazole bromide [C4mim]Br 2.5M			601.00[d]	
		1-butyl-3-methylimidazole bromide [C4mim]Br 4M			605.00[d]	
Punica granatum	Peels	Methanol	1:20, 6h	---	3.10[i]	504.80[e] (Saad et al., 2012)
Pinus pinaster	Bark	Water + 1% NaOH + 0.25% Na_2SO_3 + 0.25% $NaHSO_3$	1:9, 2h 80ºC	22.06	489.70[c]	(Chupin et al., 2013)
		Water + 5% NaOH + 0.25% Na_2SO_3 + 0.25% $NaHSO_3$		31.30	179.20[c]	
Pinus radiata	Bark	Acetone (25%)	1:20, 2h 40ºC	3.50	350.00[h]	(Ramos et al., 2013)
		Ethanol (25%)		3.00	310.00[h]	
		Acetone (25%)	1:20, 2h 120ºC	11.00	220.00[h]	
		Ethanol (25%)		10.10	250.00[h]	
Carya illinoinensis	Shells	Water	1:50, 0.5h 98ºC	32.12	36.94[h]	(do Prado et al., 2014)
		Ethanol	1:50, 1h 25ºC	32.09	412.10[h]	
Osbeckia parvifolia	Whole plant	Hexane	1:5, 24h	3.40	7.31[d]	(Murugan and Parimelazhagan, 2014)
		Ethyl acetate		4.80	10.88[d]	
		Methanol		9.20	20.32[d]	
		Ethanol		1.60	10.67[d]	
Picea abies	Bark	Water + 2% $NaHSO_3$+ 0.5% Na_2CO_3	1:20, 2h 60ºC	16.10	330.00[j]	(Kemppainen et al., 2014)
			1:20, 2h 90ºC	20.90	480.00[j]	
Mimosa hamata	Whole plant	Methanol (80%)	1:6, 48h	24.20	264.40[k]	(Saxena et al., 2014)
		Ethanol (95%)l		34.74	287.50[k]	
Pluchea indica	Leaves	Water	3h b.p	40.65	81.30[h]	(Widyawati et al., 2014)
		Methanol		38.07	911.90[h]	
		Ethyl acetate		32.97	93.10[h]	
		Ethanol		31.09	7.80[h]	
		Hexane		29.46	0.90[h]	
Spondias purpurea	Bark	Ethanol (95%)	1:30 4h	---	31.80[e]	(Baldosano et al., 2015)
			1:30 6h		73.75[e]	
			1:30 8h		181.60[e]	
Saccharum officinarum	Bagasse	Methanol (50%)	1:10, 72h	6.20	381.80[Ee]	(Vijayalaxmi et al., 2015)
		Ethanol (50%)		4.50	316.50[e]	

Castanea sativa	Peels	Water	1:4, 4h 85ºC	7.03	234.80[c]	(Aires et al., 2016)
		Water + 1% Na_2SO_3		7.74	794.90[c]	
		Water + 4% Na_2SO_3		8.67	373.80[c]	
		Water + 1% NaOH		11.63	728.70[c]	
		Water + 4% NaOH		66.59	415.00[c]	
Eucaliptus globulus	Leaves	1-butyl-3-methylimidazole bromide [C4mim]Br 0.6M	1:30, 0.33h MAE[e] 385W	---	3.40[f*]	(C. Liu et al., 2016)
		1-butyl-3-methylimidazole bromide [C4mim]Br 1M			7.15[f*]	
		1-butyl-3-methylimidazole bromide [C4mim]Br 1.2M			6.90[f*]	
Phyllantus niruri (Patiala region)	Whole plant	Ethanol	1:2, 24h	---	2.50[i]	(Kaur and Kaur, 2016)
		Methanol			16.00[i]	
Vitis vinifera	Skins	1-butyl-3-methylimidazolium bromide [C4mim]Br 0.5M	1:10, 4h 25ºC	---	60.10[j]	(Ćurko et al., 2017)
		1-pentyl-3-methylimidazolium bromide [C5mim]Br 0.5M			41.30[j]	
		1-heptyl-3-methylimidazolium bromide [C7mim]Br 0.5M			38.60[j]	
		1-decyl-3-methylimidazolium bromide [C10mim]Br 0.5M			6.60[j]	

*Results expressed in mg of tannins per gram of dry matter.
[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DE= dry extract.
[c]Tannin content in extracts expressed in mg of reactive tannins/g dry extract (Stiasny number).
[d]Tannin content in extracts expressed in gallic acid equivalents (GAE).
[e]Tannin content in extracts expressed in tannic acid equivalents (TAE).
[f]Hydrolysable tannin content in the extracts (HTC).
[g]b.p= boiling point.
[h]Content of extracts expressed in catechin equivalents (CE).
[i]Tannin content in extracts expressed in cyaniding equivalents (CYE).
[j]Condensed tannin content in the extracts (CTC).
[k]Tannin content in extracts expressed in quercetin equivalents (QE).

Table 4. Results related to the extraction of tannins via fluid at supercritical conditions

Species	Plant part	Fluid	Co-solvent	T[a] (ºC)	P (MPa)	Extraction yield (% w/w)[a]	Tannin content (mg/g_{DE}[b])	References
Tamarindus indica	Seed	CO_2	Ethanol (10%)	40	30.00	<1	0.06[c]	(Luengthanaphol et al., 2004)
				55			0.05[c]	
				88			0.02[c]	
Acacia mearnsi	Bark		Ethanol	60	25.00	---	95.00[d]	(Pansera et al., 2004)
			Water				135.00[d]	
Vitis vitfera	Seed		Methanol (30%)	80	65.50	---	600.00[e]	(Ashraf-Khorassani and Taylor, 2004)
			Methanol (35%)				720.00[e]	
			Methanol (40%)				770.00[e]	
Phyllantus niruri	Stem and aerial parts		Water	60	20.00	17.78	93.80[f]	(Markom et al., 2010b)
			Ethanol (50%)			19.83	93.60[f]	
			Ethanol (70%)			8.50	92.10[f]	
Punica granatum	Leaves		---	50	30.00	0.21-0.67	340.00[g]	(Cavalcanti et al., 2012)
Pinus pinaster	Sapwood and knotwood		---	50	25.00	1.60	19.38[g]	(Conde et al., 2013)
			Ethanol (10%)			4.10	75.61[g]	
Carya illinoinensis	Shells		Ethanol (10%)	50	10.00	0.83	0.48[h]	(do Prado et al., 2014)
					20.00	8.40	29.00[h]	
Camellia sinensis	Leaves		Ethanol	50	18.80	---	499.90[d]	(Maran et al., 2015)
Picea abies	Bark		Ethanol (70%)	40	10.00	22.5	26.38[d]	(Talmaciu et al., 2016)

[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DE= dry extract.
[c]Amount of epicatechin recovered in the extracts.
[d]Tannin content in extracts expressed in tannic acid equivalents (TAE).
[e]Amount of catechin recovered in the extracts.
[f]Total ellagitannin content in the extracts.
[g]Tannin content in extracts expressed in gallic acid equivalents (GAE).
[h]Tannin content in extracts expressed in catechin equivalents (CE).

Table 5. Results related to the extraction of tannins using water at high pressures and temperatures

Species	Plant part	Time (min)	T[a] (ºC)	P (MPa)	Extraction yield (% w/w)[a]	Tannin content (mg/g_{DE}[b])	References
Vitis vinifera	Seeds	30	50	10.34	4.20	615.47[c]	(García-Marino et al., 2006)
			100		12.40	405.67[c]	
			150		37.70	505.44[c]	
Terminalia chebula	Fruits	37.50	120	4	---	15.57[d]*	(Rangsriwong et al., 2009)
			180			21.43[d]*	
			220			3.95[d]*	
Punica granatum	Peels	5	40	10.34	43.30	21.94[c] / 610.39[e]	(Çam and Hışıl, 2010)
Phyllantus niruri	Stem and aerial parts	60	100	5	21.50	100.46[d]	(Markom et al., 2010a)
				10	23.21	102.11[d]	
				15	24.50	95.92[d]	
				25	23.35	90.36[d]	
Rosmarinus officinalis	Leaves	20	200	10.34	15.00	192.84[f]	(Plaza et al., 2010)
Thymus vulgaris					14.80	188.48[f]	
Verbena officinalis					8.00	81.14[f]	
Vitis vinifera	Pomace	30	120	8	---	12.29[c]*	(Aliakbariana et al., 2012)
				11.50		14.35[c]*	
				15		11.52[c]*	
Vitis vinifera	Pomace	5	100	10.34	---	52.90[c]	(Vergara-Salinas et al., 2013)
			200			18.30[c]	
Larix europaea	Barks	30	100	2	10.50	381.90[e]	(Ravber et al., 2015)
Phyllantus amarus	Aerial parts	15	107.60	11	---	0.54[f]*	(Sousa et al., 2016)
			150.00			3.15[f]*	
			192.40			4.14[f]*	
Viola × wittrockiana	Flowers	15	---	250	---	93.86[e]*	(Fernandes et al., 2017)
Ficus carica	Industry fermented byproducts	30	---	0.1	5.32	0.46[c]*	(Alexandre et al., 2017)
				300	6.61	0.53[c]*	
				600	7.13	0.49[c]*	
Pistacia vera	Hulls	50	110	6.9	59.10	41.46[g]	(Erşan et al., 2018)
			150		70.90	45.84[g]	
			190		65.30	31.24[g]	

*Results expressed in mg of tannins per gram of dry matter.
[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DE= dry extract.
[c]Tannin content in extracts expressed in catechin equivalents (CE).
[d]Hydrolysable tannin content in extracts (gallotannins+ellagitannins+coraligin).
[e]Tannin content in extracts expressed in tannic acid equivalents (TAE)
[f]Tannin content in extracts expressed in gallic acid equivalents (GAE)
[g]Gallotannin content in extracts obtained by HPLC

Table 6. Results devoted to the extraction of tannins assisted by microwave

Species	Plant part	Extraction conditions					Extraction Yield (% w/w)[a]	Tannin content (mg/g_{DM}[a])	References
		Solvent	S/L (g/mL)	T (ºC)	Time (min)	Power (W)			
Vitis vinifera	Seed	Methanol (90%)	1:15	73	3.33	30	15.12	429.00[c]*	(Hong et al., 2001)
Radix puerariae	Whole plant	Ethanol (70%)	1:20	---	6.50	255	---	5.75[d]	(Wang et al., 2010)
			1:30					8.00[d]	
			1:40					6.25[d]	
Cinnamomum zeylanicum	Leaves	Ethanol (50%)	1:20	50	18.00	200	---	16.79[e]	(Gallo et al., 2010)
Crocus sativus	Powder							29.39[e]	
Coriandrum sativum	Seeds							0.82[e]	
Cuminum cyminum								11.59[e]	
Agrimonia pilosa	Stems and roots	Acetone	1:35	30	15.00	300	---	99.95[e]	(Jin et al., 2010)
						500		128.65[e]	
						700		107.00[e]	
Buddleia officinalis	Whole platn	Ethanol (75%)	1:10	78	10	900	---	55.5[f]*	(Pan et al., 2010)
		Ethanol (95%)						62.00[f]*	
		Ethanol pure						58.50[f]*	
Vitis vinifera	Seeds	Ethanol (70%)	1:40	60	2.00	125	16.40	528.05[e]*	(Li et al., 2011)
Pinus radiata	Bark	Acetone (70%)	1:10	25	3.00	900	10.40	523.69[f]*	(Aspé and Fernández, 2011)
Rosmarinus officinalis	Leaves	Methanol (70%)	1:5	70	5.00	180	---	3.48[d]	(Švarc-Gajić et al., 2013)
						320		3.90[d]	
						800		3.25[d]	
Pinus pinaster	Bark	Acetone (80%)	1:20	---	3.00	100	13.60	48.98[f]*	(Chupin et al., 2015)
Myrtus communis	Leaves	Ethanol (42%)	1:32	---	1.04	500	---	32.65[g]	(Dahmoune et al., 2015)
Acacia mollissima	Bark	Water	1:20	---	5.00	150	---	47.64[h] 0.09[c]	(Naima et al., 2015)
		Ethanol						30.29[h] 0.03[c]	
Eucalyptus globulus	Leaves	Ethanol (45%)	1:30	---	4.50	340	---	4.11[f]	(Huma et al., 2018)

*Results expressed in mg of tannins per gram of dry extract.
[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DM= dry matter.
[c]Tannin content in extracts expressed in tannic acid equivalents (TAE).
[d]Rutin content in the extracts (RC).
[e]Tannin content in extracts expressed in gallic acid equivalents (GAE).
[f]Tannin content in extracts expressed in catechin equivalents (CE).
[g]CAmount of condensed tannins precipitated from extracts (CTP).
[h]Tannin content in extracts expressed in cyaniding equivalents (CyE).

Table 7. Results related to the extraction of tannins assisted by ultrasound

Species	Plant part	Extraction conditions					Extraction Yield (% w/w)[a]	Tannin content (mg/g_{DM}[b])	References
		Solvent	S/L (g/mL)	T (ºC)	Time (min)	Power (W)			
Leucaena spp	Leaves	Acetone 70%	1:50	25	15	---	---	86.10[c]	(Dalzell and Kerven, 1998)
					20			89.80[c]	
					30			88.10[c]	
Betula alleghaniensis	Foliage	Ethanol (95%)	---	20	30	750	14.80	43.00[d]*	(Diouf et al., 2009)
Averrhoa carambola	Fruit	Methanol	1:10	25	15	135	4.80	11.70[e]*	(Annegowda et al., 2012)
					30		4.70	11.20[e]*	
					45		4.30	10.90[e]*	
Vitis vinifera	Full berry	Ethanol (50%)	1:10	10	6	200	---	6.00[f]	(Carrera et al., 2012)
Vitis vinifera	Seeds	Methanol	1:10	30	15	150	---	61.80[e]	(Da Porto et al., 2013)
Areca catechu	Nuts	Acetone (80%)	1:10	---	37.50	10		44.53[e]	(Chavan and Singhal, 2013)
						50		101.60[e]	
						90		37.02[e]	
Withania somnifera	Roots	Ethanol	1:10	25	20	480	3.17	29.15[g]*	(Dhanani et al., 2013)
		Ethanol (10%)					9.08	22.12[g]*	
		Water					10.27	18.18[g]*	
Quercus brantii	Leaves	Methanol (50%)	1:20	60	45	140	21.10	104.50[e]*	(Tabaraki et al., 2013)
		Methanol (90%)					25.30	127.00[e]*	
Pistacia lentiscus	Leaves	Ethanol (40%)	1:50	---	15	130	---	35.94[f]	(Dahmoune et al., 2014)
Rubus fruticosus	Fruits	Ethanol	1:2.50	25	15	60	5.30	5.09[h]*	(Ivanovic et al., 2014)
					30		5.90	25.42[h]*	
Phyllantus amarus	Aerial parts	Deionized water	---	25	7	301	---	27.23[g]	(Sousa et al., 2016)
Cannabis sativa	Flowers, leaves and seed husks	Methanol (80%)	1:25	---	15	90	8.75	31.44[d]	(Agarwal et al., 2018)
						120	11.29	40.39[d]	
						150	9.68	39.19[d]	
Piper betle	Leaves	Ethanol (78.74%)	1:21.85	51.60	30	400	13.71	21.5[i]	(Ali et al., 2018)
Vitis vinifera (Tempranillo)	Pomace	Ethanol (44%)	1:5	50	3	500	---	86.67[f]	(Poveda et al., 2018)

*Results expressed in mg of tannins per gram of dry extract.
[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DM= dry matter.
[c]Tannin content in extracts expressed in L leucocephale proanthocyanidin equivales (LPAE).
[d]Tannin content in extracts expressed in quercetin equivalents (QE).
[e]Tannin content in extracts expressed in catechin equivalents

[f]Total content of condensed tannins in extracts (TCT).
[g]Tannin content in extracts expressed in gallic acid equivalents (GAE).
[h]Total tannin content in extracts (TTC).
[i]Tannin content in extracts expressed in rutin equivalents (RE).

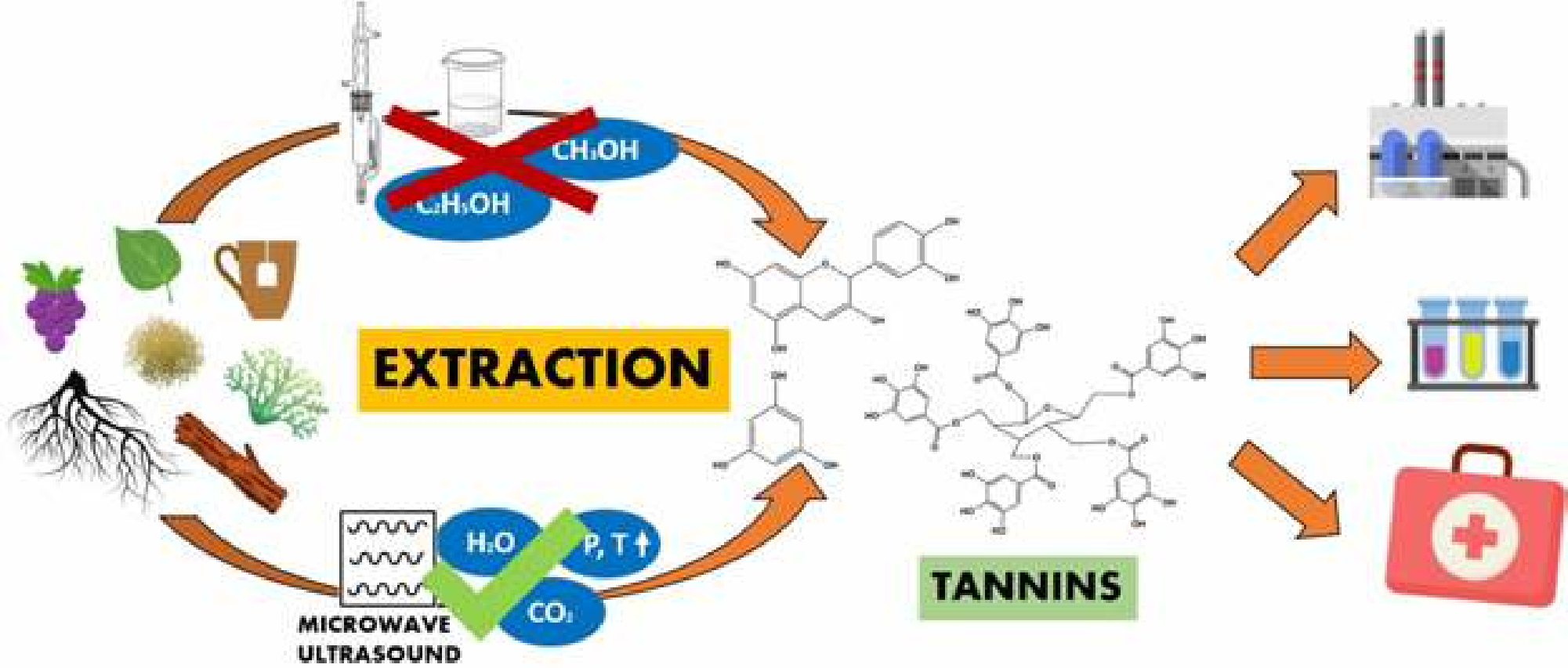
Table 8. Results devoted to the assessment and comparison of the different tannins extraction methods

Species	Plant part	Extraction technique	Extraction conditions	Extraction yield (% w/w)[a]	Tannin content (mg/g_{DE}[b])	Reference
Pistachia Vera	Hulls	SLE	Methanol-1:4 25ºC, 6h	---	32.80[d]	(Goli et al., 2005)
		SFE	$SCCO_2$[c] co-solvent-15%Methanol 45ºC-15 min. 35.46MPa		6.55[d]	
		UAE	Methanol-1:8 45 min.		32.80[d]	
Terminalia chebula	Fruit	SLE	Ethanol-1:15 78.3ºC, 240 min	---	9.92[e]	(Rangsriwong et al., 2009)
			Water-1:15 100ºC, 120 min		15.96[e]	
		PWE	Water 180ºC, 37.5 min 4MPa		21.43[e]	
Pinus radiata	Bark	SLE	Acetone (70%)-1:10 82ºC, 180 min.	12.00	62.10[f]	(Aspé and Fernández, 2011)
		UAE	Acetone (70%)-1:10 25ºC, 6 min. 85W	9.50	47.2[f]	
		MAE	Acetone (70%)-1:10 25ºC, 3 min. 900W	10.40	55.4[f]	
Galla chinensis	Whole plant	EtOH+UAE+MAE	Ethanol-1:15 Microwave 400W+ Ultrasound 50W 1 min	---	543.50[g*]	(Lu et al., 2012)
		IL+UAE+MAE	1-butyl-3-methylimidazole bromide [C4mim]Br-1:15 Microwave 400W+ Ultrasound 50W 1 min		630.20[g*]	
		MAE	Ethanol-1:15 400W 1 min		528.50[g*]	
		UAE	Ethanol-1:15 50W 1 min		491.20[g*]	
Camellia sinensis	Leaves and aerial parts	SLE	Ethanol (30%)-1:10 40ºC, 2h	---	180[g]	(Ribeiro et al., 2013)
		ILE	1-ethyl-3-methylimidazolium chloride [C2mim]Cl (50%) 40ºC, 2h, 1:10	---	300[g]	

Rubus sp.	Bagasse	SLE	Ethanol-1:31.60 50ºC, 6-8h	14.58	4.25[g]*	(Reátegui et al., 2014)
		SFE	$SCCO_2$[c] no cosolvent, 15MPa 120 min.	6.84	4.07[g]*	
		SFE+UAE	$SCCO_2$[c] no cosolvent, 15 MPa 400W, 57 min.	7.94	3.53[g]*	
			$SCCO_2$[c] cosolvent-10%Ethanol, 15MPa 200W, 57 min	18.25	12.73[g]*	
Solidago canadensis	Bark	SLE	Ethanol (50%)-1:20 25ºC, 30 min.	---	26.29[h]	(Deng et al., 2015)
		UAE	Ethanol (50%)-1:20 30 min		30.15[h]	
Myrtus comunis	Leaves	UAE	Ethanol (96%)-1:5.4 30 min. 320W	10.81	324.34[g]*	(Pereira et al., 2017, 2016)
		SFE	$SCCO_2$[c] co-solvent-Ethanol 45ºC, 700 min. 23MPa	10.80	47.28-94.56[g]*	
Berberis jaeschkeana	Fruits	SLE	Methanol 80%-1:70 70ºC-15 min.	---	21.41[d]	(Belwal et al., 2017)
		UAE	Methanol 80%-1:70 70ºC-15 min.		32.41[d]	
		MAE	Methanol 80%-1:40 5 min. 670W		24.04[d]	
Myrtus communis	Leaves	SLE	Ethanol 42%-1:50 120 min.	---	36.01[f]	(Bouaoudia-Madi et al., 2017)
		MAE	Ethanol 42%-1:30 1 min 500W		34.50[f]	
Salacia chinensis	Roots	SLE	Methanol-1:10 25ºC, 360 min.	---	43.37[d]	(Ghadage et al., 2017)
		UAE	Methanol-1:10 25ºC, 10 min.		41.29[d]	
		MAE	Methanol-1:10 25ºC, 5 min. 180W		43.54[d]	
Erica carnea	Aerial parts	SLE	Ethanol 96%-1:30 22ºC, 7 days (maceration)	15.30	57.19[g]	(Veličković et al., 2017)
		UAE	Ethanol 96%-1:20 30 min 216W	18.33	60.65[g]	

		MAE	Ethanol 96%-1:20 30 min 600W	30.65	61.70[g]	
		PWE	Water-1:20 140ºC, 30 min. 4MPa	42.66	62.53[g]	
Lavatera thuringiaca	Whole plant	SLE	Ethanol 96%-1:30 22ºC, 8h	---	65.61[g]*	(Mašković et al., 2018)
		UAE	Ethanol 96%-1:20 30 min 216W		71.78[g]*	
		MAE	Ethanol 96%-1:20 30 min 600W		71.15[g]*	
		PWE	Water-1:20 140ºC, 30 min. 4MPa		72.23[g]*	

*Results expressed in mg of tannins per gram of dry matter.
[a]Extraction yield expressed in grams of extracts per grams of material.
[b]DE= dry extract.
[c]$SCCO_2$= carbon dioxide at supercritical conditions.
[d]Tannin content in extracts expressed in tannic acid equivalents (TAE).
[e]Hydrolysable tannin content in extracts (HTC)
[f]Tannin content in extracts expressed in catechin equivalents (CE).
[g]Tannin content in extracts expressed in gallic acid equivalents (GAE).
[h]Total tannin content in the extracts (TTC).


CH₃OH
C₂H₅OH
EXTRACTION
H₂O
P, T
CO₂
MICROWAVE
ULTRASOUND
TANNINS