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Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures

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Tannins are, after lignins, the most abundant source of natural aromatic biomolecules and can be an alternative feedstock for the elaboration of chemicals, building blocks to develop polymers and materials. Tannins are present in all vascular and some non-vascular plants. One of their major issues is the versatility according to their botanical origin, extraction and purification processes. During the last few decades, tannins have been exploited and chemically modified for the development of new biobased polymers, thanks to their functionality brought by phenolic and aliphatic hydroxyl groups. After a historical overview, this review summarizes the different classes of tannins. Some generalities concerning the extraction techniques of tannins and the corresponding properties are also described. This review provides in detail the different chemical modifications of tannins which have been previously reported, with corresponding pathways and applications. Finally, the main chemical pathways to obtain polymeric materials are especially presented.

1. Introduction

After cellulose, hemicellulose, and lignin, tannins are the most abundant compounds extracted from the biomass. Tannins are, after lignins, a major source of polyphenolic components with 160 000 tons potentially biosynthesized each year all over the world.[1] Tannins are found in various proportions in all vascular plants and in some non-vascular plants, such as algae. Their role in vascular plants is defense against mushroom or insect aggression.[2] In addition, the natural astringency of tannins makes the plant not easily digestible by animals.[3] In non-vascular plants, phlorotannins are oligomers of phloroglucinol (1,3,5-trihydroxybenzene) and are found mostly

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Luc Avérous became in 2003 a Full Professor at ECPM (University of Strasbourg – France), where he teaches biopolymer science, biomaterials, composites, plastic processing & polymer characterization. During the last two decades, his research projects have dealt with "biobased and/or biodegradable polymers systems, for environmental and biomedical applications". As a leading international expert in these fields, he has developed strong collaborations with several foreign labs (Australia, Brazil, Canada, and Spain) and major companies (PSA, Soprema, Tereos, and Total). He has published hundreds of scientific communications and has co-edited 3 books during the last 5 years.

in brown algae (2% of dry mass)[4,5] and in some red algae.[6] Their chemical structures are similar to those of vascular plant tannins.[7] Phlorotannins have different metabolic roles,[8] such as cell wall construction,[9] marine herbivore defense *e.g.* against worms,[10] and UV protection.[11]

Tannins are present in each cytoplasm of all vegetable cells.[12] Contrary to lignins, tannins are mainly in soft tissues of the plant such as sheets, needles or bark.[13] According to the botanical resource, tannins are stored in different zones of the plants:[12] as the bark in pine (*Pinus* sp.), oak (*Quercus* sp.) or mimosa (*Acacia mearnsii*), the sheets in gambier (*Uncaria gambier*), or the wood in quebracho (*Schinopsis* sp.) and chestnut (*Castanea* sp.). Some tannins are very well known in everyday life, such as tannins from tea and wine.[14–17]

2. Tannin chemistry

2.1. Historical outline

The term "tannin" indicates a plant material which allows the transformation of hide into leather.[12] The history of tannins has mainly begun between 1790 and 1800.[18] At that time, there was no differentiation between tannin and gallic acid.[19] In 1787 Scheele discovered gallic acid from oak bark. Dizé continued research on galls in 1791 and Deyeux in 1793. They agreed that the isolated substance was a mixture of gallic acid, a green coloring compound, and other molecules. In 1795, Seguin did tanning experiments with oak-bark and developed the tanning principle.[20] He concluded that when he boiled hide water with an oak-bark infusion, he obtained a light-colored precipitate. The latter was insoluble in water and became dark after light exposure. Thereafter, Berzelius prepared almost pure tannin in 1798. He used a decoction of galls which formed a yellow precipitate after the addition of tin dichloride. The precipitate was decomposed in water with sulphuric acid, forming metal sulfide, which precipitated, leaving the astringent component in solution. Finally in 1834, Pelouze observed the formation of crystalline gallic acid from tannin after being boiled with sulphuric acid. In 1891, Trimble defined "tannin" as the whole class of astringent substances. Nowadays, the common definition of tannin is the one given in 1962 by Swain and Bate-Smith,[21] *i.e.*, tannins are water-soluble phenolic compounds with molecular weights between 500 and 3000 g mol^{-1}.

Tannin structures were studied in order to find their chemical organizations. The most difficult step was to obtain a pure substance, free from sugars. The early purified substances corresponded to digallic acid. In 1912, Fischer and Freudenberg showed that the tannin structure was pentadigalloyl glucose, which is the pentahydroxy gallic acid ester of glucose.[22] Nowadays, investigations are being carried out to elucidate the chemical structures of different tannins.[23–36]

2.2. Classification and chemical structures of vascular plant tannins

The word "tannin" is used to define two classes of phenolic compounds with different chemical natures: hydrolysable tannins and condensed tannins.[37] Hydrolysable tannins are subdivided into gallotannins and ellagitannins. Another class can also be considered: the complex tannins.[38] All these different classes are presented in Fig. 1.

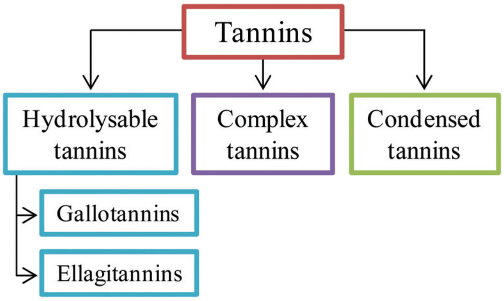


Fig. 1 Tannin classification.

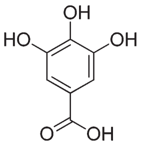
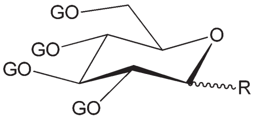
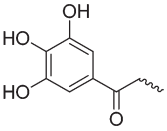
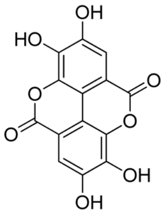
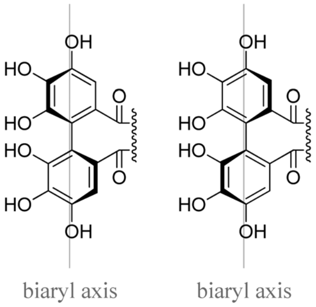
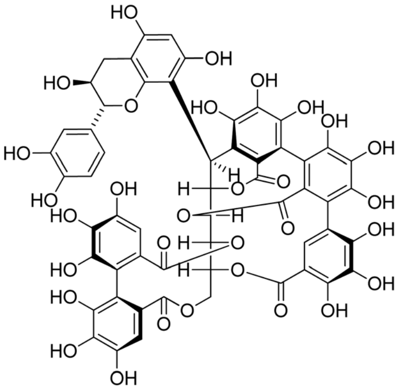
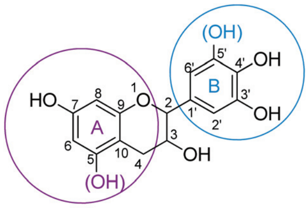
2.2.1. Hydrolysable tannins. Hydrolysable tannins are a mixture of phenols such as ellagic acid and gallic acid, esters of sugars (*i.e.*, glucose), gallic acid or digallic acid.[39] These tannins are divided into two families: the gallotannins, which produce gallic acid and its derivatives from hydrolysis; and the ellagitannins, which produce ellagic acid after hydrolysis (Table 1). These tannins are mainly used in the tanning industry. The most used are tannins of chestnut and tara. They present a weak nucleophilicity. They also present low availability with limited worldwide production (less than 10% of the world's tannin commercial production) and a relatively high price which makes them less attractive compared to condensed tannins.[40]

2.2.1.1. Gallotannins. Gallotannins are simple hydrolysable tannins resulting from polyphenolic and polyol residues. Although the nature of the polyol residues can vary, most gallotannins are attached to saccharides. The hydroxyl functions (OH) of this polyol residue can be partly or completely substituted by galloyl units. If this substitution is partial, the remaining OH can be substituted or not by other residues. For example, in Table 1, the gallotannins 2,3,4,6-tetra-*O*-galloyl-D-glucopyranose (TGG) and 1,2,3,4,6-penta-*O*-galloyl-β-D-glucopyranose (β-PGG), which are present in many plants, are key intermediaries in the biosynthesis of the hydrolysable polyphenols.[41]

2.2.1.2. Ellagitannins. Ellagitannins constitute the most known class of tannins with more than 500 identified natural products.[42] They are formed by gallotannins which lead to a monomeric unit with an axis of chirality after an oxidative coupling between at least two galloyl units. The basic monomer is the hexahydroxydiphenol (HHDP) presented in Table 1. The observed chirality is caused by the presence of bulky substituents located in the *ortho* positions of the biaryl axis and by the isomerism caused by the restricted rotation around this axis. Very often, esterification in *ortho* of the two carboxyl groups with a polyol (generally D-glucopyranose) is at the source of this chirality.

2.2.2. Complex tannins. Complex tannins are formed from an ellagitannin unit and a flavan-3-ol unit.[43] An example of

Table 1 Structure of vascular plant tannins

Type of tannins		Examples of structures
Hydrolysable tannins	Gallotannins	 gallic acid  R = α,β-OH (1) TGG R = β-OG (2) β–PGG  G = Galloyl unit
	Ellagitannins	 ellagic acid  (3) HHDP
Complex tannins		 acutissimin A
Condensed tannins		 Structure of monoflavanoid

this kind of tannin is acutissimin A (Table 1), which is composed of a flavagallonyl unit connected to a polyol derived from D-glucose by a glucosidic connection in C-1 and three other ester bonds.[44]

2.2.3. Condensed tannins. Condensed tannins represent more than 90% of the worldwide production of commercial tannins.[37] From 3 to 8 flavanoid repetition units are needed to call a compound condensed tannin. These tannins are also made up of associated precursors (flavan-3-ol, flavan-3,4-diol) of carbohydrates as well as amino and imino acid traces.[45] These tannins are generally complexed with proteins.[46,47] Their faculty of complexation changes according to their chemical nature.[48] Each flavanoid is composed of two phenolic rings having different reactivities.[12]

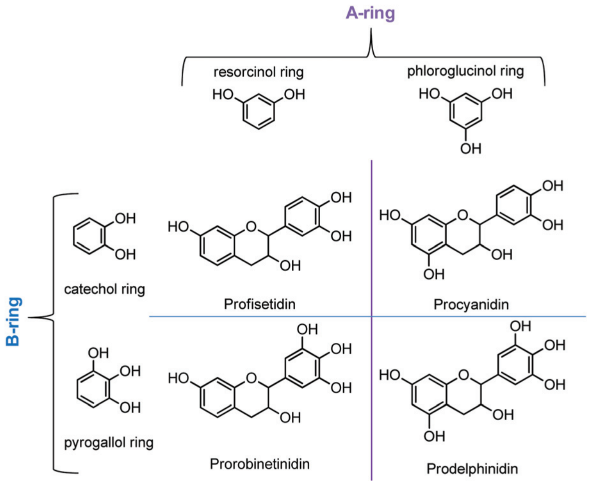


Fig. 2 Structures of the four monoflavanoid building blocks.

The structure of monoflavanoid in Table 1 shows that it is possible to have two configurations for each ring: with or without OH in positions 5 and 5′. These various configurations generate four possibilities (Fig. 2) and four corresponding basic building blocks from condensed tannins.[49]

The flavanoids from condensed tannins are mostly derived from flavan-3-ol and flavan-3,4-diol.[50] The type of connection between the various flavanoid units depends on the nature of the rings. A resorcinol type A-ring (substitution by an OH in the *meta* position) of the flavan-3,4-diol as well as the oxygen in the heterocycle create high nucleophilicity on C6 and C8 positions. Thus, the units of condensed tannins are mainly connected through C4–C6 or C4–C8 bonds. C4–C6 is prevalent in tannins mainly composed of profisetidins and prorobinetidins. C4–C8 is prevalent in tannins mainly composed of procyanidins and prodelphinidins.[51]

In a flavanoid, nucleophilic centers of the A-ring are generally more reactive than those of the B-ring. This is due to the position of the OH present on the rings, which are at the origin of this difference in reactivity. In the case of the A-ring, they involve a located activation (C6 and C8) due to the resonance structure, leading to a highly reactive nucleophilic center contrary to the case of the B-ring.[39]

2.3. Non-vascular plant tannins

Phlorotannins are present in non-vascular plant tannins. They are formed by the polymerization of phloroglucinol (1,3,5-trihydroxybenzene) and have a large range of molar masses between 126 and 650 000 g mol^{-1}.[4] However, the molar mass generally varies between 10 000 and 100 000 g mol^{-1}.[52] Phlorotannins can be easily compared to condensed tannins from vascular plants. Their roles are relatively similar as well as their chemical reactivity. For example, phlorotannins can be associated with metal ions or various biomacromolecules such as proteins, glucides or nucleic acids. However, phlorotannins are not produced by the same biosynthesis method used for other conventional tannins. That is because phloroglucinol derives from the condensation of acetate and malonate *via* an enzymatic reaction.

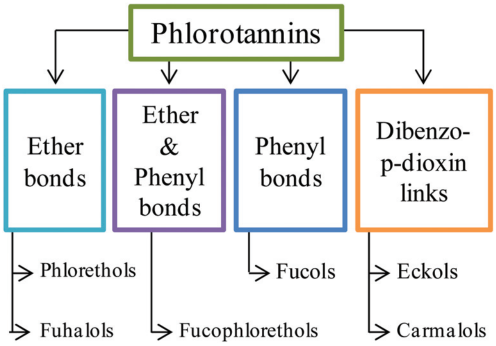


Fig. 3 Phlorotannin classification.

Phlorotannins can be subdivided into four classes according to the type of linkage between the phloroglucinol units (Fig. 3). There can be either ether bonds (fuhalols and phlorethols), phenyl bonds (fucols) or both (fucophlorethols). Finally, the last type of linkage is a dibenzo-*p*-dioxin connection (eckols and carmalols).[6]

2.3.1. Phlorotannins with ether bonds. This category is composed of fuhalols and phlorethols, which both derive from phloroglucinol units connected together by aryl–ether bonds. The corresponding molecules can be linear or not. In the case of the phlorethols, compounds are strictly made of phloroglucinol units. In the case of the fuhalols, the phloroglucinol units are connected by ether bonds having regular sequences in *ortho* and *para* positions and containing in all the rings an additional OH (Table 2).[53]

2.3.2. Phlorotannins with phenyl bonds. This class is made of compounds formed by phloroglucinol units which are only connected by aryl–aryl bonds. This group is essentially composed of fucols (Table 2).

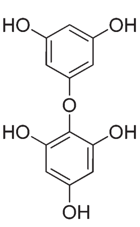
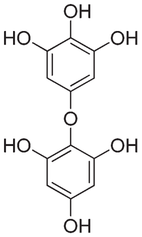
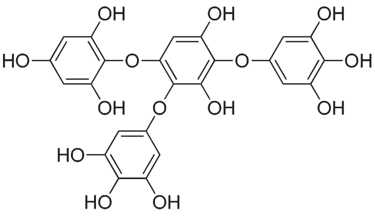
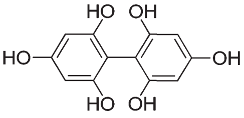
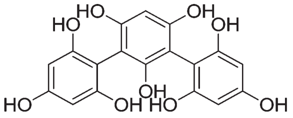
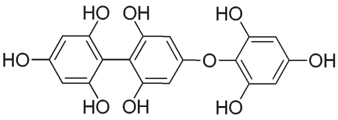
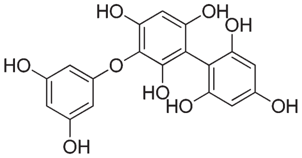
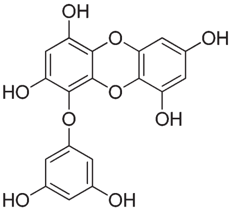
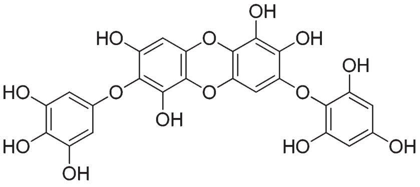
2.3.3. Phlorotannins with ether and phenyl bonds. Some compounds are made of phloroglucinol units which are connected by ether–aryl and aryl–aryl bonds. These molecules are called fucophlorethols (Table 2).

2.3.4. Phlorotannins with dibenzo-*p*-dioxin links. This class is made up of two types of molecules. The eckols are made of at least half a molecule of dibenzo-*p*-dioxin substituted by phloroglucinol in the C4 position. Carmalols are composed of one half of a dibenzo-*p*-dioxin molecule and phlorethol derivatives (Table 2).

3. Extraction of tannins

Plant preparation and extraction processes have a great influence on tannin extract composition. Phenolic compounds can be extracted from fresh, frozen or dried plant. Generally, after drying treatment, plants can be milled and homogenized.[54,55] Drying methods have a strong impact on the final composition of the tannin extracts, with *e.g.* bonding with other compounds.[56–58]

Table 2 Structure of phlorotannins

Types of phlorotannins	Examples of structures
Ether bonds	 Diphlorethol  Bifuhalol  Trifuhalol C
Phenyl bonds	 Difucol  Trifucol
Ether and phenyl bonds	 Fucophlorethol A  Fucophlorethol B
Dibenzo-*p*-dioxin links	 Eckol  Diphlorethohydroxycarmanol

Under anaerobic conditions, the free tannin content increases slightly with the temperature, whereas under aerobic conditions, there is a strong decrease in the free tannin content. Lyophilized samples are similar to those dried at a lower temperature (25 and 45 °C). Compared with other drying methods, freeze-drying seems to be one of the best methods for preserving the molar masses of the condensed tannins,[59] extracting high levels of phenolic compounds[60] and preserving the native structures.[61]

Extraction methods are usually based on solvents. The industrial method of extraction traditionally used to recover tannins starting from vegetable substances is based on boiling water. The corresponding solution is then concentrated by evaporation.[62] Wood shavings are loaded in a series of autoclaves functioning by counter-current. This system of autoclaves is used in order to solubilize tannins contained in a strong concentration in fresh wood shavings. This treatment, called scrubbing, is generally carried out with water at a fixed temperature (50–110 °C) and pressure (maximum 0.8 bar) in each autoclave for several hours (6–10 h) for a ratio of water/wood equal to 2–2.4 in mass. Generally, this process leads to a solution containing 4–5% in weight of tannins with an extraction yield of around 60–65%. After clearing by decantation, the tannin solution is concentrated by several evaporations under vacuum, to limit the oxidation of tannins, until obtaining the desired concentration (in general, 40–50% in weight). This last solution can be stored after addition of a stabilizing agent or it can undergo other treatments like being reduced to dry powder by atomization, *i.e.* by spraying with hot air (90–96% of dry mass). Water can be used alone, but most of the time organic solvents with or without water such as ethanol,[63–65] methanol,[66–68] acetone,[57,69–72] ethyl acetate[73] or mixtures of these solvents[74] are used to increase the extraction efficiency.[75] To improve the extractive yield, alkaline solutions are also used. The most studied species is pine wood.[76–82] Effects of alkaline solution extraction are also the same on chestnut and eucalyptus species[83] or on cranberry pomace.[84] Another technique for increasing the yield is by the use of an acidic solvent. Strong acids like hydrochloric acid or a weak acid like formic acid can be used.[70,75,85,86] However, these extraction methods need large volumes of organic solvents as well as long extraction times. That is why new methods have been developed over the past few years such as microwave-assisted extraction (MAE),[87–91] ultrasound-assisted extraction (UAE)[92–95] and pressurized liquid extraction (PLE), also called accelerated solvent extraction (ASE)[96,97] with water (subcritical water extraction, SWE)[98,99] or solvent (supercritical fluid extraction, SFE).[100,101] These new methods bring strong improvements in tannin extraction.

The chemicals used depend on plant parts[102,103] or species[25,64] with a variety of physical properties like polarity or solubility.[104] There are no universal extraction conditions. Each plant sample has an optimized solvent and an extraction procedure.[105] The yield and the composition of extracts[106,107] rely totally on the type of solvent (polarities),[108–110] the extraction time and the temperature of the process[98,111,112] and the sample/solvent ratio.[68,110]

Most of the time, tannins are bound with other plant components such as carbohydrates or proteins, and during extraction, various plant components can be also extracted such as sugar or organic acids. Currently, these impurities are the biggest hindrance limiting a global and successful development of tannin as the biobased resource to develop aromatic building blocks. To obtain "pure" tannins, additional and costly treatments are necessary to purify the extracted mixture like liquid–liquid extraction procedures or solid phase extractions.[54]

4. Chemical modification

4.1. General background

This section will be mainly focused on the chemical modification of condensed tannins. A wide variety of modifications, linked with their chemical structure, can be performed with these tannins. As presented in Fig. 4, the main chemical

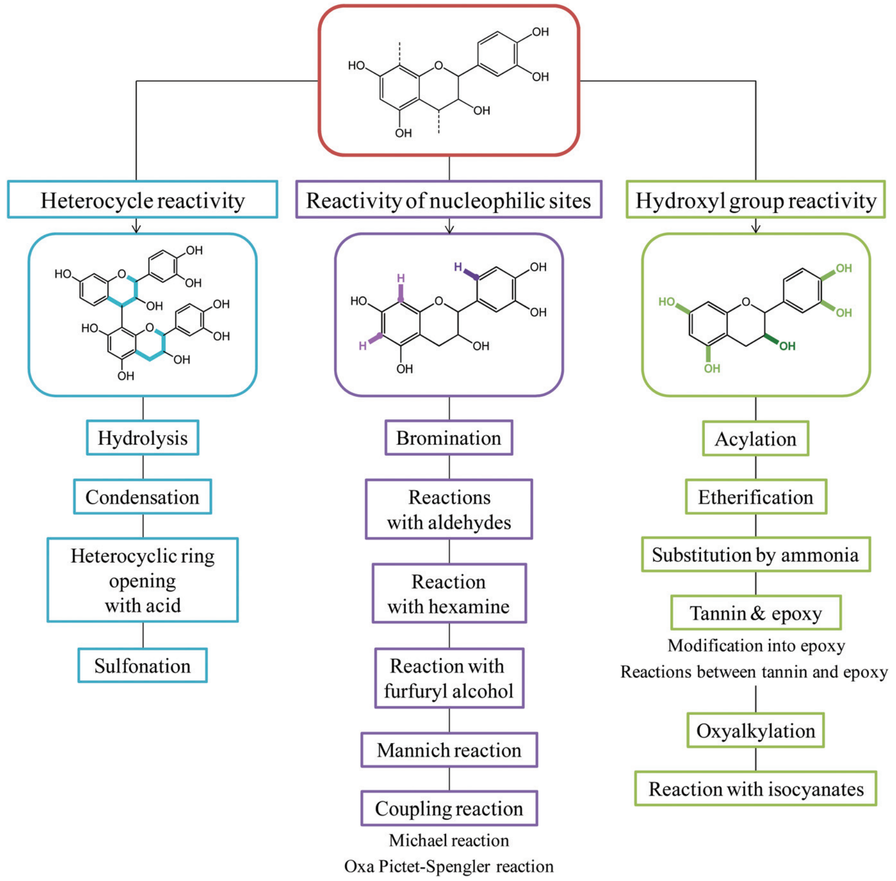


Fig. 4 Various types of reactions with catechin, applicable to condensed tannins.

modification can be classified into three main categories. The heterocycle can be opened and can lead to rearrangements of the chemical structure. Reactivity of nucleophilic sites, created by OH groups present on the aromatic rings, leads to electrophilic aromatic substitutions. Lastly, reactions can also take place directly with the OH. In each category, there are different reactions leading to new building blocks, which are of great interest for polymer synthesis.

4.2. Heterocycle reactivity

Under both acidic and alkaline conditions, catalyzed rearrangements such as hydrolysis and autocondensation are common reactions for tannins (Fig. 5). The cleavage of the interflavonoid bond can also be acid-catalyzed or induced by a sulfonation reaction.

4.2.1. Hydrolysis and autocondensation. Under strong acidic conditions, hydrolysis or autocondensation can occur. Degradation under acidic media leads to the formation of catechins and anthocyanidins. The example of biflavanoid is illustrated in Fig. 6.[113]

The second type of reaction is the condensation after heterocycle hydrolysis (Fig. 7). The formed *p*-hydroxybenzylcarbonium ions condense on the nucleophilic sites of another tannin unit. Phlobaphens or red tannins are obtained.

In the same way, under alkaline conditions different rearrangements are common. These rearrangements are based on the rupture of the interflavonoid C4–C8 bond. The reactivity depends on the nature of tannins. The formed products can autocondense, giving an alkaline condensation (Fig. 8).[114]

The second type of reaction is based on the opening of the heterocycle which increases the reactivity, resulting in partial autocondensation, as for catechin monomers (Fig. 9).[115]

4.2.2. Heterocyclic ring opening with an acid. The cleavage of the interflavonoid bonds can be acid-catalyzed. This leads

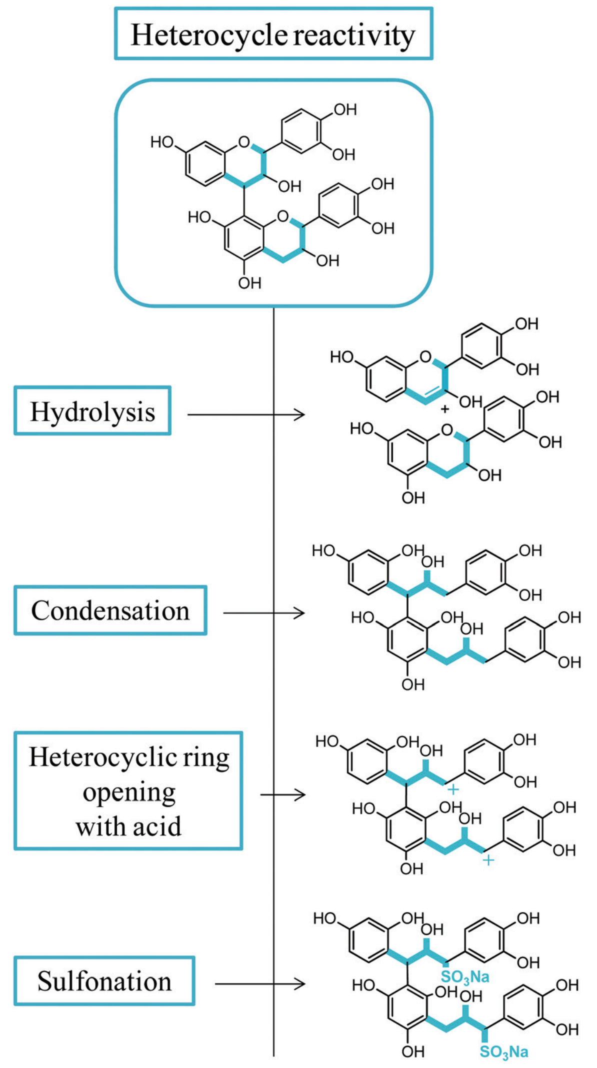


Fig. 5 Summary of the chemical reactions from tannin heterocycles.

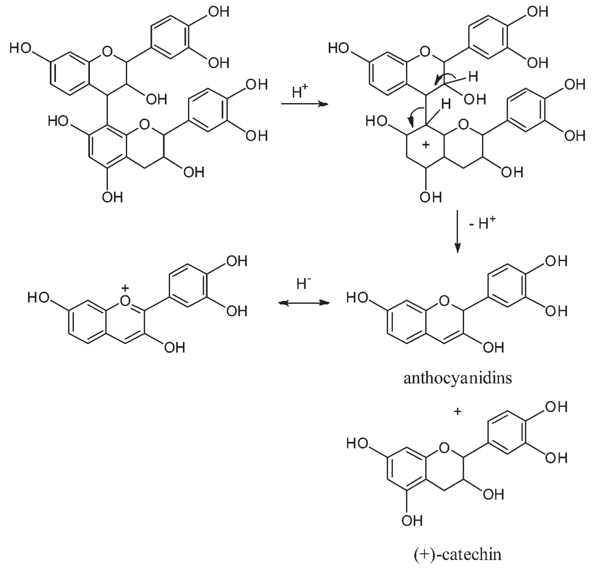


Fig. 6 Degradation of tannins in catechins and anthocyanidins.

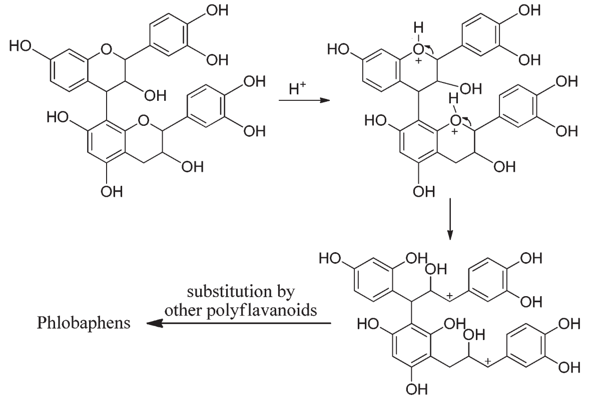


Fig. 7 Acid autocondensation by hydrolysis of the heterocycles.

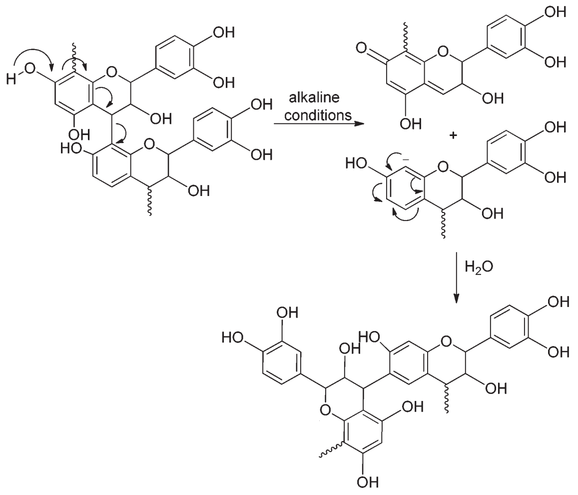


Fig. 8 Alkaline autocondensation.

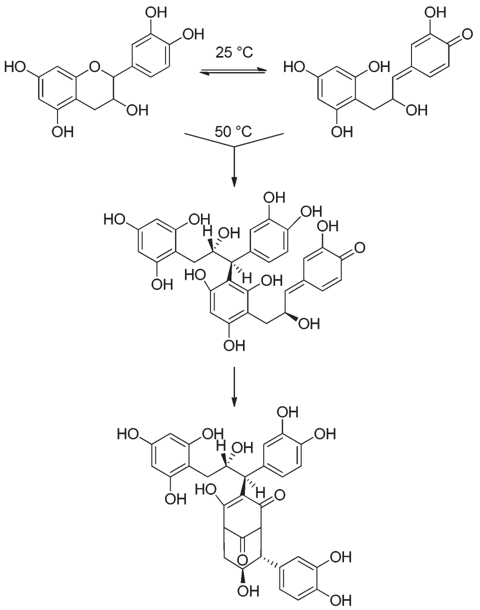


Fig. 9 Catechin rearrangement.

to a heterocyclic ring opening with the formation of a carbocation (Fig. 10), which can be captured by a nucleophile such as phenol, resorcinol, phloroglucinol or the phenolic rings of other flavonoid units present. Different acids were tested such as hydrochloric acid[116] or acetic acid catalyzed with benzyl mercaptan.[117,118]

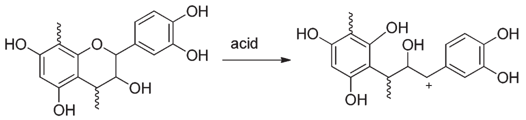


Fig. 10 Treatment of mimosa tannin with acid.

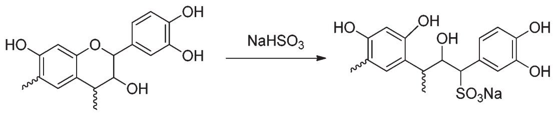


Fig. 11 Sulfonation reaction of tannin.

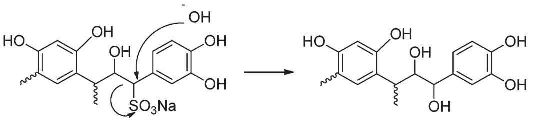


Fig. 12 Substitution of the sulphonic group by OH.

To open the heterocycle, it is also possible to treat tannins with trichloroacetic acid,[119,120] which is added in an aqueous solution of tannins, and then heated at 86 °C for 2 hours. After cooling, the reaction medium is neutralized by the addition of a sodium hydroxide (NaOH) solution.

4.2.3. Sulfonation. It is also possible to open the heterocycle by a sulfonation reaction.[121–123] The reaction takes place in the presence of sodium hydrogen sulfite or sodium hydrogenosulfate with the insertion of a sulphonic group into position 2 after the heterocyclic ring opening (Fig. 11). This polar group increases the solubility and decreases the viscosity of tannins.

This reaction is often used to facilitate the tannin extraction. Sulfited tannins can be used to produce formaldehyde resins.[124] However, sulfated tannins are moisture sensitive. When they are submitted to strongly alkaline conditions, the sulphonic group can be substituted by an OH in the presence of strong alkali *via* a bimolecular nucleophilic substitution (SN_2) reaction (Fig. 12).

4.3. Reactivity of nucleophilic sites

Nucleophilic sites are present in the tannin structure due to the phenol groups. Indeed, electrophilic aromatic substitutions can occur. In fact, OH is an electron donor which can be intensified under basic conditions in which a phenoxide ion is formed. Bromination reaction was studied to understand this reactivity. Then, different modifications were investigated to tune the tannin structure. Modifications were performed with hexamine, furfuryl alcohol, ethanolamine and different aldehydes. Due to the aromatic structure, the coupling reaction can also occur with carboxylic acid and aldehydes. All these modifications are presented in Fig. 13.

4.3.1. Bromination. To study the reactivity as well as the accessibility of the flavanoids, some model molecules resulting from phloroglucinol and resorcinol have been selectively brominated in pyridine.[49] Phenol groups are *ortho* and *para* directing. Thus, on the A-ring, C6 and C8 are both activated by the phenol groups. In the case of (+)-tetra-*O*-methylcatechin, bromination is done preferentially in the C8 position. When this site is occupied, substitution is performed in the C6 position since the B-ring is less reactive. In the case of an excess of

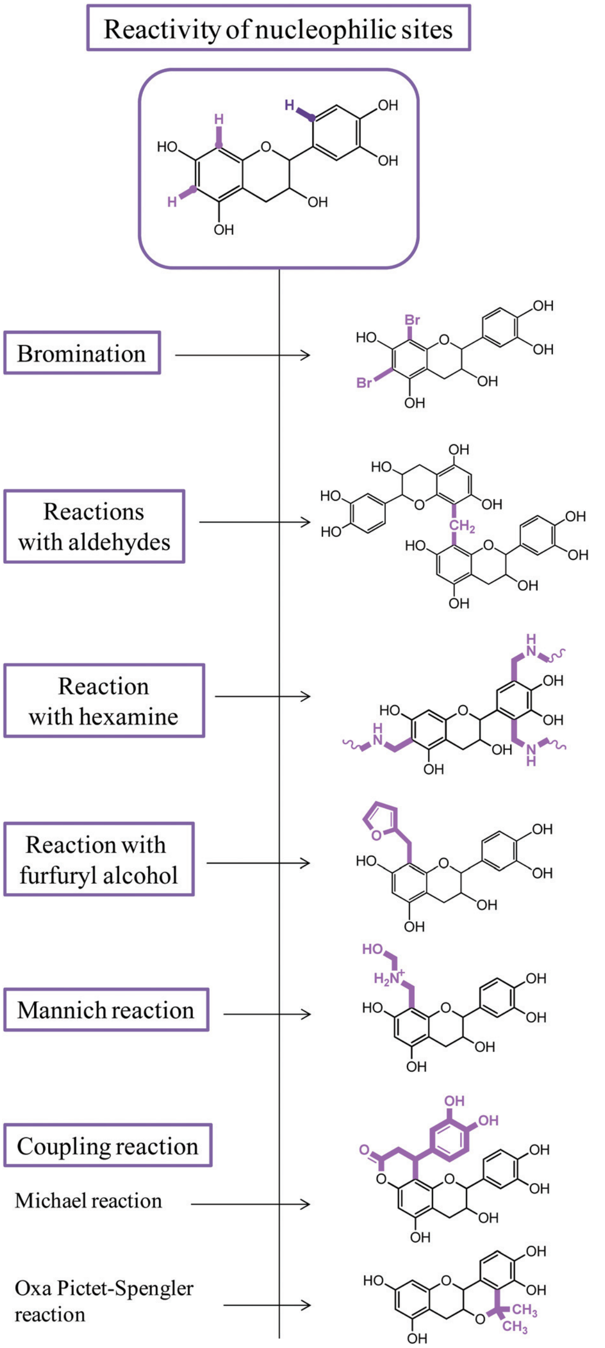


Fig. 13 Summary of the chemical reactivity of tannin nucleophilic sites.

the bromination reagent, the reaction can also take place in the C6′ position. Thus, the sequence of bromination is the following: C8, C6, and then C6′. However, for equivalent resorcinol forms, such as (−)-tri-*O*-methylfustin, the bromination sequence is different with C6, C8 and finally C6′. Preferential sites are presented in Fig. 14 depending on the flavonoids.

This preferential substitution in C8 *vs.* C6 is certainly related to the accessibility of the sites for each type of flavanoid (phloroglucinol and resorcinol, respectively).

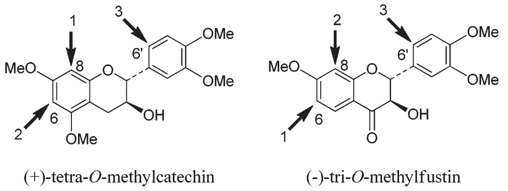


Fig. 14 Bromination reactive sites of flavonoids.

4.3.2. Reactions with aldehydes. In the case of adhesive and foam preparation, formaldehyde is the most commonly used aldehyde (see sections 5.1 and 5.2). With condensed tannins, formaldehyde reacts mainly with the A-ring to form methylene interlinks. When the A-ring is of the resorcinol type, the reactive site is in the C8 position, whereas, when the A-ring is of the phloroglucinol type, the reactive site is in the C6 position (Fig. 15).[121] When alkaline conditions are used (at pH = 8), the nucleophilicity of tannin phenols is activated with the formation of phenoxide ions.

The B-ring (pyrogallol or catechol) is less reactive compared to the A-ring. Indeed, activation due to the presence of phenol groups on the B-ring is not located on a carbon contrary to the A-ring whose activated sites are on C6 and C8. However, at high pH (approximately 10), the B-ring can be activated by anion formation. Different tannin varieties and wastewater from the tanning process have been successfully tested.[78,124–129] Thus, it is possible to carry out this reaction regardless of the type of tannin.

The reaction between the A-ring and the formaldehyde (Fig. 16) leads to the creation of a cross-linked three-dimensional network with a decrease of the molecule mobility. With a small degree of condensation, the size and the configuration of the molecules do not allow the creation of extra methylene bonds because the reactive sites are too far apart.

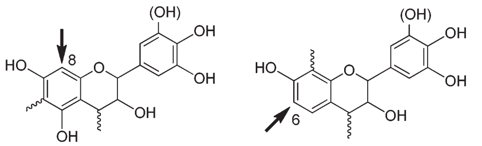


Fig. 15 Formaldehyde reactive sites.

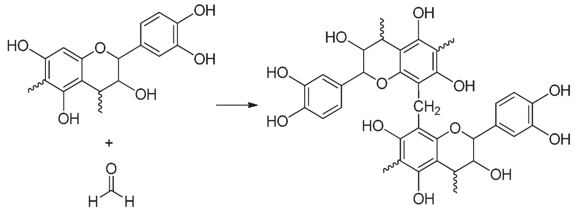


Fig. 16 Reaction between tannin and formaldehyde.

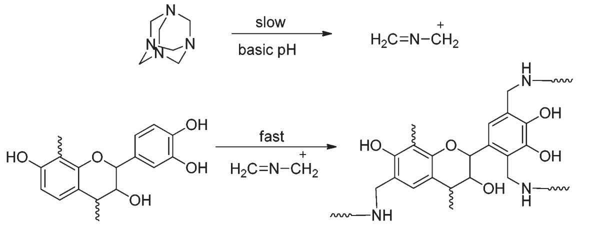


Fig. 17 Decomposition under alkaline conditions of the hexamine in methylene imine–amine, which reacts with tannins.

The kinetic differences between formaldehyde and other aldehydes were studied on tannins of pine and mimosa.[125] Formaldehyde exhibits the fastest kinetics compared to other aldehydes (acetaldehyde, propionaldehyde, iso-butyraldehyde, *n*-butyraldehyde or furfural) due to their steric hindrance.

4.3.3. Reaction with hexamine. To avoid the toxic formaldehyde, hexamethylenetetramine, also called hexamine, was studied as a substitute. When under acidic conditions, hexamine is decomposed into formaldehyde and ammonia[130] whereas under alkaline conditions, it decomposes into formaldehyde and triethylamine.[131] However, under certain conditions, it is possible to avoid the production of formaldehyde from hexamine. When molecules with nucleophilic sites such as tannins are present in the medium, amino-imine groups are formed and react with the phenolic compounds (Fig. 17). The very fast reaction between amino-methylene bases and tannins prevents the formation of formaldehyde.[132] This reaction leads to the formation of benzylamine bonds on the tannin molecules.

The decomposition of the hexamine strongly depends on pH which also has an influence on tannin reactivity. A study was also performed on autocondensation between hexamine and mimosa (condensed tannins) or chestnut tannins (hydrolysable tannins). It was shown that pH has a great influence on the reactivity.[133] At high pH, hexamine decomposition is faster than its reaction with tannin. In this case, it is possible to form formaldehyde due to the decomposition of amino-methylene.

4.3.4. Reaction with furfuryl alcohol. Tannin can react with furfuryl alcohol to give intermediates for further synthesis with *e.g.* formaldehyde. Furfuryl alcohol is a bio-sourced heterocyclic alcohol derived from hemicellulose. The reaction was studied on catechin and was carried out in the presence of acetic acid at 100 °C. The acidity of the reactive medium is necessary because at low pH, furfuryl alcohol reacts mainly with itself.[134] After purification, two products were obtained. Catechin is substituted by the furanyl group in the C8 position and in the C6 position with a yield of 4 and 1.5%, respectively (Fig. 18).

However, these reactions show low yields. This is due to the self-condensation of furfuryl alcohol under acidic conditions, leading to poly(furfuryl alcohol).[135]

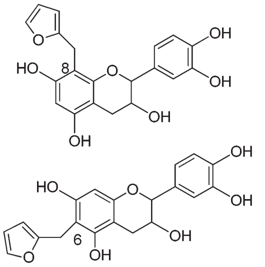


Fig. 18 Products of the reaction between catechin and furfuryl alcohol.

Some studies used formaldehyde and furfuryl alcohol to improve the alcohol reactivity.[136] Indeed, furfuryl alcohol can be converted into 2,5-bis(hydroxymethyl)furan by formylation. The latter is commonly used, mixed with tannin as a reactive species, to produce foams.

4.3.5. Mannich reaction. Under strong acidic conditions, tannins can react with ethanolamines according to the Mannich reaction (Fig. 19), and then give amphoteric tannins, which are water soluble.[121] These new compounds have flocculating properties and are used in water treatment plants to eliminate clay suspensions. After a Mannich reaction and an alkylation, the quebracho tannins have flocculating properties necessary to bleach waste waters.[137]

To understand the reactivity of this system, a study was performed on quercetin with various secondary amines such as diethylamine or piperidin. Depending on the ratio of amine–formaldehyde used, it is possible to obtain mono- or di-(aminomethyl) quercetin (yield: 45% and 46%, respectively).[138]

4.3.6. Coupling reaction

4.3.6.1 Michael reaction. Phenylpropanoids can be grafted on the A-ring of catechin (Fig. 20). This synthesis is based on a two-step pathway. A dienone-phenol rearrangement is followed by a Michael reaction type coupling.[139]

The reaction is catalyzed by trifluoroacetic acid (TFA) and sodium acetate (NaOAc). The best yields were obtained for a mixture of tetrahydrofuran (THF)–benzene 1 : 1 (v/v). Other compounds were tested such as cinnamic acid or *p*-methoxycinnamic acid but the coupling reaction did not occur. This was due to the absence of the *p*-hydroxyl group in these molecules, which would have provided the formation of the intermediate through dienone-phenol rearrangement (tautomerism). This intermediate would then react with flavan-3-ol as a Michael acceptor.

4.3.6.2 Oxa-Pictet–Spengler reaction. This reaction is derived from the Pictet and Spengler reaction which consists of β-arylethylamine cyclization after condensation with an aldehyde in the presence of an acidic catalyst. In the case of

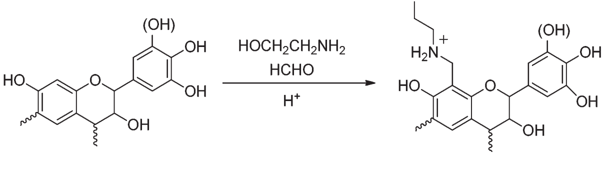


Fig. 19 Mannich reaction with tannins.

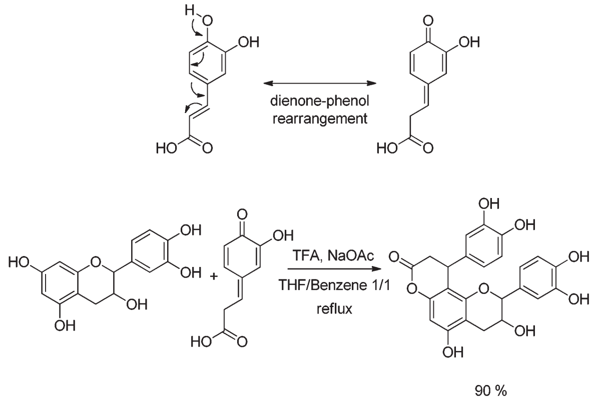


Fig. 20 Dienone-phenol rearrangement and reaction between catechin and caffeic acid.

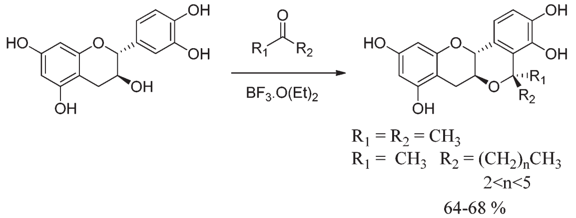


Fig. 21 Oxa-Pictet–Spengler reaction of catechin and various ketones.

the reaction Oxa-Pictet–Spengler, the nitrogen is replaced by an oxygen atom (Fig. 21). This reaction was done with different ketones and catechins.[140,141]

The conventional catalyst is boron trifluoride etherate ($BF_3{\cdot}O(Et)_2$). Catechin, ketone and a catalyst are mixed for 48 h at room temperature under a nitrogen atmosphere to form β-arylethylamine cyclization.

4.4. Functionalization of the hydroxyl groups

Phenolic and aliphatic hydroxyl (OH) groups are reactive functions which can be modified to obtain several tannin derivatives. Tannin can be modified to increase the OH chemical reactivity or its solubility in organic solvents, or to improve its processing. Two main strategies are possible to obtain new building blocks from tannin: (i) changing the nature of the reactive sites or (ii) increasing the hydroxyl group reactivity. The phenolic hydroxyl groups are the most active groups. Different modifications such as acylation, etherification, substitution by ammonia and reactions with epoxy groups or with isocyanates were performed and investigated (Fig. 22). The reactivity and the availability of phenolic functions can be increased by modification into epoxy, which can be then transformed into aliphatic hydroxyl groups.

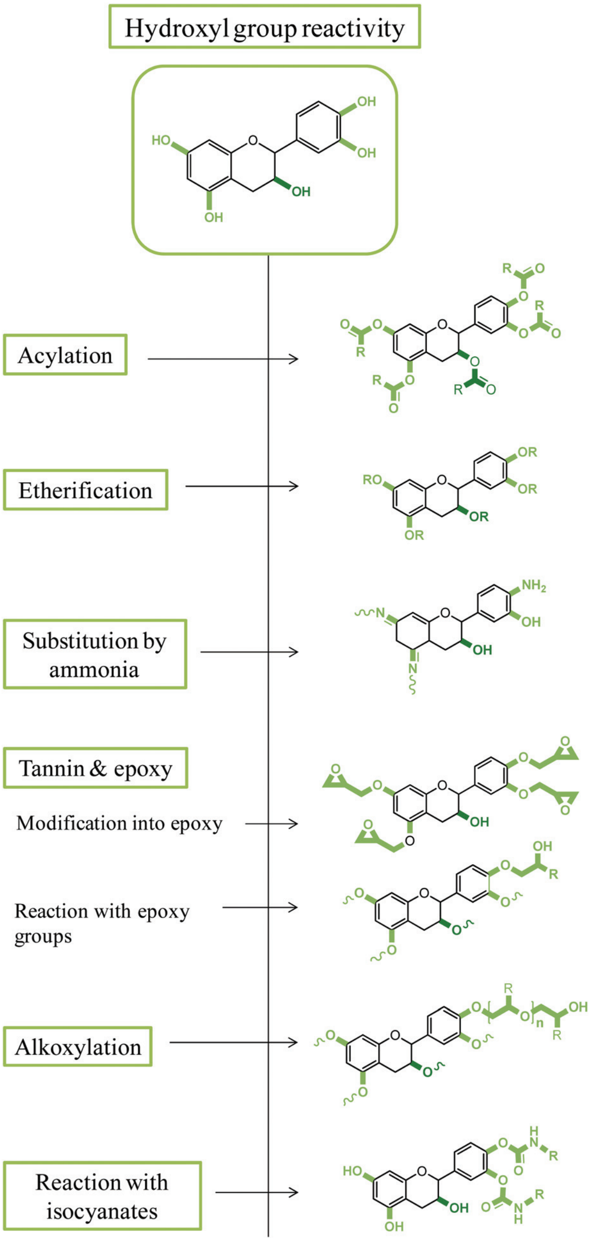


Fig. 22 Summary of the chemical reaction with tannin OH groups.

4.4.1. Acylation. Acylation of tannins is a well-known method usually employed for the tannin characterization. After reaction with acetic anhydride in pyridine, tannins become soluble in organic solvents[142] and then can be analyzed *e.g.* by NMR.[143] All OH (phenolic and aliphatic) are subjected to acylation.[144] Whatever the level of acylation, the derivative of tannin loses its water solubility and melts at around 150 °C.

Acylation agents are either carboxylic acids or more reactive derivatives, such as acyl chlorides or acid anhydrides.[145] Esters can also be used for transesterification reactions. If an acid is used, it is possible to form the corresponding anhydride *in situ* in the presence of *N*,*N*′-dicyclohexylcarbodiimide. Solvents generally used are toluene, pyridine, chloroform or acetone to solubilize, at least partially, the polyphenolic compound. The reaction was carried out in the presence of a base in order to activate the hydroxyl groups. Bases were selected from organic

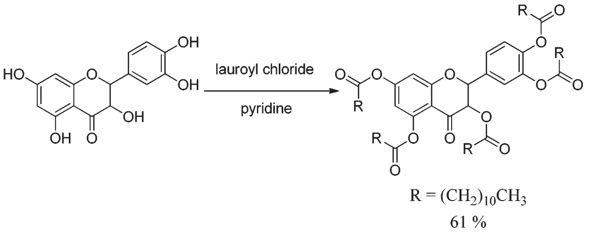


Fig. 23 Acylation of quercetin by lauroyl chloride.

or inorganic bases, such as pyridine, or potassium carbonate, respectively, when another solvent was used. The reaction preferentially takes place at solvent reflux temperature until full esterification. This reaction is considered as an opportunity to enhance the lipophilicity of tannins. For example, Fig. 23 presents the reaction between quercetin and lauroyl acid chloride, in pyridine at 100 °C for 6 hours.

A complete study was performed on quercetin acetylation.[146] In most cases, the reaction is carried out with acyl chlorides in 1,4-dioxane at 60 °C.

Tests were carried out directly on pine and quebracho tannins. In these cases, acylations were performed with stearoyl chloride and 1-methylimidazole as a catalyst in acetone.[143] The maximum degree of substitution increased with the stearoyl chloride/tannin ratio, for quebracho and pine tannins. The corresponding substitution degrees are 4.0 and 5.1, respectively.

As previously mentioned, tannins can be modified with fatty acid. Quebracho and pine tannins were esterified with lauroyl chloride to give the corresponding laureate ester.[147] Partially substituted derivatives have been obtained with a preference for substitution on the B-ring, with the formation of mono- and di-esters. The same tannins have also been esterified with acid, linoleate and acetate groups to produce tannin-fatty esters.[148] Linoleic acid is firstly modified to linoleic acid chloride which reacts with the tannins.

Pine tannin esterification using anhydrides (acetic, propionic, butyric or hexanoic anhydride) was investigated as a route to synthesize tannin esters possessing varying ester chain length and degree of substitution.[149] These tannin derivatives were used as plastic additives in *e.g.* poly(lactic acid) as anti-UV.

Tannins can be regioselectively benzoylated according to the Schotten–Baumann method (Fig. 24)[121] to decrease the number of OH per flavonoid unit. Besides, they precipitate in aqueous solution to easily separate sugars from tannins.

Adipoyl dichloride is used to introduce a carbonaceous chain between tannin molecules. The highest yield (around 75%) is obtained for molar ratios adipoyl dichloride : tannin equal to (6–10) : 1. The reaction is carried out at 75 °C for 120 min in a mixture of chloroform and 1,4-dioxane.

Various carboxylic acids were grafted (Fig. 25) on the OH in position 7 of the 5,7-dihydroxy-6-methoxy-2-phenylchromen-4-one (oroxyline A).[150] A solution containing a carboxylic acid, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDAC) and hydroxybenzotriazole (HOBt) in dichloromethane is maintained at 0 °C for 20 min under a nitrogen atmosphere. Oroxyline A, solubilized in dichloromethane (DCM) and dimethylformamide (DMF), is then added. The reaction medium is then stabilized at room temperature for 4–5 hours under a nitrogen atmosphere.

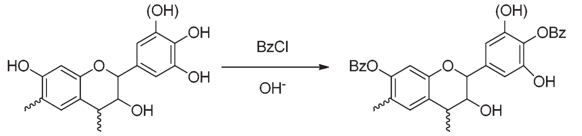


Fig. 24 Benzoylation of tannin of mimosa according to the Schotten–Baumann method.

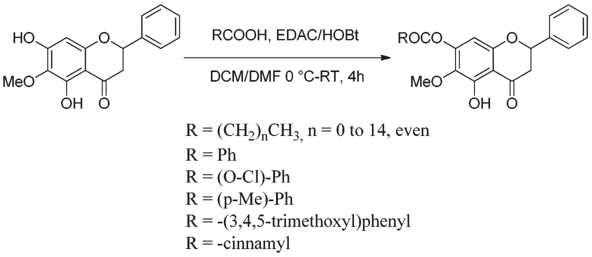


Fig. 25 Synthesis of oroxyline A derivatives.

Recently, the synthesis of urethane groups from non-isocyanate reactions was performed from hydrolysable chestnut tannins. By an aminolysis way, condensed tannins reacted with dimethyl carbonate and then with hexamethylenediamine (Fig. 26).[151,152] These promising pathways bring new routes to safely synthetize high performance polyurethane materials, without toxic isocyanates.

4.4.2. Etherification. The polyphenols can react by etherification with halogenoalkanes. Alkylation of quercetin in DMF in the presence of tetraethylammonium fluoride (Et_4NF) gives

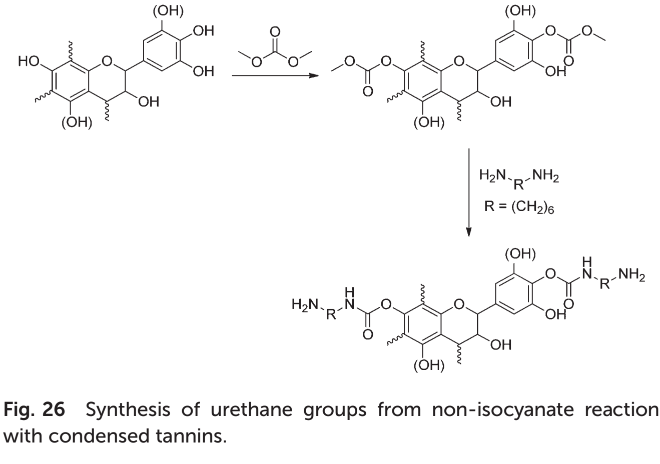


Fig. 26 Synthesis of urethane groups from non-isocyanate reactions with condensed tannins.

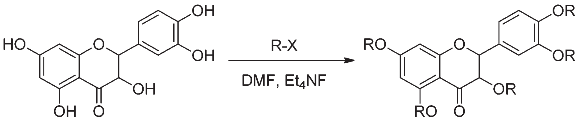


Fig. 27 Synthesis of tetra-*O*-ethyl-3,7,3′,4′-ethyl[^{3}H]-5-quercetin.

tetra-*o*-ethyl-3,7,3′,4′-*O*-ethyl[^{3}H]-5-quercetin (Fig. 27).[153] The same product can be obtained by reaction of quercetin with ethylene carbonate. Depending on the quercetin/ethylene carbonate ratio, synthesized products were more or less substituted.[154]

Quercetin was also alkylated with 1-chloro-2-propanol in the presence of potassium carbonate in DMF. Then, various hydroxypropylquercetin could be obtained.[155] It is also possible to methylate OH from the rings. The reaction was studied on chrysin with iodomethane (MeI) and K_2CO_3, as presented in Fig. 28.[156]

Under the same conditions, this reaction is often used for specific methylation of certain OH after the protection of some others. For example, in the case of the catechin, after protection of B-ring hydroxyls, it is possible to methylate catechol with dichlorodiphenylmethane.[157] When the targeted OH is methylated, deprotection can be performed. The reaction was carried out on quercetin to obtain 7-*O*-methyl quercetin (Fig. 29).[158]

Other experiments were completed with a mixture of halogenoalkanes (MeI and ethyl bromide) on oroxylin A in the presence of K_2CO_3 in acetone under reflux to develop new antibacterial agents.[150] However, many fastidious steps are necessary to produce the corresponding targeted molecule. Then, this pathway is not really industrially viable.

Investigations were directly performed on tannins. Pine and quebracho tannins were carboxymethylated by chloroacetic acid or chloroacetate sodium. A base is added into the reaction mixture: either NaOH if the reaction takes place in water, or K_2CO_3 if the reaction takes place in acetone. The best results are obtained when chloroacetic acid is used in acetone with K_2CO_3 (Fig. 30).[159]

In addition, tannins react also with the 1-bromooctane in DMF with potassium carbonate at 60 °C. The OH reacting group percentage varies between 15 and 93%. These etherified tannins are insoluble in water.[159]

4.4.3. Substitution by ammonia. Amination reactions with ammonia (NH_3) were studied. It is possible to convert a part of phenolic OH into amine functions. A study showed that amination of the pyrogallol B-ring by an ammonia solution, without a catalyst and under mild conditions, is regioselective.[160] In the case of *Acacia mearnsii* tannin composed of the pyrogallol B-ring, amination in the presence of dioxygen produces 4′-amino-3′,5′-dihydroxybenzene on the B-ring. In the case of the catechol B-ring of quebracho tannins, an amination reaction does not take place either with or without O_2.

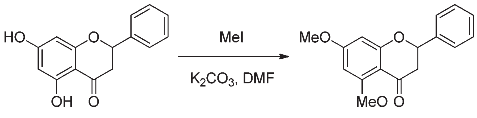


Fig. 28 Methylation of chrysin.

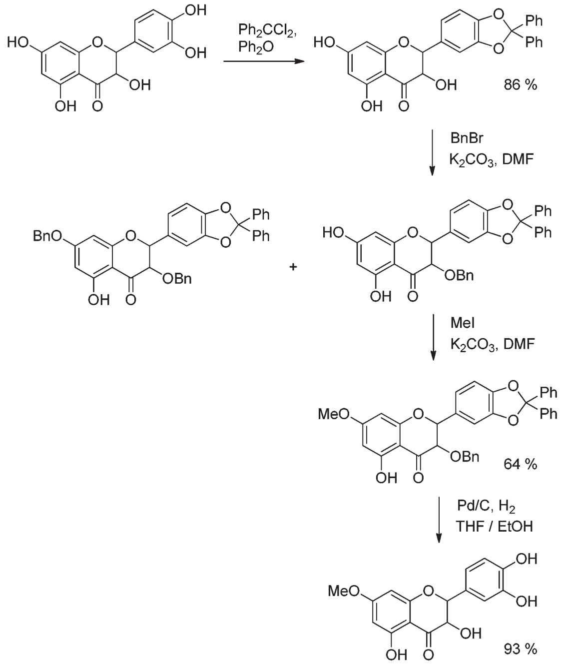


Fig. 29 Synthesis of 7-*O*-methyl quercetin.

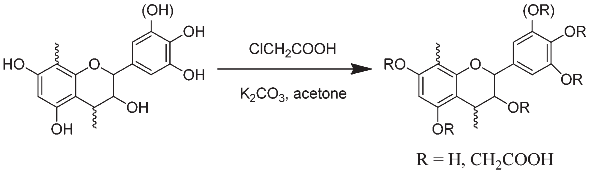


Fig. 30 Carbomethylation of pine tannin by chloroacetic acid.

Different amination conditions were tested.[161,162] A NH_3 solution containing tannins is stirred for one hour. The mixture becomes very viscous, and then placed for one day under hood at room temperature. The solid obtained is washed with water and dried. Analysis showed that a multiamination took place on a majority of phenolic hydroxyls regardless of the ring, A or B. On the other hand, an oligomerization occurred due to the formation of imine bonds between various units involving a tannin-ammonium gelation of the mixture (Fig. 31).

4.4.4. Reactions between tannin and epoxy groups

4.4.4.1. Reactions with epoxy groups. Tannins can react with various epoxies. Hydrolysable tannins were used to make ion-exchange resins after reaction with epoxy resin. Tannin OH

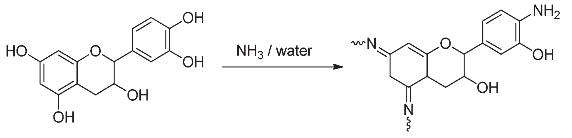


Fig. 31 Example of structure obtained after amination of catechin by NH$_3$.

reacts with epoxy groups.[163] Condensed tannins can also react with epoxy.[164] This is particularly the case with pine tannins with diglycidyl ether or polyglycidyl ether (Fig. 32).

4.4.4.2 Addition of epoxy groups. Currently, companies want to substitute bisphenol-A because of its toxicity. This compound used in epoxy-polyphenolic resins was substituted by catechin. After reaction of catechin with epichloridrin (Fig. 33), the compound thus formed can then replace the bisphenol A diglycidyl ether usually used.[165]

4.4.5. Alkoxylation. Like other biobased resources such as lignin,[166] tannins can be oxypropylated (Fig. 34). This reaction is a ring opening polymerization (ROP) of propylene oxide by the hydroxyls of the polyphenols. To optimize the conditions of synthesis, the reaction with resorcinol was used as a model. The best parameters of synthesis were applied to catechin, pine and quebracho tannins.[159] The syntheses were in mass in a reactor with triethylamine (TEA) as a catalyst at 110 °C for 24 hours. The influence of the propylene oxide content was investigated. With the increase in the load of propylene oxide, the percentage of weight gain of tannin during alkoxylation also increased.

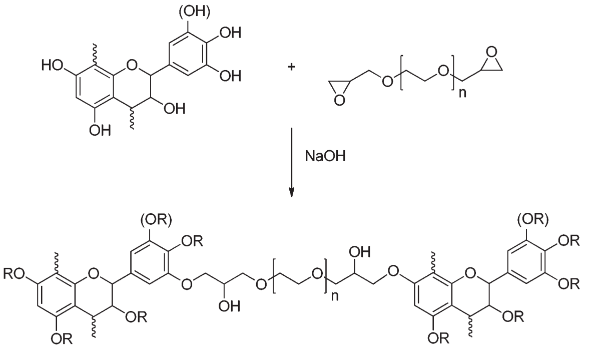


Fig. 32 Reaction of pine tannins with ethylene glycol diglycidyl ether.

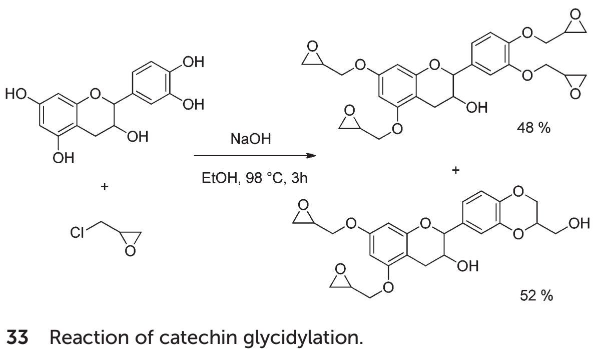
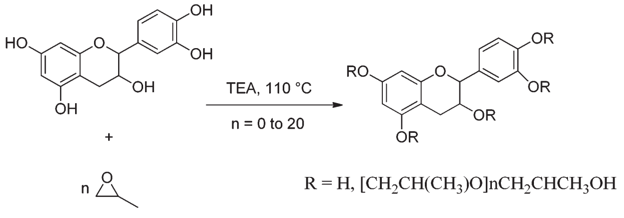


Fig. 33 Reaction of catechin glycidylation.



R = H, [CH$_2$CH(CH$_3$)O]nCH$_2$CHCH$_3$OH

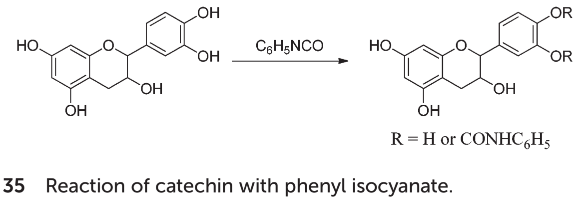
Fig. 34 Alkoxylation of catechin with propylene oxide.

Oxypropylation was tested on pine barks at room temperature in aqueous alkaline solution. Different degrees of substitution were obtained, always holding secondary hydroxyl groups at the end chain of poly(propylene oxide).[167]

Oxypropylation was also tested directly on gambier tannins with propylene oxide and butylene oxide with potassium hydroxide as a catalyst at 150 °C in a reactor.[114,168] In both cases, the reaction occurred and, by adjusting the reaction parameters, such as the oxide/tannin ratio, the length of polyether grafted chains can be controlled. Alkoxylation with butylene oxide offered an advantage to produce fully biobased polyols and was also successfully carried out with different tannins such as gambier, mimosa or pine.[168] For both oxides, whatever the tannin species, all OH present in molecules reacted. Nowadays, an alkoxylation reaction is an encouraging way to increase the value of tannins, leading to reactive polyols.

4.4.6. Reaction with isocyanates. To understand tannin reactivity with isocyanates to form urethane groups, catechin was studied as a tannin model with phenyl isocyanate.[169] The reaction is performed with acetonitrile under an inert atmosphere at 30 °C for 24 hours.

This study showed that OH from the A-ring does not react with isocyanate. It is quite surprising that only OH present from the B-ring can take part in this reaction (Fig. 35).[169] This is probably due to lower electron densities at the oxygen atoms in the A-ring compared to those in the B-ring. This suggests that only phenolic hydroxyl groups on the B-ring of a condensed tannin molecule participated in its reaction with isocyanate.



R = H or CONHC$_6$H$_5$

Fig. 35 Reaction of catechin with phenyl isocyanate.

5. Toward biobased polymers and materials

5.1. Adhesives

As mentioned, the main aldehyde to form adhesives is formaldehyde.[170] However, the resulting adhesive formaldehyde–tannins have a small number of methylene bonds, which explains the brittleness often observed. To improve the adhesive, phenol or resorcinol molecules can be added to create bonds between distant tannin sites through methylene links[120,171] with a decrease of the viscosity of the mixture. Tannins can be used in adhesive particle board resins with another natural component such as starch. A study has proved the industrial viability of using cornstarch–mimosa tannin–urea formaldehyde resin in a classic adhesive formulation in order to replace the conventional urea–formaldehyde system.[172] If cornstarch and mimosa tannin are added up to 10 and 4%, respectively, the corresponding resins for boards do not present variations in their physical and mechanical properties. Other additives can be used to improve the adhesive properties. A study was performed with glyoxal because it is not toxic and produced at an industrial scale.[173] Tests were carried out on wood panels which were glued with an adhesive formulated with tannin pine and glyoxal. Glyoxal reactivity with phenol, urea and melanin is lower than the reactivity of formaldehyde. This study also showed that cohesion between these panels was lower compared to those glued with a tannin-paraformaldehyde adhesive. However, in the case of formaldehyde prohibition, the glyoxal can be a potential substituent. Chestnut tannins were used for wood adhesives with formaldehyde, tris(hydroxymethyl)nitromethane, and with glyoxal and hexamine as hardeners.[126] This study was performed in order to substitute formaldehyde. The curing enthalpy for the adhesive with hexamine as a hardener was the highest, due to a high crosslinking density. But the highest rate of chemical curing was achieved using paraformaldehyde as a hardener to achieve complete chemical curing. Another option to synthesize adhesives without formaldehyde is with hexamine. For mimosa tannins, good adhesives for wood panels can be obtained at pH = 10. Composite materials with good properties have been elaborated starting from non-woven fiber of hemp and flax fibers with a tannin mimosa resin containing 5% of hexamine.[133] Thus, it is possible to make multi-layered compounds by binding fibers together with the resin.[174] These composites made with tannin resin reinforced with flax fibers can be used for automotive applications.[175]

Although formaldehyde gives good adhesive properties, the corresponding volatile organic compounds (VOC) bring some toxicity issues. Then, some studies were carried out with new adhesives starting from acetaldehyde, propionaldehyde, *n*-butyraldehyde or furfural. These aldehydes were formulated with mimosa tannins as adhesives for wood panels[176] which showed poor adhesion properties. However, partial substitution of formaldehyde by *n*-butyraldehyde can be carried out. The latter is water resistant due to the hydrophobicity of the carbon chain of *n*-butyraldehyde. To increase the properties, in addition to tannins and aldehydes, the formulation can contain urea such as monomethylol or dimethylol urea.[177] Another substitute for formaldehyde which was recently studied and which gives satisfactory adhesion results is furfuryl alcohol,[178] which is often used for tannin-based foams.

Acylation is also a useful chemical modification to decrease the brittleness of materials based on tannins and formaldehydes. Adipoyl dichloride is used to introduce a carbonaceous chain between tannin molecules. This inter-chain brings more flexible materials.[179]

5.2. Phenol-formaldehyde foam type

As phenol-formaldehyde foams, it is also possible to synthesize porous structures from tannins. A customary foam formulation is the following: tannins, furfuryl alcohol (used as an exothermic agent) and formaldehyde. Foams were first elaborated with catechin under acidic conditions.[134] The first foams based on tannins were synthesized with mimosa tannin and catalyzed by *p*-toluene sulphonic acid.[180] Since then, several studies have been reported to analyze different parameters such as acid and alkaline catalysis,[181] the use of boric or phosphoric acid to increase fire resistance,[182] the influence of foam carbonization,[183] the effect of the pre-activation of tannins,[184] the addition of hydroxymethylated lignin, polyurethane or an industrial surfactant.[136] The processing conditions have also been investigated. Microwaves were *e.g.* tested to accelerate the reaction and led to foams which have comparable properties to those obtained under a hot-press procedure.[185] Thus, microwave-based systems can be considered as more appropriate processes for industrial applications because of the corresponding reduced production times. Different extracts of tannins were tested.[136] In the case of tannins with a low degree of polymerization, it is not possible to obtain foams. It is in particular the case of the gambier tannin which contains too great a proportion of monoflavonoid.[186] The reactivity varies according to the nature of tannin. For instance, pine tannins are very reactive. This strong reactivity involves a shorter time of freezing which does not leave time for the foaming agents to evaporate. Only recently a formulation was successfully developed based on propylene glycol.[187]

Glyoxal was also used for foam applications as a formaldehyde substituent to prepare tannin/furanic rigid foams.[188] Glyoxal can completely substitute formaldehyde in pine foams. The corresponding insulation materials have low thermal conductivity and good mechanical resistance.[189] As previously mentioned, furfuryl alcohol can react with tannins to give tannin-furanic foams. This study investigates the integration of tannins into industrial processes to obtain light porous materials with good properties. Tannin open-cell foams had good sound absorption/acoustic insulation characteristics, compared to industrial foams.

A new foam structure can be prepared from an emulsion based on tannin, hexamine, vegetable oil and a surfactant.

After the reaction of the resin, oil is extracted and the remaining structure is pyrolysed.[190] These foams have more open structures with smaller pores and higher mechanical properties, compared to tannin-formaldehyde carbon foams.[191] A study shows that the initial concentration of tannins controls the porosity, the average cell size and the cell wall thickness of the foam.[192]

With the previous formulations, the tannin foams are either rigid or semi-rigid. Tests were carried out to synthesize flexible foams. During the preparation, glycerol is added with tannins, furfuryl alcohol and formaldehyde.[193] Glycerol acts as a non-volatile and non-toxic plasticizer.

5.3. Materials based on polyurethane

5.3.1. Polyurethane foams. Polyurethane foams were obtained starting from mimosa tannins and diisocyanates, such as the methylene diphenyl diisocyanate (MDI).[194] To increase the reactivity, tannins are initially treated by a liquefaction process based on polyethylene glycol and glycerol. Liquefaction takes place at 120 °C for 1 h. Then, the catalyst and other additives are mixed with tannin derivatives before the addition of MDI. In another study, condensed tannins are used to make flexible and open cell polyurethane foams. Quebracho was tested with ethoxylated fatty amine and polymeric MDI.[195] Foams are composed of copolymerized amine/isocyanate/tannin oligomers. From 30 up to 50% of tannins can be added with the reticulating agents. These foams slow down burning compared to conventional polyurethane foams.

Closed-cell foams were also obtained from oxypropylated tannins. Oxypropylated glycerol was replaced progressively up to 100%. The use of tannins increased the properties, *e.g.* the compressive strength and closed-cell content, leading to a reduction of the thermal conductivity.

5.3.2. Non-porous polyurethane materials. It is also possible to form polyurethane films with partially benzoylated mimosa tannins (Fig. 36).[121] Benzoylation is performed *via* the Schotten–Baumann method (section 4.4.1, Fig. 24). Bifunctional isocyanates are then used to elaborate reticulated films, which are bright with strong scratch resistance.

Crosslinked polyurethane membranes were also prepared from oxypropylated gambier tannins by a two-step procedure with isocyanate-terminated prepolymers. These were prepared from MDI with poly(propylene)glycol (PPG) or with a polyester diol from fatty acid dimers. Oxypropylated gambier tannins offer the potential of preparing a wide range of products. The nature of isocyanate-terminated prepolymers and the isocyanate/hydroxyl group molar ratio impacted the behaviour (thermoplastic *vs.* thermoset), the morphology (different crosslink densities) and the properties of the final polyurethane materials. For example, a high elongation at break with a low modulus is obtained for membranes with the longest grafted PPG chains.

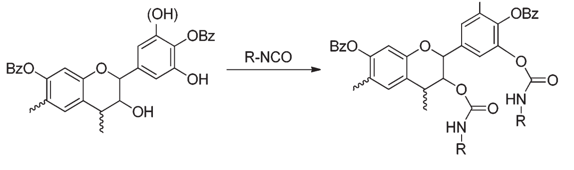


Fig. 36 Reaction between partially benzoylated mimosa tannins and isocyanates.

5.4. Materials based on polyesters

As previously mentioned, tannins can be modified with fatty acids and it is possible to obtain fully biobased polyester thermosets. Vegetable oil was used afterwards as a crosslinking agent to obtain films.[148] Tannins were esterified with linoleic acid and then crosslinked. The oxidation copolymerization was promoted with cobalt/zirconium metal driers as the catalyst. Tannin derivatives provided rigidity through polyphenolic aromatic rings and unsaturated chains as crosslinkers. A similar study was carried out with oleic acid and provided soft, flexible rubber-like materials.[196]

5.5. Materials based on epoxy resins

Hydrolysable tannins can also act as a crosslinking agent for epoxy resins. The corresponding resins have great resistance properties while being easily decomposable for the recycling.[197] These resins can be dispersed in solvent and used as a coating to protect metals from corrosion.[198] Condensed tannins can also react with di-epoxy to form resins.[164] Resins were synthesized with pine tannins with diglycidyl ether or polyglycidyl ether. The effect of the pH has been explored and, *e.g.*, it was shown that epoxy opening is favored under basic conditions with an increase of the reaction kinetics. Recently (2014), a new project called "Green Epoxy", from Bpifrance and FUI (France), was recently launched to develop a non-toxic industrial alternative to rigid epoxy resins derived from the forestry industry.

As previously mentioned (section 4.4.4.2), tannins can be modified by epichloridrin and then formulated with amines or anhydrides as reticulating agents.[199] Resins based on green tea extracts were functionalized with epichlorohydrin in the presence of benzyltriethylammonium chloride as a phase transfer catalyst.[200] To obtain epoxy resins, tannin epoxy derivatives were cured with isophorone diamine. Thermal and mechanical properties of tannin based epoxy resins are high due to a high crosslinking density.

6. Conclusion

Tannins are an abundant natural aromatic resource that has not yet been fully exploited as a renewable source to elaborate new macromolecular architectures for novel materials. The specific chemical structures of tannins allow bimolecular nucleophilic substitution, giving the opportunity to convert them into several promising aromatic chemicals and building blocks. Neat or modified tannins permit the elaboration of adhesives, foams, polyurethanes, epoxy resins *etc.* with interesting performance. However, the intrinsic properties of tannins, the resource variability, polymerization degree and chemical hyperbranched structures have hampered the development of tannin derivatives. Thus, to obtain high value tannin products, a preliminary investigation into the chemical structure of tannins as well as the use of high purity tannins are a priority.

The tannin price varies between 0.7 and 1.5 € kg^{-1}, according to the extraction, purification and drying process and depending on the botanical resource and the product purity. Such a price can be a limitation for some low-cost applications compared to some other renewable resources.

In summary, all these current developments highlight the great potential of tannins to create innovative and efficient materials in agreement with the emergent concept of sustainable development. Tannins as an aromatic building block for green chemistry to develop biobased polymers represent an important field of research. Tannins have become an encouraging and interesting renewable aromatic resource for the next few decades.

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