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REVIEW OF TANNINS CURRENTLY USED IN THE LEATHER INDUSTRY. PART 2: CONDENSED TANNINS

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Tannins are macromolecules found in different proportions in the structures of various plants and are thought to be their defense mechanisms. They have been used in the tanning and retanning processes in leather production, and their use for this purpose dates back to very old times. They are used together or with other tanning agents in the production of shoemaking, saddlery, stout leather, etc. They have become more popular recently, because they can provide the opportunity to produce metal-free leather. Therefore, they can be categorized as green, environmentally friendly materials. In addition, industrial production of tannins is also common due to the relative practicality of production and easy availability of the raw material. They are divided into three main classes—hydrolyzable, condensed, and complex (different combinations of hydrolyzed and condensed tannin monomers). This study includes condensed tannins, which are secondary metabolites in plants consisting of various mixtures of oligomeric and polymeric substances called flavan-3-ols. The chemical structures of condensed tannins and condensed tannins such as mimosa, quebracho, gambir and mangrove used in leather production and the properties they impart to the leather are explained.

Keywords: leather, tannins, condensed tannins

INTRODUCTION

The term "tannin" was first used to refer to the compounds found in vegetable extracts that turn animal hide/skin into leather. These compounds are found in plant extracts as polyphenols with different molecular sizes and complexities. All of the chemical characteristics of tannin are also present in many nonpolyphenolic substances found in plants; however, no research has been done on their ability to leather hides (Harborne, 1967; Chung *et al*., 1998).

Vegetable tannins are water-soluble phenolic compounds with a molecular weight of 500–3000 Da, according to Swain and Bate-Smith. These polyphenols have the ability to form cross-linkages with proteins and other macromolecules because they have a high number of hydroxyl or other functional groups (1 to 2 per 100 Da). Phenolic compounds with low molecular weights (less than 500 Da) and high molecular weights (more than 3000 Da) cannot be used as tanning agents. Additionally, proteins, gelatin, and alkaloids can combine with vegetable tannins to form precipitation (Swain & Bate-Smith, 1962; Chung *et al*., 1998).

In this review, the structures of condensed tannins and the most commonly used condensed tannins in leather production such as mimosa, quebracho, mangrove and gambir are explained.

Chemical Structure of Condensed Tannins

Condensed tannins, also referred to as "proanthocyanidins," are made up of oligomers or polymers of flavan-3-ol (Figure 1), a subclass of flavonoids, at its fundamental structure (Mavlyanov *et al*., 2001; Auad *et al*., 2020; Schofield *et al*., 2001; Porter, 1989; Mueller, 2001; Ekambaram *et al*., 2016; Romani *et al*., 2006).

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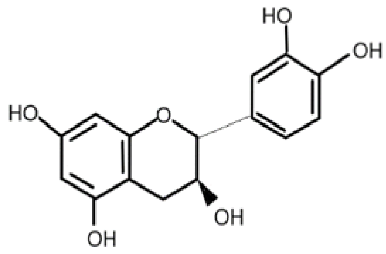

Figure 1. Chemical structure of flavan-3-ol molecule

Condensed tannins are secondary metabolites in plants. They have subunits such as catechin (C), epicatechin (EC), gallocatechin (GC), epigallocatechin (EGC), epicatechin gallate (ECG), gallocatechin gallate (GCG) and epigallocatechin gallate (EGCG). The chemical structures of these molecules are as shown in Figure 2. Studies have shown that its biological activity is related to the presence of galloyl and gallic moieties in flavan-3-ol units. EGCG contains both galloyl and gallic moieties in flavan-3-ol units, which makes EGCG the strongest ability to inhibit bacteria among condensed tannins (Huang *et al*., 2024)

Compared to hydrolysable tannins, condensed tannins have a broader molecular weight range of 500–2000 Da. Additionally, according to Hoque *et al*. (2024), they can react with aldehydes to create polymeric materials.

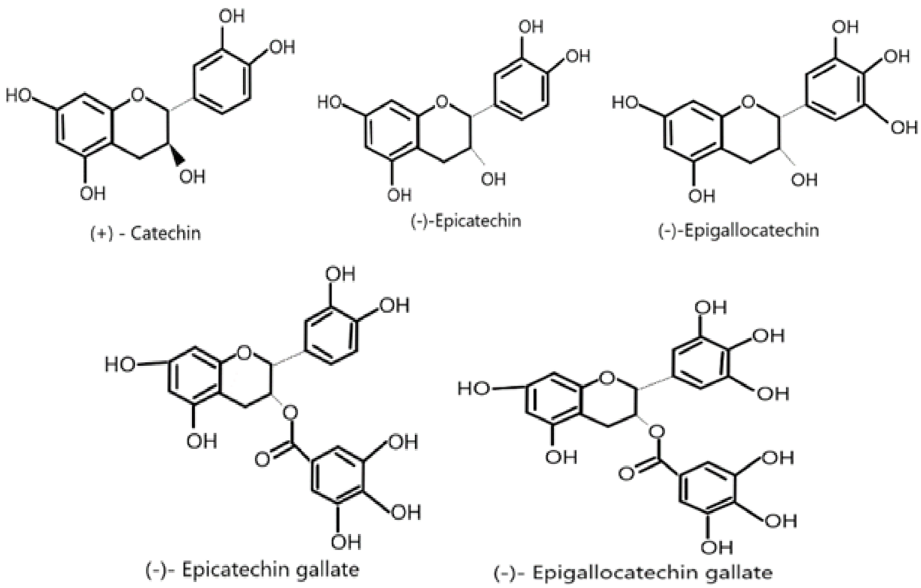

Figure 2. Condensed tannin subunits

Condensed tannins give a greenish black stain when they chemically react with iron, while hydrolyzed tannins give a bluish black stain. Condensed tannins are more astringent than hydrolysable tannins and their structures are more complex (Redwood, 2020).

Condensed tanning agents are not decomposed by enzymes and when heated they give completely pyrocatechin. Under the influence of oxidizing agents or when treated with strong acids they form high molecular weight and insoluble phlobaphenes by condensation. Their precipitation with formaldehyde, hydrochloric acid or bromine water is characteristic (Sarı, 1993).

Reddish-brown leathers with condensed tannins have a tendency to darken in the presence of light. Additionally, these leathers have a propensity to absorb air pollutants, the most harmful of which is sulfur dioxide (SO_2), which encourages the hydrolysis of collagen acid (Falcão & Araújo, 2011).

The majority of the bonds formed by both hydrolysable and condensed tanning agents with the leather are based on H bridges. The phenolic OH groups of the tanning agents act as H atom donors (Sarı, 1993).

The leather that has been tanned using condensed tannin(s) has a shrinkage temperature between 80 and 85°C. Similar to hydrolysable tannins, the Ts is characteristic, meaning that an observed shrinkage temperature greater than 80°C is highly suggestive of the use of condensed tannins. It is interesting to note how different tanning processes with different tannin types produce different results. This variation must arise from a different type of reaction, i.e., the shrinkage temperature can be measured depending on how covalency contributes to similar reactions (Covington, 2009).

Condensed Tannins Widely Used in Leather Production

Tannins attach themselves to the functional groups (COOH, $-NH_2$) of the leather protein collagen through hydrogen and covalent bonds. But these connections only happen when the tannin molecules are big enough to attach to nearby collagen chains and have enough phenol in them to create multiple cross-links. There are two steps in the vegetable tanning process: penetration and fixation. The diffusion of tannins into the leather is referred to as penetration, and the binding of the penetrated tannins to the collagen, which creates the stable material, is known as fixation. To produce the desired products, this process involves a number of variables, including temperature, pH, mechanical effects, and particle size (Tasnim *et al.*, 2024; Mia *et al.*, 2024). In terms of tanning efficiency, quality, performance, and extraction efficiency, condensed tannins from mimosa, quebracho, gambir and mangrove (Table 1) are typically utilized in commercial applications.

Table 1. Condensed tannins commonly used in leather production and their properties (Redwood, 2020)

Plant	Source of tannin	Tannin content (%)	Non-tans content (%)
Mimosa (*Acacia decurrens/mearnsii*)	Bark	22-48	7-8
Quebracho (*Quebrachia lorentzii, Schinopsis balansae/lorentzii*)	Wood	14-26	1-2
Gambir (*Uncaria gambir*)	Leaves	20-50	1-2
Mangrove (*Avicennia germinans*)	Bark, Leaves, Fruit	16-50	9-15

Mimosa

Certain acacia tree cultivars are marketed as mimosa extract because of their high tannin content. Among these, the invasive *Acacia mearnsii*, or Black Mimosa, is grown in Australia, America, and South Africa. It is a significant plantation for the wood chips industry and tannin production. It is used commercially to obtain tannin for leather tanning owing to its affinity for binding proteins (Xiong *et al*., 2016; Featherstone, 2024).

However, 68% of the *Acacia mearnsii* bark extract by weight consists of proanthocyanidins (PAC) and is an important industrial source for the production of this substance. In addition, proanthocyanidin oligomers in this extract contain 5-deoxy extender units that make interflavanyl bonds resistant to acid-catalyzed hydrolysis (Mia *et al*., 2024). It is also valued for its health-related applications, including antioxidant and antitumor effects, hair growth promotion, antihypertension and antiallergic properties (Xiong *et al*., 2016).

Teklemedhin *et al*. used commercial mimosa extract as a control group in their study investigating the usability of *Cassia singueana* bark extract in leather tanning. In this study, the pH of the mimosa extract was measured as 5.3. In addition, some properties of the leathers tanned with mimosa in the findings of this study are as indicated in the Table 2 (Tekmeledhin *et al*., 2023).

Table 2. Some properties of mimosa tanned leathers (Tekmeledhin *et al*., 2023)

	Values	Standard values	References
Tensile strength (N/mm^2)	14,8	20	IULTCS/IUP 6 (2006)
Elongation at break (%)	38,7	>%40	IULTCS/IUP 6 (2006)
Tearing strength (N/mm)	22,5	20	IULTCS/IUP 8(2016)
Shrinkage temperature (°C)	80	> 75	IULTCS/IUP 16 (2015)

Quebracho

The best species of Quebracho, which is a tree native to South America, in terms of tannin are found in the Gran Chaco region in northern Argentina and in Uruguay. Both the bark and heartwood contain tannin, and the average tannin content was determined as 14-26% in the heartwood; 22-45% in the bark. However, Quebracho extract is usually produced from the wood part. The parts left over from the construction of construction materials and railway sleepers are used for the production of tannin extract. Quebracho wood, which contains high amounts of condensed tannin, meets approximately one third of the world's total tanning material demand (Yahia *et al*., 2019; Erkan and Deniz, 2016). The most important species in terms of tannin are *Quebracho colorado (Schinopsis balansae)* and *Quebracho maco (Schinopsis lorentzii)*. Quebracho extract is soluble in hot water and can be used in the final stage of leather production in this form. When sulfite is used in the production of Quebracho, sulfite Quebracho is obtained. Sulphite Quebracho is soluble in cold water. Sulphite Quebracho has a higher penetration rate into the skin than raw Quebracho extract, less sludge formation rate and the color of the leathers produced is lighter (Yahia *et al*., 2019).

Yahia et al. used Quebracho as a control group in their study investigating the effects of the combination of Quebracho and Oxazolidine on leather tanning and obtained some properties of the leathers tanned with Quebracho as shown in the Table (Yahia *et al*., 2019).

Table 3. Some properties of quebracho tanned leathers (Yahia *et al*., 2019)

	Values	Standard values	References
Tensile strength (N/mm^2)	215±3	200	IULTCS/IUP 6 (2006)
Elongation at break (%)	55±1.5	40-65	IULTCS/IUP 6 (2006)
Tearing strength (N/mm)	50±0.8	30	IULTCS/IUP 8(2016)
Shrinkage temperature (°C)	84±0.5	>75	IULTCS/IUP 16 (2015)

Gambir

Gambir (*Uncaria gambir*) is an annual plant widely used for industrial and pharmaceutical purposes and grows in tropical regions (Bancın, 2021). Gambir (*Uncaria gambier*) plants can be obtained by boiling the leaves and branches and then pressing to extract the gum. Depending on the percentage of tannin content, gambir has various types and is included in the class of condensed tannins (Griyanitasari *et al*., 2020). Leathers tanned with gambir are soft, smooth and light colored (Andini *et al*., 2023).

Mangrove

It is found in forests in Southeast Asian countries. The leaves, fruits and bark of mangrove (*Rhizophora mucronata*), which is among the condensed tanning materials, are used to obtain tannin. The bark contains approximately 26% tannin (Pancapalaga and Nitiharjo, 2019).

Dewi et al. investigated the effects of the combination of chromium and mangrove on leather tanning. When they used 8% mangrove alone in tanning, they obtained leathers with a shrinkage temperature of 55.23 °C ± 0.49. When they used 4% basic chromium sulfate and 4% mangrove together, they measured the shrinkage temperature as 83.03 °C ± 1.86 (Dewi *et al*., 2021). As can be understood from this, the use of mangrove alone is insufficient for the leather tanning process.

CONCLUSION

The tannins found in various plants are used to make leather. Three classes of tannins are identified: hydrolyzed, condensed, and complex. They are capable of interacting with proteins. As a result, they have long been employed in the tanning of leather. The condensed tannins that are most frequently utilized for this purpose on the market are mimosa, quebracho mangrove, and gambir. They are used in the tanning and retanning processes and in the production of leathers such as shoemaking, saddlery and stout leather. Among all vegetable tanning agents, mimosa and quebracho stand out commercially in terms of the properties they provide to the leather. However, vegetable tanning agents have some disadvantages such as being hydrophilic, giving color to the leather and having a low shrinkage temperature. Therefore, they are usually used together with each other or other tanning agents.

One of the main issues of sustainable leather production is the rapid biodegradation of the finished product when it is thrown away after its useful life. The most important microorganisms of recycling in nature are fungi. It has been observed that various fungi grow easily on vegetable tanned leather. In studies conducted by inoculating fungi onto vegetable tanned leather and chrome tanned leather, it was observed that fungi developed later in chrome leather. While many fungi grow later and slower on the leather due to the oligodynamic effect of chromium, they are not compatible with fungi. However, studies generally show that molds can easily grow on the leather (Bayramoğlu *et al*., 2017, Bayramoğlu & Maltaş, 2011). While fungus formation during production is a disadvantage in vegetable tanned leather, it is an advantage to ensure rapid fungus formation and decomposition of the leather into its minerals at the end of its life. For sustainable leather production, leather that has expired and is thrown into the environment must quickly decompose and mineralize without harming the nature. In this context, the mineralization of waste leather by fungi in leather produced with vegetable tanning agents is extremely important for sustainable leather production.

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