

# Tannins market research report: industrial applications and market outlook with focus on leather tanning and spruce-bark tannin coagulants for wastewater treatment in the Nordic-Baltic Region



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# 1. Introduction to tannins

Tannins are a class of plant-derived polyphenolic compounds known for their distinctive astringent taste and ability to bind proteins. They play diverse roles in plants and have significant applications in industries ranging from food and beverages to leather tanning and biotechnology. In this introduction, we outline what tannins are and how they are classified, trace their historical usage, identify key natural sources (including coniferous and other plant species), and describe their chemical composition and properties. This provides a foundation for understanding the scientific and business significance of tannins in modern applications.

## 1.1 Definition and classification

Tannins are generally defined as high molecular weight polyphenols produced by plants that can form strong complexes with proteins, polysaccharides, and minerals [1]. They are secondary metabolites found in many parts of plants and are responsible for the dry, puckering sensation (astringency) in foods like unripe fruits, red wine, and tea due to their protein-precipitating ability [2]. **In terms of classification, tannins are broadly divided into two major groups** based on their chemical structure [1], [2]:

- **Hydrolyzable tannins (HTs):** these have a core of a polyhydric alcohol (usually glucose) esterified with phenolic acids such as gallic acid or ellagic acid. They are called "hydrolyzable" because acid, base, or enzymatic hydrolysis can cleave them into their constituent phenolic acids and sugar. HTs are further subclassified into **gallotannins** (e.g. tannic acid, composed of multiple gallic acid units) and **ellagitannins** (which contain hexahydroxydiphenoyl units derived from coupled gallic acids) [1]. These compounds tend to have molecular weights of a few hundred to a few thousand Daltons and are potent antioxidants due to their high density of phenolic hydroxyl groups [2].

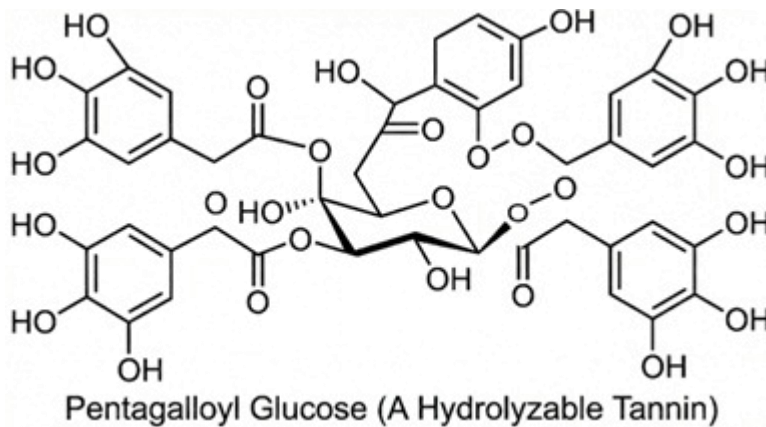


Figure 1. Structural example of hydrolysable tannins [3]

- **Condensed tannins (CTs):** also known as proanthocyanidins, these are polymers of flavan-3-ol units (flavanol monomers such as (+)-catechin or (-)-epicatechin) linked by carbon-carbon bonds [2]. Unlike hydrolyzable tannins, condensed tannins do not contain a sugar core and are not easily cleaved by hydrolysis. They can range from small oligomers to large polymers with very high molecular weights. When heated in acidic conditions, condensed tannins can yield colored anthocyanidins (hence the name proanthocyanidins). This class is very common in bark, wood, seeds, and fruits, contributing to bitterness and astringency in foods and beverages.

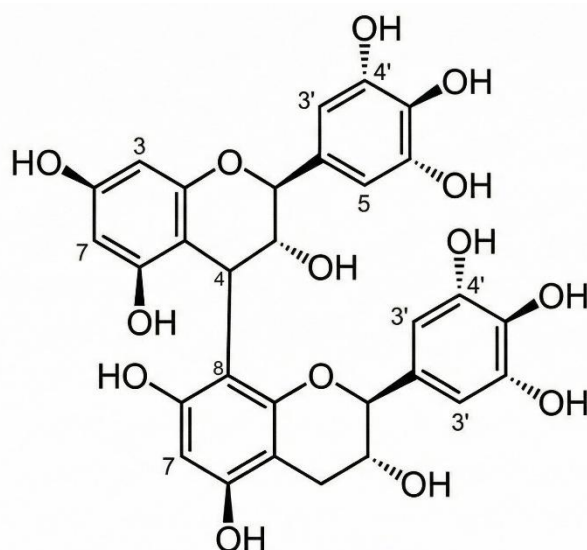


Figure 2. Structural example of condensed tannin (Procyanidin B2) [3].

In addition to these two primary groups, some literature recognizes **complex tannins** and **pseudo-tannins** as minor categories. **Complex tannins** are hybrid molecules containing elements of both hydrolyzable and condensed tannins in one structure (these are relatively rare in nature) [1]. **Pseudo-tannins** are low-molecular-weight phenolic compounds (such as simple gallic acid, catechin, or other flavonoid monomers) that are not true tannin polymers but can still exhibit tannin-like properties (e.g., the ability to precipitate proteins) [1]. Overall, all tannins share a common feature of a polyphenolic backbone with multiple hydroxyl groups, enabling them to strongly interact with proteins, enzymes, and metal ions. This shared chemistry underlies their biological activities and industrial uses [2].

## 1.2 Historical background

**Ancient use:** the use of tannin-containing materials dates back millennia. The term "tannin" itself is derived from the traditional process of tanning leather, where plant extracts were used to convert

animal hides into durable leather [4]. Historical records indicate that various cultures soaked animal skins in water with crushed bark or wood from tannin-rich trees (such as oak) to preserve and strengthen the hides – a practice known for thousands of years. For example, oak bark, sumac leaves, and gall nuts (rich in gallotannins) were used in ancient Egypt, Greece, and Rome for leather making and as medicinal astringents. These organic tanning methods were time-consuming (taking months to over a year for full curing), but they were the only means available to produce leather in pre-industrial times [4].

**18<sup>th</sup>-19<sup>th</sup> century developments:** the scientific study of tannins began in the 18<sup>th</sup> century. Researchers observed that certain plant extracts could precipitate iron salts and proteins, indicating the presence of a distinct "astringent principle." In 1795, the French chemist Seguin first quantified the tanning power of plant extracts by their ability to precipitate gelatin, essentially identifying tannins by their function. By the late 18<sup>th</sup> to early 19<sup>th</sup> century, chemists such as Carl Scheele, Antoine Fourcroy, and Joseph Proust had isolated gallic acid from galls (gall is an abnormal, tumor-like growth that develops on the external tissues of plants, fungi, or algae, caused by an external parasite) and confirmed that tannin substances contained this acid component, helping to distinguish tannins as a group of compounds [4]. The term *tannin* was introduced in the early 19<sup>th</sup> century as these compounds became “officially” recognized as a category of plant chemicals used for converting hides into leather.

The mid-19<sup>th</sup> century saw the rise of a true tannin industry. Around the 1850s in Lyon, France, factories started extracting tannins on a large scale to produce concentrated tannin extracts (e.g., from chestnut wood or mimosa bark) [4]. Initially, one major use was in dyeing (tannins were used with iron salts to produce black inks and dyes such as iron gall ink for writing) and in the blackening of silk fabrics. After fashions changed and the dye industry demand fell, tannin extract producers shifted focus to selling extracts to the leather industry. This was a pivotal change: using purified plant tannin extracts dramatically reduced the time to tan leather from many months (with raw plant materials) to a few weeks. By the late 19<sup>th</sup> and early 20<sup>th</sup> century, commercial extraction of tannins from diverse sources expanded globally. Companies in Europe established plantations or sourced bark/wood from South America (e.g. quebracho wood in Argentina) and Africa (e.g. wattle or mimosa bark in South Africa) to meet the high demand for vegetable tanning agents [4]. Tannin-rich woods like quebracho (*Schinopsis species*) and bark from the black wattle (*Acacia mearnsii*) became major export products for tanning, alongside traditional sources like oak and chestnut in Europe.

**20<sup>th</sup> century changes:** vegetable tannins remained the mainstay of the leather industry until the mid-20<sup>th</sup> century, when they began to be gradually supplanted by mineral tanning agents (particularly chromium salts). Chrome tanning, introduced in the early 1900s, could tan leather even faster and produce softer, lighter-colored leathers, which led to a decline in vegetable tanning for mass-produced goods. After World War II, the use of synthetic materials and chrome in shoe and apparel manufacturing caused many tannin extract plants to close or downscale [4].

Nevertheless, vegetable tannins continued to be used for certain high-quality leathers (e.g., for luxury leather goods, heavy leather for saddlery or tooling, where vegetable-tanned leather's durability and aesthetic are valued). In recent decades, environmental and health concerns about chromium have prompted some revival of interest in vegetable tanning. Today, vegetable-tanned leather is a premium niche, marketed as an eco-friendly and traditional alternative.

Beyond leather, tannins historically also found use in folk medicine and other applications. Tannin-rich plant extracts (like oak bark, witch hazel, or tea) were used as astringents to treat wounds or gastrointestinal issues due to their ability to precipitate proteins and “tighten” tissues. Tannins were ingredients in traditional remedies for diarrhea, throat inflammations, and as antidotes for some poisons, owing to their protein-binding properties. In the 20<sup>th</sup> century, as the chemistry of tannins became better understood (through the work of chemists like Edwin Haslam and Theodore Bate-Smith), new applications emerged. Tannins began to be studied as natural antioxidants and antimicrobial agents, and by the late 20<sup>th</sup> century researchers like Antonio Pizzi explored tannins as renewable resources for industrial products such as wood adhesives, foams, and anticorrosive coatings [4]. Thus, the historical trajectory of tannins has moved from traditional uses (leather tanning, dyeing, medicine) to modern engineered applications, reflecting their enduring economic importance and versatile functionality.

### 1.3 Sources: coniferous and other plant species

Tannins are widespread in the plant kingdom, occurring in many species of trees, shrubs, legumes, fruits, and even some aquatic plants. They are found in most higher plants as part of the plant's defense system against herbivores, insects, and pathogens (the bitter, astringent taste deters feeding and the protein-binding can inactivate microbial enzymes) [4]. The distribution of tannins in a plant can vary: they may concentrate in bark, wood, leaves, fruits, or seeds depending on the species. Below we highlight major sources of tannins, with an emphasis on coniferous (gymnosperm) plants and other important tannin-producing species:

- **Coniferous trees (softwoods):** many conifers have high levels of condensed tannins, especially in their bark. For example, **pine** species (genus *Pinus*) and **spruce** (*Picea*) have bark and heartwood rich in proanthocyanidins (condensed tannins) [4]. Pine bark extracts (e.g., from maritime pine *Pinus pinaster* or radiata pine *Pinus radiata*) are used industrially for adhesives and have been studied as antioxidants and nutraceuticals (pine bark extract known as Pycnogenol is a dietary supplement high in procyanidin tannins). **Hemlock** (e.g., *Tsuga* species) and **cedar** bark were historically used for tanning leather in North America due to their tannin content. Although conifer needles generally contain fewer tannins than bark, some conifers (like certain cedars or firs) do have tannins in needles and cones as well. Overall, coniferous sources predominantly yield condensed tannins.

- **Deciduous trees and shrubs:** a wide range of non-coniferous woody plants produce tannins. **Oak** (*Quercus* species) is a classic source: oak bark and wood contain both condensed tannins and hydrolyzable tannins, and oak galls (swellings caused by insects on oak trees) are extremely rich in gallotannins (historically used to make tannic acid and ink). **Chestnut** (*Castanea sativa*) wood is a commercial source of hydrolyzable ellagitannins (chestnut extract is used in leather tanning and wine enology) [4]. **Acacia** trees, particularly the black wattle (*Acacia mearnsii*), are cultivated for their bark which yields condensed tannins (wattle extract) used extensively in tanning and adhesive industries. **Quebracho** (*Schinopsis lorentzii* and related species), a hardwood from South America, provides a major source of condensed tannin extract (quebracho extract), valued in leather tanning for its deep reddish color and strength [4]. Other tannin-rich trees include *Mangroves* (used locally for tanning in coastal areas), *Willow* bark (contains tannins along with salicin), and *Sumac* (*Rhus* species) – sumac leaves are rich in gallotannins and were traditionally used in Middle Eastern leather tanning.
- **Fruits, nuts, and legumes:** many edible plants contain tannins, especially in their skins, shells, or seeds. For instance, **grape** skins and seeds are notable sources of condensed tannins (proanthocyanidins), which influence the taste and aging properties of red wine [2]. **Persimmon** fruit is extremely high in soluble tannins when unripe (explaining its mouth-puckering effect), and these tannins polymerize or precipitate as the fruit ripens. **Berries** such as cranberries, blueberries, and blackberries contain tannins (both condensed and small hydrolyzable types) contributing to their astringency. **Nuts** like walnuts and pecans have tannins in their skins and shells (for example, walnut husks have long been used as a natural dye/tannin source). **Legume pods** and seeds can be rich in tannins: the **tara pod** (*Caesalpinia spinosa*) from Peru is rich in gallotannins (tara is used commercially to produce gallotannic acid), and **carob** (*Ceratonia siliqua*) pods contain condensed tannins. Even some cereals and pulses have tannins in their seed coats (e.g., sorghum and certain varieties of brown beans have tannins that affect their taste and nutritional quality).
- **Leaves and other plant parts:** young leaves of many plants have high tannin content as a defense mechanism. **Tea** leaves (*Camellia sinensis*) famously contain tannins (often colloquially referred to as "tannic acid," though tea tannins are primarily flavanol polymers and gallates) which contribute to the bitterness and astringency of brewed tea [2]. **Sumac** and **witch hazel** leaves are rich in tannins (witch hazel extract is used as an astringent in skincare). In some plants, **roots** and **bark** are major tannin reservoirs (e.g., the bark of **pomegranate** roots contains punicalagins, a type of ellagitannin). Even the **wood** of certain trees not used for tanning can contain significant tannins that affect its color and durability (for example, mahogany and cedar have tannins that resist rot).

This wide occurrence means tannins are virtually ubiquitous in plant-based materials. From a business perspective, **commercial tannin production** today relies mainly on a few plant sources that are abundant and renewable: notable examples are the bark of wattle (acacia), the wood of

quebracho, the wood of chestnut, and to a lesser extent, by-products like pine or spruce bark from the lumber industry [4]. There is ongoing research into utilizing agricultural and forestry residues (such as fruit pomaces or tree barks) as sustainable sources of tannins. For instance, winery grape pomace is being explored as a source of proanthocyanidins for supplements, and spruce/pine bark extracts are studied as natural additives or adhesives. The abundance of tannin sources provides opportunities for various industries to tap into these natural polyphenols, whether for their functional properties (antioxidant, antimicrobial, binding ability) or as eco-friendly alternatives to synthetic chemicals.

## 1.4 Chemical composition and properties

**Chemical composition:** tannins are chemically characterized by their polyphenolic structure and high molecular weight relative to other plant metabolites. The exact composition varies by class:

- Hydrolyzable tannins are built from a sugar (often D-glucose) or other polyol core, esterified with multiple molecules of phenolic acids. In gallotannins, the attached units are gallic acid (3,4,5-trihydroxybenzoic acid) – for example, commercial "tannic acid" is essentially a mixture of polygalloyl glucose esters [1]. In ellagitannins, some of these gallic acid units are coupled to form larger diacid structures like hexahydroxydiphenic acid, which, upon spontaneous lactonization, yields ellagic acid when hydrolyzed. The molecular weight of hydrolyzable tannins can range roughly from ~500 up to 2000–3000 Da depending on how many galloyl or ellagitannins units are present [2]. They are generally **water-soluble** (especially smaller gallotannins) and can be hydrolyzed by dilute acid or tannase enzymes into simpler compounds (gallic acid, ellagic acid, glucose, etc.).
- Condensed tannins (proanthocyanidins) consist of flavonoid subunits (flavan-3-ols and/or flavan-3,4-diols). Common subunits include (+)-catechin, (–)-epicatechin, (+)-gallocatechin, (–)-epigallocatechin, among others, which differ in hydroxylation pattern. These subunits are linked mainly through C–C bonds (typically the C4 of one unit to C8 or C6 of another unit). Because these interflavan bonds are not readily cleaved by hydrolysis, condensed tannins do not break apart into smaller phenolics easily; strong oxidative or acidic conditions are needed to depolymerize them (yielding anthocyanidins, which is a lab test for proanthocyanidins) [1]. The degree of polymerization (DP) can vary widely: a tannin may be a dimer, trimer, or large polymer with DP > 10. As DP increases, solubility in water often decreases (very large condensed tannins become insoluble or form colloids). Condensed tannins from different sources have specific compositions – for example, grape seed proanthocyanidins are mostly procyanidins (made of catechin/epicatechin units), while those from cinnamon bark include procyanidins and prodelphinidins (with gallocatechin units) in mixed forms.

Despite their diversity, all tannins share an abundance of phenolic hydroxyl (–OH) groups. This polyphenolic nature is the key to their properties.

**Properties and reactivity:** the multiple phenolic groups allow tannins to engage in hydrogen bonding and hydrophobic interactions with proteins and other macromolecules. A hallmark property of tannins is their ability to **bind and precipitate proteins** out of solution. This happens because tannins can bind to the peptide bonds and amino acid side chains (especially proline-rich proteins, like salivary proteins or collagen) and cross-link them, leading to aggregation. In practical terms, this is why tannin-rich persimmon or unripe banana causes a dry feeling in the mouth – the tannins are precipitating salivary proteins, reducing lubrication. In an industrial context, the same property is exploited in leather tanning: plant tannins infiltrate a hide and bind to the collagen fibers, transforming the protein structure into a water-insoluble matrix that resists decomposition and imparts strength [1]. The protein-binding property also means tannins can inactivate many enzymes and microbial proteins, contributing to their antimicrobial effects (many pathogens cannot thrive on tannin-rich plants). However, this can have a negative side in nutrition: dietary tannins can complex with digestive enzymes or dietary proteins and reduce the absorption of nutrients (hence tannins are sometimes termed *anti-nutrients* in animal feeds if present at high levels).

Tannins also readily **chelate metal ions**. The ortho-dihydroxy (catechol) or tri-hydroxy (galloyl) arrangements on the phenolic rings can bind metals like iron, copper, and aluminum. A well-known example is the reaction of tannins with iron(II) sulfate to produce a dark blue-black complex, historically used as **iron gall ink** (the standard writing ink from medieval times up to the 19th century was made by combining oak gall tannins with iron sulfate) [4]. In wine, tannins can bind to iron and other trace metals, which can influence wine stability and color. The metal-binding property is also being researched for corrosion inhibition – tannin extracts applied to metal surfaces can form protective complexes that prevent oxidation of the metal.

Another key property is **antioxidant activity**. Tannins are often very effective radical scavengers due to the ease with which their phenolic groups can donate hydrogen atoms or electrons to neutralize free radicals. Both condensed and hydrolyzable tannins tend to have strong antioxidant capacity, which has drawn attention to their **health benefits**. Studies have linked tannin-rich diets (e.g., consumption of berries, tea, red wine) with lower risk of chronic diseases such as cardiovascular disease and certain cancers, partly attributing this to tannins' ability to mitigate oxidative stress [2]. Tannins also exhibit **anti-inflammatory** and **antimicrobial** properties, making them interesting candidates for nutraceuticals and functional foods [5]. For instance, epigallocatechin gallate (EGCG), a tannin-related polyphenol from green tea, is known for its anti-cancer and anti-inflammatory effects. Gallotannins have been studied for antiviral properties as well (e.g. against hepatitis and HIV, by blocking viral enzymes) [5].

From a physical-chemical standpoint, most tannins are amorphous, amorphously solid or extractable as brownish substances. They are typically soluble in water and polar organic solvents (like alcohols), especially the smaller tannins; larger condensed tannins may be soluble in hot water but less so in cold. When exposed to air and light, tannins can oxidize and darken (a phenomenon

seen in cut fruits like apples/bananas browning, partly due to tannin oxidation). They often form colloidal solutions and can interact with other plant compounds (e.g., forming complexes with pectins and starches).

**Relevance of properties to industry:** these chemical properties underline many practical uses of tannins. The protein-binding and antimicrobial traits make tannins useful as natural preservatives in food and beverages (for example, oak-derived tannins added to wine or beer can stabilize the product and add flavor while inhibiting certain bacteria). The strong antioxidant capacity is a selling point for tannin extracts in the health supplement market (grape seed or pine bark extracts are marketed for cardiovascular health due to proanthocyanidin content). In materials science, tannins' tendency to complex with proteins and cross-link under certain conditions has led to development of tannin-based adhesives and resins: tannins can react with formaldehyde or other cross-linkers to form wood glues, foams, and even composite plastics [4]. Their metal-chelating ability means tannins can serve as natural anti-corrosive agents in paints or coatings for metal protection.

It is important to note that while tannins have beneficial uses, their effects are dose dependent. In foods or feeds, a moderate level of tannins can provide antioxidants and desirable flavors, but a high level can be detrimental – causing bitterness, reducing palatability, and inhibiting nutrient absorption. For example, in animal nutrition, small amounts of certain tannins can improve protein utilization by protecting proteins from rumen breakdown, but large amounts will bind too much protein and minerals, leading to poorer nutrition. Likewise, in human diets, tannin-rich foods like tea or red wine in moderation are considered healthful, but excessive intake of tannins (or tannin supplements in high dose) may cause stomach irritation or liver stress [5].

**Key trends and developments:** contemporary research on tannins is vibrant, reflecting these compounds' potential in various fields. On one front, there is growing interest in sustainable extraction and production of tannins – for instance, using greener solvents (like deep eutectic solvents or supercritical fluids) to extract tannins from plant waste more efficiently, and developing purification methods to obtain specific tannin fractions for specialized uses. On another front, biomedical research is examining tannins as lead compounds for drug development or health products (such as antimicrobial coatings, cancer therapy adjuvants, or modulators of gut health due to tannins' interaction with gut microbiota) [5]. In the materials sector, tannins are being incorporated into advanced materials: recent studies have used tannins to synthesize foams and aerogels for insulation, as well as UV-resistant coatings and biobased polymers, highlighting tannins as a valuable resource in the push for renewable and non-toxic material components [4].

In summary, tannins are chemically complex but offer a remarkable suite of properties – astringency, binding capacity, antioxidant activity – that have been harnessed by humans historically and are still highly relevant today. Understanding their definition, types, sources, and chemistry is crucial for both scientists and business stakeholders who seek to innovate with natural

compounds. The richness of tannin research in the past five years underscores a renaissance in appreciating these natural polyphenols: from improving foods and beverages to creating green industrial products, tannins serve as a bridge between traditional knowledge and modern scientific application.

## 2. Sources of plant-based tannins

Plant-based tannins occur across a diverse range of species, from trees to shrubs and fruits. The key botanical sources of tannins include **angiosperm trees** such as oak (*Quercus* spp.), chestnut (*Castanea* spp.), and mimosa (wattle, *Acacia mearnsii*), which are traditional commercial tannin sources. Tropical species like quebracho (*Schinopsis balansae*) and mangrove (*Rhizophora* spp.) are also rich in tannins. Additionally, various fruit pods and galls (e.g. tara pods from *Caesalpinia spinosa*, oak galls) and leafy shrubs (e.g. sumac, *Rhus* spp.) contribute to the spectrum of tannin-yielding biomass. These sources yield different types of tannins – broadly classified into hydrolyzable tannins (polyesters of gallic or ellagic acid, common in oak galls and chestnut) and condensed tannins (proanthocyanidins derived from flavan-3-ols, common in bark of acacia, quebracho, etc.). Each source has characteristic tannin content: for example, wattle bark and quebracho wood can contain well above 30% tannins by dry weight in commercial extracts, mostly of the condensed type. By contrast, gallnuts and sumac contain primarily hydrolyzable tannins (gallotannins) in similarly high concentrations. This wide availability of tannin-rich materials underpins their traditional use in leather tanning and emerging use in wood adhesives and biopolymers [6].

Importantly, tannin content and composition depend on species, plant part, and even growing conditions.

### 2.1 Tannins from conifer sources

Conifers (gymnosperms) are of particular interest because their bark and wood often represent an underutilized by-product of the forestry industry yet contain significant amounts of condensed tannins. In this chapter, we will detail the key conifer species producing tannins, the methods to extract and process these tannins, comparisons of yield and quality [7].

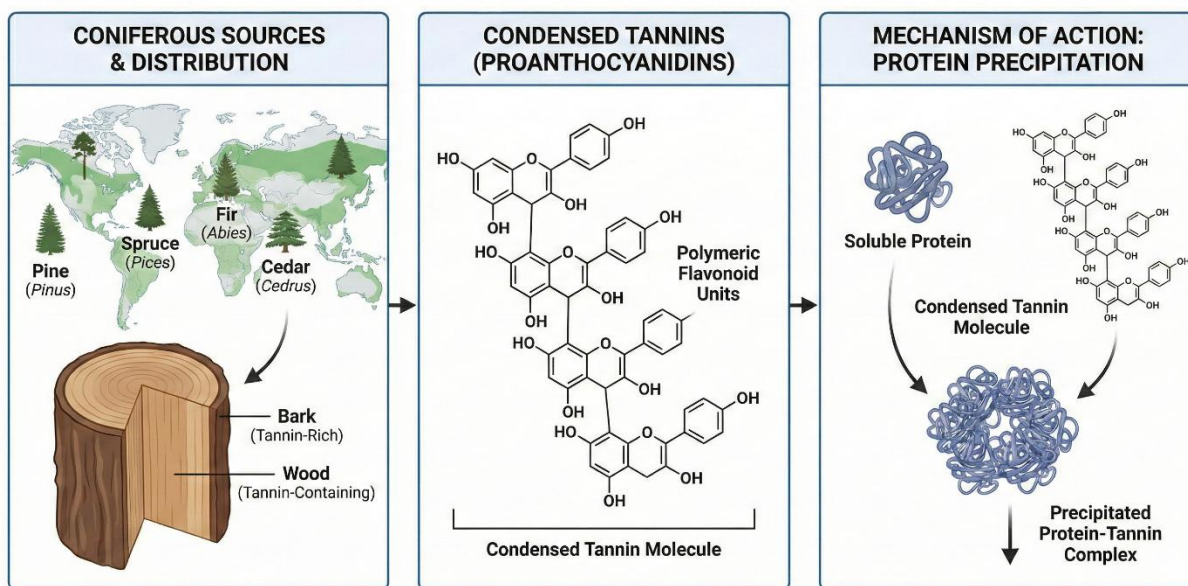


Figure 3. Origin, structure and function of coniferous tannins [8].

## 2.2 Key conifer species: pine, spruce, fir, cedar

Coniferous trees are widespread across temperate and boreal regions, and several genera are notable for their tannin content in bark and wood. The primary conifer sources of tannins include pines, spruces, firs, and cedars (including related genera). These species produce tannins predominantly of the condensed type (proanthocyanidins), which are polymeric flavonoids capable of precipitating proteins.

**Pine (*Pinus spp.*)** – pine trees are globally distributed (native to much of the Northern Hemisphere and widely planted elsewhere). Pine bark is a well-studied tannin source. Many pine species yield appreciable condensed tannins in their inner bark. For example, **Maritime pine** (*Pinus pinaster*) of the Mediterranean region is known to have a high polyphenol content: extracts can exceed 160 mg of gallic acid equivalents per gram of dry bark under optimized conditions [9]. This corresponds to roughly 15–20% of the bark mass as phenolic compounds. Other pines such as **Scots pine** (*P. sylvestris*, widespread in Europe) and **Monterey pine** (*P. radiata*, grown in e.g. Australia, New Zealand, Chile) also contain substantial tannins (often 10–18% by weight in bark) [10], [11]. Pine tannins are typically procyanidins, composed of catechin and epicatechin units, sometimes with taxifolin (a related flavonoid) also present in bark extracts [9]. Geographically, pines in drier or poorer soils may accumulate more tannins as a defense mechanism, whereas

species and age influence absolute content (e.g. young pine bark can have higher tannin percentage than older trees) [10].

**Spruce (*Picea spp.*)** – spruces dominate boreal forests in North America (e.g. white spruce *P. glauca*, black spruce *P. mariana*) and Northern Europe/Asia (e.g. Norway spruce *P. abies*). Spruce bark has long been recognized for its tannins; historically Norway spruce bark was used in Europe for leather tanning. Typical condensed tannin levels in **Norway spruce** bark average around 10–15% of dry weight, though values can range from as low as ~5% to over 20% depending on extraction conditions and bark condition [11], [12]. Notably, some studies report exceptionally high yields: *Picea sitchensis* (Sitka spruce) bark, for instance, yielded up to ~35% extractives in optimized hot water extraction, a significant portion being polyphenols [13]. Spruce bark tannins are also proanthocyanidins (mostly procyanidin type from catechin units), often accompanied by unique phenolics like stilbene glycosides (e.g. astringin and isorhapontin) which are abundant in spruce but not in angiosperm tannin sources [11], [13]. These stilbenes are not tannins per se, but co-extract as bioactive compounds. Geographically, spruce forests in colder climates tend to produce bark with higher tannin content during winter dormancy than in summer, as seasonal influences affect polyphenol levels [11].

**Fir (*Abies spp.* and related genera)** – true firs (genus *Abies*, e.g. silver fir *A. alba* in Europe, balsam fir *A. balsamea* in North America) and some fir-like conifers (e.g. Douglas-fir *Pseudotsuga menziesii*, which is botanically not a true fir but shares similar bark traits) are also notable sources of tannins. Fir bark generally contains condensed tannins and flavonoids analogous to pine and spruce. For example, Douglas-fir bark was used in the 20th century for tannin extraction in western North America; it contains around 8–15% tannins in the bark under typical conditions [12]. More recent analyses of fir bark confirm respectable yields: studies on silver fir and Chinese fir (*Cunninghamia lanceolata*) report extraction yields around 20% of bark dry weight using ethanol-water solvents, with catechin, epicatechin, and flavonol glycosides (quercetin, isorhamnetin derivatives) identified as major components [11]. This indicates firs produce a tannin profile rich in proanthocyanidins (for tanning or adhesive applications) along with smaller amounts of co-extracted compounds. The geographical distribution of *Abies* is montane and temperate zones (e.g. European Alps, North American Rockies, East Asian highlands), suggesting a wide raw material base. Douglas-fir, common in the Pacific Northwest, has its bark commercially available from sawmills, and its tannins (often blended with faster-setting mimosa or quebracho extracts) have been investigated for wood adhesives [4], [14].

**Cedar (*Cedrus spp.* and related “cedars”)** – the term *cedar* can refer to several coniferous trees; here we primarily mean true cedars (genus *Cedrus*: e.g. Atlas cedar, Deodar cedar) and also cedar-like species in the cypress family often called cedar (such as Western Red Cedar, *Thuja plicata*, or Eastern “Red” Cedar, *Juniperus virginiana*). Cedars are known for aromatic wood and resins, but their bark and heartwood also contain polyphenolic compounds that function as tannins. **True cedars** (native to the Mediterranean and Himalayas) have been less studied for tannin extraction

compared to pine or spruce. Nevertheless, Cedrus bark does contain condensed tannins along with terpenoids; in traditional medicine, decoctions of cedar bark were used as astringents, implying tannin presence. Quantitative data are sparse in recent literature, but cedar bark tannin content is likely moderate (on the order of a few percent up to ~10%). **Western red cedar** (often called cedar but actually a *Thuja* species) is noted to have unique phenolics (e.g. flavonoids and tropolones like thujaplicins) that give its extracts antimicrobial properties. These phenolics can cross-link proteins similarly to tannins, although they are structurally distinct.

Table 2.1 below provides a comparative snapshot of the main conifer genera used (or considered) as sources of bark-derived tannins, linking indicative extract/tannin yields with tannin chemistry and processing implications. Across the group, tannins are predominantly condensed proanthocyanidins, but the table highlights meaningful differences in (i) how much material is recoverable under mild aqueous extraction versus process-intensified methods (e.g., MAE or subcritical/hot-water systems), (ii) the structural type of tannins (spruce and pine largely procyanidins, while fir shows a higher prodelphinidin share), and (iii) the extent of co-extracted carbohydrates and minor phenolics that influence downstream purification and application performance. Spruce and fir stand out as particularly attractive industrial candidates due to higher tannin contents and/or more favorable tannin-to-carbohydrate balance, whereas pine can reach competitive yields primarily when intensified extraction is applied. Cedar (e.g., *Thuja*) is differentiated by strong tannin-polysaccharide association, which lowers the fraction of readily extractable tannins and can complicate isolation. Overall, the table frames species selection as a combined question of yield, tannin composition (including degree of polymerization), and extract cleanliness, which together determine suitability for end uses such as leather tanning, adhesives, and tannin-based coagulants.

Table 2.1. Key conifer tannin sources: indicative tannin contents and types in bark of pine, spruce, fir and cedar.

Conifer group (example species)	Indicative tannin / extract content in bark*	Main tannin type & composition	Comparative notes (within conifers)	Key refs.
Pine ( <i>Pinus sylvestris</i> , <i>P. pinaster</i> , <i>P. radiata</i> )	<ul style="list-style-type: none"> <li>Hot-water / mild aqueous extracts: tannin-rich extracts in same order of magnitude as other softwoods, but lower tannin fraction vs carbohydrates (e.g. <i>P. sylvestris</i>).</li> <li>Intensified methods: - <i>P. pinaster</i> MAE (hydroethanolic) <math>\approx</math> 11 wt% extract / dry bark. - <i>P. radiata</i> SHS extraction up to <math>\approx</math>17–18 wt% tannin-rich extract / dry bark.</li> </ul>	<ul style="list-style-type: none"> <li>Dominantly condensed procyanidins (catechin/epicatechin).</li> <li>Oligomeric and polymeric flavan-3-ols plus notable carbohydrates and small phenolics in hot-water extracts.</li> </ul>	<ul style="list-style-type: none"> <li>Moderate tannin source under conventional extraction.</li> <li>Process-intensified methods can yield high tannin-rich extracts.</li> <li>Generally higher extractable polyphenols than cedar, but lower tannin:carbohydrate ratio than spruce/fir in water extracts.</li> </ul>	[14], [15], [16], [17], [18]
Spruce ( <i>Picea abies</i> )	<ul style="list-style-type: none"> <li>Wood-free bark tannins <math>\approx</math> 10.7 wt% of dry bark.</li> <li>Mild aqueous extraction (60 °C): <math>\approx</math> 3.3 wt% dried extract.</li> <li>Pilot hot-water extraction: dried extract with <math>\approx</math>50 wt% condensed tannins.</li> </ul>	<ul style="list-style-type: none"> <li>Predominantly condensed procyanidins. <ul style="list-style-type: none"> <li>DP up to <math>\approx</math>13 units.</li> </ul> </li> <li>Minor stilbene glucosides and galloylated flavan-3-ols; co-extracted arabinans, arabinogalactans and glucans.</li> </ul>	<ul style="list-style-type: none"> <li>Consistently identified as high-value conifer tannin source.</li> <li>Higher tannin content and more favourable tannin:carbohydrate balance than pine.</li> <li>Technically attractive for industrial tannin (and tannin-coagulant) production.</li> </ul>	[14], [15], [16]
Fir ( <i>Abies alba</i> )	<ul style="list-style-type: none"> <li>Aqueous extraction (60 °C): <math>\approx</math> 10.1 wt% dried extract / dry bark, slightly higher than spruce under similar conditions.</li> <li>Water-extractable fraction rich in polyphenols.</li> </ul>	<ul style="list-style-type: none"> <li>Condensed tannins richer in prodelphinidins (gallocatechin/epigallocatechin) than spruce.</li> <li>DP up to <math>\approx</math>9; also contains procyanidins, stilbene glucosides, galloylated flavan-3-ols and low-molecular phenolics.</li> </ul>	<ul style="list-style-type: none"> <li>Substantial extract yields comparable to spruce.</li> <li>More strongly hydroxylated tannin structures (higher prodelphinidin share) <math>\rightarrow</math> high antioxidant and metal-chelating potential.</li> <li>Good complementary source to spruce/pine.</li> </ul>	[14], [15], [16]
Cedar (western redcedar <i>Thuja plicata</i> )	<ul style="list-style-type: none"> <li>Cold-water bark extraction: <math>\approx</math> 3.4 wt% aqueous extract / dry bark.</li> <li>Alcohol-insoluble fraction <math>\approx</math> 1 wt% of bark, containing proanthocyanidins + polysaccharides; polysaccharides <math>\approx</math> 30 wt% of that fraction.</li> </ul>	<ul style="list-style-type: none"> <li>Flavan-3-ol-derived proanthocyanidins strongly associated with neutral polysaccharides.</li> <li>Tight proanthocyanidin-polysaccharide complexes reduce “free” extractable tannin fraction.</li> </ul>	<ul style="list-style-type: none"> <li>Lower yield of readily extractable tannins (<math>\approx</math>3–4 wt% under mild conditions) than pine, spruce or fir.</li> <li>Strong tannin-polysaccharide association complicates isolation and makes cedar a less efficient industrial condensed-tannin source.</li> </ul>	[19]

In summary, while pine, spruce, and fir are the principal conifer tannin sources, cedar species contribute tannins in certain regions or niche applications. The type of tannin in cedars is also of the condensed category, though often mixed with other non-tannin phenolic constituents.

Overall, coniferous tannins are **condensed tannins (proanthocyanidins)**, in contrast to the hydrolyzable tannins of many angiosperm sources. Their content in bark ranges roughly from 5% up to 20% (occasionally more under ideal conditions) of dry weight, depending on species and conditions [10], [11]. Such variability underscores the importance of extraction techniques and resource selection, as discussed next.

Table 2.2 summarizes major tannin-bearing species, linking their native/production regions with characteristic tannin chemistries and typical applications. It highlights clear contrasts between high-yield condensed-tannin sources (e.g., *Acacia mearnsii* and quebracho) and hydrolysable ellagitannin-rich chestnut, alongside softwood bark sources (pine, spruce, fir, Douglas-fir) whose generally lower-purity condensed tannins remain valuable for adhesives and antioxidant/material uses.

Table 2.2. Key tannin-bearing species: native range and typical tannin characteristics

Species (organ typically used)	Native range / major production regions	Typical tannin characteristics	Key refs.
<i>Acacia mearnsii</i> De Wild. (black wattle, bark)	<ul style="list-style-type: none"> <li>• Native: SE Australia, Tasmania</li> <li>• Major plantations: South Africa, Brazil, China, Vietnam, other subtropical regions</li> </ul>	<ul style="list-style-type: none"> <li>• Very high <b>condensed tannin</b> content in bark (“wattle tannin”).</li> <li>• Dominant units: <b>profisetinidin</b> / <b>prorobinetinidin</b> (fisetinidol, robinetinidol).</li> <li>• High Stiasny-reactive fraction → fast reactivity in phenolic resins, strong leather-tanning efficiency.</li> <li>• Extracts show strong antioxidant and antimicrobial activities.</li> </ul>	[4], [20], [21]
<i>Schinopsis lorentzii</i> / <i>S. balansae</i> (quebracho colorado, heartwood)	<ul style="list-style-type: none"> <li>• Native: Gran Chaco (Argentina, Paraguay, Bolivia, Brazil)</li> <li>• Industrial extraction: Argentina/Paraguay for export</li> </ul>	<ul style="list-style-type: none"> <li>• <b>Highly polymerised condensed tannins</b>, mainly <b>profisetinidin-type proanthocyanidins</b>.</li> <li>• Very high tannin content in commercial extracts, strongly astringent.</li> <li>• Excellent protein- and metal-complexation; used in leather, wood adhesives, antioxidants in meat/food systems and functional materials.</li> </ul>	[4], [22], [23], [24]
<i>Castanea sativa</i> Mill. (sweet chestnut, wood & bark)	<ul style="list-style-type: none"> <li>• Native: Mediterranean basin, W Asia</li> <li>• Cultivation/production: S and W Europe (Italy, France, Spain, Portugal)</li> </ul>	<ul style="list-style-type: none"> <li>• Dominated by <b>hydrolysable ellagitannins</b> (e.g. castalagin, vescalagin and derivatives).</li> <li>• Industrial extracts: often ≥50–60 % “active” ellagitannins in dry extract.</li> <li>• Strong antioxidant and metal-chelating capacity; used in vegetable leather tanning, enology (oak/wood alternatives), animal nutrition and emerging water/material applications.</li> </ul>	[4], [24], [25]
<i>Pinus pinaster</i> Ait. (maritime pine, bark)	<ul style="list-style-type: none"> <li>• Native: W Mediterranean (Iberian Peninsula, Atlantic France, NW Africa)</li> <li>• Plantations: SW Europe, South America, S Africa, Australia, NZ</li> </ul>	<ul style="list-style-type: none"> <li>• Bark rich in <b>condensed procyanidin-type tannins</b> (catechin/epicatechin oligomers and polymers).</li> <li>• Co-occurring phenolic acids and flavonoids (e.g. taxifolin, quercetin).</li> <li>• Strong antioxidant, antihyperglycemic and anti-inflammatory activities; model conifer bark for nutraceuticals (e.g. Pycnogenol®-type extracts) and polyphenolic materials.</li> </ul>	[4], [9], [26]

Species (organ typically used)	Native range / major production regions	Typical tannin characteristics	Key refs.
<i>Pinus sylvestris</i> L. (Scots pine, bark)	<ul style="list-style-type: none"> <li>Native/abundant: boreal and temperate Eurasia (Nordic/Baltic region, Russia, Central Europe)</li> </ul>	<ul style="list-style-type: none"> <li>Hot-water bark extracts contain <b>condensed procyanidins</b> with notable co-extracted carbohydrates (arabinans, arabinogalactans, glucans) and inorganic salts.</li> <li>Tannin fraction generally lower (rel. to total extract) and less pure than in wattle/quebracho; nonetheless suitable for adhesives and as antioxidant polyphenol feedstock.</li> </ul>	[4], [14]
<i>Picea abies</i> (L.) H. Karst. (Norway spruce, bark)	<ul style="list-style-type: none"> <li>Native: boreal &amp; montane Europe (Nordics, Baltics, Central European mountains)</li> <li>Major industrial species in Scandinavian/Baltic sawmill and pulp sectors</li> </ul>	<ul style="list-style-type: none"> <li>Significant <b>condensed tannin source</b> in bark (<math>\approx 10</math> % of bark dry mass in industrial material).</li> <li>Tannins mainly <b>procyanidin-type oligomers/polymers</b> (DP up to <math>\sim 13</math>), plus stilbene glucosides (e.g. astringin, isorhapontin) and galloylated flavan-3-ols.</li> <li>Hot-water extracts show comparatively high tannin:carbohydrate ratio among softwoods, attractive for adhesives and water-treatment coagulants.</li> </ul>	[14], [15], [16], [27]
<i>Abies alba</i> Mill. (silver fir, bark)	<ul style="list-style-type: none"> <li>Native: montane Central &amp; Southern Europe (Alps, Carpathians, Balkans)</li> <li>Important regional conifer in mixed fir-spruce forests</li> </ul>	<ul style="list-style-type: none"> <li>Bark extracts rich in <b>condensed tannins with higher prodelphinidin content</b> (galloocatechin/epigalloocatechin units) than spruce.</li> <li>DP typically up to <math>\sim 9</math>; also contains procyanidins, stilbene glucosides and galloylated flavan-3-ols.</li> <li>Higher B-ring hydroxylation <math>\rightarrow</math> very strong antioxidant and metal-chelating behaviour.</li> </ul>	[14], [15]
<i>Pseudotsuga menziesii</i> (Mirb.) Franco (Douglas-fir, bark)	<ul style="list-style-type: none"> <li>Native: W North America</li> <li>Widely planted: W &amp; Central Europe, Chile, NZ</li> </ul>	<ul style="list-style-type: none"> <li>Hot-water bark extracts contain <b>condensed procyanidin tannins</b> with species-specific structural patterns.</li> <li>Bianchi <i>et al.</i> showed distinct tannin composition vs spruce, fir and pine, with implications for viscosity and reactivity in adhesives.</li> <li>Considered a promising softwood tannin source for phenolic-resin replacement and functional materials.</li> </ul>	[4], [14]

## 2.3 Extraction and processing techniques

**Extraction of tannins** from conifer biomass has been performed using both long-standing traditional methods and newer “green” technologies. The choice of extraction technique influences the efficiency (yield of tannins), the purity/quality of the extract, scalability for industry, and environmental footprint. Here we outline major techniques:

**Traditional hot water extraction:** this is the classic method used in the tannin industry for over a century. Bark or wood (coarsely ground) is cooked in hot water (often at ~70–100 °C) for several hours to leach out tannins, followed by filtration. Sometimes steam or boiling water is used in large percolation tanks. For example, historical processes for spruce or hemlock bark involved soaking or boiling the bark in water to produce tanning liquor. Hot water primarily extracts polar compounds like tannins, sugars, and acids. **Pros:** Water is non-toxic and inexpensive, and the process is simple and well-established. It can handle large volumes of material (e.g. industrial plants processing tons of bark). **Cons:** the extraction may be incomplete or slow – tannins bound in the biomass may require long extraction times.

Norway spruce bark typically yields around 6–12 % extractives with hot water alone under standard conditions, but the composition of this extract is highly sensitive to extraction parameters. In particular, recent scale-up work on hot-water extraction of spruce and Scots pine bark has shown that, under certain conditions, hemicelluloses and other non-tannin polysaccharides can account for more than 50 % of the dried extract mass, leaving tannins as only one component of a broader carbohydrate-rich mixture. This is consistent with the broader observation that hot water co-extracts substantial amounts of non-tannin substances (neutral sugars, hemicelluloses, soluble lignin fragments and low-molecular phenolics), which dilute the tannin content and influence viscosity and downstream processing behaviour of the extract [28]. As a result, process design for spruce bark must explicitly decide whether the goal is a relatively pure tannin fraction or a multifunctional polyphenol-plus-hemicellulose extract, because the same “high yield” in mass terms can correspond to quite different tannin concentrations depending on the chosen conditions.

Energy demand is another central issue: heat is required to raise large volumes of water to extraction temperature and, in most commercial settings, the resulting liquor must then be concentrated to a syrup or dried powder for storage and transport [16]. Evaporation of water is inherently energy-intensive, so the overall process energy footprint depends strongly on how concentration is achieved. Alongside conventional evaporation, membrane processes such as ultrafiltration offer an alternative route to concentrate bark extracts, allowing partial removal of water and low-molecular solutes while retaining high-molecular-weight tannins and hemicelluloses in the retentate [29]. In principle, this can reduce thermal load, enable fractionation (for example, separating high-molecular tannins from smaller sugars) and improve the energy efficiency of tannin production, especially when integrated with heat-recovery schemes.

Despite these challenges, water-based extraction remains the industrial standard. Most commercial tannin extracts from wattle, quebracho and other angiosperm sources still rely on hot water, sometimes with mild additives (e.g. sodium bisulfite) to disrupt wood structure and increase yield. In the conifer context, hot water extraction has already been successfully scaled for pine and spruce bark. For example, spruce bark treated in a pressurised hot-water extractor at around 120 °C has yielded up to ~35 % extractives, indicating that, under controlled higher-temperature and higher-pressure conditions, water alone can achieve high overall yields that approach those of more aggressive solvent systems [11]. These operating windows, however, begin to border on “pressurised” or subcritical water techniques, reinforcing the importance of optimising not only the quantity of extract but also its quality (tannin vs. hemicellulose content) and the efficiency of subsequent concentration steps.

- **Organic solvent extraction:** using organic solvents (or mixtures with water) can improve tannin recovery from conifer biomass. Common solvents include **ethanol**, **acetone**, or their water mixtures. Ethanol-water (50:50 v/v) is especially effective for proanthocyanidins, as it balances polarity to extract tannins but not too many sugars. Studies on maritime pine bark showed maximal tannin yields with ~50–70% ethanol-water at near-boiling temperatures, extracting ~17–18% of bark as dry matter with high phenolic content [9], [11]. **Pros:** organic solvents can extract a broader range of polyphenols and often faster than pure water. For example, ethanol can penetrate plant tissue better, yielding more tannins in less time. Acetone-water is noted to prevent some tannin oxidation during extraction. **Cons:** the need to recover and recycle the solvent adds cost; solvents like ethanol are flammable, and acetone or methanol (sometimes used in lab-scale) are not food-grade. In an industrial setting, ethanol-water extraction is feasible (since ethanol can be distilled off and reused), and indeed some modern tannin facilities use alcohol to improve yield. One particular approach is **pressurized liquid extraction (PLE)**, where solvents at high temperature and pressure (e.g. ethanol at 120 °C under pressure) are pumped through the biomass. PLE can achieve high yields in short times. In one case, **spruce bark PLE with water** yielded comparable or higher tannin content than a 12-hour Soxhlet extraction [16]. However, the capital cost for pressure vessels is higher. In summary, traditional solvent extraction is effective and somewhat scalable, but industries tend to favor water or water/ethanol for cost and safety unless higher yields justify solvent use.
- **Supercritical CO<sub>2</sub> Extraction (SFE):** SFE is a modern “green” extraction that uses carbon dioxide at supercritical conditions (typically >31 °C and >74 bar) as a solvent. Supercritical CO<sub>2</sub> has gas-like diffusion and liquid-like solvating power, and it leaves no solvent residue since CO<sub>2</sub> evaporates. However, CO<sub>2</sub> by itself is non-polar, which makes it a poor solvent for polar tannins. To extract polyphenols like tannins, **co-solvents** (also called modifiers) such as a small percentage of ethanol or water are added to the CO<sub>2</sub>. SFE has been tested on conifer bark: for instance, Spinelli *et al.* (2019) compared SFE vs other methods on Norway spruce

bark [13]. They found SFE (with 10% ethanol modifier) yielded only ~2–3% of dry bark as extract, with a very low total phenolic content (~0.8 mg GAE/g). This was significantly less efficient than ultrasound or pressurized water methods. **Pros:** Supercritical CO<sub>2</sub> extraction is a solvent-clean technology that avoids toxic solvent residues and waste, and its pressure/temperature settings (plus optional co-solvent) can be tuned to target specific compound classes. It is very effective for essential oils and other lipophilic extractives in wood, and in the case of bark tannins this selectivity can be advantageous: most highly hydrophilic components, including neutral sugars and other carbohydrates, are only poorly solubilised in scCO<sub>2</sub>. As a result, when tannins are extracted (typically with the aid of a polar co-solvent such as ethanol), the resulting extract is often relatively tannin-rich and low in co-extracted carbohydrates and mineral impurities compared to hot-water extracts. This high intrinsic purity can be valuable for applications where a solvent-free, low-sugar tannin fraction is required (e.g. certain food, nutraceutical or high-performance material uses), and it reduces the need for extensive downstream purification. **Cons:** The equipment (high-pressure CO<sub>2</sub> pumps, extractor vessels, heat exchangers) is capital-intensive and generally limited to smaller throughputs than conventional vat or percolation extractors. Moreover, pure CO<sub>2</sub> has low affinity for polar, high-molecular-weight tannins; even with added co-solvents, overall tannin yields are typically lower than those obtained by conventional aqueous or hydroalcoholic extraction [13], [18]. This has two important economic implications: first, the cost per kilogram of tannin recovered is high because fixed capital and operating costs are spread over a smaller product mass; second, the process remains unattractive for bulk tannin production aimed at large-volume sectors (leather, water treatment, adhesives), where crude hot-water extracts with substantial carbohydrate content are acceptable. In practice, supercritical CO<sub>2</sub> is therefore better viewed as a niche technology for producing high-purity, carbohydrate-poor tannin fractions in relatively small volumes, rather than a primary route for large-scale tannin manufacture.

- **Deep eutectic solvents (DES):** deep eutectic solvents are a newer class of designer solvents, often made by mixing a quaternary ammonium salt (like choline chloride) with a hydrogen-bond donor (like glycerol, acids, urea) to form a eutectic mixture with melting point far below that of either component. DES can dissolve many biopolymers and polyphenols and are touted as green (they are made from safe, biodegradable components). Recent research has applied DES to tannin extraction from bark. For example, choline chloride-based DES have been used on pine and spruce bark, achieving tannin yields in the range of ~12–15% of bark weight. In one comparative study, a DES composed of choline chloride and glycerol (at 60 °C) extracted ~11.4% of Norway spruce bark, with a TPC of ~17 mg GAE/g, outperforming some traditional solvents [30]. **Pros:** DES are tunable – by changing the components and ratios, one can target different types of tannins. They are non-volatile (no evaporation needed), recyclable, and often non-toxic (some DES components are even edible, like malic acid or betaine). They can provide high selectivity and yield for phenolics. **Cons:** the viscous nature of DES can make

processing and separation of the extract difficult. After extraction, the tannins are in a DES matrix, which may need dilution with water or alcohol to recover the tannins or use the extract directly in formulation. The scalability of DES is still under study; large-scale separation and reuse of DES in an economic way needs further development. Nonetheless, DES technology is promising for environmentally friendly tannin extraction, potentially allowing **one-step extraction** of tannins without the need for subsequent solvent removal (the DES-tannin mixture could be used as-is in some applications like resin synthesis).

- **Other advanced techniques:** several other extraction enhancements have been explored. **Ultrasound-Assisted Extraction (UAE)** uses high-frequency sound waves to create cavitation in the solvent, which can rupture plant cells and accelerate tannin release. UAE has been shown to reduce extraction time dramatically. For example, using an ultrasonic horn, high tannin yields from larch bark were obtained in 15 minutes that were comparable to hours of conventional soaking [11]. **Microwave-Assisted Extraction (MAE)** is another method, where microwaves rapidly heat the solvent inside the plant matrix, improving penetration. MAE of pine bark has achieved good yields in short times (e.g. <30 minutes), though care must be taken to avoid overheating which can degrade tannins. **Accelerated solvent extraction (ASE)**, a form of PLE with automated cycles, has also been effectively used on conifer bark, as noted earlier with pressurized hot water yielding very high phenolic contents. Enzyme-assisted extraction (using cellulases or pectinases to break cell walls) is a niche approach that could increase yield by freeing tannins bound in cell structures; a few studies indicate modest improvements with enzyme pretreatment, but this is not yet common practice.

**Efficiency and scalability:** traditional hot-water extraction remains the most **scalable** – industrial bark extract producers can utilize existing infrastructure (extraction tanks, boilers, spray dryers). It's efficient in processing bulk material but may leave some tannins unextracted. Modern techniques like UAE or ASE can significantly improve efficiency (higher yield in less time) and might be scaled by numbering-up (multiple smaller extraction units in parallel). SFE and DES are at a pilot stage for tannins: SFE might be reserved for high-value small-scale production (due to cost), whereas DES could potentially be scaled if separation challenges are overcome. A scientifically literate stakeholder will note the **trade-off between yield and cost/environmental impact:** for instance, adding organic solvent or using high pressure yields more tannin but at higher

capital and operational cost; greener methods avoid toxic solvents but might sacrifice some efficiency.

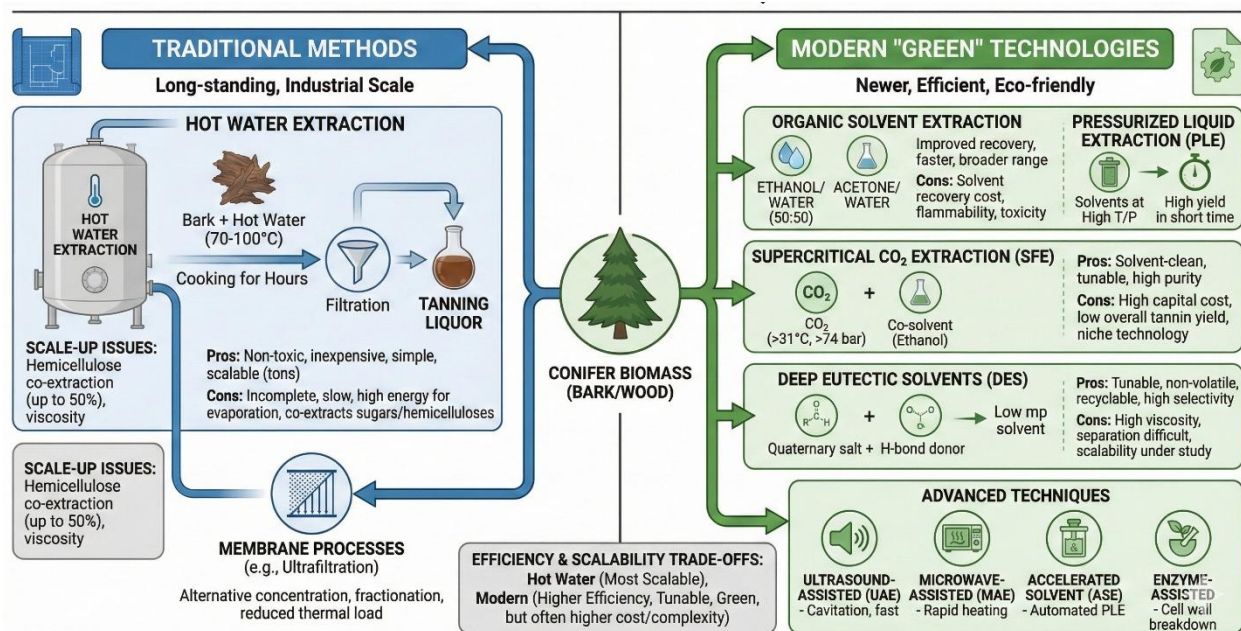


Figure 4. Extraction and processing techniques for conifer tannins.

Fig. 4 illustrates the diverse landscape of extraction and processing pathways for conifer tannins, ranging from century-old industrial standards to emerging "green" technologies. At its core, the diagram highlights the critical trade-offs between extraction efficiency, tannin purity, and environmental footprint. Traditional hot water extraction is depicted as the high-volume, cost-effective baseline, though it often results in a complex mixture where tannins are diluted by hemicelluloses and sugars. In contrast, advanced methods like Supercritical CO<sub>2</sub> and Deep Eutectic Solvents (DES) are shown as precision tools capable of producing high-purity, carbohydrate-poor extracts for niche applications. The schematic also emphasizes the role of downstream concentration - comparing energy-intensive thermal evaporation with the more efficient membrane ultrafiltration - demonstrating how process design must align with the specific requirements of the end-use industry, whether it be bulk wastewater treatment or high-performance bio-resins.

Table 2.3. Extraction techniques for conifer tannins (Norway spruce, Scots pine, etc.): indicative yields, purity and environmental aspects

Extraction method	Indicative tannin yield (% of dry bark)	Purity / composition of extract	Typical conditions & extraction time	Environmental & scale aspects	Ref.
<b>Hot water (atmospheric, 60–90°C)</b>	<ul style="list-style-type: none"> <li>Total dissolved solids (TDS) <math>\approx</math> 10–20% of bark (bench-scale spruce)</li> <li>Tannins typically <math>\approx</math> 3–6% of bark, up to <math>\approx</math> 70–90% of bark tannins recovered under optimised lab conditions</li> </ul>	<ul style="list-style-type: none"> <li>Tannins often <math>\approx</math> 30–50 wt% of dried extract; remainder mainly hemicelluloses and other carbohydrates</li> <li>Norway spruce bark extracts can contain &gt;50 wt% hemicellulosic sugars under some extraction conditions, decreasing tannin purity</li> </ul>	<ul style="list-style-type: none"> <li>60–90°C, 1–2 h; 5–15 wt% solids</li> <li>Atmospheric or slightly elevated pressure; sometimes with Na<sub>2</sub>SO<sub>3</sub> / Na<sub>2</sub>CO<sub>3</sub> to aid cell-wall opening and stabilise tannins</li> </ul>	<ul style="list-style-type: none"> <li>Solvent is water only; low toxicity effluent but rich in sugars and salts</li> <li>Main environmental burden from heating, evaporation and spray-drying; LCA for spruce bark shows evaporation/drying dominate GWP and energy use</li> <li>Ultrafiltration / nanofiltration can cut energy demand by concentrating tannins before evaporation</li> </ul>	[16], [28], [29]
<b>Pressurised / subcritical hot water (100–160°C)</b>	<ul style="list-style-type: none"> <li>Sequential pressurised steps (100–160 °C) can dissolve <math>\approx</math> 30–40% (up to <math>\approx</math> 42%) of spruce bark dry matter</li> <li>Very high recovery of non-cellulosic polysaccharides; tannins also solubilised but increasingly diluted by hemicelluloses at higher temperatures</li> </ul>	<ul style="list-style-type: none"> <li>Extracts dominated by non-cellulosic polysaccharides (arabinans, galacturonans, etc.) with a smaller condensed-tannin fraction</li> <li>High molecular-weight phenolics and “apparent lignin” may appear in TDS due to analytical co-precipitation</li> </ul>	<ul style="list-style-type: none"> <li>100–160°C, 50–100 bar (ASE or continuous reactors)</li> <li>Often 3 <math>\times</math> 20 min cycles (<math>\approx</math> 1–1.5 h net hot-water contact)</li> </ul>	<ul style="list-style-type: none"> <li>No organic solvents; good fit to kraft / biorefinery sites that already use high-pressure steam</li> <li>Higher energy intensity than atmospheric hot water; more complex equipment</li> <li>Attractive when both sugar-rich and tannin-rich streams can be valorised in an integrated bark biorefinery</li> </ul>	[31]
<b>Ethanol/water organosolv (40-70% EtOH)</b>	<ul style="list-style-type: none"> <li><b>Spruce bark (<i>Picea abies</i>):</b> 50 % EtOH/H<sub>2</sub>O at 100 °C gave <math>\approx</math> 14.8 wt% extract on bark</li> <li><b>Maritime/ Aleppo pine bark:</b> hydroethanolic Soxhlet extractions typically <math>\approx</math> 17–18 wt% extract on bark</li> </ul>	<ul style="list-style-type: none"> <li>For spruce (50 % EtOH/H<sub>2</sub>O, 100 °C): TPC <math>\approx</math> 325 mg GAE/g extract; tannin content (TTC) <math>\approx</math> 84 mg/g extract (<math>\approx</math> 8 wt%)</li> <li>For pine bark, hydroethanolic extracts show higher TPC and antioxidant activity than water or pure EtOH alone (e.g. <math>\approx</math> 73 mg GAE/g bark for hydroethanolic extract)</li> </ul>	<ul style="list-style-type: none"> <li>80–100°C; EtOH/H<sub>2</sub>O 40–70 vol%</li> <li>Batch or Soxhlet: typically 1–3 h; pilot-scale extraction of pine bark with 75 % EtOH shows good scale-up behaviour</li> </ul>	<ul style="list-style-type: none"> <li>EtOH is low-toxicity and easily recovered by distillation; solvent loops can be closed</li> <li>Organosolv tends to enrich phenolics relative to sugars, giving more phenolic-dense extracts than pure water while keeping conditions mild</li> <li>LCA for spruce bark phenolic extraction shows solvent recovery and heat integration are crucial for environmental performance</li> </ul>	[32], [33]

Extraction method	Indicative tannin yield (% of dry bark)	Purity / composition of extract	Typical conditions & extraction time	Environmental & scale aspects	Ref.
<b>Deep eutectic solvents (DES, typically choline chloride + organic acids / polyols)</b>	<ul style="list-style-type: none"> <li>For spruce bark, choline-chloride DES gave extraction yields <math>\approx</math> 11.4–27.7 wt% of bark</li> <li>DES + water systems for spruce: TPC equivalent to <math>\approx</math> 0.23–0.60 wt% gallic-acid equivalents per 100 g dry bark under mild conditions (2 h, 60°C)</li> </ul>	<ul style="list-style-type: none"> <li>DES extracts can have TPC from <math>\approx</math> 41–463 mg GAE/100 g extract (Skulcová et al.) or 233.6–596.2 mg GAE/100 g bark (Jablonský et al.)</li> <li>Composition strongly depends on hydrogen-bond donor; extracts contain condensed tannins plus other phenolics and some carbohydrates</li> </ul>	<ul style="list-style-type: none"> <li>Typical lab conditions: 60°C; 1–2 h; solid:liquid <math>\approx</math> 1:20 (w/w)</li> <li>Highly viscous solvents; agitation and mixing important for mass transfer</li> </ul>	<ul style="list-style-type: none"> <li>DES are often biodegradable and non-volatile; can operate at relatively low T and ambient pressure</li> <li>Recovery / recycling of DES is still a major technical and economic challenge; viscosity and dilution make downstream separation energy-intensive</li> <li>Attractive for “green chemistry” niches and selective phenolic fractionation, but industrial experience with bark tannins is still early-stage</li> </ul>	[34], [35], [36]
<b>Supercritical CO<sub>2</sub> (SFE, often with ethanol co-solvent)</b>	<ul style="list-style-type: none"> <li>For bark/wood phenolics in general, SFE typically recovers low overall mass (<math>\approx</math> 0.5–3 wt% of dry biomass; somewhat higher with co-solvent) but can enrich low-molecular-weight flavan-3-ols and lipophilic phenolics</li> <li>On spruce/pine bark, SFE yields of tannin-rich fractions are usually below those from aqueous or hydroethanolic extraction</li> </ul>	<ul style="list-style-type: none"> <li>Extracts are relatively phenolic-rich and carbohydrate-poor because hydrophilic sugars and most hemicelluloses are not co-extracted</li> <li>Fractionation strategies (pressure, temperature, co-solvent gradients) can separate resinous/lipophilic components from more polar flavonoid-type tannins</li> </ul>	<ul style="list-style-type: none"> <li>Typical: 30–35 MPa, 40–60°C; 1–3 h contact time</li> <li>Often uses 5–15 vol% ethanol as co-solvent to increase solubility of proanthocyanidins and polar phenolics</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> is non-toxic, non-flammable and easily removed; no solvent residues in extract</li> <li>However, equipment is capital-intensive; energy needed for gas compression and circulation is high</li> <li>Given lower yields vs. water/EtOH, SFE is currently uneconomical for bulk tannin production (e.g. water-treatment coagulants) but attractive for small-volume, high-purity nutraceutical / cosmetic fractions</li> </ul>	[37], [38]

In summary, a combination of conventional and innovative extraction techniques is available for conifer tannins. The optimal choice often depends on the intended application of the tannin (e.g. food-grade requires food-safe solvents like water/ethanol or CO<sub>2</sub>; industrial adhesive might tolerate stronger chemicals), and on economic considerations. Many recent studies aim to maximize use of green solvents and energy-efficient processes to align tannin extraction with sustainability goals, as discussed further.

## 2.4 Yield and quality comparison

Different conifer species and extraction methods produce tannin extracts with varying yields and quality. Here we present a comparative overview, including quantitative data from recent studies, to illustrate how pine, spruce, fir, and cedar rank in tannin yield and what quality indicators are used for their extracts.

**Yield comparison among species:** yields are typically reported as the percentage of oven-dry biomass that is extracted (yield %), and often the total phenolic content (TPC) or “tannin content” of that extract is measured to gauge quality. Recent literature provides benchmarks for bark tannin yields:

**Spruce vs. pine:** in a 2024 review of bark phytochemicals, Norway spruce (*P. abies*) generally showed higher extractable yields than Scots pine (*P. sylvestris*) under similar conditions [11]. For example, using a 50:50 ethanol-water solvent at near boiling, **spruce bark** yielded around 12–16% extract, whereas **pine bark** was slightly lower (around 8–12%) under identical extraction time. However, pine extracts often had a higher concentration of polyphenols within that extract. In one study, maritime pine bark gave ~18% yield with ~75% of that extract being tannins, while spruce gave ~16% yield with ~50–60% tannins [10], [14]. The **net tannin output** (mass of tannin per mass of bark) can thus be comparable. Notably, under optimized conditions (ASE with hot water), Norway spruce bark yielded up to 35.7% extract, which is exceptionally high – this included a lot of non-tannin polyphenols (stilbenes, sugars). In contrast, pine bark typically maxes out around 20% yield even with vigorous conditions, as much of pine bark’s structure (e.g. suberin, lignin) is not soluble without harsher treatment.

**Fir and larch:** data on fir bark yields are slightly scarcer but indicate firs are on par with pines. For instance, *Abies alba* bark yielded ~15% with aqueous ethanol, and Chinese fir (*Cunninghamia*) about 10–12% with water vs ~20% with ethanol present, showing the influence of solvent [11]. An interesting case is European larch (*Larix decidua*), a deciduous conifer: different studies reported a wide range of TPC from 6 up to 145 mg GAE/g, corresponding to yields from a few percent up to ~26%, highly dependent on extraction parameters [11]. Larch bark may contain very reactive tannins but also is sensitive to extraction conditions (overheating drastically lowers yield and quality, as some larch tannins decompose at >50 °C) – a reminder that quality can suffer if extraction is too harsh.

**Cedar:** quantitative yield reports for cedar are not prominent in recent literature. From analogous sources, cedar (e.g. Atlas cedar) bark likely yields on the order of 5–10% extract with conventional extraction. A study on mixed softwood bark (including cedar) showed total phenolics around 40–60 mg GAE/g in extracts [39], which suggests moderate tannin content. **Western red cedar** bark is reported to yield lower tannin percentages compared to pine or hemlock bark, partly because a portion of its extractives are non-tannin (tropolones). Historically, cedar was less favored for leather tanning because of this lower yield and the presence of resinous components. Therefore, while cedar can be a source, its yield tends to be at the lower end among the conifers discussed.

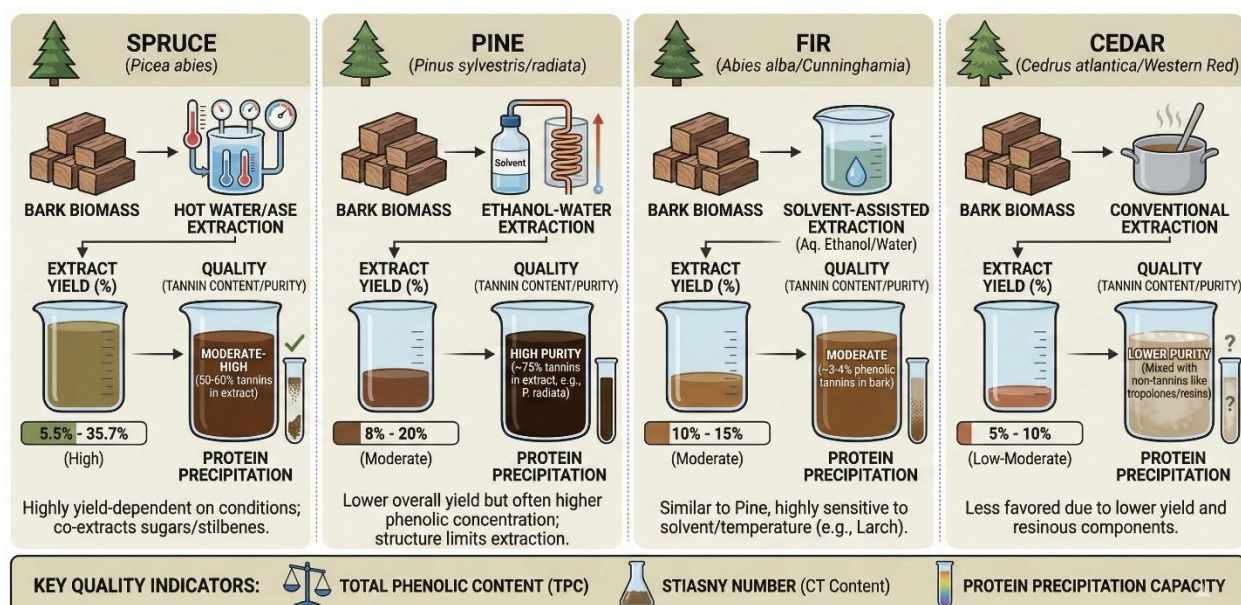


Figure 5. Conifer tannin yield and quality comparison by species and extraction methods.

Fig. 5 illustrates the comparative yield and quality benchmarks for tannin extraction across key conifer species, highlighting the fundamental trade-off between "crude mass" and "chemical purity." Norway Spruce (*P. abies*) is shown at the top of the yield hierarchy, capable of reaching exceptionally high extractive percentages (up to 35.7%), though often at the cost of higher sugar and hemicellulose dilution. In contrast, Scots Pine (*P. sylvestris*) and Maritime Pine demonstrate a "quality over quantity" profile, typically yielding less total mass but a significantly higher concentration of pure condensed tannins within that fraction. The visualization also captures the moderate standing of Fir and Larch, noting the latter's extreme sensitivity to temperature, while Cedar occupies the lower end of the spectrum due to its higher content of non-tannin extractives like tropolones. This ranking serves as a strategic guide for industrial selection, where the choice of species depends on whether the goal is maximizing raw biomass throughput or obtaining a high-potency phenolic extract.

Table 2.4. Indicative bark extract yields and tannin contents for selected conifers.

Species (bark)	Example extraction conditions (lab scale)	Indicative extract yield (% of dry bark)	Approx. tannins/phenolics in bark (% of dry bark)*	TPC / tannin quality indicators (extract)	Ref.
<i>Pinus radiata</i> (radiata pine)	Sequential solvent or hydro-ethanolic extraction of debarked bark (bench & pilot scale)	<ul style="list-style-type: none"> <li>• <b>CT-rich fraction:</b> <math>\approx 4.4\text{--}4.7\%</math> of dry bark (water-insoluble condensed tannins)</li> <li>• <b>Crude phenolic extract (EtOH/water):</b> typically <math>\approx 8\text{--}12\%</math> reported in bench/pilot studies (includes sugars + low-MW phenolics as well as CT)</li> </ul>	<ul style="list-style-type: none"> <li>• From CT fraction: <math>4.5\%</math> extract <math>\times \sim 76\%</math> CT <math>\rightarrow \approx 3\text{--}4\%</math> <b>actual condensed tannins in bark</b></li> <li>• Crude “tannin” content sometimes quoted higher (<math>\sim 7\text{--}8\%</math> on bark) when all polyphenols are counted, but this includes non-tannin phenolics.</li> </ul>	<ul style="list-style-type: none"> <li>• Water-insoluble CT fraction: <math>\sim 76\%</math> <b>tannins</b> (precipitation / CT assay) – a very high tannin purity compared with crude bark extracts</li> <li>• Total phenolics in crude radiata bark extracts often in the range <b>400–700 mg GAE /g extract</b>, depending on solvent and temperature (Folin–Ciocalteu).</li> </ul>	[40], [41]
<i>Picea abies</i> (Norway spruce)	Hot water extraction of debarked industrial bark; 60–100°C, atmospheric pressure (lab/pilot)	<ul style="list-style-type: none"> <li>• At 60°C hot water: <math>\approx 5.5\%</math> (54.5 g/kg dry bark) total extract <ul style="list-style-type: none"> <li>• Earlier boiling-water extractions: <math>\approx 11\%</math> (110 g/kg)</li> </ul> </li> <li>• Intensified/pressurized hot water at 90°C: up to <math>\approx 20\%</math> (205 g/kg) total extract under optimized conditions</li> </ul>	<ul style="list-style-type: none"> <li>• 60°C extract: 54.5 g/kg <math>\times</math> 34.2% phenolics <math>\approx 1.8\text{--}2\%</math> <b>phenolic “tannins” in bark</b> - Boiling-water data (<math>\approx 50\%</math> phenolics in 110 g/kg extract) give <math>\approx 5\text{--}6\%</math> <b>phenolic tannins in bark</b> under more severe conditions</li> <li>• 90°C high-yield extraction with <math>\approx 45\%</math> tannins gives <math>\approx 9\%</math> <b>condensed tannins in bark</b> (bench scale, acid-butanol assay).</li> </ul>	<ul style="list-style-type: none"> <li>• 60°C extracts show <b>phenolics <math>\approx 34\%</math> (as epicatechin equivalents)</b> of dry extract, i.e. <math>\approx 340</math> mg “ECE”/g</li> <li>• Pilot-scale spruce bark extracts tuned for adhesive use often report <b>Stiasny numbers in the 50–70 range</b>, reflecting a tannin-rich but carbohydrate-contaminated extract suitable for phenolic resins.</li> </ul>	[14]

Species (bark)	Example extraction conditions (lab scale)	Indicative extract yield (% of dry bark)	Approx. tannins/phenolics in bark (% of dry bark)*	TPC / tannin quality indicators (extract)	Ref.
<i>Abies alba</i> (silver fir)	Hot water extraction at 60°C on debarked stem bark (Northern–Central European material)	<ul style="list-style-type: none"> <li>60°C extraction: ≈12% (120.2 g/kg dry bark) total extract</li> <li>Other studies along the stem report roughly 9–17% phenolic-rich extractives depending on height and bark fraction (trunk vs branches).</li> </ul>	<ul style="list-style-type: none"> <li>120.2 g/kg × 27.9% phenolics ≈ 3–4% <b>phenolic “tannins” in bark</b></li> <li>Plant-physiology work on <i>A. alba</i> bark indicates that phenolic-rich extractives can reach 3–5% of bark DW, with substantial intra-tree variation.</li> </ul>	<ul style="list-style-type: none"> <li>Bianchi 2015: <b>phenolics ≈28% (ECE) of extract</b>, i.e. ≈280 mg “ECE” /g.</li> <li>Dedicated silver-fir bark extract papers (e.g. antioxidant studies) often report <b>TPC ~200–300 mg GAE /g extract</b>; Stiasny numbers are typically moderate (≈45–60), reflecting mixed tannin–carbohydrate composition.</li> </ul>	[14], [42]
<i>Cedrus atlantica</i> (Atlas cedar)	Typically: small-scale aqueous or hydro-ethanolic extraction of stem bark (pharmacological/antioxidant studies)	<ul style="list-style-type: none"> <li>Reported bark-extract yields are <b>moderate</b>, generally in the ≈5–10% range for aqueous / hydro-ethanolic systems (lab batch; values vary strongly with solvent and solid:liquid ratio).</li> <li>A working “example” value of ≈6% can be taken as mid-range for simple water or dilute-ethanol bark extraction, but published studies rarely aim at maximizing solids yield (they target bioactivity).</li> </ul>	<ul style="list-style-type: none"> <li>Detailed condensed-tannin quantification in bark is scarce; most studies report <b>total phenolics</b> rather than tannin-only.</li> <li>Based on typical conifer bark composition and reported TPC of <i>C. atlantica</i> extracts, a reasonable order-of-magnitude is ≈2–4% <b>phenolic tannins in bark</b>, lower than optimized spruce-bark systems but comparable to many non-industrial conifers.</li> </ul>	Recent work on <i>C. atlantica</i> stem bark extracts reports TPC in the ballpark of 150–300 mg GAE /g extract and significant condensed-tannin contribution to bioactivity; however, Stiasny numbers are generally not reported because the focus is pharmacological, not adhesive.	[43]

\*“Tannins in bark” here means phenolic/tannin mass that is actually recovered into solution under the cited lab conditions, expressed back on a dry-bark basis. The true total tannin pool in the bark tissue can be considerably higher (a large fraction remains unextracted or tightly bound).

Table 2.4 shows that bark-extract yields and tannin contents vary widely with species and extraction severity: *Picea abies* ranges from ~5.5% (60°C) to ~20% (intensified hot water), implying ~2–9% phenolic tannins in bark, while *Abies alba* typically gives ~12% extract and ~3–4% phenolic tannins. *Pinus radiata* yields a smaller but very pure CT-rich fraction (~4.4–4.7% extract at ~76% CT, ~3–4% CT in bark) versus higher-yield crude extracts (~8–12%) that include non-tannin phenolics, and *Cedrus atlantica* is generally moderate (~5–10% yield; ~2–4% phenolic tannins) with tannin quality more often reported via TPC than Stiasny.

**Quality indicators:** quality of tannin extracts is crucial for applications.

**Total phenolic content (TPC):** usually measured by the Folin-Ciocalteu assay, reported in mg gallic acid equivalents (GAE) per g of extract or per g of original bark. A higher TPC means the extract is rich in polyphenols (tannins and related compounds). For example, a spruce bark extract might have TPC ~100 mg GAE/g (10% phenolics by weight of bark), whereas a very pure pine tannin extract can reach >150 mg GAE/g [9]. In practice, commercial tannin extracts (like quebracho or mimosa) often have 70–80% polyphenols; similarly, conifer extracts can be concentrated to that range by removing non-tannin components.

**Stiasny number:** this is a classical test specifically for condensed tannins, indicating the fraction of tannins that can form insoluble complexes with formaldehyde (a proxy for reactive polyphenol content). It's given as a percentage of the extract. Pine and spruce bark tannins often have Stiasny numbers in the 60–80% range [10], meaning a majority of the extract are indeed tannins capable of cross-linking (important for wood adhesive use). Lower Stiasny (e.g. <50%) would indicate either many non-tannins present or tannins that are partially degraded or too small to precipitate. In one study, pine bark extracts had Stiasny numbers around 70%, slightly higher than spruce extracts ~60%, reflecting that pine extract contained fewer sugars and more flavanol polymers.

**Tannin Structure (procyanidin/prodelphinidin ratio, molecular weight):** advanced analytical indicators include the average degree of polymerization of tannins and the proportion of different building blocks (e.g. procyanidins vs prodelphinidins – the latter have an extra hydroxyl, common in some fir/larch species). Generally, pine and spruce tannins are primarily procyanidin (catechin-based). The molecular size affects reactivity: very high molecular weight tannins may be less soluble or too viscous, whereas very low molecular weight ones (dimers, trimers) might not perform as well in tanning or adhesive contexts. Quality-wise, a balance is desired. Some reports note that **spruce bark tannins** tend to have slightly lower average molecular weight than Douglas fir and Loblolly pines tannins, which can make them more suitable for certain resin formulations (lower viscosity) but possibly slightly less effective in leather tanning on their own [44].

**Non-tannin content:** this includes sugars, gums, and inorganic matter. A quality extract for industrial use will have low non-tannin content (ash <3%, sugars minimal). Conifer extracts often contain residual polysaccharides from bark if water extraction is used. A purification step or using solvents can reduce this. As an example, **spruce bark extract** obtained by cold water may contain

20–30% glucose and other carbohydrates [14], whereas hot water or ethanol extracts dramatically lower the sugar fraction. High sugar content is undesirable as it can ferment or reduce the shelf stability of extract and doesn't contribute to tanning effect. Thus, the extraction method heavily influences quality. Green methods like DES might leave some solvent residue (which could act as a plasticizer or stabilizer, depending on context) – this is a new consideration for quality when comparing to traditional extracts that are essentially pure solids.

In comparing species quality, pine and fir bark extracts often show slightly higher purity in terms of tannin vs non-tannin, because their bark typically has lower soluble sugars than, say, spruce's inner bark (spruce accumulates starch seasonally). Spruce, however, yields unique stilbenes (astringin, piceid) which add antioxidant value – so if “quality” is defined as bioactive diversity (for nutraceuticals), spruce extracts might be valued. For leather tanning or wood adhesives, the key quality is high condensed tannin content and reactivity: by that metric, **pine and mimosa bark extracts** are comparable in performance, and spruce/fir extracts have also been shown to be viable with some formulation adjustments.

To summarize: **pine and spruce** are competitive in tannin yield (commonly 8–15% yields, up to ~20% in optimal conditions), with pine perhaps giving a slightly more concentrated tannin extract. **Fir** bark yields are in a similar range, and the limited data on **cedar** suggests lower yields. The quality in terms of tannin richness is generally high for all conifer extracts if proper extraction is done (Stiasny numbers ~60–75%). Differences in secondary components (stilbenes in spruce, resin acids in pine, etc.) can distinguish the extracts. These factors influence how industries might choose one over another – for instance, pine bark extract has been studied as a partial substitute for phenol in resins [9], capitalizing on its high flavanol content, whereas spruce bark extracts have been examined for antioxidant nutraceutical ingredients because of the presence of stilbenoids [13]. The next section will consider the sustainability of obtaining these tannins, which is an equally important part of the business case in modern bioresource utilization.

## 2.5 Environmental impact and sustainability

Harnessing tannins from conifer sources must be evaluated in light of environmental sustainability and responsible resource management. This section discusses the environmental impacts of harvesting conifer bark/wood for tannin extraction and how sustainability frameworks (like FSC and PEFC certification) mitigate these impacts and ensure long-term viability of the resource.

**Use of Forestry by-products:** one key advantage of conifer tannins is that they can be sourced from forestry residues. In commercial forestry, **bark** is a significant residue generated when logs are processed – bark can constitute about 10–20% of the tree's volume. Traditionally, this bark was often burned as low-grade fuel or disposed of. Extracting tannins gives it a higher-value use. From an environmental perspective, utilizing bark that is a by-product of timber harvesting means no additional trees are cut specifically for tannin production. For example, sawmills processing pine

or spruce can supply bark to tannin extraction facilities. This synergistic use improves the overall resource efficiency of forestry. It is important, however, to manage the logistics: bark left on forest floors can have ecological roles (nutrient cycling, habitat), so removing excessive amounts could have local impacts. In practice, tannin operations typically use bark that has already been removed in industrial yards, not bark peeled directly off standing trees (except historically, as noted with hemlock bark stripping in the 1800s which led to deforestation). Today's approach is generally to integrate with existing sustainable forestry operations.

Harvesting impact is only one dimension of sustainable tannin sourcing; storage of the bark after felling is equally critical for both yield and environmental performance. If bark or wood were to be harvested solely for tannins, that could incentivize cutting of trees or stripping bark from live trees – both environmentally problematic. Therefore, sustainable tannin sourcing relies on felled trees from managed forests. Bark is best removed during wood processing; this avoids damage to standing forests. Studies show that bark removal from live trees increases susceptibility to pests and disease and is not recommended except for cork oak (a special case not related to tannins) [45]. Thus, conifer tannin producers ensure that raw material comes from already felled logs. In regions like Northern Europe or Canada, where large volumes of spruce/pine are harvested for lumber and pulp, even a fraction of bark diverted to tannin extraction can support a sizable tannin industry without extra felling. This model exemplifies a cascading use of biomass: wood for lumber/paper, bark for tannins/chemicals, and remaining residues for energy.

However, storage strongly determines how much of the tannin potential is actually recoverable from this bark side stream. Norway spruce bark is rich in hydrophilic extractives – condensed tannins, stilbenes and other phenolics – that are chemically and biologically labile. Long-term storage in industrial conditions (bark piles, exposed to rain and warm temperatures) causes rapid loss and transformation of these compounds through leaching, microbial degradation, oxidation and photodegradation. Early technical work by Lappi *et al.* documented substantial decreases in bark extractives over a 24-week storage period, with hydrophilic fractions being particularly affected, and emphasized that bark intended for extraction should be processed as soon as possible after debarking, especially during the warm season [46].

More detailed quantitative data for Norway spruce have been provided by Jyske *et al.*, who followed the fate of tannins and stilbenes in bark attached to sawlogs stored outdoors for six months. After 24 weeks, only about 5–7% of the original stilbene content and roughly 30–50% of the original condensed tannin content remained, and the average antioxidative capacity of bark extracts had fallen to around 27% of the initial level. Summer storage led to substantially faster degradation than winter storage, and outer bark deteriorated earlier than inner bark. On this basis, Jyske *et al.* concluded that intact bark on logs preserves polyphenols markedly better than debarked bark stored in piles, and explicitly recommended avoiding debarking before storage when bark is to be used for high-value extractives [47].

Complementary pile-storage experiments with debarked Norway spruce bark by Routa *et al.* underline how quickly losses occur once bark is piled. In large industrial bark piles, internal temperatures exceeded 50°C within one to two weeks, dry matter losses averaged about 6% per month, and acetone-soluble extractives fell to roughly 66% of their original amount after only eight weeks of storage, with approximately 30% of extractives lost in the first two weeks alone [48]. These losses are concentrated in the hydrophilic phenolic fraction that includes tannins, meaning that every month of uncontrolled pile storage directly erodes the tannin yield per tonne of bark. Later synthesis of storage studies for conifer bark has therefore adopted a simple rule of thumb: bark should be processed or extracted as soon as possible after debarking, and long, warm-season storage – especially in finely chipped piles exposed to rain – should be avoided if the goal is to recover tannins and other polyphenols rather than only energy.

From a tannin-producer's perspective, these results imply that feedstock logistics can be as decisive as forest management in determining process feasibility. In a cascading use model, spruce logs can be stored with bark intact, with debarking and extraction scheduled as close as possible to the extraction step, ideally in cooler seasons or under covered, controlled conditions. If bark must be stockpiled, minimizing residence time (especially the first 4–8 weeks when degradation is most intense), limiting pile temperatures, and reducing exposure to rainfall become key design parameters. Otherwise, even though bark is sourced sustainably from existing forest harvests, the effective tannin yield per unit of harvested biomass may be reduced by half or more before extraction begins, undermining both the economics and the resource-efficiency rationale of a bark-based tannin industry in spruce-rich regions such as the Baltics and Scandinavia.

**Energy and emissions:** the extraction process itself has an environmental footprint – boiling tanks or drying extracts consume energy (often derived from burning wood waste, which does emit CO<sub>2</sub> but is considered biogenic carbon). Modern extraction methods can lower energy use; for instance, using solar or waste heat to warm extraction tanks, or employing efficient presses. **Green extraction technologies** like supercritical CO<sub>2</sub> and DES, as discussed, avoid harmful solvents but may require more electricity (pressurization) or generate a difficult-to-treat effluent (in case of DES carryover). A life-cycle assessment would consider these trade-offs. Generally, water/ethanol extraction of bark has a relatively low impact, especially if waste biomass (e.g. sawdust, spent bark) is used to fuel the process. Water effluents containing organic matter from extraction need treatment – fortunately, tannins are biodegradable, but high concentrations can be toxic to aquatic life (due to oxygen depletion or direct toxicity). Effluent management (through biological treatment or recycling of water) is thus part of a sustainable tannin operation.

**Carbon footprint consideration:** using plant tannins in place of petrochemicals (e.g. replacing phenol in resins or chromium in leather tanning) can reduce the carbon footprint of those industries. Conifer tannins are renewable and can store atmospheric carbon in end products (like wood composites) for some time. However, the transport of bulky bark and the drying of extract are energy-intensive steps that need optimization to ensure the carbon gains are realized. Decentralized

extraction (near the source of bark) can minimize transport emissions, and using bark-derived energy can make the process nearly self-sufficient in thermal energy. In sum, when done thoughtfully, extracting tannins from conifer bark can be a **carbon-efficient practice**, especially compared to leaving bark to decompose (releasing CO<sub>2</sub>/CH<sub>4</sub>) or burning it outright.

**Forest stewardship and certification:** schemes like the **Forest stewardship council (FSC)** [49] and the **Programme for the endorsement of forest certification (PEFC)** [50] play a significant role in promoting sustainable sourcing of wood and bark. These certifications set strict standards for forest management, including maintaining biodiversity, preventing illegal logging, and ensuring regeneration of forests. When bark is sourced from an FSC-certified forest, stakeholders can be confident that the tree harvesting was done sustainably (e.g. not overcutting, protecting high conservation value areas, respecting indigenous rights). FSC and PEFC also encompass **chain-of-custody certification**, which can extend to products like tannin extracts – meaning a tannin product could be certified as coming from responsibly managed forests. This can be a market advantage, as buyers (e.g. eco-conscious leather producers or adhesive manufacturers) may prefer certified sustainable inputs.

In practical terms, large forestry companies that supply pine or spruce bark to tannin processors often have FSC or PEFC certification for their timber. For example, in Scandinavia and Canada, where spruce/pine bark extraction is being considered, forestry operations are predominantly certified. This ensures that tannin production does not drive unsustainable harvesting. Additionally, certification standards encourage using as much of the tree as possible (integral utilization), which tannin extraction exemplifies. Both FSC and PEFC have criteria related to non-timber forest products and ecosystem impact; removing bark is acceptable under these schemes as long as it's part of the normal harvesting process and does not harm soil or regeneration (some bark left in the forest can be beneficial, so balance is key).

**Ecosystem considerations:** harvesting conifer bark, if done as a by-product, has minimal direct impact on forest ecosystems compared to harvesting timber itself. One area of note is that bark contains nutrients (potassium, calcium) that normally return to the soil if left to decompose. Continuous removal of all bark could gradually deplete site nutrients. Sustainable practice may therefore involve leaving a portion of bark or wood residues on site or compensating via soil amendments in plantations. This is analogous to how whole-tree harvesting for bioenergy can impact soil fertility [51]. Certification schemes and forestry guidelines increasingly recognize this; for instance, recommendations might suggest leaving some slash (branches, bark) especially in nutrient-poor sites. In a tannin supply context, companies can coordinate with foresters to ensure that bark removal does not exceed what is environmentally sound for that site.

**Chemical use and worker safety:** traditional tannin extraction uses water and sometimes benign chemicals; however, if solvents are used (e.g. ethanol) or chemical modifications (like sulfiting of tannins), care must be taken to prevent negative environmental and health effects. Modern green

chemistry approaches (supercritical CO<sub>2</sub>, DES, etc.) aim to minimize hazardous chemicals. Workers in bark processing facilities should be protected from dust (bark dust can contain fungi spores) and excessive noise/heat from extraction equipment. These operational considerations are part of the social sustainability (often covered under certification or ISO process standards for manufacturing).

**End-of-life and toxicity:** tannins are natural and generally have low toxicity. Any effluent from the process can be treated biologically; spent bark (after extraction) is usually a fibrous material that can be used as boiler fuel or even as mulch. There is little in the way of hazardous waste compared to petrochemical resin production [52]. One environmental concern could be if large amounts of tannin-rich water enter streams, it might chelate metals or affect aquatic organisms. Thus, containment and proper waste management are implemented (usually not releasing strong tannin liquor into waterways without treatment). Encouragingly, tannin production can be seen as an **environmentally friendly industry** when compared with many chemical processes, especially if it upcycles waste.

In conclusion, tannins from conifer sources can be produced sustainably by aligning with certified forestry and employing clean extraction methods. The **environmental impact** is mitigated by using residue biomass, avoiding additional deforestation, and following guidelines to protect forest ecosystems. FSC and PEFC certification of raw material assures stakeholders that the tannin supply chain meets high sustainability standards – a critical factor for market acceptance in today’s bio-based economy. Moreover, developing **green extraction technologies** further reduces the environmental footprint, making conifer tannins an even more attractive component of sustainable materials and chemicals. The overall theme is one of circular economy: converting what would be waste (bark) into valuable tannins, while maintaining forest health and contributing to renewable material flows.

## 3. Applications by Industry

Tannins are versatile polyphenols that find use across a spectrum of industries. Building on the broad market applications outlined earlier, this section delves into specific sectors, highlighting both traditional uses and modern innovations. Each industry subsection covers historical context, the advantages of plant-based tannins, current market trends, and regulatory factors shaping tannin utilization.

### 3.1 Leather industry

The leather industry is the oldest and still the largest consumer of tannins. Tannins are indispensable in converting animal hides into leather, a process known as tanning (the very term “tannin” originates from this application). This sector illustrates the evolution from ancient practices to modern industrial processes.

#### *3.1.1 Historical and modern tanning processes*

For millennia, leather was produced by **vegetable tanning** – soaking hides in water with tannin-rich barks or woods [53]. Early methods were laborious: hides spent up to a year in pits layered with oak or chestnut bark to slowly absorb plant tannins. In the mid-19th century, technology advanced in Lyon (France) by using concentrated plant extracts, cutting tanning time from about 12 months to 28 days. This innovation spurred a boom in tannin extraction, with factories sourcing botanical tannins worldwide (e.g. quebracho wood from South America, mimosa bark from Africa) to supply Europe and North America. By the early 20th century, vegetable tanning had become a global industry, supporting the mass production of leather goods [53].

The late 19th century introduced **chromium tanning**, a chemical process that revolutionized leather manufacturing. Using chromium<sup>(III)</sup> salts, this method could tan hides in a matter of hours to days, producing a softer, stretchier leather suitable for finer applications like apparel. Chrome tanning quickly became dominant, and today the **majority of the world’s leather is chrome-tanned**, whereas plant-based tanning is often reserved for heavy leathers (e.g. saddlery, soles) or premium artisanal products. Modern tanneries sometimes combine techniques (e.g. “combination tanning” using both chromium and vegetable tannins) to leverage the benefits of each. Despite chrome tanning’s prevalence, the **vegetable tanning tradition persists**, bolstered by improved formulations (e.g. adding oils to produce more supple leather) and growing niche demand. In summary, leather tanning has evolved from year-long bark soaks to rapid mineral processes, with contemporary industry balancing speed, quality, and sustainability.

### 3.1.2 Advantages of plant-based tannins

Plant-based (vegetable) tannins offer several advantages in leather processing, especially as sustainability becomes a priority:

- **Renewable and natural:** unlike chromium salts derived from mining, plant tannins come from renewable sources (bark, wood, pods). They align with a bio-based economy and can utilize agro-forestry byproducts (e.g. chestnut or quebracho wood) [54]. This reduces waste and carbon footprint.
- **Lower toxicity and waste impact:** vegetable tanning avoids the heavy metal residues associated with chrome. Spent vegetable tanning liquor, while high in organic load, lacks toxic metals and can be treated biologically or used as compost after appropriate processing. Concerns over the toxicity of chromium (especially the carcinogenic hexavalent form) have spurred renewed interest in plant tannins as safer alternatives.
- **High-quality, niche aesthetics:** leather tanned with plant extracts is prized for its rich, natural hues (warm browns) and its patina – it ages gracefully, developing character over time. It tends to be firmer, which is ideal for luxury leather goods that demand structure (belts, wallets, antique-style upholstery) [25]. These unique aesthetics and tactile qualities allow vegetable-tanned leathers to command a premium in certain markets.
- **Regulatory and allergen benefits:** plant-tanned leathers are free of chromium, benefiting consumers who may have chromium allergies (chrome-tanned leather can sometimes contain trace Cr (VI) if not properly managed) [55]. This makes vegetable-tanned leather attractive for products like watch straps or children's shoes where skin contact sensitivities and safety standards are crucial.

In essence, while chrome tanning often yields more pliable leather for mass fashion, plant tannins provide an eco-friendly edge and artisanal quality that align with sustainability and heritage craftsmanship trends. Many high-end brands now highlight “vegetable-tanned” labels to cater to eco-conscious consumers seeking natural, metal-free leather goods.

### 3.1.3 Market Demand and Trends

From a market perspective, the **plant-based tannin sector has grown steadily** between 2019 and 2025, with applications diversifying into leather tanning, food and beverage stabilization, nutraceuticals, adhesives, and biopolymers [56]. The tannin market was valued at approximately USD 2.47 billion in 2022, with a projected compound annual growth rate (CAGR) of around 5–6% through 2030 [56]. Europe remains the largest regional market, primarily driven by the wine and premium leather industries, while Asia-Pacific, led by China and India, represents the fastest-

growing consumption hub. Industrial interest in tannins is further stimulated by tightening environmental regulations (e.g., REACH in the EU), favoring natural over synthetic chemicals.

The leather sector remains the **largest market for tannins**, accounting for about *62% of tannin demand in 2022* [56]. Global leather production has been buoyed by rising disposable incomes and diverse end-uses - from footwear and automotive upholstery to luxury handbags and furniture. The durability and prestige of leather drive ongoing demand: for example, automotive and furniture industries favor leather for its longevity and comfort, and consumers in emerging economies are buying more leather goods as spending power increases. This translates into robust consumption of tannins for tanning processes worldwide [57].

However, market trends are complex. **Regional shifts** are notable: Europe remains a major leather producer [58] (e.g. **Germany hosts 100+ tanneries and is among Europe's top producers** [59]), but much growth is occurring in Asia. The Asia-Pacific region is expected to see the fastest growth in tannin demand (projected  $\sim 7.5\%$  CAGR) thanks to expanding leather manufacturing in countries like China and India. These countries benefit from cost advantages and growing local markets for leather products. In contrast, traditional hubs in North America and Australia have seen **declines in leather processing** - partly due to consumer shifts toward synthetic or “vegan” leather alternatives and rising compliance costs [60]. For instance, the U.S. tanning industry has contracted as some manufacturers and consumers pivot to non-animal materials [61]. Similarly, Australian leather exports have slowed, with increased costs and a vegan lifestyle trend reducing rawhide processing domestically [62].

Despite competition from synthetics, the global leather market is still valued in the tens of billions USD and expected to grow, albeit modestly. There is a bifurcation in consumer behavior: luxury and heritage brands fuel demand for genuine leather (often emphasizing vegetable tanning and craftsmanship), whereas some mass-market segments experiment with synthetic leathers for cost or ethical reasons. This dynamic influences tannin usage - high-end leather goods sustain the need for plant tannins, while overall volume is still dominated by conventional chrome processes.

In tanning, another trend is technological innovation to improve sustainability [63]. Tanners are investing in R&D to reclaim or recycle spent tanning liquids [64], reduce water usage, and explore hybrid tannage. Several companies are trialing “**chrome-free**” **tannages** (using aldehyde or plant-based systems) [65] to produce “metal-free” leather that meets stringent environmental standards. As these green technologies develop, they could modestly increase the share of plant-derived tannins used in the industry. Notably, wood adhesives [66] and other material applications of tannins are growing faster in percentage terms, but leather will remain a key driver for tannin demand in absolute volume for the foreseeable future.

### 3.1.4 Regulatory environment

Environmental and safety regulations have a significant impact on the leather tanning industry, thereby influencing tannin usage. **Chromium regulation** is paramount: in the EU, REACH regulations tightly restrict hexavalent chromium (Cr(VI)) in consumer products, effectively mandating that tanneries manage chromium so it remains in the safer trivalent state and limiting residual Cr(VI) to very low levels [67] (typically <3 ppm in leather goods). These rules, along with strict effluent discharge standards, put pressure on tanneries to adopt cleaner practices or seek alternatives. The “*real or perceived toxicity*” of chromium has indeed driven research into alternative tanning agents, including enhanced vegetable tannin formulations and synthetic polymer tannages, to meet regulatory demands and public expectations.

**Waste management and pollution control** laws also favor plant-based tannins [68]. Tannery wastewater containing chromium and sulfides requires costly treatment; many countries mandate heavy-metal removal and safe sludge disposal. Plant tannin effluents, while still requiring treatment (due to high organic content and phenolics), do not carry the long-term toxicity of heavy metals. Regulatory frameworks in Europe encourage circular use of waste – an example being using spent vegetable tanning bark as biomass fuel or soil amendment, an approach aligned with EU waste directives and already implemented by some producers (Silvateam uses tannin extraction residues [69] to generate bioenergy). Such practices help tanneries comply with carbon emission goals and waste reduction targets.

Additionally, **occupational health standards** influence tannin choice. Chromium(VI) is a known carcinogen, so strict workplace exposure limits exist for tanneries. In jurisdictions with aggressive enforcement, some smaller tanneries have opted to switch partially back to vegetable tanning or chromium-free tanning to reduce regulatory burdens [70]. Trade regulations can play a role too: for example, export markets (EU, US) might reject leather goods if they exceed chemical limits, indirectly encouraging global suppliers to adhere to those standards (favoring cleaner tanning processes universally).

Lastly, **industry certifications and consumer pressure** act as quasi-regulatory forces. Initiatives like the Leather Working Group (LWG) [71] audit and rate tanneries on environmental performance. High ratings often require minimizing chrome impact or having modern waste treatment – prompting many tanneries to integrate vegetable tannins or innovative low-impact methods. In summary, regulations increasingly align with the strengths of plant-based tannins (renewable, less toxic) and push the leather industry toward more sustainable practices, even as compliance remains a challenge for this traditional sector.

## 3.2 Food and beverage industry

Beyond leather, tannins have a prominent presence in foods and beverages, where they contribute to flavor, color, and preservation. In this industry, tannins are both naturally occurring components and added ingredients. We examine their role in specific beverages like wine, beer, and juices, as well as emerging uses in functional foods and nutraceuticals, alongside market trends.

### *3.2.1 Tannins in winemaking, beer brewing, and juices*

In alcoholic beverages, tannins are key to defining sensory profiles. **Winemaking** is a classic example: grape tannins (largely condensed tannins from skins, seeds, and stems) impart structure, astringency, and aging potential to wine. During red wine fermentation, tannins are extracted into the wine, where they bind with anthocyanin pigments to stabilize color [72] and contribute to mouthfeel. As wine ages, tannins gradually polymerize and soften, which is why fine red wines become less astringent and more complex over years. Oenologists sometimes supplement wines with tannin extracts (from oak gall, chestnut, or grape seeds) to enhance a wine's balance, especially if the natural tannin content is low. These added enological tannins help stabilize color in red wines and even white wines (small tannin additions can prevent premature oxidation). Consumer perception ties tannins to quality: aged, tannin-rich wines are viewed as premium products, and many wine consumers associate robust tannic structure with sophistication [73]. Europe, with its deep wine culture, consequently has a high demand for tannins – not only intrinsic grape tannins but also commercial tannin additives to fine-tune wines. France, for instance, as a top wine producer, utilizes substantial tannin resources in its vineyards and wineries.

In **beer brewing**, tannins play a more nuanced role [74]. Barley malt and hops both contain tannins (polyphenols) that can leach into beer. In moderate amounts, these tannins contribute to the mouthfeel and complexity of certain beer styles (they can lend a slight astringency that balances malt sweetness, especially in some ales or stouts). However, excessive tannins in beer are usually undesirable; they complex with proteins causing haziness (the so-called chill haze) and can impart harsh bitterness. Brewers carefully manage their mashing and lautering process to avoid over-extracting tannins from grain husks [75] (keeping mash pH in check and not over-sparging are standard practices to control tannin extraction). Hops tannins, on the other hand, can aid in beer stabilization by precipitating proteins. While brewers generally do not *add* tannins externally, they sometimes use clarifying agents that remove excess tannins and proteins, yielding a clearer, more stable brew. In summary, tannins in beer must be balanced – they are a natural part of the brew from malt and hops, subtle in flavor contribution, but significant in physical stability of the final product.

In **juices and other beverages**, tannins also make their mark. Many fruit juices (especially from berries, pomegranate, apples, and grape juice) contain tannins that affect taste [76]. Apple juice, for example, gets some astringency from tannins in apple skins and seeds; cider makers pay

attention to tannin levels as they influence mouthfeel and clarifyability of the cider. Tannins in juices can act as natural antioxidants, helping preserve color and flavor during storage. However, if a juice is too tannic, it may taste overly astringent or bitter to consumers. Thus, juice processors sometimes remove tannins through fining (adding gelatin or plant protein to bind and precipitate tannins) to achieve a smoother taste, particularly in products like clear apple or white grape juice. On the other hand, **tea and coffee**, while not “juices,” are important beverages where tannins (or tannin-like polyphenols) are central: tea gets its astringency from catechins and theaflavins (often generically called “tannins”), and coffee’s slight bitterness is partly from chlorogenic acids (polyphenols) [77]. These drinks highlight how tannins influence beverage flavor profiles – from the puckering effect of a strong black tea to the drying sensation of a heavy red wine.

Overall, tannins are pivotal in beverages for **flavor and stability**. They can stabilize color and act as natural antioxidants in wine and juice, and in moderate amounts provide desirable astringency that defines traditional tastes. Producers manage tannin levels carefully: winemakers might blend wines or use oak barrels (which impart tannins) to reach the desired profile, while brewers and juice makers often fine-tune processes to avoid tannin excess. The result is a wide array of tannin expressions – from the bold tannic bite of a young Cabernet Sauvignon to the gentle, refreshing astringency of iced tea.

### *3.2.2 Functional foods and nutraceutical applications*

Beyond taste and color, tannins have attracted attention for their **health benefits**, fueling their use in functional foods and nutraceuticals. Tannins are a subset of polyphenols, many of which are known for antioxidant activity and potential protective effects against chronic diseases. As consumer interest in “food as medicine” grows, tannin-rich extracts are making their way into supplements and fortified foods.

A prominent example is **green tea extract**, rich in catechin tannins like EGCG (epigallocatechin gallate). Green tea extracts are sold as nutraceuticals for supporting metabolism, cardiovascular health, and cancer prevention. EGCG, a well-studied tannin, exhibits strong antioxidant and anti-inflammatory properties; it’s thought to help reduce inflammation and even combat certain cancers and heart disease [78]. Functional beverages like antioxidant teas, matcha drinks, or kombuchas leverage these tannins as a selling point to health-conscious consumers. Similarly, grape seed extract - a preparation high in proanthocyanidin tannins - is marketed for its beneficial effects on vascular health and skin aging. Clinical and mechanistic research supports its antioxidant, anti-inflammatory, and endothelial-protective actions, and recent human trials demonstrate measurable improvements in skin elasticity and oxidative resistance [79], [80], [81]. Another tannin-rich nutraceutical is **pycnogenol** (French maritime pine bark extract), comprised largely of procyanidins, which is used for its anti-inflammatory and circulatory benefits [82].

In the realm of **functional foods**, tannins often serve as natural preservatives or health-boosting ingredients. For instance, adding a berry extract (loaded with tannins and anthocyanins) to a beverage or yogurt can impart both color and antioxidant benefits. Certain protein bars or cereals include cocoa or tea extracts for polyphenol content. Because tannins can inhibit microbes, they are explored as natural food preservatives – e.g. incorporating tannic acid into edible films or coatings to extend shelf life by preventing bacterial growth. Tannins can also protect lipids in foods from oxidation (serving a similar role as synthetic antioxidants like BHA/BHT, but with a clean-label friendly name) [83], [84], [85].

**Market analysts consistently report strong growth in the nutraceutical and functional food sectors** - often at high single-digit CAGRs (e.g. 7-8.5% through the late 2020s) - driven by rising consumer demand for natural health-enhancing ingredients. Polyphenolic supplements, including tannin-rich extracts such as grape seed, green tea, and other fruit-sourced polyphenols, constitute a significant and rapidly expanding segment of this market (polyphenols market growth ~7.4% to 7.1% CAGR, grape seed ~44% share). Companies explicitly market tannin-based ingredients as “natural, fruit-derived, antioxidant-rich”, appealing to consumers seeking immunity or disease-prevention benefits. Functional beverages like red wine and pomegranate juice, promoted for cardioprotective polyphenols (tannins included), have contributed to increased interest and sales in functional drinks markets [86], [87], [88], [89], [90].

Consumer preferences in this area lean toward **trust in traditional remedies** as well. Many tannin-rich foods (green tea, cranberries, grape skins) have folkloric or epidemiological links to health benefits (like lower incidence of certain illnesses), which companies leverage in marketing. However, it’s also noted that excessive tannin intake can have downsides – very high levels may reduce nutrient absorption or cause digestive discomfort [91], [92], [93]. As a result, formulation is key: nutraceutical manufacturers calibrate doses to be beneficial but safe. Ongoing research, including clinical trials, continues to clarify the role of dietary tannins in health (discussed more in the pharmaceutical section) [94]. Overall, tannins occupy a dual role in foods: they are functional additives that improve shelf life and organoleptic properties, and they are bioactive compounds that enhance the health appeal of products in the booming functional food market.

### *3.2.3 Market analysis and consumer preferences*

The food and beverage sector’s use of tannins is closely tied to consumer tastes and global market trends. **Wine and premium beverages:** the global wine industry - valued at over USD 340 billion in 2023 and forecast to grow at ~4–6% annually into the 2030s - relies fundamentally on tannins for structure, aging, and sensory complexity in wines. Growth in regions like Asia-Pacific, notably China, where red wine demand among emerging middle classes is rising, indirectly boosts demand for cooperage oak and other tannin products. For example, China’s developing wine culture has led to interest in bold red wines, which in turn rely on good tannin management. Meanwhile, the craft beer movement increasingly employs barrel-aging techniques that extract wood tannins to

provide complexity in beer styles, further diversifying tannin demand beyond wine, catering to consumers seeking novel flavors [95], [96], [97], [98], [99], [100].

**Health-driven markets:** the global functional beverage market, which includes antioxidant-rich drinks like green tea, kombucha, and even moderate red wine, is expanding rapidly as consumers increasingly pivot toward health and wellness. Market research firms report the industry's value at approximately USD 150–260 billion in 2024, with projections reaching up to USD 248-466 billion by the late 2020s, implying CAGRs of ~6.5–8.9% (depending on the report and forecast period) [101]. Consumers clearly prefer clean-label, plant-derived ingredients: drinks fortified with grape seed extract, green tea extract, or other botanical antioxidants are favored over synthetic alternatives. The industry's "clean-label functional beverage ingredients" segment is projected to reach USD 15.8 billion in 2024, growing at a 9.0% CAGR through 2034 [102]. Within this broader product trend, antioxidants are a dominant ingredient class, accounting for around 27.3% of functional beverage formulations in recent reports [103].

**Taste and preference diversity:** tannins also illustrate how consumer preferences can diverge. In wines, some consumers enjoy the drying, astringent feel of a young red wine, while others prefer smoother, low-tannin varieties or heavily aged vintages where tannins have mellowed. Winemakers thus tailor styles (and use of tannin additives) to target demographics – e.g., a trend to produce "earlier drinking" reds might involve managing extraction to keep tannins soft. In tea, Western consumers often add milk or sugar to counter tannin astringency in black tea, whereas many Asian consumers appreciate the briskness of a tannin-rich brew straight. Such differences influence how products are formulated or marketed in different regions.

On the flip side, **bitterness aversion** leads some sectors to reduce tannin content. For instance, the juice industry found that removing tannins can make products more palatable to children (hence the popularity of clarified, low-tannin apple juice vs. tannin-rich cloudy cider). The beer industry's use of PVPP finings to strip polyphenols in light lagers is another case of tailoring to a preference for smooth, clear beer without the bitterness or haze tannins can cause [104], [105].

In summary, market analysis reveals that tannins in food and beverages are a double-edged sword: a key quality factor and health asset, but also a component to modulate carefully according to consumer preference. The current trend tilts toward emphasizing their **positive attributes** – leveraging their natural, healthful image in marketing, while technologists work behind the scenes to ensure the taste remains acceptable. As consumer education about polyphenols grows, tannins may increasingly become a selling point ("rich in antioxidants") for products, provided the flavor profiles are well-balanced.

### 3.3 Pharmaceutical industry

The pharmaceutical industry's interest in tannins stems from their wide-ranging biological activities. Tannins have long been used in traditional medicine for their astringent and antimicrobial properties, and modern science is validating some of these uses while exploring new therapeutic avenues. Tannins, particularly tannic acid and related gallotannins, have both established and emerging roles in the pharmaceutical domain. Historically, tannic acid formulations were used as topical astringents and burn treatments. In contemporary research, tannic acid is incorporated into nanoparticle-based drug-delivery systems under investigation for anticancer, anti-inflammatory, and antimicrobial therapies. Reviews note its use in clinical/preclinical studies of green tea and grape seed extracts, and its broader inclusion in pharmaceutical formulations across inflammation, wound care, and cardiovascular support [106], [107], [108].

#### 3.3.1 Therapeutic and medicinal applications

Historically, tannin-rich plant extracts have been used as remedies for ailments such as diarrhea, inflammation, and wound healing. Their ability to precipitate proteins underlies an **astringent effect** – they can constrict tissues and reduce secretions, which explains their traditional use to treat diarrhea or stop bleeding [109]. For example, oak bark (rich in hydrolyzable tannins) teas or powders were common in folk medicine to manage gastrointestinal issues and as topical antiseptics on wounds. Similarly, **witch hazel** extract (*Hamamelis*, high in tannins) has been used for centuries to soothe skin irritations, hemorrhoids, and minor bleeding by virtue of its astringency.

In modern medicinal products, tannins or tannin-derived compounds feature in several ways. One prominent success is **Crofelemer** (brand name Mytesi, formerly known as SP-303 or Provir) [110], an FDA-approved drug for managing HIV/AIDS-related chronic diarrhea. Crofelemer is a purified oligomeric proanthocyanidin (condensed tannin) derived from the sap of the *Croton lechleri* tree. It works by modulating chloride channels in the gut, reducing fluid loss, and exemplifies how a traditional remedy (the sap, known as “dragon’s blood,” was used for diarrhea by indigenous people) has been translated into a standardized pharmaceutical. Another area is **venotonic drugs** for chronic venous insufficiency: proprietary extracts like those from horse chestnut seed (rich in both saponins and tannins) or French oak wood are used in oral or topical medications to strengthen vein walls and reduce edema. Tannins’ protein-binding property likely helps reduce capillary permeability, alleviating swelling [111], [112], [113].

Tannins also find use as **antimicrobial agents** [114]. Their ability to inactivate viruses and bacteria by binding to surface proteins or enzymes has led to explorations in antiviral drugs. For instance, tannic acid and other gallotannins have shown activity against viruses like influenza and herpes in lab studies by blocking viral attachment or replication enzymes [106], [115]. While not yet a mainstream drug, such findings spur development of tannin-based virucidal gels or coatings.

Additionally, tannin-containing formulations are used in oral health (e.g. some mouthwashes or throat lozenges contain tannins for their anti-microbial and mucosa-tightening effect to soothe sore throats or gum inflammation).

In the realm of **dermatology**, tannins are utilized for treating skin conditions. Astringent powders or creams (often with tannic acid) are applied to treat conditions like oozing eczema or poison ivy rash, to dry out the affected area and provide relief [116]. Tannic acid has even been used in burn therapy in the past to form a protective scab, though that practice has waned due to mixed results[117]. Nonetheless, modern wound dressings sometimes incorporate plant extracts (some containing tannins) aiming to reduce infection and promote healing.

It's important to note that while many phytopharmaceutical products contain tannins, the efficacy can vary and is often still under investigation. The pharmaceutical industry tends to isolate active components, and tannins being large polyphenols present challenges – their complex structures can make it hard to pinpoint mechanisms, and their strong protein-binding can sometimes cause side effects (like constipation or reducing nutrient absorption). Still, the therapeutic potential of tannins, especially in an era searching for **natural product drugs**, is significant. They present a library of bioactive molecules that are being examined in conditions ranging from digestive disorders to cancers (e.g. ellagitannins from pomegranate are being researched for anti-tumor properties) [118]. A key theme in medicinal use is converting the broad-spectrum activity of tannins into targeted therapies with known dosing and safety profiles, as exemplified by turning “dragon’s blood” sap into Crofelemer tablets.

### *3.3.2 Antioxidant and anti-inflammatory properties*

One of the most celebrated properties of tannins is their role as antioxidants. Tannins can scavenge free radicals and chelate metal ions that catalyze oxidative reactions, thereby protecting cells from oxidative stress. This antioxidative power is linked to a variety of potential health benefits [119], particularly in preventing or mitigating chronic diseases such as cardiovascular disease, neurodegenerative disorders, and cancer. Many tannins (especially condensed tannins and gallotannins) have demonstrated the ability to inhibit lipid peroxidation – for example, tannins in green tea and grape seeds can prevent the oxidation of LDL cholesterol, a factor in atherosclerosis [120]. Such effects support the epidemiological observations that diets rich in polyphenols (red wine, tea, fruits) correlate with lower incidence of heart disease.

Tannins also exhibit **anti-inflammatory activity**, often tied to their antioxidant mechanism. By neutralizing reactive oxygen species, they indirectly reduce the activation of inflammatory pathways. Additionally, tannins can interact with cell signaling: studies have shown tannins can modulate key regulators like NF- $\kappa$ B and MAPKs, leading to decreased production of pro-inflammatory cytokines [121]. For instance, ellagic acid and EGCG have demonstrated the ability to down-regulate key inflammatory mediators in preclinical models of arthritis. Ellagic acid

suppresses NF- $\kappa$ B, TNF- $\alpha$ , IL-1 $\beta$ , and IL-6 in collagen- and adjuvant-induced arthritis models, while enhancing antioxidant markers and reducing RANKL levels [122], [123]. EGCG exhibits chondroprotective and immunomodulatory effects in animal models - ameliorating osteo- and rheumatoid-arthritis by reducing cartilage degradation enzymes (MMP-13, ADAMTS5), inflammatory cytokines (IL-6, TNF- $\alpha$ , IFN- $\gamma$ ), and regulating Th17/Treg balance via STAT3/HIF-1 $\alpha$  and Nrf-2/HO-1 signaling pathways [124], [125], [126]. Proanthocyanidins from pine bark (pycnogenol®) have undergone clinical studies demonstrating that it reduces inflammatory and oxidative markers in circulation and joints, with accompanying symptomatic relief in osteoarthritis. A topical patch study reported 64% reduction in inflammation and 66% reduction in swelling after 3 weeks, while an oral regimen significantly down-regulated cartilage-degrading enzymes and cytokines (MMP-3, MMP-13, IL-1 $\beta$ , ADAMTS-5) in osteoarthritis patients. Dose-dependent plasma antioxidant effects have been observed in healthy subjects, and meta-analyses show consistent anti-inflammatory and cardiovascular benefits across randomized controlled trials [127], [128], [129].

These properties have made tannins a focal point in developing **nutraceuticals and adjunct therapies** [130]. Supplements high in tannins are marketed for “anti-aging” or “cell protection.” In skincare (bridging pharma and cosmetics), tannin-rich extracts are applied topically to combat oxidative damage in the skin from UV radiation and pollution, thereby reducing wrinkles and inflammation (some cosmeceuticals with green tea or grape seed extract cite this mechanism). The anti-inflammatory effect also underpins the soothing action of tannin-containing creams on minor rashes or sunburn [131], [132], [133].

From a pharmaceutical research perspective, tannins’ antioxidant/anti-inflammatory profile is being harnessed in exploring treatments for metabolic syndrome and neuroprotection. For example, researchers are investigating whether tannin-rich diets or supplements can improve outcomes in diabetes by reducing inflammation in adipose tissue and the vascular system. Similarly, neuroprotective angles (as in Alzheimer’s or Parkinson’s disease) consider tannins for their potential to reduce neuronal oxidative damage [134], [135]. It should be noted that a challenge here is **bioavailability**: many tannins are large molecules that are poorly absorbed in the gut, or they may be metabolized by gut flora [136]. Scientists are thus looking at delivering tannins in more bioavailable forms or using gut microbiome products of tannins (like urolithins from ellagitannins) as the active agents [137].

In conclusion, the antioxidant and anti-inflammatory properties of tannins place them at the intersection of preventive medicine and therapeutic development. While they are not panacea, the evidence of their beneficial effects is substantial enough that tannins are key ingredients in many health supplements and are promising leads in drug discovery efforts targeting inflammation-driven diseases.

### 3.4 Water and wastewater treatment – a growth frontier for tannins

The water and wastewater sector represents one of the most promising new application domains for tannins, particularly for condensed, bark-derived tannins that can be cationised and used as coagulants. Global water-treatment practice remains dominated by inorganic salts such as aluminium sulfate, polyaluminium chloride (PAC) and ferric salts, complemented by synthetic organic polymers including polyDADMAC and polyacrylamides. These substances underpin a coagulant–flocculant market estimated at roughly 10–13 billion USD in 2023, with projected growth of about 3.8–6 % annually to around 2030–2033, depending on segment and region. Coagulants and flocculants together account for approximately 35–40 % of total water-treatment chemical sales, illustrating the scale of this market space.

Within this largely conservative sector, tannin-based coagulants (TBCs) currently occupy only a small share of volume, but are among the fastest growing families of “bio-coagulants”. This growth is driven by several converging pressures. First, utilities and industrial operators face mounting expectations to decarbonise and reduce dependence on mined metal salts and petrochemical polymers. Second, sludge management has become a central bottleneck: in many jurisdictions, regulatory limits on heavy metals, poorly degradable synthetic polymers and associated micro-pollutants in biosolids increasingly restrict land application and push up disposal costs. Third, circular-economy narratives encourage wastewater systems that generate sludges compatible with material recovery, composting or bioenergy, rather than permanent hazardous residues. In this context, plant-derived coagulants that yield low-metal, biodegradable sludge are gaining attention. Recent reviews and a SWOT analysis of TBCs conclude that the underlying technology is technically mature in several applications, but market penetration is still limited by pricing, path-dependency in plant operations and the need to further green the upstream extraction and cationisation processes.[138]

Most commercial TBCs are synthesised from condensed tannins (proanthocyanidins) extracted from bark, historically from *Acacia mearnsii* (mimosa), chestnut and quebracho, and more recently from other forest and agro-industrial residues. These tannins are typically converted into cationic polymers via Mannich-type reactions, introducing protonatable aminoalkyl substituents on the aromatic rings. The resulting polymers combine electrostatic charge neutralisation with polymer-bridging capacity, enabling effective destabilisation of negatively charged colloids, natural organic matter (NOM), dyes and microorganisms [138], [139]. Unlike classical alum or ferric salts, which have relatively narrow optimal pH windows and often require alkalinity correction, TBCs generally operate over a broader pH range (approximately pH 4–8) and have only a modest impact on treated water pH, which can reduce or eliminate the need for lime dosing [138], [140].

Chemically, the condensed tannins found in conifer bark, including spruce, pine and fir, are closely analogous to those used in existing TBC products, as described in the earlier sections on conifer tannin chemistry and extraction.

The structural differences between spruce bark tannins and more conventional mimosa or quebracho tannins lie mainly in average degree of polymerisation, substitution patterns and the presence of co-extractives such as stilbene glycosides (e.g. astringin, isorhapontin) in spruce. These factors influence reactivity during cationisation and the properties of the final TBC, but they do not represent a fundamental barrier: laboratory studies have shown that spruce-derived condensed tannins can be successfully aminomethylated to yield cationic coagulant prototypes with performance comparable to commercial bark-tannin coagulants. [138]

Systematic comparisons between TBCs and conventional coagulants indicate that, when properly formulated, TBCs can match or outperform alum and PAC in a wide range of matrix conditions. Hameed *et al.* evaluated a mimosa-based TBC in a municipal wastewater pilot plant and found turbidity and COD removals comparable to, or slightly better than, polyaluminium chloride at similar dosages (10-40 mg/L), while producing sludge with lower metal content [141]. Importantly, extended operation with the TBC as a pre-treatment to a biofilm reactor did not impair biological performance, indicating that residual tannins and their degradation products are compatible with conventional activated-sludge processes. In drinking-water applications, Schmitt *et al.* reported that two commercial bark-tannin polymers achieved up to ~90 % turbidity removal and ~86 % colour removal in Brazilian surface waters at doses of around 15 mg/L, with performance similar to aluminium sulfate but without elevating residual aluminium or significantly affecting pH [142].

Beyond removal of solids and colour, tannin coagulants can also play a role in pathogen and antibiotic-resistance control. In a comparative study on tertiary treatment of urban wastewater, Grehs *et al.* showed that both alum and a bark-tannin coagulant effectively reduced bacterial counts, but the tannin product achieved equal or superior removal of several antibiotic-resistance genes at comparable doses, while avoiding the introduction of metals into the sludge [143]. Field experience with commercial TBCs in domestic sewage polishing has also demonstrated significant reductions in thermotolerant coliforms, supporting the use of TBCs as part of a broader disinfection strategy.

Industrial effluents provide further evidence of TBC performance in more challenging matrices. TBCs have been tested in textile dyeing effluents, cassava processing water, landfill leachate and other strongly coloured waste streams, where they often achieve higher colour and COD removal than alum or ferric salts at equivalent or slightly lower doses [138], [139]. Neto *et al.* showed that a tannin-based coagulant applied to high-turbidity river water delivered robust clarification and generated sludge that met regulatory requirements for agricultural use, highlighting one of the strategic advantages of bio-based coagulants: the creation of organic, low-metal sludge more

amenable to land application or composting [144]. Meta-analyses across multiple case studies and reviews converge on the conclusion that TBCs regularly achieve >80–90 % turbidity removal, 50–80 % COD removal, and >80 % colour removal in suitable wastewaters, often with 30–60 % lower dry sludge production than conventional metal salts, though absolute performance is necessarily matrix- and formulation-dependent [138], [139], [140].

While coagulation–flocculation remains the principal use case for tannins in water treatment, the chemistry of tannins also lends itself to hybrid processes. Condensed tannins can be immobilised on solid supports such as silica, chitosan, activated carbon or polymeric beads to create selective adsorbents for metals (e.g. Cr(VI), Sb, U) and dyes [138], [140]. These materials can be integrated with TBCs in treatment trains, where a TBC performs bulk clarification and an immobilised tannin sorbent polishes residual contaminants or recovers valuable metals. From a business perspective, such hybrid systems expand tannins beyond the commodity-coagulant segment into higher-margin niche treatments, though likely with lower volumes.

### *3.4.1. Relevance to pulp and paper mill wastewater*

Pulp and paper (P&P) mills are especially interesting for tannin-based coagulants because they sit at the intersection of major water consumption, stringent effluent requirements and an abundant local supply of bark. P&P effluents are characterised by high suspended solids and fibres, substantial loads of dissolved and colloidal organics (lignin derivatives, resin acids, carbohydrates and other extractives), pronounced colour and, in some cases, adsorbable organic halides (AOX) originating from chlorinated bleaching. Kamali and Khodaparast’s comprehensive review of P&P wastewater underscores that, despite the prominence of biological treatments, coagulation–flocculation remains a critical step for colour and AOX removal and is often the limiting stage in achieving compliance with discharge limits [145].

From a conceptual standpoint, P&P wastewater and bark-derived tannins are well matched. The effluents already originate from lignocellulosic material and naturally contain phenolic species, including low levels of tannin-like compounds. Treating such streams with a coagulant derived from the same raw material family is chemically coherent and avoids introducing foreign metals or persistent synthetic polymers. Although the number of published full-scale case studies applying TBCs specifically to P&P effluents is still limited, several pieces of evidence support their feasibility. First, the successful use of TBCs in other highly coloured, aromatic-rich effluents (e.g. textile dye baths, leachates) suggests that the chromophoric lignin fragments in P&P effluents should be amenable to similar mechanisms of charge neutralisation and polymer-bridging [138], [139]. Second, experimental work on aminomethylated spruce-bark tannins has demonstrated coagulant activity comparable to commercial bark-tannin coagulants in model waters, confirming that Norway spruce tannins can be upgraded to functional TBCs. Third, the regulatory and market context of Nordic and Baltic P&P mills increasingly favours sludge streams that are compatible with circular-economy pathways such as composting, soil amendment or bioenergy. Aluminium-

and polymer-laden sludges complicate such uses, whereas tannin-based systems maintain a “forest-derived” organic character that is easier to integrate into forestry and agricultural cycles.

In an integrated Nordic kraft mill, several modes of process integration can be envisaged. One option is a fully on-site TBC plant in which debarking residues are diverted from the energy boiler to a dedicated extraction line. The tannin-rich extract, possibly concentrated and spray-dried, is then cationised on site and immediately used in primary clarifiers, dissolved-air flotation (DAF) systems or tertiary polishing units. This “closed-loop” configuration minimises logistics and maximises the narrative of a circular, self-sufficient mill. An alternative is a regional hub model, where a central tannin extraction and coagulant factory sources bark from several mills and sawmills within a reasonable radius and supplies TBCs to both industrial and municipal clients. A hybrid configuration is also plausible: mills might extract a spruce-tannin intermediate (e.g. a concentrated aqueous extract) in-house and ship this to a specialised chemical facility for cationisation and formulation, receiving finished TBCs back under long-term supply contracts [146].

Mass-balance considerations suggest that bark availability is not a limiting factor. A modern Nordic bleached kraft mill with a capacity of around 1 Mt/y of pulp typically generates approximately 100–150 kt/y of dry bark, depending on wood species and debarking practices. If spruce bark contains 10–15 % condensed tannins on a dry basis and extraction efficiency reaches 60–70 %, values consistent with previous sections of this report, the mill could produce on the order of 6–15 kt/y of tannin solids. This quantity is more than sufficient to cover its own coagulant demand, with potential surplus for neighbouring utilities or industrial sites. The fraction of bark diverted from energy generation would have to be optimised against the value of electricity and steam, but many mills already face constraints on bioenergy exports relative to material valorisation opportunities [147].

### 3.4.2. Large-scale feasibility and environmental performance

The large-scale feasibility of TBC production from bark has recently been addressed by life-cycle assessment (LCA) and techno-economic analysis (TEA). Simões *et al.* conducted an LCA for extraction of condensed tannins from Acacia bark specifically for TBC production [68]. Their system boundaries included bark transport and preparation, hot-water or water–ethanol extraction, filtration, purification via adsorption and spray drying. The study identified spray drying and solvent regeneration in purification as major environmental hotspots, primarily due to energy demand. Sensitivity analyses showed that reducing extraction water volumes, lowering final product moisture, and integrating low-carbon or waste heat sources can substantially improve environmental performance. When compared with alum and PAC production on a cradle-to-gate basis, TBCs generally exhibited lower global warming potential and toxicity indicators, particularly when sludge disposal and land-application impacts were included.

Complementary work by de Jesus *et al.* examined replacement of aluminium sulfate by a TBC in an oil-refinery water-treatment plant, combining process data with LCA and economic analysis [148]. The study found that, at equal treatment performance, the TBC reduced the environmental burdens associated with sludge disposal and, once co-benefits such as reduced pH correction and lower sludge volumes were accounted for, delivered a comparable or slightly lower cost per cubic metre of water treated, despite a higher cost per kilogram of coagulant. Together with the synthesis and scale-up studies reported for bark TBCs, which show that Mannich-type cationisation reactions can be reliably transferred from laboratory to larger reactors without loss of performance [149], these analyses suggest that the key constraints on TBC expansion are commercial rather than technical.

For spruce bark in the Baltic and Scandinavian context, the environmental picture is arguably even more favourable. Bark is already concentrated at sawmills and pulp mills, implying short transport distances and high logistical efficiency. Forestry in these regions is predominantly FSC/PEFC-certified, conferring a strong sustainability credential that can be leveraged in export markets and ESG narratives. Existing bark-fired boilers offer opportunities to integrate extraction and drying with waste-heat utilisation, partially offsetting the opportunity cost of diverting bark from combustion. At the same time, as noted in the earlier sections, bark is often oversupplied relative to local heat demand, making its conversion into higher-value chemicals an attractive bioeconomy strategy.

Taken together, the technical, environmental and feedstock conditions make large-scale production of spruce-derived TBCs for water and wastewater treatment a realistic prospect, provided suitable market entry strategies and demonstration projects are implemented.

## 4. Market trends and regional outlook

### 4.1 Global coagulant and flocculant markets: positioning tannins

The global coagulant/flocculant market forms the central arena into which TBCs must move if spruce bark tannins are to become a significant industrial product. Synthesizing recent market analyses, this combined market was valued at around 10–13 billion USD in 2023 and is projected to grow at roughly 3.8–6 % per year to 2028–2033, with some variation between municipal and industrial segments. Metal-based coagulants (alum, PAC, ferric salts) currently dominate by volume, accounting for approximately 60–70 % of coagulant use, while synthetic organic polymers represent roughly 25–35 %, mainly as flocculant aids. Natural and bio-based coagulants, including TBCs, chitosan and plant proteins, still make up less than 5 % of the market but typically exhibit the highest growth rates, with some estimates placing their compound annual growth at above 8 %.

End-use applications are split roughly half-and-half between municipal water/wastewater and industrial users, including P&P, mining, oil and gas, food and beverage, and textiles. Within this landscape, TBCs are especially competitive in scenarios where sludge management costs are high, where metal content in biosolids is tightly constrained, or where public-sector procurement criteria explicitly favour bio-based and low-toxicity chemicals. Scenario modelling in the LCA literature indicates that achieving even 1–3 % market share for TBCs by 2030 would require several hundred thousand tonnes per year of tannin solids, representing a sizeable new outlet for forest-derived tannins [138], [68]. For stakeholders in the Baltic–Scandinavian region, this implies that a relatively modest penetration of TBCs into European and global coagulant markets could already absorb the output of multiple spruce-bark extraction plants.

## 4.2. Regional perspectives

### 4.2.1. Europe

Europe is simultaneously the largest market for tannins by value, driven by wine, premium leather and specialised wood-adhesive sectors, and a regulatory frontrunner in promoting bio-based, low-impact chemistries.

Wastewater and sludge regulations in the EU, including restrictions on heavy metals, persistent polymers and micro-pollutants in biosolids, create a strong structural incentive to adopt alternatives to alum and polyacrylamide in both municipal and industrial treatment plants. Moreover, EU-level strategies on circular economy and the zero-pollution agenda increasingly emphasise nature-based solutions and the reduction of reliance on critical raw materials [150]. In this climate, TBCs can be framed not merely as niche green products but as enablers of compliant sludge valorisation and reduced dependence on imported aluminium and iron salts.

At the same time, European utilities and industrial operators are cautious adopters of novel chemistries, prioritising operational reliability and long-term supply contracts. Existing TBC deployments have been concentrated in Southern Europe and Latin America, while in Northern and Central Europe TBCs have so far been evaluated mostly in pilot and demonstration projects. For Baltic and Scandinavian producers, however, proximity to advanced water-treatment markets in the Nordic countries, Germany and the Benelux region, combined with ready access to FSC/PEFC-certified bark resources and a strong forest-bioeconomy narrative, provides a favourable context for introducing spruce-derived TBCs. The ability to market coagulants as “Nordic, forest-based, low-metal and circular” could be a differentiating factor, especially for municipal utilities and industrial clients seeking to improve ESG profiles [151].

#### 4.2.2. Asia–Pacific

Asia–Pacific is the largest and fastest-growing regional market for water-treatment chemicals, reflecting rapid urbanisation, industrialisation and persistent water-quality challenges in countries such as China, India and Indonesia [152], [153]. The region hosts substantial P&P, textile, mining and petrochemical industries, each generating significant volumes of wastewater in which coagulation–flocculation plays a central role. Despite this, the coagulant mix remains overwhelmingly dominated by low-cost inorganic salts sourced from domestic or regional suppliers, while synthetic polymers are widely used as flocculants [1].

Natural coagulants, including TBCs, are being explored in Asia–Pacific, particularly in niche segments such as eco-industrial parks, high-end food and beverage plants and demonstration “green city” projects [138]. However, adoption has so far been limited by cost sensitivity, lack of familiarity and the absence of strong regulatory drivers analogous to European sludge regulations [154]. Current deployments of TBCs in the region often rely on imported products, such as Tanfloc from South America. In the medium term, the large plantation resources of acacia and eucalyptus suggest that Asia–Pacific could develop its own tannin industry for water treatment, but for spruce-bark-based TBCs the region is more likely to constitute an export market rather than a primary raw-material base [155].

#### 4.2.3. Americas

In North America, the water-treatment chemicals market is mature and closely tied to large industrial sectors including pulp and paper, oil and gas, mining and food processing, as well as municipal utilities with ageing infrastructure [156]. Cost considerations remain paramount, and TBC uptake will depend on the ability to demonstrate equal or better performance at comparable lifecycle cost, including sludge-management savings. Environmental and ESG pressures are growing, but regulatory frameworks have, to date, been less prescriptive than in the EU regarding sludge composition, which slows the shift away from traditional metal salts and synthetic polymers [157]. Nevertheless, specific niches - such as “green” breweries, eco-certified food plants or P&P mills in environmentally sensitive regions - may offer early-adoption opportunities [158].

Latin America presents a contrasting picture. Countries such as Brazil and Argentina are both major producers of bark-derived tannins (notably mimosa and quebracho) and early adopters of TBCs in municipal drinking water and wastewater treatment, as well as in agro-industrial facilities [138]. The co-location of feedstock and markets, combined with growing regulatory expectations and public concern over water quality, has allowed TBCs to move beyond pilot projects into routine operation in some utilities. This experience is particularly valuable for Baltic and Scandinavian stakeholders because it demonstrates that TBCs can achieve commercial viability in diverse climatic, institutional and economic settings, provided that local feedstock, regulatory niches and market expectations align.

#### 4.2.4. Middle East and Africa

In the Middle East and parts of Africa, water scarcity, desalination [159] and brackish-water treatment make coagulation especially important as a pretreatment step prior to membranes and other advanced processes. Here, the primary constraints on TBC deployment are economic and logistical rather than technical [160]. Many countries lack significant bark resources suitable for large-scale tannin extraction, necessitating imports of both tannin extracts and finished TBCs. For the foreseeable future, the region is likely to adopt TBCs selectively in high-value or particularly sensitive installations rather than as mainstream coagulants [161].

### 4.3. Strategic opportunity: spruce bark tannins from the Baltics and Scandinavia

The Baltic and Scandinavian region combines three critical ingredients for a spruce-bark-based TBC industry: abundant feedstock, proximity to demanding markets and strong sustainability credentials. Norway spruce and related conifers dominate regional forests and generate large volumes of bark as a side-stream of timber and pulp production [162].

Tannin contents in spruce bark typically range from around 10–15 % of dry mass, with higher values achievable under optimised extraction conditions, making this residue a credible competitor to more established tannin sources when considered on a “waste-to-resource” basis [163].

From a market standpoint, Baltic and Nordic producers are well placed to serve both domestic P&P mills and nearby municipal and industrial customers in Northern and Central Europe. These markets are under growing pressure to reduce reliance on metal salts and synthetic polymers while improving sludge valorisation, creating a receptive environment for bio-based coagulants with robust environmental documentation. The predominance of FSC and PEFC certification in regional forestry provides an additional layer of assurance that can be leveraged in branding and procurement processes [164].

Spruce-derived TBCs could also be differentiated from incumbent Acacia-based products by emphasising regional origin, traceability and integration into the Nordic/Baltic circular bioeconomy. Co-extracted compounds such as spruce stilbenoids may open auxiliary value chains in nutraceuticals or high-value antioxidant formulations, improving overall plant economics.

Against these advantages stand several risks: the need to achieve competitive cost per cubic metre treated in sectors that are highly price-sensitive; technological and organisational inertia among utilities and mills accustomed to alum/PAC; and the energy intensity of extraction and spray-drying steps if not carefully integrated with existing mill energy systems. Nonetheless, the alignment between regional strengths and global trends suggests a favourable strategic position for developing spruce-bark-based TBCs as a flagship product of the northern forest bioeconomy [165].

## 5. Overall summary and conclusions

Tannins constitute a chemically and functionally diverse class of plant-derived polyphenols whose industrial significance has evolved markedly over time. Classical definitions emphasise their high molecular weight and ability to form strong complexes with proteins, polysaccharides and metal ions, properties that underpin their role in plant defence and explain their characteristic astringency.

Historically, these same properties were harnessed in leather tanning, dyeing and traditional medicine, long before the molecular nature of tannins was elucidated. Modern classification distinguishes hydrolysable tannins, based on galloyl or hexahydroxydiphenoyl esters of polyols, from condensed tannins, which are proanthocyanidin polymers of flavan-3-ols.

The first part of this report has shown that tannins are widely distributed in both angiosperm and gymnosperm species, with commercial production historically concentrating on oak galls, chestnut wood, mimosa and quebracho. Conifer bark, and particularly spruce, pine and fir, has emerged as an underexploited source of condensed tannins with contents typically between 5 and 20 % of dry bark.

Advances in extraction technologies, ranging from optimised hot-water and aqueous-ethanol processes to deep eutectic solvents, allow these bark resources to be converted into tannin extracts of sufficient purity for multiple applications. Environmental assessments indicate that when bark is sourced as a by-product from sustainably managed, certified forests and extraction is integrated with existing mill energy systems, the overall environmental footprint of conifer-tannin production is favourable relative to fossil-based resins or mineral tanning agents.

Against this scientific and resource background, tannins have diversified from their traditional stronghold in the leather industry into food and beverages, pharmaceuticals, nutraceuticals and advanced materials. In leather, chrome tanning remains dominant, but vegetable tannins persist in high-value, eco-labelled and artisanal segments, while syntans serve as auxiliaries. In foods and beverages, tannins shape sensory qualities and act as natural antioxidants, stabilising colour and extending shelf life, while tannin-rich extracts are increasingly used as functional ingredients in health-oriented products.

In the pharmaceutical domain, both hydrolysable and condensed tannins are being explored as active or supportive agents in a wide range of indications, from diarrhoeal disorders, where Crofelemer is an approved example, to chronic inflammatory and cardiovascular diseases, where tannin-rich extracts from tea, grape seeds and pine bark show promising antioxidant and anti-inflammatory effects in clinical and preclinical studies.

The second part of the report has argued that water and wastewater treatment is poised to become a major new outlet for tannins, especially those derived from bark. Tannin-based coagulants synthesized from condensed tannins via cationization reactions have been shown to deliver turbidity, colour and COD removal comparable to or better than conventional metal coagulants, often with lower sludge production and reduced impact on water pH [138], [139], [142], [148]. Case studies in municipal and industrial contexts demonstrate not only technical feasibility but also environmental advantages when sludge management and upstream production are accounted for.

Within this broader picture, pulp and paper mills in the Baltics and Scandinavia emerge as particularly attractive early adopters. These facilities generate large volumes of spruce bark as a side-stream and produce effluents whose composition - high colour, lignin-rich organics and suspended solids - aligns well with the mechanisms of tannin-based coagulation [145]. By establishing local value chains in which spruce bark is processed into tannin extracts and subsequently into TBCs that are used on-site or within regional clusters, mills can close a material loop, converting a low-value fuel into a higher-value treatment chemical while maintaining an organic sludge compatible with forestry and agricultural cycles.

The feasibility of such systems is supported by LCA and TEA studies for analogous bark-tannin processes, which highlight energy demand in drying and purification as key optimisation levers but generally confirm an environmental performance superior to that of metal-based coagulants when applied in suitable contexts [68], [148]. At the same time, pathway-dependent challenges remain. TBCs must demonstrate competitive cost per cubic metre treated in very cost-sensitive markets; utilities and mills may be reluctant to deviate from familiar chemistries; and process design must ensure stable product quality despite variability in bark composition and extraction conditions. These challenges underscore the importance of targeted pilot projects in real pulp-mill environments, rigorous performance benchmarking against existing coagulants, and transparent communication of LCA results to regulators and customers.

For stakeholders in the Baltics and Scandinavia considering investments in spruce-bark tannin extraction and TBC production, the key conclusion is that the underlying science and process technology are sufficiently mature to support commercial deployment. The determining factors will be strategic: selecting the right integration model (on-site versus hub-and-spoke), aligning with regulatory and market niches where the advantages of TBCs are most valued, and building partnerships with water-treatment operators, chemical distributors and technology providers. If these elements are put in place, spruce-derived tannins have the potential to transition from a minor by-product of the forest industry to a cornerstone of regional water-treatment strategies and a visible example of the forest bioeconomy in practice.

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