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TANNIN DERIVATIVES AS POTENTIAL MATERIALS: A REVIEW

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ABSTRACT

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<p>Biobased materials are leading a new trend in the development of potential applications nowadays. In this connection, sustainable green chemistry is promoted in public awareness. One of the best candidates in this concept is tannin derivatives which should not be neglected. With excellent properties related to biological, mechanical, physical, and chemical characteristics, tannin-based materials have been designed to gradually replace toxic fossil-based raw materials in certain applications. To fulfill and develop such a new formulation of tannin characteristics, condensed tannins are paid more attention due to their market and applicability.</p> <p>Apparently, the diversity of tannin derivatives is spread over a vast number of its application from pharmaceutical and nutraceutical applications to the leather manufacturing and beverage sectors. However, in the realm of tannin chemistry, there are a few promising applications which are not yet commercialized. As an example, tannin-based wood adhesives can be used to replace hazardous synthetic compounds, thereby eliminating the emissions of volatile organic substances and formaldehyde compounds. Furthermore, tannin derivatives can also be synthesized with other compounds to enhance the bio-durability properties of wood in the preservative industry. Additionally, tannin-based foaming materials can be used in the construction industry, especially insulating materials, to improve fire resistance and water repellence. Moreover, certain drawbacks in applying tannins to new promising applications are highlighted, from which further research can be conducted in the future.</p> <p>The thesis topic was taken from the Green Bioraff Solutions (GBS) project from Research and Development of Centria University of Applied Sciences. The object of this study is to stand a chance of gaining a deeper insight into tannins in the field of tannin chemistry. Furthermore, the focus of this study will be to exploit the potential applications of tannin derivatives based on the literature review, and thus no laboratory work is required in this report.</p>		

<p>Key words tannin derivatives, condensed tannins, tannin foams, tannin-based adhesives, tannin-based preservatives, winemaking, tannin market</p>
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ABSTRACT

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1 INTRODUCTION

The rise of public awareness relating to the environment and human health has resulted in seeking and developing cleaner and more sustainable alternative materials for synthetic products. Many studies have been conducted to find out the best materials that it aims to achieve the green chemistry concept, coupled with bringing better quality on potential applications. With this end in view, tannins have been analyzed and determined as one of the best choices in terms of sustainable chemistry concept, for tannins can act as substitute alternatives to hazardous compounds in recently emerging industries (Singh & Kumar 2019). For example, glue wood products used in manufacturing furniture and construction are reported, in which tannins are applied to react with aldehydes and other reagents. The more tannins are applied in the chemical formulation, the fewer toxic compounds are used in the product. (Norström, Demircan, Fogelström, Khabbaz & Malmström 2017.)

Tannins are well known by the name phenolic compounds naturally extracted from sustainable sources, in which they can be found in different plant tissues. Moreover, on account of their biological activities, tannins are also defined as bioactive compounds, applying in the manufacturing of pharmaceutical and nutraceutical products (Das, Islam, Faruk, Ashaduzzaman, Dungani, Rosamah, Hartati & Rumidatul 2019). Besides, the ability to interact with carbohydrates, proteins, enzymes, polysaccharides, and bacterial cell membranes are highlighted of their biochemical traits (Aldred 2009, 163). It is interesting to note that different plant species are results of the production of the different chemical structures of tannins, thus making compounds more difficult in the concept of polyphenol analysis. It is estimated that there are currently more than 8000 different tannins that being determined and characterized; however, that is a very incomplete part of the picture in the field of tannin chemistry. According to the University of Turku, tannin definition based on both biochemical and chemical hypotheses can be acceptable, but a leap into more correct clarification of tannins should be based on their chemical structures. (Krzyzowska, Tomaszewska, Soliwoda, Bien, Orłowski, Celichowski & Grobelny 2017, 336.)

In the realm of tannin chemistry, tannin derivatives are not yet commercial. While it is widely claimed to bring significant benefits to each potential application in terms of sustainable chemical materials and environmental-friendly compounds, it is interestingly refuted by facts that there are yet certain drawbacks and a vague acknowledgment of this sector. This study aims to make use of published literature in dissecting the meanings of tannins in new potential applications.

2 CONCEPT OF TANNINS

The word “tannin” derives inherently from the Celtic word for “oak” (Hagerman 2002), in which the name “tannin” officially has attributed to the tanning process in leather production. In this connection, tannins have been used and acknowledged for more than 400 years. Tapping into this requires a flashback to the tannins’ historical time when tannins were recognized as astringent compounds by an Italian chemist named Giovannetti in the 17th century. Many researches had been put forward in identifying the acid properties in these compounds in 1772. Soon thereafter, gallic acid was successfully extracted from these compounds by Scheele. Tannins are officially recognized as a distinct group based on their gallic acid content in the early 19th century by Proust. The era of the tannin extraction industry took place in 1850 in Lyon, France as coloring agent compounds in the fashion industry (Caller 1989 [Pizzi 2019a, 2]). In addition to the fashion industry, tannin applications have applied in the leather industry, due to its less time-consuming. The explosion in demand for tannin had a result in the establishment of manufactories in South America, and Southern and Central African in the early 20th century when the material supplies were short in Europe. However, the tannin extraction industry had undergone many drastic changes after World War II, when tannins gradually were substituted by synthetic materials in the leather industry, led to a cut in tannin production. With the continuous innovation and development, tannins today again have revived and attracted the public attention as regards the sustainable bio-sourced materials that apply in a wide range of different fields, namely medicine, construction, wood-adhesive, plant protecting agent, and other applications. (Pizzi 2019a, 1980.)

Tannins are classified as one of the subclasses of the polyphenol group, along with lignans, flavonoids, and stilbenes (Tuutti 2019, 7). Having an astringent property and a molar weight higher than 500 g/mol, tannins are often so-called substituted complex phenolics which are soluble in water, due to their chemical structures. Ashok and Upadhyaya (2012, 45) concluded that tannins exist under shapeless yellowish or light brown powder, and the astringent property of tannins creates a dryness and pucker sense as same as tasting strong tea or red wine or unripe fruit. Tannins are found in each cytoplasm of vegetable cells (Haslam 1989), thus presenting in different parts of plants, including seeds, roots, bark, wood, and leaves. In this connection, tannins play an essential role in protecting plants from natural enemies, inherently involved phenolic compounds by reason of secondary metabolites. The protein interaction and precipitation mechanism of tannins additionally cause a dramatic reduction from microorganisms such as bacteria and fungi. (Swanson 2003, 5729-5730; McGee 2004; Pizzi 2019a, 2.). More than what has mentioned above, a profound understanding of tannins is provided in this chapter.

2.1 Distribution of Tannin Resources

Since tannins are made famous by their wide distribution in different parts of the plant species, tannin resources are classified in distinct means either by plant localization or plant genus. To classify and clarify the occurrence of tannins, a few approaches are briefly mentioned here. The first distribution is based on the naturally synthesized processing of tannins in plant tissues (TABLE 1) (Ashok & Upadhyaya 2012, 46-47; Hamilton-Miller 1995, 2375-2377). The table shows where tannins are synthesized in different parts of plant materials, along with their fundamental roles in plant protection.

TABLE 1. Tannin availability and role in different position of plant tissues (Ashok & Upadhyaya 2012, 46-47; Hamilton-Miller 1995, 2375-2377)

Plant parts containing tannins	Position in plant	Role in plant
Bud tissues	The outer part of the bud	Freezing protection agents
Leaf tissues	The upper epidermis of leaves	Protection against herbivores
Root tissues	The hypodermis	Chemical barrier against pathogens
Seed tissues	The layer between the outer integument and the aleuronic layer	Creating allopathic and bactericidal agents by cooperating with the maintenance of plant dormancy
Stem tissues	The growth areas of the trees (the secondary phloem, xylem, and the layer between epidermis and cortex) and heartwood	Regulating the growth of the tree and countering the microbial activities

Another distribution approach is to describe the tannins' occurrence based on the plant species (TABLE 2). This table also based on tannins' chemical structures and wood types, briefly shows the plant species containing tannins in categories. However, it is undeniable that the numbers of plant species will be overlooked (see TABLE 2), especially softwood species which require further research. Therefore, the list contains mostly hardwood species and few different classes of tannins. (Das et al. 2019, 2-11; Tuutti 2019, 10-25; Kar 2003, 44; Kohmura, Nio & Ariyoshi 1990, 1991 [Garson 2010, 510].)

TABLE 2. Plant species containing tannins in different categories (Das et al. 2019, 2-11; Tuutti 2019, 10-25; Kar 2003, 44; Kohmura et al. 1990, 1991[Garson 2010, 510].)

Distribution	Condensed tannins	Hydrolysable tannins
Hardwood	Casuarina; Salix; Betula; Castanea, Lithocarpus, Quercus; Persea; Prunus; Acacia, Cassia, Robinia; Carapa, Xylocarpus; Excoecaria; Astronium, Rhus, Schinopsis; Camptostemon; Heritiera; Hopea; Pemphis; Sonneratia; Bruguiera, Carallia, Ceriops, Candelaria, Rhizophora; Laguncularia; Eucalyptus, Tristania; Avicennia	Casuarina; Pterocarya; Alnus, Carpinus; Castanea, Nothofagus, Quercus; Nuytsia; Nuphar; Cercidiphyllum; Drosera; Francoa, Ribes; Liquidambar; Rosoideae (Geum, Fragaria, Potentilla, Rosa, Rubus); Pterocarpus (Caesalpinia); Geranium; Tetratheca; Acalypha, Euphorbia, Ricinus; Empetrum; Coriaria; Cyrilla; Corynocarpus; Acer monspessulanum (A.ginnala); Greyia, Melianthus; Vitis; Aristotelia; Camellia, Cleyara, Gordonia, Thea; Frankenia; Tamarix; Bixa; Stachyurus; Elaeagnus, Hippophae; Lagerstroemia, Lythrum; Punica; Cassipourea (Rhizophora); Combretum (Terminalia); Agonis, Angophora, Callistemon, Eucalyptus, Eugenia, Melaleuca, Metrosideros, Myrtus, Psidium; Bertolonia, Heterocentron, Medinilla, Tibouchina; Dircaea, Fuchsia, Jussieua, Lopezia, Oenothera; Gunnera, Haloragis, Myriophyllum; Arbutus (Arctostaphylos & Vaccinium); Galax; Centropogon; Tagetes; Hypoxis
Softwood	Spruce, Pine	
	Phlorotannins	Pseudo tannins
Different classes	Brown algae (Fucus vesiculosus)	Gallic acid (Rhubarb); Catechins (Acacia, catechu, cocoa, guarana); Chlorogenic acid (Nuxvomica, coffee, mate); Ipecacuanhic acid (Ipecacuanha)

Due to the prevalence of hydrolysable tannins in nature, several plant spices are introduced to the commercial sides, which contributes to developing potential applications. Das and his co-workers (2019, 10) introduced the occurrence of commercial hydrolysable tannins, aiming to make hydrolysable tannins more noticeable in the realm of tannin chemistry. After being illustrated from the previous distribution (see TABLE 1) and (see TABLE 2), tannin resource of some native species is presented in both plant material and plant name. (TABLE 3). (Das et al. 2019, 2-11.)

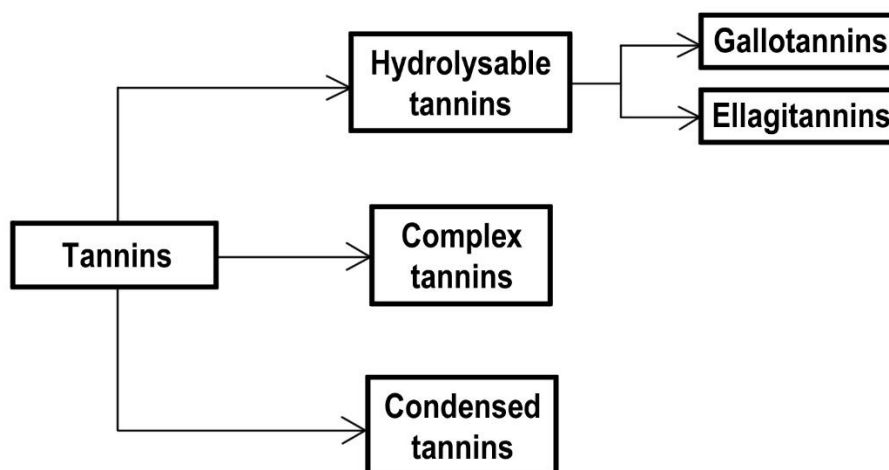
TABLE 3. Occurrence of commercial hydrolysable tannins (Das et al. 2019, 2-11.)

Name	Family	Genus	Plant Material
Chinese tannin	Anacardiaceae	Rhus semialata	Galls on leaves
Sumac tannin	Anacardiaceae	Rhus coriaria	Leaves
Myrobalans	Combretaceae	Terminalia chebula	Fruit
Turkish tannin	Fagaceae	Quercus infectoria	Galls on wood
Valonea extract	Fagaceae	Quercus valonea or Q.macrolepis	Acorn cups
Oak extract	Fagaceae	Quercus species	Wood
Chestnut extract	Fagaceae	Castanea sativa and C.dentata	Wood
Tara extract	Leguminosae	Caesalpinia spinosa	Pods
Divi-divi	Leguminosae	Caesalpinia coriaria	Pods
Algarobilla extract	Leguminosae	Caesalpinia brevifolia	Pods

2.2 Classifications and Characterizations of Tannins

Classifying tannins has more than one method in tannin chemistry; however, the two most well-known classifications of tannins are based on either chemical structures or plant formations. To present the different structural characteristics of tannins in plant species, tannins commonly are divided into two main groups, namely hydrolysable and condensed tannins (GRAPH 1). The graph additionally shows the subclasses of hydrolysable tannins, namely gallotannins and ellagitannins, along with the presence of a special class so-called complex tannins. A more detail of this classification approach can be seen in Table 4, where chemical structures of different tannins are presented. (Arbenz & Avérous 2015, 2627; Singh & Kumar 2019, 3.). Another classification of tannins based on the plant formations should not be overlooked, in which there are vascular plant tannins and non-vascular plant tannins. In other words,

this method divides tannins into three main groups, including hydrolysable tannins, condensed tannins, and phlorotannins. No matter how complicated tannin classifications are at times, professionals can point out the definition of each type of tannin (Arbenz & Avérous 2015, 2627-2629; Singh & Kumar 2019,1.)



GRAPH 1. Tannins classification based on their structural characteristics (Adapted from Arbenz & Avérous 2015, 2627)

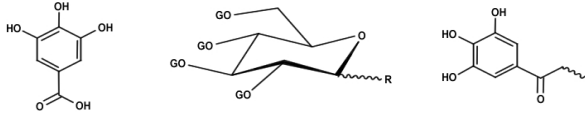
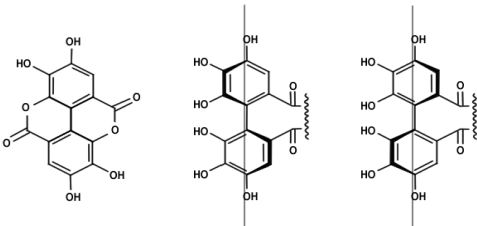
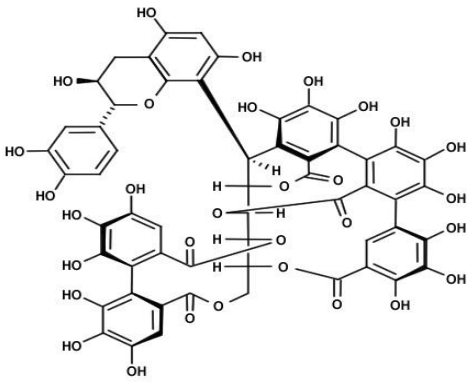
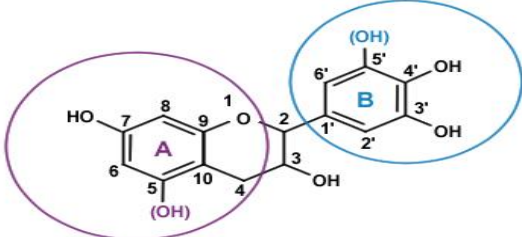
2.2.1 Hydrolysable tannins

Hagerman's definition (2002) concluded that gallic acid derivatives are hydrolysable tannins, in which galloyl units are inclined to esterify to a core polyol to form hydrolysable tannins. In other words, hydrolysable tannins are formed from a glucose with either trihydroxybenzoic acid units (gallic acid) or hexahydroxydiphenic acid units (ellagic acids). Gallic and ellagic acids and sugars can be obtained back from hydrolysable tannins by hydrolysis processing (Sjöström 1993, 105). Hydrolysable tannin occurrences are a wide distribution in nature (see TABLE 2). While some are rich in natural resources for the tannin extraction industry (see TABLE 3), it is claimed that hydrolysable tannin production has nearly only 10 percent of the world's commercial production due to its high price. (Arbenz & Avérous 2015, 2627; Singh & Kumar 2019, 3.)

The biosynthesis of both gallotannins and ellagitannins takes place either independently or together in plants with a high percentage found in angiosperms and dicots (Singh & Kumar 2019, 3). Gallotannins are one of the subclasses of hydrolysable tannins originally obtained by substituting galloyl units either

partly or completely to the hydroxy (OH) of a polyol residue. Typical examples of gallotannins are tetragalloylglucose (TGG) and pentagalloyl glucose (β -PGG) (TABLE 4). Pentagalloyl glucose is so-called 1,2,3,4,6-penta-O-galloyl- β -D-glucopyranose, having five similar ester linkages which are associated with the hydroxyl groups of the sugar. Although β -PGG has different structural characteristics compared with TGG, along with the diversity in the chemical and biochemical properties (see TABLE 4), having molecular weights (940 g/mol). The popularity of ellagitannins in the tannin industry lies in the power of their numerous natural products. Ellagitannins are obtained after oxidative coupling reactions between galloyl units from gallotannins, which inherently has resulted in the establishment of monomeric of ellagitannin with an axis of chirality. This biaryl axis (HHDP) then is esterified with a polyol residue to form ellagitannin. The general structure of this biaryl unit (hexahydroxydiphenoyl) is considered as the first stage of oxidation reactions of ellagitannins (see TABLE 4). By lactonizing in an aqueous solution, ellagic acid can be obtained from HHDP. (Arbenz & Avérous 2015, 2627; Hagerman 2002.)

TABLE 4. Classification of tannins (Adapted from Arbenz & Avérous 2015, 2628)

Type of tannins	Example of structures
Hydrolysable tannins	<p data-bbox="400 416 564 450">Gallotannins</p> <div data-bbox="730 465 1318 645">  <p data-bbox="754 611 823 633">gallic acid</p> <p data-bbox="932 600 1102 645">R = α, β-OH (1) TGG R = β-OG (2) β-PGG</p> <p data-bbox="1171 611 1273 633">G = Galloyl unit</p> </div> <p data-bbox="400 797 571 831">Ellagitannins</p> <div data-bbox="730 689 1209 976">  <p data-bbox="762 936 837 958">ellagic acid</p> <p data-bbox="932 925 1002 947">biaryl axis</p> <p data-bbox="1102 925 1177 947">biaryl axis</p> <p data-bbox="1007 947 1086 969">(3) HHDP</p> </div>
Complex tannins	 <p data-bbox="914 1491 1034 1514">acutissimin A</p>
Condensed tannins	 <p data-bbox="767 1933 1098 1955">Structure of monoflavonoid</p>

2.2.2 Condensed tannins

Needless to mention, condensed tannins are the eye of the storm in the tannins industry, since there has been a growing trend toward the worldwide production of commercial tannins, which has accounted for more than 90 percents. Unlike hydrolysable tannins, condensed tannins do not contain any sugar residues, having a stronger resistance against microbial degradation and bringing more advantages in bio-activities, such as antibacterial, antiviral, and antifungal properties (Krzyzowska et al. 2017, 336; Aldred 2009, 163). Proanthocyanidins is another name of condensed tannins, due to their ability to generate anthocyanidins under an oxidative cleavage mechanism in hot alcohol solutions. Condensed tannins are defined as polymers of flavonoids, found mostly in mimosa, quebracho, mangrove, hemlock, and other plant species (see TABLE 2) (Sjöström 1993, 105). In other words, condensed tannins are produced by the result of combined flavonoid units, with a range from 3 to 8 flavonoids. Researches on flavonoid units nowadays are based on flavan-3-ol and flavan-3,4-diol, which are precursors of condensed tannins. Flavan-3-ol is divided into (-)-epicatechin and (+)-catechin (FIGURE 1). (Das et al. 2019, 2-6; Arbenz & Avérous 2015, 2628-2629; Hagerman 2002.)

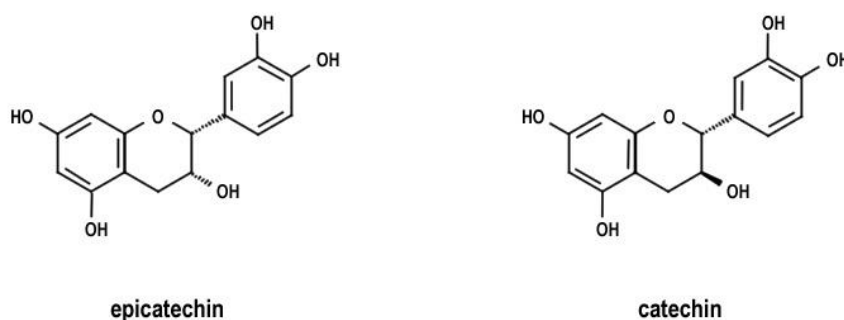


FIGURE 1. Flavan-3-ol subclasses (Adapted from Hagerman 2002)

There are two phenolic rings, which include A-ring and B-ring with different reactivities and exist in each flavonoid. As a result, the products of biosynthesis from condensed tannins are variable based on their flavonoid units (Aldred 2009, 163). The simple structure of condensed tannins is monoflavonoid, in which it includes or excludes (OH) in positions 5 and 5' (see TABLE 4). With the change of position of hydroxyl radical in both rings, this leads to the forming of four possibilities (FIGURE 2). Figure 2 indicates that there are resorcinol and phloroglucinol figurations in the A-ring, while the B-ring includes

catechol and pyrogallol figurations. All four different blocks, namely profisetidin, procyanidin, prorobinetidin, and prodelphinidin, accounts for 65 to 84 percentage of the composition of mimosa bark extraction, while the rest is known as non-tannins (Braghirolo, Amaral-Labat, Boss, Lacoste & Pizzi 2019, 3). Moreover, the nature of the rings has an influence on forming the bonds between flavonoid units. The nucleophile strength at the position of C6 and C8 is the result of the resonance structure caused by the resorcinol ring and the oxygen in the heterocycle, leading to a high active property in A-ring compared to B-ring. Furthermore, this resonance structure has resulted in forming bonds in condensed tannins via C4-C6 or C4-C8 positions. While C4-C6 positions are noted primarily in profisetidins and prorobinetidins, C4-C8 positions are reported mainly in procyanidins and prodelphinidins. (Das et al. 2019, 2-6; Arbenz & Avérous 2015, 2628-2629; Hagerman 2002.)

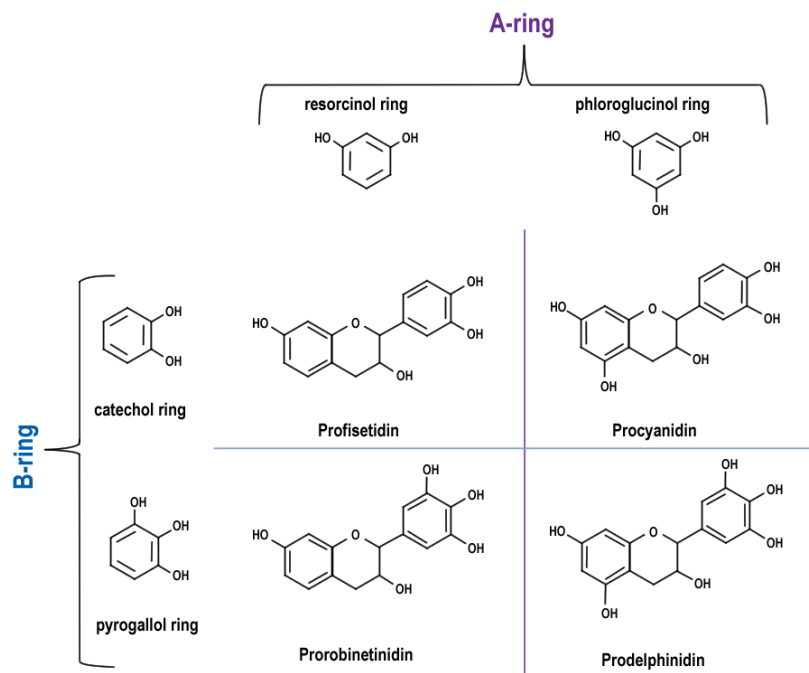


FIGURE 2. Monoflavonoid structures with four different possibilities (Adapted from Arbenz & Avérous 2015, 2629)

2.2.3 Other tannin types

The formation of complex tannins is a result of biosynthesis from either a gallotannin unit or an ellagitannin unit with a catechin unit (Khanbabaee & Ree 2001, 647; Oduka & Ito 2011, 2191-2217 [Sieniawska & Baj 2016, 202]). It is undeniable that the chemical structure of complex tannins is more difficult

to analyze compared to other tannins. To be specific, acutissimin A (TABLE 4) shows complex linkages between units, where a flavagallonyl unit is associated to a polyol originated from D-glucose by a glycosidic bond in C-1 and three other ester bonds (Ferreira & Bekker 1996, 411-433 [Arbenz & Avérous 2015, 2627-2628]).

Unlike vascular plant tannins, phlorotannins are found mostly in sea plants. There is a widespread belief that the major source of phlorotannin constituent is found in brown algae. The function of phlorotannins is to support the sea plant structure and behave as photoprotective agents. Furthermore, phlorotannins from brown algae are used in medicine and cosmetic applications owing to their bioactivities, such as antioxidant, antidiabetic, anti-inflammatory, and antitumor properties (Singh & Kumar 2019, 1). Having a broad range of molecular weight from 126 to 650000 g per mol, phlorotannins are generated by the polymerization of phloroglucinol. Phloroglucinol in sea plants is obtained from the condensation of acetate and malonate by an enzymatic reaction, leading to the difference in the biosynthesis route of phlorotannins compared to other usual tannins. In terms of classification by linkages, Singh and Bharate (2006) divided phlorotannins into four subclasses, namely ether bonds, ether and phenyl bonds, phenyl bonds, and dibenzo-p-dioxin bonds. (Arbenz & Avérous 2015, 2629; Garson 2010, 510.)

It is interesting to note that there is another subgroup of tannin with low molecular weights, and they are called pseudotannins. Some of pseudotannins obtain astringent properties as true tannins, but they are not considered as a tannin group. The origin of pseudotannins comes from cinnamic acid and their distribution in nature (TABLE 2). To indicate the presence of tannins in animal hides, the goldbeater's skin test normally is applied; however, pseudotannins show an inert property to the test. Typical examples of pseudotannins are gallic acid, catechin, and chlorogenic acid, in which their chemical structures are highlighted (FIGURE 3). (Aldred 2009, 164-165 & 338; Ashok & Upadhyaya 2012,48.)

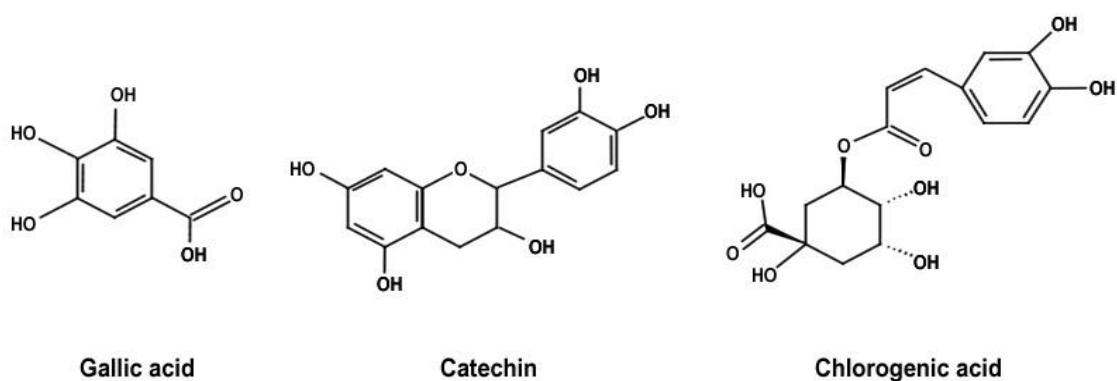


FIGURE 3. The chemical structures of some pseudotannins (Adapted from Aldred 2009, 164)

2.3 Isolation of Tannins

Tannins are considered as the most extractive materials from biomass after cellulose, hemicellulose, and lignin (Arbenz & Avérous 2015, 2626). Besides, different plant materials and species provide manufacturers different tannins' concentrations for the end-products before and after extraction. To be specific, tannins account only for 5 to 12 percent in the oak heartwood before extraction processes, while the rest is composed of cellulose, hemicellulose, and lignin. Ellagitannins contain primarily in the heartwood extractives, as well as the presence of other extractives. The constituent of these compounds in heartwoods is variable concerning the lifespan of the tree and wood tissues. For instance, the establishment of the insolubility of ellagitannins in the central of older heartwood is caused by polymerization. (Mosedale & Puech 2003, 394-395.). Furthermore, the well-known unstableness of phenolic compounds easily transforms themselves into different reaction products when the plant tissues are damaged (Izawa, Amino, Kohmura, Ueda & Kuroda 2010, 656). Therefore, the method generally in extracting tannins from plant tissues requires to be accurate, effective, and profitable, aiming to reduce loss in the extraction processes.

In the beginning of the 20th century, there is a popular process to extract tannins out of mimosa and quebracho species, which is known as sulfidation. Since sulfidation is one of the reactions of condensed tannins lowering tannins' viscosity and boosting tannins' solubility in water (Pizzi 1980; Roux 1965 [Braghirolo et al. 2019, 3-6]), the result shows a high percentage in extraction yield by 28-33%. The principle of sulfidation is summarized shortly into three steps. Firstly, crushing bark and wood chips after collecting are put into countercurrent industrial hot water (70-90 °C) with zero pressure. Secondly, small quantities of sodium sulfite or metabisulfite are added to the process, sometimes a small amount of sodium bicarbonate is applied to enhance the solubility of high molecular weight tannins. Finally, after being treated and flowed through stainless steel tanks, a low concentration of tannins is obtained prior to concentrating to 35% solids by spray drying or concentrating to 86% by vacuum drying and molding into a solid mass. It is claimed that adding urea into the stock solution will have a sharp increase in the yield content by 18-25%, and thus generating more profits, whereas the organic solvent is used in the post-treatment as a second purification for nutritional and pharmaceutical applications. (Braghirolo et al. 2019, 3-6; Sealy-Fisher & Pizzi 1992, 212-220.)

All in all, there are no rules in determining which method is the best suitable for extracting tannins, in which whether it is sulfidation extraction or new methods, namely, microwave, ultrasound, subcritical water, supercritical fluids, and other extraction methods (Dai & Mumper 2010). However, on top of that,

having an enormous influence on the extraction efficiency of tannins, certain parameters should not be overlooked, such as extraction method, time and temperature, chemicals used, and practice size of the sample. For example, water is used as solvent addition in traditional methods due to its applicability and availability, whereas acetone is applied to the process when dealing with high molecular weight tannins (Xu & Chang 2007, 159-166). In terms of time and temperature during extraction, high temperatures not only increase both the solubility and mass transfer rate, but also decrease viscosity of the solution. But treating the materials at high temperature for too long will decrease the yield extraction of tannins. (Shirmohammadli, Efhamisisi & Pizzi 2018, 317-318.)

2.4 Analysis of Tannins

The study of tannin analysis paves a wide pathway for professionals in understanding more about the characteristics of tannin compounds. Since tannin is a sub-group of polyphenols, tannin analysis involves the work of polyphenol analysis in general. According to the University of Turku, modern phytochemical methods today can be applied to determine individually tannin content in the plant tissues, applying to all the galloylglucoses and gallotannins, even to most of the ellagitannins. In fact, the biological activities of plant metabolites in tannins draw more public attraction in conducting research analysis. To illustrate, a high-performance liquid chromatography system with diode-array detection (HPLC-DAD) or ultra-high-performance liquid chromatography system with a diode array detector (UPLC-DAD) is capable of quantification for secondary metabolites in a plant. Besides, liquid chromatography- mass spectrometry (LC-MS) is used in case there is a presence of minor components overlapped by other major components in the chemical analysis. Such a case requires more concentration in conducting quantification; therefore, it is crucial to know what sample is quantified and what models of standards are used. In terms of condensed tannins and some polymeric ellagitannins, the works of quantification end up more intricate due to their molecular mass. But condensed tannins can be analyzed and characterized by the utilization of vanillin-HCl or protein precipitation methods. (Swanson 2003, 5730-5732; University of Turku.)

In the concept of polyphenol analysis, qualitative analysis is applied to decode biological functions of tannin characterization with the help of chromatographic techniques and mass spectrometry together. Professionals at the University of Turku (TU) conduct a polyphenol analysis research based on HPLC-DAD-QTOF-MS and UPLC-DAD-QQQ-MS, in which QTOF-MS and QQQ-MS represent quadrupole time-of-flight mass spectrometry and triple quadrupole mass spectrometry respectively. By applying

these techniques with the help of TU library of reference compounds, individual polyphenols are classified and interpreted into specific sub-groups. However, polyphenol purification is effectuated by gel chromatography with the support of preparative and semi-preparative LC when tannin identification is unsolved by phytochemistry and mass spectrometry techniques. In some special cases, new methods are carried out to analyze complex and large molecular tannins. In terms of quantitative analysis, various methods are capable of quantifying the original plant tissue in that the methods enable the determination of the concentration of the individual polyphenol. Beside traditional methods, UPLC-QQQ-MS/MS methods ensure the accuracy of the total polyphenol concentration. To quantify accurately as close as to the concentration of polyphenols in nature, multiple reaction monitoring (MRM) approaches are used, coupling with the authentic standards extracted from plants. However, the rapid transformation of tannin both in composition and concentration after collecting makes it impossible to match the quantitation in nature at the beginning. (Moilanen, Sinkkonen & Salminen 2013, 165-179; Engström, Päljjarvi, Fryganas, Grabber, Mueller-Harvey & Salminen 2014, 3390-3399 [University of Turku].)

Today there are numerous available methods in tannin analysis to determine the tannin characterization; however, tannin analysis not only faces limitations caused by the different responses of tannin compounds, but also finds difficulties in introducing a feasible appropriate standard. Differential response nominates the inability of a sample to represent a single value by its tannin level and rules out any single commercial compound as a universal standard. Although there are some problems needed to overcome to deepen more understanding of tannin characteristics, science today finds the answer in applying both qualitative and quantitative research when conducting tannin analysis with an innovation of phytochemistry and mass spectrometry methods. (Hagerman 2002.)

3 POTENTIAL UTILIZATION OF CONDENSED TANNINS

The focus of attention for bio-based materials today is increasingly growing in the works of R&D departments around the world, aiming to achieve fossils-based independence from raw materials. Beside other green materials, tannins have shown their unique capabilities and played a key role in developing new potential materials in view of their chemical structures, commercial and natural properties. (Luckeneder, Gavino, Kuchernig, Petutschnigg & Tondi 2016, 396.). But on top of that, condensed tannins draw more public attention than hydrolysable tannins with respect to commercial-scale and applicability. Leather tanning is not the only application of condensed tannins. Nowadays, there are various applications for condensed tannin derivatives relating to different fields, namely wood-laminating adhesives, construction materials, astringent products, protection agents, and other industries. Some applications of condensed tannin derivatives will be briefly highlighted in this chapter to provide an idea of their utilization.

3.1 Condensed tannin-sulfonate derivatives in wood-laminating adhesives

In the realm of wood adhesives, various synthetic adhesives are used to produce wood resin adhesives mostly accompanied by carcinogenic formaldehyde compounds. In this connection, they pose a considerable threat to the environment generally and human health specifically. To face this challenge, other alternative materials are put into effect. Without conducting research on new sustainable materials, bio-based materials, such as proteins, starch, other polysaccharides, lignin, and tannin, become negligible as potential alternatives. Yet applying food source materials, such as starch and protein, in the wood adhesive industry creates some ethical issues about food security in the world. (Norström et al. 2017, 50.). As a result, lignin and tannin-based materials today stand as a suitable candidate for changing the table, although only tannin-based adhesives are highlighted in this paper. Tannin-based adhesives have a better hardness ability compared to synthetic adhesives regarding the great linkages with other aldehydes or with different non-aldehyde hardeners, and lignocellulosic materials. Condensed tannins, particularly mimosa and quebracho-based tannins, have shown a great influence on reducing formaldehyde emissions. Additionally, mimosa tannin is considered the most successful material due to its ability to deal with different resin synthesis reactions and hyperactivity in wood adhesives. (Singh & Kumar 2019, 8.)

Yet another challenge when applying condensed tannins in the wood adhesive industry is the presence of non-tannins after extraction processes. For example, after being extracted from mimosa bark, the

polyphenolic pattern created by resorcinol A rings and pyrogallol B rings accounts for 70% of compositions, while the parallel pattern with the formation of resorcinol A rings and catechol B rings accounts for a quarter and the rest is known as non-tannins. These non-tannins exist under carbohydrates, hydrocolloid gums, and even a small amount of amino and imino acid fractions. (Pizzi 2003, 573-588). To a certain extent, these compounds have a negative influence on the properties of the adhesive resin. For example, carbohydrates weaken the actual solid content, and gums have an impact on the strength and water resistance ability of the resin adhesive. Therefore, certain methods, including hydrolysis and autocondensation, acidic intervention, and sulfonation, are introduced to modify condensed tannins. (Zhou & Du 2019, 4-9; Arbenz & Avérous 2005, 2632-2633.)

Sulfonation is capable of opening the heterocycle ring to modify tannin's molecular mass, which is known as the cleavage of the interflavonoid bond. By introducing sodium bisulfate to tannin under normal pH conditions, the heterocycle ring is opened to allow the addition of the sulfonate to position C-2 (FIGURE 4). After the reaction, tannin molecules are lightly degraded. On top of that, a sulfonation reaction with four mechanisms is used to increase the solubility and decrease the viscosity of tannin extracts. First step is the opening of the heterocycle ring. Second step is the addition of the sulfonate group and another hydroxyl group. Third step is the moderation in polymer rigidity, steric hindrance, and intermolecular hydrogen bonding. Final step is the hydrolysis of gums and interflavonoid bonds under acidic conditions. Yet the insertion of sulfonate group to the open ring increases the sensitivity to moisture, thereby leading to the substitution of it by an OH group under strong alkaline conditions. In that case, desulfonation is introduced with the involvement of 2,4,6-trihydroxybenzyl sulfonic acid under mild alkaline conditions. (Zhou & Du 2019, 4-9; Arbenz & Avérous 2005, 2632-2633.)

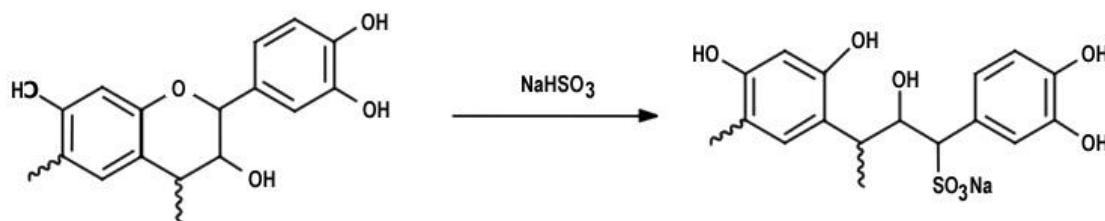


FIGURE 4. Sulfonation reaction of condensed tannin (Adapted from Arbenz & Avérous 2005, 2633)

In the preparation of resin adhesives, modified condensed tannins after sulfonation are cured with aldehyde, especially formaldehyde. The reaction of formaldehyde with condensed tannins take place primarily with the A-ring, which has resulted in the formation of methylene interlinks. Depending on the ring

type in A-ring, the reactive position with formaldehyde can be either C6 or C8 (FIGURE 5). While C6 reactive position belongs to the phloroglucinol ring, C8 reactive position is found in the resorcinol ring. In the reaction with aldehydes, B-ring, such as pyrogallol or catechol ring, is inclined to be less reactive because of hydroxyl substituents with nonlocalized effects compared to A-ring. In fact, anion formation affords the reactivity of the B-ring under high pH conditions, particularly pH of 10. Furthermore, the negative impacts of incomplete polymerization should not be overlooked, inherently resulting in the weakness and brittleness of the resin adhesives. Incomplete polymerization is the result of the immobility of tannin molecules at a low degree of condensation, and thus inhibiting the formation of methylene interlinks in the reaction. To tackle this, bridging agents are introduced to bridge the gap of available reactive sites. After curing with an aldehyde, modified condensed tannins go through setting either under high heat or at a room temperature in the preparation of wood applications. Tannin-based resin adhesives not only use as wood-laminating adhesives but also have a wide range of applications based on different settings, namely thermosetting and coldsetting. (Arbenz & Avérous 2005, 2634-2635; Zhou & Du 2019, 4-9, Pizzi 2003, 573-588.)

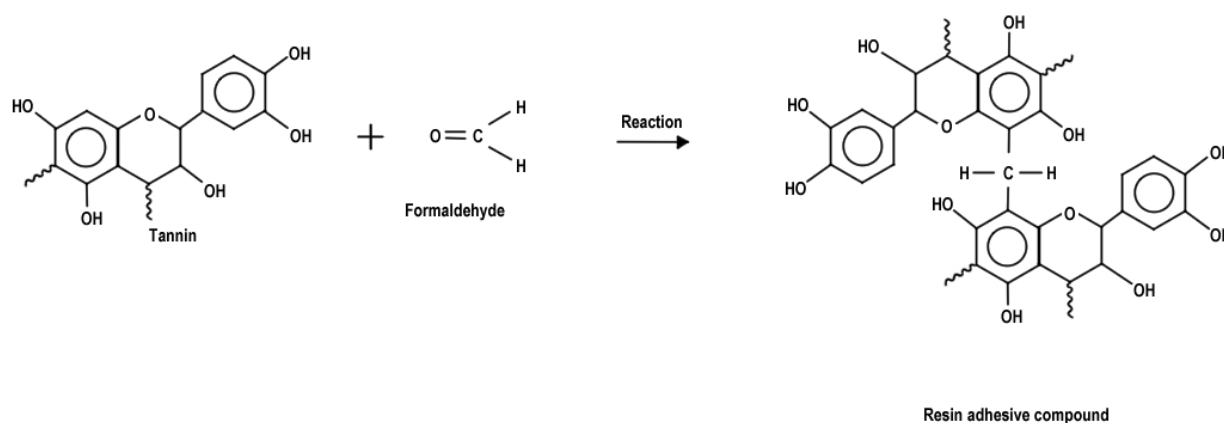


FIGURE 5. Reaction of condensed tannin with formaldehyde (Adapted from Arbenz & Avérous 2005, 2634)

The use of formaldehyde in producing resin adhesives is prevalent in the tannin industry owing to its ability to yield the fastest kinetics compared to other aldehydes. Using formaldehyde compound today is still under debate in causing harmful effects involving volatile organic compounds (VOCs) to the environment and human health, despite the attempts in lowering of formaldehyde emission by adding tannins. Not only formaldehyde, but also other curing agents, such as paraformaldehyde, hexamethylenetetramine, tris(hydroxymethyl)nitromethane, bring awareness to formaldehyde emissions (Kim &

Kim 2003, 1369-1383; Trosa & Pizzi 2001, 266-271). Many studies have been reported so far in limiting the use of formaldehyde by using glyoxal and hexamine as substituted alternatives to improve the quality of tannin-based adhesives. A study case of glyoxal, coupling with pine tannin, was carried out on wood panels. Although glyoxal showed a lower performance compared to a tannin-paraformaldehyde adhesive, it has no toxicity with a vast industrial manufacturing scale. Another study case in formaldehyde, tris(hydroxymethyl)nitromethane, along with potential alternatives, including glyoxal and hexamine as hardeners were carried out with chestnut tannins. The surprising outcome showed the highest curing enthalpy in applying hexamine as a hardener owing to its high crosslinking density. Besides glyoxal and hexamine, many attempts were proceeded in other aldehydes, including acetaldehyde, propionaldehyde, n-butyraldehyde, and furfural, to replace carcinogenic formaldehyde compound. Yet they resulted in poor adhesive properties for wood panels when formulating with mimosa tannins. But there are certain advantages properties to wood adhesives from potential alternatives, for example the water resistance of n-butyraldehyde. (Arbenz & Avérous 2005, 2640.). With this end in view, many studies are widely promoted in the future.

3.2 Tannin derivatives in wood protection and wooden composite

Tannin-based wood preservation makes a change to the wood industry as an optimal alternative, for wood products generally are easy prey for different insects, microorganisms, pathogens, and weather conditions. Tannin-based preservatives not only stand out with antibacterial, antiviral, and antifungal properties (Krzyszowska et al. 2017, 336; Aldred 2009, 163) but also reducing negative impacts on the environment and human health from substituting dangerous preservatives. With this end in view, many researches have been conducted to enhance the bio-durability properties and weather resistance properties with tannin-based preservatives in both main types of tannins, namely hydrolysable and condensed tannins. Yet it is reported that the antifungal property of condensed tannins in wood preservation is twice as intense as that of neat wood. Additionally, due to the ability of tannins to complex the protein, they successfully inhibit the biodegradation enzymes and the growth of pathogens. (Singh & Kumar 2019, 7-8; Shirmohammadli et al. 2018, 324; Zhou & Du 2019, 11-12.)

Many typical examples were carried out in the mixing of tannins and other compounds in enhancing the wood properties against natural enemies. When copper (II) ions were complexed with tannins obtained from *Pinus taeda*, it showed a significant effect against fungi (Laks, McKaig & Hemingway 1988). When mimosa tannin was treated with copper-ammonia complex, it prevented the natural decaying process

from fungal attacks for wood products (Yamaguchi & Okuda, 1998; Yamaguchi & Yoshino, 2001). Moreover, a study for impregnated wood was reported by Silveira and her co-workers in 2017, in which treating the amount 5% or 10% aqueous solution of mimosa tannin with impregnated wood made an improvement in the countering of white rotting fungus. Additionally, research on termiticidal properties of tannins (Tascioglu et al. 2012), showed that wood products treated with mimosa and quebracho tannins inhibit the invasion of underground termites under a high tannin content inside the wood by 80 to 100 kg per cubic meter of wood. (Shirmohammadli et al. 2018, 324.)

The innovation of combining hexamine and boric acid in tannin-based preservatives inside the wood was an enormous success, for it conveyed a resistance against microorganisms and herbivores even after aging periods (Tondi et al. 2012a, 2012b). Furthermore, this approach affords more water-repellent in wood products. Additionally, while studying the harden preservative of this mixture, researchers found a mechanical improvement and fire resistance in wood products (Tondi et al. 2012c, 2014). In terms of weather conditions, this approach showed high durability in manufacturing plywood panels used both in furniture and under humid conditions (Efhamisisi et al. 2016, 2017). The success of the formation of tannin-based preservatives, along with boric acid and hexamine, lied in the power of reducing in loss and exerting a good effect in wood preservatives; therefore, this approach fulfilled the requirements of the European standard EN 113 (Zhou & Du 2019, 11-12). (Shirmohammadli et al. 2018, 324.)

Yet there are certain challenges needed to overcome in the field of wood preservatives. Tondi and his co-workers (2013) concluded that tannin-based co-polymers treated woods still face degradation when exposing these products to weather-beaten conditions due to its aromaticity. Another study showed the change of color in beech wood samples treated with mimosa tannins under weather conditions (Yalcin et al. 2017). When researches on tannin-based preservatives by co-adding polymers are noted nowadays, it is promising a future for bio-based wood preservatives generally. To specific, furan or furanic resin, including furfural and furfuryl alcohol, is considered as a potential biobased polymer to harden tannins. Indeed, furanic resin is cured inside with impregnation wood, which is enabled and identified as an environmental-friendly and harmless preservative. Yet the upside-down is that to exert a powerful effect on the products requires a plethora of resins, which has a negative impact on cost-effectiveness, along with the difficulty in the decomposition of the resin due to its great water repellence and fire resistance (Pizzi 2016). But furfuryl alcohol is also familiar in the tannin adhesive industry, acting as a substitute for formaldehyde (Arbenz & Avérous 2005, 2640), thus paving a new pathway for further studies in the wood preservation industry. (Shirmohammadli et al. 2018, 324.)

3.3 Tannin foams

To overcome the shortcomings of the previous generation of foams and evolve new foam formulations, the researches on tannin foams have been developed so far to enhance their properties in new applications (Li et al. 2012b; Lacoste et al. 2013; Zhao et al. 2010). Indeed, tannin foams have attracted attention of researchers, since the first tannin-furfuryl alcohol foams were reported in 1994 (Meikkeham & Pizzi, 1994). Moreover, these new foams have been advanced to bring comparable properties based on mechanical and physical strength and to promote environmentally friendly materials, compared to synthetic polyurethane foams (Pizzi 2019a; Shirmohammadli et al. 2018, 324).

Tannin-based rigid foams conventionally can be prepared in three phases, namely mixing, expansion, and curing. Firstly, a combination of tannin extract with furfuryl alcohol, formaldehyde, blowing agent, additives, and water, is mixed mechanically to reach a homogeneous and obvious viscous phase. After mixing, an acid catalyst is added to launch the mechanism of the expansion phase. In the mixture, the furfuryl alcohol is of considerable significance as an exothermic reaction agent to provide heat to the whole reaction and its self-polymerization reaction, while foam expansion is conducted by a physical blowing agent so as to evaporate the solvents. At the same time, tannin and furfuryl alcohol are cured by the increase of the temperature in reactions. Eventually, with the presence of formaldehyde used as a hardener, the tannin system of furfuryl alcohol and formaldehyde is formed by cross-linking. This optimized formulation was invented for hardening process control, in which it ensured that the reaction neither took place too early nor too late; and thus, preventing the failure in the foaming process. (Tondi & Pizzi 2009a, 356-363; Pizzi 2016, 2019a.)

Other formulations on tannin foams also were reported in terms of properties enhancement. Applying tannin-furfuryl alcohol in polyurethane foams makes a tremendous contribution to ameliorating the product's quality, particularly more fire resistance and the use of environmental-friendly substances (Basso et al. 2014). Polyurethane foams basically can be formulated by two different approaches. The first formulation took advantage of the addition of glycerol to enhance the reactivity by treating mimosa tannins and diisocyanates such as methylene diphenyl diisocyanate (MDI) by liquefaction process. After treating tannins at 120 Celsius degree in an hour, other substances including catalyst and additives were enforced with tannin derivatives prior to adding MDI to the mixture. (Li et al. 2012a, b; Ge et al. 2003). Another method carried out in the synthesis of quebracho tannins with ethoxylated fatty amine and pol-

ymeric MDI to produce flexible and open-cell polyurethane foams (FIGURE 6). The amount of 50 percent of quebracho tannins was copolymerized into polyurethane conversion by simultaneous synthesis. In that connection, the synthesis pathway highly gave combustion-modifiable polyurethane foams with better fire resistance. (Basso et al. 2014b, c). Besides, oxypropylated tannins were gradually applied to replace total glycerol in producing closed-cell polyurethane foams, which also contributed in physical, thermal, and porous properties. (Arbenz & Avérous 2005, 2640-2641; Pizzi 2016.)

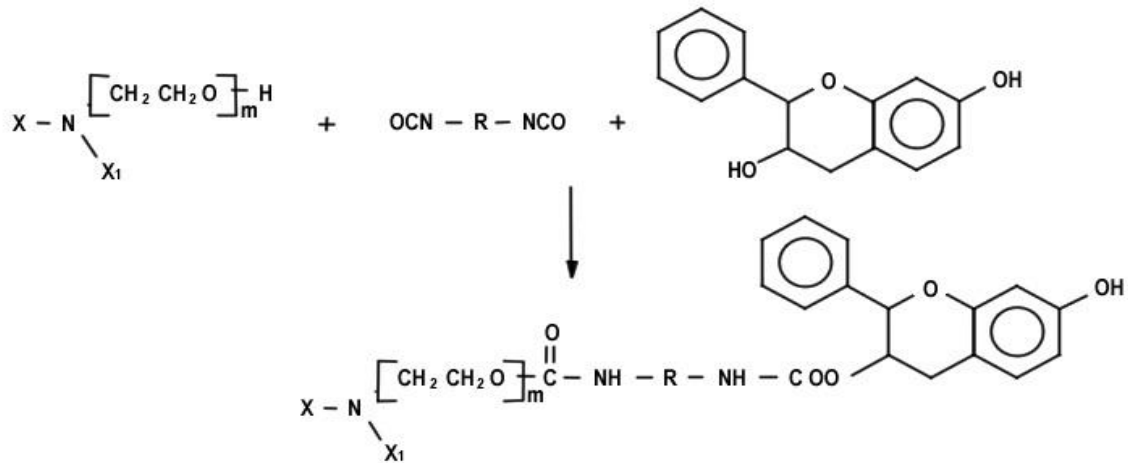


FIGURE 6. The synthesis pathway of condensed tannins with isocyanate and amine to produce flexible polyurethanes (Adapted from Pizzi 2016, 197)

Although the applicability of tannin foams has been acknowledged so far, there are still certain drawbacks related to the factors on the environment and foaming materials in the industry that should not be neglected. To illustrate, tannins with a low level of polymerization fail in producing foams, particularly gambier tannins. The high reactivity of pine tannins, for example, has an influence on the shortness of freezing time, which leads to the failure in the evaporation of foaming agents. Additionally, the water permeability and surface friability are considered as their own drawbacks (Pizzi 2019b, 481). Furthermore, the most disadvantage of tannin foams is the low mechanical strength of the foams, which still require more research to apply to their applications (Li et al. 2012c). As a result, the need for new formulations in certain types of tannin foams increases by adding new environmentally friendly compounds. More recently, optimal suggestions have been put forward to tackle the problem in properties of a few specified tannin foams and move towards green chemistry concept. A typical example is applying non-toxic glyoxal in foam applications which also can be used in other tannin applications. Glyoxal can be used to replace formaldehyde totally in pine foams, thereby putting up a low thermal conductivity

and enhancing mechanical strength for related insulation materials. Another example is applying furfuryl alcohol with tannin to prepare tannin-furanic foams, thus increasing the mechanical strength of the tannin foams to some extent (Varila, Romar, Luukkonen & Lassi 2019, 302). Moreover, the better fire resistance of doped foam today lies in the power of the addition of boric acid in which it not only plays a key role as a potential alternative to toxic compounds using in the production of conventional and expensive polyurethane foams but also contributes to the construction industry as insulating materials (Varila et al. 304). Additionally, a surprising outcome was achieved by the addition of new substances namely oligomeric precursors and glutaraldehyde, increasing more than 37 percent in compressive strength compared to the usual formulation (Li et al. 2012c). (Arbenz & Avérous 2005, 2640- 2641.)

A study case was carried out by Varila and his co-workers (2019) from the University of Oulu in determining the properties of enforced tannin-furanic foams as potential applications such as catalyst, adsorbent, and gas storing materials. More specifically, the idea of the study aimed to determine the mechanical strength of tannin foams when enforcing with boric acid (H_3BO_3) and zinc chloride ($ZnCl_2$), then treating with carbonization, and compare to the prepared reference foams at the end. In the first stage of the process, the liquid phase was obtained by mixing thoroughly water, furfuryl alcohol, surfactant Tween 885 for 30 seconds prior to adding tannin acids and stirring mechanically with 2000 rpm from 5 to 10 minutes. Soon thereafter, the addition of blowing agent and n-pentane accompanied with the presence of a catalyst was applied and mixed thoroughly to the liquid phase for 5 to 10 seconds. This technique was applied to different selected catalysts. Para-toluenesulfanoic acid (PTSA), H_3BO_3 , and $ZnCl_2$ were selected as catalysts in this process as different samples. After foaming, three different foams were placed on an oven for hardening for 24 hours at 378 Kelvin degrees. Then, all samples were cut in a size of 2 cm x 0.9cm x1.4 cm for further processes. In the second stage of the process, physical and chemical activation were applied and marked to some samples and analyzed later based on mechanical strength and other parameters. Overall, this study indicated that there is a relation between the holding time and mechanical strength during the treatment, along with the higher compressive strength in the comparison between matured foam without activation and with chemical activation when enforcing with H_3BO_3 and $ZnCl_2$. (Varila et al. 2019, 301-314.)

In general, the extension in the majority of studies on tannin foams during the last ten years aim to improve the properties of tannin foams in the favor of eliminating the use of formaldehyde, aldehydes, organic solvent, furfuryl alcohol in tannin foam production, and carrying out new formulations and approaches, namely copolymerizing with proteins or synthetic resins, operating with open cells and closed cells, increasing hydrophobic ability, foaming the mixture by heat alone. Moreover, other researches on

flexible foams, simplified foams, and procyanidin-based tannins have gained more attention (Basso et al. 2014b; Cop et al. 2014; Lacoste et al. 2013, 2014; Srivastava & Pizzi 2014). (Pizzi 2019a, 2016.). Besides, there are plenty of researches on tannin-based foams to characterize and analyze different parameters on other materials and approaches such as tannin foams enforced with boric and phosphoric acid, the use of hydroxymethylated lignin, polyurethane, isocyanate or surfactant, the influence of pre-activation of tannins, and other studies (Arbenz & Avérous 2005, 2640- 2641). These new modified foams are unceasingly designed and enhanced to meet practical applications in daily life, namely acoustic absorbing panels in soundproofing, metal ion adsorption in wastewater treatment, floral foams in the garden, porous tannin spray dried powder (PTSDP) in bone reconstruction, foam sandwich panels in construction and other applications (Lacoste et al. 2015; Tondi et al. 2009b; Basso et al. 2016; Zhou et al. 2013; Pizzi 2019a.)

3.4 Tannin derivatives in wine production

It is common knowledge that tannins are added to most beverages, particularly in wines and spirits, to enhance the astringent taste, color, and odor of the products. Yet the amount of concentration of tannin added to the products is considered and measured to avoid insipid or unpleasant feelings. In other words, the level of tannins supplied to the beverage manufacturing should not be too low or too high. The use of tannins in wine and spirit production can be applied in different approaches, namely the direct addition of tannins, the oak chips addition, and the use of oak barrels (Harbertson et al. 2012). However, the use of alternatives among other approaches in wine production, apart from barrel-aging method, faced challenges in terms of legislation of European countries. To illustrate, in the beginning, the direct addition of tannin extracts or oak chips to wine was restricted and banned by most European countries. But the limitations did not affect Southern Hemisphere manufacturers in which oak particles were applied to wine to boost its aging period, while the rest of the producers attempted to protect their market in a different way. With the aim of producing better, clearer wines and evading legal obligations, the addition of tannin additives for aging to low tannin-level wines was implemented by some secret manufacturers. The limitations for winemaking had to be revised downwards because of the French paradox. In this connection, the study showed that the regular consumption of red wines from French people surprisingly decreased the high risks of cardiovascular diseases. Indeed, the anti-cardiovascular effect of red wines lies in the power of the antioxidant property of tannins, thus bringing considerable benefits for health. More specifically, another study conducted by Corder & his co-workers (2006) pointed out that proan-

thocyanidins in tannins inhibited the production of peptides which is mainly caused atherosclerosis. Beside ant cardiovascular diseases, the polyphenol of tannins presents in wine against the oxidation processes and plays a key role as wine preservatives. However, it should be kept in mind that only purified tannins afford to add to wine products, from which other unnecessary components must be removed. On the whole, the use of tannin extracts or tannin oak chips gains legal permission in European countries nowadays. In addition to wines, beers and fruit juices are supplied by the addition of tannins to enhance the scent. But for the public awareness of the French paradox and antioxidant property of tannins, tannins would not have been acknowledged and applied greatly in beverage sectors. (Mosedale & Puech 2003, 401-402; Pizzi 2019a; Ashok & Upadhyaya 2012, 48.)

In light of researches on wine characteristics, the astringent property of tannins performs a pivotal role in enhancing the taste of red wines. The answer to this lies in the protein precipitation of tannins' property, which mainly causes the dry and puckering mouthfeel when tasting. (García-Estéver et al. 2018; Picariello et al. 2018). More specifically, the presence of flavan-3-ols and oligomeric tannins in the phenol contents are the main factors of the bitterness of wines while anthocyanidins generated from condensed tannins are of great importance in most of the color of red wines. Besides, red wines account for 1500 mg/l content of phenols that are far outweighed white wines, and thus making its name for red wine astringency. Tannins found in wine products normally are defined as either enological tannins or oenotannins. Phenolic compounds of these commercial tannins are derived from suitable plants typically oak wood, plant gall, grape skin and seed, and quebracho, which are the main means used in wine production (Sanz et al. 2008). Moreover, phenolic compounds are composed of complex flavonoids (e.g. anthocyanins and flavan-3-ols) and other non-flavonoids (e.g. resveratrol, gallic acid, and other compounds), in which flavan 3-ols, coupled with oligomeric and condensed tannins, account for the most proportion by 25-50% of the overall phenolic contents (Corder et al. 2006). In terms of chemical characterization in wines, wine properties are bound to be ameliorated by the presence of flavonoids, namely anthocyanins, flavan-3-ols, and tannins; however, it is worthy to note that nonflavonoids also contributes to both chemical and oxidation reaction of wines. (Casassa 2017; Shirmohammadli et al. 2018, 325.)

The use of oak barrels in winemaking contributes to the cooperage industry, in which beverages and a few other food products apply barrel-aging by the oak casks nowadays. Oak cask barrels used in wine aging also produce some tannins to the final products (Ashok and Upadhyaya 2012, 48). During the winemaking, red wines are placed in barrel for wine aging from 6 to 18 months prior to bottling the final product, whereas white wines are normally alcoholic fermented in the barrels. In the end, both types of wine go through malolactic fermentation (MLF), which is a conversion process of malic acid to lactic

acid in wines (Lonvaud-Funel 2010, 60-92). This approach inherently has a great impact on the flavor of wines, from which some chemical fraction of oak woods is determined. It is noted that only about 5% of lignin are found while 55% of phenolic compounds are present. Unlike mature spirits, polyphenol compounds, so-called ellagitannins are found in aging wines; however, they account for a very small proportion of percentages. Researches indicate that the interaction between these compounds with ethanol has resulted in the formation of hemiketal or ketal derivatives, which are responsible for astringent properties. Beside the above-mentioned compounds, the primary volatile compounds found in oak wood extraction are oak lactones, which are key factors for the quality of both wines and spirits. Other compounds (e.g. volatile phenols, furans, and pyrazines) should not be overlooked because they also have an influence on wine properties. In a nutshell, it is complicated to analyze the specified role of phenolic compounds in barrel-aging wines because (Ashok & Upadhyaya 2012, 48) the synthetic make-up of the tannin is as a matter of fact changed during winemaking procedures. (Mosedale & Puech 2003, 399-400.). Tapping into this requires more researches in terms of chemical characterizations and wine characteristics.

4 MARKET OVERVIEW OF THE TANNIN DERIVATIVES

The tannin derivatives market is restricted by companies and organizations in providing import and export data to outsiders, which are mainly caused a grey area for academic researchers. Indeed, it is hard to find the path in the mist, but a quick look at the facts shows a slightly vivid picture of the tannin market. Different parameters of tannins, concerning the original sources, applications, regional markets, and other factors account for the driven forces of tannins to global market consumption. Given is a summary report made by Grand View Research (2017a) to provide a short comprehension of the tannin market. In 2015, the global tannin market reached at 1076,3 kilotons, leading a potential growth estimation of the Compound Annual Growth Rate (CAGR) of 5.8% during the period from 2016 to 2025. Overall, it is interesting to note that the factors which are inclined to increase in demand, namely the leather manufacturing, pharmaceutical products, wood adhesives, and winemaking sectors (Singh & Kumar 2019, 3). It is reported that leather manufacturing had the largest proportion of the application segment by 2016 that accounted for over half of the global tannin market size. Following behind the scene was the presence of other segments, such as wood adhesives, winemaking, additives, and other sectors. The explanation for this seems to be the growth and development of new tannin applications and their biological and chemical properties. Yet that is a very incomplete part of the picture. Leather manufacturing can be used as an example, in which the explosion in demand for leather products from consumers, particularly applying in furniture, brandy clothing, and car parts, is also all about the high income from populations and user tastes.

In terms of regional markets, the tannin market size accounted for 282.4 kilotons by 2015 in the United States (US). It is expected that there has been a growing trend among products, namely hydrolysable tannins, condensed tannins, and phlorotannins, during the period from 2014 to 2025. But on top of that, the driving growth lies in the power of the leather manufacturing and pharmaceutical sectors. On the other side of the earth, Australia belonging to Oceania, was one of the majorities in the production of tannin-based wood adhesives, along with the leather manufacturing from imported tannins (Hobbs 2009, 27-28). Europe accounted for the 38% of the all-out income in 2015, becoming a new rising market for tannins and tannin products, especially winemaking products. Indeed, the growth of the winemaking sector in European countries is popular for its great success, which has resulted in the high demand of tannin supplies in the region. Following behind Europe was North America, which represented a noteworthy portion of the total revenue in 2015. Apart from that, the booming economies, such as China and India, are expected to make a major contribution in the demand anticipation of tannin global market, for there is a rapid growth in leather and food manufacturing sectors in the region of Asia Pacific. It is

further anticipated that there is a potential expansion of the tannin market in the regions of Central and South America and The Middle East and Africa. (Grand View Research 2017a, 2017b.)

In terms of tannin sources, the exceptionally rich tannin contents of black wattle, so-called *Acacia mearnsii*, account for 36-44% in the bark, monopolize the tannin market. It is noted that there is approximately half of million-hectare of wattle being grown in different countries of the world, namely South Africa, Brazil, China, India, Kenya, Tanzania, and Zimbabwe. South Africa only already accounts for 131,679 ha of wattle cultivating. With specified properties in enhancing linkages and hydrophobia abilities, the black wattle is mainly applied in producing wood adhesives. Apart from black wattle, other species are still under research in Philippines, Kenya, and South Africa. (Hobbs 2009, 27-28.)

5 CONCLUSION

It is undeniable that the key role of tannins in the development of medical products nowadays because of its promising properties, especially in terms of antibacterial, antiviral, and antifungal characteristics. Yet that is not enough to describe the untapped potentials of tannin derivatives. Apart from that, a well-known antioxidant property of tannins in winemaking showed that the industry has the potential for growth. In line with modern society, it is becoming common for the high demand from consumers in spending money on the better high quality of wines, from which antioxidant tannins are projected to bring benefits to human health. Different methods have been used to notice no matter how a difference of tannin addition to wines, it will affect the wine content in both wine characteristics and tannin chemical characterization.

Extending over virtually every aspect of wood application, tannins have become more noticeable in line with the emergence of other sustainable chemical alternatives, including glyoxal, hexamine, and n-butyraldehyde. The chemical properties of tannins enable the replacement of toxic compounds, particularly formaldehyde in glued wood productions. To illustrate, eliminating and reducing the toxicity issuing by VOCs from formaldehyde emission to the environment by seeking new alternatives with promising results pave a new way in the tannin chemistry. In terms of wood preservatives, tannin derivatives make a great contribution to improving the wood quality against herbivores and pathogens by their antifungal properties. Researches from published articles in this paper showed evidence in innovating a new formulation of wood preservatives with less hazardous compounds when co-adding polymers with tannins. However, drawbacks concerning resin cost-effectiveness and stubbornness should not be overlooked. The lack of ability of tannin preservatives to deal with weather conditions is not really surprising, in which more research activities are needed to conduct in this sector.

Furthermore, another key feature of tannin is forming foams which are considered as new materials in the construction industry. More currently, many studies have been done from tannin-furfuryl alcohol foams to other approaches in generating new formulations in the tannin foam industry. Each aspect and drawback of tannin foams have been pointed out to enhance the formulation to the best. Typical topics for these improvements of tannin foams aim to water repellence, mechanical strength, surface friability, and fire resistance. In this connection, it shows a significant growth of interest of R&D departments around the world in this field.

All in all, this paper provided a profound understanding of tannin and its promising applications in the concept of green chemistry. To some extent, there are some challenges needed to overcome to exploit the great potency of tannin derivatives as it paves a wide pathway to solve many problematic issues concerning the impact of synthetic compounds on the environment and human health. In recognition of its vitality, public awareness is encouraged to pay more attention to bio-green chemistry materials. But on top of that, many studies are subjected to be conducted and promoted to find out the next generation of tannin materials that can overcome current drawbacks.

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