



Modified Vegetable Tanning Agents for Leather Manufacture

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Abstract

Nowadays, chemically modified vegetable tanning agents are becoming increasingly popular both in the field of research and industrial sectors because of their unique advantages over traditional vegetable tanning agents. Chemical modifications of vegetable tanning leads to tuning of chemical reactivity together with physico-chemical properties of leather tanned with modified vegetable tanning agents. More importantly, these modified tanning agents may be employed in large scale applications in various industries including leather sector.

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I. Introduction

It is well-known that certain organic substances have tanning properties, which are capable to tan and transform animal skins into leather. Later, these organic substances became known as 'tannin'. The name 'tannin' originated from the French word 'tanin' which means substance that is capable of tanning. The term 'tannin' came from the German word 'tanna' which originated from the term 'Tannenbaum' representing oak or fir tree. Thus 'tannin' refers to the use of wood tannins from oak in tanning animal hides into leather; hence the words "tan" and "tanning" came for the treatment of leather. Accordingly, tannins are mostly utilized in the tanning industries. In fact, the word 'tannin' is used to denote a range of natural polyphenols. Tannins are a type of phenolic compounds extracted from the different families of the higher plants. In nature, tannins are found worldwide in many plant species such as in Chestnut and Oak wood, Divi-Divi, Sumach, Myrobalan, Trillo, Valonea or plant galls.

Now-a-days, a vegetable tanning agent comes under the category of "green tanning agent" because of its ability to undergo biodegradation. In this regard, vegetable tanning can be an effective alternative to minimize chemical hazards associated with the chromium tanning. Moreover, vegetable tanned leather is equipped with excellent fullness, molding ability, wear resistance, and air permeability. Thus, vegetable tanning plays an important part in making heavy leathers, such as furniture leather, garment leather and shoe upper leather. Accordingly, increasing attention has continuously been paid by researchers throughout the world to replace the hazardous chromium tanning agents by the vegetable tanning agents. Though vegetable tannins give leathers some properties like natural look, firmness, toughness and characteristic colour of themselves, vegetable tannins suffer from several drawbacks like colour changing and darkening caused by exposure to light for prolonged times. In fact, on prolonged irradiation with UV light, fading or darkening of vegetable tanned leather is caused due to extensive chemical modification of polyphenolic components. In this regard, darkening of vegetable tanned leather is caused by formation of quinones in the phenolic structure of the vegetable tannin, whereas lightening of vegetable tanned leather is actuated due to photo degradation of the molecules. Moreover, vegetable tannins are not suitable for manufacturing light weight leathers, as vegetable tanned leathers are of increased solidity and heavier in nature and hence cannot meet the present demand of customers for light weight fancy leather articles. Furthermore, shrinkage temperature of a vegetable tanned leather is generally lower than that of a chromium tanned leather, and hence the thermal stability of a vegetable tanned leather is relatively inferior. In addition, the inherent solubility of vegetable tannins in water is usually poor, and hence lacks the ability to penetrate deep inside a thicker leather. Moreover, highly reactive vegetable tannin molecules usually tend to deposit at the surface of tanned leather, leading to under-tanned or even untanned bulk portion.

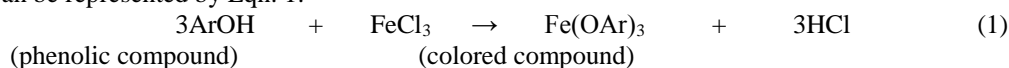
To overcome such shortcomings, chemical modifications of mimosa and quebracho tannins were executed to improve lightfastness of tanned leathers [2,3]. In the past, the usual practice was to reduce the

reactivity of condensed type vegetable tannins via sulfonation using sodium bisulfite, which also increases the solubility of tannins in water. This is the one way of modifying vegetable tannins by which the solubility of condensed tannins in water can be improved, whereas the reactivity can be reduced to achieve better penetration along with a gentle and mellow tanning. Attempts have been made to improve thermal resistance of vegetable tanned leather by introducing different types of chemical modifications on vegetable tannins. Chemical modification of tannins can be achieved via diversified *ex-situ* approaches consisting of numerous reactions, such as sulfonation, sulfomethylation, aldehyde treatment, Metal complexation, sulfanilic acid functionalization, and Mannich reaction, to obtain suitable tanning agents for leather manufacture. In addition, combination tanning methodology is still a popular and widely practiced approach to obtain a good quality leather. At the time of combination tanning, the possible *in-situ* reactions among different tanning agents within the leather matrix have also been investigated.

In this report, the attempt has been made to summarize all the techniques by which vegetable tannins are being modified till date. In this context, various classes of vegetable tannins and their chemical modifications have been discussed separately, along with the proposed or established reaction mechanisms involved during such modification process. At the end, physio-chemical characteristics of the modified tannin treated leathers have been represented in a collective form, to express the comparative property developments in the modified tannin treated leathers over conventionally tanned leather.

Tannins

In order to understand the modification of tannins, it is necessary to include a brief chemistry, classification and some physio-chemical properties of tannins. Earlier, Bate and Smith defined tannin as “water-soluble phenolic compounds, having molecular weights between 500 to 3000, giving the usual phenolic reactions (e.g. blue colour with iron (III) chloride), and having special properties such as the ability to precipitate alkaloids, gelatin and other proteins.” Actually, phenolic reaction is the conversion of compounds with a phenol group (ArOH) to a blue, violet, purple, green, or red-brown colored compound, Fe(OAr)₃, upon addition of aqueous ferric chloride (FeCl₃). This reaction can be used as a test for phenol groups. The reaction can be represented by Eqn. 1:



The other special property of tannin is its ability to precipitate protein. However, the detailed chemistry behind such precipitation is not fully understood yet. It is certain that tannins interact with proteins to form an entity or substance which is unable to remain in the solution phase. If tannin molecules are added in an aqueous dispersion of protein then the added tannin molecules will interact with the protein macromolecules to form a tannin- protein assembly (Fig.). This tannin-protein assembly should be heavier in nature and its hydrophilic character should be less. Therefore, the tannin-protein assembly is precipitated or thrown out of the solution phase.

However, definition given by Bate and Smith does not include all tannins. More recently, molecules with a molar mass of up to 20000 D (D = Dalton) have been isolated that should also be classified as tannins on the basis of their molecular structures. Griffith defined tannins as “macromolecular phenolic substances”.

In his definition, only high molecular weight phenolic substances (M.W > 1000 D) were taken into consideration. Interestingly, though morphine is an alkaloid, it cannot be precipitated by tannin. Physically, tannins may appear as light yellow or white amorphous powders (Fig.). Its appearance may also be shiny, nearly colourless, loose masses associated with a characteristic strange smell and astringent taste.

On the basis of their structural characteristics, tannins can be classified into four major groups: Gallotannins, ellagitannins, complex tannins, and condensed tannins (Fig.)

Hydrolysable tannins

In general, hydrolysable tannins include both the gallotannins and the ellagitannins. Hydrolysable tannins can be fractionated hydrolytically into their components. Such hydrolysis can be done by treatment with hot water or with tannases. In fact, tannase or tannin acyl-hydrolase catalyzes the hydrolysis of ester bonds present in these tannins.

Gallotannins

Gallotannins are those hydrolysable tannins which gives gallic acid (Fig.) on hydrolysis. Degradation of gallotannins by enzymes secreted by *Aspergillusniger* has been reported. A typical structure of a simple gallotannin (e.g. 1,2,6-trigalloyl glucose) has been depicted (Fig.). This particular gallotannin can be found in cell cultures of *Cornusofficinalis*. In this structure, three galloyl residues are linked to C-1, C-2, C-6 of glucose unit by ester linkages (Fig). Enzyme secreted by *Aspergillusniger* can cleave the ester linkages of gallotannins to produce gallic acid and glucose (Fig).

Ellagitannins

As a result of hydrolysis of ellagitannins, ellagic acid (Fig.) is obtained. A typical structure of ellagitannin, named Pedunculagin, has been depicted in Fig. One Pedunculagin molecule contains two ellagic acid molecules attached to core glucose. Hydrolysis of Pedunculagin results generation of two ellagic acid molecules and one glucose (Fig). Actually, ellagitannins are esters of hexahydroxydiphenic acid (HHDP) joined to a glucose molecule. The structure of HHDP has been depicted in Fig. In aqueous solution, HHDP is transformed spontaneously to ellagic acid by lactonization (Fig.). Therefore, these tannins are named as ellagitannins. Actually, lactonization or lactone formation occurs as a result of intramolecular esterification involving $-OH$ group and $-COOH$ group of the same molecule. Lactone formation takes place spontaneously when the ring that is formed is five- or six-membered. During the transformation of HHDP to ellagic acid, a six-membered ring is formed (Fig.). This six-membered ring is highly stable, and hence the transformation of HHDP to ellagic acid is spontaneous. Corilagin is a typical ellagitannin wherein an ellagyl residue is attached to the C-3 and C-6 of the glucose unit via ester linkages. Another gallic acid residue is linked to C-1 of glucose unit (Fig).

Condensed tannins

On the other hand, some tannins are unable to be hydrolyzed. These tannins were categorized as non-hydrolysable or condensed tannins. Basically, condensed tannins are composed of complex condensation products of flavonoid units, which form oligomers and polymers [Arbenz and Avérous 2015]. The condensed tannins represent more than 90% of the world commercial production, and are used in different industrial applications such as leather tanning. Examples of important condensed tannins for vegetable tanning are extracted from quebracho wood and mimosa bark.

Chemically, condensed tannins are based on the flavan-3-ols (Fig.). Various types of flavan-3-ol units, such as robinetinidol, fisetinidol, catechin, gallo catechin, are found in different condensed tannin molecules (Fig.). In this regard, depending on the predominance of the constituent monomeric flavan-3-ol units, condensed tannins can generally be classified into prodelphinidins, procyanidins, profisetinidins, and prorobinetidins (Fig.). For instance, prodelphinidin is a name for the polymeric tannins composed of gallo catechin/ epigallo catechin, whereas catechin/ epicatechin units are the most frequently found constituents of procyanidins. Accordingly, profisetinidins are mostly composed of fisetinidol, whereas prorobinetidins are a type of condensed tannins formed from robinetinidol. Structurally, prodelphinidins are constituted of phloroglucinol A-rings and pyrogallol B-rings, whereas procyanidin units bear phloroglucinol A-rings and catechol B-rings. On the other hand, profisetinidins have the units bearing resorcinol A-rings and catechol B-rings, whereas prorobinetidins possess the units having resorcinol A-rings and pyrogallol B-rings (Fig). Notably, both gallo catechin/ epigallo catechin and catechin/ epicatechin units bear $-OH$ group at C-5 of A-ring. Theoretically, the presence of $-OH$ group at C-5 restricts the ability of the ring system to react at the C-6 position, and hence both prodelphinidins and procyanidin type tannins tend to be linear. On the other hand, both fisetinidol and robinetinidol are devoid of $-OH$ group at C-5 of A-ring. Accordingly, due to the absence of $-OH$ group at C-5 position, both profisetinidins and prorobinetidins are branched polyphenols. For instance, mimosa mostly contains prorobinetidin and quebracho is predominantly composed of profisetinidins [7]. In fact, it was proven that quebracho extract contains no robinetinidol. More precisely, quebrachopolyanthocyanidins consist of a homologous series of one molecule of catechin (starter unit) linked to one, two, three, etc. *ent*-fisetinidol extender units [9]. Moreover, due to the absence of $-OH$ group at C-5 position of the constituent monomers, interflavanyl bonds in mimosa and quebracho become stable against acid hydrolysis. Accordingly, longevity of mimosa and quebracho tanned leathers is more than the leathers tanned by prodelphinidins and procyanidin type tannins.

Modification of tannins

Sulfonation

By means of sulfonation, heterocyclic A-ring of the condensed tannin molecule is opened. Thereafter, a modified condensed tannin molecule with rearranged chemical structure containing newly formed hydroxyl and sulfonate groups is obtained (Fig.). In fact, sulfonation of condensed tannin molecules requires the addition of sodium bisulfite or sodium bisulfate. As a result, heterocyclic ring of the condensed tannin molecule is cleaved and thereafter, sulfonate group is inserted at the C2 position of the ring. Accordingly, a sulfonated tannin molecule is produced, which shows increased polarity, hydrophilicity and solubility over the raw condensed tannin molecule. Moreover, sulfonation reduces the viscosity of vegetable tannin extracts. Lowering of viscosity is connected with the fact that the degree of polymerization of sulfited tannins is somewhat lower than those for the natural tannins. This is an indication that sulfonation cleaves the interflavonoid C-C linkages (Fig.), resulting in shorter poly-flavonoid chains. An ESI (electrospray ionization)-MS investigation of sulfited (cold-water-soluble) quebracho extract polyanthocyanidins indicates that during sulfonation, sulfite ions ($-SO_3^-$) are introduced at both C-2 and C-4 of the constituent fisetinidol monomeric moieties. In the case of C-2 sulfonation,

the pyran ring is opened, followed by formation of dimers, trimers, and tetramers (Fig.). Thereafter, the acyclic sulfonate-containing molecules react further with an additional bisulfite ion at C-4. This is associated with fission of the interflavanyl bond [10]. The reaction cascade is associated with step by step sulfitation and cleavage of interflavanyl bonds of quebracho tannin molecules (Fig). This effect is the greatest in the pine tannin, due to the well-known lability of the inter-flavonoid C-C linkage that connects procyanidin units bearing phloroglucinol A-rings and catechol B-rings [6], but sulfitation does not seem to affect the quebracho tannin to such a large extent. In contrast to pine tannin molecules, interflavanyl bonds in mimosa and quebracho becomes stable against acid hydrolysis due to the absence of –OH group at C-5 position of the constituent monomers inprofisetinidins and prorobinetidins [10]. Interestingly, mimosa tannin is proportionally affected more than quebracho but less than pine. This is unexpected as interflavonoid link cleavage is rather difficult in mimosa. In this regard, it is well established that mimosa mostly contains prorobinetinidin and quebracho predominantly composed of profisetinidins [7]. Moreover, mimosa contains branched structures bearing angular units, whereas quebracho constitutes of linear structures devoid of angular units.

Several attempts were made to incorporate sulphonate groups in the mimosa tannin molecules modified with novolac type polymers [2]. While producing such novolac modified tannins, sulphonate groups can be incorporated in the tannin moieties either before (Fig.), during (tandem)(Fig.), or after the polymerization process. Among these three options, if sulfitation of tannin moieties was carried out before or at the time of polymerization, the resulting polymeric tannins became more soluble in water. On contrary, when sulfitation of the tannin part was attempted subsequent to polymerization, the sulfitation reaction became difficult to perform owing to lower solubility of polymers in water. Among all of these three options, tandem process was economically viable as less reaction time was required to carry out sulfitation at the time of polymerization, along with lower consumption of energy. However, a sulfomethylation reaction may occur as side reaction during the tandem process. Detailed mechanism of sulfomethylation and associated reaction conditions have been discussed in the subsequent section. In addition to the study related to the variation in the sulfitation stage of tannins, another set of investigations was conducted on the individual effect of three different aromatic sulfonic acids, such as phenol sulfonic acid, naphthalene sulfonic acid and naphthol sulfonic acid, incorporated during the polymeric modification of sulfited tannins. Herein, polymer modified tannins bearing phenol sulfonic acid (Fig.) showed the higher solubility in water, as compared to the modified tannins containing either naphthalene sulfonic acid or naphthol sulfonic acid. Moreover, naphthalene sulfonic acid bearing modified tannins composed of lower tanning substances in comparison to the polymer modified tannins containing phenol sulfonic acids. Poor tanning substance in naphthalene sulfonic acid bearing modified tannins can be expected as it is well-known that naphthalene sulfonic acid based synthetic tanning agents are usually employed as auxiliary tanning agents or dispersing agents. In addition, average molecular weight of polymer modified tannins was also tuned by changing the molar ratio of ingredients such as tannin, formaldehyde and urea. Accordingly, higher molecular weight modified tannins were generated when relatively increasing proportions of formaldehyde and urea, with respect to tannins, were applied at the time of polymerization. A common trend was observed which showed that both the tensile strength and the elongation-at-break of the tanned leathers were deteriorated when modified tannins of increasingly higher molecular weight were employed for tanning (Table). Such phenomena can be possible as the bigger and bulkier tannin molecules should experience greater steric hindrance during penetration and uniform distribution of tannins throughout the collagen matrix, which in turn should encourage greater deposition at the surface rather than penetrating deep inside. As a whole, phenol sulfonic acid containing novolac modified mimosa tannins of lower molecular weight, in which sulfitation of tannin was executed either before or at the time of polymerization, showed the better tanning potency than the unmodified mimosa tannins. Similar to the condensed tannins, hydrolysable tannins like valonia extract was modified via bisulfitation and the sulfonated valonia extract has been effectively used as combination tanning agent with Oxazolidines [18].

Sulfomethylation

This technique was adopted from the sulfomethylation reaction practiced in the synthesis of amino resins based on urea and melamine. By this sulfomethylation process, sulfomethyl groups can be inserted to the unsubstituted ring carbon of phenols. In this process, sodium sulfite and formaldehyde are the essential reactants. When sulphonate groups are incorporated in the tannin moieties during (tandem) novolac making step [2], the reaction is carried out at medium temperature (80 °C) using phenol, formaldehyde, and sodium sulfite, causing the insertion of a sulfomethyl group in the aromatic ring (Fig). According to a comparative study conducted by a research group, the sulfomethylated tannins showed the best lightfastness and provided the best hydrothermal stability as compared to the other modified tannins obtained by various modification techniques, like sulfonation and formaldehyde treatment.

Aldehyde treatment

In the past, several attempts have been made to produce efficient tanning agents via chemical modification of condensed tannins by reaction with formaldehyde. In a condensed tannin extract, relative

proportion of phloroglucinol vs. resorcinol type A-rings determines the reactivity of the condensed tannin towards formaldehyde and hence their rate and extent of cross-linking. Moreover, relative proportion of pyrogallol vs. catechol B-rings can influence heterocycle pyran ring opening tendency. With condensed tannins (Fig.), formaldehyde reacts mainly with the A-rings of condensed tannin units to produce methylene links (Fig.). In fact, if A-ring of a condensed tannin unit is resorcinol type, then the formaldehyde reacts invariably with the C8 reactive site of the A-ring. On the other hand, formaldehyde reacts with the C6 reactive site of the A-ring, if the condensed tannin contains phloroglucinol type A-ring. Notably, as compared to A-ring, B-ring of the condensed tannin is relatively less reactive. Unlike A-ring, ring carbons are not the reactive sites of the B-ring. However, at a high pH (pH = 10), the B-ring can be activated via anion formation through dissociation of phenolic OH groups. Indeed, regardless of the type of tannins, it is possible to carry out the following reaction between condensed tannin and formaldehyde (Fig.) [1].

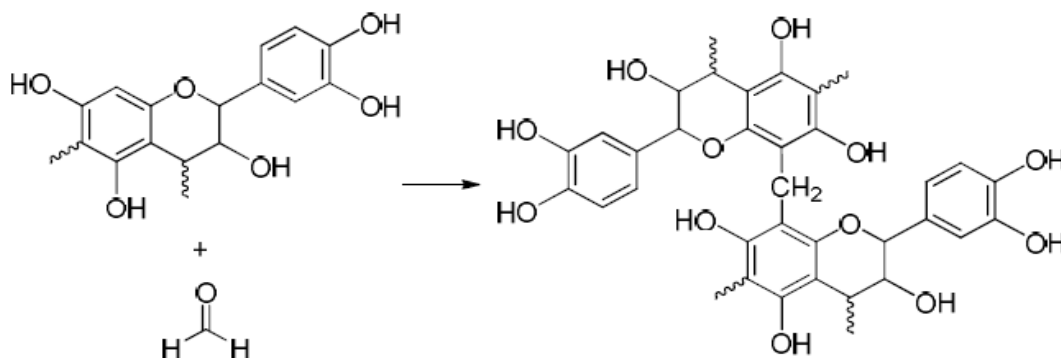


Fig.: Reaction between formaldehyde and condensed tannin

The application of a combination of condensed tannin and aldehyde and thereby possible reaction between tannin and aldehyde molecules was first proposed by Das Gupta [4]. In the past, during the commercial introduction of oxazolidine E in 1973, the following possible reactions of oxazolidine/mimosa combination tanning were postulated:

1. oxazolidine can react directly to cross-link with basic groups of collagen (Fig.)
2. oxazolidine can react with collagen in one hand and couples with mimosa on the other hand, without cross-linking, and
3. oxazolidine can react with basic groups of collagen via mimosa forming crosslinking.

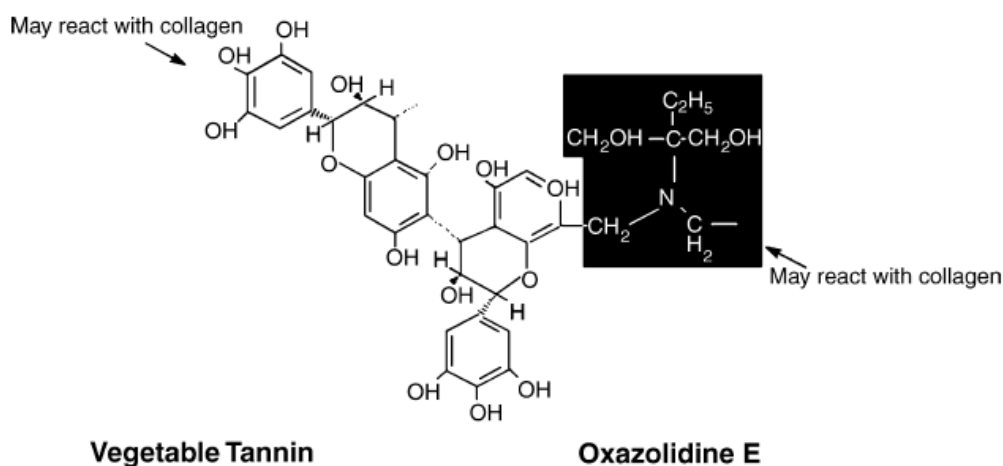


Fig. Reaction among vegetable tannin, oxazolidine E and collagen [5]

Herein, oxazolidine reacts with the C8 position of A-rings in condensed tannin units to produce methylene bridge (Fig.). In this context, an NMR study of the interaction between catechin and oxazolidine (an aldehyde containing alicyclic ring system capable of creating two N-methylol reactive sites) demonstrated that the reaction occurred at the C6 and C8 positions of the A-ring in catechin, whereas the B-ring remained unchanged. However, the structure of the B-ring can influence the reactivity of tannin with formaldehyde.

Molecular modelling of catechin and galocatechin and their reactions with formaldehyde were studied, which indicated that the C6 and C8 positions of catechin are equally reactive towards aldehydes. However, C8 position of galocatechin is more reactive than C6 towards aldehydes. Earlier, with the help of formaldehyde, Tambi et al. (2007) carried out diversified modifications of condensed tannin molecules present in mimosa tannin extract. Among all the proposed structures of the modified tanning agents, the B-rings remained unreacted, whereas both the ring carbons (i.e. C6 and C8) of the A-rings were shown to participate as the reactive sites (Fig.) [2].

Metal complexation

Among the hydrolysable tannins, chestnut and tara are the most widely used tannins. It is well established that the main component of tara tannin is a molecular species having galloylatedquinic acid structure (Fig.). In this galloylatedquinic acid structure, several units of gallic acids are linked to quinic acid via ester linkages (Fig.).

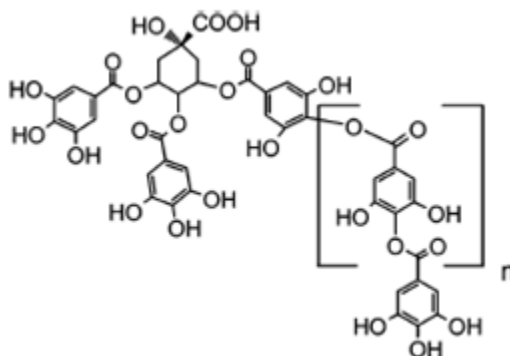


Figure X: Structure of a typical Tara gallotannin

Now-a-days, Titanium-tannin complex is used in the modern leather technology as an alternative of chromium tanning and as an effective modification of vegetable tanning. In fact, the major positive aspects of tanning by titanium-tannin complexes are that the titanium (IV) - tannin solution treated leather is very soft, flexible and possess good thermal stability. Surleva et al. (2014) synthesized and evaluated the structure of Titanium-tannin complexes suitable for leather manufacture [12]. It was proved by UV-Vis and IR spectrometry that the aromatic carboxylic oxygen (Ar-C=O) and probably phenolic oxygen of tannin are involved in coordination with titanium ion (TiO^{2+}). It was estimated that in a solid form the complex composition could be $[Ti(OH)_2TA]^+$ of which the structure of tannin part is depicted in Fig.

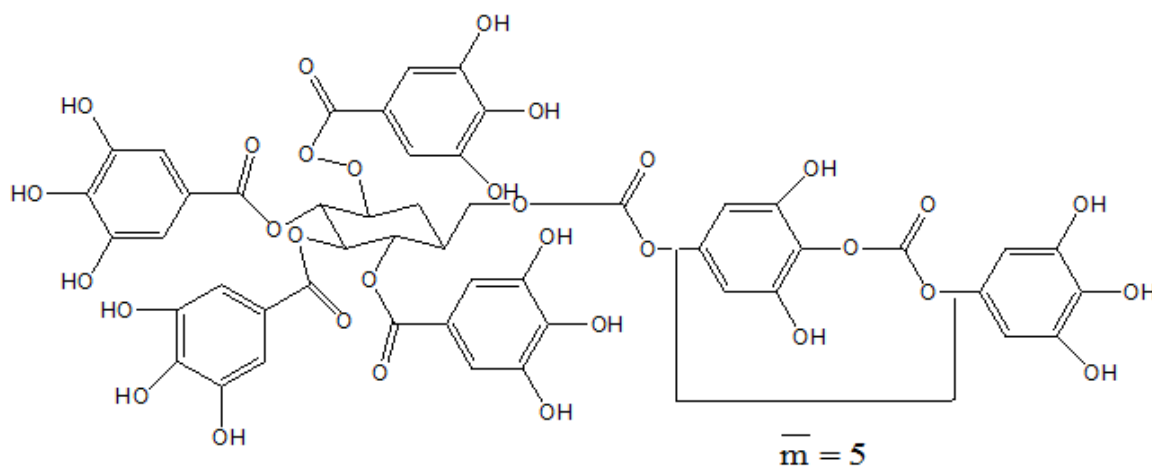


Fig.: Structure of the tannin [12]

Moreover, the titanium/tannin/formate solutions were also investigated to find out the major molecular species. Within the concentration ranging from 5×10^{-6} to 2×10^{-5} M and at pH = 4, the main titanium IV complex species is $TiO(OH)TA$. Earlier, Teng et al (2012) conducted a detailed study relating to the contribution of gallic acid content in the efficacy of combination tanning by different Ti (III) - tannic acid mixtures [13]. In this context, three different types of Ti (III) - tannic acid mixtures were prepared, in which the tannin parts were derived from *Acacia Mangium* tannin extract (no gallic acid), Oil Orange tannin extract (25% gallic acid) and Strawberry Tree tannin extract (40% gallic acid). The structures of three different tannins were depicted in Fig.

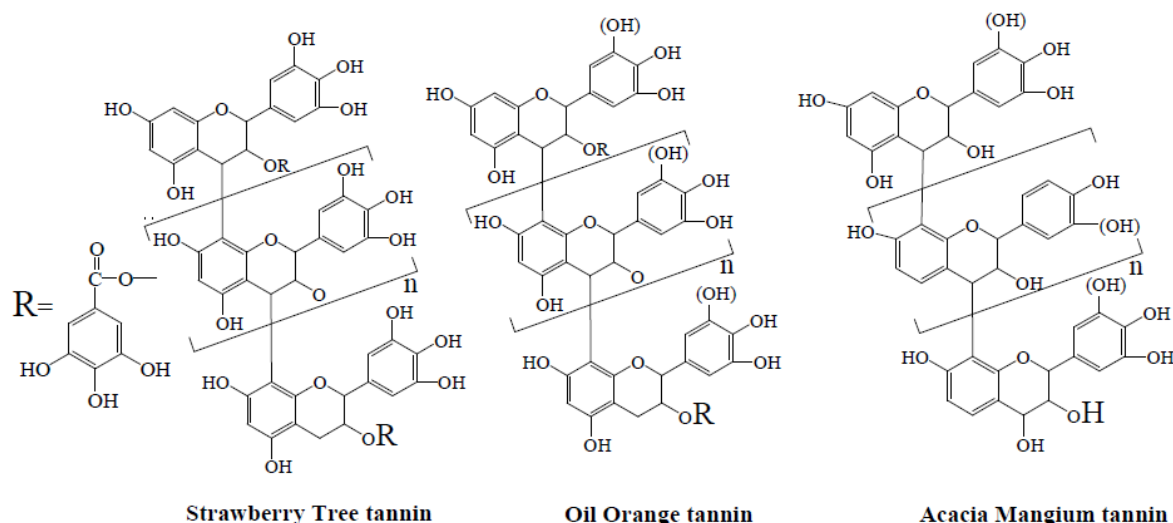


Figure 1. The structural characteristics of tannins (Chen et al., 2011)

Fig.: Structures of different tannins

All the three different Ti (III) – tannic acid mixtures, prepared from three different tannin extract containing variegated extent of gallic acid, were applied as tanning agents under different temperatures and pH conditions. It was observed that under different temperature and pH conditions, the complexation ability of tannin with Ti (III) improved when tannins contain higher portion of gallic acid. In fact, the tannin extracts containing more gallic acid, showed higher effective complexation indices and better complex forming tendency with Ti(III). Under tanning condition, the thermal stability of leather was directly dependent on the gallic acid content oftanninextracts. Basic structural unit of these tannin extracts was flavan-3-ol (Fig.), which reacted with metal ions through adjacent phenolic hydroxyl groups on B ring, thereby forming stable chelates (Fig.). In general, the ortho-dihydroxyl group on the flavonoid B-ring of condensed tannins is the main group involved in metal complexation [14]. Gallic acid group reacted with metal ions more readily through higher number of available hydroxyl groups present in the pyrogallol structure.

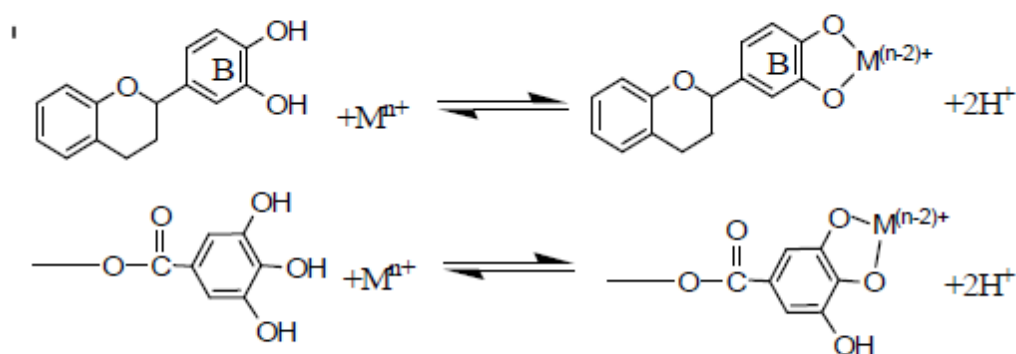


Figure 3. Reactions between tannin and metal ion

In this context, yellow colored Ti(IV)-wattle tannin complex can be used to caste a golden color on leather [14]. Also, the red-colored Mo(VI)wattle tannin complex has been used in a colorimetric method for tannin analysis. However, the formation of highly colored Fe(III)-tannin complexes can have negative features. In leather manufacture using vegetable tannins, any contact with iron surfaces (or if iron is a contaminant in the

water or other tanning chemicals) causes unsightly blue/grey stains. In these context, $\text{Fe}(\text{RH})^{-2}$ and $\text{Fe}(\text{RH})^{3-3}$ are the prevalent species that are present in the $\text{Fe}(\text{III})$ -Wattle Tannin Complexes. Fortunately, these can be removed with oxalic acid and/or EDTA. Another such problem is known as 'iron rot'. If for instance, iron nails are used in shoemaking with vegetable tanned leather, the protons released on iron-tannin complexation can cause acid hydrolysis of the hide protein.

Recently, in a Chinese patent (CN100355908C), claimed regarding fabrication of modified tara tannins via metal complexation of the raw tannins. In this regard, a series of chromium and sodium hydroxymethyl modified metal complexes were prepared through modification tara tannin extract. Application of such modified tara tannin resulted in generation of pale colored or white, soft, full eco-leathers of high strength. For instance, one attempt has been made related to chemical modification of concentrated tan liquor of tara by aluminum chloride. Initially, 100 parts of concentrated tannin extract of tara was added to a stainless steel reactor and the temperature of the extract was raised to 65 °C, followed by slow addition of 20% salt solution having 30 parts of methylsulfonate. Then the solution was heated up to 70°C and stirred for 3 h. Subsequently, the solution is cooled down to below 40°C and 3.5 parts of aluminum chloride was added. Thereafter, the mixture was stirred for 30 minutes and then spray dried to produce grey colored powder of modified Tara tanning agent. In another attempt, white colored modified Tara tanning agent was prepared by complexation with 4 parts of aluminum sulfate. In addition, another two greyish white colored modified Tara tanning agents were prepared by applying aluminium alum and zinc sulfate as complexing agents. In this regard, Al (III) does readily form complexes with numerous biomolecules, limiting the free ion concentration in solution due to interactions with O^{-} , (O,N), and (O,N,P)-containing molecular substrates, including citrate, quinate and phosphonate [8]. Therefore, complexation of Al(III) with quinate moieties of tara tannins is highly probable, leading modification of tara tannins by aluminium alum, aluminum sulfate and aluminum chloride.

Modification by sulfanilic acid

Hou and Lv (2012) studied the tanning properties of sulfanilic acid modified tannic acid and the modification was conducted by means of Horseradish Peroxidase and hydrogen peroxide (H_2O_2).

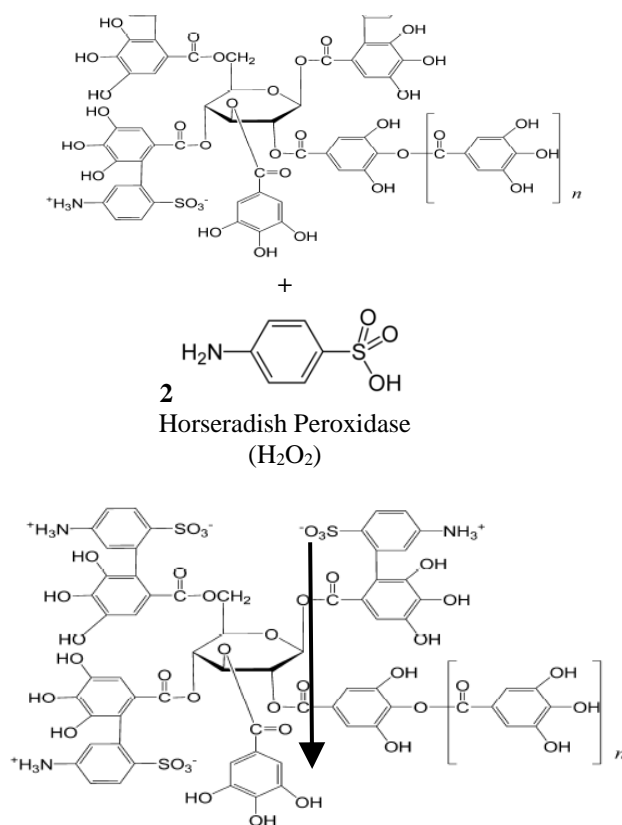


Fig.: Structure of sulfanilic acid modified tannic acid [11]

At the time of modification of tannic acid, active presence of H_2O_2 is essentially required for the catalytic oxidation of various organic substrates by horseradish peroxidase. In fact, horseradish peroxidase is a heme-containing peroxidase type metalloenzyme that functions as an oxidoreductase which catalyses the reductive cleavage of hydrogen peroxide by an electron donor. In this context, the pH of the system was

adjusted to 8.0 by sodium bicarbonate. However, the pH optimum of HRP is in the range of 6.0 - 6.5 and activity at pH = 7.5 is 84% of the maximum. Therefore, maximum catalytic effect was not sought at the time of synthesis. Nevertheless, in any case, the temperature during enzyme-assisted modification was not raised beyond 37 °C. Notably, in the structure of modified tannic acid, the galloyl moieties of the tannic acid were linked with aromatic ring of sulfanilic acid via C-C linkages. However, the presence of such C-C linkages was not detected comprehensively by FTIR. Nevertheless, the solubility of the modified vegetable tannin in water was increased owing to incorporation of sulfonate group(s) in the modified tannic acid structure [11]. However, the shrinkage temperature of the modified tannin acid treated leather was noted to be slightly less than the tannic acid treated leather (Table: Properties). This is expected since the tanning potential of the modified tannic acid was affected by the enhanced solubilizing effect by the incorporated sulfonate groups. However, when this modified vegetable tannin was applied in combination with either aluminium tanning agent [Al₂(SO₄)₃, 18H₂O] or chromium tanning agent [Cr(SO₄)₃, 6H₂O], enormous escalation of shrinkage temperature was noted in combination tanned leathers. Such enhanced shrinkage temperature was possibly attributed to the formation of stable cross-links which involves the following: 1) interaction of either aluminum or chromium complexes with the neighbouring-OHs of tannic acid to produce a stable five-membered ring and 2) usual coordination of either aluminum or chromium complexes with -COO⁻ of collagen. Nature of such complexation among aluminium tanning agent, collagen and vegetable tannins was also responsible behind the hydrothermal stability or shrinkage temperature of the combination tanned leather. Most likely, stable crosslinks should be formed of the tanning agents moieties arranged in the following sequences favourable for increasing the shrinkage temperature:

1. **Collagen-Al-Veg-Al-Collagen**

2. **Collagen-Veg-Al-Collagen**

However, such enhancement in shrinkage temperature would not be possible if the moieties are arranged in the following sequential crosslink:

3. **Collagen-Veg-Al-Veg-Collagen**

This implies that the direct attachment of collagen with aluminium tanning agent is essentially required to enhance the shrinkage temperature. In sequence 3, since the aluminium tanning agent is indirectly attached to collagen and the attachment of vegetable tannin with collagen is not strong, the moist heat and water molecules can easily cleave the weak joints between collagen and vegetable tannin, leading to easier rupture of these crosslinks. Impressive enhancement in shrinkage temperature was resulted when garad-Al combination tanning was performed. Indeed, shrinkage temperature of the garad-Al combination tanned leather was further improved when garad treatment was followed by Al₂O₃additon, as compared to the combination tanning performed in the reverse sequence, i.e., Al₂O₃additon was followed by garad treatment (Table: Properties) [15]. Though the authors have not cited any reason behind such improvement, it is most likely that the crosslinks of sequence 1 and/or sequence 2 types were more preferably formed inside the garad-Al combination tanned leather when garad treatment was followed by Al₂O₃additon. However, it was observed that the shrinkage temperature of THPS (TetrakisHydroxymethylPhosphoniumSulphate)-Tara tanned leather was comparatively higher than that of Tara-THPS tanned leather [16]. The combination tanning system using Tara and THPS results in leathers with reduced or absence of free formaldehyde in crust stage when compared to leathers tanned with THPS alone. Thus, Tara as a combination tanning agent with THPS not only improves the leather properties but also can act as a scavenger of free formaldehyde present in THPS tanned leather. Free formaldehyde scavenging action of tara tannin can be explained from the fact that the galloyl ester components of tara tannins might be reacted with the formaldehyde present in THPS tanned leather, and thereby the free formaldehyde components might be converted to bound formaldehyde. In fact, the pods of *Caesalpinia spinosa* (tara) yield an important amount of hydrolyzable tannins that could react with formaldehyde under certain conditions [17]. Thus, formaldehyde reaction can be possible at the ortho position of a sufficiently large number of galloylated rings of tara tannins.

Mannich reaction

A group of researchers have successfully prepared vinyl modified tannins by grafting the methacrylate-acrylamide based copolymer with tannins via Mannich reaction [19]. The authors have confirmed the Mannich reaction based vinyl modification of tannins by FTIR, and thereafter, comparative studies were conducted between a full chrome leather, tanned by 8 % BCS, with the combination tanned leather tanned by 6 wt% vinyl modified tannins and 2 wt% BCS. A significant improvement in tearing strength has been observed in the combination tanned leather with respect to the conventional full chrome leather, along with a marginal increment in tensile strength (Table properties). In this regard, the coordinate bonding among macromolecules and the chromium complexes can produce improved tensile and tearing strengths in the combination tanned material containing strengthened crosslinks. Moreover, considerably enhanced thickness of the combination tanned leather over full chrome leather indicates the greater fullness of the combination tanned leather containing long

macromolecules of vinyl modified tannins. However, the shrinkage temperature of the combination tanned leather has still remained inferior to that of the full chrome leather.

II. CONCLUSION

Chemical modification of vegetable tannin is becoming increasingly popular because of its several advantages including enhanced penetration, uniformity in distribution, reduced risk of casehardening, and bringing about the desired mellowness in reactivity. Thus, chemical modification of tannins can be achieved via diverse ex-situ approaches consisting of numerous reactions, such as sulfonation, sulfomethylation, aldehyde treatment, Metal complexation, sulfanilic acid functionalization, and Mannich reaction, to obtain suitable tanning agents for leather manufacture. In near future, the synthesis and application of chemically modified vegetable tannins will be one of the notable fields of study in the leather and allied sectors.

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