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► **To cite this version:**

Pedro Luis de Hoyos-Martinez, Juliette Merle, Jalel Labidi, Fatima Charrier-El Bouhtoury. Tannins extraction: A key point for their valorization and cleaner production. *Journal of Cleaner Production*, 2019, 206, pp.1138-1155. 10.1016/j.jclepro.2018.09.243 . hal-01925978

HAL Id: hal-01925978

<https://hal.science/hal-01925978v1>

Submitted on 27 Nov 2018

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Tannins extraction: a key point for their valorization and cleaner production

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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 perspectives 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 1. INTRODUCTION

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

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

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

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

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

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

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

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

9 The work structure is divided in several parts. After the introduction, section 2 is presented
10 covering a brief state of the art on the field of tannins related to the tannin extraction. Then section
11 3, describes the methodology employed for carrying out this research. Section 4 displays the main
12 results related to tannins extraction by the different methods, an in-depth comparison between
13 them and a full discussion of the major advantages and disadvantages of each one. The study is
14 concluded with the main outcomes and future perspectives.

15 **2. BACKGROUND**

16 **2.1. Tannin definition**

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

22 One of the first tannins definitions was given by A. Seguin in 1796, who described them as
23 substances in vegetable extracts used for converting animal skins into stable leather (Bele et al.,
24 2010). Nevertheless, it was not until the early 1960s that a more accurate definition of tannin was
25 introduced by Swain and Bate-Smith in 1962. They defined tannins as “*naturally occurring water*
26 *soluble polyphenolic compounds having a molecular weight between 500 and 3000, capable of*
27 *precipitating alkaloids as well as gelatin and other proteins from aqueous solutions*”(Bate-Smith
28 and Swain, 1962). This definition is the one most frequently found and cited within the literature

29 **2.2. Tannin classification**

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

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

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

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

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

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

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

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

28 *Gallotannins*: they represent the simplest kind of hydrolysable tannins and consist of
29 galloyl or digalloyl units linked to a polyol core and therefore they have the ability to yield
30 gallic acid from the hydrolysis reaction.

31 *Ellagitannins*: this kind of tannins are characterized by having one to several HHDP units
32 attached to a polyol core. Upon hydrolysis, ellagitannins are able to produce HHDP free
33 units, which spontaneously turn into the dilactone (ellagic acid).

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

1 block connected through a carbon-carbon linkage. This type represents a minority group within
2 the tannins family. A typical example of this kind of compounds is accutisim A (figure 5).
3 The other type of tannins discovered in the recent years is phlorotannins. This group is
4 prominently found in brown algae and is composed of phloroglucinol units (1,3,5-
5 trihydroxybenzene). The research carried out lately on this group of tannins, has led to the
6 structural elucidation of more than 150 compounds with a large range of molar masses between
7 126-625000 g·mol⁻¹ (Glombitza and Pauli, 2003; Lopes et al., 2012; Sathya et al., 2017).
8 Structurally phlorotannins form dehydro-oligomers and polymers of phloroglucinol moieties
9 linked via aryl-aryl (C-C) and diaryl ether bonds (C-O) (Koivikko et al., 2008).
10 Considering the previous information, it is clear tannins can display a variety of structures
11 resulting in diverse chemical compositions. This aspect, which discussed in the next point, is of
12 considerable importance, since it can have a direct impact over the extraction efficiency.

13 **2.3. Tannins abundance and occurrence in nature**

14 In nature, tannin content depends on several aspects such as the plant part and species considered.
15 Within the same species, the tannin content is reported to vary between the different parts with
16 special abundance in barks, leaves, seeds, roots and rhizomes (Bele et al., 2010). In addition, their
17 content can also vary with seasonal and environmental factors e.g. water availability, temperature,
18 light intensity and soil quality (Frutos et al., 2004). These points have a relevant importance, since
19 they can influence the results of the different extraction methods. In the literature, there are several
20 works assessing the effect of different species and plant parts on the tannin extraction results
21 (Geoffroy et al., 2017; Tabaraki et al., 2013). In this sense, it was reported by Cheng et al. (2012)
22 that the variety of the grape employed significantly influenced the amount of tannins quantified
23 in the extracts (Cheng et al., 2012). They found that the extracts of the variety *Pinot Noir* presented
24 higher amount of tannins (gallic acid equivalents) than *Pinot Meunier*. This was attributed to the
25 different viticultural practices and environmental conditions. Moreover, the amount of tannins
26 was higher in the seeds compared to skin and pomace. In another work, tannins from different
27 spices were extracted via microwave and ultrasound and significant differences regarded. Again,
28 the variety of spice was confirmed to have a major role. Thus, the extraction for *Crocus sativus*
29 resulted in a tannin amount thirty times higher than that of *Coriandrum sativum* (Gallo et al.,
30 2010). Besides, the spices were reported to provide higher tannin amounts in the extracts by means
31 of microwave assisted extraction than ultrasound.

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

1 (2015), proved that the tannin composition of the extracts from different wood barks species
2 extracted under the same conditions showed several divergences (Bianchi et al., 2015). Thereby,
3 a predominant amount of prodefininidins was determined in Silver fir, whereas a higher amount of
4 procyanidins was found for European Larch. They reported too, that the tannins composition of
5 these species substantially differ from those of tropical species such as Mimosa and Quebracho.
6 This divergences were also displayed on another work on tannin extraction from the seeds of
7 different varieties of grapes (Mattivi et al., 2009). The results showed significant variations
8 between the major tannin monomers present in the different grape species.

9 **3. METHODS AND RESEARCH DESIGN**

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

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

25 **3.1. Choice of search terms and selection of articles**

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

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

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

13 **3.2. Method of analysis and limitations of research**

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

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

23 **4. RESULTS AND DISCUSSION**

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

26 **4.1. Extraction parameters for each extraction process**

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

31 **4.1.1. Solid-liquid extraction (SLE)**

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

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

3 Concerning the use of organic solvents and their aqueous solutions, the extraction is commonly
4 carried out by means of a soxhlet apparatus whose experimental extraction procedure has been
5 described in several works (Jensen, 2007; Luque de Castro and Priego-Capote, 2010). However,
6 other techniques are also employed and reported in the literature such as infusion or maceration.

7 The extraction with water can be carried out under reflux or through simple maceration in flasks
8 or vessels. At the industrial scale it is generally performed on wood barks by percolation or open
9 diffusion (Ciesla, 1998; Myers, 1998).

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

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

1 components is proved to reach higher extraction yields compared to lower concentrations (Antwi-
2 Boasiako and Animapauh, 2012; Inoue et al., 1998). Nevertheless, the increment of the
3 concentrations can provide a lower tannin content in the extracts due to the raise of undesirable
4 non-tannin components (Ping et al., 2011). For this reason, the indiscriminate increase of the
5 alkaline compounds and salts concentrations is not desirable. Different works were found
6 underlining the importance of employing moderate amount of these compounds (Aires et al.,
7 2016; Vieira et al., 2011).

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

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

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

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

32 Concerning the time of extraction, it is seen that the increment of this parameter provides a higher
33 content of tannins extracted as presented in some of the works from literature (Baldosano et al.,
34 2015; Chowdhury et al., 2010). This is due to the longer times the solute and the solvent are in
35 contact, which favours the mass transfer between both components. Nevertheless, the increase of
36 the extraction times beyond certain values is not desirable. It was discussed by Tan et al. (2013)
37 that the amount of tannins extracted above 4.5h was dramatically decreasing towards a minimum

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

5 The temperature of extraction is observed to increase the extraction yields as displayed in the
6 results from table 3 (Kemppainen et al., 2014; Vázquez et al., 2001). This enhancement is due to
7 the increase of the mass transfer coefficient at higher temperatures (Huang et al., 2016). Moreover
8 the increment of the temperature results in the improvement of the solute solubility and diffusion
9 coefficient and also decreases of solvent viscosity, which promotes the extraction (Al-Farsi and
10 Lee, 2008). This parameter is normally regulated and optimized, since high temperatures can also
11 lead to lower amount of tannins in the extracts as showed by Ramos et al. (2013) (Ramos et al.,
12 2013). This was attributed to the denaturation of these compounds owing to the harsh conditions
13 employed. The use of too high temperatures can also result in solvent evaporation. For this reason,
14 in this kind of extraction the temperature is normally set up at the solvent boiling point.

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

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

29 **4.1.2. Supercritical fluid extraction (SFE)**

30 In this part, the extraction of tannins by using supercritical fluids is presented. The principle of
31 this method is based on the concept of critical point, which is defined as the highest temperature
32 and pressure at which a pure substance can exist in a vapour-liquid equilibrium (Ajila et al., 2011).
33 Above this point a fluid shares properties between a gas and a liquid, such as the typical weight
34 of liquids with the penetration power of gases (Azmir et al., 2013). The works found in the
35 literature related to this technique are presented in table 4. In regards to the presented results,
36 various common characteristics are identified. The most widely employed solvent among all the
37 works is carbon dioxide (CO₂). This is due to its desirable properties such as non toxicity, non-

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

5 Concerning the extraction yields and tannins extracted, the parameter with the greatest influence
6 is the utilization of a co-solvent. Thus, poor extraction yields are achieved using supercritical CO₂
7 alone whereas considerable enhancements are reported after the addition of a co-solvent
8 (Cavalcanti et al., 2012; Conde et al., 2013). This is due to the non-polar nature of CO₂ as solvent
9 and the polar nature of most of tannin compounds. The addition of co-solvents of polar nature
10 such as ethanol, methanol or aqueous mixtures help ameliorating the solvating power of CO₂
11 towards tannins and improves the extraction yields. The pressure employed also presents a major
12 role in the extraction efficiency and amount of tannins extracted. It is observed that the increment
13 of the pressure promotes the extraction of tannins (do Prado et al., 2014). The reason for that is
14 that at higher pressures the fluid density is increased, decreasing the distance between the
15 molecules and therefore improving the interactions fluid-matrix (Maran et al., 2015).

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

21 The main advantages concerning this extraction method are the utilization of mild temperatures
22 and a nontoxic solvent (CO₂) which can be easily removed and can avoid further oxidation
23 reactions by creating an oxygen free environment. On the other side, one of the main drawbacks
24 are the high investment costs, due to the high pressures needed for the extraction process (Perrut†,
25 2000). The other main problem concerning CO₂ is its non polar nature, which reduces the
26 extraction power towards tannins (low solubility of polar compounds). Consequently, the addition
27 of co-solvents such as methanol, ethanol, acetone or water, becomes an essential requirement

28 **4.1.3. Pressurized water extraction (PWE)**

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

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

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

12 The temperature plays a major role and its increment leads to higher extraction yields (Sousa et
13 al., 2016). This effect is attributed to the fact that at higher temperatures the solvent is more easily
14 diffused into the plant matrix. Moreover at higher temperatures the solute vapour pressure is
15 incremented and it is easier for the solute to free itself from the matrix (Markom et al., 2010a).
16 However, the employment of too severe temperatures was proved to have a negative effect,
17 particularly on the tannin content of the extracts (García-Marino et al., 2006; Rangsiwong et al.,
18 2009). This is associated to the possible degradation and denaturation of the different
19 polyphenolic compounds at harsh temperatures (Vergara-Salinas et al., 2013).

20 Concerning the pressure, the influence on the water properties is little as far as it stays as a liquid
21 (Plaza and Turner, 2015). For this reason, its effect on the results of extraction is normally lower.
22 Despite this fact, the increase of this parameter can result in slightly higher extraction yields and
23 tannin content in the extracts until certain pressure values (Aliakbariana et al., 2012). Above these
24 pressure values the solvent solubility is not further improve and accordingly the extraction yields
25 remain or even slightly decrease as well as the amount of tannin extracted (Markom et al., 2010a).
26 The main advantages of this method are the reduced handling time and solvent consumption and
27 the no utilisation of toxic organic solvents. Another advantage is the possibility to extract
28 selectively tannins of different polarities by the modification of the temperature, pressure or co-
29 solvent. On the other hand, the major disadvantages are related to the high temperatures and
30 pressures used (reduction of the extraction selectivity and possible degradation of the analytes)
31 and the expensive equipment required (solvent transporting pump, a pressure vessel and system
32 controller, and a collection device for the extract needed).

33 **4.1.4. Microwave assisted extraction (MAE)**

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

1 is the heating of one of the components by interaction with the other, previously heated by the
2 microwave irradiation. The effect of heating on the solvent increases its solubility, whereas on
3 the material it improves porosity allowing an easier penetration of the solvent (Routray and Orsat,
4 2012). Thereby, in either case the extraction of tannins from the cell wall of the feedstock is eased.
5 Within this section, a sample of papers focused on the tannins extraction assisted by microwave
6 is displayed (table 6). From the previous results, it is remarked the short times needed for
7 extraction (1-20 minutes), which achieved a significant level of tannin extraction. Regarding the
8 solvent employed, the volume used for the extraction has a direct impact on the amount of tannins
9 extracted. Normally a larger amount of solvent is supposed to achieve a higher quantity of tannins
10 extracted, according to the principle of equilibrium between solvents and materials. In a work by
11 Wang et al., 2010 (Wang et al., 2010), it was found that the increase of the solvent volume led to
12 the enhancement of the tannins extracted until certain point (ratio 1:30) and then decreased. This
13 was attributed to the relatively large amount of solvent employed, which resulted in a dilution of
14 the amount of the tannins in the extracts (Guo et al., 2001; Xiao et al., 2008). The nature of the
15 solvent also plays a major role on the extraction as was already mentioned in section 4.1.1
16 Accordingly, the increase of the polarity of the solvent leads to higher amounts of tannins
17 extracted (Pan et al., 2010). The effect of the microwave power was discussed in several works
18 as well (Naima et al., 2015; Švarc-Gajić et al., 2013). It is proved that the increase of the power
19 leads to higher amounts of tannins extracted. This is due to the enhancement of the solvent
20 penetration into the matrix and the faster energy transfer to the solvent and material. However,
21 above high values of microwave irradiation, the amount of tannins extracted is observed to
22 decrease. Normally, this fact is due to the thermal degradation of the tannins, which results in a
23 lower content of these compounds in the extracts (Dahmoune et al., 2015). It has been showed as
24 well that too high microwave power can provide excess of energy to the solvent and material.
25 This superfluous energy can generate abnormal molecular interaction, which affect the extraction
26 yields of tannins (Jin et al., 2010). Consequently, this parameter is normally optimized in the
27 majority of the works to achieve the highest amount of tannins recovered.
28 The main advantages of this method are the employment of considerably short extraction times,
29 and lower amount of solvents compared to traditional solid-liquid extraction. Another advantage
30 is the agitation provided by the microwave irradiation, which can ameliorate the mass transfer
31 phenomenon (Jain et al., 2013). The main disadvantages are the great costs of the equipment
32 needed (specially at larger scale) and the possibility of thermal degradation of the feedstocks and
33 tannins, especially those with high number of hydroxyl groups (Xu et al., 2017).

34 **4.1.5. Ultrasound assisted extraction (UAE)**

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

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

4 In this section, a sample of works related to the extraction of tannins assisted by ultrasound, is
5 discussed (table 7). Within the works presented, the influence of several parameters on tannin
6 extraction efficiency is observed. Again, the solvent employed has a prominent effect and
7 therefore the use of more polar solvents leads to the improvement of the extraction yields.
8 Nonetheless, it was reported that ethanol and methanol presented a higher selectivity to the
9 polyphenolic compounds, providing higher amounts of tannins in the extracts (Dhanani et al.,
10 2013; Tabaraki et al., 2013). Regarding the extraction times, not high values are needed to achieve
11 good extraction yields (below 1hour). The increment of this parameter can lead to higher
12 extraction yields and amount of tannin in the extract (Ivanovic et al., 2014). However, when the
13 extraction time is incremented above relatively high values, the extraction efficiency tends to
14 decrease. A first work by Dalzell and Kerven, (1998) showed that sonication after 30 minutes
15 decreased the tannins extraction efficiency from *Leucaena* spp. This result was attributed to the
16 possible degradation of the proanthocyanidins due to the increased temperature of the water bath,
17 provided by the prolonged sonication time (Dalzell and Kerven, 1998). In another work, the
18 decrease of the tannins extracted at high extraction times was associated to the prolonged interval
19 of sonication and the possible degradation of the tannins as well but also to the lower
20 concentration gradient of the solvent (Annegowda et al., 2012). A similar tendency is observed
21 for the sonication power. Hence, the increase of this parameter provides higher amounts of tannins
22 extracted until certain point and then began to decrease (Agarwal et al., 2018; Chavan and
23 Singhal, 2013). This is due to the chemical decomposition of tannins extracted. Taking the
24 previous phenomena into consideration, a further optimization of the conditions was carried out
25 in most of the works presented.

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

31 **4.2. Comparison of extraction methods**

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

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

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

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

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

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

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

3 **4.2.1 Technical and costs comparison**

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

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

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

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

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

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

5 **5. Conclusions**

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

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

25

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ACCEPTED MANUSCRIPT

LIST OF FIGURES:

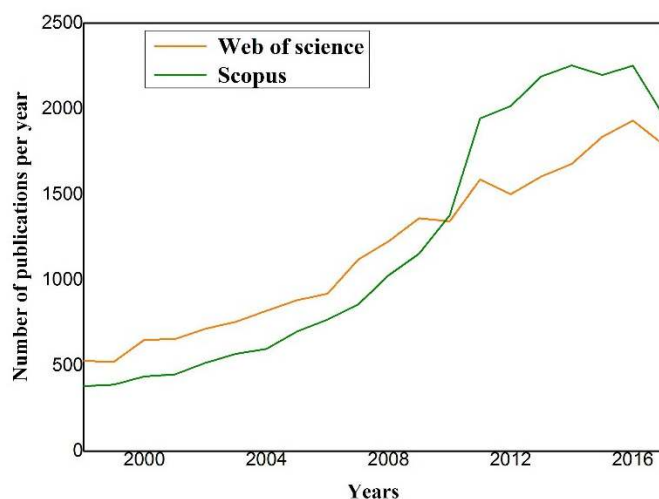


Figure 1. Number of tannins-related publications per year in the period 1998-2017 indexed in Web-of-Science and Scopus.

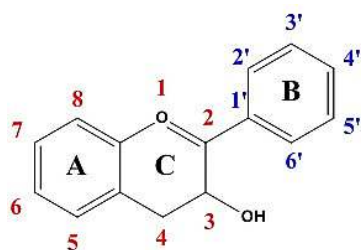


Figure 2. Structure of Flavan-3-ol and its nomenclature

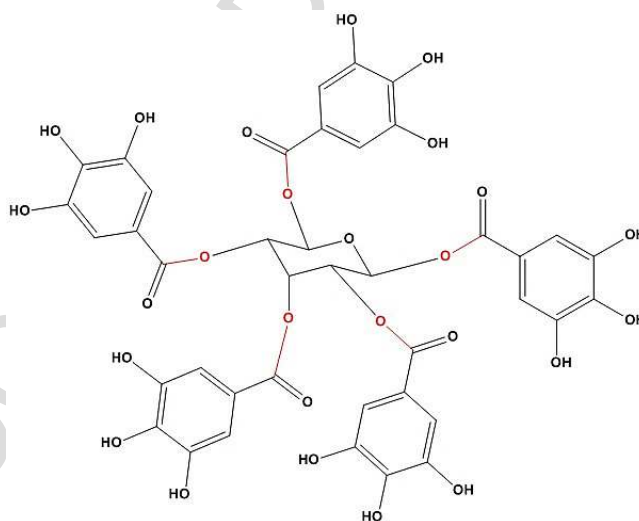


Figure 3. Example of a hydrolysable tannin unit and the linkages present (e.g. pentagalloyl glucose structure linked via ester bonds).

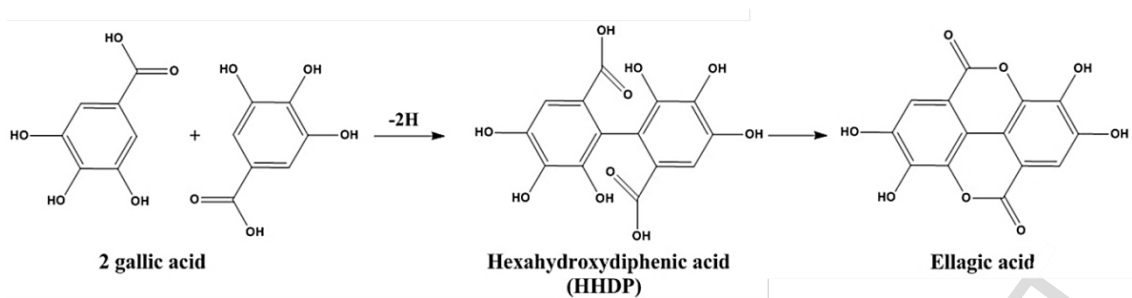


Figure 4. Transformation between the main polyphenolic acids and derivatives present in the structure of hydrolysable tannins

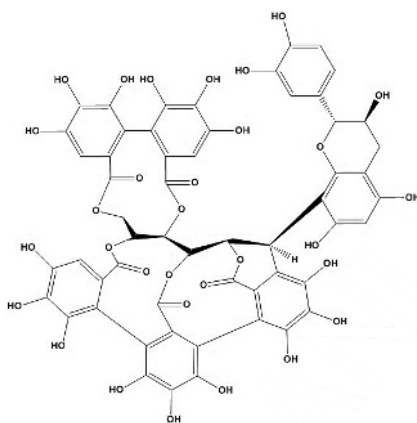


Figure 5. Acutissimin A typical complex tannins group.

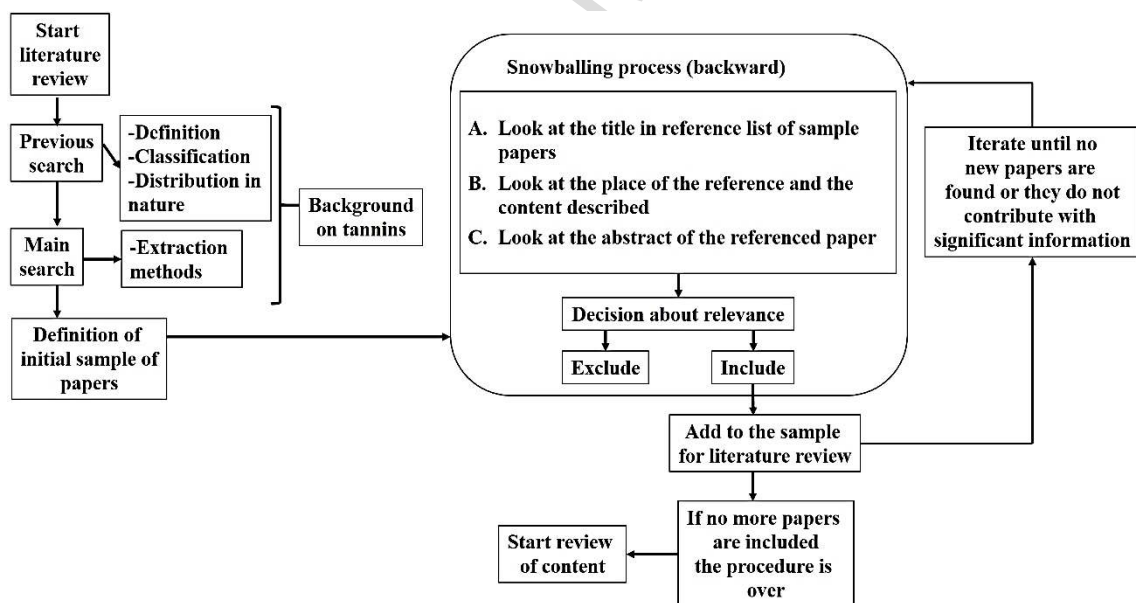


Figure 6. Literature review process

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

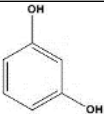
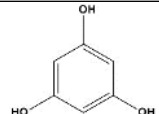
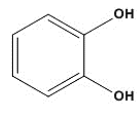
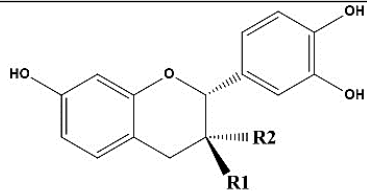
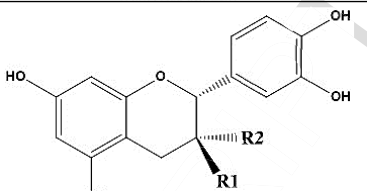
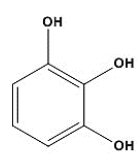
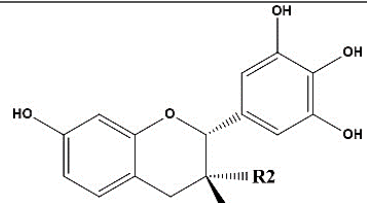
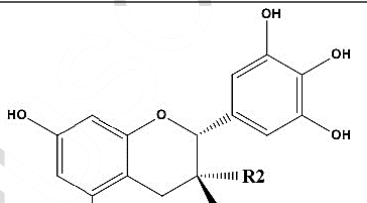
A rings B rings	 resorcinol ring	 phloroglucinol ring
 catechol ring	 R1=OH R2=H fisetinidol R1=H R2=OH epifisetinidol	 R1=OH R2=H catechin R1=H R2=OH epicatechin
 pyrogallol ring	 R1=OH R2=H robinetinidol R1=H R2=OH epirobinetinidol	 R1=OH R2=H gallocatechin R1=H R2=OH epigallocatechin

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
<i>Pinus radiata</i>	Bark	Water	1:20, 2h	19.60	887.00 ^c	(Inoue et al., 1998)
		Water+ 1% NaOH	100°C	30.50	828.00 ^c	
<i>Pinus pinaster</i>	Bark	Water + 2.5% NaOH	1:10, 0.5h	16.5	965.00 ^c	(Vázquez et al., 2001)
		Water + 5% NaOH	70°C	18.9	875.00 ^c	
		Water + 2.5% NaOH	1:10, 0.5h	23.20	963.00 ^c	
		Water + 5% NaOH	90°C	25.00	812.00 ^c	
<i>Mangifera indica</i>	Peels	Acetone (80%)	1:20, 3h	---	1.4 ^d	(Berardini et al., 2004)
	Pulp			0.2 ^d		
	Kernel			15.5 ^d		
<i>Acacia mearnsii</i>	Bark	Ethanol	1:10, 24h	---	237.00 ^e	(Pansera et al., 2004)
<i>Phyllanthus niruri</i>	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	
<i>Acacia catechu</i>	Whole plant	N,N-dimethylammonium N',N'-dimethylcarbamate (DIMCARB) (15%)	1:5, 25°C 1h	30	---	(Chowdhury et al., 2010)
			1:5, 25°C 2h	60	---	
			1:5, 25°C 16h	85	61.50 ^f	
		Water	1:10, 70°C 16h	64	28.60 ^f	
<i>Pinus radiata</i>	Bark	Acetone (70%)	1:10, 1-6h	12.00	62.10 ^h	(Aspé and Fernández, 2011)
<i>Vitis vinifera</i>	Pomace	Water + 10% NaOH	1:8, 2h 120°C	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	
<i>Endopleura uchi</i>	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	
<i>Pinus ocarpa</i>	Bark	Water	1:15, 2h b.p.	24.84	655.60 ^c	(Vieira et al., 2011)
		Water + 1% Na ₂ CO ₃		30.94	857.20 ^c	
		Water + 5% Na ₂ CO ₃		35.74	890.70 ^c	
		Water + 1% NaHSO ₃		19.86	846.40 ^c	
		Water + 5% NaHSO ₃		26.70	722.80 ^c	
<i>T. tetraptera</i>	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	
<i>Galla chinensis</i>	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		
<i>Punica granatum</i>	Peels	Methanol	1:20, 6h	---	3.10 ⁱ	504.80 ^e	(Saad et al., 2012)
<i>Pinus pinaster</i>	Bark	Water + 1% NaOH + 0.25% Na ₂ SO ₃ + 0.25% NaHSO ₃	1:9, 2h 80°C	22.06	489.70 ^c		(Chupin et al., 2013)
		Water + 5% NaOH + 0.25% Na ₂ SO ₃ + 0.25% NaHSO ₃		31.30	179.20 ^c		
<i>Pinus radiata</i>	Bark	Acetone (25%)	1:20, 2h 40°C	3.50	350.00 ^h		(Ramos et al., 2013)
		Ethanol (25%)		3.00	310.00 ^h		
		Acetone (25%)	1:20, 2h 120°C	11.00	220.00 ^h		
		Ethanol (25%)		10.10	250.00 ^h		
<i>Carya illinoensis</i>	Shells	Water	1:50, 0.5h 98°C	32.12	36.94 ^h		(do Prado et al., 2014)
		Ethanol	1:50, 1h 25°C	32.09	412.10 ^h		
<i>Osbeckia parvifolia</i>	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		
<i>Picea abies</i>	Bark	Water + 2% NaHSO ₃ + 0.5% Na ₂ CO ₃	1:20, 2h 60°C	16.10	330.00 ^j		(Kemppainen et al., 2014)
			1:20, 2h 90°C	20.90	480.00 ^j		
<i>Mimosa hamata</i>	Whole plant	Methanol (80%)	1:6, 48h	24.20	264.40 ^k		(Saxena et al., 2014)
		Ethanol (95%) ^l		34.74	287.50 ^k		
<i>Pluchea indica</i>	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		
<i>Spondias purpurea</i>	Bark	Ethanol (95%)	1:30	4h	---	31.80 ^e	(Baldosano et al., 2015)
				6h		73.75 ^e	
				8h		181.60 ^e	
<i>Saccharum officinarum</i>	Bagasse	Methanol (50%)	1:10, 72h	6.20	381.80 ^{Ee}		(Vijayalaxmi et al., 2015)
		Ethanol (50%)		4.50	316.50 ^e		

<i>Castanea sativa</i>	Peels	Water	1:4, 4h 85°C	7.03	234.80 ^c	(Aires et al., 2016)
		Water + 1% Na ₂ SO ₃		7.74	794.90 ^c	
		Water + 4% Na ₂ SO ₃		8.67	373.80 ^c	
		Water + 1% NaOH		11.63	728.70 ^c	
		Water + 4% NaOH		66.59	415.00 ^c	
<i>Eucaliptus globulus</i>	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*}	
<i>Phyllanthus niruri</i> (Patiala region)	Whole plant	Ethanol	1:2, 24h	---	2.50 ⁱ	(Kaur and Kaur, 2016)
		Methanol		---	16.00 ⁱ	
<i>Vitis vinifera</i>	Skins	1-butyl-3-methylimidazolium bromide [C4mim]Br 0.5M	1:10, 4h 25°C	---	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.

^aExtraction yield expressed in grams of extracts per grams of material.

^bDE= dry extract.

^cTannin content in extracts expressed in mg of reactive tannins/g dry extract (Stiasny number).

^dTannin content in extracts expressed in gallic acid equivalents (GAE).

^eTannin content in extracts expressed in tannic acid equivalents (TAE).

^fHydrolysable tannin content in the extracts (HTC).

^gb.p= boiling point.

^hContent of extracts expressed in catechin equivalents (CE).

ⁱTannin content in extracts expressed in cyaniding equivalents (CYE).

^jCondensed tannin content in the extracts (CTC).

^kTannin 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 (°C)	P (MPa)	Extraction yield (% w/w) ^a	Tannin content (mg/g _{DE} ^b)	References
<i>Tamarindus indica</i>	Seed	CO ₂	Ethanol (10%)	40	30.00	<1	0.06 ^c	(Luengthanaphol et al., 2004)
				55			0.05 ^c	
				88			0.02 ^c	
<i>Acacia mearnsi</i>	Bark		Ethanol	60	25.00	---	95.00 ^d	(Pansera et al., 2004)
			Water				135.00 ^d	
<i>Vitis vitifera</i>	Seed		Methanol (30%)	80	65.50	---	600.00 ^e	(Ashraf- Khorassani and Taylor, 2004)
			Methanol (35%)				720.00 ^e	
			Methanol (40%)				770.00 ^e	
<i>Phyllanthus niruri</i>	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		
<i>Punica granatum</i>	Leaves	---	50	30.00	0.21-0.67	340.00 ^g	(Cavalcanti et al., 2012)	
<i>Pinus pinaster</i>	Sapwood and knotwood	---	50	25.00	1.60	19.38 ^g	(Conde et al., 2013)	
		Ethanol (10%)			4.10	75.61 ^g		
<i>Carya illinoensis</i>	Shells	Ethanol (10%)	50	10.00	0.83	0.48 ^h	(do Prado et al., 2014)	
				20.00	8.40	29.00 ^h		
<i>Camellia sinensis</i>	Leaves	Ethanol	50	18.80	---	499.90 ^d	(Maran et al., 2015)	
<i>Picea abies</i>	Bark	Ethanol (70%)	40	10.00	22.5	26.38 ^d	(Talmaciu et al., 2016)	

^aExtraction yield expressed in grams of extracts per grams of material.

^bDE= dry extract.

^cAmount of epicatechin recovered in the extracts.

^dTannin content in extracts expressed in tannic acid equivalents (TAE).

^eAmount of catechin recovered in the extracts.

^fTotal ellagitannin content in the extracts.

^gTannin content in extracts expressed in gallic acid equivalents (GAE).

^hTannin 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 (°C)	P (MPa)	Extraction yield (% w/w) ^a	Tannin content (mg/g _{DE}) ^b		References
<i>Vitis vinifera</i>	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		
<i>Terminalia chebula</i>	Fruits	37.50	120	4	---	15.57 ^{d*}		(Rangsriwong et al., 2009)
			180			21.43 ^{d*}		
			220			3.95 ^{d*}		
<i>Punica granatum</i>	Peels	5	40	10.34	43.30	21.94 ^c	610.39 ^e	(Çam and Hışıl, 2010)
<i>Phyllanthus niruri</i>	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		
<i>Rosmarinus officinalis</i>	Leaves	20	200	10.34	15.00	192.84 ^f		(Plaza et al., 2010)
<i>Thymus vulgaris</i>					14.80	188.48 ^f		
<i>Verbena officinalis</i>					8.00	81.14 ^f		
<i>Vitis vinifera</i>	Pomace	30	120	8	---	12.29 ^{c*}		(Aliakbariana et al., 2012)
				11.50		14.35 ^{c*}		
				15		11.52 ^{c*}		
<i>Vitis vinifera</i>	Pomace	5	100	10.34	---	52.90 ^c		(Vergara-Salinas et al., 2013)
			200			18.30 ^c		
<i>Larix europaea</i>	Barks	30	100	2	10.50	381.90 ^e		(Ravber et al., 2015)
<i>Phyllanthus amarus</i>	Aerial parts	15	107.60	11	---	0.54 ^{f*}		(Sousa et al., 2016)
			150.00			3.15 ^{f*}		
			192.40			4.14 ^{f*}		
<i>Viola × wittrockiana</i>	Flowers	15	---	250	---	93.86 ^{e*}		(Fernandes et al., 2017)
<i>Ficus carica</i>	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*}		
<i>Pistacia vera</i>	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.

^aExtraction yield expressed in grams of extracts per grams of material.

^bDE= dry extract.

^cTannin content in extracts expressed in catechin equivalents (CE).

^dHydrolysable tannin content in extracts (gallotannins+ellagitannins+coraligin).

^eTannin content in extracts expressed in tannic acid equivalents (TAE)

^fTannin content in extracts expressed in gallic acid equivalents (GAE)

^gGallotannin 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 (°C)	Time (min)	Power (W)				
<i>Vitis vinifera</i>	Seed	Methanol (90%)	1:15	73	3.33	30	15.12	429.00 ^{c*}		(Hong et al., 2001)
<i>Radix puerariae</i>	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		
<i>Cinnamomum zeylanicum</i>	Leaves	Ethanol (50%)	1:20	50	18.00	200	---	16.79 ^e		(Gallo et al., 2010)
<i>Crocus sativus</i>	Powder							29.39 ^e		
<i>Coriandrum sativum</i>	Seeds							0.82 ^e		
<i>Cuminum cyminum</i>								11.59 ^e		
<i>Agrimonia pilosa</i>	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		
<i>Buddleia officinalis</i>	Whole plant	Ethanol (75%)	1:10	78	10	900	---	55.5 ^{f*}		(Pan et al., 2010)
		Ethanol (95%)						62.00 ^{f*}		
		Ethanol pure						58.50 ^{f*}		
<i>Vitis vinifera</i>	Seeds	Ethanol (70%)	1:40	60	2.00	125	16.40	528.05 ^{e*}		(Li et al., 2011)
<i>Pinus radiata</i>	Bark	Acetone (70%)	1:10	25	3.00	900	10.40	523.69 ^{f*}		(Aspé and Fernández, 2011)
<i>Rosmarinus officinalis</i>	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		
<i>Pinus pinaster</i>	Bark	Acetone (80%)	1:20	---	3.00	100	13.60	48.98 ^{f*}		(Chupin et al., 2015)
<i>Myrtus communis</i>	Leaves	Ethanol (42%)	1:32	---	1.04	500	---	32.65 ^g		(Dahmoune et al., 2015)
<i>Acacia mollissima</i>	Bark	Water	1:20	---	5.00	150	---	47.64 ^h	0.09 ^c	(Naima et al., 2015)
		Ethanol						30.29 ^h	0.03 ^c	
<i>Eucalyptus globulus</i>	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.

^aExtraction yield expressed in grams of extracts per grams of material.

^bDM= dry matter.

^cTannin content in extracts expressed in tannic acid equivalents (TAE).

^dRutin content in the extracts (RC).

^eTannin content in extracts expressed in gallic acid equivalents (GAE).

^fTannin content in extracts expressed in catechin equivalents (CE).

^gAmount of condensed tannins precipitated from extracts (CTP).

^hTannin 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 (°C)	Time (min)	Power (W)			
<i>Leucaena spp</i>	Leaves	Acetone 70%	1:50	25	15	---	---	86.10 ^c	(Dalzell and Kerven, 1998)
					20			89.80 ^c	
					30			88.10 ^c	
<i>Betula alleghaniensis</i>	Foliage	Ethanol (95%)	---	20	30	750	14.80	43.00 ^{d*}	(Diouf et al., 2009)
<i>Averrhoa carambola</i>	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*}	
<i>Vitis vinifera</i>	Full berry	Ethanol (50%)	1:10	10	6	200	---	6.00 ^f	(Carrera et al., 2012)
<i>Vitis vinifera</i>	Seeds	Methanol	1:10	30	15	150	---	61.80 ^e	(Da Porto et al., 2013)
<i>Areca catechu</i>	Nuts	Acetone (80%)	1:10	---	37.50	10	---	44.53 ^e	(Chavan and Singhal, 2013)
						50		101.60 ^e	
						90		37.02 ^e	
<i>Withania somnifera</i>	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*}	
<i>Quercus brantii</i>	Leaves	Methanol (50%)	1:20	60	45	140	21.10	104.50 ^{e*}	(Tabaraki et al., 2013)
		Methanol (90%)					25.30	127.00 ^{e*}	
<i>Pistacia lentiscus</i>	Leaves	Ethanol (40%)	1:50	---	15	130	---	35.94 ^f	(Dahmoune et al., 2014)
<i>Rubus fruticosus</i>	Fruits	Ethanol	1:2.50	25	15	60	5.30	5.09 ^{h*}	(Ivanovic et al., 2014)
					30		5.90	25.42 ^{h*}	
<i>Phyllanthus amarus</i>	Aerial parts	Deionized water	---	25	7	301	---	27.23 ^g	(Sousa et al., 2016)
<i>Cannabis sativa</i>	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	
<i>Piper betle</i>	Leaves	Ethanol (78.74%)	1:21.85	51.60	30	400	13.71	21.5 ⁱ	(Ali et al., 2018)
<i>Vitis vinifera</i> (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.

^aExtraction yield expressed in grams of extracts per grams of material.

^bDM= dry matter.

^cTannin content in extracts expressed in L leucocephale proanthocyanidin equivalents (LPAE).

^dTannin content in extracts expressed in quercetin equivalents (QE).

^eTannin content in extracts expressed in catechin equivalents

^fTotal content of condensed tannins in extracts (TCT).

^gTannin content in extracts expressed in gallic acid equivalents (GAE).

^hTotal tannin content in extracts (TTC).

ⁱTannin content in extracts expressed in rutin equivalents (RE).

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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
<i>Pistachia Vera</i>	Hulls	SLE	Methanol-1:4 25°C, 6h	---	32.80 ^d	(Goli et al., 2005)
		SFE	SCCO ₂ ^c co-solvent- 15%Methanol 45°C-15 min. 35.46MPa		6.55 ^d	
		UAE	Methanol-1:8 45 min.		32.80 ^d	
<i>Terminalia chebula</i>	Fruit	SLE	Ethanol-1:15 78.3°C, 240 min	---	9.92 ^e	(Rangsriwong et al., 2009)
			Water-1:15 100°C, 120 min		15.96 ^e	
		PWE	Water 180°C, 37.5 min 4MPa		21.43 ^e	
<i>Pinus radiata</i>	Bark	SLE	Acetone (70%)-1:10 82°C, 180 min.	12.00	62.10 ^f	(Aspé and Fernández, 2011)
		UAE	Acetone (70%)-1:10 25°C, 6 min. 85W	9.50	47.2 ^f	
		MAE	Acetone (70%)-1:10 25°C, 3 min. 900W	10.40	55.4 ^f	
<i>Galla chinensis</i>	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*}	
<i>Camellia sinensis</i>	Leaves and aerial parts	SLE	Ethanol (30%)-1:10 40°C, 2h	---	180 ^g	(Ribeiro et al., 2013)
		ILE	1-ethyl-3- methylimidazolium chloride [C2mim]Cl (50%) 40°C, 2h, 1:10	---	300 ^g	

<i>Rubus sp.</i>	Bagasse	SLE	Ethanol-1:31.60 50°C, 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*}	
<i>Solidago canadensis</i>	Bark	SLE	Ethanol (50%)-1:20 25°C, 30 min.	---	26.29 ^h	(Deng et al., 2015)
		UAE	Ethanol (50%)-1:20 30 min		30.15 ^h	
<i>Myrtus comunis</i>	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 45°C, 700 min. 23MPa	10.80	47.28- 94.56 ^{g*}	
<i>Berberis jaeschkeana</i>	Fruits	SLE	Methanol 80%-1:70 70°C-15 min.	---	21.41 ^d	(Belwal et al., 2017)
		UAE	Methanol 80%-1:70 70°C-15 min.		32.41 ^d	
		MAE	Methanol 80%-1:40 5 min. 670W		24.04 ^d	
<i>Myrtus communis</i>	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	
<i>Salacia chinensis</i>	Roots	SLE	Methanol-1:10 25°C, 360 min.	---	43.37 ^d	(Ghadage et al., 2017)
		UAE	Methanol-1:10 25°C, 10 min.		41.29 ^d	
		MAE	Methanol-1:10 25°C, 5 min. 180W		43.54 ^d	
<i>Erica carnea</i>	Aerial parts	SLE	Ethanol 96%-1:30 22°C, 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-1:20 140°C, 30 min. 4MPa	42.66	62.53 ^g	
<i>Lavatera thuringiaca</i>	Whole plant	SLE	Ethanol 96%-1:30 22°C, 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-1:20 140°C, 30 min. 4MPa		72.23 ^{g*}	

*Results expressed in mg of tannins per gram of dry matter.

^aExtraction yield expressed in grams of extracts per grams of material.

^bDE= dry extract.

^cSCCO₂= carbon dioxide at supercritical conditions.

^dTannin content in extracts expressed in tannic acid equivalents (TAE).

^eHydrolysable tannin content in extracts (HTC)

^fTannin content in extracts expressed in catechin equivalents (CE).

^gTannin content in extracts expressed in gallic acid equivalents (GAE).

^hTotal tannin content in the extracts (TTC).

