



## Review

## Chestnut tannin: New use, research and bioeconomy

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## ABSTRACT

Chestnut tannin, extracted from the bark or wood of chestnut trees, possesses unique properties that make it valuable in various industries. It serves as a natural source of tannins, which are widely used in the production of leather, textiles, and wood preservation. As research continues to explore its potential applications, chestnut tannin remains a promising resource with diverse industrial uses. Highlighting new use, research and bioeconomy aspects, this study provides a unified perspective on chestnut tannin. New advanced applications will likely emerge shortly.

## 1. Introduction

Chestnut tannin, also called “tannic acid”, is a natural product extracted from the bark or wood of chestnut trees known for its high tannin content and distinct chemical composition, offering advantages such as excellent binding capabilities and resistance to microbial degradation (Pizzi, 2019). It was first commercialized in the mid 19th century for the production of iron tannate for the black coloring of silk for women’s blouses (Pizzi, 2019). When, around 1860, the latter were no longer fashionable, chestnut tannin was used to replace oak chips to tan leather in 28 days rather than in one year (Pizzi, 2019). The word “tannin” originates from Latin word *tannum* for “oak bark”. The biophenols of tannin irreversibly bind the peptide groups of the collagen and other proteins contained in animal skin inhibiting proteolytic enzymes. As a result, animal skin is converted into chemically and biologically stable leather (Carçote et al., 2016).

Compared to tannins sourced from other woods, chestnut tannin affords excellent leather. Its environmentally friendly nature makes it a desirable alternative to synthetic tannins, promoting sustainable practices in manufacturing processes. The color imparted to skin tanned with chestnut tannin is particularly clear (all tannins give the skin a more or less intense brown color depending on the plant of origin) and the resulting leather has excellent light resistance, justifying its employment to produce luxury leathers. Until the 1960s, vegetable tanning lasted about 30 d taking place via slow tanning of hides immersed in solutions of tannins at progressively increasing concentration. Today rapid tanning takes place in rotating drums allowing to reduce tanning times to 36–48 h (BuyLeatherOnline, 2022).

Shoes, before the introduction of oil-derived polymers, were chiefly made of leather. The rapid replacement of leather with petroleum-derived synthetic rubber to make shoes, and the introduction of leather tanning with toxic but cheap Cr(VI) and Al(III) salts (Al-Mizan et al., 2020) led to a quick fall in tannin demand. Tannin manufacturers reacted by searching alternative end uses for their product. Applied research showed that condensed tannins (condensed flavans containing no sugar residues) were particularly effective replacing synthetic phenols used in adhesive manufacturing. In just two decades the global tannin industry shifted from

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hydrolysable tannins to condensed tannins chiefly extracted from black mimosa bark and quebracho wood. The latter in 1982 already constituted over 90 % of the global production (~350 000 t) of commercial tannins (Pizzi, 1982). As a consequence, most chestnut tannin production plants, chiefly located in Europe, closed. The few remaining plants continued to manufacture and supply tannin industrially sourced from sweet chestnut (*Castanea sativa* Mill.) wood, chiefly in liquid form to manufacturers of luxury leathers. Compared to mineral tanning today using toxic Cr(III) salt (Hassan et al., 2023), tanning of heavy leather and sole leather with chestnut tannin affords a compact, flexible material with good water resistance (BuyLeatherOnline, 2022). Chestnut tannin (see below), however, is the most expensive tannin. Hence, leather manufacturers generally mix it along with other wood tannins.

Biochemistry research carried out during the 1970s (Haslam, 1974) unveiled that hydrolysable tannins have high biological activity due to the uniquely high amount of *ortho*-phenolic groups inhibiting extracellular hydrolytic enzymes (cellulases, pectinases, xylanases) used by many pathogens to penetrate plant tissues (Scalbert, 1991), as well as to bind (complex) metal ions (Zhang et al., 2023). The same groups are also responsible for the high antioxidant properties of these tannins (Jung et al., 2016).

In a series of pioneering researches conducted in Yugoslavia in the late 1980s, researchers working with the national chestnut tannin company discovered that added in small dosage to forage or livestock feed chestnut tannin widely improved animal nutrition (Mirosevic, 1992). In the subsequent three decades, plentiful applied research across the world showed that chestnut tannin reduces ammonia formation, protects liver and kidney tissues against oxidation, reduces intestinal parasite and pathogenic bacteria load, and improves intestinal microbial ecosystem, and gut health (Huang et al., 2018). A few years after the new application as animal feed ingredient discovered in Yugoslavia, researchers in Italy unveiled the second practically relevant new application of chestnut tannin, namely its use as plant biostimulant and biofertilizer (Miele et al., 2020).

In brief, in about two decades (2002–2022) agriculture and animal nutrition became two unexpected and significant end markets for chestnut tannin, as well as for condensed tannins. Research on chestnut tannin, virtually absent for decades, restarted in the early 2000s and eventually (see below) it became a hot research topic. In one of the first bioeconomy study devoted to tannin as a key bioproduct of forest areas (Pagliaro et al., 2021), we suggested that the versatile chemistry and biochemistry of tannin will drive applications in many other fields beyond today's four dominant uses (leather tanning, wood adhesives, wine production and anticorrosive primers). Now, focusing on chestnut hydrolysable tannin, we provide a unified outlook of the bioeconomy of chestnut tannin. New advanced applications, we conclude, are likely to emerge shortly.

## 2. Production and chemistry

Since the early industry's days in the 1860s, the chestnut tannin extraction process relies on leaching of water-soluble tannin from chestnut wood chips in boiling water. Three major significant technology advances were achieved since the industry started production: the introduction of counter-extraction, membrane-based nanofiltration to purify and concentrate the extract, and plant automatization. The first two major advances happened in the late 1990s.

In brief, the boiling pools were replaced with counter-current extractors consisting of steel autoclaves connected in series. A typical plant today consists of a battery of eight autoclaves (each of 200 m<sup>3</sup>) connected in a circuit (Pizzi, 2008; Costa et al., 2018). The extraction is carried out with superheated fresh water heated at a temperature that generally varies from 110 to 120 °C, under moderate pressure going from 200 kPa in the first vessel to 80 kPa in the last one.

In detail, chipped wood having dimensions in the order of 20 mm × 40 mm × 5 mm are loaded into a battery of autoclaves working in counter-current, thereby undergoing a repeated leaching procedure. The biomass always remains in the same autoclave, while the extraction water is moved from one autoclave to the next (Costa et al., 2018). Each autoclave is equipped with an upper opening to introduce the chipped wood, and a lower opening to discharge the spent chips. The extraction liquid discharge from each autoclave is withdrawn below it and fed to the head of the next autoclave. The underlying concept in the entire extraction procedure is the leaching of the fresh wood with the penultimate extraction water, while spent wood undergoes the last leaching with fresh water.

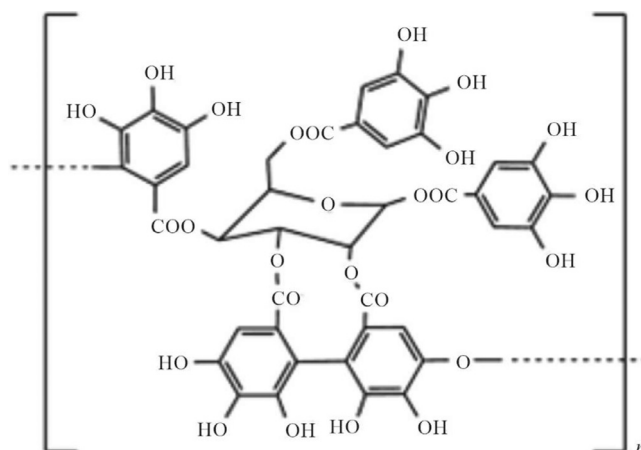
The extraction lasts about 6 h. Generally, a 4 %–5 % (w) tannin solution is obtained, with an extraction yield of about 60 %–65 %. After clarification by settling, the tannin solution is concentrated up to the desired concentration (50 % (w) and higher) either via nanofiltration or via conventional vacuum evaporation in multiple evaporators (to limit oxidation). Tannin is generally supplied to customers either as a brown powder obtained by spray-drying or as a brown-black concentrated aqueous solution.

No acid, alkali or organic solvent is used in the extraction process. Hence, the “de-tanned” chestnut wood residual after the extraction of tannin can be readily converted into wood fiber panels suitable for building insulation (see below).

The second major progress took place nearly concomitantly when an improved extraction process based on nanofiltration (trade-named “Tantec” (Available at: <http://web.tiscali.it/proras/tantectipimpita.htm>)) through polymeric membranes, requiring significantly lower energy than vacuum evaporation, was commercialized. During concentration, the temperature does not exceed 40 °C substantially improving the quality (purity) of the extracted tannin, with significant improvement also of the occupational health and safety conditions.

In general, the production (extraction and purification) process is highly energy-intensive due to the large specific heat capacity of water and to the relatively high (3.3, for example) water-to-wood weight ratio typically employed (Costa et al., 2018). As a result, the price of chestnut tannin is high, even though the selling price is far higher than the production cost. For example, by early 2024 in Italy, 1 kg of pure chestnut tannin for wine taste and color magnification (namely for human consumption) was sold at 16.59 EUR (Available at: <https://www.emporioenologico.com/it/catalogo/prodotti-enologici/tannini/tannino-di-castagno-etann-c-1-kg-513.html>).

Until a few years ago, the only revenues for the few chestnut tannin manufacturers derived from selling their tannin to luxury leather manufacturers for leather tanning. For at least three decades (1985–2015), the market experienced no supply or demand shortage. Demand from luxury leather manufacturer was growing at modest (1 %–3 %) annual growth rate as the demand of luxury



**Fig. 1.** Structure of pentagalloylglucose repeating unit undergoing oligomerization in  $n$  monomers. Adapted from Pasch and Pizzi (2002) with permission.

goods from emerging economies continued to grow. A relatively small market was dominated by a few (“incumbent”) relatively large manufacturers chiefly consisting of the companies that survived the closure of numerous small extracting plants following the fall in demand due to the introduction of leather tanning based on Cr and Al salts.

In the early 2010s, however, the demand of chestnut tannin from the livestock sector led to a sudden and quick rise in demand creating new opportunities for new players, using advanced recovery and isolation techniques. For example, one company in France invested 15 million EUR to build a new production plant in 2016–2017 in Tarn’s Labruguière (Available at: <https://www.usinenouvelle.com/article/king-tree-demarre-la-production-de-tanin-de-chataigniers-dans-sa-nouvelle-usine-tarnaise.N694134>). The company started to operate the new plant in 2018, and in 2021 it already had 4 million EUR revenues processing 20 000 t of chestnut wood. So quick was the return on the investment, that the company is currently (2024) completing construction of a second production line, costing 5 million EUR, to produce chestnut tannin for the tanning market (Available at: <https://www.helloprojets.fr/nos-actualites/king-tree-relance-le-tannage-vegetal>). It is also instructive that the aforementioned plant, with an original capacity to process 60 000 t/a of chestnut wood, requires only 12 employees (including the company’s management staff) thanks to the highly automatized production process managed by a single control room, from wood receipt to tannin packaging in 25 kg bags. Finally, the company gives back the “de-tanned” chestnut wood residual after the extraction of tannin to a wood fiber panel manufacturer located next to its plant that supplied the chestnut wood chips used as tannin source.

The latter plant automatization is the third major advance in the history of tannin manufacturing.

The history of chestnut tannin industrial use testifies to the hydrolysable tannin chemistry versatility. Said tannins were considered too unreactive to compete with condensed tannins in the phenolic resin market until the mid 1970s. Yet, chestnut tannin was used industrially between 1974 and 1980 by a Norwegian paint group subsidiary that produced phenol-formaldehyde (PF) resins in Malaysia for Southeast Asia plywood manufacturers. The company replaced up to 50 % by weight of phenol with chestnut tannin extract (Kulvik, 1976). Nearly, thirty years later Pizzi, Spina and co-workers improved this process by producing PF resins with a phenol substitution degree of up to 80 %, with excellent results in terms of the mechanical properties of the plywood obtained (Spina et al., 2013).

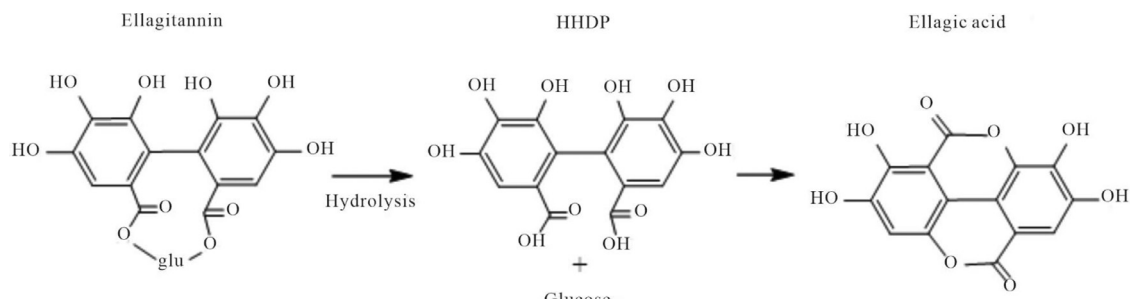
The uniquely versatile chemistry and biochemistry of chestnut tannin are due to the properties of its two main components, namely gallic acid and ellagic acid. In a milestone study on the chemistry of tannin based on the analysis of chestnut ellagitannins by matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry, Pasch and Pizzi (2002) suggested that the varying composition of chestnut tannins is actually due to the hydrolysis of the real structure of the tannin as present in nature: a high molecular weight random series of pentagalloylglucose oligomers of the repeating unit shown in Fig. 1 (Pasch and Pizzi, 2002).

The hydrolysis of said repeating units affords castalagin, vescalagin, vescalin, castalin, gallic acid and ellagic acid. Plentiful studies indeed confirm that ellagic acid (EA) from chestnut wood readily forms via hydrolysis of ellagitannin through the production of hexahydroxydiphenic acid which spontaneously converts via lactonization to EA (Fig. 2) (Vekiari et al., 2008).

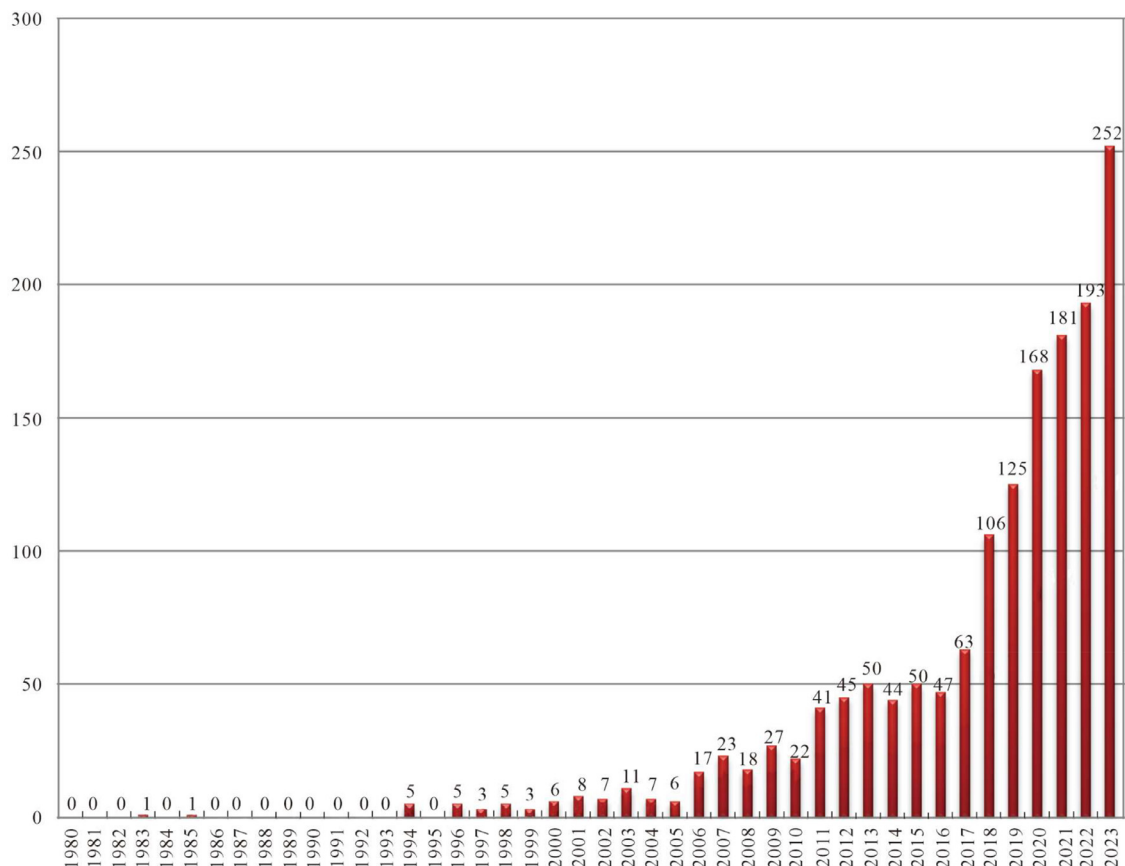
### 3. Research and new usages

Very little research on chestnut tannin was conducted in the two decades between 1980 and 2000, when only 26 documents (research article, review, book chapter, conference paper and book) were published in the international literature in English indexed by Scopus database in 2024.

A first timid growth in research interest followed 2001 (Fig. 3) with the re-discovery of the broad scope activity in animal nutrition and, a few years later, by the discovery of its applicability in agriculture. Between 2001 and 2010 research on chestnut tannin increased by nearly six times with 146 documents published in the decade. Finally, during 2011–2020, chestnut tannin became



**Fig. 2.** Hydrolysis of ellagitannin to ellagic acid through formation of hexahydroxydiphenic (HHDP) acid that spontaneously lactonizes to ellagic acid (EA). Adapted from [Vekiari et al. \(2008\)](#) with permission.



**Fig. 3.** Number of documents dealing with “chestnut tannin” during 1980–2023 indexed by Scopus.

a hot topic in contemporary bioeconomy, chemistry and biotechnology research, with 739 documents published. Following 2020, the research has further grown as shown by the 626 documents published in just three years between 2021 and 2023, most of which (499) original research articles. Along with research on the use of chestnut hydrolysable tannins in animal nutrition and in agriculture, the bioproduct is being extensively investigated in the formation of functional hydrogels.

Furthermore, biochemical research aimed at identifying pharmaceutical and nutraceutical applications also started ([Pizzi, 2021](#)). For example, scholars in Italy in 2018 discovered that hydrolysable tannin (HT) in chestnut tannin inhibits alpha-glycosidase *in vitro* ([Cardullo et al., 2018](#)). The latter enzyme regulates carbohydrates absorption making chestnut HT potentially relevant in the treatment of type 2 diabetes mellitus or low glucose tolerance.

Due to prolonged lack of research that lasted about twenty years (1980–2000), plentiful studies claim that chestnut tannin was commercialized for animal nutrition in the early 2010s. This is actually not case. Publishing a book chapter on the use of tannin from chestnut as early as of 1992 ([Krisper et al., 1992](#)), industry and academic researchers based in Slovenia reported that a chestnut

tannin extract rich in castalagin was already commercialized in Yugoslavia for prevention and treatment of diarrhea in pigs and cattle also based on the outcomes of their studies.

As mentioned above in the section of introduction, Yugoslavia's tannin state industry had patented the discovery already in 1990 (Mirosevic, 1992). The researchers ascribed the beneficial effect of the chestnut tannin extract to prevention of water losses through mucous membranes, as well as to iron chelation, influencing the metal reabsorption in the animal digestive tract.

It is also instructive that Krisper et al. (1992) reported that industrial extraction of tannin from *C. sativa* took place only in France, Italy, and Yugoslavia. The team reported an overall annual production of 30 000–40 000 t with 90 % of chestnut tannin used for hide tanning, followed by use in the recovery of germanium in the mining industry, in oil drilling, as a corrosion inhibitor, and in cosmetics.

More than a decade later, in 2003–2004 a small but rapidly increasing demand of chestnut tannin originated from the animal feed sector as an alternative to in-feed antibiotics. The results were so successful that demand in just five years rose to amount to nearly half of today's chestnut tannin market. During the 2010s researchers across the world confirmed and expanded the findings of Yugoslavian researchers. Added in small dosage to forage and to livestock feed, chestnut tannin not only can replace antibiotics (Farha et al., 2020), but widely improves cow, pig and poultry nutrition, reducing ammonia formation, protecting liver and kidney tissues against oxidation, reducing intestinal parasite and pathogenic bacteria load, eventually improving intestinal microbial ecosystem, and gut health (Kapp-Bitter et al., 2020; Caprarulo et al., 2021).

As mentioned in the introduction, the second commercially significant new application of chestnut tannin followed the discovery in Italy in the early 2000s that chestnut tannin is an effective plant corroborant, namely as enhancer of plant resistance to harmful organisms, improving also radical development by reducing damage of the root system due to parasites protecting plants in nematode-infested fields, and from bacterial disease (Bargiacchi et al., 2013).

Research continued and the team discovered that a small (1 %, w) addition of powdered chestnut tannin to urea fertilizer was also valuable in preventing nitrogen volatilization due to the exceptional urease inhibiting effect of chestnut tannin already at 0.1 mmol/L concentration (Miele et al., 2020). Remarkably, the team used chestnut aqueous extracts obtained via a purification process involving nanofiltration and membrane concentration steps capable to afford aqueous extracts of consistent composition (Campo et al., 2016).

One such powdered standardized extract with 75 % tannin titer (obtained via the same nanofiltration process) is a registered plant corroborant sold in Italy by early 2024 in 25 kg bags at 244 EUR (9.76/kg) (Available at: <https://www.agrimag.it/prodotto/tannino-di-castagno>). Approved in organic agriculture, the product is applied both by foliar spray irrigation (1.5–2.5 kg/hm<sup>2</sup>) and by fertigation (7.5–10.0 kg/hm<sup>2</sup>) in the last phase of the irrigation cycle to avoid leaks due to leaching on horticultural, floricultural and fruit crops. The activity is so high that a relatively small amount is required to treat a large number of plants every 10–20 d with 2–4 applications (Available at: <https://www.agrimag.it/wp-content/uploads/2022/07/Tannisol-PB-Scheda-tecnica.pdf>), making chestnut tannin an economically (and not only environmentally) viable alternative to agrochemicals.

Adding to its repellent action against predator insects and parasites due to altered plant tissue flavor (astringency) and hardness, chestnut tannin is also a biopesticide exerting a broad scope antimicrobial and antifungal (Romani et al., 2021) action by inhibiting the hydrolytic enzymes (cellulases, pectinases, xylanases) used by many pathogens to penetrate plant tissues (Available at: [http://life-evergreen.com/wp-content/uploads/2015/06/EVERGREEN\\_Final-Report.pdf](http://life-evergreen.com/wp-content/uploads/2015/06/EVERGREEN_Final-Report.pdf)). Remarkably, ecotoxicity assays showed that tannin chestnut extract was free of toxic effects even at the concentration of 1 g/L. Greatly enhancing its relevance and value, indeed, sweet chestnut tannin is a safe substance devoid of toxic effect and registered as such in Europe. In the European Union in 2014 its use as a feed additive up to 15 mg/kg feed was recognized as safe for all animal species, and presenting no safety risk to consumers and for the environment (EFSA Panel on Additives and Products or Substances Used in Animal Feed, 2014). The diets of cow (Kapp-Bitter et al., 2020), pig (Caprarulo et al., 2021) and poultry (Buyse et al., 2021) modified with a small amount of chestnut tannin result in vastly improved digestion and metabolism, eventually improving many parameters of the meat obtained. Not surprisingly the livestock and meat industry were quick in the uptake of chestnut tannin utilization because the aforementioned pathogens cost the cow, poultry and pig industries hundreds of millions of euros of extra costs only in Europe.

#### 4. Economic aspects

Given the aforementioned new applications in huge economic sectors such as agriculture and animal nutrition, the demand of hydrolysable tannins that between the 1960s and late 1990s had barely grown, since the early 2010s is growing at significant (and increasing) rate of annual growth.

The annual 480 million EUR per 30 000 t chestnut tannin market is currently growing at annual growth rate of 5 %–7 %. This has inevitably led to construction of new extraction factories (such as that in France mentioned above) due to the relatively lower number of extraction plants remained after the discovery of hide mineral tanning.

The price of chestnut tannin remains the highest amid all tannins, amounting to about 15–16 yuan/kg (EUR) (Available at: <https://www.emporioenologico.com/it/catalogo/prodotti-enologici/tannini/tannino-di-castagno-etann-c-1-kg-513.html>). The global yearly production, taking place chiefly in Europe (Italy, Slovenia, France, Portugal and Spain), is estimated at 30 000 t

To understand the scope of the value adding process of chestnut tannin production, it is enough to consider that in Italy alone in 2010 there were about 800 000 hm<sup>2</sup> of chestnut woods with 30 000 enterprises cultivating some 54 000 hm<sup>2</sup> producing an annual turnover of 165 million EUR for both chestnut fruit (65 million EUR) and wood (Castellini et al., 2010). Since then, production of chestnut fruits and wood in Europe has further increased, with Portugal in 2021 having become the main producer in Europe (50

000 t corresponding to 36 % of the European fruit production that year) followed by Spain, Italy, Greece and France (Santos et al., 2022).

Restricting the analysis to Italy only, the list includes tens of different products with tradenames such as Tannisol, Tannini Fiber Icas, Castannino, Nemanan, Manitan, Tannino Green Has, Castan, Tannino Estratto di Castagno Cifo, Tannino Serbios, Fertiltan P, Tannino L40, Tannino 20 P, and many others. The products are available both as liquid (aqueous) and powder formulations. Farmers across the country increasingly use these products to protect and improve horticultural, floricultural and fruit crops.

Similarly numerous chestnut tannin-based products are commercially available in the global market as feed additives for improved animal nutrition. Restricting the analysis to Europe, selected tradenames include Tanno-SAN, SaviotanFeed, Evotan, Tannin 50, Silvafeed, and Digest. A search on the world wide web (Google) even in Italian only returns over 3 500 web pages dealing with chestnut tannin in animal nutrition, showing evidence of the broad societal awareness on this relatively new use of an old natural product, including a company manufacturing a chestnut tannin-based product to improve the digestions of domestic dogs and cats (Available at: <https://www.gegpetfood.com/wp-content/uploads/2022/04/2022-04-29-Pagina-2-Unica.pdf>).

## 5. Summary and concluding remarks

In summary, in the first two decades of the 2000s a major shift occurred in chestnut tannin market, whose industrial application for decades had remained limited to the remunerative, but relatively small, market of vegetable hide tanning for making luxury leather.

Unexpected new usages first in animal nutrition and shortly afterwards in agriculture emerged in the early 2000s. The outcomes of these new applications were so successful that demand from the agriculture and animal breeding sectors started to grow to such a level to saturate the production capacity of the few remaining extraction plants, chiefly based in western Europe.

Given the large and global dimensions of the aforementioned sectors, however, such large and rapidly increasing demand creates room for numerous new extraction plants and manufacturing companies. Indeed, a first new plant targeting only the animal nutrition sector was built and started to operate in 2018 in France, a country that (likewise to Italy) until the mid 1950s hosted tens of small and medium-size chestnut tannin extraction plants. Also in this single recent case, the commercial results of producing tannin at the new plant were so successful that the same plant is currently (early 2024) building a second production line targeting this time the hide “vegetable” tanning market.

All existing plants use conventional extraction in superheated water using counter-current steel extractors, a process innovation introduced in the 1990s. Another important innovation concerning this time the product purification and isolation is the membrane-based nanofiltration first introduced in Italy in the early 2000s. The membrane-based method instead than evaporation under reduced pressure affords aqueous tannin extracts of the required purity and known composition required for optimal use in products aimed at human and animal consumption. A small but important application of high quality chestnut tannin extracts, indeed, is also in red wine clarification.

Growing demand promotes supply from both incumbent and new manufacturers using new, advanced plants in which the extraction, purification, isolation and packaging is carried out in automatized plants using state-of-the art technology that will likely involve new, green extraction technology, such as hydrodynamic cavitation in water only lately applied in Italy to obtain a newly extracted chestnut tannin that has lately shown exceptional activity as biostimulant for the nursery production of high-quality grapevine planting material (Pisciotta et al., 2024).

As unveiled in this study, chestnut tannin has become a hot research topic in many world’s countries. Given the exceptional and broad scope activity of gallic acid and ellagic acid, the main components of chestnut tannin esterified with glucose, new pharmaceutical and nutraceutical applications will likely emerge soon. Furthermore, the unique quinone-catecholate redox mechanism of tannic acid is highly promising towards the manufacturing of new Li-ion cathodes made of microporous carbon functionalized with chestnut tannin in place of graphite (Ilic et al., 2021), or of electrochemical capacitors operating in aqueous electrolytes (Lemieux et al., 2021).

## Declaration of competing interest

The Authors declare no competing interest.

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