Boosting the Integrated Use of Sawmill Wastes: Tannin-based Extractives Opportunities

Eliana I. Fernández-Sosa, Nanci Ehman, and María Cristina Area *

In the lignocellulosic biorefinery concept, by-products from sawmills have been redefined and considered as raw materials to produce high-value products. Wood extractives are not an exception despite being found in smaller proportions. The extractive-based components can offer competitive advantages over traditional market products and promote a circular economy. Tannins demonstrate applicability in adhesives, fertilizers, antioxidant food packaging, and water treatment. However, there are still challenges on an industrial scale.

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*Contact information: IMAM, UNaM-CONICET, Programa de Celulosa y Papel (PROCYP), Félix de Azara 1552, Posadas, Argentina; *Corresponding author: cristinaarea@gmail.com*

Wood Tannins, A Market Highly Influenced by Geographical Distribution?

International tannin producer distribution involves South America, Europe, South Africa, and the South Pacific. The location of the tannin industries is mainly due to the availability of raw materials. While some countries, such as Paraguay, Bolivia, Peru, southeastern Brazil, and northeastern Argentina, grow "quebracho" (*Schinopsis lorentzii* and *Schinopsis balansae*) and "tara" or "guarango" (*Caesalpinia spinosa*) species due to their arid climate, in Europe the industries employ chestnut (*Castanea sativa*) and oak woods (*Quercus robur*) that can withstand a more temperate climate to produce tannins. Mimosa (*Acacia mearnsii*) is a tree that grows in a tropical or subtropical climate like southern Africa and some areas of South America. Finally, some New Zealand and Chile industries utilize pine bark (*Pinus* spp.).

The chemical characteristics of the tannins involved in each species differ, which could influence their potential applications. For example, the quebracho that grows in more arid and hot areas generates, for protection, a type of extractive primarily composed of condensed tannins. Conversely, those plants that grow in a more temperate climate, like chestnut wood, will develop a more hydrolyzable tannin or a mixture of both. Profisetinidins are tannins mostly in quebracho and mimosa, while ellagitannins are common in oak extractives, and gallotannins in tara wood. Chestnut could include both gallotannins and ellagitannins. Some industries in the named regions are Tanac S.A. (Brazil), Silvateam (Italy), Laffort (France), Mimosa S.A. (South Africa), Tanin Sevnica (Slovenia), Kauri WI (New Zealand), *etc.*

Tannins and Circularity in the Forest Industry

Bark tree fraction is a forestry by-product, representing at least 10% of the biomass in sawmills (Neiva *et al.* 2024), where it is often used as fuel or is dumped, which causes harmful environmental impacts and constitutes a fire hazard. Due to its composition, bark can be considered a raw material for high-value product production. One possible approach towards bark valorization is the extraction process with different solvents. Coniferous bark extractives are rich in hydrophilic compounds, where condensed tannins are the main constituents of the phenolic fraction. Traditional tannins application involves the leather industry. Nevertheless, conifer tannins have potential applications in wood protection, agriculture, water treatment, adhesives in wood or corrugated cardboard manufacture, and functional coating in active packaging (Fig. 1).

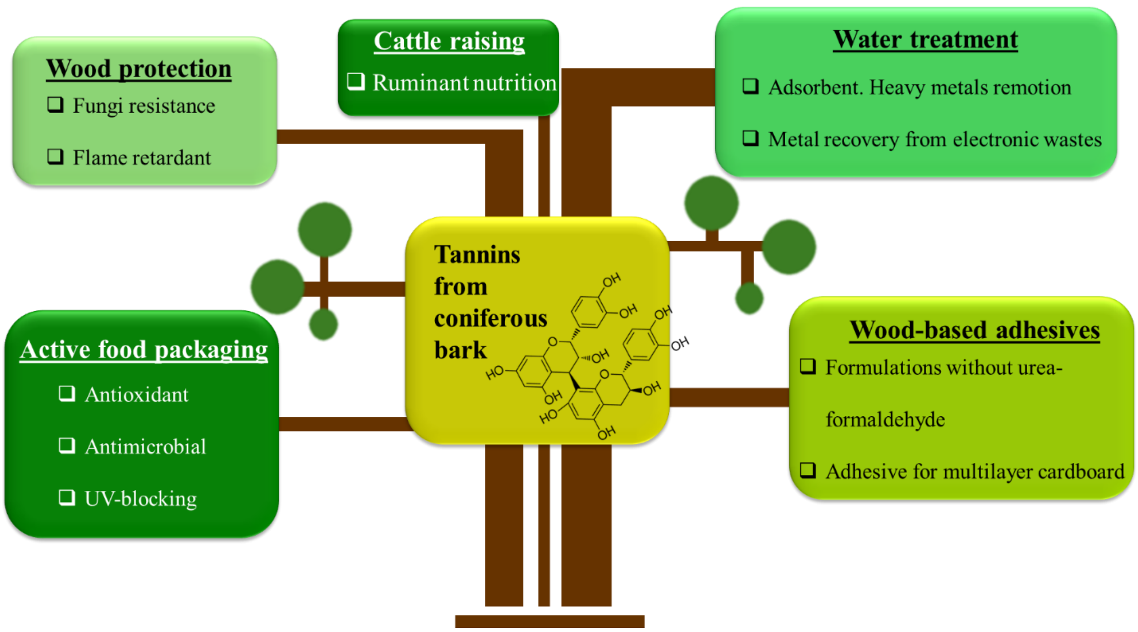

Fig. 1. Applications from coniferous tannins

Tannins cross-linked with formaldehyde lead to the formation of a polymer that could be used as an adsorbent for heavy metals removal, from aqueous solutions, and precious metals removal, like gold, from electronic and electrical waste. This contributes to purging water of potentially toxic elements and reducing waste generation through recycling and recovery. Developing bio-adsorbents from natural resources could imply lower production costs and energy consumption than conventional adsorbents.

Wood products manufacturing is on the rise, leading to a greater demand for wood adhesives. Wood adhesives obtained from condensed tannins by replacing phenol in phenol-formaldehyde adhesive formulations or even combined with other aldehydes, like glyoxal, furfural, 5-hydroxymethylfurfural, to develop formaldehyde-free resins are environmentally friendly options. Coatings from tannin extracts have also been developed as fire retardants and wood preservatives.

Tannins are recognized as safe (GRAS) by the Food and Drug Administration (FDA). Moreover, their antioxidant, antimicrobial, and UV-blocking properties make them a suitable candidate for active food packaging development. Indeed, several studies have provided promising results by incorporating tannins into different biopolymers frequently used in food packaging, improving their antioxidant activity and UV absorption, and reducing water vapor and oxygen permeability (Li *et al.* 2019; Huang *et al.* 2022; Liao *et* *al.* 2022; Deng *et al.* 2023; Şahin *et al.* 2024). Moreover, mechanical properties were not significantly affected.

Nanocellulose and Coniferous Tannins for Active Food Packaging

Tannins incorporation in nanocellulose matrices inhibit the activity of Gram-negative and Gram-positive pathogenic bacteria. Proanthocyanidins are potent antimicrobial agents and allow antiadhesive actions against bacteria in urinary and dental infections. Proanthocyanidins could inhibit some Gram (+) bacteria species such as *Staphylococcus aureus* (found in uncooked meat, chicken, fish, and egg) and *Bacillus cereus* (meat, pasta, potato, rice, vegetables, milk, and fish). Additionally, they can act in Gram (-) species, like *Salmonella* (dairy products, eggs, and uncooked meat), *Escherichia coli* (uncooked vegetables, uncooked meat), and *Pseudomonas aeruginosa* (uncooked fruits and vegetables, water, and ready-made food). As flavonols, they have a chelating action, which could limit the supply of iron to bacteria, reducing growth. In the case of *Escherichia coli*, the alpha bonds of proanthocyanidins also prevent the adhesion of the fimbriae of pathogens to the body.

Challenges in Tannin Compound Extraction

Limiting actions on the applicability of tannin extracts are the lower extraction yield and the co-extraction of other substances (organic acids and carbohydrates) due to covalent bonding. Purification steps could increase processing costs, produce a higher energy consumption, and lead to environmental impacts.

The wood bark extraction applied as a unique sequence could lead to unprofitable processing methods. In this sense, moving towards more cost-effective systems involves an integral cascade processing. For example, one possible way is the lignin recovery from the extracted bark. According to its quality and purity, it could be a product with high added value. Another processing route could be the pyrolysis of bark to obtain biochar, bio-oil, and gaseous compounds. All cases require a technical-economic and environmental impact assessment of the integral process evaluation.

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